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INFRARED SPECTRA OF BISMUTH TRIFLUORIDE
AND CHLORODIBORANE. ATTEMPTED PREPARATION
OF BISMUTH HYDRIDE FOR INFRARED STUDY.

RALPH A. TURNER, JR.

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ATTEMPTED PREPARATION OF BISMUTH HYDRIDE FOR INFRARED STUDY.

by

Ralph A. Turner, Jr.

This work is accepted as fulfilling
the thesis requirements for the degree of
MASTER OF SCIENCE

from the
United States Naval Postgraduate School

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ATTEMPTED PREPARATION OF BISMUTH HYDRIDE FOR INFRARED STUDY

by

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Lieutenant, United States Navy

NO FORN

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE

United States Naval Postgraduate School
Monterey, California

1962

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ABSTRACT

I. Bismuth trifluoride was prepared as a precipitate from the addition of potassium trifluoride to a solution of bismuth nitrate dissolved in nitric acid. Infrared spectra of Nujol mulls and cesium bromide pellets containing bismuth trifluoride gave only two of the four absorption bands expected. One band was at 523 and the other a broad band at 258 wave numbers. Due to equipment limitations, it was not possible to go further out in the infrared range below thirty-eight microns to obtain the other two absorption bands.

II. The production of sufficient quantities of bismuth hydride (bismuthine) for infrared study was attempted by two methods. The method used by Paneth in 1919 involved preparing a magnesium-bismuth alloy. The alloy was treated with acid; bismuth hydride was reported as one of the gaseous products evolved. The second method of production was proposed by Schaeffer in 1954. Lithium borohydride in aqueous solution was added to a solution of bismuth trichloride dissolved in hydrochloric acid. In both methods, mechanical detection or infrared study of the gases evolved failed to indicate the presence of any material that could be bismuth hydride.

III. The lithium borohydride used in the attempted production of bismuth hydride by the Schaeffer method was obtained commercially and contained chlorine as an impurity. The gas from the hydrolysis reaction with sulfuric acid gave the diborane spectra. The infrared spectrum of the gas evolved from the hydrolysis of the commercial lithium borohydride with hydrochloric acid, water and sodium hydroxide is thought to be that of chlorodiborane. This conclusion was based on the elimination of possible products, molecular weight determinations of the condensable gas and other physical characteristics. No spectra comparison with chlorodiborane or a similar gas produced by another method was used. Contrary to previously published data, the chlorodiborane did not dissociate to any notable degree for time periods of 120 hours.

The writer wishes to express his appreciation for the assistance and encouragement given him by Professor J. W. Schültz of the U. S. Naval Postgraduate School in these investigations.

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INFRARED STUDY OF BISMUTH TRIFLUORIDE

1. Preparation of Bismuth Trifluoride (BiF_3)

Several attempts to produce bismuth trifluoride by dissolving the bismuth oxide (Bi_2O_3) in excess hydrofluoric acid and evaporating the solution to crystallize the acid salt $\text{BiF}_3 \cdot 3\text{HF}$ followed by heating the latter until hydrogen fluoride was completely expelled /1/ produced unsatisfactory results.

Bismuth trifluoride was produced by dissolving bismuth nitrate $\text{Bi}(\text{NO}_3)_3$ in nitric acid (HNO_3) and adding potassium fluoride in aqueous solution to precipitate the bismuth trifluoride. /2/ In the actual reaction 1.1 grams of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were dissolved in 50 ml of 1.28M HNO_3 ; at room temperature vigorous stirring is required to effect the dissolving of $\text{Bi}(\text{NO}_3)_3$ in the acid. The stoichiometric amount of KF required is 0.492 grams; however, one gram of KF dissolved in 50 ml of H_2O was added to the $\text{Bi}(\text{NO}_3)_3$ solution. When the KF solution was added, a finely dispersed white precipitate of BiF_3 was obtained. The precipitate was allowed to settle, and excess liquid decanted from the precipitate. This was followed by three washings in water until the precipitate was neutral to litmus paper. The BiF_3 was then dried in an oven at 100°C . for twenty four hours. The powder was hand ground in an agate pestle and mortar. A sample of the powder was treated with water; no fluorine gas was detected. However when BiF_3 was treated with 3M H_2SO_4 , the liberated fluorine gas etched the watch glass upon which the reaction was carried out.

Spectra were obtained on a Perkin-Elmer Model 221 spectrophotometer equipped with CsBr and NaCl prism-grating interchange. Two sampling techniques were used. Nujol mulls were prepared and pressed between CsBr plates. The effect of varying the mull film thickness and the amount of BiF_3 in the mull had little effect on the observed spectrum within the limits of this sampling technique. The spectrophotometer was used with a slit program of 970×2 , attenuator speed of 7:00, drum speed of 32, gain at 6.0 and scale of 0.5 micron per centimeter for the CsBr region. No absorption bands were observed in the NaCl region.

The second sampling technique used involved making infrared transparent pellets or disks of CsBr and BiF_3 . Amounts of 0.001 to 0.003 gram of BiF_3 were mixed with 0.3 gram of finely powdered CsBr. The mixtures which gave the best pellets were obtained by subjecting the sample-filled mold to five minutes of vacuum treatment and then compressing the material at 20,000 psig for five minutes while still under the vacuum. Clearer pellets were obtained when the BiF_3 mass was held at approximately 0.001 gram. The spectrophotometer settings were the same as those used for the mulls. No bands were observed in the NaCl range. Both sampling techniques gave the same infrared spectrum for the BiF_3 in the CsBr range (Figure 1).

2. Conclusion.

Herzberg /3/ in his discussion of the trihalides of bismuth states that all these compounds studied have four fairly strong Raman lines. On this evidence it is assumed that these molecules have a structure in the form of symmetrical pyramids (point group C_{3v}). While BiF_3 was not discussed per se, it is reasonable to assume that it also has the same structure.

From the spectrum obtained there are two absorption bands at 523 and at 258 wavenumbers. The band at 258 wavenumbers is a broad band. The other two bands were below the range of the equipment. As a comparison, BiCl_3 has observed frequencies at 288, 130, 242, and 96 wavenumbers as determined by the Raman Spectrum.

The infrared study gave only two of the four principal bands of BiF_3 . Further study of this compound will require absorption spectra in the infrared range beyond 38 microns. This is not possible on the present equipment.

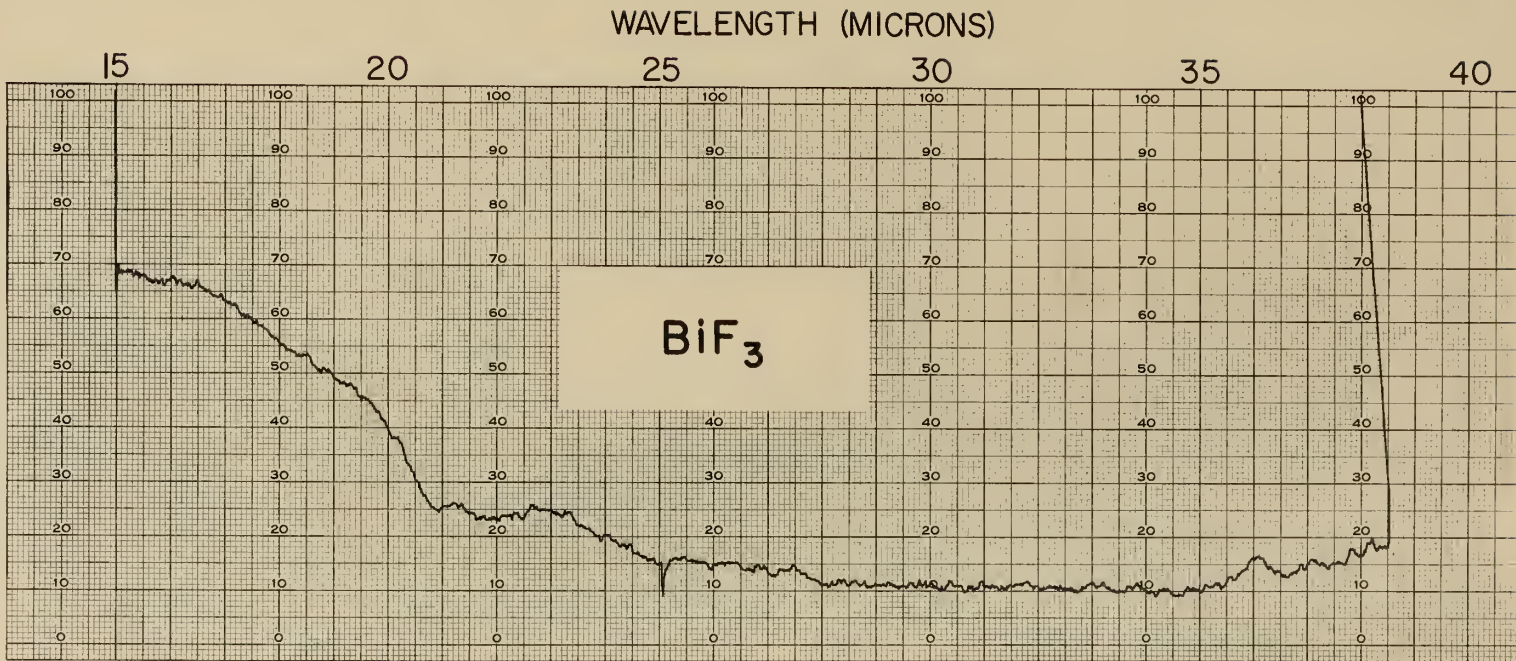


Figure 1
Infrared Spectrum of Bismuth Trifluoride

ATTEMPTED PREPARATION OF BISMUTH HYDRIDE (BISMUTHINE)

1. Introduction.

The existence of bismuth hydride (BiH_3) was proved by Paneth and Winternitz /4/ by the use of radioactive isotopes of bismuth. An alloy of Mg-Bi was prepared by heating equal weights of the powdered metals to a dark dull red glow (approximately 1200°F) for 45 minutes in an atmosphere of dry hydrogen gas. The partly fused, partly sintered alloy was powdered and then treated with 4N acid. The gases evolved were carried by dry hydrogen through a filter of wadding to a Marsh tube where the presence of the unstable hydride was detected by formation of a radioactive bismuth mirror upon heating the tube. The presence of BiH_3 was also detected by bubbling the evolved gas through silver nitrate. The bismuth reacts with the silver and precipitates as Ag_3Bi which is black in color. /5/

Pearson, Robinson and Stoddart /6/ attempted to produce BiH_3 in 1933 by the reaction of atomic hydrogen and molecular hydrogen with bismuth and were unsuccessful. G. W. Schaeffer and Sister M. Emilius, OSF /7/ in 1954 proposed a method of making the hydride using bismuth trichloride and lithium borohydride (LiBH_4) based on their work to produce the tin hydride. Their proposed basic method was used by Von Egon Wiberg and Kurt Mödritzer /8/ in 1957. An ethereal solution of BiCl_3 was mixed with LiBH_4 at -80°C , and the moderately turbulent reaction resulted in separation of elementary Bi and the violent evolution of hydrogen and diborane. The gases were trapped in liquid air and distilled off leaving only a trace of metallic Bi which the authors concluded was from the decomposition of the hydride BiH_3 .

All authors when discussing the reaction of LiBH_4 and BiCl_3 conclude that the reaction is:



2. Experiment.

In general the object of the experiment was to produce enough BiH_3 to obtain an infrared spectrum and to complete and correlate all the hydrides of the Group V elements.

(a) Paneth method.

The production of an Mg-Bi alloy required a flux to prevent the oxidation of Mg during the formation of the alloy. The flux used consisted of 34% KCl , 42% MgCl_2 , 14% CaF_2 , and 10% MgO (all weight percent) salts ground and mixed. Six attempts were made to obtain the Mg-Bi alloy using 20 grams each of Mg and Bi in each experiment. The Bismuth's greater density caused it to settle to the bottom on mixing with the lighter Mg, thereby giving two separate metal layers for two runs. The mechanical mixing of the two metals when melted resulted in such a fine dispersion of metal and flux that two additional runs were of no use. Two attempts gave reasonable appearing results. One was obtained by keeping the Mg (M.P. 1203.8°F) slug under a very thin flux for 40 minutes at 1200°F and then placing unmelted Bi (M.P. 519.8°F) metal powder over the flux and heating for an additional 45 minutes at 1200°F . The high density Bi passed through the flux giving a reasonable mixture of the Mg and Bi. The second successful alloy was obtained by placing the Bi metal powder over the Mg slug and covering the two metals with a deep flux and heating to 1200°F and holding for three hours. The Mg metal slug used in all attempts was one inch round stock slugs taken from 99%

pure Mg bars. All surfaces were shined with emery cloth to remove oxidized surfaces prior to use.

Five grams of hand-ground Mg-Bi alloy were placed in a three-necked reaction vessel. By using a dropping funnel, 4N H_2SO_4 acid was added to the alloy sample. The reaction vessel was swept with dry hydrogen flowing at about 500 ml per second. The gas evolved was swept through a pyrex tube one cm in diameter which was preheated and heated by a bunsen burner fitted with a wing tip. No bismuth mirror was deposited in five runs. No mirror was obtained using HCl or HNO_3 acid in lieu of the H_2SO_4 acid and at the same normality.

The alloy in the amount of 10 grams was added to the reaction vessel and 4N HCl acid added with the resulting gases trapped in liquid air. The condensate was kept in liquid air and the trap placed on a vacuum rack. The condensate was warmed up in the vacuum, distilled once to remove the water and examined in the infrared using a Perkin-Elmer Model 221 spectrophotometer with NaCl prism-grating interchange. The sample and reference cells were furnished with KBr windows and had a 10 cm pathlength. The spectrophotometer was used with a slit program of 890, attenuator speed of 11:00, drum speed at 16, gain at 4.7, and scale of 50 wave numbers per centimeter.

The infrared spectrum of the gaseous products revealed only the spectrum of a trace of water and a strong band of CO_2 at 2350 wave numbers.

To test the detection method of Weeks and Druce, gases evolved by the reaction of 8.6 grams of the alloy and 200 ml of 6N HCl acid were bubbled through 200 ml of 1 M $AgNO_3$ solution. No precipitate was observed.

(b) Schaeffer method.

To avoid the laborious process of producing Lithium Borohydride (LiBH_4) /9/ and to save time, LiBH_4 was purchased from the Metal Hydrides Company of Beverly, Mass. The material is listed as 90% pure. The purity is determined by a hydrogen evolution assay, and there is no analytical analysis run by the manufacturers. Their estimate of the impurities is lithium chloride and lithium borate.

LiBH_4 is an extremely hygroscopic material and will ignite when moistened. Precautionary measures were taken when handling the material to avoid burns to the user and spontaneous combustion when in contact with cellulose material. The material will dissolve in water if necessary precautions are taken to avoid combustion.

In order to carry out the proposed reaction



3.632 grams of 90% pure LiBH_4 (0.150 mole) were dissolved in 200 ml of water, and 15.7685 grams of BiCl_3 (0.050 mole) were dissolved in 150 ml of 3.2M HCl acid.

The BiCl_3 solution was placed in a 400 ml, three-necked reaction vessel equipped with a magnetic stirrer. The LiBH_4 solution was placed in a dropping funnel which was attached to one neck of the reaction vessel. Dried hydrogen gas was passed into the reaction vessel through a sintered glass filter below the surface of the BiCl_3 solution. The center connection of the reaction vessel served as the exit for the gases evolved in the reaction as well as the hydrogen gas used to sweep the reaction vessel.

The gases were passed through glass piping to a trap packed with pyrex glass wool and immersed in liquid air. The gases leaving the trap were passed through a mercury bubbler under a hood.

After the BiCl_3 solution was in the reaction vessel, the system was assembled and the reaction vessel submerged in an ice bath. The hydrogen gas was turned on and allowed to sweep the system for five minutes at an approximate rate of 500 ml per minute. With the hydrogen gas still sweeping the system the LiBH_4 solution was added initially one drop at a time. The reaction was violent with great quantities of gas evolved and the precipitation of reduced Bi metal. The magnetic stirrer and bubbling hydrogen gas kept the liquid in the reaction vessel in motion and prevented a concentration of precipitated Bi metal from settling. When the reaction had ceased, vacuum stopcocks sealed the trap which was then removed from the system and evacuated on a vacuum rack. The condensed gas was kept solid by keeping the trap submerged in liquid air during transport and evacuation. The gas was distilled once to remove water and then allowed to fill a standard 10 cm gas cell with KBr windows to pressures of 35 mm, 24 mm, and 18 mm on three successive runs. The Perkin-Elmer Model 221 spectrophotometer was used with a slit program of 927, attenuator speed of 11:00, drum speed of 16, gain at 5.6, and scale of 50 wavenumbers per centimeter.

The spectrum obtained was not readily identified as any of the expected products.

The unknown gas was also examined with the spectrophotometer equipped with the CsBr prism, but no absorption bands were seen in the range from 15 to 25 microns.

3. Conclusions.

(a) Paneth Method.

The Paneth method as outlined in the introduction gave no infrared spectrum. It is possible that the hydride of bismuth was produced in such small amounts as to be undetectable in the infrared, or that the BiH_3 produced decomposed prior to reaching the heated portion of the glassware. The AgNO_3 detection method used would also give negative results if the above assumptions were correct. The existence of BiH_3 has not been disproved by the experiments conducted; the methods used may not have permitted detection of very small amounts.

(b) Schaeffer Method.

The spectrum obtained was not that of BiH_3 as seen from molecular weight and the other experiments that are described in the following section. The failure to obtain BiH_3 could be due to the impurities in the commercial LiBH_4 used, or, as outlined for the Paneth method, due to experimental errors.

REACTIONS OF COMMERCIAL LITHIUM BOROHYDRIDE WITH VARIOUS SOLVENTS

1. Experimental.

In the reaction with BiCl_3 dissolved in HCl acid, the LiBH_4 that was added had been dissolved in water in the atmosphere. While combustion of the LiBH_4 when mixed with water was avoided by careful handling, a reaction of an exothermic nature had taken place. In order to determine what if any gaseous products were evolved, one gram of LiBH_4 was placed in a dry three-necked reaction vessel equipped with a magnetic stirrer. The system was flushed by dry hydrogen gas and with the cold trap in the line between reaction vessel and mercury bubbler, 125 ml of distilled water were added dropwise. The spectrophotometer settings were the same as for the HCl , BiCl_3 , LiBH_4 runs. The spectrum (Figure 2) was the same, but absorption bands were much weaker, using 29 mm of sample in the standard 10 cm gas cells.

As an aid to identifying the unknown gas, Raoult molecular weight determinations were made using the ideal gas law and the increase in mass of a glass bulb of known volume. Two determinations were made:

Run	Vol. of bulb (cm^3)	Pressure of gas (mm)	No. of gmoles	Molecular Wt. (g/gmole)
1	223.0	8	9.56×10^{-5}	56.49
2	252.1	17	2.335×10^{-4}	60.06

The temperature for both runs was assumed to be room temperature of 22°C . The second run from experimental considerations would appear to be more accurate as the mass of the unknown gas was greater.

To delve further into the properties of LiBH_4 , one gram of the material was placed in the reaction vessel, and the equipment was

arranged as before. The dropping funnel was filled with 200 ml of 4N H_2SO_4 acid which was added slowly. The spectrophotometer had the same settings as for the previous runs. The infrared spectrum of the condensed gaseous products was that given for diborane /10/ (B_2H_6) with no trace of the unknown (Figure 2).

To continue the investigation, one gram of LiBH_4 was again used in the same manner. The dropping funnel was filled with 200 ml of 4N HCl acid which was added to the dry LiBH_4 . The infrared spectrum was a mixture of the unknown and diborane (Figure 3).

Next the effect of the chloride ion on the production of the unknown was investigated. The equipment and procedures were modified. Water in the amount of 150 ml was added slowly to one gram of LiBH_4 , and the gas evolved was swept by dry hydrogen gas into another reaction vessel where it was bubbled through 300 ml of 0.025M KCl . The gaseous products were trapped and examined in the infrared. The spectrum was that of the unknown with very strong absorption bands using a pressure of 17 mm of the unknown gas (Figure 3).

Using the modified equipment, 150 ml of water were added to one gram LiBH_4 . The gaseous products were discarded and the liquid, when the reaction was completed, was added to 0.031M BiCl_3 dissolved in 4N HCl acid. The gaseous products of this reaction were trapped and their spectrum obtained from the spectrophotometer. The spectrum was that of the unknown but with very weak absorption bands.

The approach was modified so that the gaseous products from 150 ml of H_2O on one gram of LiBH_4 were passed through 300 ml of 0.5M KBr solution. The infrared examination showed no change in the spectrum. The intensity of the absorption bands was the same as obtained by

adding water to the LiBH_4 . There was no shift of the bands in the spectrum for two runs of this experiment.

In an attempt to effect the shift in the absorption bands by a substitution reaction, 150 ml of water were added to one gram of LiBH_4 and the gaseous products were passed through 300 ml of 0.25M KF solution. The infrared examination of the gaseous products shows a strong spectrum of the unknown gas plus a weak but definite spectrum of diborane using a pressure of 14 mm of gas (Figure 4).

In every case where acid or water was added to LiBH_4 , the first drops of liquid added caused a violent reaction with the evolution of large quantities of gas. The LiBH_4 was a powder initially, but upon the addition of a small amount of liquid the powder turned into a brittle porous mass. With the addition of more water and using a magnetic stirrer, the brittle mass was broken up and the LiBH_4 dissolved in water. After enough water (approximately 5 ml) had been added to cause the physical change from powder to brittle mass, the reaction was essentially over. The gas of interest had been evolved, and the remaining water was added to place the remaining material into solution.

The hydrolysis of LiBH_4 is catalyzed by acid /11/, and the reaction can be retarded by a basic solution./12/ In an attempt to determine the amount of chlorine that is present initially as an impurity, 100 ml of 3M NaOH were added to 1 gram of LiBH_4 . The first few drops of basic solution produced a violent reaction with the hydride, and the gas evolved gave the same infrared spectrum as the unknown (Figure 4). The powdered LiBH_4 remained powder, not a brittle porous mass as with water and acid additions, after the first few drops of NaOH

solution were added. Again the addition of approximately 5 ml of solution completed the reaction, but the still powdered material went into solution with much less physical stirring. When the remaining material had been placed in solution, 200 ml of 0.1M AgNO_3 were added to the solution in the hope of precipitating AgCl and then determining the amount of chloride present initially in the commercially prepared LiBH_4 . The experiment was unsuccessful. The gas evolved could have carried away the chlorine present as the spectrum showed strong absorption bands of the unknown. When AgNO_3 was added to the solution of LiBH_4 in NaOH , the silver was reduced to a black precipitate believed to be silver oxide (Ag_2O). Due to the explosive nature of dry Ag_2O no attempt was made to dry the precipitate to determine the presence of AgCl .

2. Conclusions.

The unknown is a high molecular weight condensable gas. Based on the experiments conducted, the gas is believed to be chlorodiborane ($\text{B}_2\text{H}_5\text{Cl}$). This conclusion was arrived at by the elimination of possible products. For all the basic reactions carried out, the number of elements present were limited to hydrogen, oxygen, lithium, boron and chlorine. To identify the unknown all likely published spectra were investigated. This led to the elimination of diborane /9/ (B_2H_6), boron trichloride /13/ (BCl_3), diboron tetrachloride /14/ (B_2Cl_4), and the high boranes as tetraborane /15/ (B_4H_{10}), pentaborane /15/ (B_5H_9), dihydropentaborane /15/ (B_5H_{11}). All these spectra have characteristic absorption bands at 4.05, 4.65, 5.54 and 6.15 microns with the band at 4.05 microns being the most consistently strong. The fact that the unknown compound is a gas at room temperature and has a

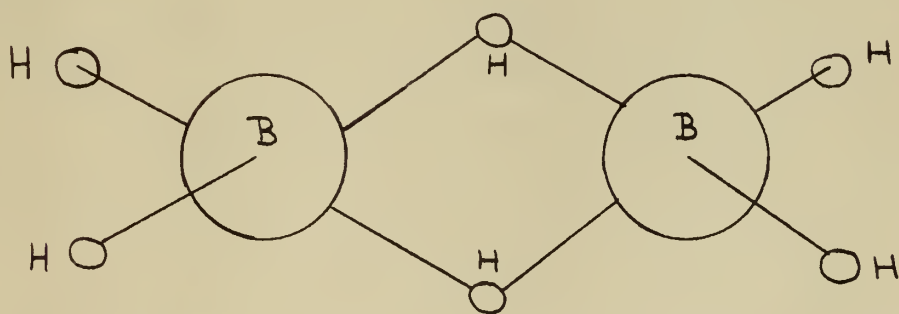
molecular weight of 60 ± 6 grams per gram mole allows the elimination of all likely compounds except chlorodiborane (B_2H_5Cl), which has a molecular weight of 62.14 and is a gas at room temperature.

The keys to the conclusion are: 1) the manufacturer's statement that the $LiBH_4$ used to produce the gas contains $LiCl$ as an impurity; 2) the hydrolysis of $LiBH_4$ is extremely rapid, and acid has a catalytic effect on the reaction.

An attempt to determine the chloride content of the commercial $LiBH_4$ in a reaction involving $NaOH$ and $AgNO_3$ was unsuccessful.

The spectrum obtained from the reaction of $LiBH_4$ and $4N H_2SO_4$ acid was that of diborane (Figure 2). In this reaction the effect of the acid was to speed an already rapid hydrolysis reaction. The reaction was so fast as to exclude the unknown reaction mechanism by which the chloride impurity joined the diborane or intermediate product.

The configuration of diborane, B_2H_6 , is shown below /16/ and has been verified by spectroscopic and other physical evidence. /17/. The molecular dimensions were obtained by a careful electron diffraction study /18/.



The hydrogen atoms having a ligancy of 1, have a H-B distance of $1.187 \pm 0.030 \text{ \AA}$. The bridging hydrogen atoms having ligancy of 2, have a B-H distance of $1.334 \pm 0.027 \text{ \AA}$. The B-B bond distance is $1.770 \pm 0.013 \text{ \AA}$.

The structure of chlorodiborane has not been reported in the literature, but it is reasonable to assume that it would have a structure similar to bromodiborane (B_2H_5Br). Pauling /19/ reports the structure of bromodiborane as essentially identical with that of diborane, except that a bromine atom replaces one of the non-bridging hydrogen atoms. Therefore in chlorodiborane the chlorine atom would take the same position.

There are no published spectra of the chloro- or bromodiboranes. Both these compounds are discussed by Stock /20/, who gives the physical characteristics of chloro- and bromodiboranes as well as successfully used methods to produce the bromodiborane. The most convenient method to prepare the bromodiborane is to allow diborane to react with less than stoichiometric amounts of elemental bromine or hydrogen bromide in a closed vessel at a high temperature for a long period of time. The reaction as reported is that of substitution. The B_2H_5Br must be separated from a product mixture of diborane and boron tribromide. The bromodiborane is reported to be the more stable and not spontaneously inflammable in the atmosphere. A similar reaction involving diborane and chlorine gas is reported to result in an explosion. The violence of the reaction was moderated by lowering the temperature. Even with only one-third the stoichiometric amount of chlorine required, BCl_3 was the predominant product of the chlorination with the majority of B_2H_6 recovered unchanged. The conclusion was that B_2H_5Cl could have been an intermediate product which dissociated so rapidly as to be undetected. D. T. Hurd /21/ proposes that B_2H_5Cl might occur as an intermediate in the

reduction of boron trichloride (BCl_3) with hydrogen gas in an electric discharge. Both authors agree that $\text{B}_2\text{H}_5\text{Cl}$ is very unstable, decomposing to B_2H_6 and BCl_3 , and that $\text{B}_2\text{H}_5\text{Cl}$ is a spontaneously inflammable gas. As no authority reports the isolation and testing of pure $\text{B}_2\text{H}_5\text{Cl}$, the reports of excess instability and spontaneous inflammability are open to question.

In the reaction of LiBH_4 and H_2SO_4 acid, diborane was the product as determined by the spectrum. The chloride content was only what existed as an impurity in the LiBH_4 and hence can be assumed relatively small. The acid catalyzed an already rapid reaction. Under these conditions of rapid reaction and low chloride content, the mechanism of reaction did not allow for the substitution of chloride ion in an amount to produce detectable quantities of $\text{B}_2\text{H}_5\text{Cl}$ by infrared studies of the gases.

When HCl acid was used in lieu of the H_2SO_4 acid under the same conditions, the spectrum was that of diborane and chlorodiborane (Figure 3), both in moderate intensity. This again is an acid catalyzed reaction and hence very rapid, but the chloride ion was in abundance from the impurity and acid. Here the preponderance of chloride ion, despite the short reaction time, allowed the substitution of chloride ion in an amount to produce detectable quantities of $\text{B}_2\text{H}_5\text{Cl}$, but not complete substitution, as diborane was also detected.

When water was added to LiBH_4 the spectrum was that of $\text{B}_2\text{H}_5\text{Cl}$; but it had very weak absorption bands (Figure 2). In this case there was no acid to catalyze the reaction, but the observed reaction was still rapid. At the slower reaction rate the small chloride impurity had more time to carry out a substitution reaction. The result is a spectrum of $\text{B}_2\text{H}_5\text{Cl}$ and no infrared detectable diborane.

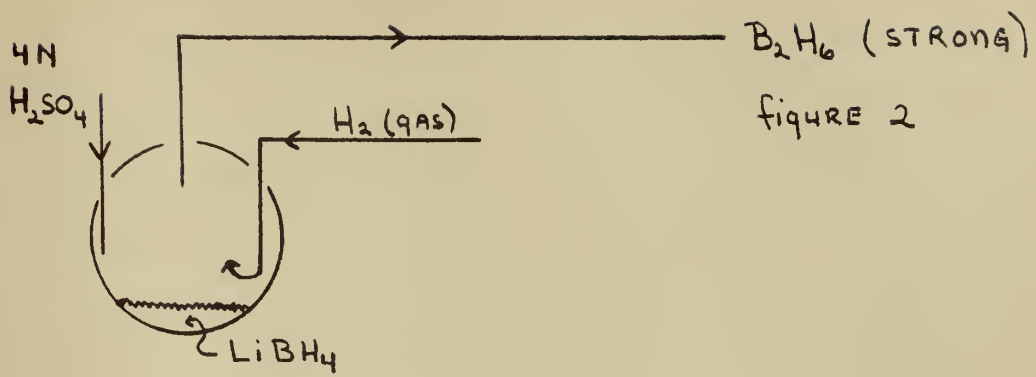


FIGURE 2

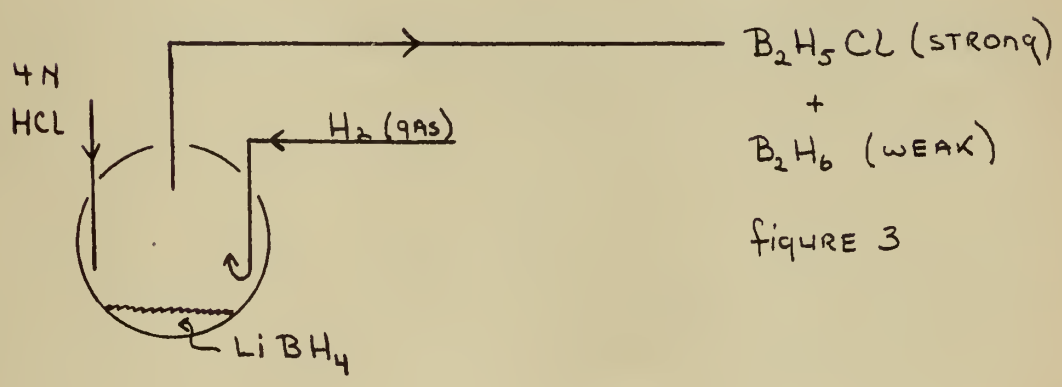


FIGURE 3

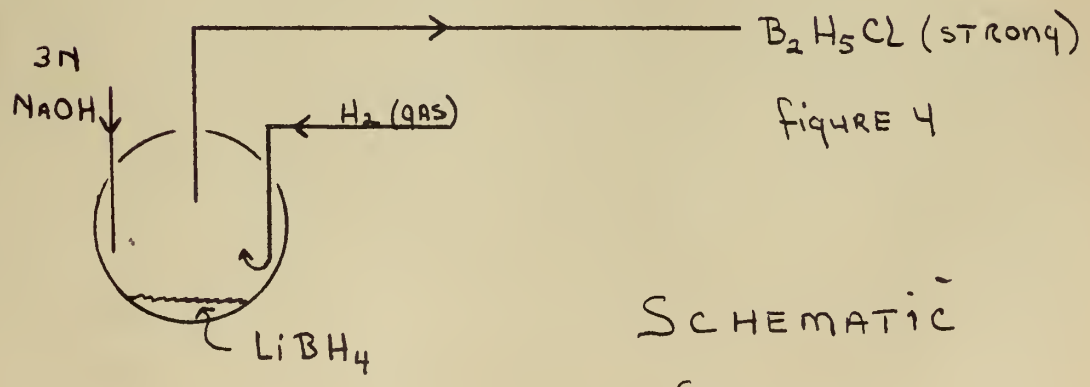


FIGURE 4

SCHEMATIC
SUMMARY

The assumption that B_2H_5Cl is produced by the substitution of a chlorine atom for a non-bridging hydrogen atom of diborane seems reasonable. The fact that diborane reacts almost instantaneously with water to produce boric acid /20/ can account for the absence of diborane spectrum from the water and $LiBH_4$ reaction. In this reaction when water was added diborane was produced. The chloride impurity of the $LiBH_4$ by substitution in diborane gave the observed spectrum. This reaction was not acid catalyzed, and the amount of diborane produced is less per unit of time than from the acid catalyzed reactions. The diborane is not evolved in a burst, but rather over a longer time. Water vapor produced by the exothermic reaction was trapped along with the diborane and B_2H_5Cl . In the subsequent heating and cooling processes of the vacuum distillation procedure, the water reacted with the diborane to produce boric acid and hydrogen.



At the beginning of the experiments, the unpacked glass traps of the vacuum system were clean, but at the end of the experimentation the trap walls were spotted with a film of white powder, with a deposit of powder in the trap well. The powder was similar in appearance to finely powdered boric acid. The small quantity of powder was not removed from the vacuum system for analysis. In the H_2SO_4 acid and HCl acid reactions, the quantity of diborane was produced in a shorter time. The small amount of water vapor trapped could not react with all the diborane and therefore allowed sufficient quantities to pass unreacted. The unreacted diborane was subsequently detected. In the light of the anomalies in the experimental procedures, the relative amounts of gases evolved from all the reactions can offer no quantitative basis of comparison. The three

experiments described above, however, do show general trends. The production of chlorodiborane seems to be favored by higher chloride ion concentrations and by neutral rather than acidic solutions.

When the gas evolved in the LiBH_4 and water reaction was allowed to escape from the reaction vessel, and the resulting solution added to a solution of bismuth trichloride and hydrochloric acid, a weak spectrum of the $\text{B}_2\text{H}_5\text{Cl}$ was observed. The gaseous diborane evolved is assumed to have been converted to boric acid in the acid solution or passed from the reaction vessel as gaseous diborane. The entire quantity of LiBH_4 was not reacted completely, and some went into solution. When this aqueous solution of LiBH_4 was added to the strongly acidic BiCl_3 solution, the reaction which followed released more diborane. The chloride ion completed the substitution reaction and gave the observed spectrum of $\text{B}_2\text{H}_5\text{Cl}$.

The diborane gas evolved along with the chlorodiborane in the water and LiBH_4 reactions to be described below can be regarded as an intermediate product. For purposes of clarity in spectrum identification, this diborane gas will be noted as X (gas).

When the chlorodiborane and diborane gas, X (gas), evolved from the water and LiBH_4 reaction was bubbled through a solution of potassium chloride, the spectrum was that of $\text{B}_2\text{H}_5\text{Cl}$. The intensity of the absorption bands however was increased approximately four-fold (Figure 3). The chloride ion reacted with the intermediate diborane gas by a substitution reaction to produce more $\text{B}_2\text{H}_5\text{Cl}$ and give stronger absorption band intensities. Any unreacted diborane must have reacted with the aqueous KCl solution or trapped water vapor to produce undetected boric acid.

When the gas evolved from the LiBH_4 and water reaction was passed through a solution of KBr, there was no noticeable change in the spectrum.

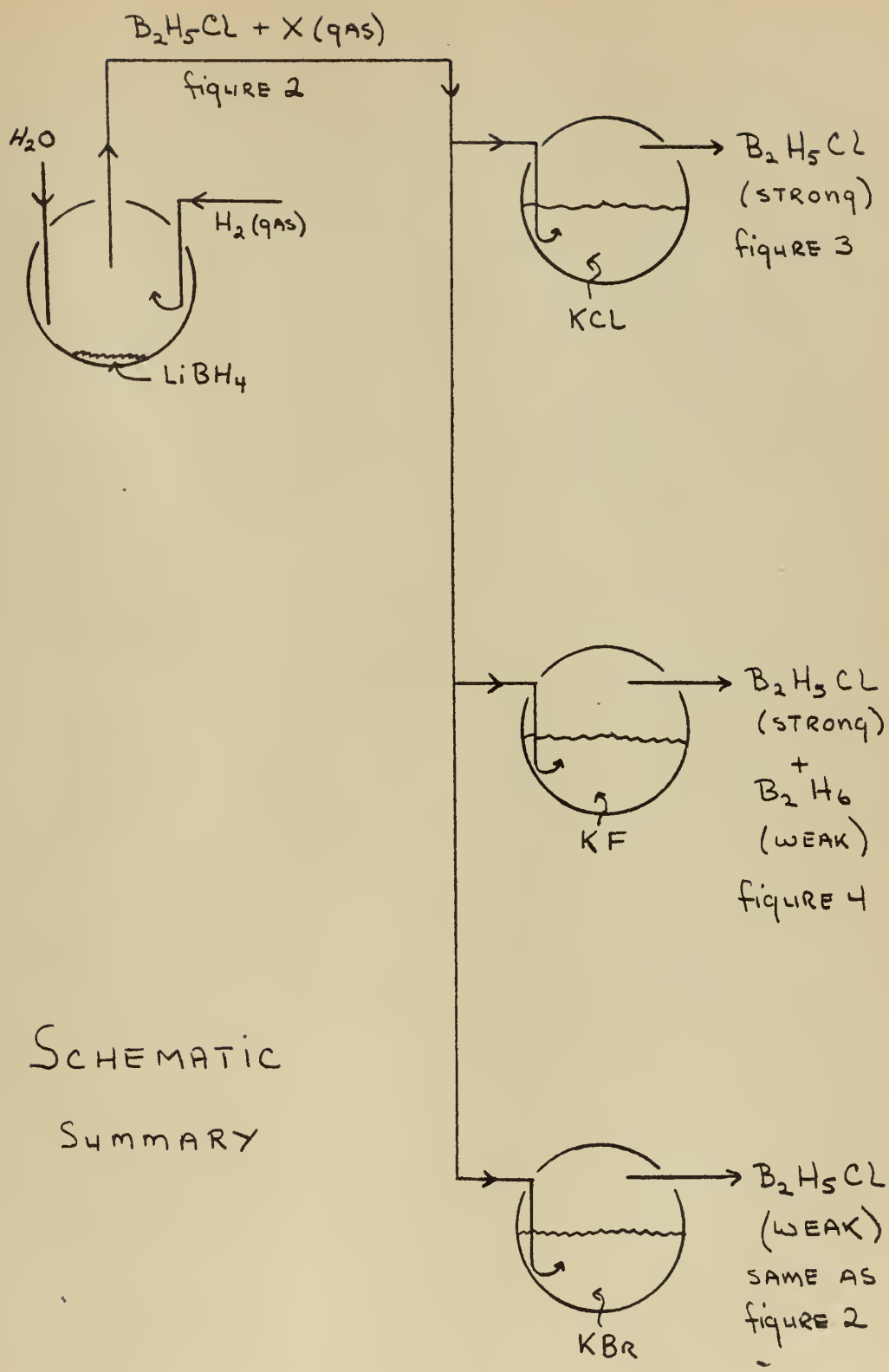
From the intensity of the absorption bands, which were the same as the bands observed from LiBH_4 and water reaction, the bromide ion effected no change on the $\text{B}_2\text{H}_5\text{Cl}$ gas or on the intermediate diborane. From electronegativity considerations it is clear that the bromide ion would stand little chance of substituting for the chlorine atom in $\text{B}_2\text{H}_5\text{Cl}$. It is possible that the bromide ion did not have sufficient time to substitute for a hydrogen atom of diborane. As stated previously, diborane and bromine gas must stand together for long periods of time at a high temperature to allow the bromine atoms to effect a substitution. The unreacted diborane underwent the reaction with water previously described to produce undetected boric acid and hydrogen gas.

When the gas evolved from the LiBH_4 and water reaction was passed through KF solution, a change in the spectrum was observed (Figure 4). The absorption bands were stronger than observed in the initial water and LiBH_4 reaction. There was no appreciable shift in any of the previously observed absorption bands to indicate formation of any compound such as fluorodiborane. Another change in the spectrum was the presence of diborane indicated by a weak absorption spectrum. In this reaction it can be assumed that the normal quantity of $\text{B}_2\text{H}_5\text{Cl}$ was produced and carried unchanged through the reaction. There was no chloride ion present to account for the increased absorption bands of $\text{B}_2\text{H}_5\text{Cl}$. The formation of a compound as $\text{B}_2\text{H}_5\text{F}$ seems most unlikely, and there was no observed shift in the spectrum to indicate its formation. This was the first time that diborane was observed in a spectrum resulting from this general type of reaction. While the other experiments were conducted at least twice, this experiment was run only once due to a limited supply of LiBH_4 . The inconsistency of this run can be attributed to the anomalies inherent in the procedure. The

hydrogen gas sweep rate might have been too high. The initial distribution of LiBH_4 in the reaction vessel and the speed in which the water was added could have been inconsistent with the previous runs. Even the effect of varying the speed of the magnetic stirrers could have affected the results. It can be concluded that the results of this experiment are subject to question and may not be reliable.

As the hydrolysis of LiBH_4 is an acid catalyzed reaction, it has been proved that the use of a basic solution will retard the reaction./12/ In this line of investigation 3M NaOH solution was added to LiBH_4 , and the gas evolved was observed in the infrared (Figure 4). The spectrum was that of the $\text{B}_2\text{H}_5\text{Cl}$ with moderately strong absorption bands. In this case the basic solution did not apparently retard the reaction sufficiently to prevent the evolution of $\text{B}_2\text{H}_5\text{Cl}$. The basic solution could have slowed the reaction sufficiently to allow more of the chloride impurity to be used in the reaction and hence yield more $\text{B}_2\text{H}_5\text{Cl}$ accounting for the increased absorption bands.

In the references $\text{B}_2\text{H}_5\text{Cl}$ is reported to be very unstable and spontaneously inflammable. No attempt was made to expose large quantities of the gas to the atmosphere. However, in working with the vacuum system small quantities of the gas, as detected by the disagreeable hydrogen sulfide-like odor, were exposed to the atmosphere during breaking connections, and no combustion reactions were observed. Several methods were employed to test the stability of $\text{B}_2\text{H}_5\text{Cl}$. A gas sample was added to a 10 cm pathlength cell resulting in a gas pressure of 28 mm. The sample was viewed periodically over a time span of 120 hours. There was no apparent change in the spectrum with the cell at room temperature. A glass bulb of 252 cm volume was filled with a gas sample of 8 mm pressure. The bulb was submerged in a water



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bath at 60°C for 20 hours, and again there was no apparent change in the spectrum. The 10 cm pathlength gas cell was used with 15 mm pressure of sample. The total pressure in the bulb was increased to 68 mm by adding dry hydrogen gas. At the end of 48 hours the sample had the same spectrum as before, indicating no change. The three procedures used to decompose B_2H_5Cl were unsuccessful, despite the attempts to increase the decomposition kinetics by adding heat or increasing the collision rate by added molecules.

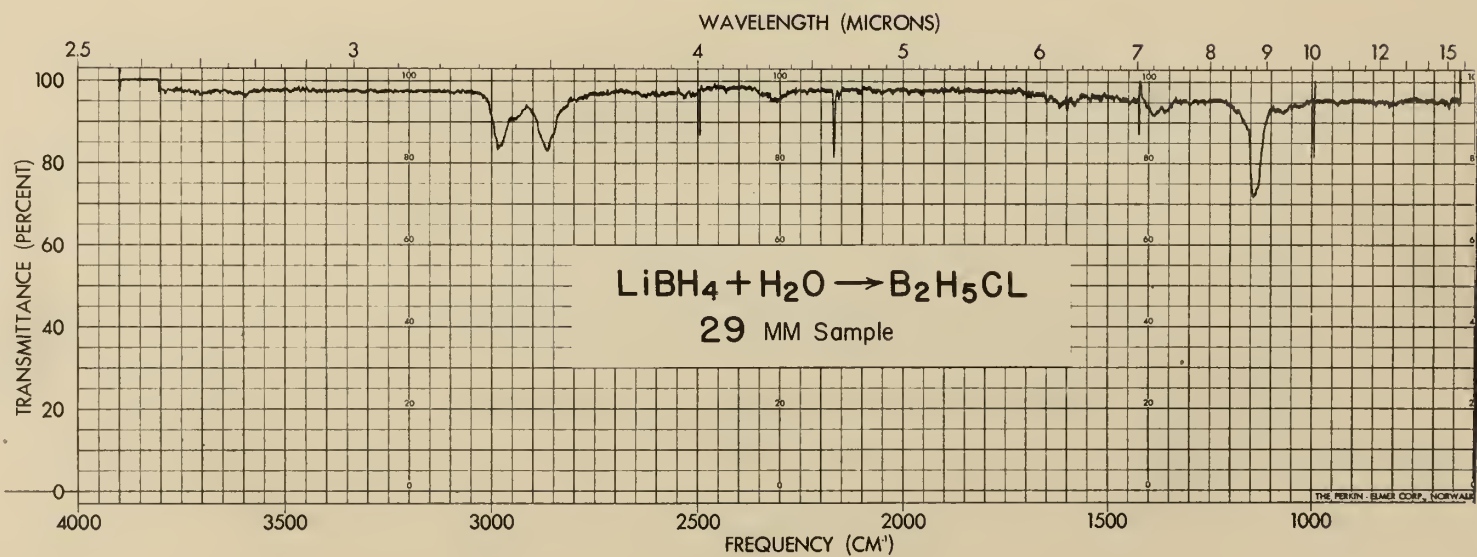
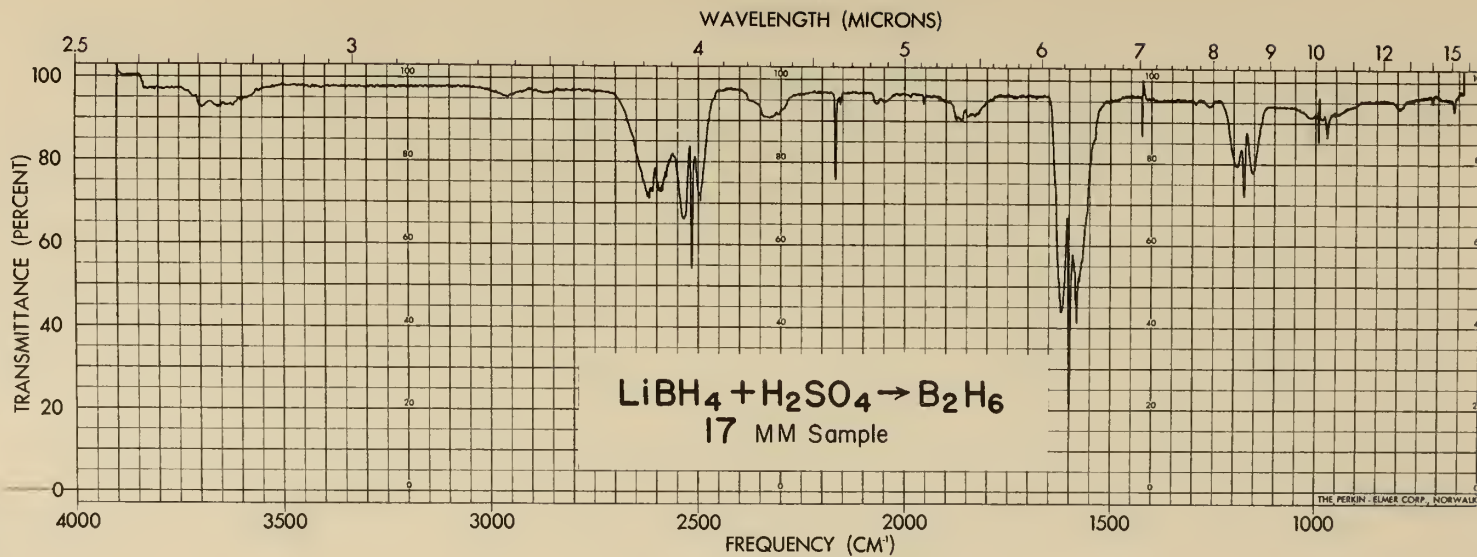


Figure 2
Infrared Spectra of Diborane From $\text{LiBH}_4\text{-H}_2\text{SO}_4$ Reaction
and Chlorodiborane From $\text{LiBH}_4\text{-H}_2\text{O}$ Reaction

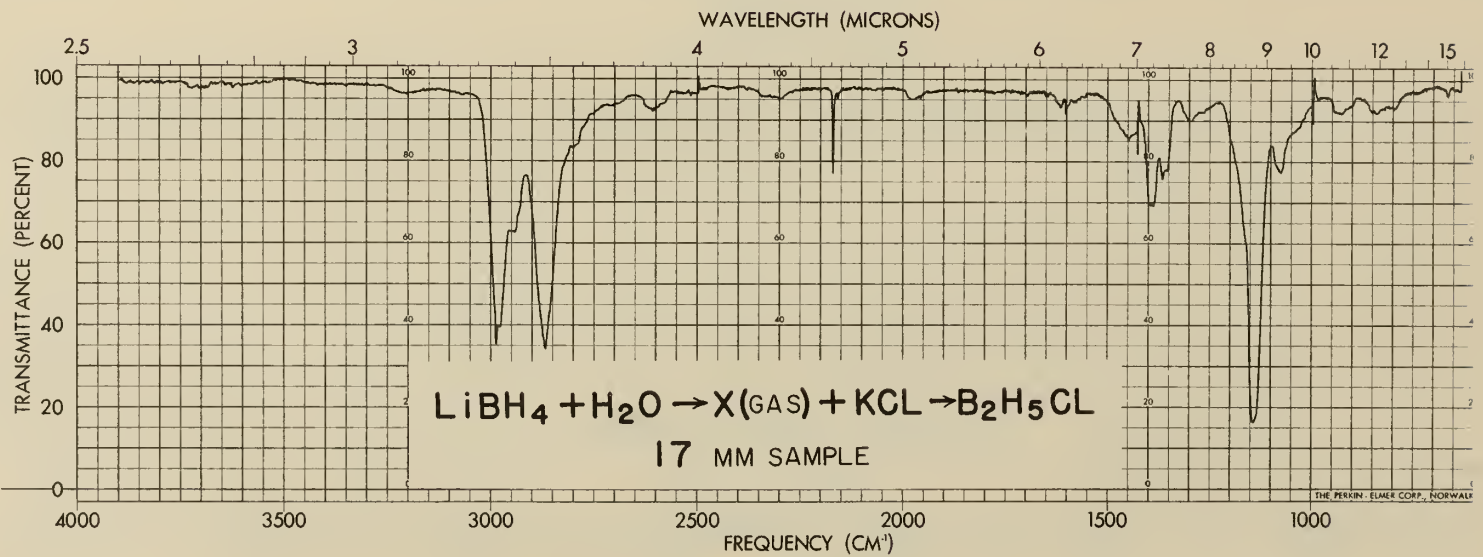
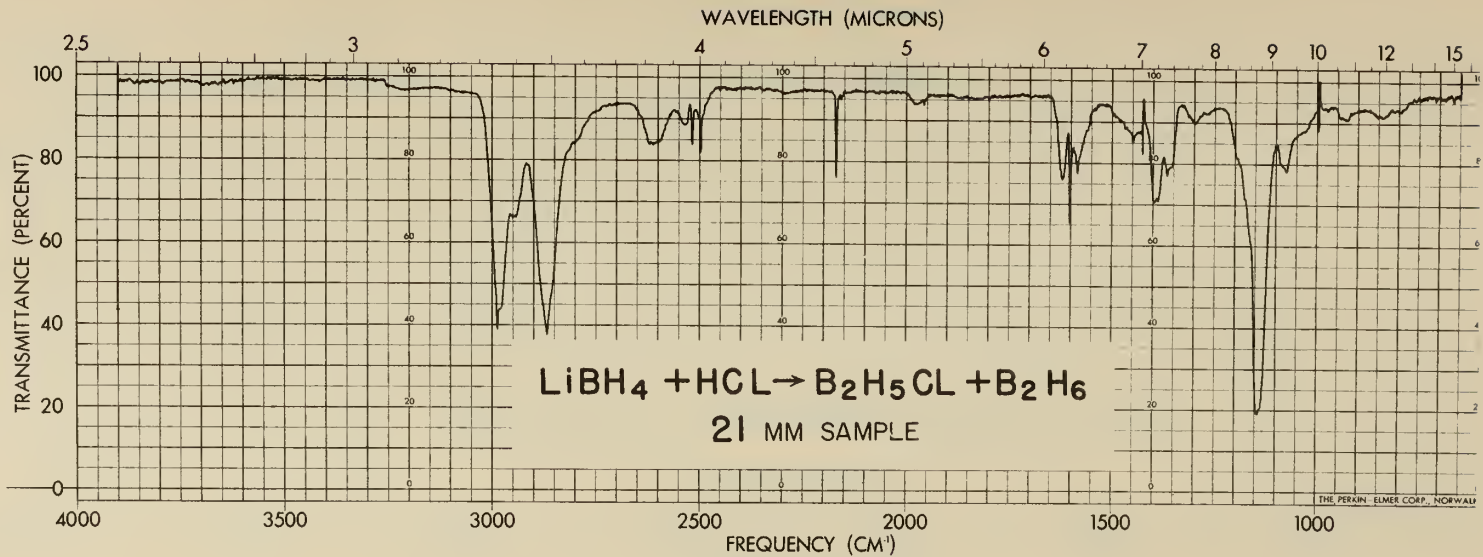
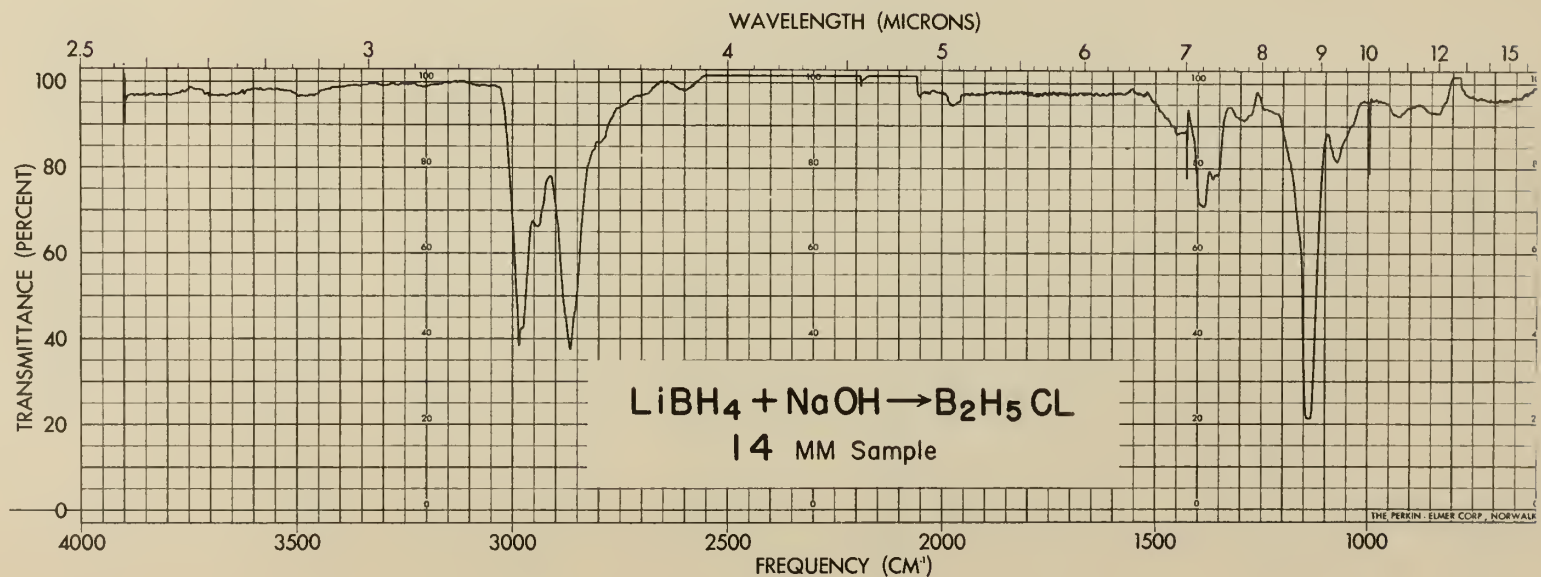
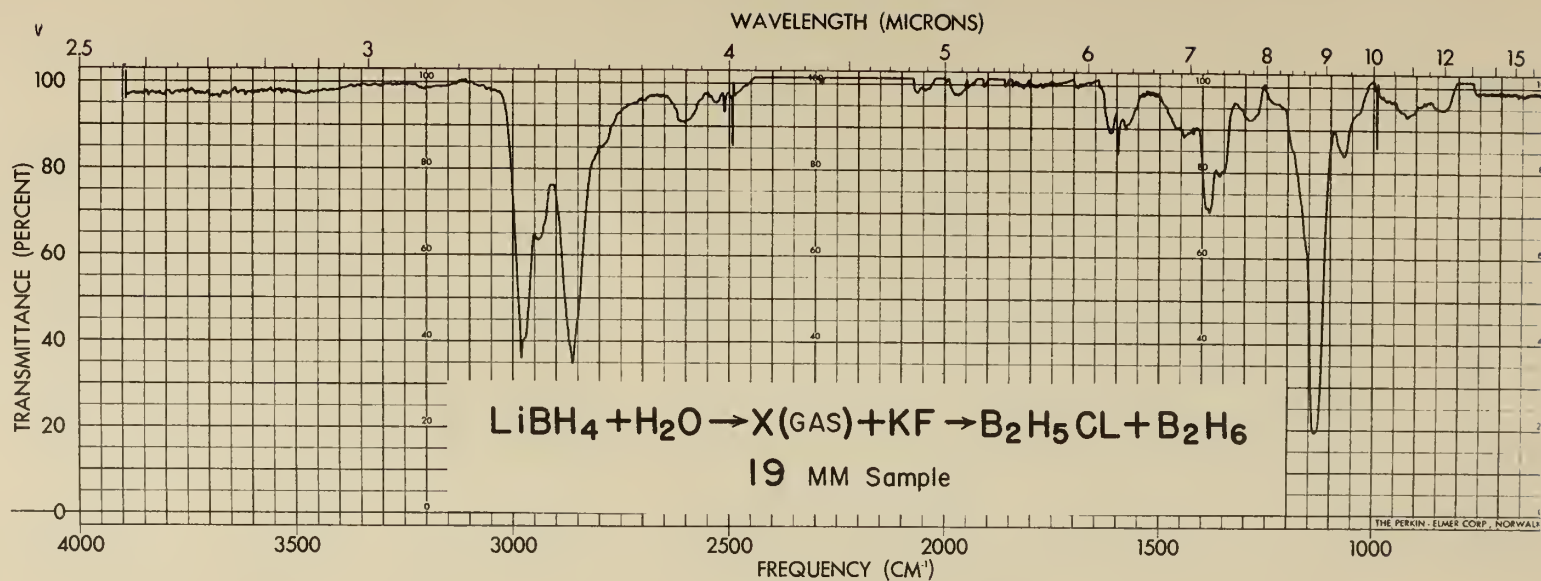


Figure 3

Infrared Spectra of Chlorodiborane From $\text{LiBH}_4\text{-HCL}$
 Reaction and From $\text{LiBH}_4\text{-H}_2\text{O}$ Reaction gas
 Passed Through KCL Solution

Figure 4
 Infrared Spectra of Chlorodiborane From $\text{LiBH}_4 - \text{NaOH}$
 Reaction and From $\text{LiBH}_4 - \text{H}_2\text{O}$ Reaction gas passed
 Through KF Solution



4. Suggestions for further study.

Due to time limitations, the experimental work done involving the commercial LiBH_4 was not completed. In dealing with the product gas $\text{B}_2\text{H}_5\text{Cl}$ the following procedures could be used to aid in positive identification:

- (1) Produce $\text{B}_2\text{H}_5\text{Cl}$ from diborane and chloride gases. This is reported as an explosive reaction, but might be feasible at low temperatures using small quantities of gaseous reactants. A positive identification could be possible from this procedure.
- (2) Produce $\text{B}_2\text{H}_5\text{Br}$ for a comparison spectrum. The reaction of diborane and bromine gases for long periods of time in a sealed container at a high temperature might yield enough $\text{B}_2\text{H}_5\text{Br}$ to be used in a comparison. These gases reportedly mix without violent reaction, and large quantities could be used.
- (3) Determine the chloride impurity in the commercial LiBH_4 to allow quantitative study of the chloride content of reactants and products.
- (4) If quantitative data could be obtained on the chlorine content, the reactions involving the commercial LiBH_4 and water, acids and base could be studied on a quantitative basis with regard to the chloride participation.
- (5) The reactions were carried out in a hydrogen atmosphere. Change the sweeping gas to helium, perhaps, and see if the hydrogen gas affected the reaction.
- (6) All studies would be made easier if the LiBH_4 hydrolysis reaction could be slowed down, as by the use of low temperatures.

- (7) In place of aqueous solutions, carry out the reaction in ethereal solutions or other solvents.
- (8) Attempt to analyze the residual powder left in the vacuum system in an effort to determine the nature of the intermediate product.

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