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## Electro-oxidation of Trihydrohydroxyborate Ion. 2. Kinetic Studies of a Chemical Reaction between two Electrochemical Reactions in Oxidation of Trihydrohydroxyborate Ion

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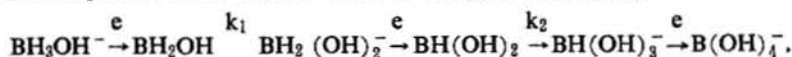
**Electro-oxidation of Trihydroxyborate Ion. II.**  
**Kinetic Studies of a Chemical Reaction between two Electrochemical**  
**Reactions in Oxidation of Trihydroxyborate Ion**

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Kinetic parameters for the reaction,  $\text{BH}_2\text{OH} + \text{OH}^- = \text{BH}_2(\text{OH})_2^-$ , which has been proposed to exist between two electrochemical reactions in electro-oxidation of trihydroxyborate ion, were evaluated by chronopotentiometric method. The pseudo first order rate constants at 0°C are 27.5, 35.0 and 0.34  $\text{sec}^{-1}$  in the solution with 0, 0.0002 and 0.0005% Triton X-100, respectively.

1. Introduction

In the previous paper<sup>1)</sup>, we proposed the mechanism for electro-oxidation of trihydroxyborate ion,  $\text{BH}_3\text{OH}^-$ . The electron transfer and chemical processes of  $\text{BH}_3\text{OH}^-$  proposed may be schematically expressed by two successive ECE processes (chemical reaction interposed between two electron transfer reactions),

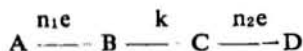


The  $\text{BH}_2(\text{OH})_2^-$  and  $\text{BH}(\text{OH})_3^-$  generated by the two chemical reactions can be oxidized at the same potential as  $\text{BH}_3\text{OH}^-$  itself. However,  $\text{BH}_2\text{OH}$  and  $\text{BH}(\text{OH})_2$  are oxidized at more anodic potentials.

The present study was undertaken to evaluate the rate constant  $k$  for the first chemical step,  $\text{BH}_2\text{OH} + \text{OH}^- = \text{BH}_2(\text{OH})_2^-$ , by chronopotentiometric method.

2. Theory

The theory for the processes similar to our present case has been discussed by Testa and Reinmuth.<sup>2)</sup> These processes may be represented in a general way by the reaction sequence

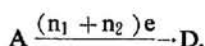


where  $k$  is a first order or pseudo first order rate constant. In this three-step process, the parent species A undergoes an  $n_1$ -electron oxidation (or reduction) to species B which, in turn, reacts chemically to yield product C, and the latter species is oxidized (or reduced) in an  $n_2$ -electron reaction to give D. When species C reacts at the same potential as species A, but species B reacts at a different potential, the chronopotentiometric transition time is expressed by Testa-Reinmuth equation corrected by Alberts and Shain<sup>3)</sup>,

$$\frac{i \tau_{\infty}^{1/2}}{i \tau^{1/2}} = 1 + \rho \left( \frac{\pi}{4k\tau} \right)^{1/2} + \frac{\rho^2 \exp\left(\frac{k\tau}{\rho} - \frac{1}{\rho}\right)}{(k\tau)^{1/2} (1 - \rho^2)^{1/2}} \int_0^{\rho} \frac{\rho (k\tau)^{1/2}}{(1 - \rho^2)^{1/2}} \exp(u^2) du$$

$$+ \frac{1}{\rho} \left( \frac{\pi}{4k\tau} \right)^{1/2} \int_0^{(k\tau)^{1/2}} \frac{\exp(u^2) du}{(1-\rho^2)^{1/2}}$$

In this relation,  $i$  is the current,  $k$  is the first order rate constant,  $\rho = n_2 / (n_1 + n_2)$ ,  $\tau$  is the experimentally observed transition time, and  $\tau_\infty$  is the predicted transition time for an infinitely large rate constant. When the rate constant  $k$  is infinite, species A is oxidized or reduced to the final product D (at the potential where A is oxidized or reduced to B) through chemically generated species C, and the transition time  $\tau_\infty$  corresponds to the transition time for the reaction,



It is possible to calculate the rate constant  $k$  from experimentally obtained transition times with the aid of the equation. However, Alberts<sup>4)</sup> has tabulated values of the right-hand side of the equation for various values of  $k\tau$ . Therefore, it is now a simple matter, in spite of the complicated form of the equation, to calculate the rate constant  $k$  from experimentally obtained values of  $(i\tau_\infty^{1/2}) / (i\tau^{1/2})$  from this table.

### 3. Experimental

All chemicals were reagent grade except sodium borohydride (98% purity), and were used without further purification. Deionized water was used for the preparation of all solutions. The sample solutions were prepared by the method described in the previous paper<sup>1)</sup>, and the concentration of  $\text{BH}_3\text{OH}^-$  was determined polarographically.

The experiments were carried out with an electronic chronopotentiometer which was designed and constructed by Dr. Longerich.<sup>5)</sup> This instrument can provide currents constant to within 0.2%. The constant current was measured by observation of the potential drop across a precision resistor (0.05%) with a digital voltmeter, Model 481, Non-Linear Systems, Inc. Transition times were measured graphically from the recorded chronopotentiograms. Chronopotentiograms with transition times longer than 2 seconds were recorded on a Honeywell 520 XY recorder; those with shorter transition times were displayed on a dual-beam oscilloscope, 520A, Tektronix, Inc. and were photographed with a Tektronix C-12 camera loaded with Polaroid Land roll film, Type 47.

The electrolysis cell was placed on a rubber platform to minimize mechanical vibrations. The temperature of the cell was controlled by circulation of thermostated water through the outer jacket. The working electrode was a hanging mercury drop electrode. It was fabricated by the method described by Shain and coworkers.<sup>6)</sup> The area of the electrode was calculated from the weight of the drops to be 0.0605 cm<sup>2</sup> on the assumption that the electrode was a perfect sphere. The auxiliary electrode was a length of platinum wire placed in a glass-tube compartment containing pure supporting electrolyte solution and separated from the sample solution by a fine-porosity fritted-glass disk. The saturated calomel reference electrode was separated from the test solution by a U-tube filled with 4% agar-saturated potassium chloride.

The solution-side end of the U-tube was brought into contact with the test solution by means of a Luggin probe.

#### 4. Results and Discussion

Number of steps of oxidation of  $\text{BH}_3\text{OH}^-$  observed in chronopotentiometry is influenced by the experimental conditions. Generally speaking, high current densities (short transition times) give three waves and low current densities (long transition times) do two waves. Fig. 1 shows typical chronopotentiograms at these two current densities.

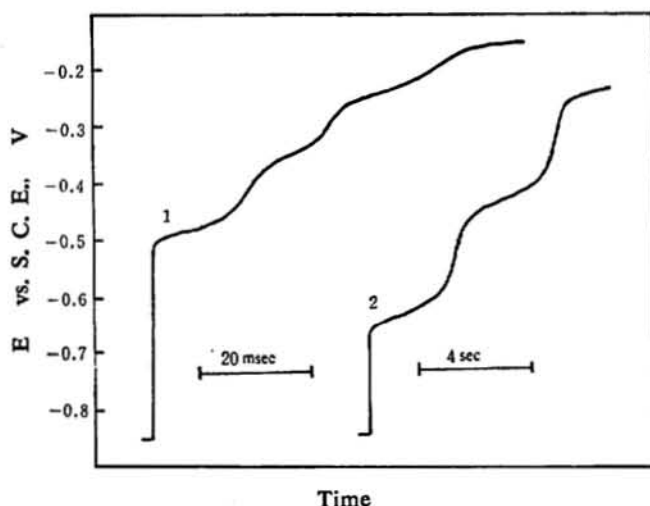


Fig. 1. Chronopotentiograms for oxidation of  $1.48 \times 10^{-2}$  M  $\text{BH}_3\text{OH}^-$  in 0.1 F KOH solution without Triton X-100.  
1:368  $\mu\text{A}$ , 2:32.2  $\mu\text{A}$

The present kinetic experiments were carried out with the solution of  $1.48 \times 10^{-3}$  M  $\text{BH}_3\text{OH}^-$  in 0.1 F KOH. Three series of experiments were performed at various current densities for 0.0, 0.0002, and 0.0005% Triton X-100 at  $0^\circ\text{C}$ . Transition time  $\tau_1$  for the first wave is presented in Table 1.

Since Testa-Reinmuth equation is valid only for a first order or pseudo first order chemical reaction, the dependence of the height of the first polarographic wave on the concentration of  $\text{BH}_3\text{OH}^-$  was investigated to ensure that the reaction is first order in the  $\text{BH}_3\text{OH}^-$  concentration. The experiment was carried out in 0.1 F potassium hydroxide medium in the presence of 0.002% Triton X-100 at  $0^\circ\text{C}$ . The resulting limiting current is plotted against concentration in Fig. 2. The constancy of the ratio  $i/C$  for the first wave over the concentration range from  $2.95 \times 10^{-4}$  to  $2.95 \times 10^{-3}$  M indicates that the reaction between  $\text{BH}_2\text{OH}$  and  $\text{OH}^-$  is pseudo first order. From these data the diffusion coefficient was also calculated to be  $1.34 \times 10^{-5}$   $\text{cm}^2/\text{sec}$  at  $0^\circ\text{C}$  from the Lingane-Loveridge equation.<sup>7)</sup>

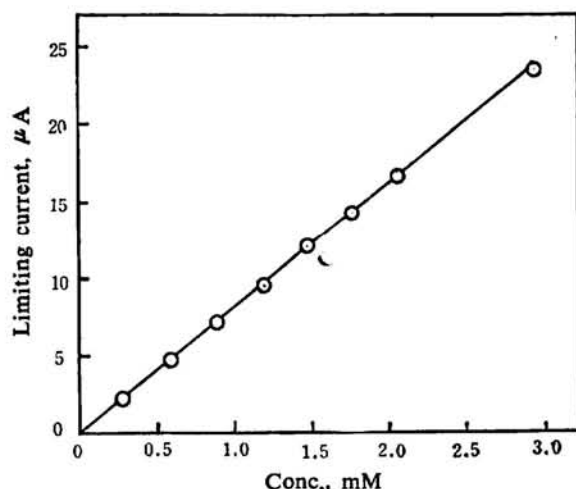


Fig. 2. Polarographic limiting current measured at  $-0.57$  V. vs S. C. E. For the first wave of  $BH\ OH^-$

The rate constant was calculated from the table provided by Alberts for the Testa-Reinmuth equation after transition time data were corrected for the effects of spherical diffusion and charging of the electrical double-layer by the methods described by Evans<sup>8)</sup> and Lingane<sup>9)</sup>, and the results are presented in Table 1. For the

Table 1. Chronopotentiometric determination of the rate constant for the chemical reaction coupled to oxidation of  $BH.OH^-$

(1) 0.0% Triton X-100			
$i, \mu A$	$\tau_1, sec$	$i\tau_\infty^{1/2}/i\tau_1^{1/2}$	$k, sec^{-1}$
39.4	2.02	1.060	29.1
68.5	0.55	1.133	25.9
			Average 27.5 $\pm$ 1.6
(2) 0.0002% Triton X-100			
$i, \mu A$	$\tau_1, sec$	$\tau_\infty^{1/2}/i\tau_1^{1/2}$	$k, sec^{-1}$
32.1	3.24	1.050	24.7
46.2	1.47	1.055	47.6
55.0	0.960	1.089	28.7
68.5	0.560	1.128	27.4
90.5	0.280	1.201	22.0
134.8	0.116	1.240	34.5
181.4	0.0567	1.306	53.0
218.5	0.0294	1.507	42.5
			Average 35.0 $\pm$ 9.5
(3) 0.0005% Triton X-100			
$i, \mu A$	$\tau_1, sec$	$\tau_\infty^{1/2}/i\tau_1^{1/2}$	$k, sec^{-1}$
20.2	3.29	1.658	0.216
31.8	1.14	1.730	0.438
34.0	0.88	1.825	0.346
53.8	0.31	1.919	0.364
			Average 0.341 $\pm$ 0.063

$i\tau_\infty^{1/2}$  has been corrected for spherical diffusion and for charging of the electrical double-layer.  
 $i\tau_\infty^{1/2} = 5.60 \times 10^{-5}$  amp. sec<sup>1/2</sup>.

calculation of the rate constant, it was assumed that the main contribution to the excess of the first transition time resulted from the first chemical step and that the contribution from the second chemical step was negligibly small because the present chronopotentiometric constants are below the theoretical value for  $n=2$ . The value of  $i\tau_{\infty}^{1/2}$  was calculated from the Sand equation<sup>10)</sup> for  $n=2$ ,  $D=1.34 \times 10^{-5}$  cm<sup>2</sup>/sec, and  $A=0.0605$  cm<sup>2</sup>.

As seen from the table, the rate constant for the solution without Triton X-100 is smaller than that for the solution with 0.0002% Triton X-100, and this result seems to be against the prediction from the polarographic studies. The reason may be due to the streaming effect which was observed with the solution without Triton X-100.

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