

possible base catalyzed exchange, hydrolysis of the borazole was so extensive that no recovery could be made.

After reaction with deuterated ethanol at  $-45^\circ$  for five minutes, recovered borazole showed that no exchange had taken place.

Borazole neither reacted with nor exchanged with acetylene-*d*<sub>2</sub> in the liquid phase at  $-50^\circ$  in 10 minutes, in the gas phase at room temperature in 5 minutes, nor in the gas phase at  $80^\circ$  in 30 minutes.

### Discussion

Clearly at least two mechanisms are operative in the isotope exchange reactions of borazole since exchange occurs so selectively either on the boron or nitrogen atoms. Any detailed discussion of possible mechanisms would not be warranted on the basis of presently available information. Perhaps the most significant and singular conclusion that can be drawn concerning exchange mechanisms arises from the deuterium chloride studies. Thus it has been established that the adduct B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>·3HCl does not decompose to borazole under the conditions of the exchange nor does it exchange with borazole once formed. Since exchange occurs when borazole and deuterium chloride are mixed, at least one reversible step must be involved before the final removal of material as the nonvolatile, unreactive adduct. Thus, it may well be that reaction takes place by electrophilic attack at the nitrogen atom followed by transfer of chloride to the boron to complete addition or abstraction of the adjacent hydrogen attached to nitrogen by the chloride ion resulting in exchange.

Relatively pure samples of B<sub>3</sub>D<sub>3</sub>N<sub>3</sub>H<sub>3</sub>, B<sub>3</sub>H<sub>3</sub>N<sub>3</sub>D<sub>3</sub> and B<sub>3</sub>D<sub>3</sub>N<sub>3</sub>D<sub>3</sub> have been prepared. The perdeuterio compound is most readily prepared by reaction of diborane-*d*<sub>6</sub> with ammonia-*d*<sub>3</sub>. The B-deuterated compound is most readily prepared by exchange of borazole directly with deuterium as reported above. The N-deuterated compound is most readily prepared from the perdeuterio compound by back exchange with hydrogen to remove the deuterium attached to boron. Unfortunately, a mass spectrometrically pure N-deuterated borazole was not obtained in this fashion.

Comparison of the three heaviest ions formed by electron bombardment of B<sub>3</sub>H<sub>3</sub>N<sub>3</sub>H<sub>3</sub>, B<sub>3</sub>D<sub>3</sub>N<sub>3</sub>H<sub>3</sub>, B<sub>3</sub>H<sub>3</sub>N<sub>3</sub>D<sub>3</sub> and B<sub>3</sub>D<sub>3</sub>N<sub>3</sub>D<sub>3</sub> (81, 80, 79; 84, 83, 82; 84, 83, 82; and 87, 86, 85, respectively) provides interesting qualitative information. The necessary data are given in Table I. Both of the N-

TABLE I  
PARTIAL MASS SPECTRA OF ISOTOPIC BORAZOLES

	<i>(Relative intensities)</i>		
	<i>M</i> <sup>a</sup>	<i>M</i> <sup>a</sup> - 1	<i>M</i> <sup>a</sup> - 2
B <sub>3</sub> H <sub>3</sub> N <sub>3</sub> H <sub>3</sub>	34.3	100.0	63.1
B <sub>3</sub> D <sub>3</sub> N <sub>3</sub> H <sub>3</sub>	41.2	34.8	100.0
B <sub>3</sub> H <sub>3</sub> N <sub>3</sub> D <sub>3</sub>	28.9	87.8	100.0
B <sub>3</sub> D <sub>3</sub> N <sub>3</sub> D <sub>3</sub>	39.2	35.8	100.0

<sup>a</sup> *M* is the highest isotopic peak in each case (81, 84 or 87).

deuterated materials were known to be somewhat contaminated with N-H derivatives. Nevertheless, it is qualitatively apparent that when hydrogen is attached to boron the intensities of ions with mass one less than the parent ion are greater than when deuterium is bonded to boron. In the case of B<sub>3</sub>D<sub>3</sub>N<sub>3</sub>H<sub>3</sub> a partial analysis of the spectrum (using a <sup>10</sup>B/<sup>11</sup>B ratio of <sup>20</sup>/<sub>80</sub>) shows that an ion of composition B<sub>3</sub>D<sub>3</sub>N<sub>3</sub>H<sub>2</sub><sup>+</sup> is only 9.6% of the parent peak. If a similar ratio may be applied to B<sub>3</sub>N<sub>3</sub>H<sub>6</sub> itself, one can calculate that about 95% of the first ionization of hydrogen is accounted for by loss of hydrogen from boron. No allowance for an isotope effect has been made. It would be valuable to compare the above calculation with one based on B<sub>3</sub>H<sub>3</sub>N<sub>3</sub>D<sub>3</sub>, but no sample of sufficient isotopic purity has been prepared in these Laboratories. It is interesting to observe that the conclusion reached above is in agreement with the interpretation of Loughran, *et al.*, based on the relatively low (11.5 volt) appearance potential for the B<sub>3</sub>N<sub>3</sub>H<sub>5</sub><sup>+</sup> ion.

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## The Isotopic-Exchange Reactions of B<sub>2</sub>H<sub>6</sub> with DT, HT and HD

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The isotope effects of the diborane-hydrogen exchange and in the pentaborane-diborane exchange reactions have been studied using deuterium and tritium as tracers. In the former reaction an inverse isotope effect was observed, whereas in the latter a normal isotope effect was obtained. The effects are interpreted in terms of previously proposed mechanisms.

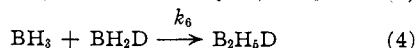
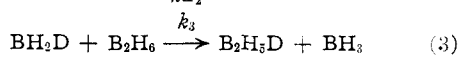
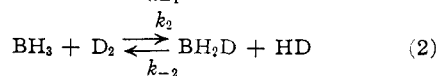
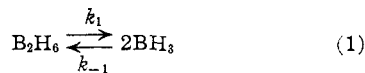
### Introduction

A number of exchange reactions involving boron hydrides have been studied; however, in none of these studies has the isotope effect been investigated. In view of the fact that a large isotope effect may influence mechanistic conclusions drawn from exchange data, it was decided to investigate the difference in exchange rates of deuterium and tritium in boron hydrides. The reaction selected for this initial study was the hydrogen-diborane exchange. This reaction was first studied by

Maybury and Koski<sup>1</sup> using deuterium as a tracer. It was found that the reaction was 3/2-order with respect to diborane and the deuterium order was dependent upon the initial deuterium concentration. At low initial deuterium concentrations the reaction was first order with respect to deuterium while at high initial concentrations it had a zero order dependence on deuterium. The reaction also showed a weak but definitely measurable surface dependence.

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

The following mechanism was proposed to account for these experimentally determined parameters. It was assumed that step 2 was surface dependent.



Later the reaction data was re-interpreted by Marcus<sup>2</sup> and it was shown that it was not necessary to assume heterogeneity to explain the observed order dependence. However, no explanation was proposed for the small but readily measurable surface dependence. This study was therefore undertaken not only to obtain information on the magnitude of the isotope effect in a boron hydride exchange reaction but also to see whether the isotope effect was consistent with the above mechanism proposed for the exchange.

### Experimental

The diborane used in this work was synthesized by the standard method.<sup>3</sup> The diborane and pentaborane were purified by means of a trap-to-trap high vacuum distillation. The purity of these materials was checked periodically by means of an infrared spectrometer. The diborane labelled with deuterium and tritium was prepared by exchange between diborane and hydrogen containing appropriate amounts of deuterium and tritium.

There were two series of experiments performed in this investigation. In Series I the reactants consisted of diborane and an equilibrated deuterium-tritium mixture at concentrations of 0.00579 and 0.00978 mole/liter, respectively. The equilibration of the deuterium and the tracer amounts of tritium were realized by passing the mixture over hot uranium. In this experiment the hydrogen reactants were D<sub>2</sub> and DT.

In Series II the reactants were 0.00665 mole/liter of diborane and 0.00992 mole/liter of hydrogen, which consisted of an equilibrated mixture of 98% H<sub>2</sub>, 2% D<sub>2</sub> and tracer amount of tritium. The reactants here were therefore HT and HD.

The procedure consisted of thoroughly mixing the two reactants, permitting the reaction to proceed at  $55 \pm 0.05^\circ$  and then quenching the reaction at various times by immersing the reaction bulb in liquid nitrogen. The hydrogen was removed and analyzed for its deuterium and tritium content. Spot-check analyses also were made on the diborane fraction. The analyses were performed by using thermal conductance for deuterium determinations.<sup>4</sup> When the deuterium was present in small amounts, as in the Series II experiments, a type 21-611 Consolidated mass spectrometer was used and the intensity of the mass 3 peak was monitored as the reaction proceeded. The tritium analyses were made by mixing a measured fraction of the recovered hydrogen with methane and this mixture then was used as a counting gas in a proportional counter. After each analysis the counter was pumped out and flushed out with hydrogen. The counter background was determined just prior to each measurement.

### Results and Discussion

The results of this work are interpreted in terms of the first order rate law given by the equation

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

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

(3) A. E. Finholt, A. C. Bond and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

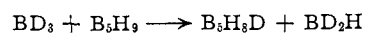
(4) N. R. Trenner, *J. Chem. Phys.*, **5**, 382 (1937).

where  $a$  and  $b$  are the concentrations of the exchangeable atoms in gram atoms/liter in each of the reactants.  $R$  is the rate and  $F$  is the fraction of exchange at the time  $t$ .

Typical results obtained in this study are given in Fig. 1 where  $\log(1-F)$  is plotted vs.  $t$  for the Series I exchange and in Fig. 2 where the deuterium and tritium exchange between diborane and pentaborane is graphically illustrated. It is evident from Fig. 1 that the tritium rate is greater than the deuterium exchange rate. The ratio of the two rates is 1.6. In the second series of experiments the ratio of tritium to deuterium exchange was found to be 2.9. In most cases the lighter isotope reacts faster than the heavier one so it is clear in this case that one is dealing with an inverse isotope effect.

Several possible sources of this inverse effect were examined experimentally. It is possible that if the reaction was a surface one such an effect may be expected, depending on the mechanism. A study of the magnitude of the isotope effect as a function of surface failed to substantiate this explanation. A question also arose as to whether the tritium radiation could be responsible for the effect since it has been observed that boron hydrides are very radiation sensitive.<sup>5</sup> To test this, the ratio of tritium to deuterium exchange was studied as a function of the tritium content. Varying the tritium activity by a factor of ten failed to influence the ratio.

Another possible explanation for the sign of the isotope effect that suggested itself was inherent in the nature of the boron hydrides. The postulated rate-determining step is between borane (BH<sub>3</sub>) and diborane. In BH<sub>3</sub> one is dealing with a planar species with terminal B-H bonds. It is conceivable in going from a terminal-like position in the planar borane to a bridge-like position in the activated complex that the difference in zero point energies could be such that the heavier isotopic species could react at a faster rate than the lighter one. To investigate this possibility an exploratory exchange was carried out between deuterated and tritiated diborane and pentaborane of normal isotopic content. The pentaborane-diborane exchange reaction was studied<sup>6</sup> and found to be half-order with respect to diborane and first order with respect to pentaborane. The exchange involved only the terminal hydrogen positions in pentaborane. It was postulated that the rate-determining step was



It is reasonable to assume that the activated complex would involve bridge bonds in this case. The results of D,T exchanges between diborane and pentaborane are summarized in Fig. 2. It is clear here that one is observing a normal isotope effect.

The most attractive explanation of the inverse isotope effect in the diborane-hydrogen exchange seems to arise as a consequence of the sequence of reactions listed above and proposed earlier as a mechanism. Step 2 is a rapid equilibrium in which exchange takes place; however, the rate-

(5) H. Schmied and W. S. Koski, unpublished work.

(6) P. C. Maybury and W. S. Koski, unpublished work.

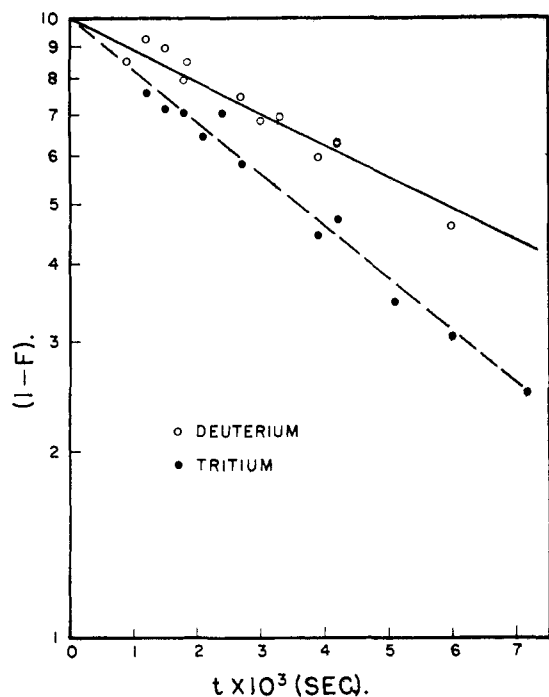


Fig. 1.—Log  $(1 - F)$  vs. time for the B<sub>2</sub>H<sub>6</sub>-D<sub>2</sub> and B<sub>2</sub>H<sub>6</sub>-DT exchange reactions. Diborane and deuterium concentrations are  $5.79 \times 10^{-3}$  and  $9.78 \times 10^{-3}$  mole/liter, respectively;  $T = 55.0 \pm 0.05^\circ$ .

determining step is (3). The concentration of BH<sub>2</sub>T will be greater than BH<sub>2</sub>D mainly as a result of the difference between the zero point energies of the reactants in the forward and reverse steps. If one uses the method developed by Marcus<sup>2</sup> for relating the rate ( $R$ ) to the elementary rate constants, one obtains

$$R = \frac{k_2 c a k_3 b / 3}{k_{-2} a + k_3 b / 3}$$

where  $a$  and  $b$  are the concentrations of H<sub>2</sub> and B<sub>2</sub>H<sub>6</sub> in equivalents per liter and  $c$  is the borane concentration. In arriving at this equation it was assumed that the rate of chain termination is appreciably less than rate of chain propagation. This is generally true for chain reactions. Applying this relation to the tritium and deuterium exchange, taking a ratio of the two and expanding in a series, one obtains

$$\frac{R_T}{R_D} = \frac{K_4 k_5}{K_2 k_3} \left\{ 1 + \frac{k_3 b}{k_{-2} 3a} - \frac{k_5 b}{k_{-4} 3a} + \dots \right\}$$

where  $k_5$  and  $k_{-4}$  are the tritium analogs of  $k_3$  and  $k_{-2}$ , respectively. Since  $k_3 \ll k_{-2}$  and  $k_5 \ll k_{-4}$  this reduces approximately to the equation

$$\frac{R_T}{R_D} = \frac{K_4 k_5}{K_2 k_3}$$

where  $K_2$  and  $K_4$  are the equilibrium constants corresponding to the elementary reaction 2 when deuterium and tritium are used as tracers, respectively.

The formalism for calculation of equilibrium constants of isotopic exchange reactions has been developed by Bigeleisen and Mayer.<sup>7</sup> The equilibrium constant is given by

(7) J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

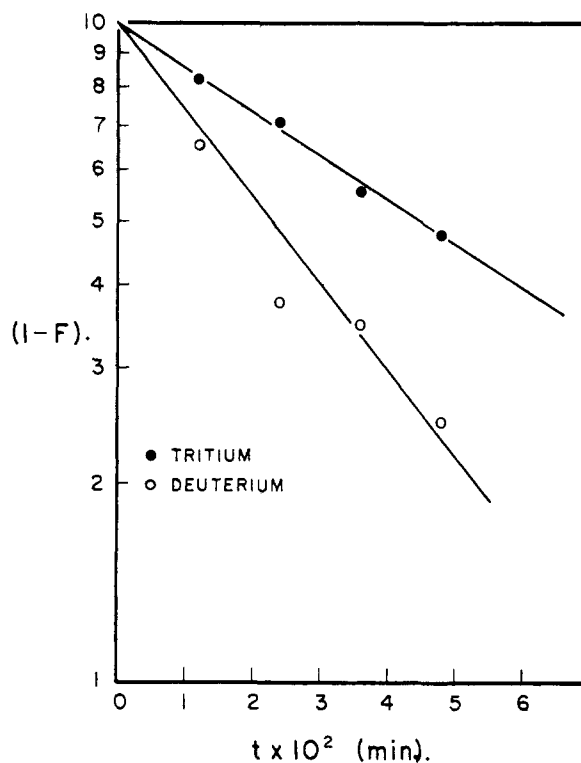


Fig. 2.—Log  $(1 - F)$  vs. time for the exchange reaction between pentaborane and deuterated and tritiated diborane. Pentaborane and diborane concentrations are  $4.20 \times 10^{-3}$  and  $9.97 \times 10^{-3}$  mole/liter, respectively;  $T = 80.0 \pm 0.05^\circ$ .

$$K = \frac{\Pi Q(\text{products})}{\Pi Q(\text{reactants})}$$

where the  $Q$ 's are partition functions. The ratio of the partition functions is given by

$$\frac{Q_2}{Q_1} = \frac{S_1}{S_2} \prod_{i=1}^{3n-6} \frac{u_{2i}}{u_{1i}} e^{(u_{1i} - u_{2i})/2} \frac{(1 - e^{-u_{1i}})}{(1 - e^{-u_{2i}})}$$

where

$$u_i = \frac{hc}{kT\omega_i}$$

and  $\omega_i$  is the appropriate vibrational frequency in wave numbers and the other symbols have their usual significance.

For hydrogen the above equation must be multiplied by the ratio of the rotational partition functions to take into account the rotational contribution. For small  $\sigma$  this contribution is

$$\frac{Q_{2r}}{Q_{1r}} = 1 + \frac{\sigma_2 - \sigma_1}{3} + \frac{(\sigma_2 - \sigma_1)^2}{18} + \frac{\sigma_2^2 - \sigma_1^2}{90}$$

where  $\sigma_i = hc/kTB_i$  and  $B_i$  is the appropriate rotational constant.

In order to calculate the ratio of equilibrium constants from the above expressions, the vibrational frequencies of BH<sub>3</sub>, BD<sub>3</sub>, BH<sub>2</sub>D and BH<sub>2</sub>T must be determined. The frequencies and force constants of BH<sub>3</sub> and BD<sub>3</sub> have been determined<sup>8,9</sup> from infrared spectra thought to be due to BH<sub>3</sub>. The frequencies of BH<sub>2</sub>D and BH<sub>2</sub>T were calculated assuming C<sub>2v</sub> symmetry and valence forces.

(8) J. Morey and G. Hill, Technical Report No. 1, Contract AF 49(638)-28 Fuel Technology Department, Univ. of Utah (1958).

(9) S. H. Bauer, *J. Am. Chem. Soc.*, **76**, 265 (1954).

The same force constants were used as in  $\text{BH}_3$  except for the force constant related to the out-of-plane vibration. The results of these calculations are summarized in Table I. The force

TABLE I

FUNDAMENTAL VIBRATIONAL FREQUENCIES OF  $\text{BH}_3$ ,  $\text{BD}_3$ ,  $\text{BD}_2\text{D}$  AND  $\text{BH}_2\text{T}$  ASSUMING VALENCE FORCES

Vibration	Frequency (cm. <sup>-1</sup> )			$\text{BH}_2\text{T}$
	$\text{BH}_3$	$\text{BD}_3$	$\text{BH}_2\text{D}$	
$\omega_1$	2310	1635	1756	1143
$\omega_2$	1527	1190	2386	2377
$\omega_3$	2470	1860	1156	767
$\omega_4$	1190	872	1134	801
$\omega_5$			2403	2391
$\omega_6$			1418	1382

constants for the  $\text{BH}_3$  and  $\text{BD}_3$  cases are  $k_1 = 3.16 \times 10^5$ ,  $k_8/l^2 = 0.25 \times 10^5$  and  $k_{\Delta}/l^2 = 1.08 \times 10^5$  dyne cm.<sup>-1</sup> for the stretching, bending in-plane and bending out-of-plane force constants, respectively. The same constants were used for the  $\text{BH}_2\text{D}$  and  $\text{BH}_2\text{T}$  with the exception of  $k_{\Delta}/l^2$  which was  $0.86 \times 10^5$  dyne cm.<sup>-1</sup>.

The vibrational and rotational constants of  $\text{H}_2$ ,  $\text{HD}$ ,  $\text{D}_2$  and  $\text{HT}$  were obtained from published literature.

Substituting this information into the basic equations, one obtains for experiments I and II

$$\left(\frac{R_T}{R_D}\right)^I = 2.0 \frac{k_8}{k_3} \text{ and } \left(\frac{R_T}{R_D}\right)^{II} = 4.3 \frac{k_8}{k_3}$$

In order to evaluate the ratio of the tritium to deuterium rates, one must evaluate the ratio of rate constants  $k_8/k_3$ . This can be done in principle but in practice rather drastic assumptions have to be made. We have chosen therefore to obtain an approximate value of this ratio from experimental data. In the rate-determining step of the hydrogen-diborane exchange, borane forms a complex with diborane which is probably  $\text{B}_3\text{H}_9$  and a terminal bond from the  $\text{BH}_3$  becomes a bridge bond in the complex. In the  $\text{B}_2\text{H}_6$ - $\text{B}_3\text{H}_9$  exchange, again  $\text{BH}_3$  interacts with  $\text{B}_3\text{H}_9$  forming a complex which involves converting terminal bonds to bridge bonds. It is assumed that the magnitude of the

isotope effect in these two reactions is not very different. A normal isotope effect would be expected for both of these elementary reactions. In the  $\text{B}_2\text{H}_6$ - $\text{B}_3\text{H}_9$  exchange two steps are involved. One is the equilibrium process between  $\text{BH}_3$  and  $\text{B}_2\text{H}_6$  which in turn is followed by the rate-determining process in which the exchange takes place. An isotope effect is expected for the equilibrium process since the vibrational frequencies for the planar  $\text{BH}_3$  are expected to be lower than those for diborane. Assuming that the magnitude of the isotope effect is about the same in each and since the over-all ratio of deuterium to tritium exchange is about 2.0 (see Fig. 2) in this reaction, a reasonable value for the ratio of the constants for the rate-determining steps  $k_3/k_8$  is approximately 1.6. Applying these values to the cases in question, one obtains 1.3 and 2.7 for the ratio of tritium to deuterium rates for series I and II, respectively. These are to be compared with the experimental values 1.6 and 2.9, respectively. The agreement is as reasonable as one can expect and indicates that the magnitude of the inverse isotope effect observed for the hydrogen-diborane reaction is not incompatible with the proposed mechanism. It remains to make some comment on the origin of the observed weak surface dependence of this reaction. Marcus<sup>2</sup> obtained the following relation between the rate  $R$  and the elementary rate constants for the reaction sequence

$$R = \frac{k_2ca}{\frac{k_{-2a}/2}{k_{6c} + k_3b/6} + 1}$$

listed above. If one assumes that the chain-terminating step takes place at least partly on the walls, the magnitude of the surface effect expected from the above relation is not incompatible with the observed results.

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[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS]

## Primary and Secondary Deuterium Isotope Effects on Rate of Mutarotation of Fully Deuteriated Glucose and Mannose<sup>1</sup>

BY NORMAN C. LI,<sup>2</sup> ARLENE KAGANOVE, HENRY L. CRESPI AND JOSEPH J. KATZ

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The rates of mutarotation of glucose, fully deuteriated d-glucose, d-glucose-1-d, d-mannose and fully deuteriated d-mannose in  $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$ - $\text{D}_2\text{O}$  mixtures, and in the presence of 0 to 0.05 *M* perchloric acid, at 25°, have been studied. The decrease in rate in  $\text{D}_2\text{O}$  represents a primary isotope effect in that O-H and O-D bonds are broken and reformed. The secondary isotope effect on mutarotation is a consequence of the presence of C-D rather than C-H bonds in the molecule and also results in a decrease in the rate of mutarotation. For fully deuteriated glucose, the secondary isotope effect amounts to about 17% in water and about 16% in  $\text{D}_2\text{O}$  in neutral solution. The secondary isotope effect is essentially the same as for d-glucose-1-d, and may be accounted for by the supposition that the principal effect on the rate of mutarotation is due to the replacement of D for H in the carbon-hydrogen bond at carbon atom 1.

### Introduction

Most hydrogen ion-catalyzed reactions are faster in  $\text{D}_2\text{O}$  than in  $\text{H}_2\text{O}$ .<sup>3</sup> Moelwyn-Hughes and Bon-

hoeffer<sup>4</sup> have postulated the mechanism of specific acid catalysis to be

(2) Department of Chemistry, Duquesne University, Pittsburgh, Pa.

(3) K. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission. Presented at the New York A. C. S. Meeting, Sept., 1960.

(4) E. A. Moelwyn-Hughes and K. F. Bonhoeffer, *Z. Elektrochem.*, **40**, 469 (1934); K. F. Bonhoeffer and O. Reitz, *Z. physik. Chem.*, **A179**, 135 (1937).