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Deuterium Exchange between Deuteriodiborane and Aluminum Borohydride

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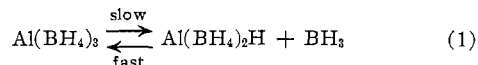
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The kinetics of the exchange of deuterium between diborane and aluminum borohydride were studied over a temperature range of -7 to 20° , and the orders of reaction were found to be dependent on the relative proportions of B_2D_6 and $Al(BH_4)_3$. When the pressure of B_2D_6 is less than four times the $Al(BH_4)_3$ pressure, the reaction order was found to be 0.52 with respect to $Al(BH_4)_3$ and 1.2 with respect to B_2D_6 . At ratios greater than four the order of reaction with respect to $Al(BH_4)_3$ changed to 0.8 and the order with respect to B_2D_6 changed to -1.2 . The activation energy was found to be 14 ± 1 kcal./mole. A mechanism is proposed involving the thermal dissociation of both $Al(BH_4)_3$ and B_2D_6 followed by a rate-determining collision of B_2D_6 with borane radicals. The changing orders of reaction are consistent with a derived steady-state expression for this exchange. Direct experimental evidence was obtained to prove that the boron atoms are undergoing exchange in this reaction by the use of boron-10 enriched B_2D_6 .

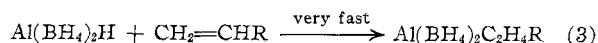
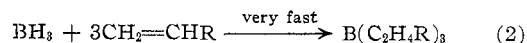
Introduction

Information obtained about the structure and chemical binding in the metal borohydrides²⁻⁷ indicates that these compounds, especially the more covalent ones, aluminum and beryllium, are similar in behavior to the boron hydrides. Infrared absorption studies of aluminum borohydride⁸ show a similarity in structure to that of diborane by giving evidence for the presence of bridge hydrogens. Longuet-Higgins has shown⁹ that a prismatic arrangement of the borohydride groups about the Al atom is compatible with a "protonated" double bond structure (bridge) in which three 120° coplanar π -bonds radiate from the Al atom.

A study of the kinetics of the reaction between aluminum borohydride and olefins¹⁰ has also indicated a similarity to diborane. The reaction mechanism proposed involves the BH_3 radical in an intermediate rate-determining step (eq. 1).

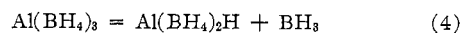


In the presence of an olefin the following fast reactions were proposed



Ogg¹¹ has reported a study of the nuclear magnetic resonance spectrum of aluminum borohydride and concludes that the molecule is characterized by a bridge bond structure, analogous to B_2H_6 , but that a dynamic process renders bridge and terminal protons indistinguishable.

In recent work¹² on the exchange reaction between $Al(BH_4)_3$ and D_2 , the kinetics showed fractional order dependence with respect to aluminum borohydride. A mechanism was suggested that involved the dissociation of $Al(BH_4)_3$ in the initial step



The reaction then proceeded by collisions between borane radicals and deuterium. This work emphasized the role played by the borane intermediates and showed the similarity of aluminum borohydride chemistry to that of the boron hydrides.

The present work described in this paper is a study of the exchange of deuterium between deuteriodiborane and aluminum borohydride. In view of the previous results of other isotopic exchange reactions involving

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(1) Department of Chemistry, University of South Florida, Tampa, Florida.

(2) H. I. Schlesinger, R. T. Sanderson, and A. B. Burg, *J. Am. Chem. Soc.*, **62**, 3421 (1940).

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diborane,^{13,14} it was expected that this exchange reaction should proceed by an interchange of borane radicals.

Experimental

Materials. $\text{Al}(\text{BH}_4)_3$.—Aluminum borohydride was prepared by the reaction of aluminum chloride and lithium borohydride. The apparatus and procedure were similar to that used by Schlesinger.¹⁵ The $\text{Al}(\text{BH}_4)_3$ was purified by distilling it from a -45° bath through a -63.5° bath and then by pumping on it at -140° to remove all traces of diborane. After preparation the $\text{Al}(\text{BH}_4)_3$ was stored in a glass bulb attached to an all glass-metal system by a Monel packless valve and stored at -80° to prevent decomposition.

B_2D_6 .—Deuteriodiborane was prepared by the reaction of boron trifluoride with lithium aluminum deuteride in an ether solution. The apparatus and procedure described by Shapiro¹⁶ were used with only minor modifications. Samples of from 96.3 to 98.0% lithium aluminum deuteride obtained from Metal Hydrides, Inc., were used in the reaction. The B_2D_6 was purified by several successive distillations from a -120° bath to liquid nitrogen-cooled traps and then stored at room temperature in glass bulbs with stopcocks. To determine the deuterium content, a sample of the B_2D_6 was quantitatively decomposed¹⁷ by passing it through a uranium furnace at 600° and the resulting isotopic composition of the hydrogen-deuterium gas mixture was determined by a thermal conductivity method. The deuterium content of the B_2D_6 used in this exchange study was determined to be 96%.

$\text{B}_2^{10}\text{D}_6$.—The $\text{B}_2^{10}\text{D}_6$ was prepared by the reaction of B^{10}F_3 etherate with lithium aluminum deuteride. The lithium aluminum deuteride was obtained from Metal Hydrides, Inc. The B^{10}F_3 was prepared from $\text{CaF}_2\text{B}^{10}\text{F}_3$ containing 96% B^{10} and obtained from the Atomic Energy Commission. The $\text{CaF}_2\text{B}^{10}\text{F}_3$ was placed in a copper tube which had previously been treated with gaseous HF overnight. The copper tube was attached to a vacuum system containing several traps. The tube was heated to 100° and degassed; the temperature was then raised to 300° and the B^{10}F_3 which was generated passed through a trap at -78° into a trap at -195° where it condensed out. The -78° trap served to remove any HF which might have been formed in the reaction. Diethyl ether was condensed on the B^{10}F_3 and the resulting product was used to prepare $\text{B}_2^{10}\text{D}_6$ as in the general preparation of diborane. The $\text{B}_2^{10}\text{D}_6$ prepared in this manner contained 96% B^{10} and 96.5% deuterium.

B_2H_6 .—The B_2H_6 used was obtained from Callery Chemical Corporation. The diborane was purified by passing it through a -140° trap and collecting it in a -195° trap.

Apparatus and Procedure. 1. B_2D_6 - $\text{Al}(\text{BH}_4)_3$ Exchange.—The high-vacuum system used in this work was partly constructed with Monel tubing and Hoke high-vacuum Monel metal valves because of the reactivity of the aluminum borohydride with stopcock lubricants.

The rate of the $\text{Al}(\text{BH}_4)_3$ - B_2D_6 reaction was more rapid in a borosilicate glass reaction vessel not previously exposed to $\text{Al}(\text{BH}_4)_3$ than in a vessel after subsequent exposure to $\text{Al}(\text{BH}_4)_3$. In previous work on the $\text{Al}(\text{BH}_4)_3$ - D_2 exchange¹² it was found that reproducible results would be obtained if the reaction vessels were exposed to 5 cm. pressure of $\text{Al}(\text{BH}_4)_3$ for a period of 60 hr. at 50° . This conditioning process was carried out in five 12-hr. intervals with intermediate pumping. By use of this process for conditioning of reaction bulbs, it was possible to obtain reproducible results for the $\text{Al}(\text{BH}_4)_3$ - B_2D_6 reaction and a kinetic study of this reaction was readily carried out.

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(15) H. I. Schlesinger, H. C. Brown, and E. K. Hyde, *ibid.*, **75**, 209 (1953).

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The kinetics of the reaction were studied by filling the reaction bulb with the desired concentrations of $\text{Al}(\text{BH}_4)_3$ and B_2D_6 , respectively, and then a constant temperature bath was raised into position. After the desired interval of time, the reaction was stopped by opening the reaction bulb valve and freezing the products into a -195° precooled trap. Separation of the products was effected by placing a -120° bath around the trap and collecting the diborane in a liquid nitrogen trap. This diborane was decomposed by passing it through a uranium furnace and analyzing the resulting hydrogen-deuterium mixture by the thermal conductance method.

Surface studies of this reaction were carried out in all Monel metal reaction vessels and also in borosilicate bulbs packed with glass rods to increase the surface to volume ratio by a factor of 13.

2. **Procedure Used in $\text{B}_2^{10}\text{D}_6$ - $\text{Al}(\text{BH}_4)_3$ Exchange.**—In order to compare the exchange of hydrogen and boron between diborane and aluminum borohydride, $\text{B}_2^{10}\text{D}_6$ was prepared. Samples of known isotopic composition were prepared by mixing $\text{B}_2^{10}\text{D}_6$ and B_2D_6 in different amounts (Table I). These samples were analyzed by a mass spectrometer (Consolidated Type 21-102C) and the results utilized to test the method used to study the boron-10 exchange between $\text{B}_2^{10}\text{D}_6$ and $\text{Al}(\text{BH}_4)_3$.

TABLE I
CONCENTRATIONS OF REACTANTS PREPARED FOR CALIBRATION WORK

Run no.	$\text{B}_2^{10}\text{D}_6$, cm.	B_2D_6 , cm.
C-1	5.00	
C-2	4.00	1.00
C-3	3.00	2.02
C-4	2.00	3.00
C-5	1.02	4.00
C-6		5.00

After calibration a series of exchange reactions between $\text{B}_2^{10}\text{D}_6$ and $\text{Al}(\text{BH}_4)_3$ was carried out (Table II) in a manner similar to the previous exchange studies. After reaction, the diborane was separated from the $\text{Al}(\text{BH}_4)_3$ by fractional distillation. This separation must be carried out at -120° in order to ensure that no further exchange occurs. The diborane fraction was then divided into two portions. One part was decomposed in a uranium furnace and the resulting H_2 - D_2 mixture was analyzed by means of a thermal conductance method. The other part was analyzed by a mass spectrometer. These samples were kept refrigerated until analyzed in order to minimize decomposition.

TABLE II
CONCENTRATIONS OF REACTANTS USED IN $\text{B}_2^{10}\text{D}_6$ - $\text{Al}(\text{BH}_4)_3$ EXCHANGE WITH REACTION TIMES AT 20°

Run no.	$\text{Al}(\text{BH}_4)_3$, cm.	$\text{B}_2^{10}\text{D}_6$, cm.	Reaction time, min.
C-9	5.00	10.0	15.5
C-10	5.00	10.0	25.0
C-11	5.00	15.0	10.0
C-12	5.00	15.0	20.0
C-13	5.00	20.0	10.0
C-14	5.00	20.0	20.0

Results

1. **$\text{Al}(\text{BH}_4)_3$ - B_2D_6 Exchange.**—The kinetics of the isotopic exchange of deuterium in this reaction have been interpreted in terms of the first-order rate law

$$R = -1/t(ab/a + b) \ln(1 - f) \quad (5)$$

where a and b are the gram-atom concentrations of the aluminum borohydride and deuteriodiborane molecules,

R is the rate of exchange, t is the time (minutes), and f is the fraction exchanged and is equal to $(D_0 - D_t/D_0 - D_\infty)$, where the D is the specific deuterium content of the analyzed compounds at times indicated by the subscripts. The orders of reaction with respect to reactants were determined by varying independently the concentrations of the reactants.

The rate of reaction is proportional to the product of the concentration of reactants raised to their respective powers.

$$R = ka^{\alpha}b^{\beta} \quad (6)$$

Taking logarithms of both sides of eq. 6 yields

$$\log R = \alpha \log a + \beta \log b + \log k \quad (7)$$

From eq. 7 it is apparent that a plot of $\log R$ vs. \log of one of the concentrations (while the other concentration is held constant) produces a slope which is equal to the order of the reaction with respect to the first reactant. The average results of a series of experiments carried out to determine the orders of reaction with respect to aluminum borohydride and deuteriodiborane are shown in the data plotted in Fig. 1 and 2. The orders of reaction are given in Table III.

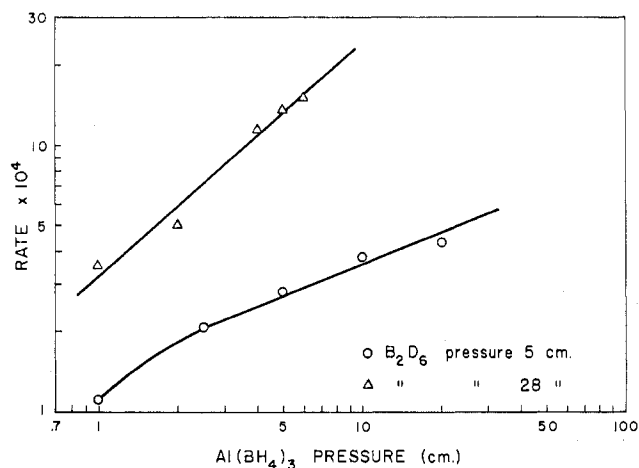


Fig. 1.—A plot of $\log R$ vs. \log pressure showing the Al(BH₄)₃ dependence at constant pressures of B₂D₆.

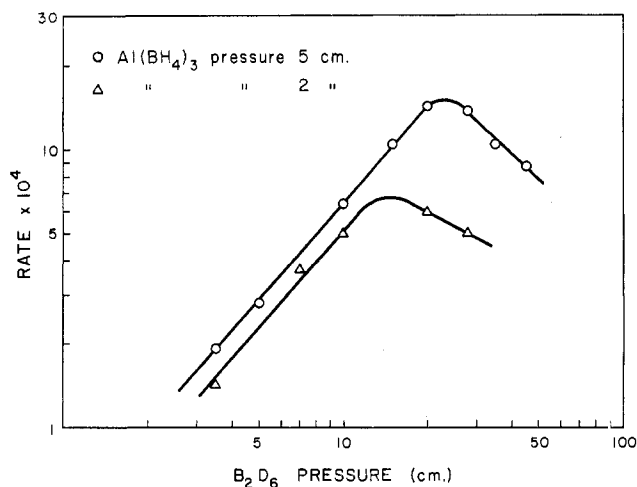


Fig. 2.—A plot of $\log R$ vs. \log pressure showing the B₂D₆ dependence at constant pressures of Al(BH₄)₃.

TABLE III

ORDERS OF EXCHANGE REACTION Al(BH₄)₃-B₂D₆ AT 20°

Al(BH ₄) ₃ pressure, cm.	B ₂ D ₆ pressure, cm.	Order
5	3.5-15	1.2 ^a
5	28-45	-1.2 ^a
2.5-20	5	0.52 ^b
1-6	28	0.80 ^b

^a Order of reaction with respect to B₂D₆. ^b Order of reaction with respect to Al(BH₄)₃.

The rate constants, k , were calculated from eq. 6, which, with proper substitution of the experimentally determined parameters, becomes

$$R = k[B_2D_6]^{1.2}[Al(BH_4)_3]^{0.52} \quad (8)$$

Where ratios of diborane concentration to aluminum borohydride concentration are greater than four, eq. 8 becomes

$$R = k[B_2D_6]^{-1.2}[Al(BH_4)_3]^{0.80} \quad (9)$$

The rate constants calculated from eq. 8 and 9 are given in Table IV. Those rate constants calculated from eq. 9 are marked by a superscript a . All other values of k were calculated from eq. 8.

Typical runs are indicated in Fig. 3, where $\ln(1 - f)$ is plotted vs. time. These straight line plots indicate a normal behavior for the first-order rate law. Isotopic analysis of reacted samples of aluminum borohydride after long reaction times have shown that all twelve hydrogen atoms of the molecule are involved in exchange.

Typical data for this reaction from -7.0 to 20.0° are plotted in Fig. 4. The temperature dependence of the rate indicates an apparent activation energy of 14 kcal./mole. Several experiments were carried out in the pretreated packed bulbs to test the effect of increased surface on the reaction rate and these results are listed in Table V. It can be seen that no

TABLE IV

RATE CONSTANTS OF THE Al(BH₄)₃-B₂D₆ EXCHANGE AT 20°

Al(BH ₄) ₃ concn., equiv./l. (a)	B ₂ D ₆ concn., equiv./l. (b)	$t_{1/2}$, min.	k
0.0065	0.0162	30.3	0.162
.0162	.0162	27.2	.232
.0323	.0162	26.8	.220
.0646	.0162	23.9	.209
.1290	.0162	23.5	.168
.0065	.0941	11.7	.191 ^a
.0129	.0941	15.7	.155 ^a
.0258	.0941	12.3	.202 ^a
.0323	.0941	12.3	.200 ^a
.0387	.0941	12.7	.193 ^a
.0323	.0113	30.2	.231
.0323	.0162	26.8	.220
.0323	.0323	17.5	.212
.0323	.0486	12.9	.217
.0323	.0646	10.5	.211 ^a
.0323	.0941	12.3	.201 ^a
.0323	.1130	16.8	.182 ^a
.0323	.1450	21.2	.194 ^a

^a Calculated from eq. 9.

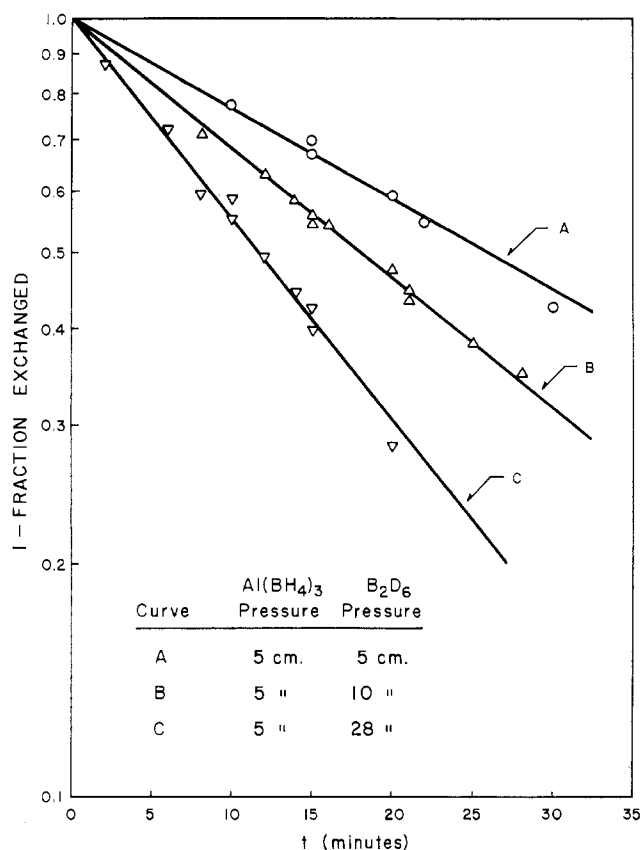


Fig. 3.—Typical curves for the exchange reaction $\text{Al}(\text{BH}_4)_3\text{-B}_2\text{D}_6$ at 20° .

TABLE V
INFLUENCE OF SURFACE ON RATE OF EXCHANGE

Temp., °C.	B ₂ D ₆ concn., cm.	Al(BH ₄) ₃ concn., cm.	10^5R	Surface change ^a
0.0	5.00	5.00	5.33	None
0.0	5.00	5.00	5.37	Monel reaction bulb
-7.0	5.00	5.00	2.21	None
-7.0	5.00	5.00	2.24	Increased s/v by 13 with Pyrex
20	10.00	5.00	63.8	None
20	10.00	5.00	61.8	Increased s/v by 13 with Pyrex

^a s/v indicates surface to volume ratio.

appreciable change in rate was obtained. These results indicate that this reaction is proceeding by a homogeneous gas phase mechanism. Several runs were carried out in Monel reaction vessels and these results are also given in Table V. The use of a pretreated Monel surface did not seem to affect the rate of this reaction.

2. $\text{Al}(\text{BH}_4)_3\text{-B}_2^{10}\text{D}_6$ Exchange.—In view of the fact that we propose that this exchange reaction involves the radical borane, it was felt that direct proof of the exchange of boron should be obtained. It was possible to determine this by preparing $\text{B}_2^{10}\text{D}_6$ and allowing this to exchange with aluminum borohydride.

In order to obtain accurate results and maximum information a simultaneous study of both boron and hydrogen exchange between diborane and aluminum borohydride was made. It was possible to measure

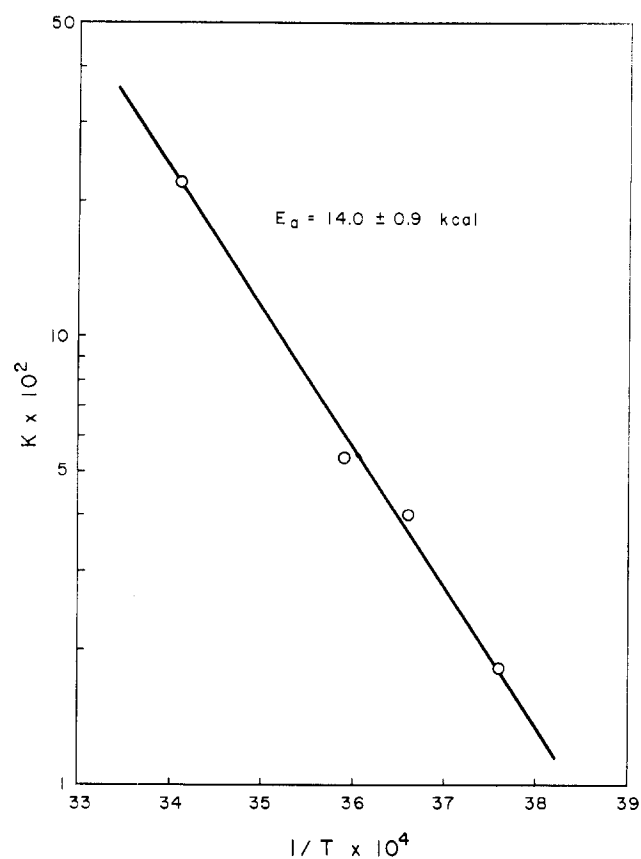


Fig. 4.—Temperature dependence of the $\text{Al}(\text{BH}_4)_3\text{-B}_2\text{D}_6$ exchange.

both the boron and hydrogen exchange of the sample by dividing it into two parts after reaction and measuring the isotopic percentages of the tracer isotopes.

The mass spectrum of $\text{B}_2^{10}\text{D}_6\text{-B}_2\text{H}_6$ mixtures yields a complicated fragmentation pattern with mass peaks from 10 to 34. A method has been devised to obtain the $\text{B}^{10}/\text{B}^{11}$ ratio in the reaction samples in order to compare the rates of exchange between boron and hydrogen in the $\text{Al}(\text{BH}_4)_3\text{-B}_2^{10}\text{D}_6$ exchange.

The hydrogen-deuterium ratio for each exchange was determined from thermal conductance measurements. For a given hydrogen-deuterium ratio it was possible to calculate the isotopic constitution of each positive ion fragment by the method used by Norton.¹⁸

The isotopic constitution of each positive ion fragment thus obtained was multiplied by the percentage of the monoisotopic boron fragments that would contain one, two, or three deuteriums. The resulting products yielded the relative abundance of each fragment. The combination of the experimental data with the relative abundances of like mass numbers was stated in terms of simple algebraic equations of the form

$$X(a) + Y(b) = C$$

where X and Y are unknown constants; a and b are the relative abundances of B^{10} and B^{11} fragments, respectively; and C is the experimental peak height

(18) F. J. Norton, *J. Am. Chem. Soc.*, **71**, 3488 (1949).

for the given mass number. Simultaneous solution of a set of these equations made it possible to calculate the B¹⁰/B¹¹ ratio. The results of these calculations for the calibration samples are found in Table VI. The first column lists the percentage boron calculated from the known isotopic abundance and the second column includes the calculated values determined by the procedure described above.

TABLE VI

MASS SPECTRUM ANALYSIS OF KNOWN DIBORANE MIXTURES

Sample	% B ¹⁰ (known)	% B ¹⁰ (calcd.)
C1	96.0	95.0
C2	80.8	79.8
C3	65.4	66.5
C4	50.4	50.7
C5	35.3	37.6
C6	20.0	23.5

Six runs were carried out with different initial concentrations of B₂¹⁰D₆ and Al(BH₄)₃ and the diborane fractions were analyzed to obtain the B¹⁰ and the H concentrations. These results are shown in Table VII. The per cent H found in each sample was obtained by use of the thermal conductance analyzer. The per cent B¹⁰ was calculated according to the procedure described above. The rates of reaction for both H and B¹⁰ were calculated by using eq. 5. The initial percentages of H and B¹⁰ in the B₂¹⁰D₆ samples were 4.5 and 96.5, respectively. The last column presents a comparison of the rate of exchange of H to the rate of exchange of B¹⁰ in the diborane fraction. This ratio, which is seen to range from 3 to 4, indicates that three to four hydrogens are exchanging per boron atom.

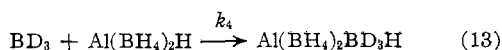
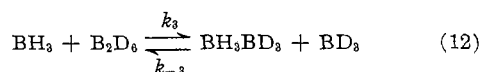
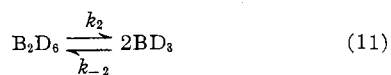
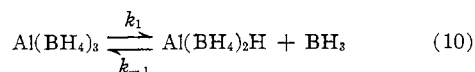
TABLE VII

ANALYSIS OF DIBORANE FRACTION AFTER EXCHANGE

Run no.	%B ¹⁰ (calcd.)	%H (T.C.)	10 ⁵ R (H)	10 ⁵ R (B ¹⁰)	R _H /R _{B¹⁰}
C9	77.4	29.2	76.0	24.8	3.06
C10	64.6	41.7	97.1	28.0	3.47
C11	82.2	24.4	122.0	34.8	3.52
C12	73.3	30.3	131.0	41.5	3.16
C13	83.5	22.6	182.0	46.0	3.96
C14	79.8	28.0	146.0	35.8	4.08

Discussion

The results obtained in these experiments suggest the following set of equations



In order to derive a theoretical expression consistent with the experimental results and the proposed mech-

anism the method recently developed by Marcus¹⁹ was employed. Using this method for relating the rate (*R*) to the elementary rate constants, one obtains

$$R = \frac{k_2 k_4 a d + k_3 k_4 a c d}{k_{-2} c + k_{-3} a / 6 + k_4 d} \quad (14)$$

where we have set $a = 6(\text{B}_2\text{D}_6)$, $b = 12[\text{Al}(\text{BH}_4)_3]$, $c = \text{BH}_3$, and $d = \text{Al}(\text{BH}_4)_2\text{H}$, since a and b denote concentrations in equivalents per liter while (B_2H_6) and $[\text{Al}(\text{BH}_4)_3]$ denote molar concentrations.

The constant k_3/k_{-3} can be evaluated in terms of the partition functions of the components of the equilibrium reaction (eq. 12). The result after simplification is obtained in terms of symmetry numbers²⁰

$$\frac{k_3}{k_{-3}} = \frac{\sigma_{\text{B}_2\text{H}_6} \sigma_{\text{BH}_3}}{\sigma_{\text{B}_2\text{H}_6} \sigma_{\text{BH}_3}} = \frac{4/3 \times 6}{4 \times 2} = 1 \quad (15)$$

therefore, $k_3 = k_{-3}$. The label * indicates a molecule with one deuterium atom in accordance with the method of Marcus.¹⁹

Equation 14 can be further simplified when the following equilibrium relations are introduced.

$$c = (k_2 a / 6 k_{-2})^{1/2} \text{ and } d = k_1 / k_{-1} (6 k_{-2} / k_2 a)^{1/2} b / 12$$

The ratio k_{-1}/k_4 is estimated from the symmetry numbers of the components and is set equal to 3. Thus one obtains the equation

$$\frac{1}{R} = \frac{6}{k_1 b} + \frac{1}{k_2 a + k_3 (k_2 / 6 k_{-2})^{1/2} a^{3/2}} \quad (16)$$

There are two cases derived from eq. 16 that should be considered. Case I, where $k_2 a \gg k_3 (k_2 / 6 k_{-2})^{1/2} a^{3/2}$, and case II, where $k_2 a \ll k_3 (k_2 / 6 k_{-2})^{1/2} a^{3/2}$. Case I applies when a is relatively high; R is then independent of a and proportional to b . When a is low case II applies such that R is proportional to $a^{3/2}$ and is independent of b . This behavior is consistent with the experimental data obtained in this exchange study.

For those experiments where the concentration of a is low (case II) a plot of $1/R$ vs. $1/b^{3/2}$ should be a straight line with a slope equal to $1/k_3 (k_2 / 6 k_{-2})^{1/2}$ and an intercept equal to $6/k_1 b$. This plot is seen in Fig. 5 and from these data, $k_3 (k_2 / 6 k_{-2})^{1/2}$ is calculated to be 0.21. The intercept depends upon the concentration of b and for the two curves in Fig. 5 k_1 is determined to be 0.326 sec.⁻¹.

It is possible to check this value of k_1 by considering those experiments where a is high (case I). Under this condition a plot of $1/R$ vs. $1/b$ should be $6/k_1$. Within experimental error this plot is found to be linear as seen from Fig. 6 and k_1 is determined to be 0.33 sec.⁻¹.

In our previous work¹³ on the isotopic exchange reaction between diborane and deuterium, we obtained results that are consistent with case II. It is worth expressing case II in physical terms in order to more clearly relate the earlier work with this exchange. First, if BD_3 were in equilibrium with B_2D_6 then we

(19) R. A. Marcus, *J. Chem. Phys.*, **23**, 1107 (1955).

(20) $\text{B}_2\text{H}_6^* = (1/3\sigma_1 + 2/3\sigma_2)\text{B}_2\text{H}_6^*$ ($\sigma_1 = *$ in bridge position; $\sigma_2 = *$ in terminal position). There are twice as many terminal positions as bridge positions, therefore $1/3 \times 2 + 2/3 \times 1 = 1/3$.

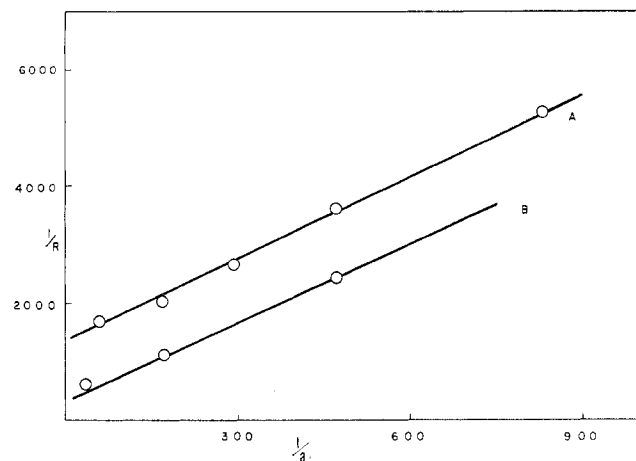


Fig. 5.—Dependence of $1/R$ vs. $1/a^{3/2}$ at 20° : curve A, $\text{Al}(\text{BH}_4)_3 = 2$ cm.; curve B, $\text{Al}(\text{BH}_4)_3 = 5$ cm.; a = deuteriodiborane concentration

would have $k_2(\text{B}_2\text{D}_6) = k_{-2}(\text{BD}_3)^2$. Case II then becomes

$$k_2(\text{B}_2\text{D}_6) \ll [(\text{BD}_3)^2/6(\text{B}_2\text{D}_6)]^{1/2}(\text{B}_2\text{D}_6)^{3/2}$$

$$k_2(\text{B}_2\text{D}_6) \ll (k_3/\sqrt{6})(\text{BD}_3)(\text{B}_2\text{D}_6)$$

This suggests that most of the B_2D_6 decomposes by means of reaction 12 rather than 11. This is the result that one would have predicted from our earlier published work. It is also possible to compare the value of $k_3(k_2/6k_{-2})^{1/2}$ obtained in this exchange with the earlier diborane work. The value of $k_3(k_2/6k_{-2})^{1/2}$ obtained from the earlier diborane work is 0.161, which compares favorably with the value 0.216 obtained in this exchange. This comparison serves as an additional test of the mechanism and provides a correlation of the two exchange reactions.

The preceding analysis shows that the usual dependence of R on a and b is consistent with a homo-

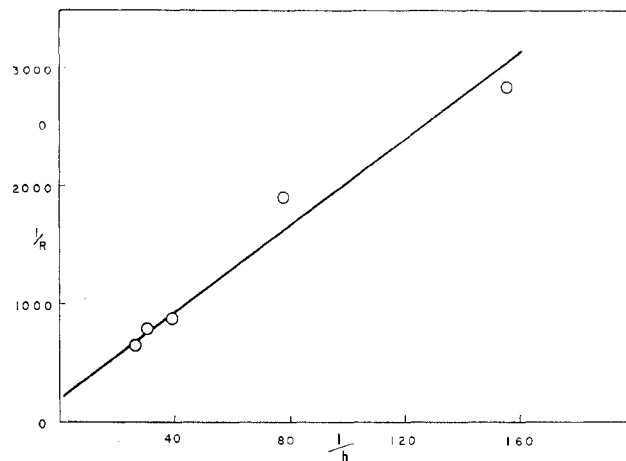


Fig. 6.—Dependence of $1/R$ vs. a/b at 20° ; b = aluminum borohydride concentration.

geneous mechanism. The results of the boron-10 exchange studies provide evidence that the boron atoms are undergoing exchange and a comparison of the rates of exchange of H to B¹⁰ provides evidence for the probable existence of borane (BH_3) as an intermediate in the exchange.

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Alkylation of Pentaborane-9 Catalyzed by Lewis Acids^{1a}

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Substitution of alkyl groups for hydrogen at the apex boron atom of pentaborane-9 was accomplished by the reaction of olefins or alkyl halides in the presence of aluminum chloride, iron(III) chloride, or tin(IV) chloride. The direction of attack and the nature of the substituted alkyl group are consistent with an electrophilic attack on pentaborane-9. The following compounds were prepared and characterized: 1-methyl-, 1-ethyl-, 1-isopropyl-, and 1-*sec*-butylpentaborane-9, as well as 1-methyl-2-*sec*-butylpentaborane-9.

The alkylation of pentaborane-9 with ethylene, using aluminum(III) chloride as a catalyst,² has recently

been reported. The work reported here confirms this result and also demonstrates that olefin addition to pentaborane-9 may be accomplished with a variety of olefins using anhydrous iron(III) chloride as a catalyst. Alkyl halides may also be used with aluminum(III) chloride to attach alkyl groups to a B_5 skeleton, chlorides and bromides reacting more readily than iodides.

(1) (a) Abstracted from the Ph.D. Dissertations (Ohio State University) of S. W. H. (1956) and E. J. M. (1957); (b) Department of Chemistry, University of Florida, Gainesville, Florida.

(2) N. J. Blay, I. Dunstan, and R. J. Williams, *J. Chem. Soc.*, 430 (1960). Our work was completed prior to 1957, but publication was delayed by security restrictions.