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Polarography of the Tetrahydroborate Ion. The Effect of Hydrolysis on the System

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A BH_3 -containing species, which is a relatively stable intermediate in the hydrolysis of sodium tetrahydroborate (NaBH_4) solutions, has an important effect on the polarographic behavior of the system. Controlled potential electrolysis of solutions rich in this species has shown that it is responsible for the anodic polarographic wave at -0.64 v. vs. s.c.e. and that it is oxidized in a three-electron over-all process which yields hydrogen. The presence of an electrooxidizable hydrolysis product explains the abnormal polarographic behavior of unbuffered alkaline NaBH_4 solutions and is consistent with other electrochemical studies and nuclear magnetic resonance spectroscopy of partially hydrolyzed solutions.

Introduction

The polarographic waves which stem from the electro-oxidation of alkaline solutions of tetrahydroborate (borohydride, hydroborate, BH_4^-) ion have been studied by Marshall and Widing,^{2a} Pecsok,^{2b} and Mochalov and Gil'manshin.³ Marshall and Widing reported two waves, at -0.15 and -0.64 v. vs. s.c.e., the first of which was larger than the second by a factor of about 65. They recognized the more positive wave as the major wave due to the oxidation of hydroborate ion, assigned it an n value of 4, where n designates the number of electrons transferred per BH_4^- ion, and attributed the second, small, wave to the electrooxidation of an impurity or a "less hydrated" form of hydroborate. Pecsok studied the wave at -0.15 v. further, showed its dependence on concentration of hydroborate ion, and estimated the n value for the process to be 8. He did not, however, confirm the existence of the wave at -0.64 v. and suggested that it was due to an impurity. Mochalov and Gil'manshin studied alkaline sodium, potassium, and lithium borohydride solutions and reported only one polarographic wave at -0.65 v. for any of the systems studied. These authors ascribed the wave to an intermediate in the hydrolysis of hydroborate ion in the bulk solution and not to hydroborate ion itself. Thus, the reported results of polarographic investigations of hydroborate solutions are highly discordant.

Related to this problem is work by Elder and Hickling⁴ on the oxidation of hydroborate ion on platinum and a study by Elder⁵ on the process at various electrodes by an oscillographic technique. For electrolysis at a platinum electrode the former authors found fewer than the eight equivalents of electricity per mole of hydroborate required by the polarographic results of Pecsok. They postulated BH_3OH^- as an intermediate in the system and recog-

nized the importance of the competition between electrolysis and hydrolysis in the over-all process. Elder's work, which included studies on mercury, showed that hydrogen ionization was the essential electrochemical step in the oxidation of hydroborate ion; a stable intermediate, postulated to be BH_3OH^- , was also indicated by Elder's data.

The purpose of the present article is to report electrochemical experiments which confirm the existence of a BH_3 -containing intermediate in the hydrolysis of hydroborate ion and to discuss the polarography of hydroborate solutions with emphasis on the effect of the homogeneous hydrolysis reaction on the system. In addition to characterizing an intermediate in the hydrolysis reactions, it is hoped that this will clarify some of the contradictions which are found in the polarographic literature.

Experimental

Test Solutions.—Sodium borohydride (98%, Metal Hydrides, Inc.) was used as received. A sample recrystallized from liquid ammonia gave polarographic results indistinguishable from the starting material. Since the impurities in the compound are doubtless products of some slight hydrolysis and the experiments described herein were all conducted in aqueous media, special purification of the NaBH_4 was not employed. Buffer solutions were prepared as indicated in each experiment and checked by measurement by means of a glass electrode pH meter, standardized with National Bureau of Standards buffer solutions.

Solutions which contained a relatively high concentration of the BH_3 -containing intermediate species are designated herein as "base-stabilized, partially hydrolyzed" solutions and were prepared as follows: NaBH_4 was dissolved in an ammonium ion-ammonia buffer solution of pH 9.1 to give 0.02 – 0.05 M ($\mu = 0.2$) and was allowed to hydrolyze at 25° for 5.5 min. At the end of this period the pH was adjusted to 12.5 or greater by the addition of 19.8 M NaOH . This solution, the preparation of which was suggested by, and is consistent with, the known kinetics of the formation and decay of the intermediate species,⁶ contains approximately a 25-fold excess of hydroborate ion over the intermediate species. The half-life of the latter in this medium was 3.7 hr.

Polarography.—Polarograms were recorded on a Leeds and Northrup Electrochemograph, Type E, according to conventional techniques. In determining αn_a values, where *maximum* values of limiting currents were required,⁷ a Bristol Dynamaster 1-mv.

(1) Allied Chemical Foundation Fellow, 1963–1964. Taken in part from the Ph.D. Dissertation of J. A. G., The Ohio State University, 1964.

(2) (a) E. D. Marshall and F. A. Widing, "Polarography of Sodium Borohydride," A.E.C.D. 2914 (1950); (b) R. L. Pecsok, *J. Am. Chem. Soc.*, **75**, 2862 (1953).

(3) (a) K. N. Mochalov and G. G. Gil'manshin, *Dokl. Akad. Nauk SSSR*, **132**, 134 (1960); (b) *Zh. Fiz. Khim.*, **36**, 1089 (1962).

(4) J. P. Elder and A. Hickling, *Trans. Faraday Soc.*, **58**, 1852 (1962).

(5) J. P. Elder, *Electrochim. Acta*, **7**, 417 (1962).

(6) J. A. Gardiner and J. W. Collat, *J. Am. Chem. Soc.*, **87**, 1692 (1965).

(7) L. Meites and Y. Israel, *ibid.*, **83**, 4903 (1961).

recorder with a pen response speed of 0.4 sec. was used without damping. Capillaries had open circuit characteristics of 1.61, 1.71, 2.43 $\text{mg.}^{2/3} \text{ sec.}^{-1/2}$. All applied voltages and half-wave potentials are reported *vs.* the saturated calomel electrode, and have not been corrected for iR drop in the cell, because the cell resistance was always less than 100 ohms. In experiments reported below in which polarography was used solely as an analytical tool for the determination of the concentration of the BH_3 -containing intermediate species, concentrations were obtained from diffusion currents measured at 25° and -0.5 v. by use of the value $9.35 \mu\text{a. mM}^{-1} \text{ mg.}^{-2/3} \text{ sec.}^{1/2}$ for the diffusion current constant of the intermediate species. Since the intermediate species has never been isolated, the evaluation of this constant depended on measurement of the polarographic current and calculation of the concentration of the intermediate species from experimentally determined rate constants.⁶

Solutions were deaerated with high-purity tank nitrogen before polarographic examination, and, except where otherwise noted, polarograms were obtained at 25° .

Hydrogen Evolution.—The hydrolysis of the intermediate species occurred appreciably faster than that of hydroborate ion. It was experimentally studied by collecting the hydrogen evolved from a base-stabilized partially hydrolyzed solution of sodium hydroborate over a period of about 200 min.; 200 ml. of a sample solution, prepared as described above, was split into two aliquots. One was placed in a polarographic H-cell for the determination of the initial concentration of the intermediate. The other was put into a bulb and attached to a vacuum line. It was outgassed by application of vacuum and allowed to hydrolyze undisturbed for at least 200 min. The hydrogen evolved was collected by a Toepler pump after passage through liquid nitrogen traps. The final concentration of the intermediate was determined polarographically. In a blank experiment the amount of hydrogen resulting from the simultaneous hydrolysis of hydroborate ion was determined. The procedure was the same as above except that the test solution was prepared by addition of NaOH to the ammonia buffer before the addition of the sodium hydroborate. Thus, the amount of the intermediate in the blank was negligible.

Controlled-Potential Electrolysis with Coulometry.—Controlled potential electrolysis of basic hydroborate solutions and base-stabilized partially hydrolyzed solutions of hydroborate ion was employed as a means of identifying the process by which hydroborate ion is electrooxidized and as a means of characterizing the intermediate species. In most experiments a 250-ml. tall-form electrolysis beaker served as the cell. Thus, the mercury pool anode had an area of about 30 cm.^2 . The electrode-solution interface was stirred by a magnetic stirrer. The working cathode was a platinum wire in another beaker joined to the first by a U-tube filled with 3% agar-saturated KCl. The potential of the anode was observed *vs.* a saturated calomel reference electrode by means of a d.c. electrometer (Kiethley Instruments, Inc., Model 610). The applied voltage was adjusted manually during an experiment to maintain the desired anode potential. Current was recorded as a function of time, and the amount of electricity passed was calculated by graphical integration. The exact procedure of the electrolysis varied as follows.

(a) **Alkaline Solution of Hydroborate Ion.**—After careful adjustment of pH, 150 ml. of test solution was pipetted into the electrolysis cell. Argon was used to deaerate the sample for 30 min. The cell was completely sealed by coating all glass to rubber joints with an adhesive material (General Electric Co. adhesive 7031). After an electrolysis period of 30 min. the pH of the solution was again measured, a sample of gas in equilibrium with the solution was admitted to a previously evacuated bulb, and the decrease in hydroborate ion concentration was determined polarographically. The gas samples were examined for the presence of hydrogen by means of a mass spectrometer (Consolidated Engineering Corp., Model 21-620).

(b) **Base-Stabilized, Partially Hydrolyzed Solutions.**—Test

solutions were prepared as described above. Since these solutions hydrolyzed at a significant rate, the following procedure was adopted to provide an estimate of the loss of intermediate species through hydrolysis. A 200-ml. sample solution was divided into two aliquots. One was kept in a polarographic H-cell and the change in its polarographic diffusion current at -0.5 v. with time was ascribed wholly to hydrolysis. The other was put into the electrolysis cell and subjected to conventional controlled-potential electrolysis with the anode potential at -0.45 v. *vs.* s.c.e. At the end of the electrolysis period of 30 min., the difference between diffusion currents at -0.5 v. measured in the unelectrolyzed solution and in the electrolysis solution was taken for use in calculating the loss of intermediate species solely through electrolysis. Mass spectrometric gas analysis was not employed in this series of experiments, but in certain of them the gas which was evolved was collected and measured in a gas buret. In these cases the electrolysis cell was attached to the vacuum line, and the technique of recovering the gas and measuring its volume was similar to that described in the section "Hydrogen Evolution."

Results

Polarography.—The main hydroborate oxidation wave ($E_{1/2} = -0.11$ v. at pH 9.1) has been studied in ammonia-ammonium ion and carbonate-bicarbonate buffer solutions and in dilute NaOH supporting electrolytes. As reported by Pecsok, the anodic diffusion current is proportional to the concentration of BH_4^- ; however, our value for the diffusion current constant of BH_4^- at -0.01 v. is $22.2 \mu\text{a. mM}^{-1} \text{ mg.}^{-2/3} \text{ sec.}^{1/2}$ in contrast to Pecsok's value of 26.0. The former value applies to buffer solutions of pH 9.1 to 10.2 and ionic strengths from 0.2 to 1.0, and to NaOH solutions in which the $[\text{OH}^-]/[\text{BH}_4^-]$ ratio is at least 4.44.

The anodic wave with $E_{1/2} = -0.64$ v. has been correlated with the presence of a BH_3 -containing intermediate in the hydrolysis of BH_4^- .⁸ Its height, postulated to be proportional to its concentration in the aforementioned buffer systems, shows a time dependence which has permitted the evaluation of the diffusion current constant of the species.⁶ The wave in dilute KOH appears to be identical with that in the buffer solutions, provided that the ratio of OH^- concentration to concentration of the intermediate exceeds about 1000. The greater magnitude of the critical ratio for the intermediate, compared to BH_4^- , probably reflects its greater chemical reactivity, and that of its oxidation products, at the surface of the mercury drop, which, in an unbuffered medium, is less basic than the bulk of the solution.

The definition and reproducibility of the waves are improved by the addition of 0.01% gelatin as maximum suppressor.

The ratio of diffusion current constants for BH_4^- and the intermediate species of 2.37 is consistent with the ratio of n values of 8:3, which is indicated by controlled-potential coulometry.

In unbuffered solutions the limiting currents of hydroborate measured at -0.01 v. are strongly affected by the concentration of hydroxyl ion. Figure 1 shows how sharply the slope of the current-concentration plot changes when the ratio $[\text{OH}^-]/[\text{BH}_4^-]$ falls below 4.44.

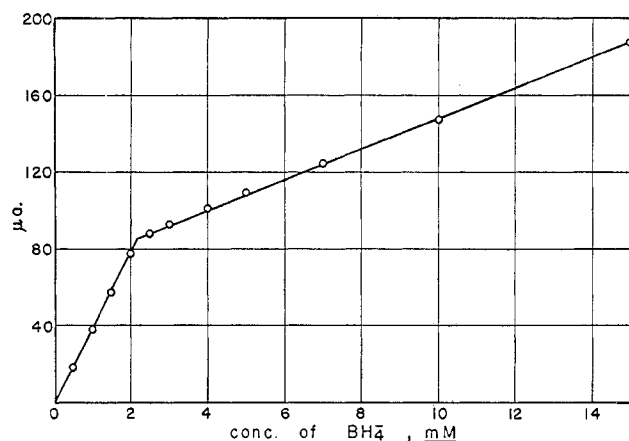
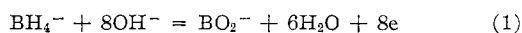


Figure 1.—Dependence of current at -0.01 v. on concentration of NaBH_4 . Supporting electrolyte: $0.10\text{ }M$ KCl , $0.010\text{ }M$ NaOH ; capillary characteristics: $1.71\text{ mg.}^{2/3}\text{ sec.}^{-1/2}$.

Assuming $CD^{1/2}$ to be proportional to flux at the surface of the d.m.e. and using the values 5.23×10^{-5} and $2.1 \times 10^{-5}\text{ cm.}^2\text{ sec.}^{-1}$ for D_{OH^-} and $D_{\text{BH}_4^-}$, respectively, this concentration ratio corresponds to a flux ratio of 7.0 at which the slope changes. This is in good agreement with the value of 8.0 required by the equation for the eight-electron process first suggested by Pecsok.



In an unbuffered medium the pH at the surface of the d.m.e. may easily be low enough to make the actual product HBO_2 rather than BO_2^- ; thus one less OH^- would be required by reaction 1. The positive slope of the current-concentration plot for a ratio of $[\text{OH}^-]/[\text{BH}_4^-]$ less than 4.44 indicates that there are one or more processes by which electrooxidation can occur, even when free hydroxyl is not available in the stoichiometric amounts required by eq. 1. This process also requires fewer than eight electrons per mole and doubtless involves hydrolysis steps as well as electron-transfer steps. The latter is highly probable because the surface of the d.m.e. is rendered acidic through depletion of hydroxyl ion, and the hydrolysis proceeds sufficiently rapidly at low pH to change the nature of the reducible species. Hydrogen is a product of the electrooxidation when the $[\text{OH}^-]/[\text{BH}_4^-]$ ratio is low. This is indicated by controlled potential electrolysis (last experiment of Table I). It is not possible now to give a more detailed account of the electrode process responsible for the main wave in unbuffered solutions with the ratio $[\text{OH}^-]/[\text{BH}_4^-]$ less than 4.44.

Values of αn_a , where α represents the transfer coefficient, n_a , the number of electrons transferred in the rate-limiting step, and $k^0_{f,h}$, the heterogeneous rate constant for the oxidation at 0.0 v. vs. s.c.e. , were determined for the two waves according to the method of Meites and Israel.⁷ Concentrations of BH_4^- and BH_3OH^- were 0.8 and 0.16 mM , respectively, and the supporting electrolyte was $0.2\text{ }M$ KOH . Plots of $E_{a.e.}\text{ vs. } \log i/(i_d - i)$ gave excellent straight lines for both waves. For oxidation of BH_4^- , αn_a was -1.91 ± 0.04 with an $E_{1/2}$ of $-0.195\text{ v. vs. s.c.e.}$ ($t_d = 4.30$

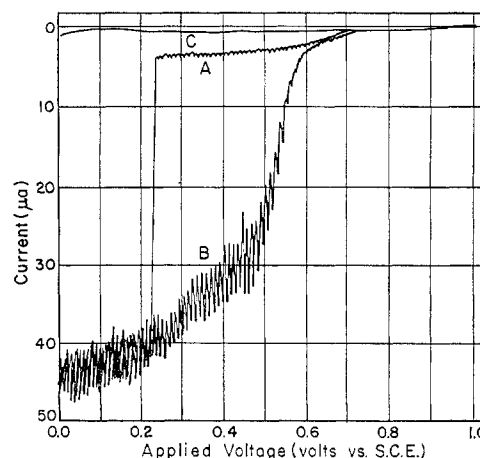


Figure 2.—Illustration of the "scan effect." Test solution: $0.005\text{ }M$ NaBH_4 , $0.001\text{ }M$ NaOH , $0.10\text{ }M$ KCl , 0.01% gelatin. A: positive-going applied voltage; B: negative-going applied voltage.

sec., corresponding to $k^0_{f,h} = 2.9 \times 10^3\text{ cm./sec.}$). For oxidation of BH_3OH^- , αn_a was -0.95 with an $E_{1/2}$ of $-0.672\text{ v. vs. s.c.e.}$ ($t_d = 4.23\text{ sec.}$ corresponding to $k^0_{f,h} = 1.0 \times 10^8\text{ cm./sec.}$). The lack of an independent determination of α precludes any definite statement about n_a for the processes. α is usually approximately 0.5; if this is true here, n_a values for BH_3OH^- and BH_4^- are 2 and 4, respectively. The latter is clearly too large for a single step and may indicate that the basic premise for this treatment, a single rate-controlling step, is not fulfilled. Alternatively, the unusually large value of 0.95 for α may be assumed for both oxidations and n_a values of 2 and 1 calculated for BH_4^- and BH_3OH^- , respectively. Since the assignment of α is arbitrary, we present αn_a and $k^0_{f,h}$ values only as parameters of the waves for the specified conditions.

In unbuffered solutions the appearance of polarograms of sodium hydroborate depends radically on the direction in which voltage is applied to the d.m.e. Figure 2 shows the strikingly different waves obtained upon reversing the direction of polarization, which we refer to as the "scan effect." On the basis of numerous qualitative experiments we have concluded that the abrupt current surge found with positive-going polarization of the d.m.e. at about -0.25 v. is the result of the autocatalytic decomposition of hydroborate to the BH_3 -containing entity which is made possible by depletion of hydroxyl ion in the neighborhood of the d.m.e. The onset of the rapid conversion of BH_4^- to the oxidizable BH_3 -containing intermediate is probably triggered by the start of another hydroxyl-consuming reaction, which could be the oxidation of hydroborate according to reaction 1, a process which begins close to the potential of the current surge. It may also be an electrooxidation yielding hydrogen, which has been shown to be produced in a controlled potential electrolysis of a solution of a similar hydroxyl to hydroborate ratio. In the hydroxyl-poor solution at the drop surface, this is doubt-

less the same process which gives rise to current discussed above for $[\text{OH}^-]/[\text{BH}_4^-]$ ratios less than 4.4.

When polarograms are recorded with negative-going applied voltage, reaction 1 occurs at the start (0.0 v. *vs.* s.c.e.), limited by the amount of hydroxyl ion available. Because of the lack of hydroxyl ion originally and its consumption by reaction 1, the pH at the surface of the d.m.e. declines and some hydroborate is rapidly hydrolyzed to BH_3OH^- . The latter is electrooxidized and continues to be electrooxidized, even as the voltage is scanned past -0.25 v. It also continues to be formed in the vicinity of the drop, which must have a pH substantially lower than the bulk of the solution. This condition of depleted hydroxyl ion concentration persists while the voltage is swept, at the common rate of 200 mv./min., into the range where only the oxidation of BH_3OH^- can occur. Thus, an abnormally high current due to BH_3OH^- oxidation is observed in the applied voltage region of -0.25 to -0.6 v. *vs.* s.c.e.

The following facts are adduced in support of this explanation of the scan effect: (1) The scan effect is not observed in a buffer solution. (2) It is not observed in a solution where the ratio $[\text{OH}^-]/[\text{BH}_4^-]$ is high. Enough hydroxyl ion to satisfy eq. 1 is present in such solutions and formation of BH_3OH^- cannot proceed in them at a significant rate. (3) The scan effect is highly dependent on the immediately previous history of the solution. For example, upon applying a constant applied voltage of -0.5 v., the current surge may appear after about 2 min. When the experiment is repeated at once, the time of appearance is sharply reduced. When the solution is allowed to stand for at least 0.5 min., the original delay is observed. (4) The time delay preceding the current surge upon polarization at a constant applied voltage is dependent upon the voltage. It decreases from several minutes at -0.5 v. to less than one drop-life at -0.25 v. It should be added that the time delays and potentials of the current surge are not precisely reproducible quantities, but because they depend on a concentration gradient of hydroxyl ion in the neighborhood of the drop they are affected by all the variables which produce convection.

Controlled Potential Electrolysis.—Table I shows data for controlled potential electrolysis of sodium hydroborate solutions at -0.06 v. *vs.* s.c.e. These experiments are cited in support of the over-all electrode reaction of eq. 1, that is, the eight-electron oxidation originally suggested by Pecsok. The last experiment was attempted under conditions of a low ratio, $[\text{OH}^-]/[\text{BH}_4^-]$. It shows that hydrogen is produced under these conditions, probably through the participation of hydrolysis in the over-all process. The results of this experiment are in marked contrast to those where the supply of hydroxyl ion was adequate to support reaction 1.

Tables II and III list results of similar experiments in a very different system, the base-stabilized, partially hydrolyzed solution of sodium hydroborate. These

TABLE I
CONTROLLED-POTENTIAL ELECTROLYSIS OF ALKALINE
 NaBH_4 SOLUTION^a

Soln. compn.	Anode pot., v. <i>vs.</i> s.c.e.	mmoles of BH_4^- consumed	mequiv. elec. passed	Equiv. of elec./mole of BH_4^-
0.1 N NaOH	-0.06	0.0649	0.509	7.8
0.0010 M NaBH_4				
0.01 N NaOH ^b				
0.0010 M NaBH_4	-0.06	0.0476	0.391	8.2
0.001 N NaOH				
0.005 M NaBH_4				
	-0.35 ^c	0.475	0.237	0.5 ^d

^a Solutions were also 0.1 M in KCl. Volume 150 ml. ^b pH values: initial, 12.19; final, 12.00. ^c Adjusted so that the large current observed in the scan effect flowed. pH of solution changed from 11.00 to 9.7 during electrolysis. ^d Hydrogen analysis was positive in this experiment; it was negative in other experiments.

TABLE II
CONTROLLED-POTENTIAL ELECTROLYSIS OF
THE HYDROLYSIS INTERMEDIATE^a

$[\text{BH}_4^-]$, M	pH of electrolyte	Electricity passed, mequiv.	Intermed. consumed, mmoles	Equiv. of elec./moles of intermed.
0.010	12.6 ^b	0.137	0.0445	3.08
0.020	12.5 ^b	0.217	0.0714	3.04
0.050	12.65 ^c	0.136	0.0405	3.36

^a Composition of original solution: 0.0334 M NH_4^+ , 0.0167 M NH_4OH , 0.150 M KCl, concentration of NaBH_4 shown in column 1. pH was raised to values shown in column 2 after hydrolysis time. Anode potential -0.45 v. *vs.* s.c.e. Volume of test solution 100 ml. ^b Hydrolysis time 5.5 min. ^c Hydrolysis time 60.0 min.

TABLE III
CONTROLLED-POTENTIAL ELECTROLYSIS OF THE HYDROLYSIS
INTERMEDIATE WITH COLLECTION OF HYDROGEN^a

Electricity passed, mequiv.	Hydrogen collected, ml. S.T.P.	Intermediate consumed, mmoles	Equiv. of elec./moles of intermed.
0.123	0.90	0.0331	3.7
0.105	1.15	0.0326	3.2
0.0741	0.90	0.0229	3.2
0.000	0.53 ^b		

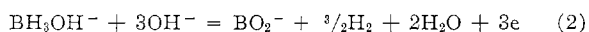
^a Composition of original solution: 0.020 M NaBH_4 , 0.0334 M NH_4Cl , 0.0167 M NH_4OH , 0.150 M KCl. Hydrolysis at pH 9.11 was stopped after 5.5 min. and pH was adjusted to 12.5 in first and third experiments and to 12.6 in second and fourth experiments. Time of electrolysis was 30 min.; volume electrolyzed was 50 ml. ^b Blank.

electrolyses were designed to clarify the electrode process which yields the small polarographic wave at -0.64 v. These data show that a three-electron oxidation process occurs at that potential, in agreement with the inference from the diffusion current constant. Furthermore, they show that hydrogen is evolved in the electrolysis, although the amounts collected were so small, after correction for the hydrolysis blank, that inferences about the stoichiometry of hydrogen evolution were precluded.

It should be noted that in the experiments of Tables II and III the hydrolysis intermediate, which was the starting material, was produced by conversions of from 1.3 to 6% of the sodium hydroborate taken. During the time of the electrolysis about 15% of the total decrease in the amount of intermediate species must be

attributed to hydrolysis, except in the cases of the experiments shown in Table III where, because of the increased time required to collect hydrogen, this figure rose to 27–36%. The hydrolysis correction may, in general, have been too large because the concentration of intermediate hydrolyzing in the blank solution was always larger than that in the electrolysis cell. The correction has, nevertheless, been used, since it would have been impracticable to improve upon it. This may contribute to the slightly high values of the ratio, equivalents of electricity/moles intermediate, shown in Tables II and III.

For the electrooxidation of the intermediate species we postulate the following over-all reaction.



Hydrolysis.—The data of Table IV show that 1 mole of the intermediate species yields 3 moles of hydrogen upon hydrolysis. The hydrolysis is much faster than the complete hydrolysis of hydroborate; however, since the concentration of hydroborate in the base-stabilized partially hydrolyzed solution exceeded that of the intermediate by about 17-fold, the blank correction given in Table IV was significant.

TABLE IV
HYDROLYSIS OF THE INTERMEDIATE SPECIES^a

pH	Hydrogen collected, ml. S.T.P.	Intermed. consumed, mmoles	Moles of H ₂ /moles of intermed.
12.6	3.88	0.0586	2.7
12.65	3.97	0.0582	2.8
12.55 ^b	0.28	...	...

^a Composition of original solution: 0.020 *M* NaBH₄, 0.0334 *M* NH₄Cl, 0.0167 *M* NH₄OH, 0.150 *M* KCl. Hydrolysis at pH 9.11 was stopped after 5.5 min. and pH was adjusted to values shown. Volume 100 ml., temperature 28 ± 1°, total hydrolysis time ~220 min. ^b Blank. pH adjusted to 12.55 before addition of NaBH₄.

Discussion

The conclusion that the hydrolysis of hydroborate ion proceeds stepwise, with the formation of an electrooxidizable intermediate containing the BH₃ group, rests on the following mutually consistent findings: (1) the kinetic scheme which fits the hydrolyzing hydroborate system⁶; (2) the magnitudes of the diffusion current constants of BH₄⁻ and the intermediate species; (3) the B¹¹ n.m.r. spectrum of the intermediate species⁸; (4) controlled potential electrolysis of BH₄⁻ and the intermediate; and (5) the stoichiometry of the hydrolysis reaction of the intermediate. The presence of the intermediate in the hydrolysis mixture is also consistent with the results of earlier electrochemical work; the BH₃-containing intermediate described

herein is clearly the one which caused the small arrests in charging curves on mercury reported by Elder.⁵

Two effects, both related to the electrode material, must be considered in comparing the results of this investigation with the previous work of Elder and Hickling. (1) The hydrolysis of hydroborate ion is catalyzed by metals, especially platinum. To some extent, then, the large amounts of hydrogen obtained by Elder and Hickling and the low *n* value for hydroborate oxidation may be attributed to this process accompanying the electrolysis. Indig and Snyder⁹ concluded that the BH₄⁻ oxidation was a four-electron process on a nickel anode. However, these authors also reported that nickel catalyzed the hydrolysis reaction, and therefore the same arguments may apply to explain the low *n* value. This catalysis must be negligible on a mercury surface since the kinetics of the hydrolysis obtained from polarographic measurements agree well with the results obtained by chemical analysis.⁶ (2) Although data on hydrogen oxidation at a mercury anode are lacking, we can assume that a higher overvoltage is required for oxidation of hydrogen to hydronium ion on mercury than on platinum. Thus, in the present work, we find a potential region, from -0.25 to -0.6 v., where hydrogen was the preponderant electrolysis product and at more oxidizing potentials we find oxidation of hydrogen. On platinum, Elder and Hickling reported hydrogen ionization from hydroborate and BH₃OH⁻ as the major electrolytic steps. It is reasonable that this ionization should be facilitated at a platinum surface. The difference in overvoltages for the two electrode materials doubtless also explains the absence of a reproducible static potential for a mercury electrode in alkaline hydroborate solution, which was observed by Elder and Hickling with platinum.

Mochalov and Gil'manshin⁸ worked with very concentrated solutions of sodium hydroborate (up to 0.08 *M*), and although they claimed to have examined the potential range between 0.2 and -2.0 v., they failed to confirm the existence of the wave at -0.1 v. They may have overlooked it because of its great height in solutions of high concentration; thus, it might appear to be the final current rise due to mercury oxidation. The wave described in their articles is due to the BH₃-containing intermediate. Its time dependence parallels that reported by us for different buffer systems. These authors recognized the importance of hydrolysis in the electrooxidation of hydroborate solutions, but their conclusion that the electroactive intermediate is BH(OH)₃⁻ is not supported by the results reported here or by n.m.r. spectra of solutions rich in the intermediate.

(9) M. E. Indig and R. Snyder, *J. Electrochem. Soc.*, **109**, 1104 (1962).