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

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The kinetics of the deuterium exchange between diborane and dimethylaminodiborane (DMADB) have been studied. The course of the reaction was followed by means of gas density measurements. The concentrations of both reactants were varied over a 20-fold range in order to establish the orders of the reaction. The reaction was found to be first order with respect to dimethylaminodiborane and half-order with respect to diborane. The activation energy was found to be 27.8 ± 3 kcal. By variation of the surface-to-volume ratio it was determined that, to within experimental error, the reaction is homogeneous. A mechanism has been proposed in which the rate-determining step is the reaction between the intermediate BH_3 and DMADB. The rather high activation energy is consistent with a postulated symmetrical intermediate in the rate-determining step.

Introduction

There have been a number of reactions studied involving isotopic exchange between the various boron hydrides. Among those studied are the B_2H_6–D_2 exchange,[2a] the B_2H_6–B_2D_6 exchange,[2a] the B_4H_{10}–B_2D_6 exchange,[2b] the B_5H_{11}–B_2D_6 exchange[3] and the B_5H_{11}–$B^{10}{}_2H_6$ exchange.[3] Studies such as these have indicated that there exists a rapid equilibrium between borane and diborane and that the borane is an important intermediate in boron hydride chemistry. It is therefore of interest to us to extend these studies to other boron-hydrogen compounds and this paper is a report of results obtained by a kinetic study of the exchange of deuterium between deuterated diborane (diborane-d_6) and dimethylaminodiborane.

Experimental

Preparation of Materials.—Diborane-d_6 was prepared by the reaction of lithium aluminum deuteride with boron trifluoride in ether. The preparation has been described in detail previously.[4] Diborane prepared in this manner was approximately 97% deuterated.

Dimethylaminodiborane (DMADB) was prepared by the reaction between dimethylamine and diborane *via* the intermediate dimethylaminoborine ($(CH_3)_2NBH_2$). The details of this preparation and the apparatus involved are described by Burg and Randolph.[5]

Both reactants were purified periodically. Their purities were checked by means of infrared spectrometry, thermal conductimetry and gas density measurements.

Isotopic Analysis.—As the reaction between these two reactants proceeds, the deuterium content in both reactants changes. Accompanying this change in deuterium content is a change in the molecular weights of both reactants. The method used to measure the deuterium content of the reactants was based on this changing molecular weight, that is, gas density measurements.

A gas density balance was constructed which was capable of measuring accurately and precisely the density of a very small sample ($\sim 7 \times 10^{-5}$ mole diborane). The balance beam was constructed out of quartz and was equipped with a boron carbide knife edge. The over-all length of the balance beam, from the buoyancy bulb ($\sim$1 cm.^{3}) to the pointer end, was approximately 8 cm. When in operation the balance beam sat on a sapphire optical flat; otherwise, it sat on an arrestment support.

Throughout this work the balance was used as a null instrument. A gas of unknown molecular weight was determined relative to a gas of known molecular weight. The reference gas was introduced into the balance enclosure and the pressure was adjusted until the balance pointer came to a certain position. The pressure was adjusted by means of a plunger in an open-end manometer. The pressure was then read from an additional mercury manometer by means of a cathetometer. The unknown gas then was introduced into the balance enclosure and the pressure was adjusted until the pointer came to the same position as it had come to with the reference gas. The pressure required to do this was read and recorded. With the two pressures and the known molecular weight, the molecular weight of the unknown gas could be determined. A knowledge of the molecular weight meant a knowledge of the deuterium content provided, of course, the sample was pure. Care was taken to use freshly purified materials.

The choice of the reference gas was dependent upon the known gas to be analyzed. When diborane of unknown deuterium content was to be analyzed, B_2H_6 was used as the reference gas. The diborane used as the reference gas was always purified immediately before use. When dimethylaminodiborane of unknown deuterium content was to be analyzed, $(CH_3)_2NB_2H_5$ was used as the reference gas.

An optical system was devised to read the balance position which made a knowledge of the absolute position of the balance-beam pointer non-essential. This was achieved by watching both ends of the balance beam simultaneously. Thus a knowledge of the relative position of the ends of the beam was sufficient.

Before the balance was put into use as an analytical device, an extensive series of experiments was performed to determine both its accuracy and precision. To determine the reproducibility of the balance, a series of experiments was performed in which repeated measurements were made on one gas. For each measurement, the gas was introduced into the balance housing and the pressure was adjusted until balance was obtained. The degree of constancy of the pressure required to obtain balance from measurement to measurement indicated the degree of reproducibility of the balance. The largest variation in pressure reproducibility was 0.2%. Nitrogen, diborane and dimethylaminodiborane were used as test gases.

A second series of experiments was performed in which samples of diborane of known deuterium content were analyzed with the balance. These experiments were designed to establish the accuracy of the balance. A comparison was made between the mass spectroscopically determined deuterium content and that obtained with the gas-density balance. The maximum discrepancy did not exceed 0.6% and in general it was much closer.

Experimental Procedure.—Known amounts of freshly purified samples of B_2D_6 and $(CH_3)_2NB_2H_5$ were condensed into the reaction vessels with liquid nitrogen. These reaction bulbs were then placed in a constant temperature bath. To allow the bulbs to warm up from liquid nitrogen temperature, 90 seconds were allowed to pass before timing began. At the desired time the bulbs were removed and the reaction was quenched in liquid nitrogen.

The separation of the reactants for analysis *via* the gas-density balance was a critical step. In most cases the diborane fraction was analyzed so a small impurity in the form

(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) (a) P. C. Maybury and W. S. Koski, *J. Chem. Phys.*, **21**, 742 (1953). (b) J. E. Todd and W. S. Koski, THIS JOURNAL, **81**, 2319 (1959).

(3) T. E. Larson and W. S. Koski, "Resumédes Communications XVI the International Congress of Pure and Applied Chemistry," Vol. I, 1958, p. 157.

(4) I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L. Smith, THIS JOURNAL, **74**, 901 (1952).

(5) A. B. Burg and C. L. Randolph, *ibid.*, **71**, 3451 (1949).

of DMADB could seriously affect the results. The procedure for separation was the following: the diborane was expanded from the reaction bulb at −78° (Dry Ice–acetone) through a trap at −119° (ethyl bromide–liquid nitrogen) into a trap at −195°. After sufficient time was allowed for any dimethylaminodiborane that had escaped from the reaction bulb to be condensed out in the trap at −119°, the diborane was expanded back through the trap at −119° and into a Toepler pump from which it was pushed with mercury into the gas-density balance.

Results

Early in the course of this work, experiments were carried out which were designed to establish the number of positions in the dimethylaminodiborane that were active in the exchange. These experiments consisted of running the reaction until equilibrium had definitely been established and then analyzing the reactants for deuterium. From the knowledge that all six sites in B_2H_6 are active to exchange, one can calculate the number of active sites in the DMADB. These results, shown in Table I, indicate five exchangeable hydrogens in DMADB.

TABLE I

DETERMINATION OF THE NUMBER OF EXCHANGEABLE HYDROGEN SITES IN DIMETHYLAMINODIBORANE

Experiment	1	2	3
Pressure B_2D_6 (cm.)	8.14	5.00	5.00
Pressure DMADB (cm.)	10.00	5.00	5.00
Method of analysis[a]	T. C.	G. D.	G. D
Calculated % D_2 at $t = \infty$ based on four sites in DMADB	53.8	58.3	58.3
Calculated % D_2 at $t = \infty$ based on five sites in DMADB	48.4	52.6	52.6
Experimental % D_2 at $t = \infty$	47.0	52.0	52.3

[a] T. C. = thermal conductivity; G. D. = gas density.

The results of this work have been interpreted in terms of the first order rate law originally derived by McKay.[6]

The rate, R, at which an atom X exchanges from one species AX_n to another species BX_m is

$$R = -\frac{1}{t}\frac{ab}{a+b}\ln(1-F) \qquad (1)$$

where a and b are the concentrations of the reactants in gram atoms of the exchanging element per unit volume, t is the time and

$$F = \frac{\%\ D_2(t=0) - \%\ D_2(t=t)}{\%\ D_2(t=0) - \%\ D_2(t=\infty)} \qquad (2)$$

In order to determine the parameters of kinetic significance, the concentrations of both reactants, the temperatures at which the reactions were run and the surface conditions were varied. The DMADB concentration was varied over a 20-fold range while the B_2D_6 concentration was held constant. The measurements were carried out at 25°. The results of these runs are summarized in Fig. 1. Likewise, at 25°, the B_2D_6 concentration was varied over a 20-fold range while the DMADB concentration was held constant. The results of these runs are shown in Fig. 2. These results summarize the dependence of the reaction on pressure and indicate that the exchange obeys the first order law to within experimental error.

(6) H. A. C. McKay, *Nature*, **142**, 997 (1938).

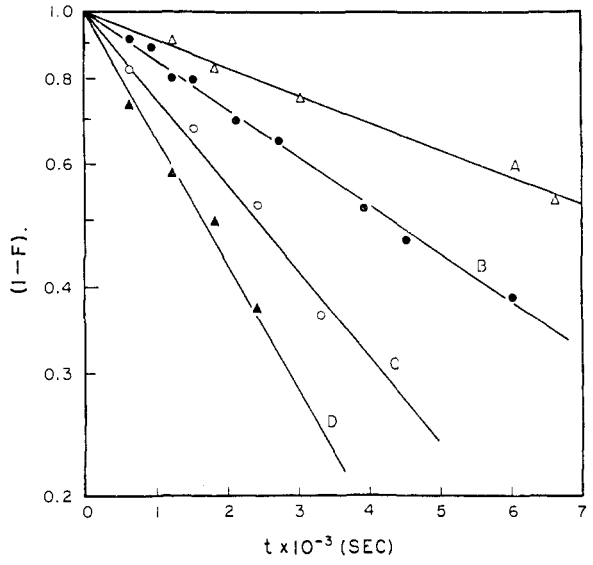


Fig. 1.—Rate of reaction of the B_2D_6–DMADB exchange at 25° as a function of the DMADB pressure. Diborane pressure = 5 cm. DMADB pressure is 1, 5, 10 and 20 cm. for A, B, C and D, respectively.

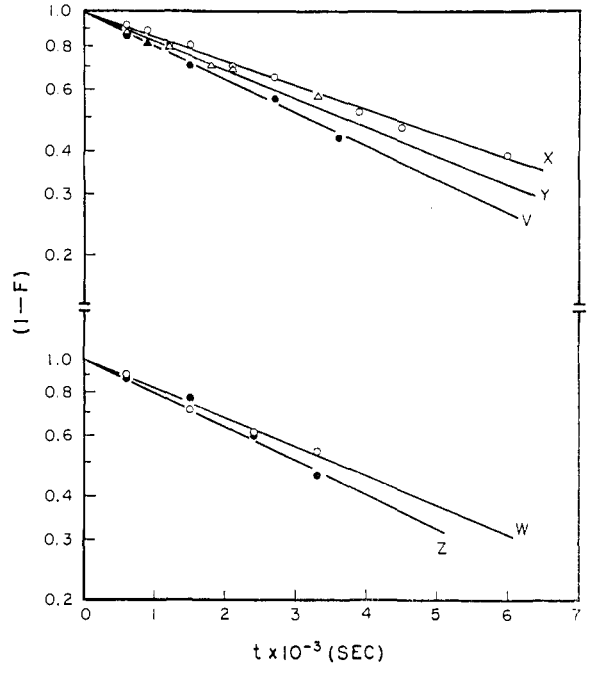


Fig. 2.—Rate of reaction of B_2D_6–DMADB exchange at 25° as a function of B_2D_6 pressure. DMADB pressure = 5 cm. B_2D_6 pressure = 1, 2, 5, 10 and 20 cm. for V, W, X, Y and Z, respectively.

The rate, R, is functionally dependent upon the concentrations of the reactants. This functional dependence takes the form

$$R = k[a]^{\alpha}[b]^{\beta} \qquad (3)$$

where α is the order with respect to a and β is the order with respect to b. Taking logarithms of both sides of equation 3 yields

$$\log R = \alpha \log [a] + \beta \log [b] + \log k \qquad (4)$$

From equation 4 it is apparent that a plot of log R *versus* log of one of the concentrations (while

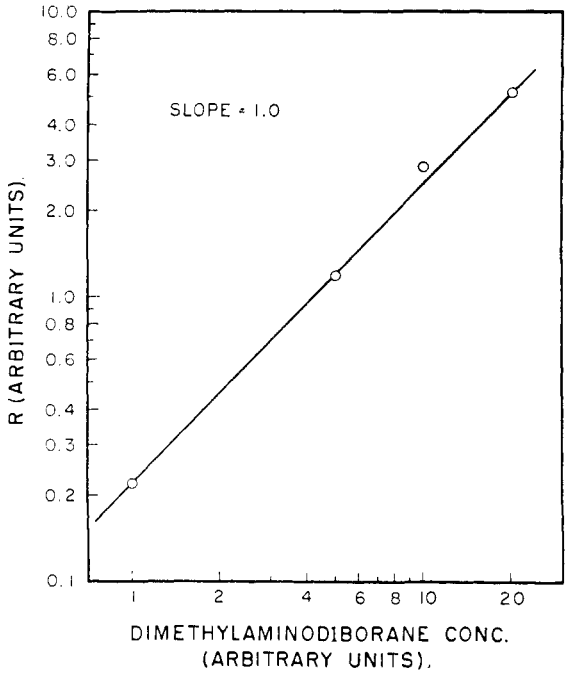


Fig. 3.—Order determination with respect to DMADB.

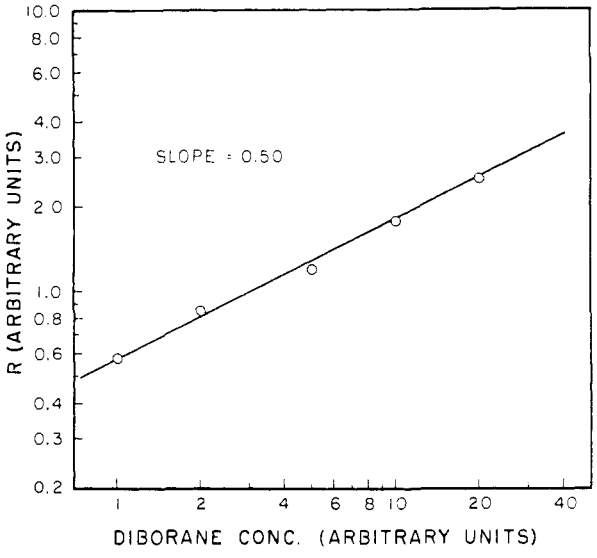


Fig. 4.—Order determination with respect to diborane

the other concentration is held constant) yields a slope which is identified with the order of the reaction. The data for such plots are given in Figs. 3 and 4. The slopes obtained from these plots were 1.0 for DMADB and 0.49 diborane indicating that the reaction is first order with respect to dimethylaminodiborane and half-order with respect to diborane.

The rate constants, k, were calculated from equation 3 which after substitution of experimentally determined parameters becomes

$$R = k[(CH_3)_2NB_2H_5][B_2D_6]^{1/2} \quad (4)$$

The rate constants calculated from this expression are given in Table II and indicate the degree of constancy typically obtained in this study. The concentrations of DMADB and diborane are expressed in gram atoms of hydrogen per liter.

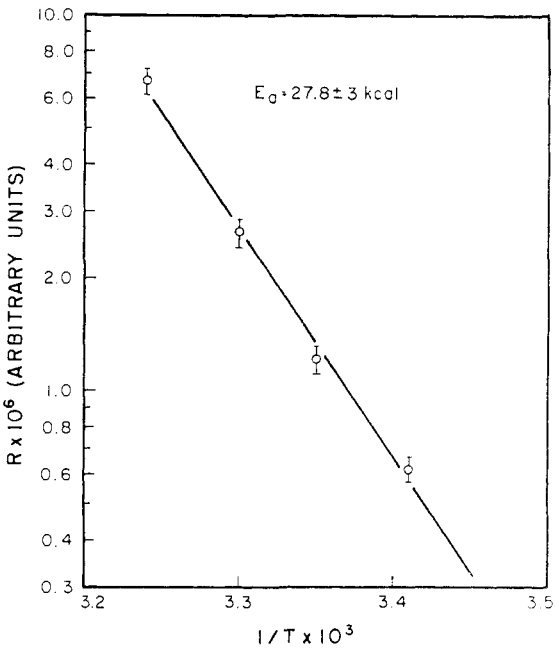


Fig. 5.—Rate *vs.* $1/T$ plot for the B_2D_6-DMADB exchange reaction.

TABLE II

TYPICAL RATE CONSTANTS OBTAINED FOR THE DEUTERIUM EXCHANGE BETWEEN DIBORANE AND DIMETHYLAMINODIBORANE

$B_2D_6 \times 10^2$	DMADB $\times 10^2$	$k \times 10^4$
1.60	0.293	6.5
1.60	1.34	7.2
1.64	2.70	8.2
1.61	5.37	7.6
0.320	1.34	7.7
0.648	1.35	7.8
1.60	1.34	7.2
3.19	1.33	7.4
6.41	1.34	7.3

In order to determine the temperature coefficient of the reaction, experiments were run at four different temperatures covering a range of 15°. From the results obtained the Arrhenius plot shown in Fig. 5 was obtained. The activation energy determined from this plot is 27.8 ± 3.0 kcal./mole.

The surface dependence of the reaction was investigated by varying the surface-to-volume ratio by packing reaction bulbs with Pyrex rods. The surface-to-volume ratio was changed conveniently in this way by a factor of ten and under such conditions the reaction rate remained constant to within experimental error, indicating that the reaction was very probably a homogeneous one.

Discussion

Any exchange mechanism proposed for this reaction must account for the following experimentally determined results: (1) five positions in the dimethylaminodiborane are actively participating in the exchange, and (2) the reaction is first order with respect to dimethylaminodiborane and half-order with respect to diborane.

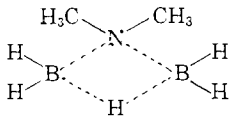
The fractional order with respect to diborane indicates that the diborane is dissociating into two fragments one of which in turn reacts with the dimethylaminodiborane. A mechanism consistent with these results is

$$(1)\quad B_2D_6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2BD_3$$

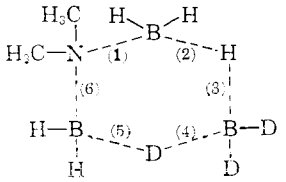
$$(2)\quad BD_3 + (CH_3)_2NB_2H_6 \xrightarrow{k_2} (CH_3)_2NB_2H_3D_3 + BH_3$$

$$(3)\quad BH_3 + BD_3 \xrightarrow{k_3} B_2H_3D_3$$

It is interesting to note that once again the kinetic results of this study have forced one to assume the existence of a BH_3 intermediate. The nature of the intermediate in the rate-determining step is also of interest. The structure of dimethylaminodiborane is represented by



When one considers this, an intermediate which would be consistent with the results of this work would be a structure represented by



A triangular intermediate such as this has been mentioned previously. A plausible structure for such a species has been given[7] to be three BH_2 groups held together with three bridge hydrogens.

If we let the above structure represent the intermediate, then the products formed are dependent upon which bonds rupture. The rupture of bonds numbered (1) and (3) would lead to dimethylaminodiborane which is deuterated in two terminal positions and in the bridge position. The rupture of bonds numbered (4) and (6) would lead to dimethylaminodiborane which is deuterated in two terminal positions only. The rupture of bonds numbered (2) and (4) would lead to deuteration of the bridge position only, while the rupture of bonds numbered (3) and (5) would represent no isotopic change.

The observed activation energy was 27.8 kcal. The observed value of course includes the heat of reaction of elementary step 1 above. Then

$$E_{\text{obsd.}} = 27.8 \text{ kcal.} = E_2 + {}^1/_2(E_1 - E_1)$$

The quantity $(E_1 - E_{-1})$ has been estimated[8] to be equal to 28.4 ± 2 kcal. Assuming this is correct, the activation energy for the rate-determining step, E_2, would equal 13.6 kcal.

Compared to results obtained from studies of similar systems such as the self-deuteration of diborane, this activation energy is quite high and probably arises in part from the difference in strengths of the B–H–B bond in DMADB and diborane.

The consistency of this exchange mechanism and the nature of the intermediate is amenable to further experimental confirmation by studying the kinetics of boron isotopic exchange in this reaction. It is expected that such measurements will be made in the near future.

(7) W. H. Eberhardt, B. Crawford and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

(8) S. H. Bauer, THIS JOURNAL, **78**, 5775 (1956).

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The Fluorescence of Sulfur Dioxide[1]

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Fluorescence spectra of SO_2 are obtained for the first time by direct optical excitation to the second electronic state above the normal state. Transitions are observed to vibrational levels of the normal state from vibrational levels of both the second and the first excited electronic states. The latter state could not be populated directly because of low absorption coefficients. The fluorescence spectrum of microcrystalline SO_2 at 77°K. was found to be identical with the vapor spectrum. The mean lifetime associated with transitions from the second to the normal state was found to be a linear function of the pressure in the range 0.017 to 0.0005 mm. The lifetime extrapolated to zero pressure is 4.2×10^{-5} second. The lifetime of the first excited state could not be determined from the vapor because of low intensity, but a value of about 5×10^{-4} second was obtained from the solid at 77°K. Only the order of magnitude of this value may have qualitative significance.

Introduction

Absorption spectra of SO_2 have shown the existence of several electronic transitions in the spectral region 1800 to 3900 Å. The transition to the first excited electronic state above the normal state has an origin at 3880 Å. and a maximum intensity at 3740 Å.[3] The intensity of the transition as a whole is very weak. The origin of the transition to the second excited state above the normal state is at 3376 Å., with a maximum intensity at 2940 Å.[4] The intensity of this transition is quite strong. These two transitions have been

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(2) Eastman Kodak Company Fellow, 1958–1959.

(3) N. Metropolis and H. Beutler, *Phys. Rev.*, **57**, 1078 (1940).

(4) N. Metropolis, *ibid.*, **60**, 295 (1941).