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Electro-oxidation of Trihydrohydroxyborate Ion. 1. Mechanistic Studies of Oxidation of Trihydrohydroxyborate Ion at Mercury Electrode

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Electro-oxidation of Trihydrohydroxyborate Ion. I.
Mechanistic Studies of Oxidation of
Trihydrohydroxyborate Ion at Mercury Electrode

Akio KINJO*

Mechanism of electro-oxidation of trihydrohydroxyborate ion was studied in aqueous alkaline solutions. The results of combined study of ^{11}B n. m. r. spectroscopy and controlled potential coulometry indicated that the overall reaction includes three electron process. In polarographic study, the stepwise oxidation of the ion was observed when the condition was chosen appropriately. The experimental results are plausibly explained by several intermediate processes including electrochemical and chemical reactions.

1. Introduction

The hydrolysis of borohydride ion has been studied by many investigators.¹⁾ The ion is stable in alkaline media, but the hydrolysis reaction occurs when the pH of the solution is lowered.

Several intermediates have been postulated to be formed during the hydrolysis reaction. Mikheeva and Fedneeva²⁾ suggested that lithium borohydride hydrolyzes through a stepwise replacement of hydride ions by hydroxide ions,



but there was a lack of evidence to support their proposal of the intermediates.

Gardiner and Collat^{3,4)} recently examined the hydrolysis reaction of sodium borohydride. Their ^{11}B n. m. r. spectrum of a partially hydrolyzed solution of sodium borohydride indicated the existence of trihydrohydroxyborate ion, BH_3OH^- . The other intermediate species have not been confirmed in spite of endeavor to detect or synthesize them. In relation to the hydrolysis reaction, Freund⁵⁾ has discussed the possibilities that intermediates such as BH_2OH , $\text{BH}(\text{OH})_2^-$ and $\text{BH}(\text{OH})_2$ may be formed during the reduction of ferric cyanide ion with borohydride.

We undertook the present mechanistic study of electrooxidation of trihydrohydroxyborate ion in hoping that the study shed light on the hydrolysis reaction of borohydride ion because hydrolysis is essentially oxidation of borohydride ion by hydrogen ion.

2. Experimental

Sodium borohydride (98% purity, Metal Hydride, Inc.) was used without further purification to prepare the sample solutions. All other chemicals were of reagent grade quality and were used without further purification. All solutions were prepared from deionized water.

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*Dept. of General Education

Since compounds of trihydrohydroxyborate have not been isolated, it is possible to obtain this species in sufficiently high concentration for n. m. r. experiments only in a partially hydrolyzed solution of sodium borohydride. The following procedure was empirically established to prepare such a sample solution. Three grams of sodium borohydride was dissolved in 10 ml of water at 0°C. After complete dissolution, 1 ml of 6 F hydrochloric acid was added, and the solution was allowed to undergo hydrolysis for 10 seconds. Then 1 ml of 50 % sodium hydroxide solution was rapidly added to quench the hydrolysis (the resulting solution was approximately 1 F in sodium hydroxide). This solution contained about 0.3 M trihydrohydroxyborate ion.

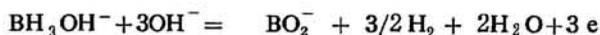
The experiments were carried out at 0°C when it was necessary to prevent deterioration of trihydrohydroxyborate ion because the sample solution was stable for several hours at this temperature.

The ^{11}B n. m. r. spectra were recorded at 19.3 megahertz with a Varian Model 4300 B high-resolution spectrometer. The areas under the spectral peaks were measured with a Model V3521 integrator attached to the spectrometer. A 15-mm (o. d.) Pyrex glass tube was used as a sample holder. The controlled-potential coulometry was performed with a Model ORNL-2005-X50 controlled-potential coulometric titrator manufactured by the Indiana Instrument and chemical Co. The working electrode was a mercury pool with an area of approximately 7 cm². The auxiliary electrode was a length of platinum wire placed in a compartment containing pure supporting electrolyte and separated from the sample solution by a fine-porosity fritted-glass disk. The saturated calomel reference electrode was separated from the sample solution by a U-tube filled with agar gel saturated with potassium chloride. The mercury electrode-sample solution interface was stirred with the aid of a magnetic stirrer, and individual trials could be completed in about 10 minutes. Polarographic experiments were carried out with a three-electrode polarograph, Model ORNL-1988, built by the Indiana Instrument and Chemical Co.

3. Results and Discussion

(1) Determination of number of electrons involved in the electro-oxidation of trihydrohydroxyborate

For the anodic oxidation of trihydrohydroxyborate ion, BH_3OH^- , Gardiner and Collat⁶⁾ have determined the n-value by means of controlled-potential coulometry. These workers estimated the concentration of BH_3OH^- in a partially hydrolyzed solution of sodium borohydride from kinetic data assuming that the hydrolysis rate of trihydrohydroxyborate ion is first order. As a result of this study, Gardiner and Collat proposed that trihydrohydroxyborate undergoes a three-electron oxidation



to yield borate and hydrogen gas.

The present investigation was undertaken to determine the number of electrons for this process by a more direct method because it was of prime importance for the mechanistic studies.

Boron-11 nuclear magnetic resonance spectroscopy was employed to determine the

concentration of the trihydroxyborate ion in a partially hydrolyzed solution of borohydride ion; then, the n -value was determined with the aid of controlled-potential coulometry.

The ^{11}B n. m. r. spectrum of the sample solution is shown in Fig. 1. The large

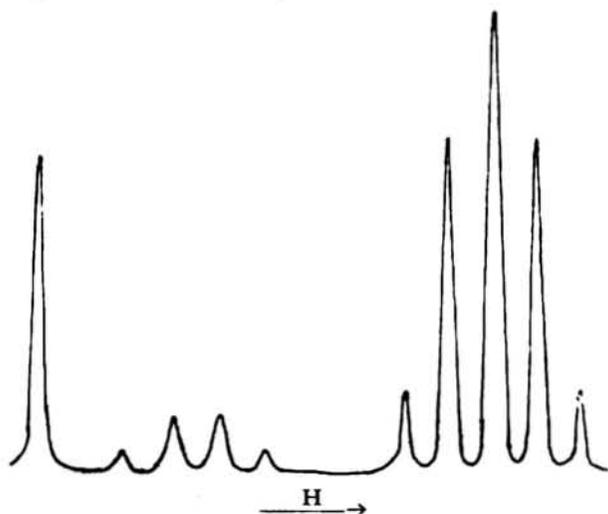


Fig. 1 The ^{11}B n. m. r. spectrum of a partially hydrolyzed solution of sodium borohydride

quintet at high field, due to the unreacted borohydride ion, has a chemical shift of $+43.0$ p. p. m. relative to boron trifluoride etherate, a boron-proton coupling constant of 83 c. p. s., and a relative peak intensity ratio of $1:4:6:4:1$, in agreement with the published spectrum.⁷⁾ The singlet at low field has a chemical shift of -1.5 p. p. m. and is attributable to the basic form of boric acid, $\text{B}(\text{OH})_4^-$ (or BO_2^-).⁸⁾ The quartet at intermediate field is due to the trihydroxyborate ion. Its chemical shift is $+14.0$ p. p. m., the boron-proton coupling constant is 91 c. p. s., and the relative peak intensity ratio is $1:3:3:1$.

Using the spectrum and knowing the total concentration of all boron-containing species, one can calculate the concentration of each individual ion, particularly trihydroxyborate, by assigning the total concentration to each species in proportion of their relative spectral area. The results are shown in Table 1. The

Table 1. Band area of the n. m. r. spectrum and concentration of the individual boron species

Species	Band area*	Concentration, M
BH_4^-	$90.8 \pm 0.2^{**}$	4.49 ± 0.01
BH_3OH^-	6.7 ± 0.2	0.33 ± 0.01
BO_2^-	17.3 ± 0.2	0.86 ± 0.01
Total	114.8 ± 0.2	$5.68 \pm 0.01^{***}$

* arbitrary units

** average value of three measurements

*** obtained by separate experiment

total concentration of all boron-containing species was determined titrimetrically after all species were changed to boric acid by the careful adjustment of pH of the sample solution.⁹⁾

Five milliliters of the original sample solution, a part of which was used for the n. m. r. experiment, was diluted to 250 ml with 1 F sodium hydroxide solution which had been cooled to 0°C beforehand to avoid decomposition of the trihydroxyborate ion during dilution. A 10-ml aliquot of this diluted solution was used for each coulometric experiment, and the temperature was controlled at 0°C. Control potentials were selected by inspection of a polarogram for oxidation of trihydroxyborate in 1 F sodium hydroxide medium. The results are presented in Table 2, confirming that number of electrons is three.

Table 2. Controlled-potential oxidation of BH_3OH^-

Moles of BH_3OH^-	Quantity of Electricity, coulombs	n-value	Control Potential V vs. S. C. E.
6.6×10^{-5}	18,978	2.98	-0.40
"	20,918	3.28	-0.40
"	19,789	3.11	-0.45
"	18,199	2.86	-0.45
"	18,595	2.92	-0.50
"	19,805	3.11	-0.50

Average: 3.04 ± 0.12

2 Polarographic study of BH_3OH^-

Polarographic curves of BH_3OH^- are greatly influenced by experimental conditions. In this section, the effects of pH and maximum suppressor on the polarographic current-potential curve were investigated in order to elucidate the mechanism of electro-oxidation of BH_3OH^- .

Effect of pH. Polarograms of BH_3OH^- usually exhibit a large maximum. However, if the concentration of BH_3OH^- is decreased to as low as 7×10^{-5} M, normal polarograms are obtained without the use of a maximum suppressor. Quantitative information concerning the polarographic behavior of BH_3OH^- at different pH values is presented in Table 3.

Table 3. Effect of pH on polarographic behavior of BH_3OH^- . Concentration = 7×10^{-5} M

Solution Compositions	pH	First Wave			Second Wave		
		$E_{1/2}, \text{V}$	$i_1, \mu\text{A}$	$\Delta E_{1/2}/\text{pH}$	$E_{1/2}, \text{V}$	$i_1, \mu\text{A}$	$\Delta E_{1/2}/\text{pH}$
1 F KOH	14*	-0.688	1.64		
				0.0			
0.1 F KOH	13*	-0.687	1.07		-0.510	1.64	
				0.0			0.076
0.01 F KOH	12*	-0.687	0.90		-0.434	1.67	
				0.0			0.049
0.05 F KHCO_3							
0.045 F KOH	10.70**	-0.689	0.91		-0.370	1.60	
0.905 F KNO_3							
				0.0			0.054
0.05 F KHCO_3							
0.035 F KOH	10.00**	-0.693	1.12		-0.332	1.58	
0.915 F KNO_3							

* pH calculated assuming activity coefficient to be unity.

** pH measured with a Leeds and Northrup pH meter.

i_1 : measured at -0.57 V

i_t : measured at -0.30 V

Quite obviously, the polarographic behavior of BH_3OH^- is profoundly affected by the pH of the solution. In 1 F potassium hydroxide solution, a single wave is observed, but it splits into two waves in 0.1 F potassium hydroxide solution and in media of lower pH. The half-wave potential of the first wave is independent of pH, whereas the second wave shifts in an anodic direction, by from 50 to 80 millivolts per pH unit, as the solution pH decreases. Although the height of the first wave, i_1 , is influenced by the pH of the solution, the total limiting current, i_t , always corresponds to a three-electron oxidation. The latter fact is evident if one compares the total limiting currents for the lower pH media with that for the 1 F potassium hydroxide medium. The occurrence of a three-electron oxidation was confirmed for 0.01, 0.1, and 1.0 F potassium hydroxide media by means of controlled-potential coulometry.

There is a tendency for the limiting current for the first wave to decrease with decreasing pH. This effect is clearly evident for the 1.0, 0.1, and 0.01 F potassium hydroxide solutions. However, the limiting current seems to increase again at pH 10.7 and 10.0, but the significance of this trend is obscured by the fact that, at these pH values, considerable hydrolysis of BH_3OH^- occurs during the recording of a polarogram.

Effect of Triton X-100. Triton X-100, which is widely used maximum suppressor, has a profound influence on the polarographic behavior of BH_3OH^- . In most of the work to be described, the effect of Triton X-100 was studied for a 1.0 F potassium hydroxide medium. With 4×10^{-4} M BH_3OH^- solution, Triton X-100 at a concentration level from 0 to 0.0015 % caused a single wave, 0.0015 to 0.0025%

caused two waves, and a concentration above 0.0025% caused three waves. Furthermore, the amount of Triton X-100 required to produce these effects depends upon the concentration of BH_3OH^- . If the concentration of BH_3OH^- is higher than 4.0×10^{-4} M, less Triton X-100 is required to cause a given splitting. However, the general pattern of the effect is similar to the case of 4.0×10^{-4} M BH_3OH^- .

Since the detailed effect (definition of waves) was more pronounced with higher concentrations of BH_3OH^- , a 1.0×10^{-3} M solution of BH_3OH^- in 1 F potassium hydroxide was employed for the majority of the studies. Polarographic data obtained in the presence of various concentrations of Triton X-100 are presented in Table 4. As seen from the table, the height of the first wave relative to the second wave is approximately 2 to 1 when enough Triton X-100 has been added (about 0.001%) to

Table 4. Effect of Triton X-100 on polarographic curve of BH_3OH^- in 1.0 F KOH. Concentration = 1.0×10^{-3} M

% Triton X-100	Number of Waves	First Wave		Second Wave		Third Wave		Relative Wave Height		
		$E_{1/2}$, V	i , μA	$E_{1/2}$, V	i , μA^*	$E_{1/2}$, V	i , μA^*	i_1	i_2	i_3
0.001	2	-0.676	17.1	-0.547	23.8	2.16	0.84	...
0.0012	2	-0.676	15.0	-0.547	23.0	1.96	1.04	...
0.0014	2	-0.671	14.9	-0.540	23.0	1.94	1.06	...
0.0016	2	-0.664	13.4	-0.524	22.0	1.83	1.17	...
0.0018	2	-0.656	12.0	-0.515	21.5	1.68	1.32	...
0.002	2	-0.657	11.1	-0.510	21.2	1.57	1.43	...
0.0025	3	-0.650	8.9	-0.513	17.5	-0.410	20.5	1.30	1.26	0.44
0.0030	3	-0.653	7.2	-0.521	15.3	-0.394	20.1	1.07	1.21	0.72
0.0035	3	-0.651	6.1	-0.516	13.0	-0.371	18.9	0.97	1.10	0.93
0.004	3	-0.650	5.94	-0.521	12.5	-0.360	17.8	1.00	1.10	0.90

i under first wave; measured at -0.57 V

i under second wave; total limiting current measured at -0.46 V

i under third wave; total limiting current measured at -0.30 V

*Decrease of total limiting current with increasing Triton X-100 is probably due to hydrolysis.

just suppress the maximum. This ratio gradually decreases with increasing concentration of Triton X-100, and the second wave then splits into two waves; that is, there are three waves in all. For approximately 0.003% Triton X-100, the relative heights of the three waves are approximately 1:1:1, and this ratio remains about the same upon further increase in the concentration of Triton X-100. Results up to a maximum suppressor concentration of 0.004% are shown in the table, but the ratio of wave heights appeared to remain essentially unchanged beyond 0.004% Triton X-100. However, Triton X-100 concentrations above 0.004% obscure the definition of the waves so that meaningful measurements were not possible.

Effects due to Triton X-100 similar to those encountered in 1 F potassium hydroxide solution were also observed in 0.1 F potassium hydroxide and lower pH media. The influence of pH on the polarographic curve of 1.48×10^{-3} M BH_3OH^- was studied

in the presence of 0.0035% Triton X-100 at 25°C, the experimental results being presented in Table 5. At pH 10.0 the second and third waves are merged into that

Table 5. Effect of pH on the polarographic curve of BH_3OH^- in the presence of 0.0035% Triton X-100, Concentration = 1.48×10^{-3} M*

Solution	pH	First Wave			Second Wave			Third Wave																				
		$E_{1/2}, \text{V}$	$i, \mu\text{A}$	$\Delta E_{1/2}/\text{pH}$	$E_{1/2}, \text{V}$	$i, \mu\text{A}$	$\Delta E_{1/2}/\text{pH}$	$E_{1/2}, \text{V}$	$i, \mu\text{A}$	$\Delta E_{1/2}/\text{pH}$																		
1 F KOH	14	-0.65	12.2		-0.51	25.4		-0.38	36.0																			
				0.0			0.07			0.07																		
0.1 F KOH	13	-0.65	11.2		-0.44	27.6		-0.31	37.2																			
				0.0			0.07			0.06																		
0.01 F KOH	12	-0.64	11.6		-0.37	30.6		-0.25	41.0																			
				0.0			0.03			0.025																		
0.05 F KHCO_3 0.045 F KOH 0.905 F KNO_3	10.70	-0.64	12.8		-0.33	30.2		-0.22	39.2																			
				0.0																								
0.05 F KHCO_3 0.035 F KOH 0.915 F KNO_3	10.00	-0.65	13.4																		
<table border="1"> <thead> <tr> <th colspan="3">Relative Wave Heights</th> </tr> <tr> <th>i_1</th> <th>i_2</th> <th>i_3</th> </tr> </thead> <tbody> <tr> <td>1.02</td> <td>1.10</td> <td>0.83</td> </tr> <tr> <td>0.90</td> <td>1.32</td> <td>0.77</td> </tr> <tr> <td>0.85</td> <td>1.39</td> <td>0.76</td> </tr> <tr> <td>0.98</td> <td>1.33</td> <td>0.69</td> </tr> </tbody> </table>											Relative Wave Heights			i_1	i_2	i_3	1.02	1.10	0.83	0.90	1.32	0.77	0.85	1.39	0.76	0.98	1.33	0.69
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*The limiting current for the first wave was measured at -0.57 V vs. S. C. E., whereas the limiting currents for the second and third waves were measured at the midpoint of the appropriate plateau region.

*Some foreign electrolytes, notably potassium chloride, obscure the third wave; therefore, the ionic strength of the 0.1 and 0.01 F potassium hydroxide media was not adjusted upward.

for borohydride oxidation. The half-wave potential for the first wave is independent of pH, but, on the other hand, that of the second and third waves is shifted anodically by 0.06 to 0.07 volt per pH unit with decreasing pH, indicating participation of hydroxide ion in these two latter electron-transfer reactions.

Proposed mechanism of the electro-oxidation of BH_3OH^- The various observations concerning the polarographic oxidation of BH_3OH^- which were described in the previous sections may now be summarized to facilitate visualization of the entire reaction scheme.

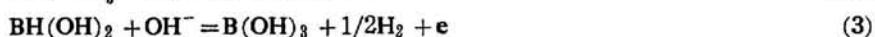
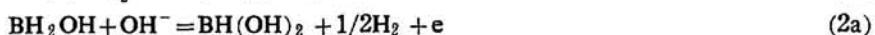
- 1) In the presence of 0.0025% and higher concentration of Triton X-100, polarograms for BH_3OH^- oxidation exhibit three waves in alkaline media.
- 2) The half-wave potential for the first wave is independent of the pH of the solution. On the other hand, the half-wave potentials for the second and

third waves are shifted as the pH decreases to more anodic potentials by approximately 0.05 to 0.08 volt per pH unit.

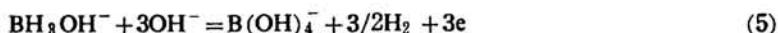
- 3) The limiting currents for the first and second waves seem to contain some kinetic current, whereas the total limiting current is diffusion-controlled.
- 4) The limiting current for the first wave decreases with decreasing pH. The effect of pH on the second limiting current is not clear from the present data.

These phenomena indicate that the electrode reactions proceed in a fashion similar to the case treated theoretically by Koutecky¹⁰⁾ and by Tachi and Senda¹¹⁾, that is, a chemical reaction interposed between two electron transfer reactions in which the species produced by the chemical reaction is more easily reducible or oxidizable than the initial species.

The present experimental results for the oxidation of BH_3OH^- in alkaline media are plausibly explained by the occurrence of the following processes:



The overall three-electron oxidation of trihydrohydroxyborate,



is seen to be a combination of the above stepwise reactions.

It is proposed that BH_2OH^- produced by direct oxidation of BH_3OH^- (reaction 1a) is not oxidized at the potential of the first wave and, likewise, that the intermediate $\text{BH}(\text{OH})_2$ is oxidized (reaction 3) at a more anodic potential than the potential of the second wave. On the other hand, the $\text{BH}_2(\text{OH})_2^-$ and $\text{BH}(\text{OH})_3^-$ intermediates produced by chemical reactions (1b) and (2b) are believed to be more readily oxidizable than BH_3OH^- (and instantaneously oxidized at the electrode surface whenever they are formed) because the hydridic character of hydrogen attached to boron is enhanced by the greater number of electron-releasing oxygens bound to boron.

According to the preceding sequence of reactions, when the polarographic curve for oxidation of BH_3OH^- is split into three waves, the electron-transfer reactions (1a) and (1c) cause the first wave, reactions (2a) and (2c) the second wave, and reaction (3) the third wave. Note that the limiting current for the first wave is enhanced through reaction (1c) by the amount of $\text{BH}_2(\text{OH})_2^-$ formed by chemical reaction (1b). In addition, the pH dependence of the first limiting current is explained by participation of hydroxide ion in chemical reaction (1b). Though no clear infor-

mation is available concerning the dependence of the second limiting current on pH, hydroxide ion is included in chemical reaction (2b), in analogy with reaction (1b). The dependence of the half-wave potentials of the second and third waves on solution pH is explained by the participation of hydroxide ion in electron-transfer reactions (2a) and (3).

When the polarogram for BH_3OH^- oxidation is split into only two waves, chemical reaction (2b) is presumed to be fast enough to preclude electron-transfer reaction (3). When the pH of the solution is increased to the value corresponding to that of 1 F potassium hydroxide (without Triton X-100), chemical reactions (1b) and (2b) proceed very rapidly, and electron-transfer reactions (1a), (1c), and (2c) occur simultaneously at the potential of the first wave so that only a single polarographic wave is observed.

Finally it should be noted that Triton X-100 is believed to retard two chemical reactions, (1b) and (2b).

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