KINETICS AND MECHANISM OF THE OXIDATION OF ACETALDEHYDE BY BROMATE ION IN AQUEOUS PERCHLORIC ACID

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ABSTRACT

The stoichiometry, kinetics and mechanism of the oxidation of acetaldehyde by bromate ion in aqueous perchloric acid have been investigated. The reaction follows the empirical rate law;

$$-d[CH_2CHO]/dt = \{a + b[H+]\}[CH_3CHO][BrO_3^-]$$

Where $a = 2.14 \times 10^{-2} M^{-1} s^{-1}$, $b = 2.71 \times 10^{-1} M^{-2} s^{-1}$ *at* 23.0 ± 0.1°*C,* $[H^+] = 0.05\text{-}0.15M$ *and* $I = 1.0M(NaClO_4)$*. The mechanism of the reaction is discussed in terms of the outer-sphere mechanism.*

INTRODUCTION

Several studies into the redox reactions involving metal ion complexes and a wide range of substrates have been reported[1-11]. Our interest has mostly been focused on the reactions involving oxyanions and metal ion complexes[1-3,6]. The reactions of oxyanions with some aldehydes and ketones have also started receiving some attention[12-15]. In order to gain more information into their chemical and biochemical activities, we have initiated kinetic studies into the reactions of aliphatic aldehydes and ketones with selected oxyanions[16,17]. In this paper, we report the results of the reaction between CH_3CHO and the versatile oxidizing agent, bromate ion[1,3,18,19,21].

EXPERIMENTAL

Reagents

Standard solutions of acetaldehyde (Analar) were usually prepared before use. Sodium bromate (Analar) solution was prepared and standardized according to the method described by Birk and Kozub[18,19]. $HClO_4$ was used as the acid medium and $NaClO_4$ was used to maintain a constant ionic strength.

Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titration, using the mole ratio method. Reaction mixtures containing CH_3CHO and BrO_3^- solutions at $[H^+] = 0.1M$ and $I = 1.0M$ ($NaClO_4$), were allowed to stand until the reaction had gone to completion. The absorbances of the solutions were measured at 390nm and the stoichiometry was evaluated from the plot of the absorbance versus mole ratio.

Kinetic measurements

All rate measurements were made using Unicam SP 1750 uv-visible spectrophotometer. The reaction rates were monitored under pseudo-first order conditions, by following the rate of change of absorbance of the reaction mixture at 390nm. The pseudo-first order rate constants were obtained from the slope of the plots of $\log(A_t - A_0)$ versus time (where A_t and A_0 are the absorbances of the reaction mixtures at time t and time zero respectively). The temperature was kept constant at 23.0 ± 0.1°C for all the runs, $[H^+] = 0.1M$, $I = 1.0M$ ($NaClO_4$), unless otherwise stated.

RESULTS AND DISCUSSION

Stoichiometry

The stoichiometry of the reaction between acetaldehyde and bromate ion was found to be in the ratio 5:2, so that the overall equation can be written as;

$$5CH_3CHO + 2BrO_3^- + 2H^+ \rightarrow 5CH_3COOH + Br_2 + H_2O \quad \text{.......... (1)}$$

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A similar stoichiometry was reported for the reaction between HCHO and $Mn0_4^-$[16] and for that between HCHO and $Br0_3^-$[17]. The products of the reaction were qualitatively identified [1,3,17]. The ether extract of the reaction mixture gave an effervescence in the presence of $NaHCO_3$. The evolved gas turned lime water milky, suggesting CO_2, which confirmed the presence of a carboxylic acid. The brownish yellow colour of the reaction mixture was decolorized in the presence of cyclohexene, also suggesting Br_2 as one of the reaction products.

Table 1: Second order rate constants for the oxidation of acetaldehyde by bromate ion in aqueous perchloric acid at 23.0 ± 0.1°C $[BrO_3^-] = 0.42M$, λ_{max} = 390nm.

$10^2[CH_3CHO]$, (M)	$[H^+]$, (M)	I, (M)	10^2k_2, ($M^{-1}s^{-1}$)
0.8	0.1	1.0	5.73
1.0	0.1	1.0	5.65
1.2	0.1	1.0	5.77
1.5*	0.1	1.0	5.57
1.7	0.1	1.0	5.55
1.9	0.1	1.0	5.51
2.5	0.1	1.0	5.78
1.5	0.05	1.0	3.47
1.5	0.15	1.0	6.40
1.5	0.2	1.0	7.13
1.5	0.3	1.0	11.00
1.5	0.1	0.4	4.07
1.5	0.1	0.52	4.89
1.5	0.1	0.75	5.02
1.5	0.1	1.0	5.10
1.5	0.1	1.25	5.37
1.5	0.1	1.5	5.77
1.5	0.1	2.0	5.99
1.5	0.1	2.2	6.77

Rate law

Pseudo-first order rate constants, k_o, show a linear dependence on $[CH_3CHO]$ at constant $[H^+]$, from which the second order rate constants, k_2, were evaluated (Table 1). The linearity of the pseudo-order rate plots and the plot of log k_o versus log$[CH_3CHO]$, indicates that the reaction, under our experimental conditions, is first order each in $[CH_3CHO]$ and $[Br0_3^-]$. Thus, the rate equation for the reaction is

$$-d[CH_3CHO]/dt = k_2[CH_3CHO][Br0_3^-] \quad \text{...........(2)}$$

$$k_2 = (5.65 + 0.11) \times 10^{-2}M^{-1}s^{-1}$$

Effect of acid

The effect of acid on the rate of the reaction was determined by keeping all other conditions constant while varying the acid concentration in the range 0.05 - 0.15M. A plot of k_2 versus $[H^+]$ was linear (r = 0.98), with a positive intercept, suggesting that k_2 vary with $[H^+]$ according to equation (3)

$$k_2 = a + b[H^+] \quad \text{.....................(3)}$$

$$a = 2.14 \times 10^{-2}M^{-1}s^{-1}, \quad b = 2.71 \times 10^{-1}M^{-2}s^{-1}$$

When the expression for k_2 in equation (3) is substituted into equation (2), the rate equation for the reaction becomes

$$-d[CH_3CHO]/dt = \{a + b[H^+]\}[CH_3CHO][Br0_3^-] \quad \text{................(4)}$$

Effect of added anions

The effect of added formate and nitrate ions on the rate of the reaction was investigated and the results, as presented in Table 2, show that both anions enhanced the rate. The enhancement of the rate is in the order $k_o(HCOO^-) > k_o(NO_3^-)$, similar to that observed for the $HCHO/Br0_3^-$ system[17]. Least squares plots of k_o versus $[X^-]$, (X^- = HCOO or NO_3), were linear and fitted into equation (5).

$$k_o = p + q[X^-] \quad \text{...........................(5)}$$

where $p(HCOO^-) = 7.27 \times 10^{-4}s^{-1}$,
$q(HCOO^-) = 8.54 \times 10^{-2}M^{-2}s^{-1}$
$p(NO_3^-) = 7.11 \times 10^{-4}s^{-1}$,
$q(NO_3^-) = 2.28 \times 10^{-2}M^{-2}s^{-1}$

Table 2: Anion dependent rate constant for the oxidation of acetal dehyde by by bromate ion in aqueous perchloric acid $[H^+] = 0.1M$, $[Br0_3^-] = 0.32M$, $[CH_3CHO] = 1.5 \times 10^{-2}M$, $I = 1.0M$ ($NaCl0_4$), Temp = 23 ± 0°C λ_{max} = 390nm

$10^3[X^-]$, (M)	10^2k_2, ($M^{-1}s^{-1}$)	
	($HCOO^-$)	(NO_3^-)
3.0	6.63	-
5.0	7.85	5.67
7.0	8.75	6.30
10.0	10.50	6.47
15.0	-	6.93
20.0	-	7.59

Effect of ionic strength

The effect of ionic strength on the rate of the reaction was studied over the range 0.40 - 2.2M, using $NaCl0_4$, while keeping all other conditions constant. The results presented in Table 1, show that the rate constants increase with increase in ionic strength, suggesting a positive Bronsted-Debye[22,23] salt effect.

Reaction mechanism

The rates of redox reactions of many oxyanions show strong dependence on acid concentration[1,3,24]. The $[H^+]$ terms commonly encountered in reactions of $Br0_3^-$,[18,19,21,25-27], has been attributed in the formation of $HBr0_3$, which reacts with the reductant in the rate determining step. In reaction systems[17,26] similar to the titled reaction, the H^+ dependence has also been ascribed to the substantial and rapid hydration of the aliphatic aldehydes and ketones. From the above reasoning, the reaction scheme proposed below, accounts for the experimental results.

$$CH_3CHO + H_20 \xrightarrow{K_2} CH_3CH(OH)_2 \quad ...(6)$$

$$Br0_3^- + H^+ \xrightarrow{K_1} HBr0_3^- \quad ....(7)$$

$$CH_3CH(0H)_2 + HBr0_3 \xrightarrow{k_1} CH_3COOH + H_20 + HBr0_2 \quad ....(8)$$

$$CH_3CH(OH)_2 + Br0_3^- \xrightarrow{k_2} CH_3COOH + H_20 + Br0_2^- \quad ....(9)$$

$$CH_3CHO + HBr0_3 \xrightarrow{k_3} CH_3COOH + HBr0_2 \quad ....(10)$$

$$CH_3CHO + Br0_3^- \xrightarrow{k_4} CH_3COOH + Br0_2^- \quad ....(11)$$

$$Br0_2^- + H^+ \rightarrow HBr0_2 \text{ (Fast)} \quad ....(12)$$

$$2HBr0_2 + 3CH_3CH0 \rightarrow 3CH_3COOH + Br_2 + H_20 \text{ (Fast)} \quad ....(13)$$

From the above, the rate of loss of CH_3CHO is given by equation (14)

$$-d[CH_3CHO]/dt = \{[k_2K^1_H + k_4) + (k_1K_1K^1_H + k_3K_1)[H^+]\} [CH_3CHO] [Br0_3^-] \quad ....(14)$$

where $k^1_H = K_H[H_20]$ and K_1 has been reported as *ca* $10^{-11}M^{-2}$ [23].

Equation (14) is analogous to equation (4) and is consistent with the experimental results.

A key point of interest is whether this reaction occurs via the inner- or the outer-sphere mechanism or a combination of both. Cases have been reported[18,21], where the reaction of $Br0_3^-$ has been explained in terms of parallel outer- and inner-sphere pathways, with the acid dependent path occuring via the outer-sphere mechanism. In some other cases[19], the $Br0_3^-$ reduction by Fe(III) complexes involve two parallel outer-sphere paths and that by $IrCl_6^{2-}$, involve essentially diffusion controlled outer-sphere processes. This issue was addressed as follows;

(a) The spectra of the reaction mixtures taken 2 minutes after initiation of the reaction did not show any shift in the λ_{max} suggesting that there is no inner-sphere complex formation[1,17]. This observation indicates the occurrence of the outer-sphere mechanism.

(b) Addition of acrylonitrile to the partially oxidized reaction mixture of CH_3CHO and BrO_3^- showed no gel formation, even on addition of large excess of methanol[29,30]. This suggests the absence of free radicals in the reaction.

(c) From Table 2, it can be observed that the rate of the reaction was enhanced by the presence of added formate and nitrate ions in the following order; $k_o(HCOO^-) > k_o(NO_3^-)$. This anion catalysis is in support of the outer-sphere mechanism[3,24,31]. Similar anion catalysis has been observed for other BrO_3^- systems[1,27].

(d) A Lineweaver-Burk modification[3,32] of Michaelis-Menten plot of $1/k_o$ versus $1/[CH_3CHO]$ was linear with an insignificant intercept. This also suggests that inner-sphere intermediates are unimportant in this reaction.

From the above reasoning (a) - (d), it can be inferred that the spectroscopic and catalytic evidence are in support of the occurrence of the outer-sphere mechanism in the titled reaction.

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