delate, the values of x ranging from 0.00 to 0.20. The optical densities of these solutions were measured at a number of different wave lengths, and in every case, after correction for the free cupric ion and the slight absorbance of the mandelate solution, the residual absorbance was 0.000 ± 0.002. Together with the polarographic evidence and the results of the acidimetric titration, this constitutes conclusive proof that the supposed complex does not exist in appreciable concentrations in aqueous solutions.

Acknowledgment.—I am greatly indebted to Dr. John E. Ricci for a large number of valuable suggestions dealing with both the rigor and completeness of the theory and the presentation of the experimental data. It is a pleasure to be able to express my appreciation of his interest and assistance

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Polarographic Studies on the Oxidation and Hydrolysis of Sodium Borohydride[1]

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Sodium borohydride in solutions buffered at pH 9 or greater yields a single, highly irreversible anodic polarographic wave, corresponding to the oxidation to hydrogen ion and borate ion, and involving eight electrons per mole. The polarographic data have been utilized to reaffirm the hydrolysis reaction and to measure its rate. The standard e.m.f. of the half reaction has been calculated to be 1.23 v. *vs.* the standard hydrogen electrode.

The reducing properties of sodium borohydride have been investigated in connection with both inorganic[2,3] and organic[4,5] reactions. The hydrolysis of sodium borohydride has been studied as a potential source of limited amounts of hydrogen gas.[6] The kinetics of the similar hydrolysis of lithium borohydride were determined in sulfuric acid solutions by an oscillographic measurement of the hydrogen evolved.[7] Strong reducing agents are expected to yield an anodic wave at the dropping mercury electrode. Such behavior has been reported for sodium borohydride in alkaline buffers.[8] Most of our knowledge of the preparation, properties and reactions of sodium borohydride has been collected in an excellent series of articles recently published by Schlesinger and his co-workers.[9]

This paper clarifies and extends the work of Marshall and Widing.[8] The polarographic data obtained have been interpreted to give the electrode half reaction and to confirm the hydrolysis reaction and to measure its rate. Although the standard oxidation potential of sodium borohydride could not be measured, it has been calculated from available data.

Experimental

Solutions of sodium borohydride were prepared freshly as needed from the commercially available product (approximately 95% pure) dissolved in 0.01 M sodium hydroxide. Both air-free and air-saturated solutions were used; no significant difference was noticed. Solutions stored at pH 12 decomposed only a few tenths of a per cent. per day. The solutions were standardized by the addition of an excess of calcium hypochlorite, followed by the addition of potassium iodide, acidification and titration with thiosulfate to determine the excess hypochlorite. This method yields results comparable to the recently reported iodate method[10] and details will be reported separately.

Polarograms were recorded in the conventional manner[11] with a Sargent Model XXI Polarograph. The H-cell contained a saturated calomel electrode and was maintained at 25 ± 0.1°, except where noted. Nitrogen, purified by passage through a vanadous solution, was used to deaerate the solutions, usually before the addition of the borohydride.

Measurements of pH and e.m.f. were performed with a Beckman Model G pH meter. The buffers contained phosphate, pyrophosphate, borax, or ammonium chloride-ammonium hydroxide, at approximately 0.1 M concentrations.

Results and Discussion

Oxidation at the Dropping Mercury Electrode.—In solutions buffered at pH 9 or greater, or containing excess sodium hydroxide, sodium borohydride yields a single anodic wave. The previously reported[8] second wave at −0.60 v. *vs.* the S.C.E. was not obtained under any conditions and was presumably caused by impurities. In solutions more acid than pH 9 the borohydride decomposes so fast that polarograms are meaningless. Above pH 9, the half-wave potential is related to the pH by the equation

$$E_{1/2} = +0.105 - 0.013\,p\text{H} \qquad (1)$$

No theoretical interpretation can be given to the coefficient −0.013.

The plot of the function $\log (i - i_d)/i$ *vs.* $E_{\text{d.e.}}$ yields a straight line with a slope of 0.045. Since the electrode reaction proposed below involves eight electrons, the slope of the log plot is expected to be 0.0075. Therefore, the polarographic oxidation is highly irreversible, making it impossible to calculate thermodynamic properties from polarographic data alone.

Furthermore, the limiting current is not entirely diffusion controlled. The ratio $i_d/h^{1/2}$, which is independent of the height of the mercury column for

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(1) Presented at the 123rd National Meeting of the American Chemical Society, Division of Physical and Inorganic Chemistry, Los Angeles, Calif., March 16, 1953.

(2) A. C. Stewart, Master's Thesis, University of Chicago (1948).

(3) G. W. Schaeffer and J. W. Frank, unpublished.

(4) M. B. Mathews, *J. Biol. Chem.*, **176**, 229 (1948).

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(6) H. I. Schlesinger, *et al.*, *ibid.*, **75**, 215 (1953).

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

(8) E. D. Marshall and R. A. Widing, A.E.C.D. 2914 (June 1950).

(9) H. I. Schlesinger, *et al.*, THIS JOURNAL, **75**, 186 ff. (1953).

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

(11) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Edition, Interscience Publishers, Inc., New York, N. Y., 1952.

diffusion controlled currents, was 5.67 at 40 cm. and 6.65 at 80 cm. The oxidation undoubtedly proceeds through several intermediate stages involving relatively slow reaction rates.

Nevertheless, the polarographic wave is well formed with a flat, easily measurable plateau. It is proportional to the concentration of borohydride over wide ranges in solutions in which the borohydride is stable. For a capillary with $m^{2/3}t^{1/6}$ = 1.92, the diffusion current constant is 26.0. Although the Ilkovic equation is applicable only to strictly diffusion controlled processes, the deviations noted above do not invalidate the use of the equation to determine n, the number of electrons involved in the electrode reaction. If n is assumed to be eight, the diffusion coefficient of the borohydride ion is approximately 3×10^{-5} cm.^{2} sec.$^{-1}$, a reasonable value compared to the diffusion coefficients of other ions.[12] Marshall and Widing[8] concluded that n is equal to four, which would yield a diffusion coefficient of 10×10^{-5} cm.^{2} sec.$^{-1}$, a value larger than that for hydrogen ion.

The proposed net reaction for the polarographic oxidation is therefore

$$BH_4^- + 8OH^- = BO_2^- + 6H_2O + 8e^- \qquad (2)$$

Hydrolysis Products.—One of the most important reactions of sodium borohydride is its "hydrolysis." This interesting reaction involves not only the separation of water into its ions, but also its apparent reduction to hydrogen gas. A closer inspection reveals that this is not a true reduction, but rather the formation of the very weak acid $H^+ \cdot H^-$ from the hydrogen ions of water and the hydride ions of sodium borohydride. The polarograph has been used to aid in establishing the products.

Cupric ion was polarographed in a number of supporting electrolytes, including the "hydrolysis" products. The half-wave potential of copper and its dependence upon pH were identical in solutions of the "hydrolysis" products and sodium borate only. Similar work has been reported by Marshall and Widing[8] who used ammonia-ammonium chloride buffers. They did not obtain unequivocal results because of the amminocupric complexes present. These results further support the hydrolysis reaction first proposed by Hoekstra[13]

$$BH_4^- + H^+ + 2H_2O = HBO_2 + 4H_2 \qquad (3)$$

Rate of Hydrolysis.—The rate of reaction was measured in solutions of constant ionic strength, μ = 0.1, at 15, 25 and 35°. Each solution contained initially 0.1 M potassium chloride, 0.01 M pyrophosphate buffer and approximately 0.001 M borohydride. The pH of the buffer was adjusted and the oxygen was removed before adding the borohydride. The pH was varied over the range yielding a measurable reaction rate and was measured immediately before and/or after the reaction. The potential of the dropping mercury electrode was maintained at −0.05 v. *vs.* the S.C.E., well on the anodic diffusion plateau. The current *vs.* time curve was recorded until the reaction was essentially complete, or for at least several hours at high pH where the reaction is slow. For all runs lasting more than a few minutes, the electrode was polarized (and current allowed to pass) at appropriate intervals for short periods of time so that there could be no appreciable loss of borohydride due to the polarographic current. For each run, a reproducible, smooth logarithmic curve resulted. Plots of the logarithm of the borohydride concentration *vs.* time at 25° are reproduced in Fig. 1.

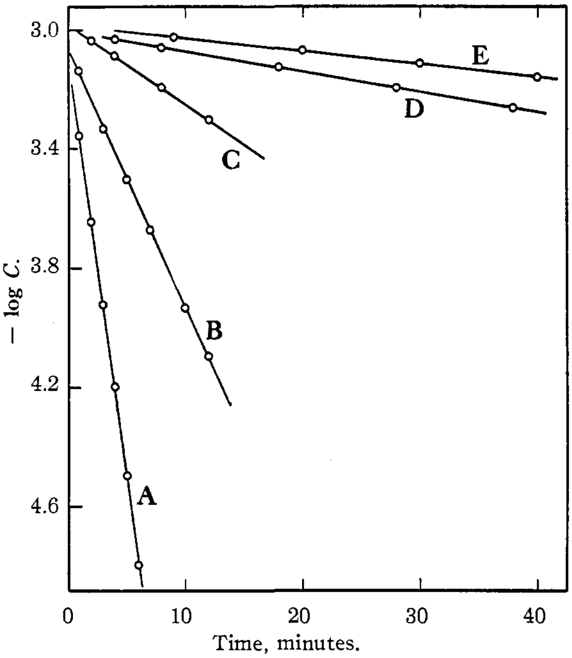

Fig. 1.—Decomposition of sodium borohydride as a function of time and pH. Ordinate is molar concentration of borohydride; all temperatures, 25°: A, pH 7.7; B, pH 8.2; C, pH 9.0; D, pH 9.3; E, pH 9.5.

Similar plots with different slopes were obtained at 15 and 35°. The linearity of the curves in Fig. 1, indicates the hydrolysis reaction is first order in borohydride concentration; the slopes of the lines represent k' in the rate equation

$$-\frac{d(BH_4^-)}{dt} = k'(BH_4^-) \qquad (4)$$

The constant, k', is a function of pH. If the reaction is also first order in hydrogen ion, k' should be directly proportional to the concentration of hydrogen ion. Since the latter varied over several powers of ten, log k' was plotted *vs.* pH, yielding a straight line for each temperature, as shown in Fig. 2. The slopes of these lines represent k in the rate equation

$$-\frac{d(BH_4^-)}{dt} = k(BH_4^-)(H^+) \qquad (5)$$

The values of k are 8.7×10^6 at 15°, 1.5×10^7 at 25° and 2.4×10^7 at 35°.

Admittedly, this procedure is approximate. While the polarograph measures the *concentration* of borohydride, the pH meter measures the *activity* of hydrogen ion. Nevertheless, the relative values of the data are considered to be well established. The hydrolysis must involve the rate controlled formation of a species with the formula $HBH_4 \cdot xH_2O$.

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(12) Reference 11, p. 52.

(13) H. R. Hoekstra, A.E.C.D. 2144 (June 1947).

This intermediate loses hydrogen instantaneously, leaving an aquated borine radical which is known to hydrolyze rapidly.

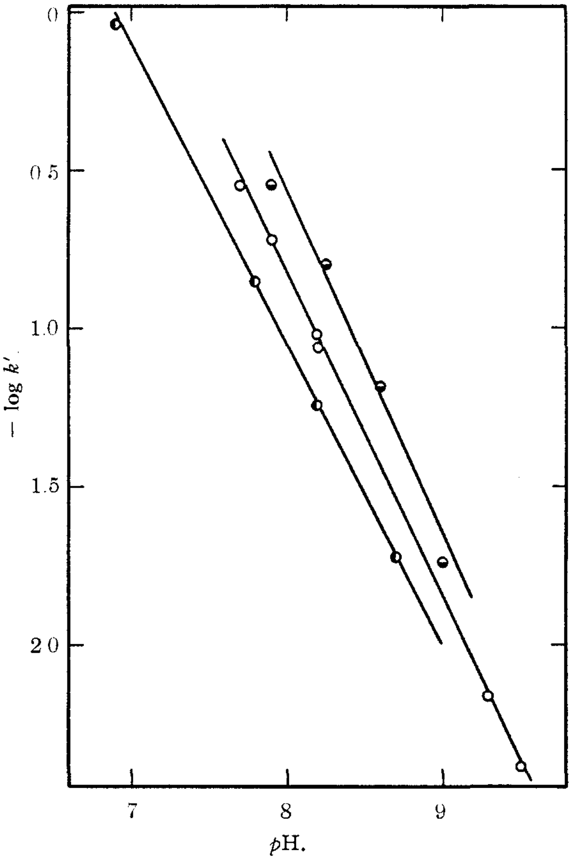

Fig. 2.—Rate constant of equation (4) as a function of temperature and pH: ◐, 15°; ○, 25°; ◓, 35°.

Standard E.M.F.—One of the reasons for the polarographic study of sodium borohydride was an effort to measure the standard e.m.f. of the half reaction involving its oxidation to sodium borate. There appears to be no way of measuring this directly. Polarographic waves were highly irreversible in all supporting electrolytes. Repeated attempts to titrate potentiometrically using a variety of electrode systems and a number of oxidants yielded surprisingly reproducible systems, but none that could be shown to be reversible electrodes. It is, however, possible to calculate the standard e.m.f. for the half reaction (2) from known thermodynamic data. The heat of hydrolysis for the reaction

$$H^+ + BH_4^- + 3H_2O = H_3BO_3 + 4H_2 \qquad (6)$$

has been measured by Davis,[14] who reported the value −63.9 kcal./mole. The entropies of all species involved are known except that for the borohydride ion. Using an estimated entropy of 40 for the latter (which is the entropy of the fluorborate ion)[15] one calculates the free energy of the hydrolysis reaction to be −91,400 cal. With the additional reactions[15]

$$H_3BO_3 = HBO_2 + H_2O;\ \Delta F^\circ = 0 \qquad (7)$$

$$HBO_2 = H^+ + BO_2^-;\ \Delta F^\circ = -12{,}600 \text{ cal.} \qquad (8)$$

$$8OH^- + 4H_2 = 8H_2O + 8e;\ \Delta F^\circ = -153{,}000 \text{ cal.} \qquad (9)$$

one can add reactions (6) through (9) to obtain the free energy of the half reaction (2), which is −231,000 cal. The standard e.m.f. is thus 1.23 v. *vs.* the standard hydrogen electrode. The assumption of 40 for the entropy of the borohydride ion is not critical, inasmuch as the value 18, calculated from the Powell–Latimer formula for monatomic ions,[16] yields a value for the e.m.f. of 1.25 v. The only previously reported value for the reduction potential of sodium borohydride is −1.37 v.[17]

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