Complex Dynamical Behavior in the Oxidation of Hydroxylamine by Bromate

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Abstract

Complex dynamical behavior has been observed in the oxidation of hydroxylamine by bromate in acidic sulfate medium. The reaction shows clock type kinetics in closed conditions and an aperiodic oscillations if gaseous products are removed from the system with a constant flow-rate. The reduction kinetics of bromate ions with excess hydroxylamine has been studied in the presence of allyl alcohol. The observed pseudo-first-order rate constant k_{obs} has been found to follow the expression

$$k_{obs} = \frac{kK_1[H^+][\text{hydroxylamine}]}{(1 + K_1[H^+])K_2}$$

where [hydroxylamine] is total initial hydroxylamine concentration, $K_1 = 0.5\ M^{-1}$, $K_2 = 10^6\ M^{-1}$, and $k = 2.57 \times 10^3\ M^{-1}\ s^{-1}$ at 298.15 K and $I = 2.0$ M.

The rate constant for the bromine oxidation of hydroxylamine in sulfuric aqueous solution has been determined. © 1994 John Wiley & Sons, Inc.

Introduction

Exotic kinetic behavior has been found in both iodate and periodate oxidations of hydroxylamine. In acidic medium the oxidation of hydroxylamine by iodate or periodate ion is an oligo-oscillatory reaction [1]. Iodide ion concentration shows several extrema as a function of time. When these reactions take place in a continuous flow stirred-tank reactor (CSTR) and the pH is not kept constant, but changes freely, pH regulated oscillation is observed under favorable conditions [2,3]. The iodate-hydroxylamine oscillator has a number of fascinating features, one of them is extremely long period of oscillation, 2–6 h. Iodine appears as an intermediate during the oscillation and its concentration changes periodically. The reaction between iodine and hydroxylamine is, therefore, an important component process of the oscillatory reaction and was also studied [4–6].

No kinetics studies have been performed on the oxidation of hydroxylamine by bromate. We describe the dynamical behavior of this reaction and report here a kinetic and mechanistic study of this reaction.

Experimental

All reagents (Merck) were of the highest purity available and were used without further purification. Stock solutions were prepared with deionized water by dissolving accurately weighed amounts of chemicals.

The reduction kinetics of bromate ions with hydroxylamine in the medium of H_2SO_4 was followed polarographically, the limiting diffusion current of bromate

ions at $-1,3$ V against saturated mercurous sulfate electrode (MSE) was recorded as a function of the time. Measurements were done on an OH-105 and LP-7 type polarographs in a Kalousek cell with a thermostated mantle piece and with a dropping mercury electrode. The temperature was kept constant to within $\pm 0.1°C$. The reaction solution was deaerated by bubbling nitrogen. $NaHSO_4$ was used to adjust the ionic strength. The reaction system was also studied spectrophotometrically: the time dependence of the absorbancy at 400 nm, corresponding to the absorption maximum of bromine ($\epsilon = 172$ cm^{-1} M^{-1}) was recorded on a Specord UV VIS apparatus (Carl Zeiss, Jena).

Stopped-flow experiments were carried out using an Aminco-Morrow instrument modified by On-Line systems. The consumption of bromine was measured at 400 nm. In order to reach pseudo-first-order conditions an excess of $NH_3{}^+OH$ over bromine was employed.

The physical method of removal of gaseous products from the reaction system consisted simply in bubbling of the solution with nitrogen. The reaction proceeded in a cylindrical glass vessel (diameter 3.5 cm height 7.2 cm), the volume of the reaction solution was 20 cm^3. The rate of flow of the nitrogen was measured by a flowmeter of the type TG 400 GDR. In both closed batch and nitrogen flow experiments a bright platinum electrode and a mercurous sulfate reference electrode were used to monitor redox potential. Potentiometric measurements were performed with a Radelkis OH-105 polarograph.

When hydroxylamine was in excess, bromate was reduced completely to bromide, while a majority of the hydroxylamine was oxidized to dinitrogen oxide and no nitrite ion was detected as a reaction product.

$$2BrO_3{}^- + 6NH_2OH \longrightarrow 2Br^- + 3N_2O + 9H_2O$$
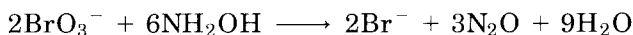
Results and Discussion

Reaction Dynamics

The closed reaction system of sodium bromate and hydroxylamine sulfate shows a peculiar kinetic behavior. The reaction dynamics are very complex, being dependent both on the ratio of the initial concentrations of bromate and hydroxylamine and on the initial acid concentrations. When $[BrO_3{}^-]_0/[NH_2OH]_0 = 1$ the potential platinum redox electrode shows several extrema as a function of time, although only one oxidant and one reductant are initially present (Fig. 1). An increase of the hydrogen ion concentration leads to the disappearance of this peculiar phenomenon (Fig. 1, curve e).

The closed reaction system of sodium bromate and hydroxylamine behaves like a clock reaction, exhibiting a pronounced increase in absorbance at a time that depends strongly upon the reactant concentrations and sulfuric acid concentrations. The increase in absorbance in the visible range indicates the formation of bromine. The induction period decreases with the increasing concentration of H^+ (Fig. 2a,b). The accumulation of bromine is transient and Br_2 disappears in a reaction with the remaining hydroxylamine (Fig. 2(a)). At higher ratio of bromate and hydroxylamine $[BrO_3{}^-]_0/[NH_2OH]_0 = 20$ bromine becomes the final product (Fig. 2(c)).

The largest set of clock systems has the general form in equations (A)–(C) [7]. This set of equations summarizes the common characteristics of the halogen based systems,
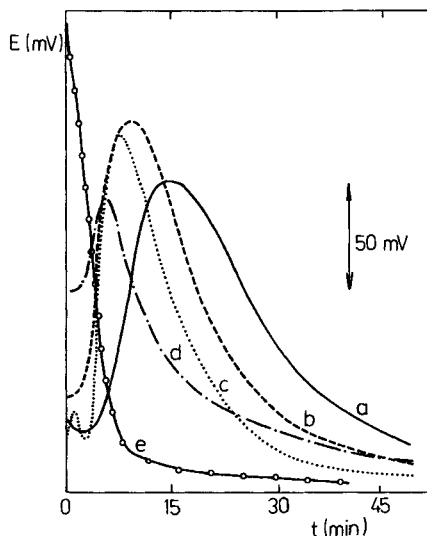
Figure 1. Redox potential traces at different acid concentrations in a closed reactor. Initial concentrations: $[NH_2OH]_0 = 5 \times 10^{-3}$ M, $[NaBrO_3]_0 = 5 \times 10^{-3}$ M. (a) $[H_2SO_4]_0 = 0.2$ M; (b) $[H_2SO_4]_0 = 0.3$ M; (c) $[H_2SO_4]_0 = 0.4$ M; (d) $[H_2SO_4]_0 = 0.5$ M; and (e) $[H_2SO_4]_0 = 1$ M.

X = halogen, A = reductant, e.g., NH_2OH

(A) $$XO_3^- + 3A_{Red} \xrightarrow{\text{very slow}} X^- + 3A_{ox}$$

(B) $$XO_3^- + 5X^- + 6H^+ \xrightarrow{\text{slow}} 3X_2 + 3H_2O$$
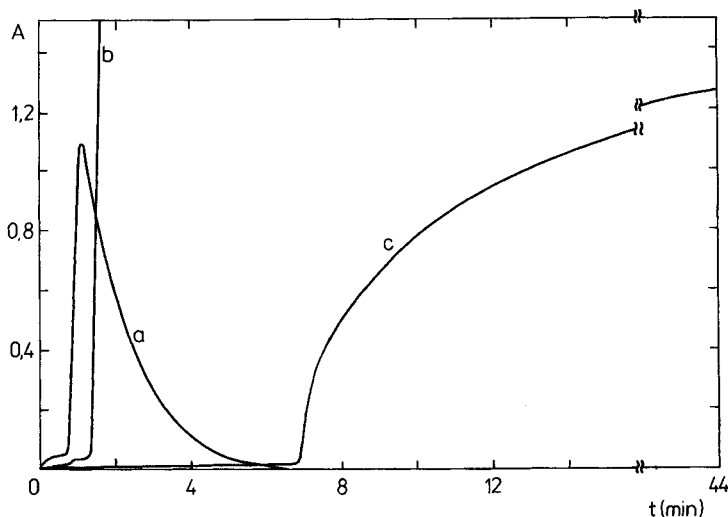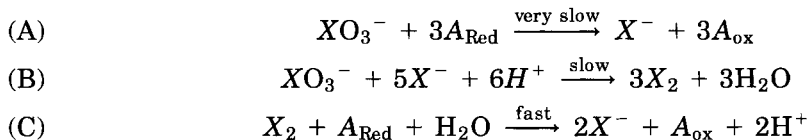
(C) $$X_2 + A_{Red} + H_2O \xrightarrow{\text{fast}} 2X^- + A_{ox} + 2H^+$$

Figure 2. Absorbance traces (400 nm) for the bromate-hydroxylamine reaction. $[NH_2OH]_0 = 2.8 \times 10^{-2}$ M, $[NaBrO_3]_0 = 0.1$ M. (a) $[H_2SO_4]_0 = 8 \times 10^{-2}$ M; (b) $[H_2SO_4]_0 = 6 \times 10^{-2}$ M; and (c) $[NH_2OH]_0 = 5 \times 10^{-4}$ M, $[NaBrO_3]_0 = 1 \times 10^{-2}$ M, $[H_2SO_4]_0 = 0.1$ M, 298.15 K.

When the physical removal of the volatile components is introduced into the system
by a constant inert gas bubbling (pseudo CSTR) the dynamics becomes even more
complicated.

After the first large reproducible maximum (the preoscillatory period) an aperiodic-
ity appears in the redox potential traces (Fig. 3). The system is sensitive to changes in
the sulfuric acid concentration. At 0.2 M H_2SO_4 aperiodic behavior is not observed. If
sulfuric acid in the system is replaced by nitric acid the aperiodic oscillations change to
nearly periodic oscillations. Under "exactly the same" initial conditions, the character
of the oscillations may be a little different.

Redox Reaction between Bromate and Hydroxylamine (A)

Kinetics in the absence of scavenger of allyl alcohol. In the presence of an excess of
hydroxylamine the reaction shows autocatalytic behavior (Fig. 4(a)), because bromate
ions are consumed not only by the reaction with hydroxylamine but also with bromide
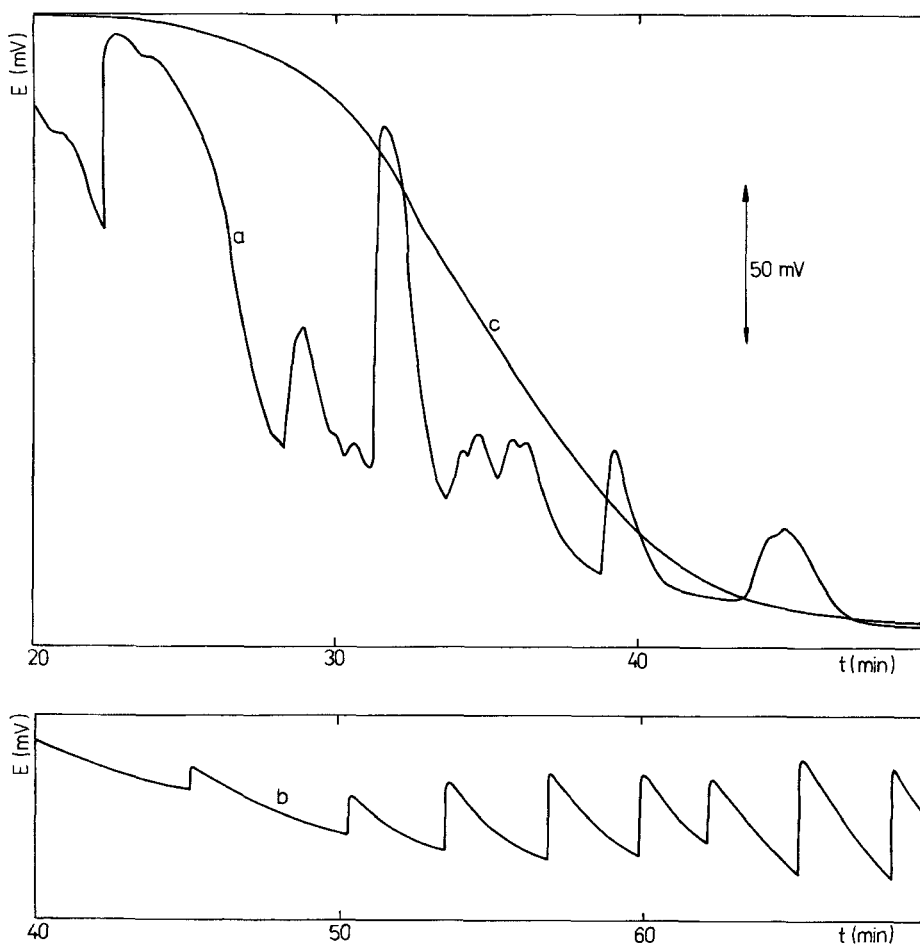

Figure 3. Aperiodic oscillations in the potential of a platinum redox electrode
$[NH_2OH]_0 = 2 \times 10^{-2}$ M, $[NaBrO_3]_0 = 0.1$ M. (a) $[H_2SO_4]_0 = 0.4$ M; (b) $[HNO_3]_0 = 0.4$ M; (c) $[H_2SO_4]_0 = 0.2$ M; and Nitrogen flow rate $= 300$ cm^3 min^{-1}, 298.15 K.

ions. Since the sigmoid curves are symmetrical, the inflection times can be determined sufficiently accurately, and the rate constants of the noncatalyzed reaction k_1 and of the catalyzed reaction k_2 can be evaluated by using the Schwartz method [8]. The rate constant $k_1 = 6 \times 10^{-4}$ s^{-1} is in accord with the rate constant of the reduction of bromate ion with hydroxylamine measured in the presence of allyl alcohol and the rate constant $k_2 = 7$ M^{-1} s^{-1} is in accord with the rate constant of the reduction of bromate with bromide (B) in 1 M H$_2$SO$_4$ [9] and at temperature 308.15 K.

Kinetics in the presence of allyl alcohol. The additional experiments were conducted in the presence of allyl alcohol. Allyl alcohol is an effective scavenger for hypobromous acid through rapid addition at the double bond of the alcohol [10]. No bromide ion is released in this reaction and consequently there is no interference from bromate-bromide reaction in the rate studies and the over-all reaction loses its autocatalytic character (Fig. 4(b)). Allyl alcohol reacts very slowly with bromate ions under the conditions of our experiments.

The time dependence of the limiting diffusion current of BrO$_3^-$ ions in the form $\ln I_0/I = f(t)$ is linear and indicates that the process is pseudo-first-order with respect to bromate ions. The value of the experimental rate constant was determined by a nonlinear regression analysis. The experimental rate constant increases linearly with hydroxylamine concentration (in the range of 0.01 to 0.4 M) and passes through the origin of coordinates, an evidence that the reaction is of the first-order also with respect to the hydroxylamine concentration. The rate equation for constant concentration of hydrogen ions, thus is

$$(1) \qquad -\frac{d[\mathrm{Br(V)}]}{dt} = k_{\mathrm{II}}[\mathrm{Br(V)}][\text{hydroxylamine}]$$

The second-order rate constant, for 1 M-H$_2$SO$_4$, is $k_{\mathrm{II}} = 1.55 \times 10^{-3}$ M^{-1} s^{-1} at 308.15 K.

The reaction is acid catalyzed, and at a constant ionic strength the rate constant increases with increasing concentration of H$^+$ ions. The actual concentration of H$^+$ ions, in the reaction solution of H$_2$SO$_4$, NaHSO$_4$, and NH$_2$OH $\cdot$ (1/2) H$_2$SO$_4$ was
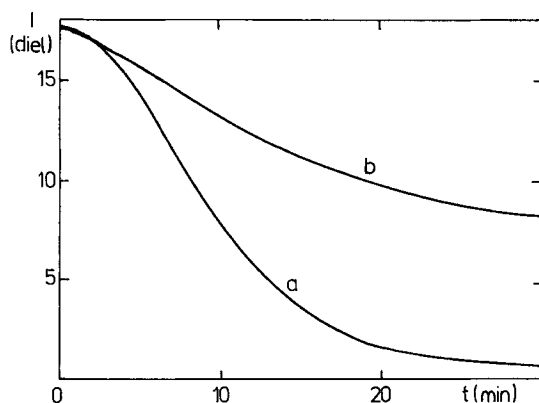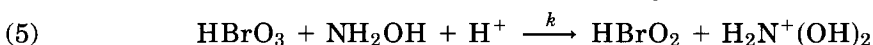

Figure 4. Time change of the concentration of BrO$_3^-$ ions in the reaction with hydroxylamine in 1 M H$_2$SO$_4$. Initial concentrations: [NH$_2$OH]$_0$ = 0.5 M, [NaBrO$_3$]$_0$ = 5 $\times$ 10^{-4} M. (a) Without allyl alcohol and (b) [allyl alcohol]$_0$ = 10^{-3} M 308.15 K.

calculated by using equation

$$(2) \quad [H^+] = \frac{1}{2} \cdot \left(C_1 - \frac{C_3}{2} - K_A \right) + \left[\left(\frac{1}{2} C_3 - C_1 + K_A \right)^2 + 4K_A(2C_1 + C_2) \right]^{1/2}$$

where C_1, C_2, and C_3 are concentrations of H_2SO_4, $NaHSO_4$, and $NH_2OH \cdot (1/2) H_2SO_4$, respectively, and K_A is dissociation constant of $NaHSO_4$ (K_A ca. 0,1) [11,12].

We suggest the following probable mechanism

$$(3) \qquad\qquad\qquad BrO_3^- + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} HBrO_3$$

$$(4) \qquad\qquad\qquad NH_2OH + H^+ \underset{}{\overset{K_2}{\rightleftharpoons}} NH_3^+OH$$

$$(5) \qquad HBrO_3 + NH_2OH + H^+ \overset{k}{\longrightarrow} HBrO_2 + H_2N^+(OH)_2$$

The equilibrium (3) and (4) are rapid, $K_1 = 0.5$ M^{-1} [13] and $K_2 = 10^6$ M^{-1} [14], reaction (5) is rate-determining. Further steps of the conversion of $HBrO_2$ and $H_2N^+(OH)_2$ are rapid and do not influence the kinetics of the whole process. By assuming that the total Br(V) and hydroxylamine concentrations are $[BrO_3^-]$ + $[HBrO_3]$ and $[NH_2OH]$ + $[NH_3^+OH]$, respectively, and taking into account that $K_2[H^+] \gg 1$, it can be deduced that

$$(6) \qquad\qquad\qquad 1/k_{II} = K_2/k + K_2/kK_1[H^+].$$

The dependence of $1/k_{II}$ on $1/[H^+]$ was found experimentally to be linear and the rate constant k for reaction (5) was calculated from the slope of this dependence. This dependence measured at three different temperature 298.15 K, 308.15 K, and 318.15 K leads to the following values of k, M^{-1} s^{-1} (ionic strength = 2.0 M) 2.57 × 10^3, 6.2 × 10^3, 18.9 × 10^3, respectively.

The corresponding activation parameters were determined as $\Delta H^{\neq} = 76 \pm 2$ kJ mol^{-1} and $\Delta S^{\neq} = -75 \pm 3$ JK^{-1} mol^{-1}.

The comparison of the rate constants of the BrO_3^- − NH_2OH and the IO_3^- − NH_2OH reactions is not possible because the latter reaction was not measured. In the study of oligooscillatory behavior in the IO_3^- − NH_2OH reaction, Beck and Rabai [1] used an estimated rate constant ($k' = 0.15$ M^{-1} s^{-1}) to simulate the observed behavior.

Our value of activation entropy is closed to the activation entropy for the oxidation of hydrazoic acid by bromate ion ($\Delta S^{\neq} = -78$ JK^{-1} mol^{-1}) where interaction among $HBrO_3$, N_3H, and H^+ is also considered in rate determining step [15].

The Oxidation of Hydroxylamine by Bromine (C)

The fast reaction of bromine with hydroxylamine was investigated by stopped-flow method. The linear plots of ln A_t against t indicate that the consumption of bromine during the reaction follows pseudo-first-order kinetics in excess of hydroxylamine. The measured rate constant increases linearly with hydroxylamine concentration and passes through the origin of coordinates, an evidence that the reaction is of the first order also with respect to the hydroxylamine. The slope of this dependence gives the rate constant $k_{Br} = 1.7 \times 10^3$ M^{-1} s^{-1} (1 M H_2SO_4, 298.15 K). We found that added H^+ ions have a small inhibitory effect on k_{Br}.

A more detailed study is needed in order to deduce the mechanism of the oxidation of hydroxylamine by bromine.

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