

Kinetics of the Stepwise Hydrolysis of Tetrahydroborate Ion

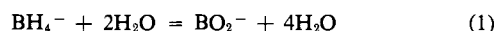
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The hydrolysis of sodium tetrahydroborate (NaBH_4) has been investigated, and a kinetic scheme which consists of a series of two pseudo-first-order reactions was used to interpret the data. The concentration of the BH_4^- has been followed by measurement of the diffusion current of its anodic polarographic wave with $E_{1/2} = -0.15$ v. vs. s.c.e., and the concentration of an intermediate in the process has been measured by the polarographic wave at $E_{1/2} = -0.64$ v. vs. s.c.e. The reaction, both steps of which are subject to general acid catalysis, has been studied in the pH range 9.1–10.2 in ammonia, ammonium ion, and carbonate–bicarbonate buffer solutions. When constants for the reaction, $\text{BH}_4^- \xrightarrow{k_1'} \text{intermediate} \xrightarrow{k_2'} \text{products}$, are defined thus: $-d \ln [\text{BH}_4^-]/dt = k_1' = \sum k_{1,\text{HA}_i} [\text{HA}_i]$, and $d[\text{intermediate}]/dt = k_1'[\text{BH}_4^-] - k_2'[\text{intermediate}]$, $k_2' = \sum k_{2,\text{HA}_i} [\text{HA}_i]$, the following specific rate constants for $\mu = 0.5$ at 25° can be reported (in $l. \text{mole}^{-1} \text{sec}^{-1}$): $k_{1,\text{HCO}_3^-} = 1.3 \pm 0.3 \times 10^{-3}$; $k_{1,\text{NH}_4^+} = 2.9 \pm 0.5 \times 10^{-4}$; $k_{1,\text{H}_3\text{O}^+} = 6.0 \pm 0.3 \times 10^5$; $k_{1,\text{H}_2\text{O}} \sim 10^{-7}$; $k_{2,\text{HCO}_3^-} = 2.2 \pm 0.3 \times 10^{-1}$; $k_{2,\text{NH}_4^+} = 4.7 \pm 0.3 \times 10^{-2}$; $k_{2,\text{H}_3\text{O}^+} \sim 10^7$; $k_{2,\text{H}_2\text{O}} \sim 10^{-5}$. The temperature coefficients of specific rate constants indicate the following Arrhenius activation energies for reactions of BH_4^- with HCO_3^- , NH_4^+ , and H_3O^+ , respectively: 13 ± 3 , 23 ± 2 , 11 ± 1 kcal. mole^{-1} . Similarly, for the intermediate, values of 9 ± 1 , 16 ± 4 , and 12 ± 8 kcal. mole^{-1} were obtained. Variation of ionic strength altered the specific rate constants in a way consistent with a negatively charged intermediate, which, together with B^{11} n.m.r. spectra indicating the presence of the $-\text{BH}_3$ group, suggested BH_3OH^- as the formula of the intermediate.

Introduction

The hydrolysis of sodium tetrahydroborate, (sodium hydroborate, sodium borohydride, NaBH_4), according to reaction 1, has been studied by investigators^{2–6}



who early showed the importance of pH on the rate of reaction. More recently, it has been shown that the reaction is subject to general acid catalysis and that a pseudo-first-order rate law describes the disappearance of the reducing power of a well-buffered sodium hydroborate solution.^{7–10}

(1) Allied Chemical Foundation Fellow, 1963–1964; taken from the Ph.D. dissertation submitted by J. A. G. to the Graduate School of The Ohio State University, 1964.

(2) H. R. Hoekstra, Atomic Energy Commission, Document No. 2144, 1947.

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(4) M. Kilpatrick and C. D. McKinney, *ibid.*, **72**, 5474 (1950).

(5) J. B. Brown and M. Svenson, *ibid.*, **79**, 4241 (1957).

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(7) R. E. Davis and C. G. Swain, *J. Am. Chem. Soc.*, **82**, 5949 (1960).

(8) R. E. Davis, E. Bromels, and C. L. Kibby, *ibid.*, **84**, 885 (1962).

At the dropping mercury electrode (d.m.e.), sodium hydroborate solutions yield a well-defined anodic polarographic wave at an $E_{1/2}$ of -0.15 v. vs. s.c.e. The height of this wave is proportional to the concentration of hydroborate ion; by means of this wave, the rate of disappearance of hydroborate in a hydrolyzing solution rather than the total reducing power of the solution has been determined.¹¹ A hydrolyzing solution of sodium hydroborate also exhibits another, smaller polarographic wave at $E_{1/2}$ of -0.64 v. vs. s.c.e.¹² It has already been suggested¹³ that this second wave arises from the electrooxidation of a species which is an intermediate in the hydrolysis, because the wave is larger as the pH of the solution is decreased and its height decreases as the hydrolysis proceeds. We have postulated that the height of this smaller polarographic wave is proportional to the concentration of the intermediate in the hydrolysis mixture and have re-investigated the kinetics of the hydrolysis as a stepwise process. Experiments directed toward identifying the intermediate have been reported earlier¹⁴; this article will be concerned with the rates of its formation and decomposition.

Experimental

Reagents. Sodium tetrahydroborate (98%) was used as supplied by Metal Hydrides, Inc. (Beverly, Mass.). A sample of this material, purified by extraction with liquid ammonia, was found to give the same polarographic results as the starting material; thenceforth the commercial material was used directly. Constituents of buffer solutions and the KCl used to adjust ionic strength were commercially available reagents. Carbonate–bicarbonate buffer solutions were prepared by dissolving weighed amounts of the sodium salts; ammonia buffers were prepared by mixing weighed amounts of ammonium chloride with measured volumes of standard KOH or NaOH. The pH values of buffer solutions were measured by means of a Beckman Model G pH meter, which was standardized by 0.01 *M* sodium borate solution. For lack of activity coefficient data at high ionic strengths, concentrations of hydrogen ion have been calculated from pH values under the assumption of unit activity coefficient.

Polarography. Conventional polarographic techniques were used for measuring anodic diffusion currents at -0.01 v. vs. s.c.e. and -0.5 v. vs. s.c.e., which were proportional, respectively, to the concentrations of

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(10) W. L. Jolly and R. E. Mesmer, *Inorg. Chem.*, **1**, 608 (1962).

(11) R. L. Pecsok, *J. Am. Chem. Soc.*, **75**, 2862 (1953).

(12) E. D. Marshall and R. A. Widing, Atomic Energy Commission Document No. 2914, 1950.

(13) (a) K. N. Mochalov and G. G. Gil'manshin, *Dokl. Akad. Nauk SSSR*, **132**, 134 (1960); *Proc. Acad. Sci. USSR, Chem. Sect.*, **132**, 467 (1960); (b) K. N. Mochalov and G. G. Gil'manshin, *Russ. J. Phys. Chem.*, **36**, 578 (1962); *Zh. Fiz. Khim.*, **36**, 1089 (1962).

(14) J. A. Gardiner and J. W. Collat, *J. Am. Chem. Soc.*, **86**, 3165 (1964).

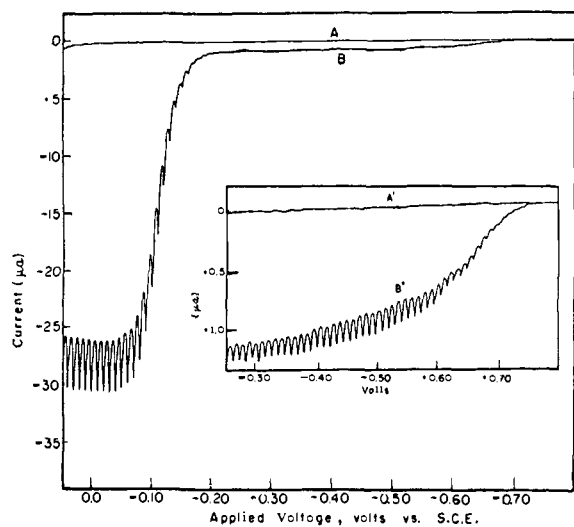


Figure 1. Polarogram of NaBH_4 in an $\text{NH}_4\text{OH-NH}_4^+$ buffer solution of pH 9.11. $[\text{BH}_4^-]_0 = 0.0015 M$; $0.0334 M \text{NH}_4^+$, $0.0167 M \text{NH}_4\text{OH}$, $0.150 M \text{KCl}$. The time after mixing was 35 min. A and A', residual current curves; B and B', after adding NaBH_4 . Inset shows wave at -0.64 v. , magnified ($\mu = 0.20$, 25.0° , $m^{2/3}t^{1/2} = 2.43 \text{ mg.}^{2/3} \text{ sec.}^{-1/2}$).

BH_4^- and the intermediate. A Leeds and Northrup Electrochemograph, Type E was used in conjunction with an H-cell of about 75-ml. capacity. A glass electrode was inserted in the stopper of the cell to make possible pH measurements at any time during the hydrolysis. Two polarographic capillaries were used; their open circuit characteristics were 1.71 and $2.43 \text{ mg.}^{2/3} \text{ sec.}^{-1/2}$.

A typical kinetic experiment was begun by standardizing the glass electrode with borate buffer. Then 55 ml. of the buffer to be used was added; it was purged with pure nitrogen and allowed to reach temperature equilibrium. The pH was noted and a weighed amount of solid sodium hydroborate on a small watch glass was added quickly. The solid dissolved and dispersed, with the help of agitation by nitrogen bubbles, within 10 sec. at the most. A stopwatch was started when the solid was added. The d.m.e. was inserted into the cell and, for the brief periods when diffusion currents were measured, the nitrogen stream was diverted over the solution.

Because the intermediate was never present in a hydrolyzing solution to an extent greater than a few per cent of the initial hydroborate ion concentration, it would have been inconvenient to measure diffusion currents due to hydroborate ion and those due to the intermediate on the same sample solution. Thus, when it was desired to measure the disappearance of hydroborate ion, approximately $0.002 M \text{NaBH}_4$ solutions were used. The applied voltage interval -0.4 to 0.0 v. vs. s.c.e. was scanned, and the limiting current at -0.01 v. was measured. The correction for residual current and the small current due to the intermediate, never more than 3% of the limiting current, was obtained by extrapolating the nearly linear current between -0.4 and -0.2 v. The diffusion current at -0.01 v. , $i_{\text{BH}_4^-}$, was the difference between the limiting current and this correction term. For studies of the intermediate the initial concentration of sodium hydroborate was 0.005 to $0.020 M$. Larger concentra-

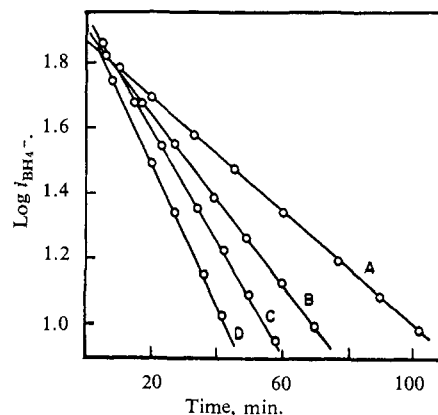


Figure 2. Plot of $\log i_{\text{BH}_4^-}$ vs. time for a $\text{HCO}_3^- \text{--CO}_3^{2-}$ buffer solution of pH 9.39. $[\text{BH}_4^-]_0 = 0.0015 M$. Bicarbonate ion concentrations in runs A, B, C, and D were, respectively, 0.1 , 0.2 , 0.3 , and $0.4 M$ ($m^{2/3}t^{1/2} = 2.43 \text{ mg.}^{2/3} \text{ sec.}^{-1/2}$, 25.0° , $\mu = 1.00$).

tions could not be used because the amount of hydrogen evolved in such solutions interfered with current measurement at the d.m.e. Limiting currents at -0.5 v. were measured as a function of time after mixing without scanning the entire voltage range of the polarogram. These currents were corrected for the (cathodic) residual current of 0.04 to $0.09 \mu\text{A.}$ at -0.5 v. , and the corrected current was called i_t . The time intervals between measurements were 2 to 5 min., depending on the rate of reaction, and each measurement required about 0.5 min.

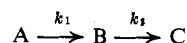
The temperature was controlled to $\pm 0.1^\circ$. Current measurements at -0.01 v. are believed to be accurate within $\pm 2\%$, while those at -0.5 v. may have an uncertainty of $\pm 5\%$. Time measurements were accurate to about $\pm 5 \text{ sec.}$, i.e., the approximate drop time of the capillary.

Standard deviations, σ , were calculated from the expression $\sigma = [\sum(x_i - m)^2/(N - 1)]^{1/2}$, where $x_i - m$ represents the deviation from the mean of an individual run and N is the number of runs.

Results

Rate Constants from Polarographic Currents. Figure 1 shows a typical polarogram for a hydrolyzing solution of sodium hydroborate. This polarogram shows only two waves; the larger at an $E_{1/2}$ of -0.15 v. stems from the oxidation of hydroborate ion; the smaller, at an $E_{1/2}$ of -0.64 v. , from the oxidation of the postulated intermediate.

Figure 2 shows the logarithmic plot of $i_{\text{BH}_4^-}$ vs. time. Figure 3 shows the time dependence of i_t , the current at -0.5 v. caused by the oxidation of the intermediate. In each buffer solution studied, $\log i_{\text{BH}_4^-}$ showed a linear time dependence, and i_t increased from zero through a maximum and then decayed. A similar time dependence of this diffusion current has been reported by Mochalov and Gil'manshin.^{13b} This behavior is characteristic of a system where the concentration of B is initially zero and the reactions are first order.¹⁶



(15) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961.

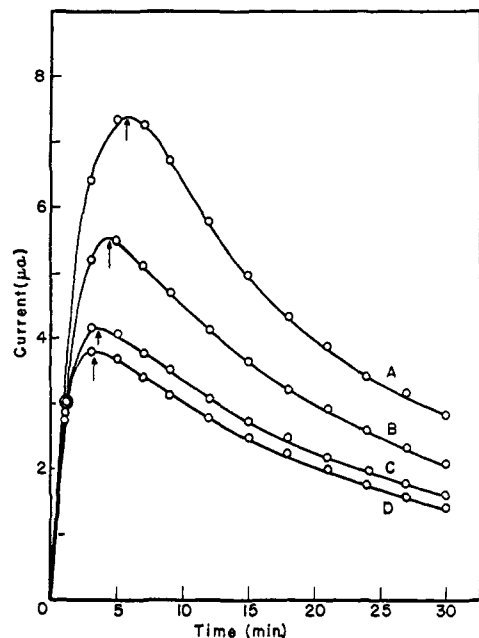


Figure 3. Plot of i_I vs. time for an $\text{NH}_4\text{OH-NH}_4^+$ buffer solution of pH 9.11, $\mu = 0.20$. $[\text{BH}_4^-]_0 = 0.0050 \text{ M}$. Ammonium ion concentrations in runs A, B, C, and D were, respectively, 0.0334, 0.0668, 0.1022, and 0.1334 M (25°). Arrows indicate t_{max} predicted by use of eq. 8, with $R_I = 22.7 \mu\text{a. l. mmole}^{-1}$.

It has been shown⁸ that the disappearance of hydroborate ion follows the rate law

$$-\frac{d[\text{BH}_4^-]}{dt} = [\text{BH}_4^-] \sum_i k_{\text{HA}_i} [\text{HA}_i] \quad (2)$$

By controlling the pH and by employing a large excess of the acidic component of the buffer, the disappearance of hydroborate ion appears to be first order. To distinguish the first stage of the hydrolysis we define a pseudo-first-order rate constant k_1'

$$-\frac{d \ln [\text{BH}_4^-]}{dt} = k_1' = \sum_i k_{1,\text{HA}_i} [\text{HA}_i] \quad (3)$$

Thus hydroborate ion corresponds to A in the above general scheme. Because of the time dependence of i_I , we have postulated that the formation of the intermediate depends on the first-order reaction of hydroborate ion and its disappearance depends on a reaction which is first order in intermediate. Thus, the intermediate, I, corresponds to B in the general scheme. We define k_2' for the second stage of the hydrolysis thus

$$\frac{d[\text{I}]}{dt} = k_1' [\text{BH}_4^-] - k_2' [\text{I}] \quad (4a)$$

$$k_2' = \sum_i k_{2,\text{HA}_i} [\text{HA}_i] \quad (4b)$$

General acid catalysis was found to be extremely important in this step.

The instantaneous concentrations of hydroborate and I, $[\text{BH}_4^-]$, and $[\text{I}]$ are given by the relations

$$[\text{BH}_4^-] = [\text{BH}_4^-]_0 e^{-k_1' t} \quad (5a)$$

$$[\text{I}] = \frac{[\text{BH}_4^-]_0}{\kappa - 1} (e^{-\tau} - e^{-\kappa\tau}) \quad (5b)$$

where $[\text{BH}_4^-]_0$ indicates the initial concentration of BH_4^- , $\kappa = k_2'/k_1'$, $\tau = k_1' t$, and the initial concentration of B is 0. If t_{max} designates the time when $[\text{I}] = [\text{I}]_{\text{max}}$

$$\tau_{\text{max}} = \frac{1}{\kappa - 1} \ln \kappa \quad (5c)$$

Experimentally measured currents can be related to concentrations by the following relations

$$i_{\text{BH}_4^-} = R_{\text{BH}_4^-} [\text{BH}_4^-] \quad (6a)$$

$$i_I = R_I [\text{I}] \quad (6b)$$

where $R_{\text{BH}_4^-}$ and R_I are constants for a given temperature and polarographic capillary. Equation 6a has been experimentally verified by Pecsok¹¹ and by us for the case of buffered solutions. Equation 6b was originally simply assumed to be true; later evidence showed that this assumption was valid. Equation 5 can be rewritten

$$i_{\text{BH}_4^-} = R_{\text{BH}_4^-} [\text{BH}_4^-]_0 e^{-k_1' t} \quad (7)$$

$$i_I = R_I \frac{[\text{BH}_4^-]_0}{\kappa - 1} (e^{-\tau} - e^{-\kappa\tau}) \quad (8)$$

A plot of $\log i_{\text{BH}_4^-}$ vs. time yielded a slope from which k_1' could be derived by multiplying by -2.303 . Therefore, k_1' was determined in a procedure which made no assumption about the mechanism of the reaction. Figure 2 is an example of the plots from which values of k_1' were derived.

For a given buffer solution, eq. 5c permits a calculation of k_2' from a measurement of t_{max} and the previously determined value of k_1' for the particular buffer solution. Equation 8 can then be solved for R_I , which, if determined accurately once and for all, makes possible an alternative calculation of k_2' in other experiments by use of eq. 8. The procedure for determining R_I was as follows. The experimentally obtained value of k_2' was introduced into eq. 8 with i_I data for several values of $t > t_{\text{max}}$, and R_I values so derived were averaged. This value of R_I was applied with data from an entirely different experiment to arrive at a value of k_2' which, substituted in eq. 5c, yielded a predicted t_{max} for this second experiment. A comparison of this t_{max} with that found in the experiment was used to judge the quality of the k_2' . The consistency of R_I for a number of experiments supports the assumption of eq. 6b. Figure 3 shows how predicted t_{max} values calculated from an R_I originally determined in a bicarbonate-carbonate buffer solution agree with experimental results from an ammonia-ammonium ion buffer system. The value of R_I was 18.5, 22.7, and 26.3 $\mu\text{a. l. mmole}^{-1}$ at 15, 25, and 35°, respectively, with a capillary whose $m^{2/3}l^{1/6}$ value was 2.43 $\text{mg.}^{2/3} \text{sec.}^{-1/2}$. These values of R_I have been used for all experiments reported. The accuracy of the rate constants depends on the value of R_I . In some experiments (see Figure 3), rate constants can be calculated from eq. 5c without use of R_I . In these cases the results agree well with calculations made with the above values of R_I substituted into eq. 8. R_I was obtained in a procedure, the precision of which is difficult to estimate; however, we believe these values are accurate to $\pm 5\%$.

Table I. k_1' and k_2' for Bicarbonate-Carbonate Buffer Solutions^a

| $[\text{HCO}_3^-],^b$ M | $k_1' \times$ $10^4, \text{sec.}^{-1}$ | $k_2' \times$ $10^3, \text{sec.}^{-1}$ |
|---|---|---|
| pH 9.63, $\mu = 0.20$, $[\text{CO}_3^{2-}] = 0.5[\text{HCO}_3^-]$ | | |
| 0.020 | 1.90 | 7.99 |
| 0.040 | 2.19 | 14.0 |
| 0.060 | 2.42 | 19.1 |
| 0.080 | 2.63 | 24.5 |
| pH 10.23, $\mu = 0.20$, $[\text{CO}_3^{2-}] = 2[\text{HCO}_3^-]$ | | |
| 0.0072 | 0.540 | 2.80 |
| 0.0144 | 0.605 | 3.96 |
| 0.0216 | 0.680 | 5.68 |
| 0.0287 | 0.744 | 7.08 |
| $\mu = 0.5$ (see Figures 4 and 5) | | |
| pH 9.39, $\mu = 1.00$, $[\text{CO}_3^{2-}] = 0.5[\text{HCO}_3^-]$ | | |
| 0.100 | 3.32 | 28.5 |
| 0.200 | 4.93 | 51.8 |
| 0.300 | 6.49 | 73.3 |
| 0.400 | 8.16 | 95.7 |
| pH 10.00, $\mu = 1.00$, $[\text{CO}_3^{2-}] = 2[\text{HCO}_3^-]$ | | |
| 0.0357 | 0.919 | 9.68 |
| 0.0714 | 1.33 | 18.3 |
| 0.107 | 1.77 | 26.9 |
| 0.143 | 2.20 | 35.4 |
| pH 9.61, $\mu = 0.50$, 15° , $[\text{CO}_3^{2-}] = 0.5[\text{HCO}_3^-]$ | | |
| 0.0400 | 1.04 | 7.43 |
| 0.200 | 2.11 | 28.6 |
| pH 10.20, $\mu = 0.50$, 15° , $[\text{CO}_3^{2-}] = 2[\text{HCO}_3^-]$ | | |
| 0.0143 | 0.306 | 2.20 |
| 0.0714 | 0.600 | 9.31 |
| pH 9.42, $\mu = 0.50$, 35° , $[\text{CO}_3^{2-}] = 0.5[\text{HCO}_3^-]$ | | |
| 0.0400 | 5.07 | 21.7 |
| 0.200 | 9.85 | 80.1 |
| pH 10.02, $\mu = 0.50$; 35° , $[\text{CO}_3^{2-}] = 2[\text{HCO}_3^-]$ | | |
| 0.0143 | 1.41 | 6.66 |
| 0.0714 | 2.70 | 26.1 |

^a At 25° except where noted. ^b Calculated from weights of the sodium salts.

Tables I and II present the results of experiments in bicarbonate-carbonate and ammonium ion-ammonia buffer solutions, respectively. It may be noted that exact duplicate runs under identical conditions were seldom made. Instead, the precision of a specific rate constant, $k_{1,\text{HA}}$, was determined by the agreement between slopes of k_1' vs. $[\text{HA}]$ plots for various pH values. This procedure, which would surely reveal any seriously discordant data, also provided necessary additional data. The current-time data from which the rate constants have been derived are available.¹⁶ Figures 4-7 show some of these results graphically. The type of plot illustrated in these figures was constructed for all the entries of Tables I and II for the purpose of deriving specific rate constants and $k_{\text{intercept}}$ values. Tables III and IV show the results of this graphical procedure for the carbonate, bicarbonate and ammonia, and ammonium ion systems, respectively.

Additional experiments have been performed to determine the effect of $[\text{BH}_4^-]_0$ on i_1 and t_{max} . At pH 10.10, it was found that t_{max} was independent of $[\text{BH}_4^-]_0$ when the latter was varied from 0.01 to 0.04 M, and i_1 was proportional to $[\text{BH}_4^-]_0$. At pH 9.75, t_{max} was constant for a variation of $[\text{BH}_4^-]_0$ from 0.005 to 0.05 M; however, because of copious hydrogen evolution, i_1 increased by about 15-fold. Furthermore, for certain experiments listed in Table II ($\mu = 1.0$, pH 9.21), k_1' was derived from i_1 data and eq. 8 by plotting $\log i_1$

Table II. k_1' and k_2' for Ammonium Ion-Ammonia Buffer Solutions^a

| $[\text{NH}_4^+],^b$ M | $k_1' \times$ $10^4, \text{sec.}^{-1}$ | $k_2' \times$ $10^3, \text{sec.}^{-1}$ |
|---|---|---|
| pH 9.11, $\mu = 0.20$, $[\text{NH}_4\text{OH}] = 0.5[\text{NH}_4^+]$ | | |
| 0.0334 | 5.77 | 8.47 |
| 0.0668 | 6.03 | 11.5 |
| 0.100 | 6.22 | 15.2 |
| 0.1334 | 6.42 | 17.1 |
| pH 9.40, $\mu = 0.20$, $[\text{NH}_4\text{OH}] = [\text{NH}_4^+]$ | | |
| 0.025 | 2.99 | 5.82 |
| 0.050 | 3.13 | 8.09 |
| 0.075 | 3.18 | 9.79 |
| 0.100 | 3.32 | 12.5 |
| $\mu = 0.5$ (see Figures 6 and 7) | | |
| pH 9.21, $\mu = 1.00$, $[\text{NH}_4\text{OH}] = 0.5[\text{NH}_4^+]$ | | |
| 0.1667 | 3.56 | 10.2 |
| 0.333 | 3.92 | 16.0 |
| 0.500 | 4.38 | 22.7 |
| 0.6667 | 4.81 | 30.3 |
| pH 9.51, $\mu = 1.00$, $[\text{NH}_4\text{OH}] = [\text{NH}_4^+]$ | | |
| 0.125 | 1.99 | 9.24 |
| 0.250 | 2.24 | 15.1 |
| 0.375 | 2.54 | 20.1 |
| 0.500 | 2.81 | 24.5 |
| pH 9.47, $\mu = 0.5$, 15° , $[\text{NH}_4\text{OH}] = 0.5[\text{NH}_4^+]$ | | |
| 0.0834 | 1.22 | 4.00 |
| 0.333 | 1.46 | 8.55 |
| pH 9.77, $\mu = 0.5$, 15° , $[\text{NH}_4\text{OH}] = [\text{NH}_4^+]$ | | |
| 0.0625 | 0.662 | 2.79 |
| 0.2500 | 0.792 | 5.32 |
| pH 8.86, $\mu = 0.5$, 35° , $[\text{NH}_4\text{OH}] = 0.5[\text{NH}_4^+]$ | | |
| 0.0834 | 16.3 | 44.3 |
| 0.333 | 19.1 | 64.1 |
| pH 9.17, $\mu = 0.5$, 35° , $[\text{NH}_4\text{OH}] = [\text{NH}_4^+]$ | | |
| 0.0625 | 8.28 | 21.4 |
| 0.2500 | 10.4 | 42.6 |

^a At 25° except where noted. ^b Calculated from weights of NH_4Cl and NaOH .

vs. t for $t > t_{\text{max}}$, under which condition only the first term of eq. 8 is important. These k_1' values agreed to better than 9% with those derived from $i_{\text{BH}_4^-}$ data and eq. 7. These results confirm the validity of

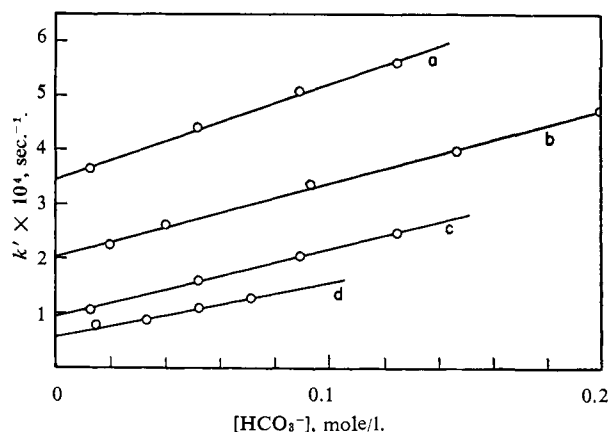


Figure 4. Plot of k_1' vs. concentration of HCO_3^- (25° , $\mu = 0.5$). pH values for a, b, c, and d were, respectively, 9.26, 9.50, 9.80, and 10.11. The ratios $[\text{CO}_3^{2-}]/[\text{HCO}_3^-]$ for a, b, c, and d were, respectively, $1/4$, $1/2$, 1, and 2.

the stepwise kinetic scheme and the assumption of proportionality of i_1 with concentration of intermediate.

(16) J. A. Gardiner, Ph.D. Dissertation, The Ohio State University, 1964.

Table III. Values of $k_{1,\text{intercept}}$, $k_{2,\text{intercept}}$, k_{1,HCO_3^-} , and k_{2,HCO_3^-} ^a

| pH | μ | $k_{1,\text{intercept}} \times 10^4, \text{sec.}^{-1}$ | $k_{2,\text{intercept}} \times 10^3, \text{sec.}^{-1}$ | $k_{1,\text{HCO}_3^-} \times 10^3, \text{M}^{-1} \text{sec.}^{-1}$ | $k_{2,\text{HCO}_3^-} \times 10^1, \text{M}^{-1} \text{sec.}^{-1}$ |
|--------------------|-------|--|--|--|--|
| 9.63 | 0.20 | 1.68 | 2.73 | 1.1 ± 0.2^b | 2.4 ± 0.5^b |
| 10.23 | 0.20 | 0.47 | 1.22 | | |
| 9.26 | 0.50 | 3.45 | 7.37 | | |
| 9.50 | 0.50 | 2.03 | 1.40 | | |
| 9.80 | 0.50 | 0.93 | 1.80 | 1.3 ± 0.3 | 2.2 ± 0.3 |
| 10.11 | 0.50 | 0.55 ₅ | 0.92 | | |
| 9.39 | 1.00 | 1.71 | 6.55 | 1.4 ± 0.3 | 2.3 ± 0.1 |
| 10.00 | 1.00 | 0.49 | 1.13 | | |
| 9.61 ^c | 0.50 | 0.77 | 2.15 | 0.6 ± 0.1 | 1.3 ± 0.1 |
| 10.20 ^c | 0.50 | 0.23 | 0.41 | | |
| 9.42 ^d | 0.50 | 3.87 | 7.10 | 2.6 ± 0.5 | 3.5 ± 0.2 |
| 10.02 ^d | 0.50 | 1.09 | 1.80 | | |

^a At 25° except where noted. ^b Rate constants with estimated σ . ^c 15°. ^d 35°.

Diffusion control of i_1 was indicated by the effect of mercury pressure on this current.¹⁷ A hydrolyzing bicarbonate buffer solution of sodium hydroborate at 25° was studied, and currents were measured as a function of height h of the mercury reservoir. The experi-

ture coefficient of R_1 at 25° of 1.9% per degree is of the correct magnitude for a diffusion-controlled current. This is independent support for the assumption of eq. 6b, since diffusion currents are proportional to concentration of depolarizer.

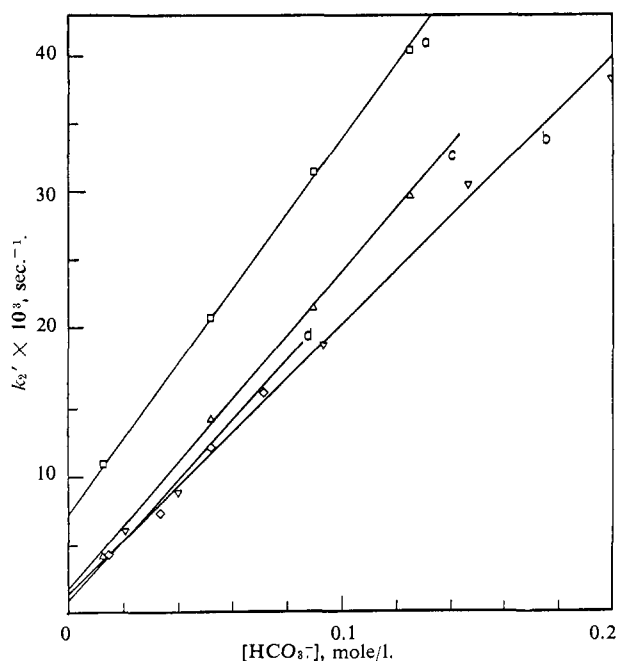


Figure 5. Plot of k_2' vs. concentration of HCO_3^- (25°, $\mu = 0.5$). pH values for a, b, c, and d were, respectively, 9.26, 9.50, 9.80, and 10.11. The ratios $[\text{CO}_3^{2-}]/[\text{HCO}_3^-]$ for a, b, c, and d were $1/4$, $1/2$, 1, and 2.

ment was performed at a time greater than t_{max} , and it was shown that hydrolysis affected the currents only slightly during the time the data were taken. i_1 varied with $h^{0.40}$ in satisfactory agreement with $h^{1/2}$, which is the predicted dependence. Moreover, the tempera-

(17) P. Zuman in "Advances in Analytical Chemistry and Instrumentation," Vol. 2, C. N. Reilly, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 225 ff.

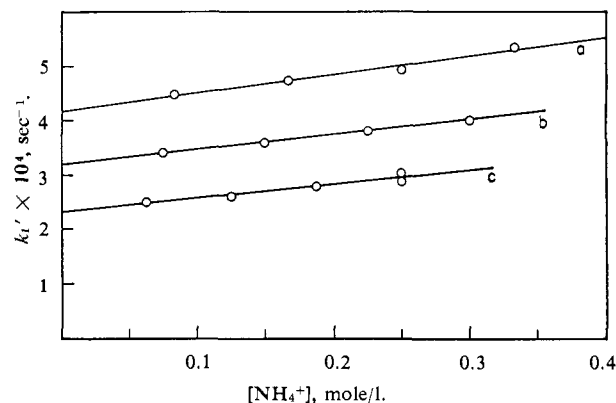


Figure 6. Plot of k_1' vs. concentration of NH_4^+ (25°, $\mu = 0.5$). pH values for a, b, and c were, respectively, 9.16, 9.29, and 9.44. The ratios $[\text{NH}_4\text{OH}]/[\text{NH}_4^+]$ for a, b, and c were, respectively, $1/2$, $2/3$, and 1.

Derivation of Specific Rate Constants. Specific rate constants were derived from the relations

$$k_1' = k_{1,\text{HA}}[\text{HA}] + k_{1,\text{H}_3\text{O}^+}[\text{H}_3\text{O}^+] + k_{1,\text{H}_2\text{O}}[\text{H}_2\text{O}] \quad (9a)$$

and

$$k_2' = k_{2,\text{HA}}[\text{HA}] + k_{2,\text{H}_3\text{O}^+}[\text{H}_3\text{O}^+] + k_{2,\text{H}_2\text{O}}[\text{H}_2\text{O}] \quad (9b)$$

where HA indicates the acidic component of the buffer solution, which was bicarbonate ion and ammonium ion in the two cases reported herein.

The slope of a plot of k' vs. $[\text{HA}]$, at constant pH and $[\text{H}_2\text{O}]$, yields k_{HA} directly. Figures 4-7 show such graphs for bicarbonate and ammonium ion general acids. The extrapolation of these plots to $[\text{HA}] = 0$

Table IV. Values of $k_{1,\text{intercept}}$, $k_{2,\text{intercept}}$, k_{1,NH_4^+} , and k_{2,NH_4^+} ^a

| pH | μ | $k_{1,\text{intercept}} \times 10^4, \text{sec.}^{-1}$ | $k_{2,\text{intercept}} \times 10^3, \text{sec.}^{-1}$ | $k_{1,\text{NH}_4^+} \times 10^4, M^{-1} \text{sec.}^{-1}$ | $k_{2,\text{NH}_4^+} \times 10^2, M^{-1} \text{sec.}^{-1}$ |
|-------------------|-------|--|--|--|--|
| 9.11 | 0.20 | 5.58 | 5.68 | 5 \pm 2 ^b | 8.7 \pm 0.1 ^b |
| 9.40 | 0.20 | 2.90 | 3.64 | | |
| 9.16 | 0.50 | 4.16 | 4.34 | 2.9 \pm 0.5 | 4.7 \pm 0.3 |
| 9.29 | 0.50 | 3.20 | 5.23 | | |
| 9.44 | 0.50 | 2.32 | 4.61 | | |
| 9.21 | 1.00 | 3.11 | 3.10 | | |
| 9.51 | 1.00 | 1.71 | 4.51 | 2.4 \pm 0.2 | 4.1 \pm 0.1 |
| 9.47 ^c | 0.50 | 1.14 | 2.48 | | |
| 9.77 ^c | 0.50 | 0.62 | 1.95 | 0.8 \pm 0.2 | 1.6 \pm 0.3 |
| 8.86 ^d | 0.50 | 15.4 | 37.7 | | |
| 9.17 ^d | 0.50 | 7.59 | 14.3 | 11.1 \pm 0.1 | 10 \pm 2 |

^a At 25° except where noted. ^b Rate constants with estimated σ . ^c 15°. ^d 35°.

defines $k_{i,\text{intercept}}$, which is used to evaluate $k_{\text{H}_3\text{O}^+}$ by means of the relation

$$k_{i,\text{intercept}} = k_{\text{H}_3\text{O}^+}[\text{H}_3\text{O}^+] + k_{\text{H}_2\text{O}}[\text{H}_2\text{O}] \quad (10)$$

Thus, $k_{i,\text{intercept}}$ plotted vs. $[\text{H}_3\text{O}^+]$ should yield a straight line whose slope is $k_{\text{H}_3\text{O}^+}$ and whose intercept is $k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]$. Figure 8, which is a plot of $k_{i,\text{intercept}}$ vs. $[\text{H}_3\text{O}^+]$ for $\mu = 0.5$, illustrates how $k_{1,\text{H}_3\text{O}^+}$, $k_{2,\text{H}_3\text{O}^+}$, $k_{1,\text{H}_2\text{O}}$, and $k_{2,\text{H}_2\text{O}}$ were obtained. The excellent fit of $k_{1,\text{intercept}}$ data to a straight line is characteristic of plots of these data under all conditions, as is the poorer fit of $k_{2,\text{intercept}}$

in evaluating specific rate constants. In cases where the buffer capacity of the solution was low, for example in the most unfavorable case shown in Table I (pH 10.23, $\mu = 0.2$, $[\text{HCO}_3^-] = 0.0072 M$, where $[\text{BH}_4^-]_0$ was 0.020 M for measurement of k_2'), the concentration of boric acid produced by complete reaction would have been considerable in comparison with the concentration of bicarbonate ion, and the significant loss of bicarbonate would have vitiated the assumption

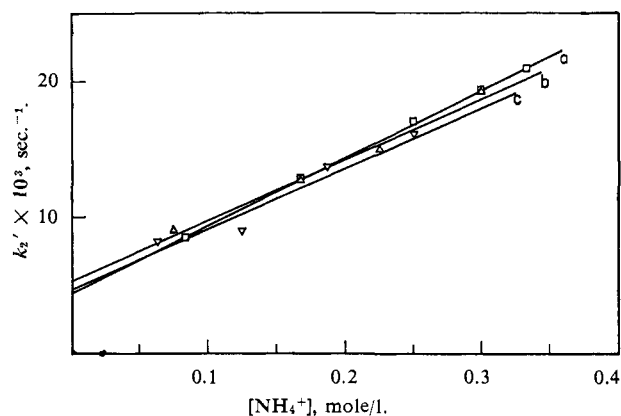


Figure 7. Plot of k_2' vs. concentration of NH_4^+ (25°, $\mu = 0.5$). pH values for a, b, and c were, respectively, 9.16, 9.29, and 9.44. The ratios $[\text{NH}_4\text{OH}]/[\text{NH}_4^+]$ for a, b, and c were, respectively, $1/2$, $2/3$, and 1.

data. A notable exception to the latter generalization is the excellent fit of $k_{2,\text{intercept}}$ data at $\mu = 0.2$. $k_{\text{H}_2\text{O}}$ values, read from the intercepts of graphs such as Figure 8, were the most uncertain of the specific rate constants, and are regarded as order of magnitude estimates.

It must be recognized that eq. 9 should include terms for general acid catalysis by boric acid, since boric acid is the final product of the hydrolysis reaction. We have tried to conduct experiments in such a way that reaction with boric acid is slight in comparison with the other acids, and we have neglected this term

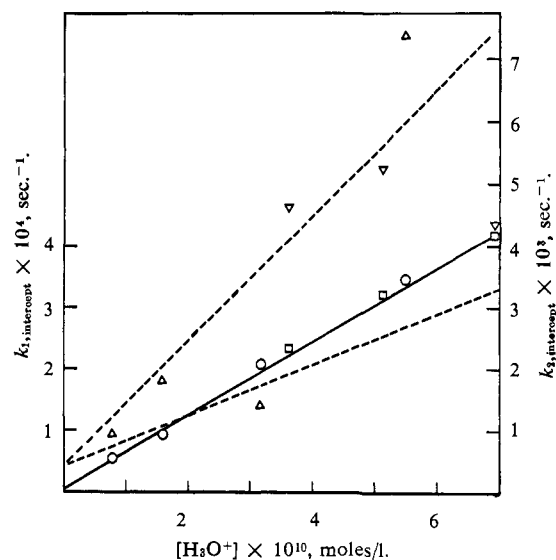


Figure 8. Plots of $k_{1,\text{intercept}}$ and $k_{2,\text{intercept}}$ vs. $[\text{H}_3\text{O}^+]$ ($\mu = 0.5$, 25°). Solid line, $k_{1,\text{intercept}}$ data; \circ , from HCO_3^- solutions; \square , from NH_4^+ solutions. Broken lines: limits for $k_{2,\text{intercept}}$ data; \triangle , from HCO_3^- solutions; ∇ , from NH_4^+ solutions.

of constancy needed for evaluating k_2' . In this buffer solution $t_{1/2}$ for hydroborate ion was 214 min., and i_1 was at its maximum value at 24 min. i_1 was measured for 60 min., during which time only about 18% of the original hydroborate had been consumed. During this period, therefore, we have assumed that the buffer capacity of the solution was adequate. More generally, when k_2' was sought, i_1 was measured until 40–60% of the original hydroborate ion was consumed. When k_1'

Table V. Specific Rate Constants^a

| Constant | $\mu = 0.2$ | $\mu = 0.5$ | $\mu = 1.0$ |
|------------------------------|------------------------------|------------------------------|------------------------------|
| k_{1,HCO_3^-} | $1.1 \pm 0.2 \times 10^{-3}$ | $1.3 \pm 0.3 \times 10^{-3}$ | $1.4 \pm 0.3 \times 10^{-3}$ |
| k_{1,NH_4^+} | $5 \pm 2 \times 10^{-4}$ | $2.9 \pm 0.5 \times 10^{-4}$ | $2.4 \pm 0.2 \times 10^{-4}$ |
| $k_{1,\text{H}_3\text{O}^+}$ | $7.2 \pm 0.2 \times 10^5$ | $6.0 \pm 0.3 \times 10^5$ | $4.9 \pm 0.6 \times 10^5$ |
| $k_{1,\text{H}_2\text{O}}$ | 6×10^{-8} | 1×10^{-7} | 4×10^{-9} |
| k_{2,HCO_3^-} | $2.4 \pm 0.5 \times 10^{-1}$ | $2.2 \pm 0.3 \times 10^{-1}$ | $2.3 \pm 0.1 \times 10^{-1}$ |
| k_{2,NH_4^+} | $8.7 \pm 0.1 \times 10^{-2}$ | $4.7 \pm 0.3 \times 10^{-2}$ | $4.1 \pm 0.1 \times 10^{-2}$ |
| $k_{2,\text{H}_3\text{O}^+}$ | $6 \pm 2 \times 10^5$ | $8 \pm 3 \times 10^5$ | $4 \pm 9 \times 10^5$ |
| $k_{2,\text{H}_2\text{O}}$ | 2×10^{-5} | 8×10^{-6} | 4×10^{-5} |

^a In l. mole⁻¹ sec.⁻¹, at 25°, with estimated σ .

Table VI. Specific Rate Constants^a

| Constant | 15.0° | 25.0° | 35.0° |
|------------------------------|------------------------------|------------------------------|-------------------------------|
| k_{1,HCO_3^-} | $0.6 \pm 0.1 \times 10^{-3}$ | $1.3 \pm 0.3 \times 10^{-3}$ | $2.6 \pm 0.5 \times 10^{-3}$ |
| k_{1,NH_4^+} | $0.8 \pm 0.2 \times 10^{-4}$ | $2.9 \pm 0.5 \times 10^{-4}$ | $11.1 \pm 0.1 \times 10^{-4}$ |
| $k_{1,\text{H}_3\text{O}^+}$ | $3.3 \pm 0.2 \times 10^5$ | $6.0 \pm 0.3 \times 10^5$ | $11.3 \pm 0.9 \times 10^5$ |
| $k_{1,\text{H}_2\text{O}}$ | 3×10^{-8} | 1×10^{-7} | Negative |
| k_{2,HCO_3^-} | $1.3 \pm 0.1 \times 10^{-1}$ | $2.2 \pm 0.3 \times 10^{-1}$ | $3.5 \pm 0.2 \times 10^{-1}$ |
| k_{2,NH_4^+} | $1.6 \pm 0.3 \times 10^{-2}$ | $4.7 \pm 0.3 \times 10^{-2}$ | $10 \pm 2 \times 10^{-2}$ |
| $k_{2,\text{H}_3\text{O}^+}$ | $7 \pm 3 \times 10^5$ | $8 \pm 3 \times 10^5$ | $28 \pm 11 \times 10^5$ |
| $k_{2,\text{H}_2\text{O}}$ | 5×10^{-6} | 8×10^{-6} | Negative |

^a In l. mole⁻¹ sec.⁻¹, $\mu = 0.5$, with estimated σ .

was determined, $i_{\text{BH}_4^-}$ was measured until 90% or more of the original hydroborate ion had disappeared.

Values of $k_{\text{H}_3\text{O}^+}$ and $k_{\text{H}_2\text{O}}$ which are shown in Tables V and VI are the result of combinations of rate constants obtained in two different buffer media. The results have been grouped in these tables to emphasize the effects of temperature and ionic strength on the two rate-limiting steps of the reaction. The precision of the specific rate constants varies widely. In general, the extent to which a given acidic species reacts with the substrate governs the precision of the specific rate constant. Thus, in an ammonia buffer of pH 9.1, and 0.04 M NH_4^+ , the hydronium ion term in the rate expression is about thirty times the ammonium ion term. This yields precise values of $k_{1,\text{intercept}}$ and good precision for $k_{1,\text{H}_3\text{O}^+}$, while the uncertainty in slope of the plot of k_1 vs. concentration of ammonium ion leads to a less precise value of k_{1,NH_4^+} . In the second step, on the other hand, the intermediate reacts with ammonium ion more extensively than with hydronium ion, and the precision of k_{2,NH_4^+} is superior to that of $k_{2,\text{H}_3\text{O}^+}$.

Table VII. Arrhenius Activation Energies^a

| Reaction | E_a , kcal. mole ⁻¹ |
|--|-------------------------------------|
| $\text{BH}_4^- + \text{HCO}_3^-$ | 13 ± 3 |
| $\text{BH}_4^- + \text{NH}_4^+$ | 23 ± 2 |
| $\text{BH}_4^- + \text{H}_3\text{O}^+$ | 11 ± 1 |
| Intermediate + HCO_3^- | 9 ± 1 |
| Intermediate + NH_4^+ | 16 ± 4 |
| Intermediate + H_2O^+ | 12 ± 8 |

^a $\mu = 0.5$.

Activation energies, determined from Arrhenius plots of the data of Table V, are shown in Table VII. The value of 11 ± 1 kcal. mole⁻¹ for the reaction between BH_4^- and H_3O^+ is in fair agreement with values of 9.1

reported by Pecsok,¹¹ 7.2 reported by Freund,¹⁸ 9 ± 1 reported by Stockmayer, *et al.*,⁹ and 7.7 reported by Jolly and Mesmer.¹⁰ Other activation energies are not available for comparison, although Stockmayer, *et al.*, predicted a value of 20 kcal. mole⁻¹ for the reaction of BH_4^- with NH_4^+ .

Discussion

Much previous work on the kinetics of the hydrolysis of sodium hydroborate has depended on the iodate volumetric method¹⁹ for the analysis of hydroborate remaining in solution. Thus, the disappearance of reducing power of the solution has been equated with the disappearance of hydroborate ion. This procedure includes any intermediates in the process in the total reducing power determination and is incapable of discerning individual steps in a hydrolysis when the total concentration of intermediate is less than a few per cent of the hydroborate concentration. The polarographic rate determination of Pecsok¹¹ employed the hydroborate wave ($E_{1/2} = -0.15$ v. vs. s.c.e.) and thereby yielded a true rate of disappearance of hydroborate ion. Although Pecsok did not state how diffusion currents were measured in the rate work, our experience with the small intermediate wave indicates that by ignoring it only a few per cent error would be introduced into the diffusion currents measured by Pecsok. Measurement of the polarographic diffusion current for hydroborate ion alone yields, therefore, kinetics very similar to those obtained through the iodate determination of reducing power.

The present work, by using the polarographic diffusion current of the postulated intermediate, introduces into the kinetic scheme information about another step of the over-all process. Two facts about this should be emphasized. First, the identity of the intermediate is not of any importance in determining the

(18) T. Freund, *J. Inorg. Nucl. Chem.*, **9**, 246 (1959).

(19) D. A. Lyttle, E. H. Jensen, and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).

Table VIII. Reported Rate Constants^a

| Rate constant | $M^{-1} \text{ sec.}^{-1}$ | Temp., °C. | μ | Analytical method | Ref. | |
|-------------------------------|-----------------------------|------------------------------|------------------------------|-------------------|--------|--------|
| $k_{\text{H}_3\text{BO}_3}$ | $2.0 \pm 0.2 \times 10^6$ | 0 | 0.16 | Iodate | 9 | |
| | 1.45×10^6 | 15 | 0.10 | Polarog. | 11 | |
| | $0.57 \pm 0.02 \times 10^6$ | 15 | | Iodate | 6 | |
| | 2.50×10^6 | 25 | 0.10 | Polarog. | 11 | |
| | $1.00 \pm 0.04 \times 10^6$ | 25 | 0.10 | Iodate | 8 | |
| | $8 \pm 1 \times 10^6$ | 25 | 0.16 | Iodate | 9 | |
| | 1.0×10^6 | 25 | 0.16 | Iodate | 18 | |
| | $2.30 \pm 0.07 \times 10^6$ | 25 | 0.0 ^b | Iodate | 8 | |
| | 1.6×10^6 | 25 | 1.0 | Iodate | 10 | |
| | $1.22 \pm 0.03 \times 10^6$ | 25 | | Iodate | 6 | |
| | 0.77 ^c | 24–28 | 3.7–9.3 | Gasomet. | 4 | |
| | 4.00×10^6 | 35 | 0.10 | Polarog. | 11 | |
| | $2.62 \pm 0.05 \times 10^6$ | 35 | | Iodate | 6 | |
| | $k_{\text{HCO}_3^-}$ | $9 \pm 4 \times 10^{-6}$ | 25 | 0.10 | Iodate | 7 |
| | | $k_{\text{NH}_4^-}$ | $1.5 \pm 0.4 \times 10^{-3}$ | 25 | 0.16 | Iodate |
| $k_{\text{H}_2\text{O}}$ | 2×10^{-9} | | 25 | 0.10 ^d | Iodate | 8 |
| | 1.2×10^{-9} | 25 | 1.0 | Iodate | 10 | |
| $k_{\text{H}_2\text{PO}_4^-}$ | $1 \pm 4 \times 10^{-2}$ | 25 | 0.10 | Iodate | 7 | |
| | $k_{\text{H}_3\text{BO}_3}$ | $2.3 \pm 0.2 \times 10^{-4}$ | 0 | 0.16 | Iodate | 9 |
| $2.0 \pm 0.3 \times 10^{-3}$ | | 25 | 0.16 | Iodate | 9 | |
| $8 \pm 4 \times 10^{-4}$ | | 25 | 0.20 | Iodate | 8 | |
| $1 \pm 5 \times 10^{-4}$ | | 25 | 0.50 | Iodate | 8 | |

^a Rate expression: $-\frac{d}{dt} \ln [\text{BH}_4^-] = \sum_i k_{\text{H}_i\text{A}_i} [\text{HA}_i]$. ^b Extrapolated. ^c This constant was determined in a H_2SO_4 medium, where the hydrolysis process may not be comparable to that in alkaline buffer solutions. See also ref. 7 for a discussion of the effect of the rate of establishment of hydrogen solubility equilibrium on this constant. ^d Estimated.

kinetics. Secondly, the addition of another rate-limiting step to the kinetics does not imply that there are not further steps before borate is formed; k_2 refers to the disappearance of the intermediate, not to the appearance of borate ion. Even at very high initial concentrations of hydroborate, however, no more than one polarographic wave attributable to an intermediate was found in this system. Presumably any more extensively hydrolyzed intermediates present existed for such a brief duration that our method of analysis could not detect them. Moreover, the kinetic scheme does not require that the intermediate be formed in a single step from hydroborate, but only that there be only one rate-limiting step in its formation.

The rate constants for the stepwise hydrolysis can, in principle, be determined without a knowledge of concentrations, or in this case without knowledge of the constants, R , of eq. 6. It has been advantageous to determine R_1 from the kinetic data for use in calculating k_2' for the following reasons. Use of a single value of R_1 for all experiments eliminates bias in the estimation of t_{max} which in experiments where it is small (2 min.) is difficult anyway. Furthermore, the correlation of many data from experiments of differing pH, ionic strength, and general acid, by means of a single value of R_1 , lends support to the assumptions of the kinetic scheme. While R_1 is a polarographic constant ordinarily determined by calibration with solutions of known concentrations, it should be emphasized that in this work it has been evaluated from kinetics and the assumption that i_1 is proportional to $[I]$. No assumption has been made about the polarographic n value or the value of the diffusion coefficient D of the intermediate. The product $nD^{1/2}$ is calculable from R_1 and the Ilkovic equation.

Comparison of Kinetic Results. $k_{1,\text{HA}}$ values derived in this work can be compared to results of other workers,

even though those results were obtained without allowance for the presence of an intermediate. This situation arises because the intermediate is never present to an extent greater than a few per cent of the hydroborate, and this uncertainty in instantaneous values of hydroborate concentration introduces negligible error into measured values of k_1' . The results of previous workers are collected in Table VIII for comparison with the results of the present study (Tables V and VI). For experiments at similar ionic strengths, $k_{1,\text{H}_3\text{O}^+}$ values are in excellent agreement. It must be noted that our result for k_{1,HCO_3^-} is about 10 times larger than $k_{\text{HCO}_3^-}$ reported by Davis and Swain,⁷ and our value of k_{1,NH_4^+} is about one-third that of Stockmayer, *et al.*⁹ Even after extrapolating to the same ionic strengths and allowing for the large uncertainties in some of these rate constants, these large unexplained discrepancies remain. The agreement on $k_{\text{H}_2\text{O}}$ among the various workers must be considered fortuitous in view of the highly derived nature of this constant.

The degree to which the H-A bond is broken in the transition state of the hydroborate-general acid reaction has been discussed by Davis, *et al.*,⁸ Stockmayer, *et al.*,⁹ and Jolly and Mesmer¹⁰ by means of the Brønsted catalysis law. The data of Table VII confirm the conclusion of these authors that the Brønsted α -value is nearly unity and, thus, that the HA bond of the attacking acid is almost completely broken in the transition state. For the second step of the hydrolysis, a similar conclusion is reached by evaluating α from k_{2,NH_4^+} and $k_{2,\text{H}_2\text{O}}$ in the relation $\alpha = d \log k / d \log K$ where k is the specific rate constant for reaction with an acid whose dissociation constant is K . Values of about 0.9 are obtained for these cases, in close analogy to the results for k_1 .

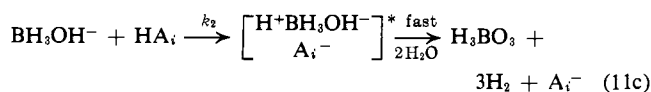
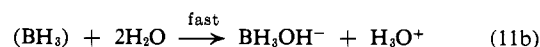
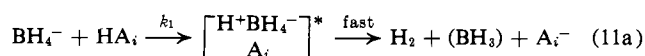
The Intermediate. The identity of the intermediate, while not needed for the calculation of rate constants

by the methods of this work, is of interest in understanding the chemistry of hydroborate ion. The most straightforward inference from the stepwise kinetics shown herein is that the intermediate is a $-\text{BH}_3$ containing species, *i.e.*, one formed through the loss of one hydridic hydrogen from hydroborate. Postulation of a $-\text{BH}_2$ or a $-\text{BH}$ containing entity would require one or more fast steps in addition to the rate-limiting step in the hydrolysis of hydroborate before the proposed intermediate was reached. Moreover, we have reported¹⁴ the n.m.r. spectrum of a species which occurs in solutions which also show the polarographic wave at $E_{1/2}$ of -0.64 and is undoubtedly due to the postulated intermediate. This spectrum indicates that the intermediate contains the $-\text{BH}_3$ group. Results of electrolytic experiments, which support this conclusion, will also be reported. The purely kinetic data of Table V, however, permit a tentative conclusion about the formula of the intermediate.

The Brønsted–Christiansen–Scatchard equation¹⁵ predicts that the rate constant increases or decreases with $\mu^{1/2}$ depending on whether the product of charges on the reacting species, $Z_A Z_B$, is positive or negative. The relation is valid only for solutions of low ionic strength, which cannot be used when polarography is the method of analysis; for the data presented here we

shall show only that the trends in k_1 and k_2 as ionic strength is changed are the same. This suggests that the charge on the intermediate species is the same as that on the hydroborate ion. Reference to Table V shows that k_{1,HCO_3^-} and k_{2,HCO_3^-} change little with ionic strength, while k_{1,NH_4^+} and k_{2,NH_4^+} both decrease appreciably. While the uncertainty in $k_{2,\text{H}_3\text{O}^+}$ is great, it seems to decrease, as does $k_{1,\text{H}_3\text{O}^+}$, with increasing ionic strength. On the basis of the similarity of behavior for $k_{1,\text{HA}}$ and $k_{2,\text{HA}}$, we prefer for the formula of the intermediate a negatively charged $-\text{BH}_3$ containing species, of which BH_3OH^- seems the most probable.

A mechanism for the stepwise hydrolysis reaction consistent with these results and those of other workers^{8–10,18} can now be postulated.



Carbonium Ion Salts. IX. Hydrogen Dihalides^{1,2}

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Contribution from the Department of Chemistry, Harvey Mudd College,
Claremont, California. Received August 12, 1964

Reaction of tropenyl methyl ether with excess hydrogen halide in ether solvent yields tropenium hydrogen dihalide and hydrogen dibromide as easily preparable, stable, stoichiometric salts. Sublimation of the hydrogen dichloride affords an excellent route to tropenium chloride. Observations on the charge-transfer spectra of the hydrogen dihalides and the light sensitivity of the chloride are reported. Tetrabutylammonium hydrogen diiodide has been synthesized; this is the first characterized salt of this anion to be reported. Equilibrium dissociation vapor pressure measurements have been carried out on four hydrogen dibromides and indicate that factors other than cation size affect the stabilities of such salts.

Exploration into the question of the possible stability of hydrogen dihalide salts was almost over before it had fairly begun. In two unfortunately often overlooked papers⁴ Kaufler and Kunz, in 1909, reported

the synthesis and analysis of 29 hydrogen dihalides and dihydrogen trihalides, and—in a remarkable piece of reasoning considering the information available to them—correctly deduced both the anionic nature and the order of bonding in the XHX^- moiety. Thus, several rediscoveries^{5,6} of tetramethylammonium hydrogen dichloride and a recent communication by Tuck and Woodhouse⁷ claiming the synthesis of the first reported hydrogen dibromide seem a bit after the fact.

Of the higher hydrogen dihalides the hydrogen dichloride is the best known. Both organic^{4–6,8,9} and inorganic^{10–12} salts have been prepared, and the symmetrical structure of the anion has been established by physical studies.^{6,9,13} Reported compounds^{4,7} of the hydrogen dibromide anion are all of the ammonium

(1) Supported by the Petroleum Research Fund and the National Science Foundation.

(2) Reported in part in a communication: K. M. Harmon and S. Davis, *J. Am. Chem. Soc.*, **84**, 4359 (1962); and a correspondence: K. M. Harmon and P. A. Gebauer, *Inorg. Chem.*, **2**, 1319 (1963).

(3) (a) National Science Foundation Scholar; (b) American Chemical Society–Petroleum Research Fund Scholar.

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