depicted by a number of kinetically indistinguishable postulates. The assumption previously made of a rapid and reversible hydrolytic pre-equilibrium is not overly attractive in the light of the equilibrium experiments. Although it is possible to formulate an entity such as $Np(OH)_2^{++}$ and attribute the observed isotope effect to the hydrolytic equilibrium, it is equally plausible to assume that if hydrogen is split off in the activated complex a deuterium effect of similar magnitude would be obtained. It is not readily apparent that the isotope effect can distinguish between these two possibilities.

In contrast to the Np(IV)–Np(VI) reaction, the rate of the Np(V) disproportionation is increased by D_2O. It has been suggested that for the Np(V) reaction, as well as for the kinetically similar U(V) and Pu(V) disproportionation, the first step in a reasonable mechanism would be an equilibrium

$$MO_2^+ + H^+ \overset{K}{\rightleftarrows} MO_2H^{+2} \qquad (10)$$

This would be followed by one or more steps

$$MO_2^+ + MO_2H^{++} \xrightarrow{k_2} \text{products} \qquad (11)$$

$$MO_2H^{++} + MO_2H^{++} \xrightarrow{k_3} \text{products} \qquad (12)$$

Since the species MO_2H^{++} would be a strong acid, no isotope effect would be expected for the pre-equilibrium. Logically then one would interpret the observed isotope effect as arising from a tighter bonding of hydrogen in the activated complex than in reactant species such as MO_2H^{+2} or MO_2HSO_4. It does not appear feasible to define further the condition of the hydrogen in the activated complex or draw any conclusion as to detailed mechanism of a hydrogen atom transfer from the isotope data.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

Kinetics of the Exchange of Deuterium between Diborane and Tetraborane[1]

BY J. E. TODD AND W. S. KOSKI

RECEIVED NOVEMBER 1, 1958

The kinetics of the exchange of deuterium between diborane and tetraborane have been found to be complex. The results indicate that the exchange proceeds by two different paths—one involves two hydrogen positions in tetraborane and the other involves the remaining eight or all ten hydrogen positions. The major reaction is interpreted in terms of a rate-determining reaction of BD_3 from diborane with B_4H_{10} while the minor reaction is envisaged as a rate-determining activation of two sites in tetraborane followed by rapid deuterium exchange with B_2D_6. Boron atoms also exchange in this system although detailed kinetics studies have not been made.

Introduction

The equilibria which are the bases for understanding interconversion reactions of the boron hydrides have been investigated by two types of chemical or quasi-chemical investigations. The purely chemical method consists of studies of product formation whereas the quasi-chemical method involves kinetic studies of isotope exchange. In either case the equilibria involved are deduced by proposing mechanisms compatible with the observed change of the system.

The advantage of directness inherent in the chemical method is frequently offset by complications introduced by product interference so that, in many systems, only initial-rate studies are feasible. Frequently, isotope exchange experiments may be performed under such conditions that any chemical change is either negligible or corrigible. Moreover, the elementary steps contributing to the mechanisms of both types of reactions are often the same so that the equilibria involved may be elucidated more directly by the isotope exchange method. An example of this is the B_2H_6–BH_3 equilibrium which has been postulated in both chemical and isotope exchange reactions involving diborane.[2,3]

In less ideal situations the exchange results may yield information about the lability of atoms of the exchanging isotope which is chemically significant. The B_2D_6–B_4H_{10} exchange reaction, reported in the following paragraphs, appears to fall in this category as well as the former. In addition, it appears to be the first gas-phase exchange reaction in which atoms of the same element in one compound exchange at two measurably different rates.

Experimental

A. **Preparation of Materials.**—Diborane (B_2H_6, B_2D_6 and $B^{10}{}_2H_6$) was prepared by treating lithium aluminum hydride or deuteride with boron trifluoride in ether. The details of the preparation and purification have been described previously.[4] Deuterium resulting from the thermal decomposition of the diborane ranged from 95–98% pure, and the diluent is hydrogen.

Tetraborane was prepared by the B_5H_{11}–H_2 reaction. The apparatus and procedure for this preparation are described by Burg and Stone.[5] The tetraborane was purified by distillation from a trap at about −78° (Dry Ice–acetone) to one at −119° (melting ethyl bromide) with continuous pumping to remove diborane. Tetraborane purified in this manner was free from impurities as indicated by its infrared spectrum. The purification procedures used for both B_4H_{10} and B_2D_6 were spot-checked by vapor-phase chromatography and found to be free of detectable amounts of impurities.

B. **Isotopic Analysis.**—Two methods were used in analyzing the boron hydrides for their specific deuterium content. (The term specific deuterium content is herein defined as the total number of deuterium atoms in a sample of compound divided by the total number of atoms of hydrogen and deuterium in the sample.) In the more fundamental

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF 18(600)-1526. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] R. P. Clarke and R. N. Pease, THIS JOURNAL, **73**, 2132 (1951).

[3] P. C. Maybury and W. S. Koski, *J. Chem. Phys.*, **21**, 742 (1953).

[4] W. S. Koski, P. C. Maybury and J. J. Kaufman, *Anal. Chem.*, **26**, 1992 (1954).

[5] A. B. Burg and F. G. A. Stone, THIS JOURNAL, **75**, 228 (1953).

procedure pure samples of gases with unknown deuterium content were decomposed by passage through a tube containing hot uranium turnings.[4] Boron remains in the tube and the hydrogen–deuterium sample may be removed and analyzed by relative thermal conductivity measurements, as described by Trenner.[6] The apparatus used was calibrated by measurements on prepared samples which were subsequently analyzed by mass spectrometry. Subsequent analyses by both methods have assured the constancy of calibration.

The secondary method of determining specific deuterium content was by gas-phase infrared absorption measurements of tetraborane with a Perkin–Elmer Model 21 C Infrared Spectrometer. This method was standardized by relative thermal conductivity measurements on samples prepared both by exchange of tetraborane with deuterated diborane and by synthesis from samples of diborane containing varying amounts of deuterium. There was no significant dependence of the calibration on the mode of preparation of the tetraborane.

The analysis for specific B^{10} content in boron hydrides *via* the B^{10} $(n,\alpha)Li^7$ reaction has been reported elsewhere.[7] In this study, diborane was analyzed at a pressure of 7.0 cm.

Procedure.—Freshly purified samples of B_4H_{10} and B_2D_6 gases were measured volumetrically and condensed into a cylindrical reaction bulb precooled to −195°. (Great care was exercised to ensure that the diborane was free of tetraborane which is formed slowly at room temperature.) The reaction bulb then was placed in a constant temperature bath and timing was started one minute after immersion. After a period of not less than 20 minutes the bulb was removed, plunged into liquid nitrogen and the contents roughly separated by distillation of the diborane from a −119° bath to one at −195°. The remaining B_4H_{10} was then carefully purified and analyzed by infrared absorption measurements. After establishing that there was no loss of tetraborane, the gases were recombined and allowed to react further and the analytical process was repeated.

In the experiments in which the surface to volume ratio was varied the above procedure was used except that the reaction bulbs were packed with 0.5 g. of Pyrex wool and heated to 350° *in vacuo* until degassing had ceased.

Results and Discussion

If there is a simple isotopic exchange between two molecular species and if the concentrations remain constant, it has been demonstrated by numerous investigators[8] that the course of the exchange is given by

$$Rt = -\frac{AB}{A+B}\ln(1-F) \qquad (1)$$

where A and B are the gram-atom concentrations of the exchanging molecules as diborane and tetraborane, R the rate of exchange, t the time, and

$$1 - F = \frac{D_0 - D_t}{D_0 - D_\infty}$$

where the D's are the specific deuterium contents of the analyzed compound at times indicated by the subscripts. The exchange rate R obeys the usual kinetic relation

$$R = k'A^\alpha B^\beta$$

where α and β are the orders of the reaction with respect to A and B. k' is not the collision theory rate constant but may be related to it by a procedure developed by Marcus.[9]

In a preliminary investigation of the exchange of deuterium between diborane and tetraborane, the exchange data did not yield the expected straight line in a plot of ln $(1 - F)$ *versus* t. Curvature was evident after a very short time in early experiments where the concentrations of exchangeable atoms in B_4H_{10} and B_2D_6 were in a ratio of 1:2. Rates calculated for various times from eq. 1 from a typical exchange are presented in Table I.

Table I

B_2D_6–B_4H_{10} Exchange at 45°

B_2D_6 = 10.0 cm. Hg, B_4H_{10} = 3.00 cm. Hg

Time (min.)	% D in B_2D_6	R (g. atoms/l./min.) $\times 10^5$[a]
0	96.0	..
10	91.1	17.6
20	88.4	14.5
30	86.5	12.4
40	85.4	10.8
50	84.4	9.8
60	83.6	8.6
70	83.0	7.8
80	82.4	7.4
90	81.8	6.9
100	81.4	6.5

[a] Rates calculated from eq. 1 for various times.

There are several possible causes for the observed drift in exchange rate indicated by the data in Table I: (1) non-equivalence of the exchanging isotope due to molecular environment; (2) slow production of exchangeable intermediates; (3) isotope effect; (4) net chemical reaction. Of these possibilities (4) had been eliminated by preliminary exploratory experiments with B_4H_{10} and B_2D_6 which indicated that decomposition was negligible under the conditions employed and that the two reactants produced no chemically distinct products. There was no experimental evidence for (2).

The isotope effect could not be completely eliminated at first but experience with closely analogous systems[3,10] and later results using an excess of B_2D_6 indicate that (3) is, at most, a minor cause of difficulty. Consequently this paper is based on the assumption that the drift in the rate of exchange and the deviation of the ln(1 − F) *versus* t plot from linearity as indicated in Fig. 1 is due to the contribution of two different mechanisms proceeding at different rates. In such situations it has been shown by Abell, Bonner and Goishi[11] and others[12] that it is possible, at least in principle, to resolve the composite curve into its two components as is customarily done in radioactive decay. This resolution is a considerably less accurate and more difficult procedure in the exchange case because the precision of measurement becomes rather poor as the reaction proceeds and the interpretation of the results is not straightforward. A typical resolution of such a composite curve is given in Fig. 1. Using the symbolism of Abell, *et al.*, the course of the exchange may be represented by

$$(1 - F_a) = Q_1 \exp[-(q + p)t] + Q_2 \exp[-(q - p)t] \qquad (2)$$

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(6) N. A. Trenner, *J. Chem. Phys.*, **5**, 382 (1957).

(7) R. P. Hamlen and W. S. Koski, *Anal. Chem.*, **28**, 1631 (1956).

(8) O. E. Meyers and R. J. Prestwood, "Radioactivity Applied to Chemistry," edited by A. C. Wahl and N. A. Bonner, John Wiley and Sons, Inc., New York, N. Y., 1951, Chapter I.

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

(10) T. E. Larson, Doctoral Dissertation, The Johns Hopkins University, Baltimore, Md., 1956.

(11) P. F. Abell, N. A. Bonner and W. Goishi, *ibid.*, **27**, 658 (1957).

(12) L. R. Darbee, F. E. Jenkins and G. M. Harris, *ibid.*, **25**, 605 (1956).

where

$$Q_1 = \frac{1}{2pA}\left[-A(q-p) + \frac{(R_{ab}+R_{ac})S_a^0 - R_{ab}S_b^0 - R_{ac}S_c^0}{S_a^0 - S_a^\infty}\right]$$

$$Q_2 = \frac{1}{2pA}\left[A(q+p) - \frac{(R_{ab}+R_{ac})S_a^0 - R_{ab}S_b^0 - R_{ac}S_c^0}{S_a^0 - S_a^\infty}\right]$$

A, B, C refer to concentrations of the three non-equivalent species of exchanging element. S_a, S_b, S_c are specific deuterium contents of species A, B, C [*e.g.*, $S_a = D_a/(H_a + D_a)$]. R_{ab}, R_{ac}, R_{bc} the exchange rates between the indicated species.

$$2q = \left(\frac{A+B}{AB}\right)R_{ab} + \left(\frac{A+C}{AC}\right)R_{ac} + \left(\frac{B+C}{BC}\right)R_{bc}$$

$$r = (R_{ab}R_{ac} + R_{ab}R_{bc} + R_{ac}R_{bc})\left(\frac{A+B+C}{ABC}\right)$$

$$p^2 = q^2 - r$$

and

$$F_a = \frac{S_a - S_a^0}{S_a^\infty - S_a^0}$$

Equation 2 is general for the case of three exchanging species. In application of (2) to the B_2D_6–B_4H_{10} exchange, the following experimental conditions hold: (a) two species, B and C for instance, cannot be analyzed separately by any of the techniques used since they correspond to different hydrogen sites in tetraborane. The number of sites in each species is not known, but all ten sites are capable of exchanging. (b) One of the three rates may be eliminated since only two exchange rates were observed. An attempt to detect exchange between B and C by infrared spectra of freshly exchanged tetraborane was unsuccessful. Moreover, both exchange reactions were first order in tetraborane, so it was concluded that the rate of exchange between B and C is zero. (c) Only diborane contained deuterium at the start of an experiment so $S_b^0 = S_c^0 = 0$.

Three independent quantities, two slopes and one intercept, may be determined by resolving the experimental $\ln(1 - F)$ curve into two straight lines. It is necessary to establish two rates and the number of sites exchanging at each of these rates. If it is assumed that n sites exchange at one rate and $(10 - n)$ sites exchange at the other, then sufficient information is available to establish the desired information. The data of Table I were analyzed graphically to determine the number of exchangeables. It was found that self-consistent results were obtained for the rates if it was assumed that two hydrogen sites belonged to one exchanging species and (presumably) eight to the other.

It is possible in principle to determine the various rates of interest from eq. 2 and the experimental data. However, because of the complex dependence of the rates on the slopes, the results so obtained were rather inaccurate and in practice the rates were determined from a limiting form of the exchange-rate equation.

By increasing the ratio of diborane to tetraborane to a large value, the limiting form of eq. 2 is obtained. This permits the assumption that there is negligible change in the deuterium content of diborane. Then by appropriate substitution in (2), one obtains

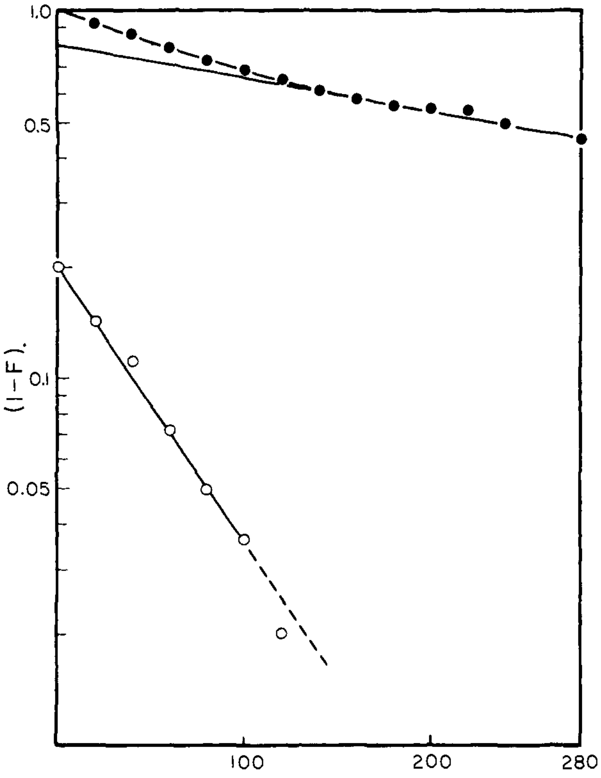

Fig. 1.

$$(1 - F) = \left(\frac{B}{B+C}\right)e^{-(R_{ab}/B)t} + \left(\frac{C}{B+C}\right)e^{-(R_{ac}/C)t} \qquad (3)$$

In the present case, $B = 2(B_4H_{10})$ and $C = 8(B_4H_{10})$ so that $Q_1 = n/10$ and $Q_2 = (10 - n)/10$.

Figure 2 shows the results of a series of experiments at various concentrations of the reactants. In most cases the resolution of the experimental curve into two straight lines easily was accomplished. The value of n obtained in this manner was 2 ± 0.5 and agreed with the number of exchangeables inferred from data at non-limiting concentrations. In cases where the experimental curve does not become reasonably linear during the period of observation, the knowledge of n enables the complex curve to be resolved into linear portions with little difficulty.

The exchange rates obtained from the experimental curves in Fig. 2 are listed in Table II. The exchange reaction involving two B_4H_{10} hydrogen positions is denoted as reaction I and the other, involving eight positions, as reaction II. In Fig. 3 these rates are plotted against the pressure of the reactant varied on a logarithmic grid. The variation of tetraborane at constant diborane is shown in the top left pair of lines; reaction I is the faster. The orders with respect to B_4H_{10} are 1.15 and 1.04 for reactions I and II, respectively. The lower pair of lines representing a variation of diborane gives clear indication of a sub-unity concentration dependence of the rates, although the loci of the experimental points are not as obviously

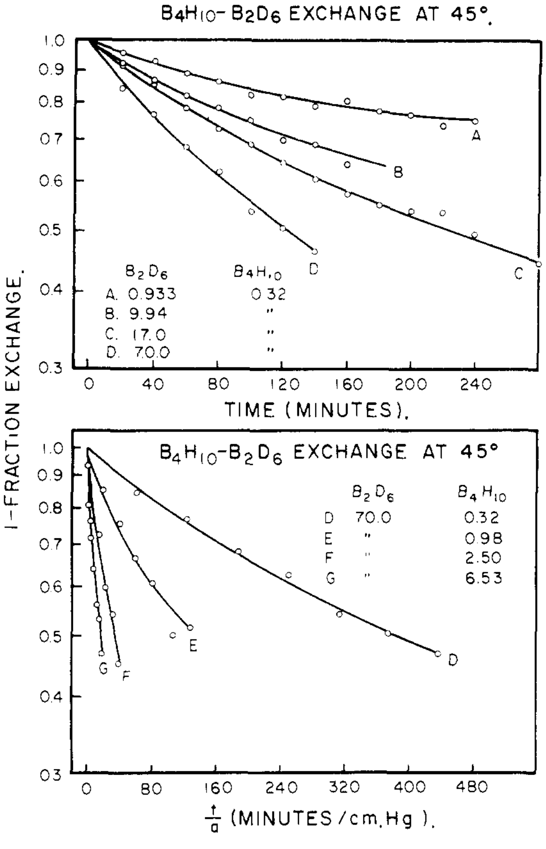

Fig. 2.

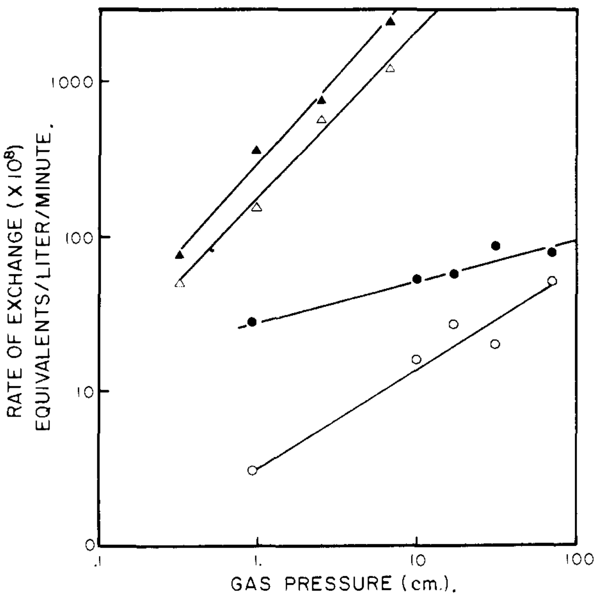

Fig. 3.

linear as above. Reaction I showed a 0.25 order dependence, while reaction II showed a 0.6 order dependence on diborane concentration.

Some preliminary B^{10} exchange experiments have been performed. The results, though qualitative, do indicate that the boron exchange occurs at a rate which implicates it in one (or both) of the reactions resulting in H–D exchange. Unfortunately, it is not possible at present to state whether this exchange also proceeds by two mechanisms.

Table II

B_4H_{10}-B_2D_6 Exchange Rates at Various Pressures

Curve (Fig. 2)	B_2D_6 (cm.)	B_4H_{10} (cm.)	R_1 (g. atoms/l./min.) × 10^6	R_2 (g. atoms/l./min.) × 10^6	m_1 (min.$^{-1}$) × 10^3	m_2 (min.$^{-1}$) × 10^3
D	70.0	0.32	7.7	5.1	23.9	3.9
E	70.0	0.98	36.9	16.0	37.0	3.9
F	70.0	2.50	76.0	57.0	30.1	5.7
G	70.0	6.53	250.0	120.0	37.6	4.5
A	0.93	0.32	2.8	0.31	10.0	0.32
B	9.94	.32	5.3	1.6	16.5	1.24
C	17.0	.32	5.7	2.7	17.0	2.1
H[a]	31.0	.32	8.5	1.5	26.2	1.2
D	70.0	.32	7.7	5.1	23.9	3.9

[a] Not shown in Fig. 2.

Rates calculated from the simple exchange law for the B^{10} exchange ranged from 2.5 to 6 × 10^{-5} (g. atoms B^{10}/l.-min.). The conditions employed were the same as those used to obtain the deuterium exchange data of Table I. It may be seen that the rates are comparable in magnitude. To make a quantitative comparison it would be necessary to multiply the B^{10} exchange rate by an unknown factor equal to the number of hydrogens carried along with each boron.

Surface effects were studied by increasing the surface-to-volume ratio one-hundred fold under conditions allowing a direct comparison with data in Table I. The rate of exchange was found to be 15 × 10^{-5} (g. atoms/l. min.) for points analyzed at 15 and 30 minutes. In this time the smaller surface exhibited rates ranging from about 12 to about 17 × 10^{-5} (g. atoms/l. min.) indicating that there is no serious surface dependence in these exchange reactions.

The activation energies were determined from rates of exchange at 25.0, 34.5 and 45°. These data are shown in an Arrhenius plot in Fig. 4 and are listed in Table III.

Table III

Temperature Dependence of Rates in the B_2D_6–B_4H_{10} Exchange Reaction

Temp. (°C.)	25.0	34.5	45.0
$R_1 \times 10^6$	0.365	1.62	5.3
$R_2 \times 10^6$	0.365	0.74	1.6

The narrow temperature range was used to obviate the complication of decomposition of tetraborane, which is significant above about 50°, and to allow both rates to be measured. It is probable that at lower temperatures reaction I (E_a = 25.5 kcal.) would be indiscernible since its rate falls off much faster than reaction II (E_a = 14.1 kcal.).

The question now arises as to whether one can reconcile the above results with the known structure and chemistry of tetraborane. The exchange studies indicate that tetraborane has two hydrogen positions that exhibit different reactivity from the other hydrogens in the molecule. There are several other indications reported in the literature which tend to support this. The early work of Stock[13] on the preparation of the potassium salt of

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(13) A. Stock and H. Laudenklos, *Z. anorg. allgem. Chem.*, **229**, 178 (1936).

tetraborane can be cited in this connection. Work on the mass spectra of tetraborane shows that the parent ion corresponding to $B_4H_{10}^+$ does not appear. However, $B_4H_8^+$ does, indicating that two of the tetraborane hydrogens apparently comes off rather easily on electron impact. In a recent investigation of the thermal decomposition of tetraborane by Pearson and Edwards,[14] it was found necessary to assume equilibria (1) and (2) to explain the observed results

$$B_4H_{10} \rightleftarrows B_4H_8 + H_2 \qquad (1)$$

$$B_4H_{10} \rightleftarrows B_3H_7 + BH_3 \qquad (2)$$

These steps are then followed by a complicated series of reactions that results in the formation of most of the higher hydrides. Since the higher hydride formation appears to proceed by two different mechanisms and since reaction 1 could possibly explain the exchange data indicating two exchangeables, these two equilibria were carefully considered in the over-all mechanism for the exchange reactions. Reaction 1 does not seem to play a significant role in the exchange reactions reported on here because when deuterium gas is mixed with tetraborane the appearance of the heavy hydrogen isotope in the latter molecule proceeds at a much slower rate than the B_4H_{10}–B_2D_6 exchange. Furthermore if the equilibrium existed under the exchange conditions, then one might expect that the exchange would proceed between H_2 and B_2D_6 in the B_4H_{10}–B_2D_6 reaction and hence the latter reaction should have properties in common with the former one. The exchange of deuterium between hydrogen gas and diborane has been investigated.[3] This reaction showed a weak but readily measurable surface effect, whereas the B_2D_6–B_4H_{10} shows no such surface dependence. If equilibrium (1) were a rapid one followed by a rate-determining collision between H_2 and B_2D_6, one would expect the B_2D_6–B_4H_{10} exchange to be slower than the B_2H_6–D_2 exchange. Such is not the case. Also one would expect fractional-order kinetics with respect to tetraborane in the former exchange, whereas the measurements indicate an order of about unity. For these reasons it appears unsuitable to assume that either equilibrium 1 or 2 plays a significant role in the B_2D_6–B_4H_{10} exchange under the conditions studied. The role of these reactions in the tetraborane decomposition is not being questioned since that work was done at higher temperatures (60° and above) whereas the exchange studies were made at 25–45°. These different conditions may be the explanation for the non-applicability of the Pearson–Edwards equilibria to the exchange reactions. However, these studies of tetraborane decomposition are of interest since they indicate, if the mechanisms are correct, that the molecule has two hydrogens which are somewhat more easily detached than the remaining ones.

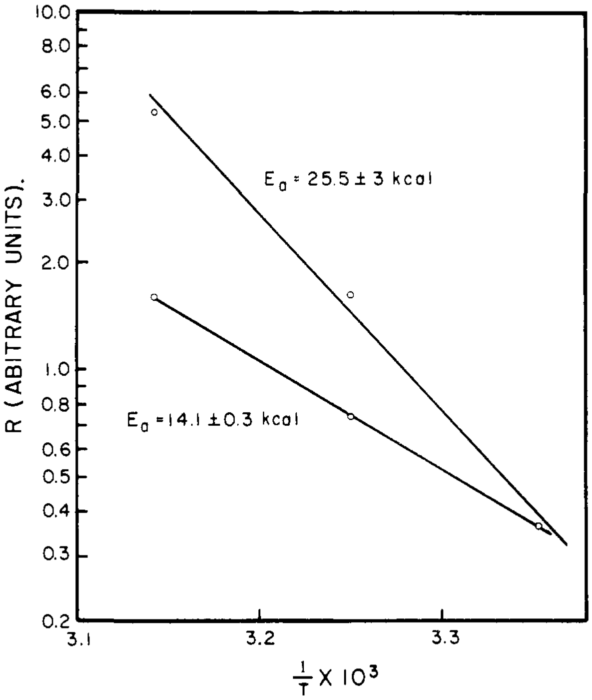

Fig. 4.

If one assumes that these two hydrogens in tetraborane can be excited vibrationally by collision with like or different molecules so they can produce the exchange on bimolecular collision with B_2D_6, then one can account for the kinetics of reaction 1 by the series of reactions

$$B_4H_{10} + B_4H_{10} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} B_4H_{10}^* + B_4H_{10}$$

$$B_4H_{10} + B_2D_6 \underset{k_{-3}'}{\overset{k_3}{\rightleftarrows}} B_4H_{10}^* + B_2D_6$$

$$B_4H_{10}^* + B_2D_6 \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} B_4H_8D_2 + B_2D_4H_2$$

Applying the usual steady-state assumptions and using the procedure of Marcus,[13] one arrives at expression (4) for the rate of disappearance of protiated tetraborane

$$\frac{-\mathrm{d}(B_4H_{10})}{\mathrm{d}t} = k_4 \frac{k_3(B_4H_{10})^2 + k_3'(B_4H_{10})(B_2D_6)}{k_{-3}(B_4H_{10}) + k_{-3}'(B_2D_6)} \times (B_2D_6) \qquad (4)$$

Examination of the above expression shows that the order of the reaction can be greater than one for tetraborane and can range from zero to one for diborane depending on the relative values of the rates of activation and deactivation in the above series of reactions. These values are not incompatible with the observed results.

The second of the two deuterium exchanges in the B_2D_6–B_4H_{10} exchange can be accounted for by the series of reactions

$$B^{10}{}_2D_6 \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} 2B^{10}D_3$$

$$B^{10}D_3 + B_4H_{10} \xrightarrow{k_6} B^{10}D_3B_3H_7 + BH_3$$

$$BH_3 + B^{10}D_3 \xrightarrow{k_7} BH_3B^{10}D_3$$

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[14] R. J. Pearson and L. J. Edwards, 132nd Meeting, American Chemical Society (Abst. No. 39, Div. Inorg. Chem.), New York, N. Y., 1957.

Again applying the usual steady-state assumptions and Marcus' approach one obtains

$$\frac{-\mathrm{d}(\mathrm{B}_4\mathrm{H}_{10})}{\mathrm{d}t} = k_6\left[\left(\frac{k_5}{k_{-5}}\right)(\mathrm{B}^{10}{}_2\mathrm{D}_6)\right]^{1/2}[\mathrm{B}_4\mathrm{H}_{10}] \quad (5)$$

This series of reactions is compatible with the observed orders and at the same time could account for the boron exchanges. In view of the fact that the first exchange reaction does not permit boron exchange, whereas the second one does, a significant test of the proposed mechanisms could be realized by careful B^{10} exchange studies and such work is under way.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Isotopic Exchange Reactions in Liquid Sulfur Dioxide. V. The Acid Halide-catalyzed S^{35}-Exchange between Thionyl Chloride and Sulfur Dioxide[1]

BY DAVID E. BURGE[2] AND T. H. NORRIS

RECEIVED SEPTEMBER 23, 1958

A study has been made of the kinetics of catalysis by antimony pentachloride of the radiosulfur exchange reaction between thionyl chloride and liquid sulfur dioxide. The process is interpreted as a case of acid catalysis in contrast to the previously investigated basic chloride catalysis. Exchange rates are only about one-hundredth as large as in the basic catalysis. The indicated rate law is rate = $k(\mathrm{SO_2})(\mathrm{SOCl_2{\cdot}SbCl_5})$, where the last term represents a complex formed in a rapid preliminary reaction with a formation equilibrium constant $K \approx 0.8$ at 0°, and $\Delta H^0 \approx 3.6$ kcal./mole. The rate constant is given by $k = 0.875 \times 10^2 \exp(-10{,}400/RT)$ l. mole^{-1} sec.$^{-1}$. The entropy of activation is -51.6 e.u. K and k appear to be essentially unchanged throughout the complete solvent range from excess sulfur dioxide to excess thionyl chloride. An activated complex involving a double chlorine, oxygen bridge between sulfurs is postulated, reminiscent of that proposed for the basic chloride case. The greater complexity of the acid complex may account for the lower exchange rates observed. The occurrence of catalysis by aluminum chloride at a ten-fold lower rate is confirmed and briefly discussed.

Previous work in this Laboratory,[3,4] has shown that the radiosulfur exchange between thionyl halides and liquid sulfur dioxide is subject to a strong basic catalysis by ionic halide solutes. Preliminary experiments in the same research[4] suggested that an acid catalysis might also occur. While no effect could be observed with hydrogen chloride, aluminum chloride appeared to show a weak catalysis for the thionyl chloride–sulfur dioxide exchange, giving rates of the order of one thousandth those with tetramethylammonium chloride. We have now investigated the kinetics of the catalysis of this exchange by antimony pentachloride, the occurrence of acid catalysis being confirmed. The experiments cover the entire range of solution composition from excess sulfur dioxide to excess thionyl chloride. The observed rates are much smaller than with basic chlorides but significantly greater than with aluminum chloride.

Results

The Rate Law.—The results of all the experiments are recorded in Table I. The first twenty-four form a set at one temperature in which the concentrations of all three reactants were varied over considerable ranges in an effort to arrive at a rate law. Although preliminary treatment of the data indicated that separate empirical rate laws could be demonstrated for excess sulfur dioxide[5] and excess thionyl chloride[6] solutions, respectively, there was every indication in the case of the basic chloride catalysis of this exchange that the same mechanism prevails in excess of either substance.[4] It was tempting, therefore, to try to show a similar situation in the present instance. It develops that a quite simple interpretation of the reaction will suffice for this purpose. One may assume that antimony pentachloride tends to form a complex with thionyl chloride and that this complex then reacts with sulfur dioxide in the rate-determining step. The rate law thus becomes[7]

$$\text{Rate} = k(\mathrm{SO_2})(\mathrm{SOCl_2{\cdot}SbCl_5}) \quad (3)$$

where the concentration of the complex will be governed by the equilibrium constant expression

$$\frac{(\mathrm{SOCl_2{\cdot}SbCl_5})}{(\mathrm{SOCl_2})(\mathrm{SbCl_5})} = K \quad (4)$$

In attempting a quantitative test of the validity of this interpretation, one is confronted with the problem that both k and K are unknown. This difficulty has been resolved by least squares analysis of the data[8] so as to obtain simultaneously optimum values for the two constants. In so doing, however, a further problem arises. It is by no means certain that these constants will be numerically the same both in excess sulfur dioxide and excess thionyl chloride. Such a situation, for example, was *not* found for the basic chloride catalysis. For this reason the two sets of data have first been treated separately. The excess sulfur dioxide data consist of all experiments where thionyl chloride was less than 2 molar and lead to the constants $k = 1.75 \times 10^{-3}$ l. mole^{-1} hr.$^{-1}$ and $K = 0.6$ l. mole^{-1}. The excess thionyl chloride

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(1) Oregon State College, Research Paper No. 348, School of Science, Department of Chemistry.

(2) Taken from the thesis of David E. Burge, submitted in partial fulfillment of the requirements for the Ph.D. degree at Oregon State College, June, 1958.

(3) R. H. Herber, T. H. Norris and J. L. Huston, THIS JOURNAL, **76**, 2015 (1954).

(4) B. J. Masters and T. H. Norris, *ibid.*, **77**, 1346 (1955).

(5) Rate = $k(\mathrm{SbCl_5})(\mathrm{SOCl_2})(\mathrm{SO_2})^2$ (1).

(6) Rate = $k(\mathrm{SbCl_5})(\mathrm{SO_2})$ (2).

(7) Assuming the equilibrium constant K fairly close to unity, the consistency of this rate law with the preliminary rate laws 1 and 2 is readily shown.

(8) For details of calculation methods see the Ph.D. thesis of David E. Burge, Oregon State College, 1958.