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REACTIONS OF THE HYDROBORATE ION IN ACIDIC SOLUTIONS

Theresa Schmitt

(M. S. Thesis)

January 1966

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January 1966

ABSTRACT

When potassium hydroborate was added to aqueous 7.8 M hydrochloric acid at -60° , a species with the power to reduce iodine to iodide was formed. Upon warming, the species decomposed with evolution of hydrogen. Procedures for preparing and analyzing 1.5-2.0 N reducing solutions were developed, and B^{11} and proton NMR studies were made. The ratio of the hydrogen evolved as a known amount of solution decomposed, to the boron in the solution, was measured. The possibility of obtaining BH_4^- by disproportionation of the reducing species upon neutralization of the solution was also investigated. Attempts were made to extract the species into ether, and to prepare an adduct with trimethylamine. A reducing solution was also prepared from diborane and cold 7.8 M hydrochloric acid. From the results of these experiments, a BH_2^+ reducing species seems possible.

I. INTRODUCTION

When stannane, SnH_4 , was prepared in aqueous solution according to the procedure of Jolly and Drake,¹ the author observed a fleeting yellow precipitate in the reaction flask as the basic stannate-hydroborate solution came in contact with a large excess of hydrochloric acid at 0° . This material was stabilized for a longer period of time, enabling its investigation, by repeating the preparation at -60° .^{*} Measurement of the ratio of the moles of hydrogen evolved as the yellow material decomposed on warming to room temperature, to the moles of tin present gave values of 3.4 to 3.7.

The experiment was then repeated with the omission of stannate ion, all other experimental conditions and reactants being kept the same. Thus, a basic solution of hydroborate was added to the low temperature acid, the hydrogen formed from reaction of the BH_4^- with the acid was pumped off, and then the hydrogen liberated when the solution was warmed to room temperature was measured. It was found that practically the same amount of hydrogen was liberated as a result of this experiment as was liberated when tin was present. Investigation of another solution, prepared in the same way but not allowed to warm up, revealed that it had the ability to reduce I_2 to I^- .

This phenomenon was of considerable interest, because at room temperature, potassium and sodium hydroborate react rapidly with acid³⁻⁵ to produce boric acid, a species with no further reducing power. Intermediates in the hydrolysis have not been isolated or identified in acid media, although in neutral and basic solutions species such as BH_3OH^- , BH_2OH , and

^{*} The freezing point of aqueous 7.8 M (eutectic composition) hydrochloric acid is -88° .²

$\text{BH}(\text{OH})_2^-$ have been reported.^{6,7}

Species such as $(\text{Me}_3\text{N})_2 \text{BH}_2^+ \text{I}^-$, as well as other compounds containing BH_2 and BH_3 groupings have been prepared in organic solvents, and by anhydrous high-pressure high-temperature techniques.^{8,9} It is interesting to note that, once formed, $(\text{Me}_3\text{N})_2 \text{BH}_2^+ \text{I}^-$ is found to be extremely stable in acidic solution, even at room temperatures and above,⁸ being unaffected by concentrated sulfuric, hydrochloric, and nitric acid, as well as by 10% sodium hydroxide and 30% hydrogen peroxide.

Many workers^{3,5,7,10,11} believe that their data point to reaction mechanisms for the hydrolysis of hydroborate to boric acid via BH_3 (aquated or unaquated) or BH_5 species. Since a knowledge of the composition of this low-temperature stabilized reducing species might shed some light on the truth or falsity of these mechanisms, it was thought especially important that an investigation of this species be made.

Because of increasing difficulties in the work with the unstable yellow tin material, this work was abandoned and the boron work was taken up. (The progress which had been made with the tin problem is given in the appendix, however.)

II. EXPERIMENTAL

A. Preparation and Analysis of Acidic Reducing Solutions

1. Preparation

A one-liter 4-neck flask was equipped with a nitrogen inlet tube, an overhead stirrer, a thermometer capable of reaching temperatures as low as -100° , and an addition tube containing potassium hydroborate, as shown in Fig. 1.

Two hundred ml of a 7.8 M^* hydrochloric acid solution was added to the flask, and cooled to -65° to -70° by means of a dry-ice-acetone bath contained in a 4 liter wide-mouth Dewar. The cooling process was usually hastened by blowing nitrogen, which had been cooled by passage through a copper coil immersed in liquid nitrogen, over the solution.

The potassium hydroborate (16 g.) was then added to the cold acid solution slowly, keeping the temperature of the solution below -60° at all times. Cold nitrogen was blown over the solution during the hydroborate addition, both to provide an inert atmosphere above the solution, and to hasten cooling by eliminating the warm air blanket on the top surface of the solution.

When all the hydroborate had been added, the stirring, nitrogen flow, and cooling were continued until about half the solution became frozen. The unfrozen portion was then poured into the pre-cooled filtration apparatus (Fig. 2), and filtered. Cold nitrogen was blown over the

* This solution (1000 ml) was prepared by diluting 645 ml of concentrated (12.1 M) HCl with enough water to make one liter of solution. The acid which was not needed in this reaction was stored and used (1) in the preparation of the iodine solution used in the analysis titration later in the experiment, and (2) for additional runs.

apparatus during the filtration, for the reasons previously mentioned.

The filtrate thus prepared contained the reducing species, in concentrations of 1.3 to 2.0 N, as determined by the analytical procedure which follows.

It was noted that the quantities of reagents employed in this experiment could be doubled, with no apparent effect on the percentage yield (i.e., normality) of the reducing species.

2. Analysis of Reducing Power

Part of the cold filtrate (25 to 30 ml) was poured into a pre-cooled graduated vessel, immersed in a dry ice acetone bath, and the total volume noted. Approximately 20 ml of this was then poured into a pre-cooled 500 ml round-bottom flask also immersed in a dry ice acetone bath, for titration, and the final volume in the graduated vessel noted, after allowing sufficient time for the viscous liquid adhering to the walls to return to the bulk of the solution. The difference in the volumes of solution in the graduated vessel before and after removing the part of the reducing solution to be titrated, was the volume of reducing solution being titrated.

Two procedures were found to be acceptable for titrating the reducing species, both involving the use of an iodine solution which was approximately 0.1 N in I_2 , .07 M in I^- , and 7.8 M in HCl. (500 ml of this solution was a sufficient amount for a given titration.)

a. Volumetric method. The iodine solution described above was cooled in a dry-ice-acetone bath, and then aliquots of known volume were delivered to the reducing solution by means of a graduated Mohr pipet. Enough iodine solution was added, with stirring, to cause the red-brown iodine color to persist in the solution. (It should be pointed out that care had to be

taken to avoid a false end point, however, since reaction and decolorization of the iodine is slow near the end of the titration.)

The titer of the iodine solution was determined by removing 20 ml aliquots of it during the course of the titration. After allowing these to warm to room temperature, they were titrated with standardized 0.1 N sodium thiosulfate solution (the latter was prepared according to the procedure given by Vogel¹²).

b. Gravimetric method. The iodine solution and its stoppered container were weighed, and then cooled in a dry-ice-acetone bath. The solution was then added (either by pouring directly or by pipeting) to the reducing solution, until the red-brown color of the iodine solution persisted, again being careful to avoid false end points. The unused iodine solution was then allowed to warm to room temperature, and the stoppered container and contents were weighed again.

The titer of a given weight of iodine solution was determined in either of two ways: 1) Portions of the cold iodine solution were poured into weighed vessels during the course of the titration, warmed to room temperature, weighed, and then titrated with standardized thiosulfate, or 2) since the concentration of iodine and iodide in the solution did not exceed their solubilities at even the low temperatures, and hence remained the same after the solution was cooled, weighed aliquots removed from the bulk iodine solution before the solution had been cooled (prior to titration of the reducing solution), were used in titration against standardized sodium thiosulfate.

Whenever the end point was overreached in either the volumetric or gravimetric methods, the solution was warmed to room temperature and back-titrated with standardized thiosulfate. (Although it appears that

the iodine titrations could be performed more simply by adding a large excess of iodine solution to the reducing solution, and then back-titrating more leisurely with sodium thiosulfate, this method had to be applied with some care, since sodium thiosulfate decomposes in strongly acidic solutions. The solution had to be stirred very well to prevent large local concentrations of sodium thiosulfate from building up in the solution, with subsequent decomposition, and error in the titration. To minimize the chances of error from this source as much as possible, large excesses of iodine were avoided.)

All titrations had to be performed under an inert atmosphere to avoid air oxidation. (The latter effect seemed to be unimportant in solutions of fairly high concentration (close to 0.1 N), however, since two aliquots of the iodine solution, removed at the same time from a flask containing the cold solutions, but titrated 1/2 hour apart, were of exactly the same normality.)

CALCULATIONS

VOLUMETRIC METHOD:

$$\begin{aligned} \underline{N} \text{ of the Iodine Solution} &= \frac{\left(\begin{array}{l} \text{ml of Na}_2\text{S}_2\text{O}_3 \\ \text{required to titrate} \\ \text{iodine solution} \end{array} \right) \times \left(\begin{array}{l} \text{Normality of the} \\ \text{standardized} \\ \text{Na}_2\text{S}_2\text{O}_3 \text{ solution} \end{array} \right)}{20 \text{ ml (i.e., volume of iodine solution titrated)}} \\ \underline{N} \text{ of Reducing Solution} &= \frac{\left(\begin{array}{l} \text{ml of iodine} \\ \text{solution used} \end{array} \right) \left(\begin{array}{l} \underline{N} \text{ of iodine} \\ \text{solution} \end{array} \right) - \left(\begin{array}{l} \text{ml of Na}_2\text{S}_2\text{O}_3 \text{ required} \\ \text{in back titration} \end{array} \right) \left(\begin{array}{l} \underline{N} \text{ of Na}_2\text{S}_2\text{O}_3 \\ \text{solution} \end{array} \right)}{\text{ml of reducing solution titrated.}} \end{aligned}$$

GRAVIMETRIC METHOD:

$$\begin{aligned} \text{Millequivalents of Iodine} &= \frac{\left(\begin{array}{l} \text{ml Na}_2\text{S}_2\text{O}_3 \\ \text{required to} \\ \text{titrate} \end{array} \right) \times \left(\begin{array}{l} \text{Normality of the} \\ \text{standardized Na}_2\text{S}_2\text{O}_3 \end{array} \right)}{\text{g. of iodine solution titrated}} \\ \underline{N} \text{ of reducing solution} &= \frac{\left(\begin{array}{l} \text{g. of iodine} \\ \text{solution required} \end{array} \right) \left(\frac{\text{milliequiv. of Iodine}}{\text{gram solution}} \right) - \left(\begin{array}{l} \text{ml of Na}_2\text{S}_2\text{O}_3 \\ \text{required in} \\ \text{back titration} \end{array} \right) \left(\begin{array}{l} \underline{N} \text{ of Na}_2\text{S}_2\text{O}_3 \\ \text{solution} \end{array} \right)}{\text{ml of reducing solution}} \end{aligned}$$

Solutions of normality 1.3 to 2.0 were generally obtained.

B. Procedure for Cross-Checking the Iodine Analytical
Method for Reducing Power - H₂ Evolution Method

A stoppered 100 ml round bottom flask containing 50 ml of 7.8 M hydrochloric acid was cooled to -60° or lower in a dry-ice acetone bath. An iodine solution (400 ml) which was 0.1 N in I₂, 0.7 M in I⁻, and 7.8 M in HCl was then prepared. Two Erlenmeyer flasks (250 ml) with stoppers and two 25 ml Mohr pipets were weighed, and some of the iodine solution was poured into each of the two Erlenmeyer flasks for standardization; the latter were then weighed again and set aside. The remainder of the iodine solution was then weighed in a stoppered 500 ml round-bottom flask and cooled in a dry-ice acetone bath.

The apparatus indicated in Fig. 3 was set up. Argon was passed through the side arm, creating a slight pressure on the solution and preventing premature filtration. Nitrogen, cooled by passage through a copper coil immersed in liquid nitrogen, was passed over the top of the apparatus.

The precooled HCl was then poured into the funnel part of the apparatus, and the stirrer turned on. Potassium hydroborate (1.6g) was added slowly to the HCl solution, care being exercised not to allow the temperature of the solution to rise above -60°.

When all the KBH₄ had been added, the stopcock was turned to allow vacuum to be applied to the flask, and the solution was filtered into the smaller compartment of the lower flask.

While the solution was filtering, the weighed-out iodine solutions were titrated with standardized 0.1 N Na₂S₂O₃ solution (see Vogel¹² for standardization procedure).

When the solution had all been filtered, the apparatus was raised in the bath until only the part below the horseshoe clamp was immersed. The clamp and the upper half of the apparatus were removed, and a slow stream of Argon was passed over the lower flask. The vessel was then tipped (while immersed in the bath), enough to allow 10-15 ml of the reducing solution to fill the larger bulb. The flask was then straightened and secured in the bath.

While maintaining the argon flow over the vessel, aliquots of the cooled iodine solution were removed with one of the pipets, and were added to the solution in the larger compartment, until the red-brown iodine color no longer disappeared (care had to be taken to avoid a false end point). A glass stirring rod was used to stir the solution during the titration. At the end of the titration, as much of the titrated reducing solution as possible was removed (with the second pipet) into a weighed stoppered container and set aside. The pipet was also set aside and both the flask and pipet were weighed after reaching room temperature. (The titrated solution was removed in order to avoid freezing and thawing unnecessarily the large volume of solution and to avoid the necessity of pumping dissolved gases from both solutions.)

The flask containing the remainder of the titrated and the untitrated reducing solutions was quickly transferred into a 4l wide-mouth Dewar containing liquid N_2 , and attached to a vacuum line, by the connection shown in Fig. 4. Silicone grease was used on the o-ring.

The unused portion of the iodine solution was removed from its cold bath, and was allowed to warm up. The first pipet was also set aside and allowed to warm up. When the pipet and the iodine solution reached room temperature, they were each weighed again, so as to obtain the weight of

the titrant by difference.

When the solutions in the flask immersed in liquid N_2 were frozen, the volume above them was evacuated. A Dewar with dry-ice-acetone was then substituted for the one containing liquid N_2 . The solution was allowed to thaw and to warm up to dry-ice-acetone temperatures, while evacuating carefully, periodically (not steadily) to prevent frothing. (Note: if pressure of evolving gases was large at dry-ice acetone temperatures, the stopcock above the solution was closed, the solution re-frozen in liquid N_2 , the gas above it pumped off, the stopcock closed and the solution thawed in a dry-ice-acetone bath again. This procedure was repeated as often as necessary to get solution pumped down without decomposing it.) When the solution had been sufficiently pumped down, the pump was closed off from the system. The dry-ice-acetone bath was removed from around the flask, and the solutions were allowed to warm up to room temperature, after making sure to allow sufficient volume to safely accommodate the H_2 which would be evolved. After the solution had all decomposed (i.e., when effervescence had ceased and solution was at room temperature), it was cooled in a dry-ice acetone bath again.

The H_2 liberated in the decomposition was then pumped off with a Toepler pump (after passage through three or four U-traps immersed in liquid N_2), and the amount of H_2 was measured.

The bottom flask was then disconnected from the vacuum line at the o-ring joint, care being taken not to tip the contents, and it was loosely stoppered.

After allowing it to warm to room temperature, the assembly was weighed. The traces of the contents which remained in the larger compartment (i.e., titrated side) were wiped out with a "Kimwipe". The vessel

was then weighed again. The contents were removed from the other side next, and the vessel reweighed.

The calculations were then carried out to determine, 1) the reducing power per g. of reducing solution, 2) moles H_2 evolved per g. of red solution, 3) ratio of 2) and 1). The results of two such experiments, as well as a sample calculation, are given below.

Run		No. 1	No. 2
1.	Weight of iodine solution and flask before titration	864.348	932.460
2.	Weight of iodine solution and flask after titration	688.601	824.717
3.	Weight of Erlenmeyer flasks (empty)	1 111.386 2 107.106	107.110 133.074
4.	Weight of Erlenmeyer flasks containing iodine solutions	1 154.203 2 140.890	131.212 168.093
5.	Ml of $\text{Na}_2\text{S}_2\text{O}_3$ req. to titrate	1 40.17 2 31.90	23.90 34.65
6.	\underline{N} of $\text{Na}_2\text{S}_2\text{O}_3$ solution	0.1007	0.1007
7.	Weight of iodine solution clinging to first pipet	.049g	0.082
8.	Weight of titrated solution removed	188.730	112.292
9.	Weight of titrated solution clinging to second pipet	.040	0.362
10.	Ml of $\text{Na}_2\text{S}_2\text{O}_3$ used in back-titration	0	4.5
11.	Weight of double-bulbed flask at end of run	363.857	373.640
12.	Weight of flask after larger compartment was wiped out	362.796	371.399
13.	Weight of flask after solution from smaller compartment was removed	344.466	346.743
14.	Millimoles of H_2 Toepfered	11.15	16.883

CALCULATIONS: RUN NO. 1

N of Iodine Solution

g. of solution titrated

No. 1	154.203	No. 2	140.890
	<u>-111.386</u>		<u>-107.106</u>
	42.817		33.784

ml of $\text{Na}_2\text{S}_2\text{O}_3$

Required:	40.17		31.90
-----------	-------	--	-------

N of $\text{Na}_2\text{S}_2\text{O}_3$: 0.1007

milliequivalents
of iodine

=	$\frac{40.17 (.1007)}{42.817}$	=	$\frac{31.90 (.1007)}{33.784}$
---	--------------------------------	---	--------------------------------

g. solution

=	0.095	=	0.095
---	-------	---	-------

N of Reducing Solution

wt. of iodine solution
before titration 864.348

wt. after titration -688.601
175.747

wt. of iodine solution
clinging to pipet - 0.049

g. of iodine solution
used 175.698

wt. of apparatus at end
of expt. 363.857

wt. of apparatus, less
soln from larger
compartment -362.796

wt. of titrated soln not
pipeted from flask after
titration 1.061

wt. of soln. clinging to
second pipet + .040

wt. of titrated soln
removed +188.730

RESULTS OF RUN NO. 2

1. Milliequivalents of Reducing Agent/g. of solution: = 1.46

2. Millimoles of H_2 /g. of solution = .685

3. Ratio of (1) to (2) = 2.1

Average ratio obtained from runs No. 1 and 2 = 2.03

C. Proton Nuclear Magnetic Resonance Studies

1. Reducing Solution

Spectra of solutions prepared in the manner described in Part A were recorded using a Varian A-60, 60 mc. NMR spectrophotometer. The sample cavity was cooled to the desired temperature (as low as -100°) by means of nitrogen gas which had been cooled by passage through a coil immersed in liquid nitrogen. The temperature was measured by means of a copper-constantan thermocouple which was placed in the cavity prior to inserting the sample, and then removed when the temperature had been measured. In this way the temperature could not be monitored continuously, but it was estimated that the temperature varied by $\pm 2^{\circ}$ (maximum) during the time the sample was in the cavity. During the recording of all spectra, the temperature was maintained at -50 or -60° (-60° was used in early experiments to insure that the compound was not decomposing. In later experiments -50° was used, since increase in viscosity of the solutions with decreasing temperature had to be minimized).

The entire region from 2000 cycles downfield of tetramethylsilane to 500 cycles upfield of it was scanned. No lines, other than those attributable to water or isopropyl alcohol,* were ever observed, even at very high amplitude (amplitude such that the water peak at its base was 200-300 cycles wide, including the large first and second sidebands).

Since the reducing solution was very viscous, even at -50° , it was thought that spectral peaks might be more readily seen if a less viscous solvent were used. Thus, acidic solutions prepared by diluting 12.1 M

* This was believed to have been caused by condensation of a slight amount of acetone (from the cold-bath) into the solution, and subsequent reduction of it to isopropanol.

HCl to 7.8 M with methanol were used as the solvent in the preparation of the reducing solutions (the rest of the procedure was carried out as described in Part A, except for the fractional freezing step which was omitted). No unaccounted-for lines were seen, however.

2. Disproportionation of the Reducing Species Upon Neutralization

A room-temperature spectrum of KBH_4 in 0.5 M KOH could be recorded at BH_4^- concentrations as low as 0.05 M (Fig. 5). (The center of gravity of the four peaks is approximately 315 cycles or 5.25 ppm upfield of H_2O ; the coupling constant is 86 cycles.) Because of the sensitivity of detection of BH_4^- in these solutions, a solution which was approximately 1.5 N in the unknown reducing species initially, would be expected to give an observable hydroborate spectrum, if any was formed by disproportionation of the reducing species in a neutralized or basic solution. Thus, 10 ml of a solution which was 1.6 N was added dropwise to liquid nitrogen, forming solid pellets of reducing agent. These were then dropped into a cooled NaOH solution (20 ml) which was 5 M (20% by wt.) in NaOH. This is the eutectic composition of a water-NaOH mixture, f.p. = -28° .¹³ The pellets were then allowed to warm up to the temperature of the sodium hydroxide solution, and then the solution was warmed to room temperature. An NMR spectrum of the resulting solution was then recorded on the A-60 spectrometer. No peaks were observed. This experiment was repeated several times with the same results. (Note: Another experiment for detection of BH_4^- using Co^{++} was also employed, and will be described in a later section.)

3. Deuterated Solvent

Since the concentration of protons from the water and acid was always quite a bit greater than the normality of the reducing species, the high

amplitudes used to try to observe peaks due to the latter always made the water signal appear very broad at the baseline (200-300 cycles wide). Since peaks due to the reducing species might lie largely beneath the peak and be obscured by it, it was decided to prepare the reducing solution in a DCl-D₂O solvent, rather than in HCl-H₂O, enabling one to scan the regions under the normal H₂O peak. (Since the D₂O used in the preparation of the DCl and of the solution was only 99.85% enriched, a peak due to water would still be expected, but it would be greatly diminished in size.)

DCl was prepared according to the procedure of Brown and Groot¹⁴ using 4 ml of D₂O and 160 ml of benzoyl chloride.

After purification of the DCl by distillation (in vacuo) through a U-tube immersed in a carbon disulfide slush, the gas was allowed to come in contact with 33 ml of D₂O which had been previously attached to the vacuum line. (It was desired to make 33 ml of concentrated (12.1 M) acid, or 50 ml of 7.8 M acid upon suitable dilution.) The flask containing the D₂O solution was shaken occasionally (while attached to the vacuum line) to speed the solution process. When the pressure on the manometer in the system stopped decreasing, indicating that little more DCl was being taken up, the D₂O-DCl solution was disconnected from the vacuum line. When this solution was cooled in a dry ice acetone bath, it froze at about -40°, indicating that the composition was not very far from 7.8 M (the eutectic composition; the slope of the curve of composition vs freezing point is very steep near the eutectic point). Thus, only 2 ml of D₂O was added to the solution. The reducing solution was then prepared in the usual way, except that it was scaled down in quantity. The final solution was not titrated, since there was not a sufficient amount of

solution available at the end of this preparation for this purpose; a qualitative test on 2 ml of it showed that it possessed reducing power, however. The solution was then transferred to several NMR tubes, the tubes were sealed, and spectra were recorded at -50° . A much diminished water peak was seen, but no unexplained lines were obtained.

D. B¹¹ Nuclear Magnetic Resonance Studies

¹¹B NMR spectra were recorded using a Varian variable frequency (VF-16) wide-line instrument. Samples were kept cold during the recording of spectra, by passing a stream of nitrogen regulated to the proper temperature over them. (The proper temperature was obtained by combining the right amount of room temperature nitrogen with gas which had been cooled by passage through heat-exchanger coils immersed in a dry-ice-acetone bath.) Temperatures were monitored periodically by means of a copper-constantan thermocouple permanently placed in the gas stream below the sample tube.

Spectra of several solutions of the unknown reducing species were recorded including 1) solutions prepared in HCl-H₂O solvent as described in Part A (1.45 and 2.04 N reducing solutions), 2) solutions prepared in HCl-H₂O-CH₃OH solvents, where the acid solution was prepared by diluting concentrated (12.1 M) HCl with enough methanol to make the final solution 7.8 M (1.66, and 1.72 N reducing solution) and 3) a solution made with a 20% concentrated HCl-80% methanol solvent. In each case, a very broad signal could be seen, using high radiofrequency power.

Since the spectrum of boric acid, into which KBH₄ (and thus probably the reducing species) decomposes, also consists of a very broad peak at

these temperatures, chemical shift studies on both the known boric acid and on the reducing solution, relative to some standard material, had to be made, in order to ascertain that the peaks attributed to the reducing species were not simply due to boric acid. The solutions prepared in the 7.8 M HCl-H₂O-CH₃OH solvent were the ones studied, since these solutions were thought to be less viscous than the straight HCl-H₂O ones, and yet not so greatly different from them as to cause doubt as to whether the species being examined was the same as that prepared in the usual HCl-H₂O solvent.

Chemical shift studies on the reducing solutions were made with samples equilibrated at -45°. This temperature was used because, 1) a convenient cold bath (chlorobenzene) could be made and used to equilibrate (and keep equilibrated) the reducing solution, the boric acid solution, and the reference compound, when not in the NMR cavity, 2) the solution was less viscous at -45° than at -50°, and higher peaks were obtainable, 3) although there was some effervescence (decomposition) of the sample at this temperature, it was not intolerable since the intensity of the peaks did not diminish greatly with time. Enough reducing solution was made initially to fill several tubes, and the ones not in use were stored in a dry-ice acetone bath to inhibit decomposition. During the course of the experiment a fresh, undecomposed sample tube was used to replace the partially decomposed one periodically.)

Spectra for chemical shift measurements were recorded using the technique of sample exchange. The region of the field containing the peaks from the reducing solution was scanned. Then, without stopping the machine or varying the sweep rate after the desired reducing solution peaks were recorded, the sample was quickly removed and was replaced with a pre-

equilibrated tube containing liquid boron trichloride, which was used as the reference material.* The sample was always exchanged in time to record the second and third sidebands of the BCl_3 (the center band of BCl_3 overlaps part of the broad peaks of the materials whose chemical shifts were being measured, and so this was not recorded. It was because of this overlap that the external reference technique (in which a capillary tube of a reference material is placed inside the larger sample tube) could not be used. Use of side bands was also more convenient in this case, however, since at the high power being used, the BCl_3 center band was very intense, and the center of it could only be found with difficulty).

Since the modulation frequency was 411 cycles (i.e., the distance between adjacent sidebands, and between center band and first side band, was 411 cycles), the position of the center band of BCl_3 could be found. The distance between the center bands of the unknown (or of boric acid) and the BCl_3 (i.e., the chemical shift) could then be measured, in cycles. The radiogrequency was 16.234 megacycles, from which the shift in parts per million could be calculated. The chemical shifts of the reducing solution peaks, recorded at -45° are given in Table II.

The solubility of boric acid in a 7.8 M methanol - HCl solution is quite low at -45° , and measurement of chemical shifts at this temperature was quite difficult. Thus, before the latter was undertaken, a study was made of the chemical shift of boric acid with temperature in the hope that room temperature data for boric acid could either be used directly or

* BCl_3 was used as the reference here rather than $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ which is more conventional, because the shift between it and both the reducing species and boric acid is greater, and there is more time available for the samples to be exchanged.

Table II. Chemical Shift of Reducing Species at BCl_3 , at -45° (Cycles)

478
446
419
458
433
467
439
510
513
521

av = 468 cycles = 28.8 ppm

Table III. Chemical Shift of Boric Acid vs BCl_3 at Various Temperatures (Cycles)

25°	0°	-23°	-45°
516	444	428	337
450	398	396	368
469	445	381	332
475	388	390	334
481		435	322
av = 478	av = 419	av = 406	419
			390
			351
			346
			300
			av = 350 cycles = 21.6 ppm

Table IV. Chemical Shift of Reducing Species Which has been Decomposed, Recorded at -45° (Cycles)

326	337	342
358	370	372
398	403	
362	381	
		av = 365 cycles = 22.5 ppm

extrapolated to the proper value at -45° . The results of this study are given in Table III. A trend of decreasing shift with decreasing temperature was indicated from results at $+25^{\circ}$, 0° , and -23° , although no linear relationship between shift and temperature was apparent. Thus it was decided that only data which could be obtained at -45° from boric acid could be used. These are also given in Table III.

Finally, the unknown reducing solution was allowed to decompose completely by warming it to room temperature, and then, after all effervescence had ceased, it was cooled to -45° again. Spectra were recorded and the chemical shifts measured. The results are given in Table IV.

(Note: The data given here are consistent within themselves since they were measured under similar conditions, on the same instrument. Care must be taken in comparing these values with those in the literature, however, since shifts vary with the environment (solution) of the species being examined, as well as (apparently) the temperature.) Because of the broadness of the peaks the values given are estimated to be accurate only to ± 2 ppm.

E. Reducing Solution from Diborane

To investigate the possibility that potassium hydroborate might consist of, or have passed through a borane intermediate in forming the unknown reducing species, an attempt was made to prepare an acid reducing solution beginning with diborane, B_2H_6 .

Diborane was prepared according to the procedure of R. Schaeffer¹⁵ by the reaction of potassium hydroborate (1.08g; .02 moles) with 85% phosphoric acid to which sufficient P_4O_{10} had been added to react with all the water present. V. P. of the final product = 225 mm at the temperature of melting CS_2 (-112°).

The diborane was allowed to remain in contact with approximately 2 ml of a 7.8 M solution, which had been cooled to dry-ice-acetone-temperatures, for 8 hours.

The excess gases were pumped off (in case unreacted B_2H_6 persisted in the system), and the HCl solution was disconnected from the vacuum line. More than 4 ml of a precooled iodine solution (approximately 0.1 N) was added to the cold acid solution before the red-brown color of the iodine persisted, indicating that a reducing species had formed in the solution as a result of letting B_2H_6 come in contact with cold 7.8 M HCl.

F. Trimethylamine Adduct-Attempted Preparations and Isolation

Since there was a possibility that the unknown reducing species was a BH_2^+ (or aquated BH_2^+) ion, and since the trimethylamine complex of BH_2^+ is a very stable material at room temperature and above, even in strongly acidic solutions,⁸ attempts were made to prepare such an adduct from the reducing solution.

Thus far, $[(CH_3)_3N]_2BH_2^+$ has only been prepared in high-pressure anhydrous reactions, or in anhydrous organic solvents. (The material is often recrystallized from aqueous solutions,⁸ however, in which it is quite soluble and stable.) Thus the feasibility of this method of preparation of the bistrimethylamine adduct of BH_2^+ , even if the BH_2^+ species did exist in the reducing solution was not certain.

Since trimethylamine readily forms the quaternary trimethylammonium chloride salt in HCl solutions, the solution of the reducing species had to be neutralized before the trimethylamine could be passed in.

The acidic reducing solution (200 ml) was prepared in the usual manner, except that 12.1 M HCl which had been diluted to 7.8 M with methanol was used as the solvent (to keep the solution from freezing during neutralization, as little water and as much alcohol as possible was desirable). Phenolphthalein indicator was added to the final solution, and the latter was titrated with an approximately 8 M methanolic KOH solution, slowly enough to keep the temperature of the solution below -50° at all times. (This required 4 to 5 hours.) When the solution was first slightly basic (pH 8), gaseous trimethylamine was passed into the flask, with swirling, for about 10 minutes.

The solution was then warmed to room temperature, while maintaining a slow flow of trimethylamine. When the solution reached room temperature, the trimethylamine flow was stopped. The white precipitate (probably KCl) which had formed in the flask during the neutralization was filtered off when the solution reached room temperature, and discarded. (The adduct is very soluble in water at room temperature and would not have been precipitated with the mass of other material.) The alcoholic filtrates obtained were then treated in one of two ways.

- 1) The filtrate was boiled down to 75 to 100 ml (to remove all the alcohol and some of the water). More white precipitates settled out. The solution was allowed to cool to room temperature and the supernatant liquor was then shaken with a volume of methylene chloride which was double the existing volume of solution. The methylene chloride phase (the lower one) was then separated from the 2-phase system in a separatory funnel, and was dried using anhydrous sodium sulfate. The solution was filtered (by gravity) and then boiled down to a very small volume (25 ml). The rest of the solvent was then allowed to evaporate in air, at room temperature. Infrared

spectra of the resulting solid, as well as of the white precipitate which had settled out upon concentration of the aqueous solution, were recorded. Comparison of these spectra (see Figs. 6 and 7) with one taken of a known sample of $[(\text{CH}_3)_3\text{N}]_2\text{BH}_2^+\text{I}^-$ (Fig. 8) did not reveal the presence of this adduct in any of the solids obtained from the reducing solution. (In particular, a peak at 4 microns which appears in the spectrum of the known compound, and is typical of the B-H stretching mode, was absent from the other spectra.)

2) The filtrate was boiled completely to dryness, and the resulting solid was powdered and shaken with 200 ml of methylene chloride. The solution was dried with anhydrous sodium sulfate (to remove any excess water in the solid from the boiled-down solution), filtered and evaporated to dryness as before. A very small quantity of solid material was obtained, but again, the infrared spectrum did not coincide with that of the known compound.

G. Attempted Detection of a B-H Bond by Hydrogen Evolution

Since only a small amount of the $[(\text{CH}_3)_3\text{N}]_2\text{BH}_2^+\text{Cl}^-$ adduct might have been formed by the procedure in Section F, among the relatively large quantity of salts, an infrared spectrum may not have been a sensitive enough tool for detection of an adduct. It was decided that since the adduct could not be readily separated from the other salts (if it was present), a test would be made to see if the presence of a B-H bond could be detected among all the solids.

The bistrimethylamine- BH_2^+ complex is extremely inert (as was mentioned previously) and it is reported to be recoverable from a solution of concentrated sulfuric acid which had been heated at 100° .

It was decided that since the compound must decompose eventually, the hydridic hydrogens attached to boron should liberate hydrogen gas when the compound was decomposed in an acidic solution. Accordingly, a sample of the solid, obtained by boiling down completely the filtrate prepared in F, was added to concentrated sulfuric acid and inserted in a tube such as that shown in Fig. 9. To determine the feasibility of the method, a sample containing 25 mg (0.1 mmoles) of known $[(CH_3)_3N]_2BH_2^+I^-$ was added to approximately 10 ml of concentrated sulfuric acid in an identical tube (the volume of which was approximately 40 ml). Both tubes were evacuated through the left arm of the tube and were then heated at approximately 70° for several hours, until the pressure in the system was only several microns (the BH_2^+ adduct would not be decomposed at these temperatures and the HCl and other gases generated when sulfuric acid was added to the crude solid from the reducing solution had to be removed before the tube was sealed.) The tubes were then sealed under vacuum and heated at 240° for 16 hours. They were then cooled and connected to a mass spectrometer. The break-seal was broken and the mass spectrum of the gases in the tube were recorded. No hydrogen was found in either tube. (Note: There was a more-than-sufficient amount of the known material in its tube to give an observable hydrogen spectrum if it had decomposed to form hydrogen.)

H. Spot Tests for Hydroborate

It was desirable to know whether hydroborate could be regenerated from the reducing solution by a disproportionation reaction. The NMR detection of the presence of hydroborate ion has already been discussed, and is good for concentrations as low as 0.05 M. A more sensitive de-

tection method was desirable, however, and spot tests with cobalt (II) and nickel (II) ions were used.

It was found that a 0.1 M solution of Ni^{++} or Co^{++} ion could detect concentrations of hydroborate ion as low as 3×10^{-3} M in a 0.1 N NaOH solution. The Co^{++} or Ni^{++} solution was added to an equal volume of the solution being tested. The hydroxide of Co^{++} or Ni^{++} precipitates at first, but after about a minute an opaque black slurry (possibly containing the nickel or cobalt borides) results. This disappears shortly thereafter and hydrogen evolution is noted. (A blank sodium hydroxide solution may give a brown precipitate due to air oxidation of the metal ions, but the black opaque precipitate forms only when BH_4^- is present.)

When this test was applied to a solution prepared from the low temperature neutralization of the reducing solution, no black precipitate was obtained.

I. Boron Analyses

1. Solubility of H_3BO_3 in Low Temperature Acid Solutions

One gram of boric acid was dissolved in 50 ml of 7.8 M HCl, and the mixture was cooled to -50° in a dry-ice acetone bath. Much of the boric acid precipitated out; after allowing it to settle, 10 ml of the clear supernatant liquor was pipeted into a 250 ml preweighed filter flask. The solution was allowed to warm to room temperature and then the solvent was carefully distilled off at reduced pressure at room temperature. The flask was weighed again and found to contain 0.020g of H_3BO_3 . (The procedure was repeated and found to be reproducible.) Since the solubility of boric acid was only .02 g/10 ml of acid solution, it was decided that a boron analysis on a reducing solution of known volume and normality

could be used to determine the ratio of the milliequivalents of reducing species to mmoles of boron in the reducing solution.

2. Analysis of Reducing Solutions Prepared as in Section A

Freshly prepared samples of reducing solutions were titrated, and known volumes of them were allowed to decompose to boric acid. The solutions were then analyzed for boron content, according to the method of Corner¹⁶ (a procedure involving the use of mannitol). The results of these determinations are given in Table V. To test the accuracy of the method, the procedure was run on two samples of known boric acid content:

	Wt of H_3BO_3 analyzed	Wt of H_3BO_3 found	% error
No.1	0.5008 g	0.4920	1.8%
No.2	0.8098 g	0.7955	1.8%

3. Analyses of Reducing Solutions Prepared from Methanolic-Hydrochloric Acid Solvent

Freshly prepared samples of reducing solutions, prepared in methanolic hydrochloric acid solvent (made by diluting 12.1 M HCl with sufficient methanol to make the final solution 7.8 M in HCl) were titrated, and known volumes of them were allowed to warm up to room temperature and to decompose to boric acid. The solutions were then cooled to dry-ice-acetone temperatures again, and were filtered through a fritted Hirsch funnel (small aliquots were filtered quickly with the use of suction to avoid warming of the solutions as much as possible.) The filtrate was then discarded, and the solid (boric acid) was transferred to a 250 ml beaker (by removing as much solid as possible to the beaker with a spatula, and then slowly filtering deionized water through the frit to remove solid

Table V.

	mmoles of B in sample* (found)	original volume of samples (ml)	mmoles of B in sample, corrected for boric acid content	meq. of reducing agent/ml of un- decomposed solution (N)	meq/ml mmoles B/ml
Run No. 1	10.854	22.0	10.15	1.60	3.5
Run No. 2	5.157	14.0	4.71	1.10	3.3
Run No. 3	9.260	19.0	8.65	1.309	2.9

*

Uncorrected for solubility of boric acid = $.02\text{g}/10\text{ ml} = .032\text{ millimoles/ml}$

clinging to the pores, and transferring the filtrate to the beaker also). The solution was then analyzed for Boron according to the method of Corner.¹⁶ The results of these determinations are given in Table VI.

Table VI

	mmoles of B in the sample	original volume of solution (ml)	meq of reducing agent/ml of un- decomposed sol'n	$\frac{\text{meq/ml}}{\text{mmoles}}\frac{\text{B/ml}}{\text{B/ml}}$
1	13.584	32.0	2.03	4.78
2	7.635	32.3	1.05	4.44

J. Extraction with Ether

If the reducing species consisted of a non-polar species, it would be expected to be soluble in ether. Thus, a freshly prepared reducing solution was shaken with a cold ether solution several times. (The ether had been distilled from sodium to eliminate peroxides.) The ether layer was then separated off from the solution, and a cold solution of iodine in ether was added dropwise. None of the iodine color disappeared, however, indicating that the ether solution contained no reducing species.

K. Stability of the Reducing Species

Effervescence of the reducing solution was observed at temperatures as low as -48° , indicating that the solution was evolving H_2 slowly at these temperatures and decomposing. (At -60° , this effervescence was not observed.)

Yields of the reducing material were greater when a stream of nitrogen was passed over the solution during preparation. A solution kept at -78° in a flask purged with nitrogen had lost only 15-20% of its reducing

power after 30 hours. A sealed ampule of reducing solution, opened after four days, had only lost 19% of its reducing power during this time. Thus, the reducing species is probably sensitive to air oxidation, but its lifetime can probably be prolonged by storage and use under an inert atmosphere such as nitrogen or argon.

L. Materials

The potassium and sodium hydroborate used were reagent grade (97 and 98% purity, respectively) and were usually used directly as received from Metal Hydrides, Inc. (One reducing solution was prepared with NaBH_4 which had been recrystallized from isopropyl amine however. A typical reducing solution (1.38 N) was obtained, indicating that reducing power of the solution was not due to any impurity in the starting material.) The sodium and potassium hydroxide, sodium thiosulfate, anhydrous sodium sulfate, boric acid, mannitol, hydrochloric acid, absolute methanol, phosphoric acid and phosphorous pentoxide used were all reagent grade chemicals supplied by the Baker and Adamson division of Allied Chemical Corporation. The sodium iodide was supplied by the same company but was USP grade (pharmaceutical quality). Benzoyl chloride, and iodine were Mallinckrodt Analytical reagents. D_2O , 99.85%, was supplied by the Bio Rad Laboratories. The gaseous trimethylamine used was supplied by the Matheson Company. The sample of known $[(\text{CH}_3)_3\text{N}]_2\text{BH}_2^+\text{I}^-$ was supplied by Dr. Arlan Norman.

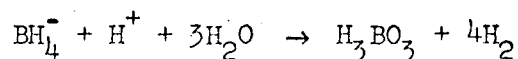
NMR tubes used for the A-60 NMR machine were standard 5 mm Varian tubes. Those used for the B" work consisted of standard 9 mm pyrex tubing with one end sealed off.

Infrared spectra were recorded on a Perkin-Elmer Infracord Spectrophotometer.

III. DISCUSSION AND RESULTS

A. Preparation and Analysis of Reducing Solutions

A large amount of the potassium hydroborate consumed in the preparation of the low temperature reducing solutions does not go into the formation of the reducing species. Instead, it is probably hydrolyzed completely, according to the reaction

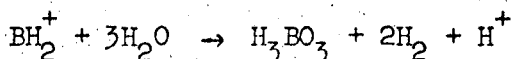
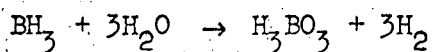
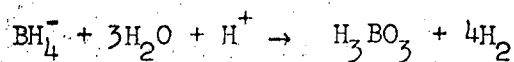


Finding a procedure which yielded reducing solutions in concentrations as high as 1.5 to 2 N posed a problem at first, since concentrations of only about 0.2 N were generally obtained when the reaction was first discovered. Since NMR and other studies required the use of more concentrated solutions, an investigation of conditions necessary for preparing more concentrated solutions was undertaken. It was found that a 10° to 15° decrease in the preparation temperature, from the -45° or -50° used initially to the -60° now used, had a profound effect on concentration. (Since later studies showed that the solution effervesces at -45°, indicating some thermal instability and decomposition at these temperatures, this is not unreasonable.) Although the necessity for partially freezing the solutions before filtration has not been positively demonstrated, concentrations of greater than 1.4 N have never been obtained where this technique was not employed. (Where alcoholic 7.8 M HCl was used, high concentrations were obtained without freezing, but other effects might be responsible for the increase in concentration.) The flow of cold nitrogen appears to be beneficial in forming more concentrated solutions, probably because it helps to insulate the solution from the warm air above it, as well as to keep away oxygen, which appears

to have a detrimental effect on the reducing species, away.

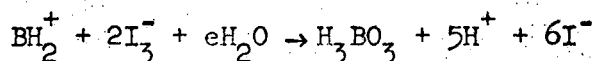
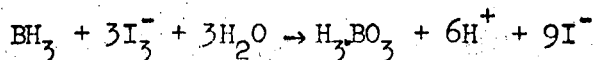
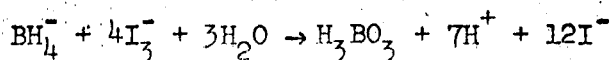
The use of an acidic iodine solution to measure the reducing power of these solutions was found to be satisfactory since 1) the reduced form (I^-) is colorless while the unreduced form (I_2 or I_3^-) is highly colored, (and thus, the transition can be easily observed), 2) the I_3^- complex is soluble in cold 7.8 M HCl solution to the extent of at least 0.1N, permitting the reducing solution to be titrated with a cold solution, and thus prevent warming and decomposition of the former, and 3) the analysis procedure is simple to use. Unfortunately there are also two drawbacks in the use of the iodine solution, namely 1) reaction of the iodine with the reducing species is slow near the end point, and lengthy persistence of the iodine color may cause one to believe that the end point has been reached when this is not really the case, and 2) the sodium thiosulfate used to standardize the acidic iodine solution decomposes at a moderate rate in acid solution; thus care must be taken to swirl the solution vigorously during the titration to avoid a local buildup and subsequent decomposition of the thiosulfate.

The results obtained with the iodine method appear to be reliable, however. The results were verified by measuring the hydrogen evolution from decomposition of a known volume of solution of known normality. As one would expect, twice as many equivalents of reducing agent were observed as millimoles of hydrogen liberated for the same volume or weight of solution. [That this must be so can be seen from considering the following three equations, which represent possible hydrolysis reactions:



In each case there are twice as many electrons transferred (8, 6, and 4, respectively) as molecules of H_2 produced (4, 3, and 2, respectively).]

The equations for the iodine titrations are



Since the hydrolysis reaction for the reducing species occurs to an observable extent only when the temperature of the solution is above about -45° , the titration reactions occur essentially exclusively when a cold reducing solution is titrated with a cold iodine solution.

(Note: To get a rough idea of the % yield of reducing species, consider the following: Since 8g (0.148 moles) of KBH_4 were used per 100 ml of solution, a 2 N solution of reducing species would represent a yield of 33.8% if the species were BH_2^+ , or 22.5% if it were BH_3 .)

B. Nuclear Magnetic Resonance Studies

In principle, B^{11} and proton NMR spectroscopy are the most powerful tools available for elucidating the composition of the unknown reducing species. If the fine structure of the B^{11} spectrum can be observed, $(2n+1)$ peaks will be seen, where n is equal to the number of hydrogen atoms bound to the boron nucleus.

Measurements had to be made at -50° , where, unfortunately, the viscosity of the solvent was quite high. Increased viscosity causes more facile relaxation processes, which leads to broadening of the spectral lines. In the case of B^{11} spectra in particular, the peaks are also broadened because of the effect of the electric quadrupole moment of boron. Since spectral fine structure cannot be observed when the line width is greater than the coupling constant of the material, no fine structure was observed in the B^{11} spectra of the reducing solution. (Coupling constants for B-H coupling are typically 120 cycles, while the observed peak was greater than 1000 cycles wide.) From the fact that a peak was observed at all, however, one was able to conclude that the solution contained a boron species. Chemical shift measurements of the reducing solution, as well as of boric acid with reference to BCl_3 , were then made, in order to prove that the boron species observed in the reducing solution was not simply dissolved boric acid. Since the data showed that the chemical shift of the reducing solution was different from that of known boric acid, it was concluded that the reducing species contained boron and was different from boric acid. From the relative shifts, it was also noted that the peak of the reducing solution lay upfield of both boric acid and boron trichloride. Spectra of a reducing solution which had been allowed to decompose were then recorded. Chemical shift studies indicated that the value of the shift, within experimental error, was the same as that for boric acid. Thus, it was concluded that the reducing species decomposes into boric acid on warming.

Attempts were made to reduce the viscosity of the solutions by using partially alcoholic solvent systems, but these did not vary the lines appreciably, and splitting still could not be observed.

Since B^{11} has a nuclear spin of $3/2$, its interaction with hydrogen atoms attached to it would give a proton NMR spectrum containing four equally-spaced equal-sized peaks. Such was the case with a solution of KBH_4 in KOH at room temperature. No such peaks were observed with the cold reducing solution however, even when it was prepared in an alcoholic-HCl solution.

Since KBH_4 is a symmetrical molecule, where quadrupole effects are unimportant, one would not expect other B-H species with unsymmetrical structures to be seen as readily, particularly at lower temperatures, where the proton-boron interaction would be greater and the peaks broader.

Proton NMR spectra were then recorded for a solution which was 0.8 M in $[(CH_3)_3N]_2BH_2^+ I^-$, an unsymmetrical molecule containing a known B-H bond. Cold 7.8 M HCl was used as the solvent, in order to duplicate conditions of the reducing solution spectra as closely as possible. The expected four equivalent peaks were not observed, however. Even a room temperature 2 M solution of this compound, in 7.8 M HCl, did not yield the expected peaks. In light of this, it was not too surprising that spectra of the reducing solution did not show these peaks. Rapid exchange between the hydrogen atoms attached to the boron and those in the solvent is a possible explanation for this behavior. $[(CH_3)_3N]_2BH_2^+ I^-$ is extremely inert,⁸ even in very strong acid solutions at elevated temperatures, implying that there is little hydridic character in the boron-bound protons. In addition, the work of Jolly and Mesmer,¹⁷ indicates that the hydridic hydroborate ion, even in basic solution, exchanges somewhat with the protons in the solvent. The rate of exchange increases with a decrease in pH, indicating acid catalysis. Thus, it is quite conceivable that the protons attached to boron in a species such as BH_2^+

might exchange rapidly with the solvent.

Since spectra usually are recorded at high amplitude to enable the expected small peaks due to the B-H interaction to be seen, the width of the water peak at the baseline (including the large first sidebands) was often several hundred cycles wide. Since the expected peaks might lie in this region (at least in part), a reducing solution was made using D_2O -DCl in place of the H_2O -HCl solvent. The H_2O peak was very much diminished (there is a small amount of H_2O present in the D_2O), but again, no group of four peaks was observed. This data points further to the possibility of an exchange reaction (although broadening due to increased viscosity might also account for the same phenomena.)

The spectrum of a room temperature sample of BH_4^- (in basic solution) can easily be seen, even with BH_4^- concentrations as low as 0.05 M (probably for two reasons: 1) Because BH_4^- is a symmetric molecule, and quadrupole effects would not be important and 2) in basic solution BH_4^- does not exchange very rapidly.¹⁷ When the spectrum of the solution prepared by plunging pellets of reducing solution into cold sodium hydroxide (-10 to -20°) was recorded, no BH_4^- (or other B-H species) was observed, indicating that the concentration of BH_4^- was less than .05 M and possibly that none was formed. The latter situation implies that disproportionation of the reducing species to hydroborate and boric acid upon neutralization does not occur.

The spot tests with Co^{++} and Ni^{++} also indicated the absence of BH_4^- in the neutralized reducing solution. (Tests which were sensitive to about $3 \times 10^{-3} M$ BH_4^- were used, but no BH_4^- was found.)

C. Chemical Tests: Diborane Reaction, Ether Extraction

When diborane came in contact with cold 7.8 M HCl, a reducing species was formed. This indicates that the unknown reducing species whose composition we are trying to determine, might consist of or have gone through, a borane intermediate.

If the unknown consisted of a borane intermediate however, one might expect it to be extractable into ether. This was not found to be the case. One cannot eliminate the BH_3 composition on this basis however, since the possibility of extraction into ether would depend on the relative strengths of the solvent-solute interaction (i.e., the distribution coefficient) of BH_3 with respect to each solvent.

D. Boron Analyses

The results of the analyses of boron content in a cold, filtered solution of reducing agent are consistent with a BH_2^+ composition, although they do not point to this with certainty. The ratio of the milliequivalents of reducing agent to the millimoles of boron gave values of 3 to 4 for the aqueous hydrochloric acid system, and values between 4 and 5 for the alcohol acid system. Since the results in the former case might be somewhat low, and those in the latter case somewhat high, a ratio of four seems likely. This means that the ratio of hydrogen to boron in the reducing species is two.

The results obtained for the ratio in the aqueous acid system may be somewhat low because there may have been excess boron present in the solution (due to supersaturation of the solution with boric acid). The correction used for the solubility of boric acid would then be too small, giving a value for the ratio which is too large. (This supersaturation

consideration is plausible since the solution is viscous and precipitation would be inhibited. In addition, boric acid does not precipitate from a reducing solution which has been allowed to decompose, until the temperature is quite high (perhaps -20°). Finally, B^{III} spectra could be recorded for boric acid when a room temperature solution of the known compound was cooled to -45° , where its solubility is quite low.)

The results obtained for the ratio in the alcoholic acid solution may be somewhat high because of losses in obtaining the solid boric acid to be analyzed. The technique used for analysis of the alcoholic solution involves precipitation of the boric acid, filtration, and analysis of the solid. It is possible that some of the solid may have been washed through the filter and not have been analyzed. In addition the alcoholic solution may have warmed sufficiently during filtration, to dissolve more H_3BO_3 than would be soluble at the original temperature of the reducing solution. As a result the boron content which was found might be low and the ratio of hydrogen to boron, high.

Thus, the average of the values obtained for the ratio by the two methods, would be about 4, the ratio of hydrogen to boron would be about 2, and the composition would be BH_2^+ . Because of the magnitude of the deviations of these values from the mean, however, it is felt that one cannot conclude with certainty that the unknown species is BH_2^+ . Rather, one can say that this composition is consistent with the data.

E. Trimethylamine Adduct

Since the unknown species might be aqueous BH_2^+ , and since the known bistrimethylamine complex of BH_2^+ is stable at elevated temperatures, even in strong acids and 10% NaOH, the preparation of this complex from

the reducing solution was attempted. $[(\text{CH}_3)_3\text{N}]_2\text{BH}^+\text{I}^-$ has never been prepared in aqueous solution however, organic solvents or high pressure techniques usually being invoked. Thus the feasibility of this experiment was somewhat uncertain.

If the complex can indeed be formed by passing trimethylamine into a cold neutralized solution of the reducing agent, other problems arise in the detection of such an adduct. Huge quantities of KCl from the neutralization, as well as excess NaOH, and probably some boric acid and trimethylammonium chloride as well, are formed. Since the adduct would be present in small quantities, and is soluble in water, separation would be extremely difficult. Some attempt was made at separation, or at least concentration, of the adduct by extractions with methylene chloride, in which the adduct is reported to be soluble.⁸ An infrared spectrum of the solids obtained by boiling the methylene chloride solution to dryness were recorded and compared with that of the known adduct (see Figs. 6-8). A peak at 4 microns typical of the B-H stretching mode, was absent in the unknown solid, however.

The attempts at isolation of the solid by the methylene chloride extractions may have been unsuccessful for the following reasons. Extraction of the adduct from an aqueous solution into methylene chloride depends on there being a high distribution coefficient between the two layers, which is not necessarily the case. Extraction with methylene chloride of the solid formed from completely boiling down the alcoholic solution, although offering the possibility of more success if the adduct is present, also relies on the fact that the adduct is not destroyed on boiling the crude bulk solution to dryness. Since a proton NMR spectrum indicates that the known solid complex may decompose upon warming to 60°

in 40% NaOH, this change could also occur as the bulk salt solution is concentrated and boiled to dryness, since excess NaOH is present.

Attempts at demonstrating the existence of a B-H band in the bulk of material obtained by boiling the neutralized solution to dryness were also unsuccessful. Neither a known sample of the adduct, nor the crude bulk of material just mentioned, when heated in concentrated sulfuric acid at 240°, for 16 hours yielded any hydrogen. Thus either the conditions for destruction of the adduct were not severe enough, or the hydrogen atoms attached to boron are non-hydridic and will never react with acid to produce hydrogen.

IV. SUMMARY

An attempt was made to identify the reducing species formed when potassium hydroborate is added to a cold hydrochloric acid solution, after procedures for preparing fairly concentrated solutions and analyzing them had been worked out and checked. B^{11} NMR indicated that the species contains boron, and that it resonates at higher field than either boric acid or boron trichloride. Proton NMR studies, including the use of deuterated solvent systems, as well as methanolic ones, revealed no information about the compound, but indicated the possibility of exchange of boron-linked hydrogens with those of the solvent. It was then found that a reducing solution can be synthesized from cold acid and diborane, indicating the possibility of a borane intermediate in either the formation of the reducing species or as the reducing species itself. Disproportionation of the reducing species to hydroborate and boric acid could not be detected. The reducing material was found not to be extractable into ether in any appreciable quantity. A boron to hydrogen analysis on the unknown reducing species was consistent with a BH_2^+ composition for the unknown, but there is some uncertainty associated with the results. Finally, attempts at preparation of a $[(CH_3)_3N]_2BH_2^+ I^-$ species from the unknown reducing species, and subsequent isolation or identification of the compound were unsuccessful.

It seems possible that the unknown material is a BH_2^+ species, but until better procedures for preparation and isolation of a stable adduct can be worked out, the question remains unresolved.

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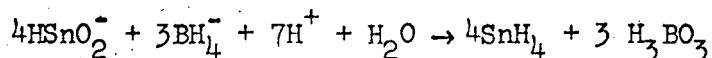
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APPENDIX

Investigations of an Unstable Yellow Tin Compound

Stannane, SnH_4 , can be prepared by addition of a stannate (II)-hydroborate solution to 6 M hydrochloric acid at 0° , according to the reaction:



(where stannate (II) ion is prepared by slowly adding a solution of stannous^S chloride to a solution of potassium hydroxide).

As soon as the stannate (II)-hydroborate solution touches the acid solution, a transient yellow solid is formed. It is likely that this yellow material is an intermediate in the formation of SnH_4 from Sn(II) , and thus its composition was of interest.

Before the yellow species could be studied, however, it had to be stabilized for longer periods of time. It was found that if a 7.8 M HCl solution was used in place of the 6 M one, a temperature of about -88° could be obtained before the solution froze (7.8 M corresponds to a eutectic composition of the hydrochloric acid-water system). The yellow material was found to be quite stable at temperatures of about -45° , persisting for at least several hours at this temperature, with no apparent darkening. It was also found that the material could be prepared in air, as well as in vacuo.

The yellow material forms a suspension in the cold acid in which it is formed, and early attempts to collect it by filtration were unsuccessful, due to its high viscosity. Methanolic acid solutions were also used in an attempt to make the solution less viscous and more filterable, but these also were unsuccessful.

A more careful study of the stability of a methanolic solution of this yellow material revealed that upon warming, the yellow color persisted until about -20° , and then faded gradually until about -12° , when the remaining color disappeared rapidly. Since a cold room, thermostatted at about -27° , was available, isolation of the yellow material from the solution was attempted in this environment. Conventional filtration of the solution was not successful. However, centrifuging the solution in a centrifuge machine which had been pre-cooled to the temperature of the cold room, did succeed in concentrating the solid in the bottom of the tube.

When the solid thus obtained was allowed to warm up and decompose, the residue consisted of a small amount of black material (probably Sn or SnO), mixed with some white material (probably boric acid and potassium chloride).

If boric acid could be eliminated from among the solids filtered with the yellow material, a boron spot test and/or a quantitative analysis for boron on the unknown solid, or on the decomposed solid, would reveal whether or not the yellow material contained boron. Thus various alcohols were used in an attempt to find a solvent in which boric acid would be soluble enough at low temperatures to prevent precipitation (1g./50 ml). None was found to be very effective, however. Even when mannitol, which forms a complex with boric acid, was added to the 7.8 M acid solution, the solubility was only increased by an estimated 10%.

Later analysis of the white material mentioned above showed that it consisted predominantly of KCl. (The infrared spectrum of the white material did not show the peaks at 8.4 and 18.3 microns, which are typical of boric acid. Flame tests on some of the solid revealed potassium

(purple flame), but no boron (green flame). Finally, the melting point of the solid was greater than 330° , while boric acid melts with decomposition at 185° , and boils with loss of $1\frac{1}{2}$ H_2O at 300° .¹⁸⁾

When the reaction was run using NaCl and $NaBH_4$ instead of the potassium salts (in an attempt to eliminate KCl precipitation), NaCl was obtained in large amounts, although its solubility was expected to be considerably greater than that of KCl at these temperatures. (The slope of the solubility vs temperature curve for KCl is much greater than that for NaCl.)

A measurement of the ratio of hydrogen to tin in the yellow material was attempted next. The yellow material was prepared in HCl solution on the vacuum line, in the original manner. When all the gases formed in preparing the yellow material were pumped off, the latter was warmed to room temperature, decomposed, and the amount of hydrogen evolved measured with a Toeppler pump. (A trap immersed in liquid nitrogen trapped any SnH_4 that may have been formed. This was then decomposed to Sn and $2H_2$ per SnH_4 , by heating the closed trap to 150° . The trap was then cooled in liquid nitrogen, opened, and the non-condensable gases pumped off and measured.) The original weight of tin in the system was known and, assuming 100% conversion to this yellow material, the ratio of the moles of hydrogen to the moles of tin in the compound was calculated. Values of 3.4, 3.4, and 3.7 were obtained from three runs. (Very little of the material went to form stannane, but a correction for the amount of tin lost in this way was made.)

Since these ratios were quite a bit different from integral values, it was decided that a blank run, without tin, but with everything else the same as in previous runs, would be made (the difference between the

hydrogen solubility at room temperature and that at dry-ice temperatures, for example, might be considerable). Thus, a basic solution of KBH_4 was added slowly to the cold HCl solution. After pumping off all gases which had been formed (from hydrolysis of the BH_4^- , etc.), the solution was warmed to room temperature, and the non-condensable gases measured. Practically the same amount of hydrogen was obtained as before, when the stannate (II) solution had been used. Since this amount of hydrogen was too great to be attributed to solubility differences of the gas at the different temperatures, the formation of a species at the low temperatures, which liberated hydrogen upon warming, was suspected. Since it was possible that this species was a reducing agent, a cold solution of I_2 in 7.8 M HCl was added. It was reduced to I^- , as shown by the disappearance of the red-brown iodine color, confirming that a reducing species was present in the cold solution.

Although no further experiments on the yellow tin material were performed subsequent to this discovery, at least two suggest themselves:

1) The isolated yellow solid should be tested for the presence of boron. (If Sn^{++} formed a complex with the boron species which was the main subject of this thesis, the complex would be expected to be stable at temperatures as high as -20° , while the boron species without stannous decomposes at temperatures above -50° .) If the yellow material could not be isolated in pure enough form to make a boron analysis meaningful, attempts could be made to prepare the yellow material with other reducing agents in place of BH_4^- . (If a yellow ppt resulted in any of these cases, it would be evident that boron was not necessary for formation of the yellow material.)

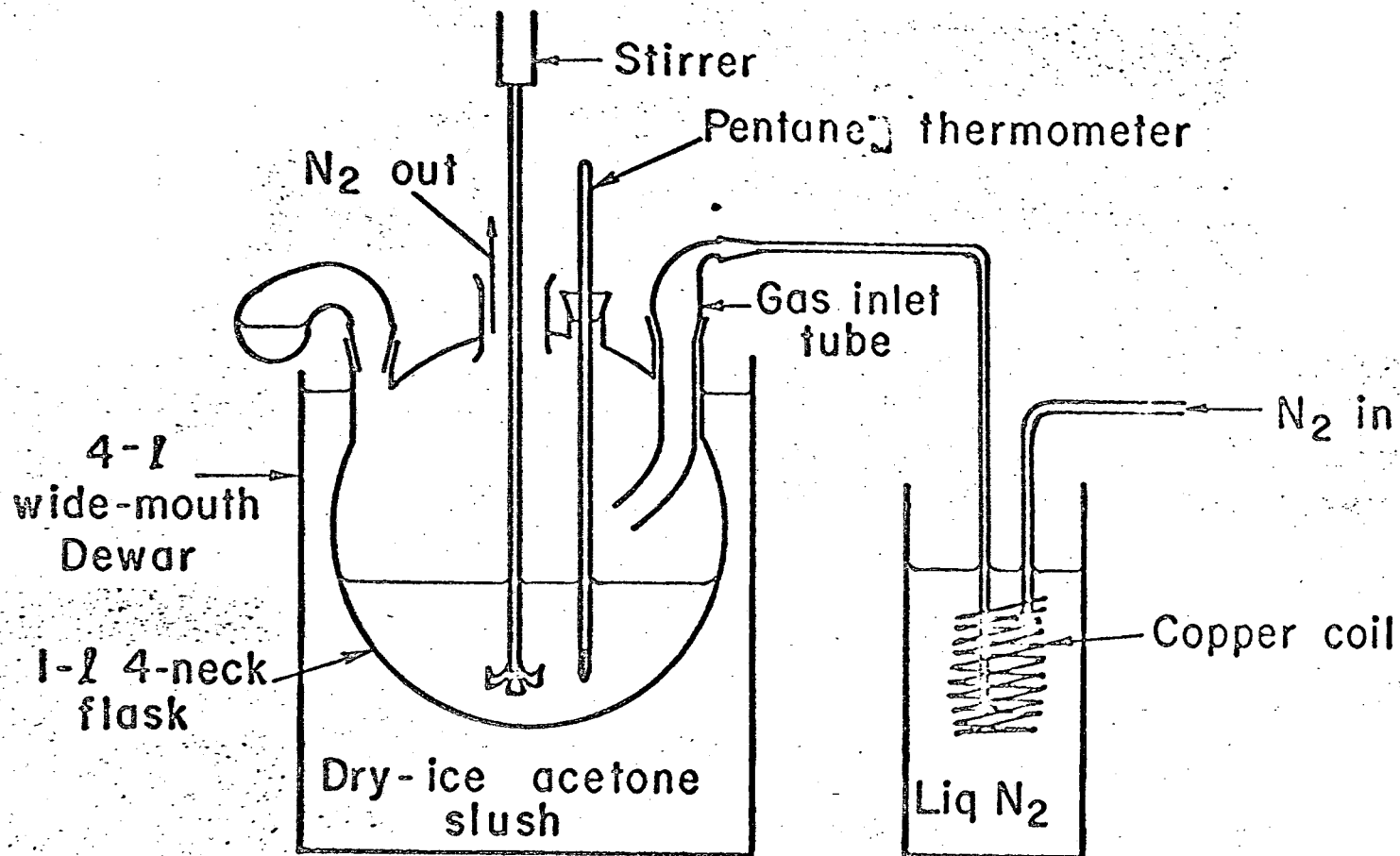
2) If the yellow material did not contain boron, and thus did not contain the unknown reducing species, the solid (still containing some

KCl and some H_3BO_3 , since these wouldn't interfere and needn't be removed) could be centrifuged, filtered, and then attached to a vacuum line, either in dry form or slurried in a 7.8 M HCl. The yellow material could then be decomposed, the hydrogen measured, and the amount of tin present analyzed by a suitable quantitative analysis scheme. (The yellow material would have to be separated from the solution in which it was prepared, prior to the H_2 analysis, however, because the boron-containing reducing species which would also be formed would also liberate hydrogen on warming.) (It might be found that the unknown consisted of SnH_2 , which is analogous to the known (yellow) germanium compound, GeH_2 .)

FIGURE CAPTIONS

- Fig. 1 Apparatus for Preparation of Reducing Solution.
- Fig. 2 Filtration Apparatus.
- Fig. 3 Crosscheck Apparatus.
- Fig. 4 Flask-to-Vacuum-Line Connector.
- Fig. 5 Proton NMR Spectrum of 0.05 M KBH_4 in 0.5 M KOH.
- Fig. 6 Infrared Spectrum of Methylene Chloride Extract.
- Fig. 7. Infrared Spectrum of Aqueous Layer Concentrate.
- Fig. 8 Infrared Spectrum of Known $[(\text{CH}_3)_3\text{N}]_2 \text{BH}_2^+ \text{I}^-$.
- Fig. 9 Sample Tube for B-H Bond-Breaking Experiment.

Fig. 1.



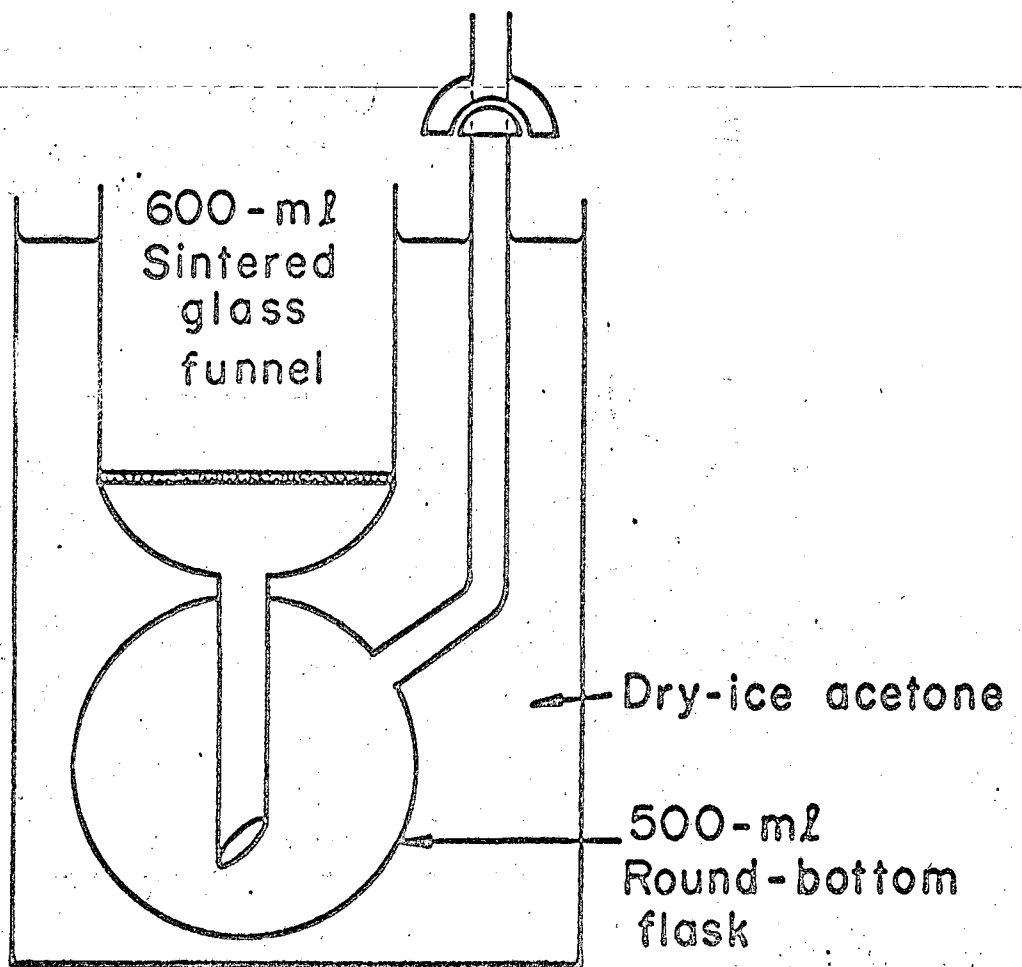


Fig. 2.

Filtration Apparatus

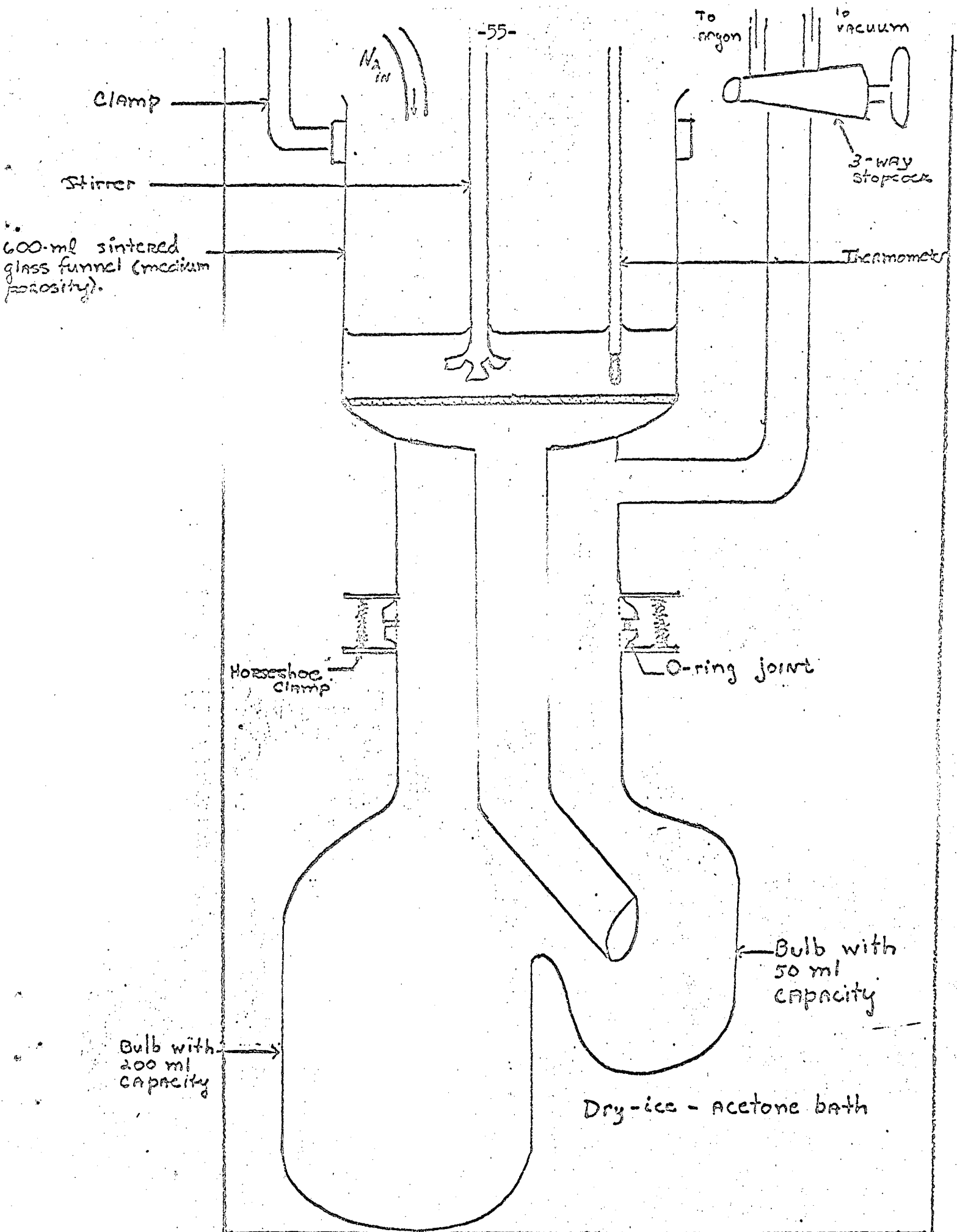


Fig. 3 Crosscheck Apparatus.

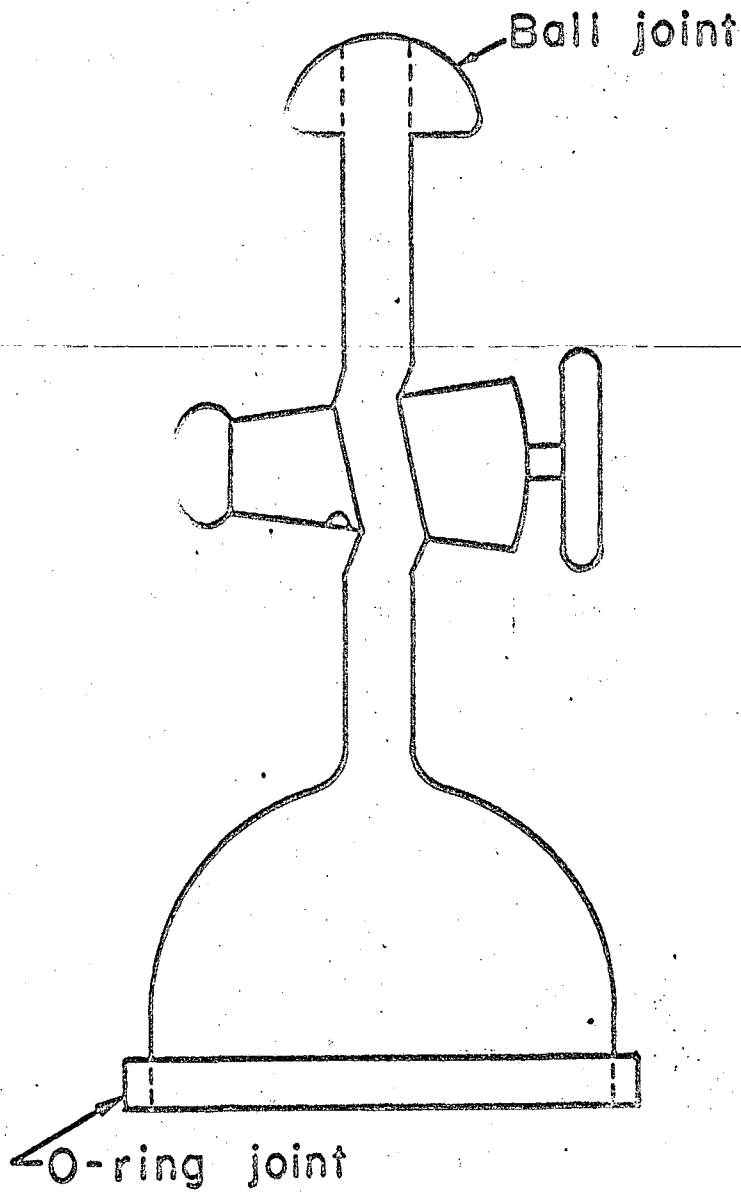


Fig. 4.

Flask-to-Vacuum-Line Connector

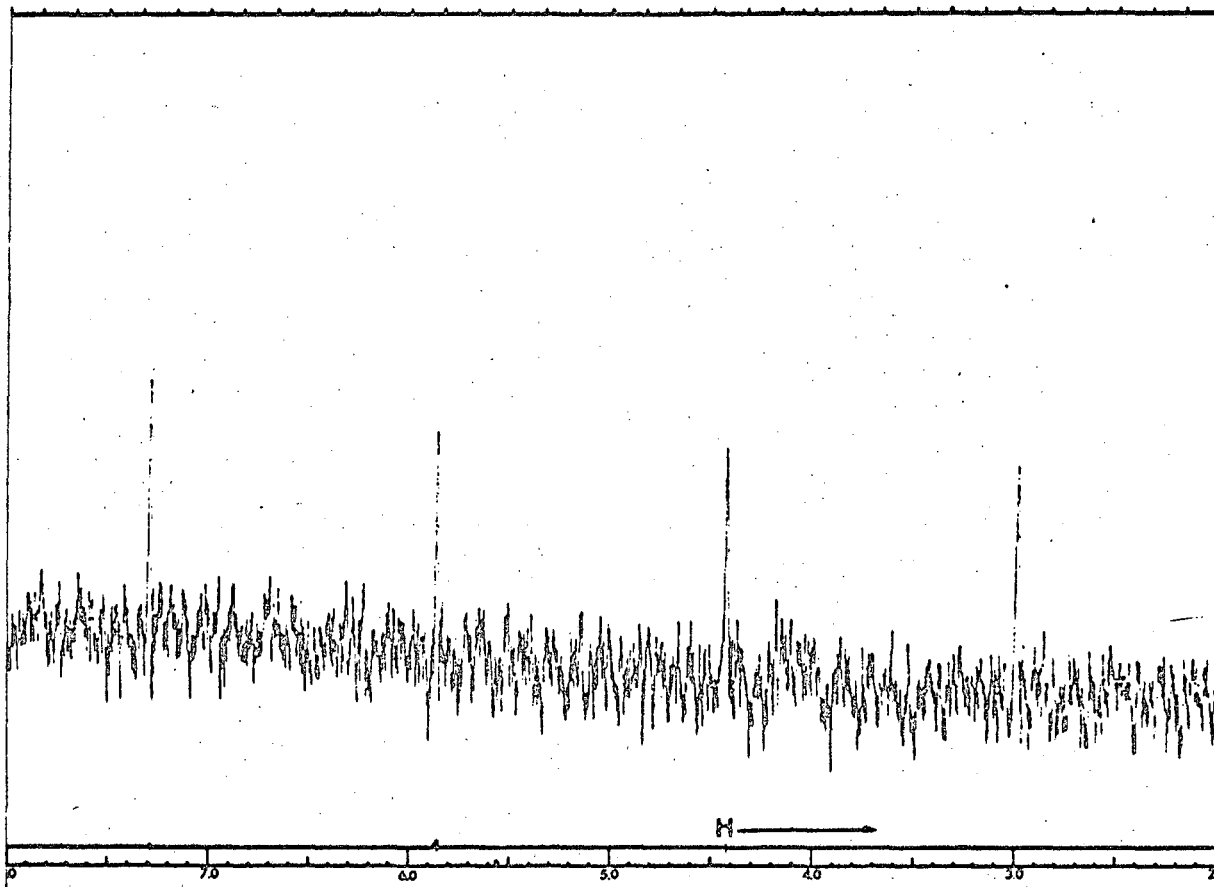


Fig. 5.

Proton NMR Spectrum of 0.05 M KBH_4 in 0.5 M KOH .

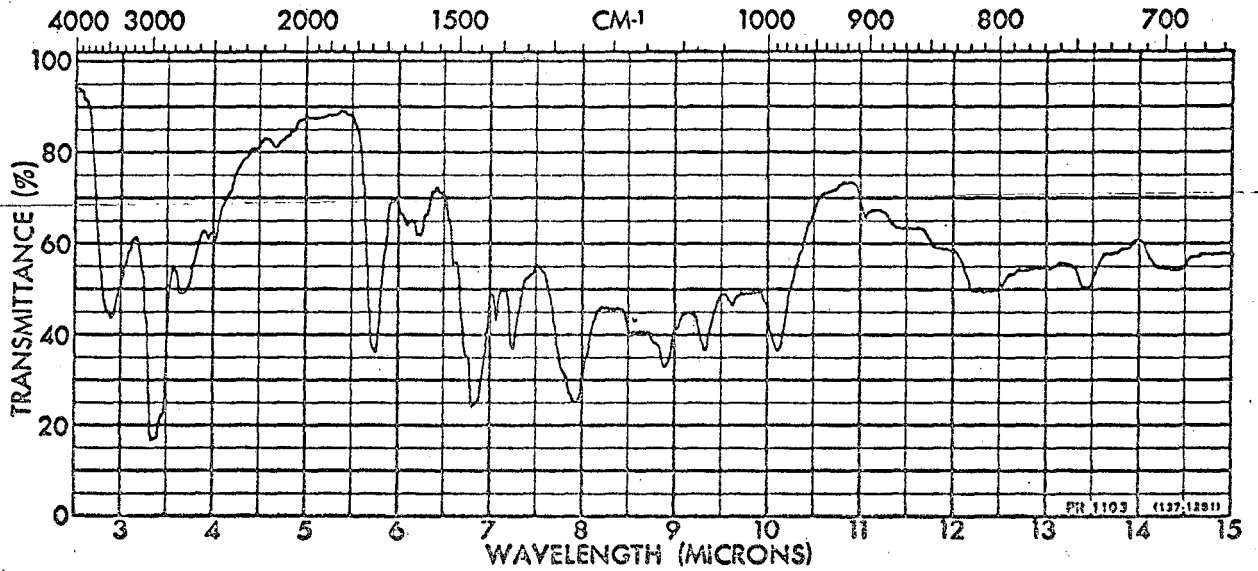


Fig. 6.

Infrared Spectrum of Methylene Chloride Extract.

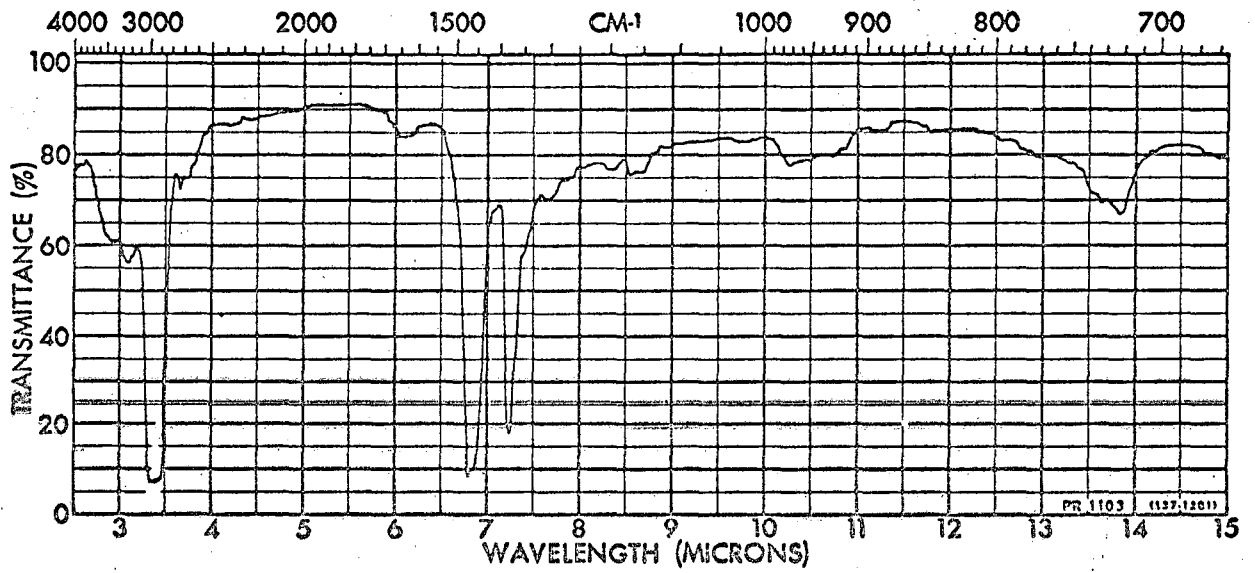


Fig. 7.

Infrared Spectrum of Aqueous Layer Concentrate.

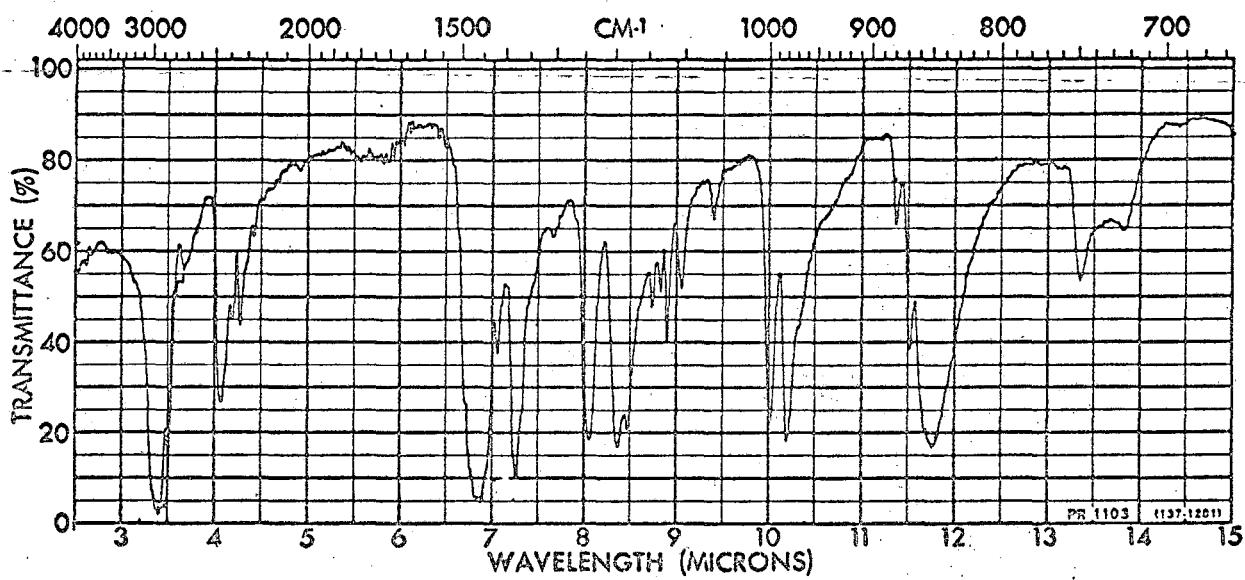


Fig. 8.

Infrared Spectrum of Known $[(\text{CH}_3)_3\text{N}]_2 \text{BH}_2^+ \text{I}^-$.

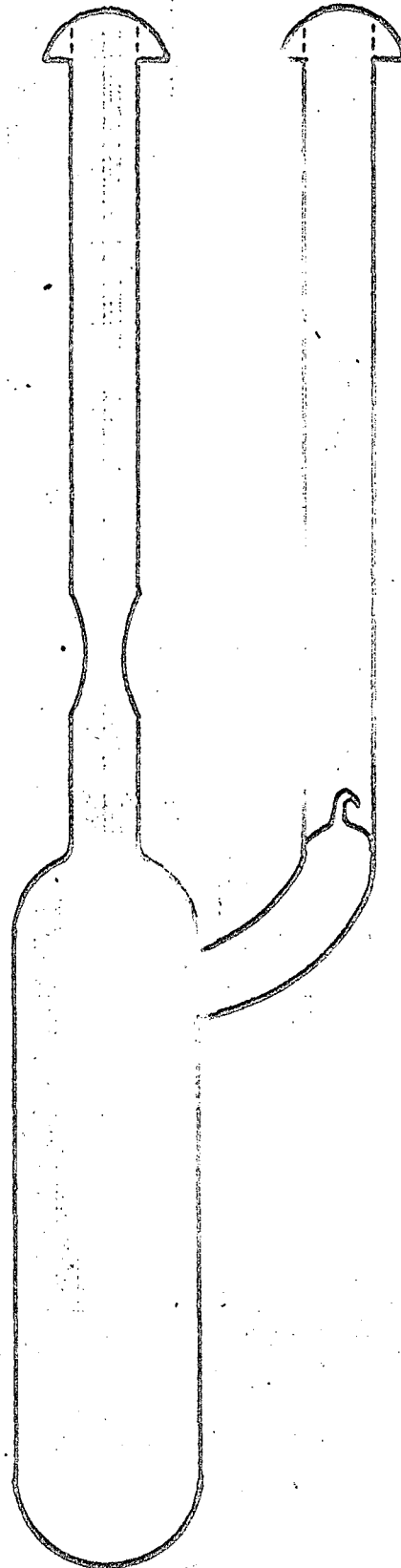


Fig. 9

Sample Tube for B-H Bond-Breaking Experiment.

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