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Boron Hydrides. III. Hydrolysis of Sodium Borohydride in Aqueous Solution¹

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The hydrolysis of sodium borohydride in aqueous buffer solutions at 25° is catalyzed by general acids. The Brønsted constant is nearly 0.9. Salt effects and solvent isotope effects have been measured. A mechanism involving a rate-determining proton transfer from a general acid onto the borohydride ion is consistent with the data of numerous investigators. One reactive intermediate has been trapped by hydrolyzing sodium borohydride in aqueous trimethylamine. Trimethylamine borane was produced in $1.45 \pm 0.09\%$ yield while the remainder of the borohydride gave hydrogen gas. Hydrolysis of sodium borodeuteride occurs faster than the hydrolysis of sodium borohydride. The primary inverse isotope effect, k_H/k_D , is 0.70 ± 0.02 at 25°. The isotope effect for the boron-hydrogen bond has been calculated using the method of Bigeleisen and Wolfsberg. Several likely models of the activated complex give values of k_H/k_D from 0.60 to 0.95. A simplified model predicts 0.65 if the amount of primary bond breaking is proportional to the amount of secondary bond stiffening. The possible role of steric effects on secondary hydrogen isotope effects has been estimated on a static model. The results show that both normal and inverse secondary isotope effects can be explained in this manner.

Introduction

Sodium borohydride has found wide usage as a powerful reducing agent.³ It is quite stable in basic solution but liberates hydrogen by reducing the hydronium ion as the pH is lowered. The rate of hydrolysis has been studied by Jensen,⁴ Kilpatrick,⁵ Pecsok,⁶ J. B. Brown,⁷ Freund⁸ and Stockmayer.⁹

Current interest in proton and hydride transfer reactions is quite great. Borohydride represents a system in which both types of reactions occur. The wide usage of borohydride in aqueous solution

also dictates the importance of a study of this ion in water.

Experimental

Materials.—Sodium borohydride (Metal Hydrides, Inc.) was recrystallized from diglyme.¹⁰

Likewise, potassium borohydride and lithium borohydride were obtained from Metal Hydrides, Inc. The purified samples³ were stored in sealed bottles in a desiccator to prevent further hydrolysis by atmospheric moisture.

Buffer Solutions.—All aqueous solutions were prepared from triply distilled conductivity water using reagent grade salts previously dried to constant weight. The buffers were prepared using recommended procedures.¹¹⁻¹³ The ionic strength was adjusted to 0.10 in most solutions with pure potassium chloride or sodium chloride (see Table I). The pH was measured using a Beckman Model G Meter. Sodium ion corrections were made when necessary.

The pH range was covered by the following materials: potassium dihydrogen phosphate-sodium hydroxide (pH 7.4-8.0), boric acid-sodium hydroxide (7.8-10.0), borax-hydrochloric acid (9.0-10.0), ammonium chloride-sodium hydroxide (8.2-9.2), borax-sodium carbonate (9.2-11.0), borax-sodium hydroxide (9.2-12.4), disodium hydrogen phosphate-sodium hydroxide (11-12) and sodium hydroxide (> 12). Only at the high pH range with sodium

(1) Preliminary report of these data has been made in Papers I and II: R. E. Davis and C. G. Swain, *J. Am. Chem. Soc.*, **82**, 5949 (1960), and R. E. Davis, C. L. Kibby and C. G. Swain, *ibid.*, **82**, 5950 (1960).

(2) (a) National Science Foundation Undergraduate Summer Research Participant, 1960. (b) National Science Foundation Cooperative Fellow, 1961-1962.

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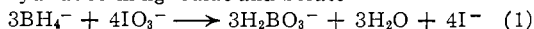
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(12) H. T. S. Britton, "Hydrogen Ions," Vol. I, 4th Ed., Chapman and Hall, Ltd., London, 1955.

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hydroxide did the ionic strength rise above $\mu = 0.10$ unless the effect of ionic strength was being studied.

Volumetric Analysis for Borohydride Concentration.—The iodate analysis¹⁴ as recommended by Lyttle has been used for most of the present study. Iodate reacts with borohydride forming iodide and borate



The excess iodate can then be converted to iodine in acidic media and titrated with standard thiosulfate with starch indicator.

Kinetic Experiments.—The initial concentration of borohydride ion was varied from 0.001 to 0.050 *M*. The buffer solution was thermostated ($\pm 0.01^\circ$ by NBS thermometers) in a flask and oxygen-free nitrogen bubbled through the system. The nitrogen reduced the supersaturation of the hydrogen gas. Even so, the flask was shaken before an aliquot was taken. Gas bubbles caused more of a problem below *pH* 9 (half-times less than 690 seconds). In this case, the aliquots were withdrawn on a weight basis rather than a volume basis.

Pyrex vessels were used to study reactions when the *pH* was below 12.0. Above *pH* 12.0 vented 6 oz. polyethylene bottles and Pyrex flasks were used as containers. After the polyethylene bottles had been used with basic borohydride, no difference was detected in reaction rate.

"*pH* Stat" Experiments.—The rate of disappearance of acid was measured using a "*pH* Stat." A type SBR2-SBU1-TTA2 titration apparatus (Radiometer, Copenhagen, Denmark) was used to automatically add dilute hydrochloric (0.01 or 0.10 *N*) acid or sulfuric acid from a micro syringe to maintain a constant *pH* at a constant temperature.

Hydrolysis in the Presence of Trimethylamine.—The mechanism postulated produces aquated borine as a reactive intermediate. An experiment was designed to trap it. A solution of 100 g. of trimethylamine (1.7 mole) in 500 ml. of water was prepared. This solution then was poured over 37.8 g. (1.0 mole) of sodium borohydride. The hydrogen gas was collected (98% of the borohydride). The trimethylamine borane in the aqueous solution was detected and analyzed using a F and M Model 609 gas chromatographic apparatus with a flame ionization detector. A 61-cm. silicone rubber column at 60° with nitrogen gas as carrier separated the residual trimethylamine in solution from the trimethylamine borane. The retention time for the amine was 0.50 \pm 0.03 minute and 1.50 \pm 0.05 minutes for the amine borane. Comparison of the chromatogram with standards of the amine borane in water allowed an analysis of the original solution. A total of 1.10 \pm 0.07 g. of amine borane was present in the original solution. This represents a 1.45 \pm 0.09% yield. Extraction with ether gave a solution from which 0.60 g. of trimethylamine borane (0.8%), m.p. 93–94°, was isolated. The infrared spectrum was identical with authentic sample. The mixed melting point (corrected) was undepressed. Trimethylamine borane was stable in the basic solution. In a control experiment trimethylamine borane was dissolved in 500 ml. of water and extracted with ether in the same apparatus. The borane was recovered quickly without hydrolysis.

Correction for the Heat of Reaction 4.—The heat of reaction 4 is quite large. At moderate concentrations of borohydride and with faster reactions, a marked temperature rise was noted. At low *pH*, smaller amounts of borohydride were used. Agitation of the solution with nitrogen increased the rate of heat transfer and maintained the temperature of the solution at that of the thermostat.

Possible Reduction of Oxygen by Borohydride.—Preliminary kinetic experiments under air gave a somewhat erratic result. Slower and more reproducible rates were obtained when pure nitrogen was bubbled through the system. The air effects were examined. Absorption of carbon dioxide was found to increase the rates as the *pH* was lowered. The possible reaction of oxygen with borohydride was considered. The heat of this reaction can be



calculated to be about –348 kcal./mole. Energetically, the reaction is very favorable. Another possible reaction would be the reduction of oxygen to form hydrogen peroxide

which is stable to further reduction.^{4,15} However, basic borohydride solutions absorbed no oxygen gas in one day at 50° at 2600 lb. pressure. The borohydride ion concentration was unchanged at the end of the experiment. Thus reactions 2 and 3 are of no importance *in strong base*.

Sodium Borodeuteride.—Sodium tetramethoxyboron was prepared by the method of Brown¹⁶ and then treated with a slight excess of diborane-*d*₆ in tetrahydrofuran on the vacuum line.¹⁶ The diborane-*d*₆ was generated on the vacuum line by the reaction of lithium aluminum deuteride (Metal Hydrides, Lot LPO 912 113) with purified boron trifluoride etherate.¹⁶ The sodium borodeuteride then was recrystallized from diglyme *in vacuo*. Yields of 80–83% were obtained using millimole quantities. Analysis of the material gave Na_{1.00}B_{0.99}D_{3.98}H_{0.021}.

Hydrolysis in Heavy Water Buffers.—Buffers in heavy water (99.6%) were prepared from buffers in light water. The light water was removed by sublimation of the frozen solution and the inorganic residue dried *in vacuo*. The residue then was moistened with a little heavy water and taken to dryness. This procedure was repeated three times. The residue now was taken up in the appropriate amount

TABLE I
HYDROLYSIS OF SODIUM BOROHYDRIDE IN AQUEOUS BUFFERS AT 25°, VOLUMETRIC METHOD

<i>pH</i> ^a	Buffer ^b	Ref.	<i>k</i> ₁ , sec. ^{-1c}
7.40	Phosphate	<i>d</i>	4.0 \pm 0.3 $\times 10^{-2}$
7.60	Phosphate	<i>d</i>	3.2 \pm .3 $\times 10^{-2}$
7.80	Borate	<i>e</i>	6.2 \pm .2 $\times 10^{-2}$
8.00	Phosphate	<i>d</i>	9.2 \pm .4 $\times 10^{-3}$
8.47	Borate	<i>e</i>	3.64 \pm .03 $\times 10^{-3}$
8.77	Borate	<i>e</i>	2.05 \pm .03 $\times 10^{-3}$
9.00	Ammonia	<i>f</i>	1.02 \pm .02 $\times 10^{-3}$
9.32	Borate	<i>g, m</i>	5.25 \pm .03 $\times 10^{-4}$
9.70	Borate	<i>g</i>	1.96 \pm .04 $\times 10^{-4}$
9.71	Borate	<i>g, m</i>	1.94 \pm .02 $\times 10^{-4}$
9.96	Borate-carbonate	<i>h</i>	1.02 \pm .02 $\times 10^{-4}$
10.00	Borate	<i>g</i>	1.00 \pm .02 $\times 10^{-4}$
10.20	Borate-carbonate	<i>h</i>	5.87 \pm .008 $\times 10^{-5}$
10.46	Borate-carbonate	<i>h</i>	4.18 \pm .04 $\times 10^{-5}$
10.60	Borate-hydroxide	<i>i</i>	3.20 \pm .04 $\times 10^{-5}$
10.75	Borate-carbonate	<i>h</i>	2.50 \pm .03 $\times 10^{-5}$
11.00	Borate-hydroxide	<i>i</i>	1.04 \pm .02 $\times 10^{-5}$
11.26	Borate-hydroxide	<i>i</i>	6.05 \pm .08 $\times 10^{-6}$
11.45	Borate-hydroxide	<i>i</i>	4.4 \pm .1 $\times 10^{-6}$
11.70	Phosphate-hydroxide	<i>j</i>	2.91 \pm .05 $\times 10^{-6}$
12.01	Phosphate-hydroxide	<i>j</i>	1.42 \pm .07 $\times 10^{-6}$
12.30	Hydroxide	<i>k</i>	7.1 \pm .3 $\times 10^{-7}$
12.65	Hydroxide	<i>k</i>	4.2 \pm .2 $\times 10^{-7}$
13.00	Hydroxide	<i>k</i>	2.50 \pm .07 $\times 10^{-7}$
13.2	Hydroxide	<i>k, l</i>	2.10 \pm .05 $\times 10^{-7}$
13.4	Hydroxide	<i>k</i>	1.74 \pm .04 $\times 10^{-7}$
13.7	Hydroxide	<i>k</i>	1.3 \pm .06 $\times 10^{-7}$
14.0	Hydroxide	<i>k</i>	1.01 \pm .02 $\times 10^{-7}$
14.4	Hydroxide	<i>k</i>	7.87 \pm .10 $\times 10^{-8}$
14.7	Hydroxide	<i>k</i>	5.45 \pm .05 $\times 10^{-8}$

^a *pH* \pm 0.02 as measured at 25.00 \pm 0.01°. ^b Ionic strength maintained at 0.10 with salts except above *pH* 12.7. ^c First order rate constant, *k*₁, rate = *k*₁(BH₄⁻). Deviations are given in terms of σ . At least two identical runs were made. In some cases five runs were made varying the initial (BH₄⁻). ^d KH₂PO₄-NaOH-KCl. ^e H₂BO₃-NaOH-KCl. ^f NH₄Cl-NaOH-KCl. ^g NaBO₂-HCl-NaCl. ^h NaBO₂-Na₂CO₃-NaCl. ⁱ NaBO₂-NaOH-KCl. ^j Na₂HPO₄-NaOH-NaCl. ^k NaOH. ^l *pH* above 13.2 calculated from activity data of Bates.¹¹ ^m LiBH₄ also used at this *pH*.

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TABLE II
HYDROLYSIS OF SODIUM BOROHYDRIDE AT 25°, pH STAT METHOD

pH ^a	Initial solution, ^b M	Titrant, M	k ₁ , sec. ^{-c}
8.00	0.0005 NaHCO ₃ + 0.09 NaCl	0.10 M HCl	1.02 ± 0.06 × 10 ⁻²
8.80	.0005 Na ₂ CO ₃ + .09 NaCl	.10 M HCl	2.23 ± .07 × 10 ⁻³
9.50	.0005 Na ₂ CO ₃ + .05 NaCl	.10 M HCl	4.31 ± .09 × 10 ⁻⁴
10.00	.0005 Na ₂ CO ₃ + .10 NaCl	.10 M HCl	1.03 ± .04 × 10 ⁻⁴

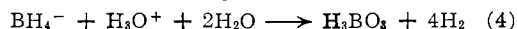
^a pH ± 0.03 at 25°. ^b The initial solution was added to the cell and 0.10 M HCl added until the pH read the value at which the run was to be made. Sodium borohydride was then added and the pH automatically maintained by the addition of the titrant from a micro syringe. ^c $\frac{-d(\text{BH}_4^-)}{dt} = \frac{-d(\text{H}_3\text{O}^+)}{dt} = k_1 (\text{BH}_4^-)$.

of heavy water. N.m.r. spectra showed less than 0.5% of hydrogen. The pD of the solution was measured with a Beckman Model G meter. The equation: pD = meter reading + 0.40 was used to estimate¹⁷ pD. The pK value used for heavy water¹⁸ was 14.71 at 25°. The rate of decomposition of borohydride was measured by the iodate technique.

Hydrolysis in Heavy Water Using the "pH-Stat."—A more convenient technique used the "pH-Stat." Sodium chloride was added to maintain an ionic strength of 0.10. The titrant was prepared by dissolving sulfur trioxide ("Sulfan B") in heavy water.

Results

The reaction of borohydride ion with acid



can be followed conveniently by the rate of loss of reducing power of the solution. The volumetric iodate method¹⁴ has been employed the most in the present study (Table I). The rate of disappearance of acid (Table II) has also been measured and found equal to the rate of disappearance of borohydride. Reaction 4 has been found⁴⁻⁹ to have the rate expression

$$\text{rate} = \frac{-d(\text{BH}_4^-)}{dt} = \frac{-d(\text{H}_3\text{O}^+)}{dt} = k(\text{BH}_4^-)(\text{H}_3\text{O}^+) \quad (5)$$

where *k* is the second order rate coefficient. Examination of the rate data of Table I, most of whose data were presented graphically in Paper I of the series,¹ demonstrated that equation 5 is certainly the most important from pH 7.4 to 12.5. However, above pH 12.5 the rate of reaction becomes much less sensitive to the concentration of the hydronium ion. This general behavior has been noted in the previous investigation.⁴⁻⁸

TABLE III
SALT EFFECTS AT pH 9.50 ± 0.02 AT 25°

Solution, M	μ ^a	k ₁ × 10 ⁴ sec. ^{-1b}
.....	0.000	7.4 ^c
0.0005, borax	.0050	6.0 ^{d,f}
KCl	.0200	5.42 ^e
KCl	.0500	4.47 ^e
0.05, borax	.100	3.80 ^f
.05, borax	.150	3.61 ^f
.05, borax	.200	3.41 ^f

^a Ionic strength maintained with KCl as needed. ^b Rate = *k*₁(BH₄⁻). ^c Extrapolated. ^d Initial rate. ^e pH Stat method; titrant 0.01 N HCl. ^f Volumetric method.

From these data, it is concluded that borohydride is experiencing *general acid catalysis*¹⁹ rather than specific hydronium ion catalysis. Thus the rate expression is more accurately ex-

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(18) W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **32**, 1397 (1936).
(19) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 191-223.

TABLE IV
SALT EFFECTS ON THE HYDROLYSIS AT VERY HIGH pH AT 25.00 ± 0.01°

NaOH, M	Added salt	Salt concn., M	μ ^a	k ₁ , sec. ^{-1b}
0.0113	0.0113	1.21 × 10 ⁻⁶
.0113	KCl	0.050	.061	1.20 × 10 ⁻⁶
.0113	KCl	.100	.111	1.12 × 10 ⁻⁶
.0113	KCl	.20	.211	1.09 × 10 ⁻⁶
.0113	KCl	.50	.511	0.94 × 10 ⁻⁶
.0113	NaCl	.50	.511	1.02 × 10 ⁻⁶
.0113	NaCl	1.00	1.01	0.92 × 10 ⁻⁶
.0113	LiCl	0.10	0.111	1.31 × 10 ⁻⁶
.0113	LiCl	0.50	0.511	1.48 × 10 ⁻⁶
.0113	LiCl	1.00	1.01	1.64 × 10 ⁻⁶
.113	0.113	2.4 × 10 ⁻⁷
.113	NaCl	1.00	1.11	2.0 × 10 ⁻⁷
.113	NaCl	4.00	4.11	1.2 × 10 ⁻⁷
.113	KCl	1.00	1.11	1.5 × 10 ⁻⁷
.113	LiCl	1.00	1.11	2.5 × 10 ⁻⁷
.113	LiCl	4.00	4.11	4.3 × 10 ⁻⁷
1.09	1.09	9.9 × 10 ⁻⁸
1.09	KCl	1.00	2.09	9.7 × 10 ⁻⁸
1.09	NaCl	0.50	1.59	9.8 × 10 ⁻⁸
1.09	NaCl	0.99	2.08	9.4 × 10 ⁻⁸
1.09	NaCl	2.02	3.11	9.0 × 10 ⁻⁸

^a Ionic strength. ^b $\frac{-d(\text{BH}_4^-)}{dt} = k_1 (\text{BH}_4^-)$ via the iodate method.

pressed as rate = *k*_{H₃O⁺}(BH₄⁻)(H₃O⁺) + *k*_{H₂O}(BH₄⁻)(H₂O) + *k*_{HA}(BH₄⁻)(HA) or

$$\text{rate} = (\text{BH}_4^-) \sum_i k_{\text{HA}_i} (\text{HA}_i) \quad (6)$$

where HA_{*i*} is a general acid. The hydronium ion term predominates below pH 12.5 and only above pH 13 does the water term, (*k*_{H₂O})(BH₄⁻)(H₂O), enter to a significant amount.

Further insight into the mode of hydrolysis is given by the effect of inert salts upon the rate. In the low pH region, the rate can be expressed in terms of the Brönsted-Christiansen-Scatchard equation. A plot of log *k*₁ versus the square root of the ionic strength, μ^{1/2}, gives a nearly linear plot (data of Table III). The slope of this line approaches -1 at low ionic strength. Thus the charges on the ions reacting to form the activated complex are +1 and -1, the product, *z*_A*z*_B = (-1)(+1), being the slope. The rate expression 6 would predict that at very low hydronium ion concentration the rate should be independent of the pH. This was not observed (Table I). This is interpreted as due to a small negative salt effect upon the term

$$\text{rate} = k_{\text{H}_2\text{O}} (\text{BH}_4^-)(\text{H}_2\text{O}) \quad (7)$$

This is shown by the data on the salt effects at high

pH values (Table IV). Sodium, potassium and lithium chloride were used as inert salts. The rate at a constant hydroxide ion concentration is depressed as either potassium or sodium chloride is added. It should be noted that the addition of lithium chloride in large amounts actually increases the rate of hydrolysis. At lower pH values lithium ion in low concentration has no effect upon the rate (Table I). No doubt in solutions of very high ionic strength, ion aggregates are present. Lithium borohydride is ether soluble and a more powerful reducing agent in organic systems because of the small size of the lithium ion and its close approach to the tetrahedral borohydride ion.²⁰⁻²²

TABLE V
VARIATION OF BUFFER CONCENTRATION AT CONSTANT IONIC STRENGTH. $\mu = 0.50$ AT 25°

pH	Buffer	HA, M^2	k/k_0^c
9.32	Borax-KCl	0.00 ^b	$1.00 \pm 0.02 = k_0$
		.050	$1.02 \pm .03$
		.100	$1.03 \pm .04$
		.150	$1.03 \pm .03$
		.250	$1.08 \pm .04$

^a Concentration of H_3BO_3 . ^b Extrapolated. ^c Ratio of first order rate constants. $k_{H_3BO_3} = 1 \pm 5 \times 10^{-4} M^{-1} sec^{-1}$. Deviations are in terms of σ .

TABLE VI

VARIATION OF BUFFER AT $\mu = 0.20$

pH	Buffer	HA, M^2	k/k_0^c
9.32	Borax-NaCl	0.00 ^b	$1.00 \pm 0.02 = k_0$
		.050	$1.02 \pm .03$
		.080	$1.04 \pm .03$
		.105	$1.08 \pm .02$
		.175	$1.17 \pm .03$

^a Concentration of boric acid. ^b Extrapolated. ^c Ratio of first order rate constants. $k_{H_3BO_3} = 8 \pm 4 \times 10^{-4} M^{-1} sec^{-1}$. Deviations are in terms of σ .

TABLE VII

GENERAL ACID RATE CONSTANTS AT 25°

Acid	$k_2, M^{-1} sec^{-1}$	μ
H_3O^+	$1.00 \pm 0.04 \times 10^{+6}$	$\mu = 0.10$
H_2O^+	$2.30 \pm 0.07 \times 10^{+6}$	$\mu = .00^a$
H_2O	$2 \pm 1 \times 10^{-9}$	$\mu = .10^a$
H_2O	$2 \pm 1 \times 10^{-9}$	$\mu = .50$
H_3BO_3	$1 \pm 5 \times 10^{-4}$	$\mu = .50$
H_3BO_3	$8 \pm 4 \times 10^{-4}$	$\mu = .20$

^a Extrapolated. See Table III.

A determined search has been made for the other terms of expression 4. The problem of detecting these terms can be quickly appreciated. At an ionic strength of 0.10, $k_{H_3O^+} = 1.00 \pm 0.04 \times 10^6 M^{-1} sec^{-1}$.²³ The value of k_{H_2O} has been esti-

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(21) J. Kollonitsch, P. Fuchs and V. Gabor, *Nature*, **173**, 125 (1954); **175**, 346 (1955).

(22) H. C. Brown, E. J. Mead and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209 (1955).

(23) This value of the rate constant is nearly five times larger than that reported by Pecsok.⁸ A value of $1.0 \times 10^{+6} M^{-1} sec^{-1}$ was calculated from the activation parameters given by Freund.⁹ W. H. Stockmayer²⁴ has privately communicated results on the hydrolysis of potassium borohydride in buffer solutions near pH 9. Their value at 25° is $0.8 \pm 0.1 \times 10^6 M^{-1} sec^{-1}$ at $\mu = 0.15$ which is in agreement with the present value.

The disagreement between the rate constant of Kilpatrick⁵ with those of the other workers has been explained previously.¹ It is a

estimated to be in the neighborhood of $2 \times 10^{-9} M^{-1} sec^{-1}$. Thus the Brønsted α is near unity. Thus, the buffer terms would only be expected to be of the order of a few per cent. of the over-all rate. This is the case as the data of Tables V and VI demonstrate. The effects are small.

Stockmayer^{9,24} obtained a value of the boric acid term $k_{H_3BO_3}$ of $2.0 \pm 0.3 \times 10^{-3} M^{-1} sec^{-1}$, at 25° and $\mu = 0.16$ with potassium borohydride. This value is much larger than the general acid catalyst term reported earlier.¹ However, variation of the boric acid concentration at $\mu = 0.20$ gives a value of $k_{H_3BO_3} = 8 \pm 4 \times 10^{-4} M^{-1} sec^{-1}$ (Table VII). The apparent effect of the ionic strength upon the boric acid term appears to be abnormally large, if real. The total effect in per cent. reaction with hydronium ion compared to the undissociated boric acid is still very small (Tables V and VI). The specific salt effects are large and thus complicate the accurate determination of catalysis constants.

Isotope Effects.—Synthesis of the pure sodium borodeuteride allowed a measurement of the primary isotope effect with the effect of three α -deuterium atoms superimposed. The data are presented in Table VIII. The k_H/k_D is less than one, being 0.70 ± 0.02 at $\mu = 0.10$. The inverse isotope effect is not a function of the pH (Table VIII) nor is it due to trace metal catalysis.²⁵

TABLE VIII

HYDROLYSIS IN AQUEOUS BORATE BUFFERS AT 25.00 \pm 0.01°, ISOTOPE EFFECTS

pH \pm 0.02	μ	$NaBH_4$ $10^4 k_1, sec^{-1}$	$NaBD_4$ $10^4 k_1, sec^{-1}$	k_H/k_D
9.70	0.10	1.74 ± 0.02	2.62 ± 0.02	0.67
9.96	.05	$1.02 \pm .02$	$1.33 \pm .03$.77
10.20	.10	$0.587 \pm .008$	$0.835 \pm .007$.70
10.20 ^a	.10	$0.59 \pm .01$	$0.84 \pm .01$.70

^a Infinity solutions crossed.

This point is confirmed by the last entry in Table VIII. Sodium borohydride was decomposed in a borate buffer at pH 10.20 and the rate constant k_H was measured. After the hydride had completely disappeared ($> 10t_{1/2}$), sodium borodeuteride was added and another rate constant k_D was measured. The reverse experiment was also tried in which sodium borohydride was decomposed in the infinity solution of a borodeuteride run. The rate constants were not altered and the kinetic data gave straight lines to 90% reaction. The k_H/k_D ratio was the same as in separate experiments. As the rate constant does not drift during a reaction, we conclude that the borodeuteride ion is not exchanging (*i.e.*, more than 5%) with the protons of the solvent (*vide infra*).

The solvent isotope effect, k_{H_2O}/k_{D_2O} , was measured using the iodometric procedure (k_{H_2O}/k_{D_2O} significant point to make that the difference is 10% fold and is caused solely by supersaturation of the solution by the hydrogen gas.

(24) W. H. Stockmayer, R. R. Miller and R. J. Zeto, personal communication.

(25) H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra and E. K. Hyde, *J. Am. Chem. Soc.*, **75**, 215 (1953). These investigators reported that the hydrolysis of sodium borohydride is accelerated by salts of manganese(II), iron(II), cobalt(II), nickel(II) and copper(II).

TABLE IX
HYDROLYSIS OF SODIUM BOROHYDRIDE IN HEAVY WATER

Range	μ	Average k_2 , $M^{-1} \text{ sec.}^{-1}$
pH 9.00-10.00	0.10	$1.00 \pm 0.02 \times 10^{6a}$
pD 9.00-10.00	.10	$0.209 \pm .005 \times 10^{6b}$
pD 9.00- 9.40	.10	$0.33 \pm .09 \times 10^{6b,c}$

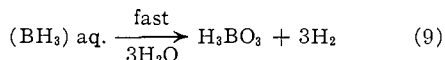
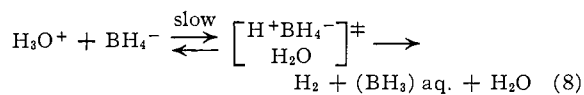
^a Measured by the iodate method in borate buffers.
^b Rate = $k_2(\text{BH}_4^-)(\text{D}_3\text{O}^+)$. ^c "pH-Stat."

= 4.9) and the "pH-Stat" (3.0). The data have been presented in Table IX.

Discussion

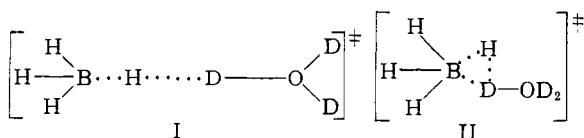
Part I.—Any mechanism postulated for the hydrolysis of borohydride must account for the following facts. The reaction order is unity in borohydride concentration and unity in the concentration of general acid. The salt effects indicate that the activated complex is formed from borohydride ion and hydronium ion. Substitution of deuterium for hydrogen in each ion produces sizable kinetic isotope effects. One intermediate, borine, has been trapped as the trimethylamine borane adduct.

A Mechanism.—A mechanism consistent with these data and the data of other workers⁴⁻⁹ can now be postulated.¹



The Nature of the Activated Complex.—It has been observed that the reaction of borohydride with deuterium oxide gives over 90% of HD.⁸ Thus the hydride hydrogens on the borohydride ion do not exchange significantly with the protons of the acidic solvent. This is also suggested by the demonstration of general acid catalysis. The fact that the rate constant for the disappearance of sodium borodeuteride in light water remains constant to better than 90% reaction can also be cited as evidence. Thus an electronically unlikely molecule, DBH_4 , of high symmetry (as a trigonal bipyramidal structure) is ruled out. Such a molecule would be expected to decompose by a statistical process (as modified by an isotope effect) to give both H_2 and HD.²⁶

Two activated complexes appear reasonable. One would have a linear boron-hydrogen-hydrogen arrangement (I) while the other would have a triangular arrangement (II). The geometry of the transition state cannot be uniquely described at present by these data. A linear activated complex



(26) It should be pointed out that lithium borohydride exchanges with hydrogen gas containing tritium at 200° in the absence of solvent.²⁷ Various derivatives of diborane will also exchange with hydrogen gas and in some cases the exchange is moderately rapid at low temperatures.

(27) N. H. Smith, K. E. Wilzbach and W. G. Brown, *J. Am. Chem. Soc.*, **77**, 1033 (1955); W. G. Brown, L. Kaplan and K. E. Wilzbach, *ibid.*, **74**, 1342 (1952).

would give only HD but a triangular complex (II) would only give HD if one postulates that the deuterium remains partially positive and never equivalent with the hydride until molecular hydrogen is formed. Lewis^{28,29} favors hydride transfers as having triangular activated complexes. The small isotope effects generally found in hydride transfer reactions only mean that a hydride is firmly bound in the activated complex. In terms of a three center linear or triangular system this means that the degenerate ν_2 mode and the ν_1 mode are both of high frequency. It is the ν_3 mode that leads to products in each case. Support for triangular configuration can be given by considering the rather stable³⁰ H_3^+ ion and other three center two electron systems as olefin-silver ion complexes.³¹

A four center activated complex also should be considered. The analogy can be drawn from the postulated four center complex in the hydroboration of olefins. Such a configuration has been postulated by Dessy for the reaction of borohydride with phenol.³² However, it has been found that the four center complex is not consistent with the data in aqueous solution if the general acid is trimethylammonium.³³

No quantum mechanical calculations have been reported for the systems I, II or the four center model. All of these configurations would be represented on the phase space of the transition state potential energies surfaces and are therefore activated complexes. Unfortunately, only speculation can be given at the present time on which is of lowest energy and therefore the most probable as the systems react on the energy surfaces.

An Intermediate.—Aquated borine is postulated as a reactive intermediate. The reaction of trimethylamine with lithium borohydride in anhydrous ether produces trimethylamine borane in good yield.³⁴ Weiss and Shapiro³⁵ have prepared diborane in high yield from alkali borohydrides in concentrated sulfuric acid or methanesulfonic acid. The yield decreases as the water content increases.

Therefore an experiment was designed to trap the borine in aqueous solution. The hydrolysis of sodium borohydride in 3.4 molar aqueous trimethylamine gave only a $1.45 \pm 0.09\%$ yield of trimethylamine borane. In aqueous solution water and trimethylamine compete for the ephemeral aquated borine. It is well established that diborane is extremely sensitive to moisture.^{36,37}

Diborane has been found to be instantaneously hydrolyzed in the presence of water or water vapor. If diborane is absorbed in an aqueous potassium

(28) E. S. Lewis and M. C. R. Symons, *Quart. Rev.*, **12**, 230-249 (1958); (b) p. 246.

(29) M. F. Hawthorne and E. S. Lewis, *J. Am. Chem. Soc.*, **80**, 4296 (1958).

(30) J. L. Hirschfelder, *J. Chem. Phys.*, **6**, 795 (1938).

(31) For a brief discussion of multicenter bonds, see K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Inc., New York, N. Y., 1953, pp. 191-194.

(32) R. E. Dessy and E. Grannen, Jr., *J. Am. Chem. Soc.*, **83**, 3953 (1961).

(33) Paper IV, R. E. Davis, *ibid.*, **84**, 892 (1962).

(34) G. W. Schaeffer and E. R. Anderson, *ibid.*, **71**, 2143 (1949).

(35) H. G. Weiss and I. Shapiro, *ibid.*, **81**, 6167 (1959).

(36) H. I. Schlesinger and H. C. Brown and collaborators, *ibid.*, **75**, 186-224 (1953).

(37) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, New York, 1933.

hydroxide solution, large amounts of hydrogen, potassium borate and moderately small amounts of the "potassium hypoborate" are formed. The "hypoborate" is stable in base, liberates hydrogen upon acidification and has strong reducing properties. The same material can be formed in larger amounts when tetraborane is decomposed in potassium hydroxide.^{38,39} Several structures have been proposed and various boron hydrates have been postulated by Freund⁸ to be intermediates during the hydrolysis of borohydride. Little is known concerning the hydroxy derivatives of diborane.

The Inverse Isotope Effect.—The hydrolysis of sodium borodeuteride occurs faster than the hydrolysis of the borohydride.¹ Jolly⁴⁰ has confirmed the isotope effect in hydrolysis in aqueous media. Brown⁴¹ has observed an inverse isotope for the reduction of ketones in alcoholic solution. Dessy has communicated results indicating that the methanolysis of lithium borohydride in diglyme also shows an inverse isotope effect.³²

It is highly unusual for a compound that is breaking a hydrogen bond to show an inverse isotope effect rather than a normal effect.⁴² We have ascribed¹ this effect to a secondary isotope effect of the *other* three hydrogens or deuteriums that are not undergoing the protonolysis reaction in the rate-determining step. The boron-hydrogen bond that is breaking is contributing a small normal primary isotope but a larger inverse secondary isotope makes the ratio, k_H/k_D , less than one. There is a greater reluctance of the BH⁻ bonds to change to BH (uncharged) in aquated borane than that of BD⁻ to change to BD. The effect is analogous to the greater basicity and nucleophilicity of DO⁻ compared to HO⁻. Infrared data suggest that DO⁻ and HO⁻ do not exert a solvent isotope effect by changing the structure of liquid water since the librational band is undisturbed. The differences between DO⁻ and HO⁻ are due to differences in the vibrational and rotational states of these ions.

Thus the non-reacting hydrogen or deuterium atoms have more zero-point vibrational energy in the activated complex than in the ground state. As the borohydride ion (symmetry T_d) forms an activated complex which resembles one-half of the diborane molecule, the vibrational fundamentals shift to higher frequencies.⁴³⁻⁴⁷ The A_1 (ν_1) boron-hydrogen stretching vibration occurs at 2264 cm^{-1} in borohydride (Table XI). The non-bridge hydrogens in diborane have a stretching frequency of 2524 cm^{-1} [$A_g(\nu_1)$ mode]. Since borohydride ion is a simple molecular system with only four normal modes and diborane is a system having D_{2h} symmetry with eighteen fundamen-

tal frequencies belonging to eight species, it is possible to estimate the isotope effect from theory.

Part II. Calculation of the Isotope Effect.—The theory of the kinetic isotope effect has been developed successfully from transition state theory by Bigeleisen.⁴⁸ The approximate equation

$$\frac{k_1 S_2 S_1^{\ddagger}}{k_2 S_1 S_2^{\ddagger}} = \frac{\nu_{11}^{\ddagger}}{\nu_{21}^{\ddagger}} \left[1 + \frac{1}{24} \left(\frac{hc}{KT} \right)^2 \sum_i^{3n} (m_{1i}^{-1} - m_{2i}^{-1})(a_{ii} - a_{ii}^{\ddagger}) \right] \quad (10)$$

can be obtained from theory where k is the specific rate constant; the S 's are symmetry numbers; the subscript 1 refers to the lighter isotope and 2 to the heavier species; ν_1 refers to the vibrational frequency of the activated complex (\ddagger) along the reaction coordinate; m_i 's represent the masses of the atoms; and the a_{ii} 's refer to the diagonal force constants for Cartesian displacements. Wolfsberg⁴⁹ has applied equation 10 to secondary hydrogen isotope effects in certain simple model reactions. As borohydride, BH_4^- , represents a simple chemical species, application of equation 10 can be made with not too many severe approximations.

First consider the maximum isotope effect to be expected in a given situation. For the types of bonds of interest in the present investigation, the method yields the data of Table X. As the X-H

TABLE X

MAXIMUM VALUES OF THE DEUTERIUM ISOTOPE EFFECT, k_H/k_D , AT 25°

Bond	Primary		Secondary	
	I ^a	II ^b	Normal	Inverse
O-H	10.6 ^c	28	2.02 ^d	0.37 ^d
N-H	8.5 ^c	23	1.87	.41
C-H	6.9 ^c	18 ^d	1.74 ^d	.46 ^d
B-H	5.3	14	1.54	.51

^a Calculated using a diatomic model which represents the complete loss of the vibrational stretching frequency. In each case an average X-H bond is used. ^b Value of $\frac{k_H S_D S_B^{\ddagger}}{k_D S_H S_D^{\ddagger}}$

based on a polyatomic model using equation 10 and assuming complete loss of all vibrational activity of the X-H bond. ^c Reported by Wiberg.⁴² ^d Values reported by Bigeleisen and Wolfsberg.⁴⁸ The remaining values have been calculated during the present investigation.

stretching frequency moves to lower frequency, the effects approach unity from above with normal effects and from below with the inverse effect. Following Bigeleisen's suggestion, the secondary effects have been rather arbitrarily calculated on the basis of decreasing the force constants in half for the normal effect and doubling the force constants for the inverse effect. Thus, in loose terminology, the nonreacting X-H bonds loosen in the activated complex for the normal effect and stiffen for an inverse effect. The maximum for the primary isotope effect in column I of Table X has been calculated using a two atom model and therefore represents only the complete loss of the

(48) J. Bigeleisen and M. Wolfsberg, "Theoretical and Experimental Aspects of Isotope Effects in Chemical Kinetics," "Advances in Chemical Physics," Vol. I, I. Prigogine, ed., Interscience Publishers, Inc., New York, N. Y., 1958, pp. 15-76.

(49) M. Wolfsberg, *J. Chem. Phys.*, **33**, 2 (1960).

(38) A. Stock and C. Massenez, *Ber.*, **45**, 3529 (1912).

(39) L. Klemm and W. Klemm, *Z. anorg. Chem.*, **225**, 258 (1935).

(40) W. Jolly, private communication.

(41) Unpublished data from these Laboratories.

(42) K. E. Wiberg, *Chem. Revs.*, **65**, 713 (1955).

(43) W. C. Price, *J. Chem. Phys.*, **17**, 1044 (1949).

(44) R. C. Taylor, D. R. Schultz and A. R. Emery, *J. Am. Chem. Soc.*, **80**, 27 (1958).

(45) A. R. Emery and R. C. Taylor, *J. Chem. Phys.*, **28**, 1029 (1958).

(46) R. C. Taylor and A. R. Emery, *Spectrochim. Acta*, **10**, 419 (1958).

(47) R. C. Lord and E. Nielsen, *ibid.*, **19** (1951).

stretching mode. In column II the value of $k_H S_D S_H^\ddagger / k_D S_H S_D^\ddagger$ is given which should represent the upper limit to be expected in a normal reaction.

Assuming typical models of the activated complex and only considering the frequency changes within the borohydride, equation 10 can be used to calculate the isotope effect. The infrared and Raman data (Table XI) can be used to estimate the force constants.⁵⁰ Allowing that in the activated complex the three hydrogen atoms bonded to the boron resemble those of diborane and that the amount of primary boron-hydrogen bond breaking is proportional to the amount of secondary bond stiffening, the value of k_H/k_D is 0.65. Experimentally the value is 0.70. In spite of the severe limitations of the calculation, it is implied that the vibrational modes of the activated complex are still harmonic and perhaps that the boron-hydrogen bond has not been appreciably broken. Several other reasonable models of the activated complex give reasonable values of 0.95 to 0.60. If one does not allow for the secondary effect, the calculated value is greater than unity.

TABLE XI
VIBRATIONAL FREQUENCIES AND FORCE CONSTANTS OF
BOROHYDRIDE^a

Fundamentals	¹¹ BH ₄ ⁻	¹⁰ BD ₄ ⁻
A ₁ ν ₁	2264	(1570) ^b 1604 ^c
E ν ₂	1210	855
F ₂ ν ₃	2244	1696
ν ₄	1080	823
Symmetry constants	10 ⁵ dynes/cm.	
F ₁	3.0511	
F ₂	0.2897	
F ₃	2.6737	
F ₄	0.2905	
F ₃₄	0.0150	
Valence force constants ^a	10 ⁵ dynes/cm.	
k _γ	2.768	
k _{γγ}	0.094	
k _α k _{αα}	.290	
k _α k _{αα'}	.291	
k _{γα} k _{γα'}	.011	

^a See ref. 46 for notation and definition. ^b Shifted by Fermi resonance. ^c Calculated.

It should be stressed that the calculated value, k_H/k_D , is not very sensitive to the assumed geometry. As stated earlier, isotope effects⁵¹ cannot uniquely distinguish between a linear and a triangular complex even in a three atom system like H-H-Cl.

Part III. Steric Effects and Secondary Isotope Effects.—A growing list of reactions now shows secondary inverse isotope effects. The causes of such inverse effects and normal secondary isotope effects are at present vigorously debated. The fact that the effects are small tends to obscure quantitative estimate of their magnitude. Vibrational effects,⁵²⁻⁵⁴ rotational effects,⁵⁴⁻⁵⁶ differential inductive effects,⁵⁷ anharmonicity effects and

steric effects⁵⁸ have been proposed. *It should be emphasized that all these effects and others can be included in the partition functions in the Bigeleisen formulation.* Bartell^{59,60} has signalled attention to the mass-sensitive amplitudes of vibration or the steric effect. We have used a simpler static model of non-bonded repulsions to independently predict that the steric effect of replacing a hydrogen by a deuterium can give rise to normal secondary isotope effects and also inverse secondary isotope effects. The range of $\Delta\Delta F^\ddagger$ was from about -200 to +200 cal./mole.⁶¹⁻⁶³

Comparison of Rate Constants and Activation Parameters.—The rate constant $k_{H_2O^+}$ was first reported to be $0.77 M^{-1} \text{ sec.}^{-1}$ as measured by a gas evolution technique in 1-3 *N* sulfuric acid.⁵ The values obtained by subsequent workers have been at least 10⁵ times larger. Pecsok⁶ reported $k_{H_2O^+} = 2.5 \times 10^5 M^{-1} \text{ sec.}^{-1}$ as obtained by a polarographic technique in the *pH* region of 7 to 10. Jensen's value^{3,4} is also in the same order of magnitude. Freund⁸ reports data from which the calculated constants are in agreement to within 10% of the value in Table VII. Stockmayer's value^{9,24} is also in good agreement with our value of $1.00 \pm 0.04 \times 10^6 M^{-1} \text{ sec.}^{-1}$ at $\mu = 0.10$. The 10⁵ fold difference in rate between the gas evolution technique and the other methods was explained¹ in terms of the Setchenow equation^{64,65} relating the

(52) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

(53) R. E. Weston, Jr., *Tetrahedron*, **6**, 31 (1959).

(54) K. T. Leffek, J. A. Llewellyn and R. E. Robertson, *J. Am. Chem. Soc.*, **82**, 6315 (1960).

(55) A. Llewellyn, R. E. Robertson and J. M. W. Scott, *Chemistry & Industry (London)*, 723 (1959).

(56) K. T. Leffek, J. A. Llewellyn and R. E. Robertson, *Can. J. Chem.*, **38**, 2171 (1960).

(57) E. A. Halevi, *Tetrahedron*, **1**, 174 (1957).

(58) V. J. Shiner, Jr., *ibid.*, **5**, 243 (1958).

(59) L. S. Bartell, *Tetrahedron Letters*, No. **6**, 13 (1960).

(60) L. S. Bartell, private communication, and papers in press to *J. Am. Chem. Soc.*

(61) The interaction, ϕ_{ij} , between two non-bonded atoms *i* and *j* is expressed in Mie's formulation. The various parameters are estimated from scattering potentials or Lennard-Jones and Morse curves. Most force constants are considered in the harmonic approximation and all off-diagonal elements are set nearly equal to zero. The overall energy, E_H of an assembly of atoms is then calculated. Then one distance is shortened 0.001 to 0.010 Å. to account for the anharmonicity upon substitution of deuterium for hydrogen. A new energy value E_D is now calculated. The difference $E_H - E_D$ is then the estimate of the steric effect. The model ignores some kinetic energy terms. *The important conclusion is that the steric effect may be of the same order of magnitude as predicted on the basis of hyperconjugative or inductive effects.*

(62) Mislow has claimed that a steric explanation based on the size of deuterium compared to hydrogen is not compatible with data on reduction of ketones. This reaction is of *very low steric* requirements as seen comparing the ΔF observed (170 cal./mole.) upon substitution of a methyl group for a hydrogen. Using amineboron complexes as a reference and then estimating the parameters of methyl-hydrogen-interaction in Mislow's reduction, a crude estimate of the potential function for ketone reduction can be made. On such a basis, the maximum steric isotope effect k_H/k_D is estimated to be only 1.0006 which is to be compared with the observed value of 1.0000 ± 0.0002 . It is concluded that Mislow's system is too insensitive to the steric effects and does not constitute a crucial experimental case to rule upon the nonexistence of such effects.

(63) A more detailed discussion of the theory was made before the Indiana Academy of Science, Oct., 1961: R. E. Davis, *Proc. Ind. Acad. Sci.*, in press.

(64) M. Setchenow, *Ann. chim. phys.*, **6**, 25, 226 (1892).

(65) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 531.

(50) E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, pp. 145 ff., 265 ff.

(51) J. Bigeleisen, F. S. Klein, R. E. Weston, Jr., and M. Wolfsberg, *J. Chem. Phys.*, **30**, 1340 (1959).

solubility of a gas to the concentration of electrolytes in solution. It is to be expected that the rate of attainment of equilibrium between the gas phase and solution will also obey an expression of this form. This is completely analogous to the quasi-thermodynamics used in the theory of absolute rates. Expanding the Setchenow equation into a power series gives an expression which will predict an apparent first-order dependence of the rate of evolution on the electrolyte concentration over a narrow range.

Jolly⁶⁶ has recently investigated the hydrolysis of borohydride in the pH region of 7 to 3.5 using a flow apparatus. The rate constant is in agreement with that reported in this paper. At one molar acid, the lower limit of $10^4 M^{-1} \text{sec.}^{-1}$ was placed upon the rate constant.

The present study has been performed at 25°. However, Pecsok⁶ reports $E_a = 9.1$; Freund⁸ reports $E_a = 7.2$; Stockmayer²⁴ reports 9 ± 1 and Jolly⁶⁶ reports 7.7 kcal./mole for the $k_{\text{H}_3\text{O}^+}$ term. A best average value would be 8.4 ± 0.9 kcal./mole. From this datum the value of $\Delta H^\ddagger = 7.8$

(66) R. Mesmer and W. Jolly, Annual A.E.C. Report, private communication, March, 1961.

± 0.9 kcal./mole and $\Delta S^\ddagger = -6 \pm 3$ cal./mole deg. can be calculated. The entropy of activation is abnormally lower than that expected for the unopposite charge type as represented in reaction 8.

The thermodynamic functions for reaction 4 have been measured. The heat of reaction,⁶⁷ ΔH , is -63.87 kcal. The ΔH^0 at 298°K. is -63.73 kcal.; ΔS^0 is 103.0 e.u.; and ΔF^0 is -94.45 kcal.⁶⁸ The half-cell potential, E^0 , has been estimated to be $+1.24$ volts⁶⁸ and $+1.23$ volts.⁵ The standard entropy S^0 of aqueous borohydride ion is 25.5 ± 1 e.u.⁶⁸

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(67) W. D. Davis, L. S. Mason and G. Stegeman, *J. Am. Chem. Soc.*, **71**, 2775 (1949).

(68) W. H. Stockmayer, D. W. Rice and C. C. Stephenson, *ibid.*, **77**, 1980 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

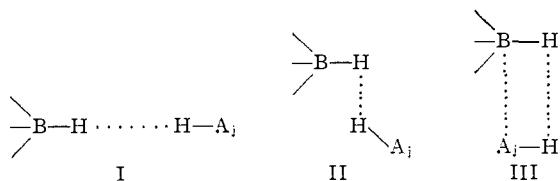
Boron Hydrides. IV. Concerning the Geometry of the Activated Complex in the Hydrolysis of Borohydride Ion by Trimethylammonium Ion

BY ROBERT EARL DAVIS

RECEIVED JULY 14, 1961

The rate of hydrolysis of sodium borohydride in aqueous solution at constant pH and constant ionic strength is increased by trimethylammonium ion. The amount of trimethylamine borane produced is much less than the theoretical amount predicted on a four center activated complex. On this basis the four center complex is rejected. Brief discussion has been made concerning a three center complex. The mean life time of a caged molecular system of borine, hydrogen and trimethylamine is estimated.

The hydrolysis of sodium borohydride in aqueous solution has been discussed in the preceding paper.¹ Three simple geometric relationships suggest themselves (I–III). The theoretically cal-



culated values¹ of the kinetic isotope effects have been found to be rather *insensitive* to the assumed geometry. The boron-hydrogen isotope effect, $k_{\text{H}}/k_{\text{D}}$, is in the range of 0.95 to 0.60 for various models. Experimentally the value^{1,2} is 0.70.

A simple experimental test can be made between a three center complex (I or II) and a four center complex (III) if the product, $\text{H}_3\text{B}-\text{A}_j$, is stable under the conditions of the hydrolysis and if it can be quantitatively determined. In the present re-

port we wish to demonstrate that the four center complex (III) is incorrect when A_j is trimethylamine.

Predictions from the Geometrics of I–III.—The most interesting system would be when A_j is a water molecule. However, aquated borine, H_3BOH_2 , is not stable in water³ nor could one determine that it formed from the hydronium ion or from the water in the solvation sphere of the borohydride ion. When A_j is trimethylamine, the adduct is very stable in aqueous solution and hydrolyzes only slowly in acidic solutions.⁴ Trimethylamine borane has a high fugacity and can be determined in aqueous solution by gas chromatography using a sensitive flame ionization detector.

Models I and II predict that a molecule of hydrogen will be formed between the borine and the newly formed trimethylamine molecule.⁵ The

(3) H. I. Schlesinger, H. C. Brown, *et al.*, *ibid.*, **75**, 186 (1953).

(4) G. E. Ryschkewitsch, *ibid.*, **82**, 3290 (1960).

(5) An analogy can be made with the solvent separated ion-pair⁶ and decomposition of azo compounds in which a stable nitrogen⁷ molecule is formed between the two radical fragments in the solvent cage.⁵

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(1) R. E. Davis, E. Bromels and C. L. Kibby, *J. Am. Chem. Soc.*, **84**, 885 (1962), Paper III.

(2) R. E. Davis, C. L. Kibby and C. G. Swain, *ibid.*, **82**, 5950 (1960), Paper II.