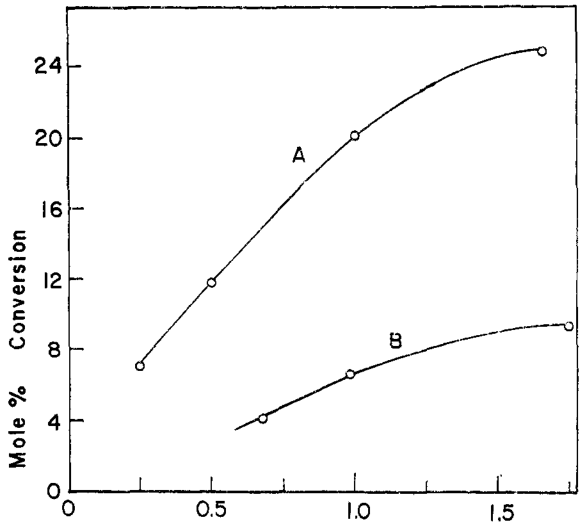

Figure 6. Conversion of *n*-heptane to toluene as a function of contact time

A. At 500° C. over 5% Re on Al_2O_3
B. At 550° C. over 0.1% Re on Al_2O_3

Because of the leveling of the curves with increasing contact time and the relatively small amount of heptane remaining after 1.4 seconds (Table I), the contact time used most often with the rapid sampling technique was 1.0 second.

Benzene accounted for 13 to 23 mole % of the aromatic hydrocarbon fraction in Table I. Some additional data on the composition of the aromatic hydrocarbon fraction are given in Table II. The toluene in this fraction under most conditions was between 70 and 90 mole %, but under some extreme conditions this value decreased. Higher temperatures and longer contact times with the platinum catalyst resulted in more benzene than toluene. Although less pronounced, the same trend was observed with the rhenium catalysts (48% toluene at 600° C. and 1.4 seconds).

Methylcyclohexane with the platinum catalyst showed a decrease in the toluene-benzene ratio as a function of contact times at 550° C. With the rhenium catalyst this decrease was not observed.

Conclusions

Rhenium catalysts show activity in the dehydrocyclization of *n*-heptane to toluene. Other reforming reactions also occur. Platinum is more selective for dehydrocyclization than rhenium. Rhenium is cheaper than platinum (*1*), but a higher percentage of rhenium is needed on the alumina support. These observations suggest that rhenium may merit further consideration in the catalytic reforming of hydrocarbons.

Acknowledgment

Appreciation is gratefully expressed to the Kennecott Copper Corp. for the financial support of this work, and to H. Smith Broadbent for permitting this work to begin as part of the rhenium research program he supervised at Brigham Young University.

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HYDROGENATION OF BORON TRICHLORIDE TO DICHLOROBORANE

A New Route to Diborane

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Dichloroborane, $BHCl_2$, has been synthesized in quantitative yields by the thermal hydrogenation of boron trichloride. The various parameters affecting the reaction of boron trichloride with hydrogen have been investigated and the rates of the reverse reaction have also been determined. Dichloroborane disproportionates quantitatively to diborane and boron trichloride under suitable conditions. Equilibrium studies were made of the disproportionation.

Several methods for the synthesis of chloroboranes have been described: the reaction of gaseous boron trichloride with hydrogen in an electric discharge at low pressure (*13*); the reaction of boron trichloride with hydrogen in the presence of reactive metals as halogen acceptors (*5, 7*); the reaction of gaseous diboron tetrachloride with hydrogen (*14, 15*); the reaction of diborane with boron trichloride in ethers to produce the corresponding chloroborane-etherates (*2, 3, 11*); and the reaction of boron trichloride and diborane in the absence of solvent (*6, 9, 12*).

In 1958 a new process was developed in this laboratory in which boron trichloride is hydrogenated to dichloroborane simply by reaction with hydrogen at elevated temperatures in the gas phase (*1, 10*). The process does not employ metals or metal hydrides as halogen acceptors. Thermal energy is used rather than an electric discharge. Yields are essentially

Table I. Hydrogen–Boron Trichloride Reaction Data at Atmospheric Pressure

Expt. No.	*Temp., ° C.*	*Residence Time, Sec.*	*Mole Ratio (H_2/BCl_3)*	*Conv. to $BHCl_2$, %*	*Yield of $BHCl_2$, %*	*Catalyst*
1	620	0.2	14.0	3.6	...	None
2	700	0.76	14.0	24.4	100.0	None
3	700	1.75	14.0	34.1	97.9	None
4	700	3.51	15.6	41.8	99.9	None
5	620	0.2	14.0	32.1	66.0	Copper
6	620	0.65	14.0	25.6	87.3	Carbon
7	620	0.48	14.0	22.4	72.4	Pd on C
8	620	0.61	14.0	20.7	57.1	Pt on C
9	700	0.2	13.9	34.3	101.9	Silver
10	700	0.5	15.1	36.3	97.3	Silver
11	700	0.5	15.6	36.9	100.0	Silver
12	700	0.5	15.9	35.7	100.8	Silver
13	700	0.5	15.9	36.7	101.4	Silver
14	700	0.8	13.4	35.1	101.0	Silver
15	700	0.8	13.6	34.5	100.6	Silver
16	750	0.2	12.3	38.2	89.9	Silver
17	750	0.5	15.8	37.3	93.4	Silver
18	750	0.55	2.75	21.2	101.3	Silver

quantitative and thus the process constitutes an important new route to diborane.

The process has been successfully demonstrated in a pilot plant designed to produce 50 pounds per day of diborane on a continuous basis. Since only liquids and gases were involved, the pilot plant unit resembled a petroleum refinery in operation and appearance. Over-all simplicity was achieved by employing boron trichloride as the absorbent liquid for separation and purification of dichloroborane, hydrogen, and hydrogen chloride. Diborane and hydrogen chloride were obtained in purities of 99%, and yields, based on boron trichloride, of 95%.

The scale-up and pilot plant work were conducted by AFN, Inc., a joint effort of American Potash and Chemical Corp., FMC Corp., and National Distillers and Chemical Corp., under sponsorship of the U. S. Air Force. The prepilot plant scale-up and the pilot plant design and operation will be described in papers from FMC Corp. and American Potash and Chemical Corp.

Results and Discussion

During an investigation of the synthesis of diborane from a thermal reaction of boron trioxide with hydrogen (*4*) conducted in a flux of molten sodium aluminum chloride, it was observed that dichloroborane was produced. The product was determined to arise from the vapor phase reaction of hydrogen with boron trichloride which was generated by the action of the chloride melt on the boron oxide. Subsequent study of the vapor phase reaction of boron trichloride with hydrogen at elevated temperatures showed that dichloroborane could be made in quantitative yields and in relatively high conversions, in accordance with the reaction:

$$BCl_3 + H_2 \leftrightarrows BHCl_2 + HCl \tag{1}$$

This reaction is reversible and the composition reached at equilibrium depends on the reaction conditions chosen. It is endothermic and the degree of conversion to dichloroborane increases with rising temperature. At ambient temperature, the equilibrium is displaced almost completely to the left, and isolation of product depends on the fact that the reverse reaction proceeds extremely slowly at ordinary temperatures. The hydrogen chloride produced in this process may be recycled by various known methods. A new process developed in this laboratory for the production of boron trichloride (*8*) permits direct recycle of the hydrogen chloride. In this method boron oxide, hydrogen chloride, and carbon are made to react at 1200° to 1400° C.

The dichloroborane can be quantitatively disproportionated to diborane and boron trichloride, according to the equation:

$$6BHCl_2 \leftrightarrows B_2H_6 + 4BCl_3 \tag{2}$$

This reaction is also reversible and can be driven all the way to the right by continuously removing the more volatile diborane from the other components.

The effects of pressure, temperature, mole ratio of H_2/BCl_3, catalysts, and residence time on the conversion of boron trichloride to dichloroborane were investigated. The results showed that the rate of reaction varies with temperature, pressure, and catalyst, and that the extent of conversion is a function of temperature, mole ratio of reactants, and residence time. The yield was found to depend on the temperature, residence time, and mole ratio of reactants. Some catalytic materials also affect the yield.

Reaction Conditions for Hydrogenation of Boron Trichloride

Below 400° C. the degree of conversion is very small, while above 750° C. decomposition may take place with the production of elementary boron. The reaction is reversible and, in fact, slow cooling of the reaction gases leads to diminishing conversions because of reversal. The successful operation of the reaction depends on the rapid decline in the rate of the back reaction with decreasing temperature. In Table I the results of a number of typical runs are given. The yields of dichloroborane are quantitative, but above 750° C. a tendency toward reduced yields is observed, with simultaneous formation of boron, particularly at high ratios of hydrogen to boron trichloride and with excessive residence times. The effect of high partial pressures of hydrogen in reducing the yield at temperatures above 750° C. may be due to the formation of a more highly hydrogenated compound (possibly BH_2Cl) which decomposes more readily than does $BHCl_2$. Materials tested as catalysts, other than silver, reduced the yields.

The conversions and yields are based on chemical analyses, the procedures for which are described in the experimental section. The number of boron-hydrogen bonds were determined by hydrolysis of the products and measurement of the evolved hydrogen, while the total boron and chloride contents were determined titrimetrically. This analytical procedure did not distinguish the types of boron hydride or chloride

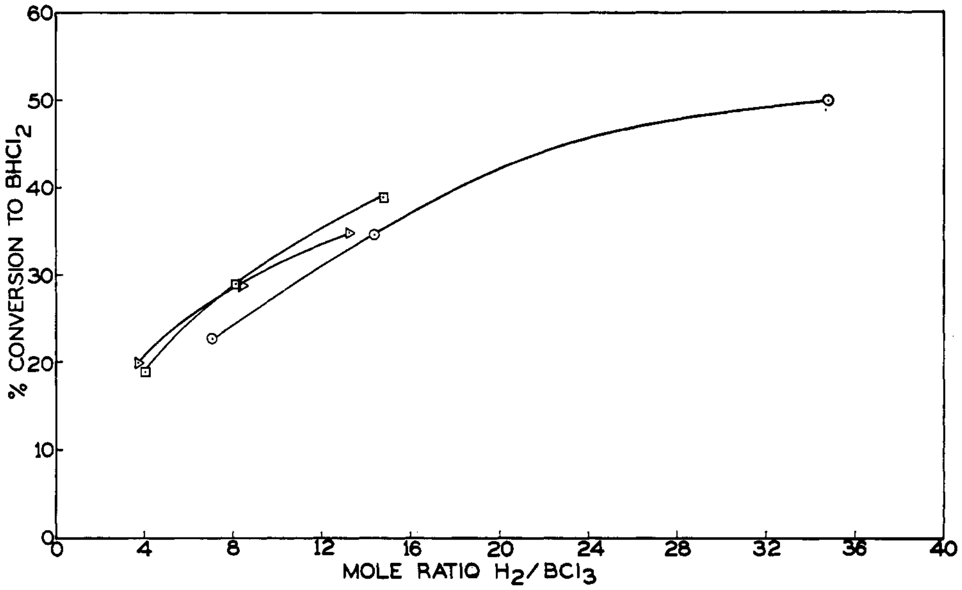

Figure 1. Effect of mole ratio H_2/BCl_3 on conversion of BCl_3 to $BHCl_2$

Silver screen catalyst, 700° C., 1 atm.
Residence time, second
○ 0.2
□ 0.5
△ 0.8

compounds present. Experimental determinations of the boron balance may be inaccurate by as much as 1 or 2%. When yields were that close to 100%, it was considered that they were essentially quantitative. This was supported by the fact that under those conditions the infrared spectra showed no constituents other than those accounted for in the chemical analysis, and no boron or higher boron hydrides were found in the reactor. On the other hand, when yields were lower, boron was found in the reactor.

When a gas sample from the reactor was examined by infrared the only species observed were dichloroborane, boron trichloride, diborane, and hydrogen chloride. The spectrum of dichloroborane showed a singlet B-H absorption at 2620 $cm.^{-1}$ and doublets at 1098, 1084 $cm.^{-1}$ and at 898, 885 $cm.^{-1}$ in accordance with information supplied to us privately by Stern and later published (*7*). Stern had confirmed that the compound was dichloroborane by determination of its molecular weight. The infrared spectra were employed for analysis of gas mixtures when it was necessary to determine the relative amounts of the components.

In Figure 1 experimental data are plotted showing the effect of H_2/BCl_3 mole ratio on conversions to dichloroborane at 700° C. The effect of residence time is also shown; the maximum conversions were obtained at 0.2 to 0.5 second when a silver screen catalyst was used. The conversions (based on boron trichloride) can be increased greatly by employing higher and higher partial pressures of hydrogen, but a point of diminishing returns is reached because the greater amount of hydrogen to be handled requires larger equipment and bigger heating and cooling loads, and difficulties in separation of products are greatly enhanced.

Within the optimum temperature range of this reaction (600° to 700° C.) it is possible to employ contact times great enough to achieve complete thermodynamic equilibrium with-

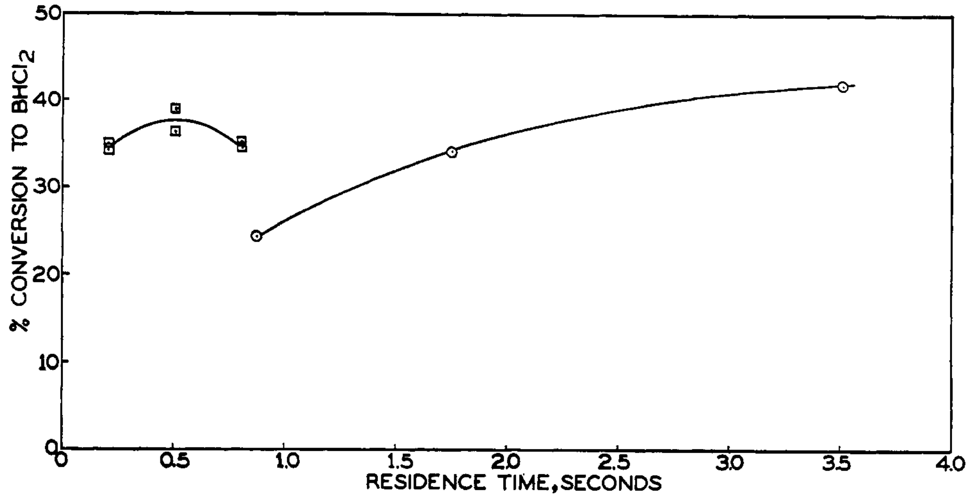

Figure 2. Effect of silver catalyst on reaction rate of hydrogenation of BCl_3

Mole ratio H_2/BCl_3 14, 1 atm.
□ Silver screen catalyst at 700° C.
○ No catalyst at 750° C.

Table II. Reaction Rate Constants for Back Reaction in Vapor Phase

Temp., ° C.	*Reaction Rate Constants, Liter/Mole Sec.*
25.6	2.21×10^{-6}
30.6	2.74×10^{-6}
53.0	3.71×10^{-6}
400	6.20×10^{-3}
500	3.04×10^{-2}

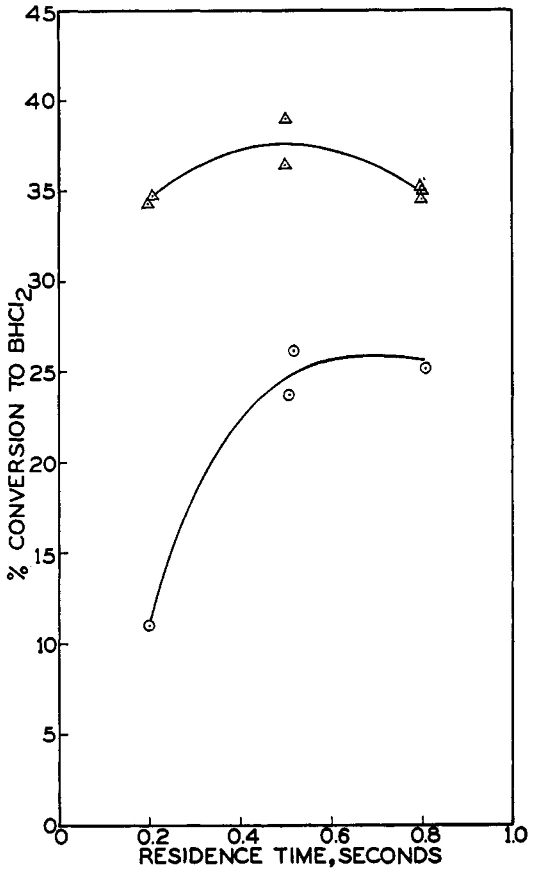

Figure 3. Effect of temperature on conversion of BCl_3 to $BHCl_2$

Silver screen catalyst, mole ratio H_2/BCl_3 14, 1 atm.
△ 700° C.
○ 620° C.

out decomposition of the dichloroborane. However, it has been found possible to increase the rate of reaching equilibrium about tenfold at atmospheric pressure by using silver as a catalyst. The use of the catalyst therefore permits a considerable reduction in the size of reactor employed. The effect of the silver catalyst in increasing the rate of reaction is shown in Figure 2. Other catalysts tried—copper, carbon, palladium-on-carbon, and platinum-on-carbon—also accelerated the reaction but caused considerable reductions in yield. The silver, on the other hand, did not affect the yield and remained bright and effective for long periods of time, apparently indefinitely. When the reactor was packed with silver in the form of fine granules (40- to 60-mesh), the particles sintered together in time and caused channeling, but when layers of silver screen (16-mesh) were employed instead, this difficulty was avoided. Figure 3 shows the variation in conversion with residence time at 620° and 700° C.

In Figures 2 and 3 the extent of conversion in the catalyzed reactions at 700° C. declines with increased residence times. This decrease is not due to a diminished yield, since the dichloroborane is formed quantitatively with respect to the boron trichloride consumed, but rather is attributed to the slower passage of the gases from the reactor zone through a zone of intermediate temperatures (because of nonuniform heating in the reactor) where there was an opportunity for reversal of the reaction (back reaction) to occur. When a reactor was constructed with an exit tube of small diameter immediately following the reactor zone, this effect, of diminished conversions with increased residence times, was greatly reduced because it provided rapid passage of the gases through the zone of intermediate temperature.

Use of pressure would not be expected to increase the extent of conversion because the number of moles of product is equal to the number of moles of reactants, but an increase in the reaction rate would be expected because of the higher concentrations of reactants. The increased rates were observed, as shown in Figure 4, but an actual decrease in the extent of conversion arose from the increased rate of back reaction at higher pressure, where rapid cooling of the gases is clearly more critical.

Back Reaction

Some efforts were made to study the rate of the back reaction—that is, the rate of reaction of $BHCl_2$ with HCl to yield BCl_3

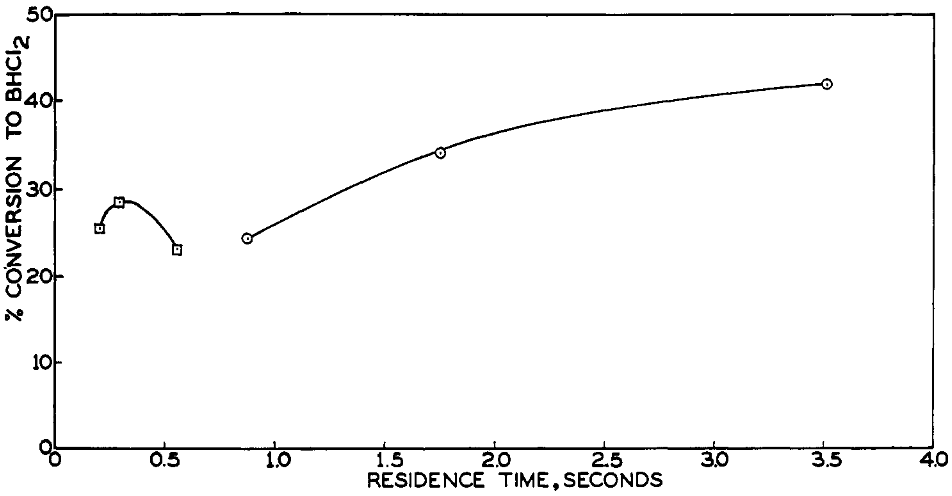

Figure 4. Effect of pressure on rate of hydrogenation reaction

No catalyst, mole ratio H_2/BCl_3 14, 750° C.
○ 1.0 atm.
□ 10.2 atm.

Table III. Thermodynamic Values at Standard Conditions for Hydrogenation Reaction and for $BHCl_2$

$\Delta H°_{(298)}$ reaction	14.2 kcal./mole
$\Delta F°_{(298)}$ reaction	12.1 kcal./mole
$\Delta S°_{(298)}$ reaction	6.96 E.U.
$\Delta H°_{f(298)}$ of $BHCl_2$	−60.9 kcal./mole
$\Delta F°_{f(298)}$ of $BHCl_2$	−58.6 kcal./mole
$S°_{(298)}$ of $BHCl_2$	62.8 E.U.

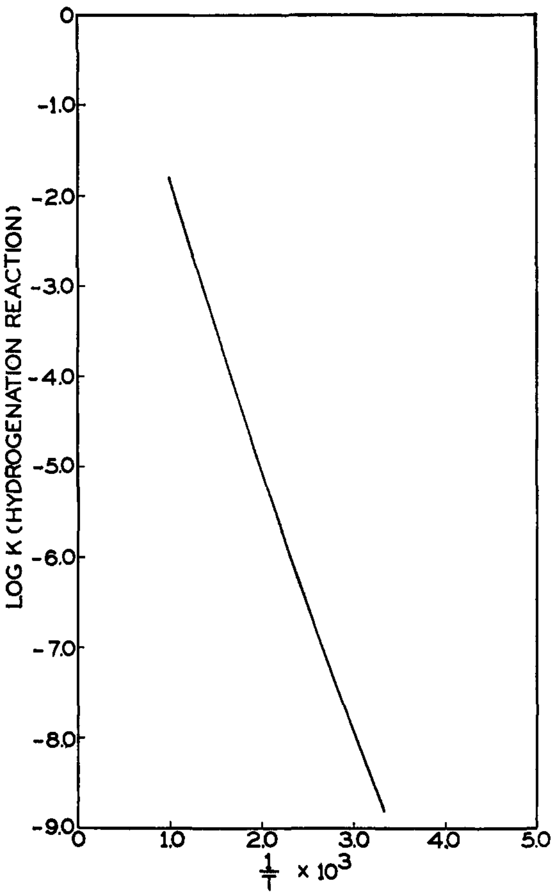

Figure 5. Variation of equilibrium constant of hydrogenation reaction with temperature (°K.)

and H_2. Studies were made in the vapor phase at temperatures ranging from 25.6° to 53.0° C. and from 400° to 500° C.

The reaction rates at 25.6°, 30.6°, and 53.0° ± 1.0° C. were measured by following the rate of $BHCl_2$ disappearance. The concentration of $BHCl_2$ was determined by measuring the absorbance of its absorption band at 9.12 microns. It was observed that the reaction

$$BHCl_2 + HCl \rightarrow BCl_3 + H_2 \qquad (3)$$

followed first-order kinetics with respect to the partial pressure of HCl and $BHCl_2$.

$$\frac{-d[BHCl_2]}{dt} = kp_{BHCl_2}p_{HCl} \qquad (4)$$

The rate constants are given in Table II.

The back reaction at elevated temperatures was rapid enough to reduce the effective conversion when the exhaust gases were not cooled quickly. The rates of the back reaction at high temperatures were determined by passing the gases from a reactor at 700° C. through a borosilicate glass coil held at controlled temperatures and at predetermined residence times. From data obtained at 400° and 500° C., the reaction rate constants at those temperatures were calculated, and are given in Table II.

From the Arrhenius plot of log k *vs.* $1/T°$ C. and by using the rate constants shown in Table II the activation energy of the back reaction in the vapor phase is estimated to be 9.1 kcal. per mole. The magnitude of the rate constants at 400° and 500° C. shows why rapid cooling is required to prevent loss of conversion. It is also of interest to observe how rapidly the rate increases in passing from 400° to 500° C.

Thermodynamic Data

Some thermodynamic quantities have been calculated from an evaluation of the equilibrium data obtained on the hydrogenation reaction in the temperature range of 600° to 700° C. and from an equilibrium study of the disproportionation reaction at 0° C. Thermodynamic quantities at standard conditions are given in Table III.

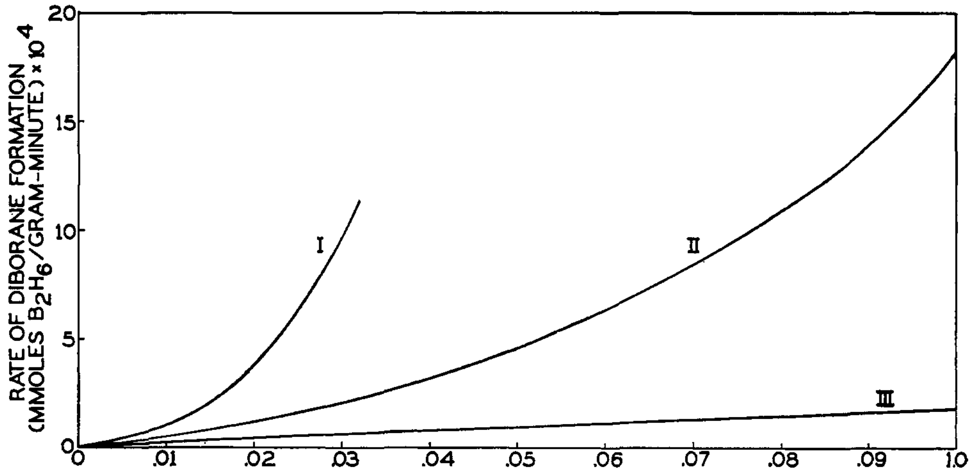

Figure 6. Rate of diborane formation as function of liquid composition

Refluxed at atmospheric pressure

Curve	Boil-Up Rate, Drops/Min.
I	224, fractionation column
II	275, no column
III	100, no column

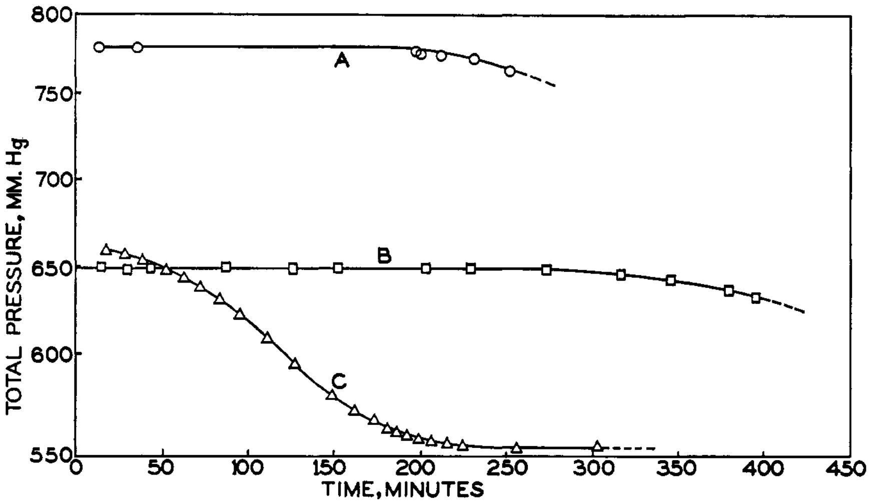

Figure 7. Rate of hydrogen-chlorine exchange between B_2H_6 and BCl_3 in liquid BCl_3 at 0° C.

	Initial Mole Fraction B_2H_6
A	0.0152
B	0.0085
C	0.0084

(mole fraction $BHCl_2$ at start 0.0051)

Figure 5 is a plot of the logarithm of the equilibrium constant *vs.* the reciprocal of temperature for the hydrogenation reaction

$$K = \frac{p_{BHCl_2} \times p_{HCl}}{p_{BCl_3} \times p_{H_2}} \qquad (5)$$

Since the experimental data used to calculate the thermodynamic quantities were obtained at 0° C. and in a temperature range of 600° to 700° C., less reliability can be placed on values calculated for intermediate temperature ranges.

Disproportionation of Dichloroborane

The dichloroborane disproportionates to boron trichloride and diborane in accordance with Equation 2. An experimental study of the disproportionation reaction showed that the reaction could be driven completely to the right by taking advantage of the high volatility of diborane and continually removing it from the system as it formed. It was sufficient to reflux a solution of boron trichloride and dichloroborane, using a reflux condenser cooled to −78° C., and to collect the diborane issuing as a gas from the top of the condenser. The rate of diborane evolution could be increased by employing a higher boil-up rate and using a fractionating column. These results are illustrated in Figure 6. The boil-up rates as shown are actually drops per minute of reflux. The fractionating column was 15 × 1.2 cm. packed with stainless steel Heli-Pak.

While disproportionation of dichloroborane was being studied, it was observed that liquid boron trichloride and diborane react with each other at an appreciable rate. Recently (*6, 9, 12*), some aspects of the reaction of boron trichloride and diborane have been reported. In this laboratory it was found that reaction occurs after induction periods dependent on the partial pressure of the diborane, as shown in Figure 7 (curves *A* and *B*). The reaction was found to be autocatalytic, since introduction of some dichloroborane at the start of reaction eliminated the lag (*C*, Figure 7). The S-shaped curve is characteristic of autocatalytic reactions.

The equilibrium composition of the mixture of diborane, dichloroborane, and boron trichloride was determined at 0° C. in order to establish the equilibrium constant for the disproportionation. This information also could be used for the calculation of other thermodynamic quantities. A mixture of diborane and liquid boron trichloride was equilibrated at 0° C. and from the final pressure of the respective components it was

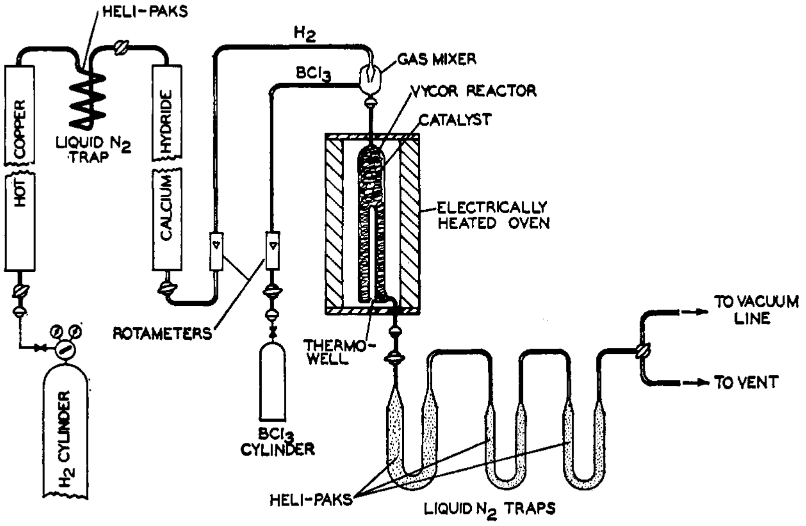

Figure 8. Apparatus

possible to determine the composition of the liquid, from which the equilibrium constant, $K_{x(\text{dis})}$, for the liquid phase reaction could be calculated.

$$K_{x(\text{dis})} = \frac{X_{\text{B}_2\text{H}_6} \times X_{\text{BCl}_3}{}^4}{X_{\text{BHCl}_2}{}^6} \tag{6}$$

where X is the mole fraction. The equilibrium constant for the vapor phase reaction, $K_{p(\text{dis})}$, could be calculated from the relation

$$K_{p(\text{dis})} = K_{x(\text{dis})} \frac{F_{\text{B}_2\text{H}_6} \times F_{\text{BCl}_3}{}^4}{F_{\text{BHCl}_2}{}^6} \tag{7}$$

where F is the fugacity. The fugacities of boron trichloride and of diborane are available in the literature. The fugacity of dichloroborane at 0° C. was determined by measurements on an equilibrium mixture of diborane and liquid boron trichloride. From these data it was possible to calculate the fugacities of both boron trichloride and dichloroborane. The calculated values of the fugacity of boron trichloride at 0° C. were 479 and 482 mm. (literature value, 477 mm.); the values determined for dichloroborane were 2.0 and 1.96 atm. The average value of 1.98 atm. was employed for calculation of the equilibrium constant of the disproportionation.

The value obtained for $K_{x(\text{dis})}$ at 0° C. was 12.52×10^3 (average of three determinations). The corresponding value of $K_{p(\text{dis})}$ at 0° C. was 872.3 atm.^{-1} This value was employed in the calculation of thermodynamic quantities for the hydrogenation reaction and for dichloroborane which are given above. The free energy decrease for the disproportionation reaction is found to be -2.48 kcal. per mole at 25° C. and the equilibrium constant in the vapor phase at that temperature is 66.4 atm.^{-1}

Experimental

Hydrogenation of Boron Trichloride. A high vacuum system and standard vacuum techniques were employed. In early studies, with silver catalyst, the reactor was made of Corning No. 1740 ignition glass. It was U-shaped, with an inlet arm smaller in diameter than the reactor arm, and contained 40.6 grams of granular silver (40- to 60-mesh) with a free volume of 30 cc. The hydrogen was metered by rotameter and passed through hot copper to remove oxygen, then through a trap cooled by liquid nitrogen, and finally through a tower of granular calcium hydride to remove water. The hydrogen then passed through a bubbler containing liquid boron trichloride, which was adjusted to the temperature needed to produce the desired molar ratio of hydrogen to boron trichloride. The gas mixture then passed through the reactor which was inside an electrically heated furnace. The exhaust gases were condensed in a train of three traps cooled by liquid nitrogen.

In later work (see Figure 8) a straight Vycor reactor tube (16.5-mm. i.d.) was used which had an exit tube of small diameter (5-mm. i.d.) to allow the exit gases to leave intermediate temperature zones rapidly. The reactor was provided with a thermocouple well and contained 35 grams of silver screen (16-mesh). The free volume of the reactor was 11.7 cc. Boron trichloride and hydrogen were separately metered through rotameters. The boron trichloride, which had been purified by fractional condensation at $-112°$ C., was taken from a small stainless steel cylinder which could be weighed before and after each experiment. The reactor was heated in an electric tubular furnace.

The studies at elevated pressure were conducted in two different stainless steel reactors. One was a tube 10.2 cm. long and 0.8 cm. in i.d. The other was the same length but had an inside diameter of 0.64 cm. The reactions were studied with the tube empty (no catalyst) and also packed with silver granules. The hydrogen flow was metered and passed through a stainless steel bubbler containing boron trichloride, the amount of the latter transported being determined by the temperature. The hydrogen was pretreated as before and the exhaust gases were collected in traps cooled by liquid nitrogen. The reactors were heated in an electric furnace.

Analytical. CHEMICAL. The procedure employed for chemical analysis involved condensing the condensable components into a vessel containing water frozen at $-196°$ C., sealing the vessel, and then allowing the water and products to reach ambient temperature. The hydrolysis products consisted of boric acid, hydrochloric acid, and hydrogen. The hydrogen was passed through three U-tubes immersed in liquid nitrogen and collected in a calibrated volume by means of a Toepler pump and measured. The total boron and hydrochloric acid were determined titrimetrically. From these data, the boron hydrides content was found and the conversion and yield were calculated, based on the boron and chlorine balance.

$$\%\ \text{conversion} = \frac{\text{BHCl}_2}{\text{total BCl}_3\ \text{introduced}} \times 100 \tag{8}$$

$$\%\ \text{yield} = \frac{\text{H}_2\ \text{from hydrolysis}}{\text{boron consumed}} \times 100 = \frac{\text{BHCl}_2}{\text{BHCl}_2 + \text{B lost}} \times 100 \tag{9}$$

INFRARED SPECTROSCOPY. Distinct infrared absorption bands specific for each component present can be observed. Unfortunately, pressure-broadening effects to a significant degree were observed with these materials—that is, the presence of each component affected the absorption curves of the other components present. Consequently, to obtain reliable results it was necessary to set up a series of calibration curves which delineated the mutual interacting effects.

An infrared calibration curve of BHCl_2 in the presence of BCl_3 was prepared. A mixture of BHCl_2 and BCl_3 of known hydride content (as determined by the hydrolysis) was used in the determination of the absorbances of BHCl_2 at various total pressures. Knowing the partial pressures of BCl_3, the differences from total pressures were considered those of BHCl_2. From these data the absorbances of BHCl_2 were determined and the extinction coefficients calculated. For a 1-cm. cell at 25° C. with sodium chloride windows and with double slits, the following values were obtained:

	Wavelength, Microns	*Extinction Coefficient, k*
BCl_3	10.10	1.9×10^{-2}
BHCl_2	9.12	1.2×10^{-2}

The absorbance of BHCl_2 was linear with respect to its partial pressure up to 6 mm. The partial pressures of BCl_3 in the mixtures were adjusted not to exceed 45 mm. A 1-cm. cell was employed for this work because the absorption of BCl_3 was too strong in a larger cell, unless very low pressures were used.

Diborane could not be measured in the 1-cm. cell and it was therefore not possible to determine its effect on the BHCl_2 calibration curve.

Further studies on infrared spectra showed the following: Hydrogen has no pressure-broadening effect on BHCl_2 at the 9.12-micron band nor on BCl_3 at the 10.1-micron band; hydrogen chloride has no pressure-broadening effect on BHCl_2 at 9.12 microns nor on BCl_3 at 10.1 microns.

Infrared analysis of known mixtures of BCl_3 and B_2H_6 showed that B_2H_6 could be measured accurately (using the 2.8-micron band) in the partial pressure range of 10 to 120 mm. in the presence of BCl_3. The latter exerts no pressure-broadening effect on B_2H_6. Within the same range of pressures there was observed a scatter of points with respect to the determination of BCl_3 in the presence of B_2H_6. Apparently there is no specific pressure-broadening effect. When pure BCl_3 was put into the infrared cell, on standing, the band of 8.3 microns increased in intensity with time. This effect was produced rapidly by the addition of a slight amount of water, and accordingly it is attributed to a species, such as $BCl_2(OH)$, Cl_2BOBCl_2, or $Cl_3O_3B_3$, which might result from hydrolysis. It is considered that the scatter of points which appears when B_2H_6 is present may be due to this effect, it being assumed that during the process of introducing the B_2H_6 sample the extra manipulations and extra time permitted a greater effect of trace moisture. The bands at 7.05 microns (preferred) and 6.85 microns were employed for the determination of BCl_3 in the presence of B_2H_6, but they are also affected to a slight extent when the band at 8.3 microns increases.

Reaction of Hydrogen Chloride with Dichloroborane (Back Reaction). VAPOR PHASE REACTION NEAR AMBIENT TEMPERATURE. Back-reaction data at near ambient temperature in the vapor phase were obtained by following the rate of disappearance of dichloroborane in an infrared cell. In these experiments, mixtures of dichloroborane and boron trichloride were placed in a 1-cm. infrared cell and the partial pressure of dichloroborane was determined by infrared analysis. The cell was then pressurized with hydrogen chloride and the rate of consumption of dichloroborane was followed by measuring the absorbance of the band at 9.12 microns. Reaction rates were measured at 25.6°, 30.6°, and 53.0° ± 1.0° C. The data obtained in a typical experiment are shown in Table IV.

VAPOR PHASE REACTION AT ELEVATED TEMPERATURES. This study was conducted by dividing the gases emerging from the reactor at 700° C. into two streams, one being passed through a heated borosilicate glass coil maintained at a controlled temperature, and the other, the bypass, quenched immediately in a trap cooled by liquid nitrogen. The gases leaving the heated coil were also cooled with liquid nitrogen. The products from the coil and from the bypass were analyzed and compared. Measurements were made at 400° and 500° C. over a range of residence times. The data obtained are given in Table V.

DISPROPORTIONATION OF DICHLOROBORANE. In one experiment a solution of 40.52 mmoles of dichloroborane in 245.56 mmoles of liquid boron trichloride was placed in a 25-ml. distillation flask, which was attached to a fractionation column (15.0- × 1.2-cm. i.d.) packed with stainless steel Podbielniak Heli-Pak (0.050 × 0.100 × 0.100 inch). The latter was connected to a reflux condenser cooled by dry ice–acetone. The solution was refluxed under dry hydrogen at atmospheric pressure. The noncondensable diborane issuing from the top of the condenser was collected in a trap cooled by liquid nitrogen. At a boil-up rate of 224 drops per minute, 6.15 mmoles of diborane were collected at the end of 3.5 hours; at the end of 7.25 hours the total diborane collected was 6.60 mmoles, and at the end of 9.25 hours the total was 6.70 mmoles. The last value represents a 99.3% recovery of $BHCl_2$ as B_2H_6.

Equilibrium Constant of Disproportionation Reaction. Measured quantities of diborane were added to known quantities of liquid boron trichloride at 0° C., and arranged to give a small vapor phase volume compared to the volume of liquid. The change of pressure was noted as the solution reached its equilibrium concentration at the temperature. In three separate determinations the quantities of materials used and the equilibrium pressures at 0° C. were:

BCl_3, Mmoles	*B_2H_6, Mmoles*	*Equil. Press., Mm.*
1155.7	16.56	620
1155.7	23.60	668
330.15	5.09	604

The fugacity of dichloroborane at 0° C. was determined in an equilibrated mixture of liquid boron trichloride and diborane at 0° C. The total pressure of the system was measured and the vapor phase was analyzed for boron trichloride and dichloroborane (diborane by difference). Data used in determination of the fugacity of dichloroborane are given in Table VI.

Table IV. Back-Reaction Data in Vapor Phase at 53° C.

Infrared cell. 10.5 mm.
Pressure of BCl_3 + $BHCl_2$ before addition of HCl. 149 mm.
Partial pressure of $BHCl_2$ as determined by IR. 13.30 mm.
Total pressure after addition of HCl. 332 mm.
Infrared cell temperature. 53° ± 1.0° C.

Time, min.	0	9	13	17	27	36	48
$BHCl_2$ pressure, mm. Hg	13.30	13.24	13.14	13.09	12.88	12.78	12.46

Table V. Back-Reaction Data in Vapor Phase at 400° and 500° C.

(Mole ratios of H_2/BCl_3 = 2.75 to 3.19)

Conversion in Reactor at 700° C., %	*Temp. of Coil, ° C.*	*Residence Time in Coil, Sec.*	*Conversion after Coil, %*
19.3	400	1.4	19.7
16.5	400	2.8	16.2
17.7	400	5.1	15.7
16.5	400	10.5	16.0
18.1	400	11.0	17.4
17.9	400	24.8	16.7
18.1	400	52.7	15.1
16.5	500	7.5	14.4
16.7	500	17.3	13.4
17.3	500	29.5	11.9
17.6	500	31.7	12.3
17.0	500	36.8	12.3

Table VI. Data for Fugacity of Dichloroborane

Initial total charge of BCl_3. 1155.7 mmoles
Initial charge of B_2H_6. 23.6 mmoles
Total volume of apparatus. 2105.0 ml.
Estimated liquid phase volume. 94.0 ml.
Total pressure. 633 mm.
Temperature. 0° C.

	Composition of Vapor, Mole %	
	After 8 hr.	*After 10 hr.*
BCl_3	71.3	71.6
$BHCl_2$	13.9	14.0
B_2H_6 (by difference)	14.8	14.4

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