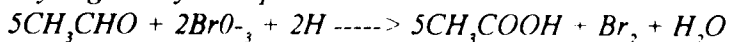


# KINETIC STUDIES OF THE OXIDATION OF ACETALDEHYDE WITH BROMATE ION IN AQUEOUS PERCHLORIC ACID

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## ABSTRACT

The oxidation reaction of acetaldehyde with bromate ion has been investigated in aqueous perchloric acid. The stoichiometry is given by the equation below:



The reaction obeys the empirical rate law:  $-d[\text{CH}_3\text{CHO}]/dt = \{a + b[\text{H}^+]\} [\text{CH}_3\text{CHO}]^2 [\text{BrO}_3^-]$   
 $a = 3.45 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ,  $b = 1.6 \times 10^{-2} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$  at  $27.0 \pm 1.00^\circ\text{C}$ ,  $[\text{H}^+] = 0.03 - 0.15 \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3} (\text{NaClO}_4)$  and  $\lambda = 410 \text{ nm}$

The rate law suggests that the reaction occurs via two pathways, involving protonated and unprotonated species of bromate ion. The inhibition of the rate by the presence of added  $\text{CH}_3\text{COO}^-$  ion and the linearity of the plots of  $1/k_{\text{obs}}$  versus  $1/[\text{CH}_3\text{CHO}]^2$  and  $1/k_{\text{obs}}$  versus  $1/[\text{BrO}_3^-]$  are suggestive of outer sphere mechanism while the second order dependence on  $[\text{CH}_3\text{CHO}]$  is also indicative of an inner sphere mechanism. No clear cut mechanism is yet proposed for this reaction.

## INTRODUCTION

There has been a lot of interest in the study of the oxidation-reduction reactions involving oxyanions with metal ion complexes<sup>(1-10)</sup>. Attention has also begun to be focused on their reactions with some aliphatic and aromatic aldehydes and ketones<sup>(11-14)</sup>. Recently, we have embarked on the study of the reactions of formaldehyde and acetaldehyde with some reagents like permanganate and dichromate ions<sup>(15)</sup> and bromate ion<sup>(16)</sup>. It is in continuation for the search for more knowledge into the reactions of these systems that we report the results of the investigation into the reaction of acetaldehyde with the versatile oxidizing agent, the bromate ion<sup>(2,3,8,9,16-19)</sup>.

## EXPERIMENTAL

Sodium bromate (BDH Analar) solution was prepared and standardized as described by Birk and Kozub<sup>(2,3)</sup>. Solutions of perchloric acid and sodium perchlorate (Analar) were standardized titrimetrically and gravimetrically respectively. Standard solutions of redistilled acetaldehyde were usually prepared before use. All other reagents were used without further purification.

## Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titration, using the mole ratio method. Reaction mixtures containing acetaldehyde and bromate solutions at constant hydrogen ion concentration and ionic strength were allowed to stand until the reaction had gone to completion. The absorbances of the solutions were measured at 410nm and the stoichiometry was evaluated from the plot of absorbance versus mole ratio.

## Kinetic Measurements

All kinetic measurements were made under pseudo-first order conditions for each of the reactants, by monitoring the rate of change of absorbance of the reaction mixture at 410nm using SP20 spectrophotometer. Pseudo-first order rate constants in each case were obtained from the plots of  $\log(A_t - A_0)$  versus time, which were linear to about 80% at various reactant concentrations (where  $A_t$  and  $A_0$  are absorbances at time  $t$  and at time zero respectively). The temperature was kept constant at  $27.0 \pm 1.0^\circ\text{C}$  and the ionic strength maintained constant at  $0.5 \text{ mol dm}^{-3} (\text{NaClO}_4)$ .

**RESULTS**

**Stoichiometry**

The stoichiometric studies showed that the overall reaction may be represented by equation (1), which is similar to that proposed for the reaction between acetaldehyde and  $MnO_4^{-(15)}$  and that between formaldehyde and  $BrO_3^{-(16)}$

$$5CH_3CHO + 2BrO_3^- + 2H^+ \rightarrow 5CH_3COOH + Br_2 + H_2O \dots(1)$$

**Product Analysis**

The products of the reaction were identified by chemical tests as follows; the ether extract of the reaction mixture gave an effectiveness in the presence of  $NaHCO_3$ . The evolved gas turned lime water milky, suggesting carbondioxide, which confirmed the presence of carboxylic acid as one of the products. The colour of the reaction mixture was decolorized in the presence of cyclohexene, also suggesting bromine as one of the reaction products.

**Determination of Order**

Pseudo-first order rate constants obtained from plots of  $\log(A_t - A_o)$  versus time showed a linear dependence on each of the reactant concentrations. Values of the observed rate constants are given in Table 1. A plot of  $\log k_{obs}$  versus  $\log [CH_3CHO]$  was linear with a slope of 1.93, indicating that the reaction is second order in  $[CH_3CHO]$ . The second order was confirmed by plotting  $k_{obs}$  versus  $[CH_3CHO]^2$ , which was linear and passed through the origin.

A plot of  $\log k_{obs}$  versus  $\log [Br_3^-]$  was linear ( $r = 1.12$ ) indicating first order in  $[Br_3^-]$ . This first order was also confirmed by a plot of  $k_{obs}$  versus  $[Br_3^-]$ , which gave a straight line passing through the origin.

The calculated values of  $k_3$  from the  $k_{obs}$  in each case were fairly constant, consistent with third order overall for the reaction. Thus the rate equation for the reaction is represented by equation (2).

$$-d [CH_3CHO] / dt = k_3 [CH_3CHO]^2 [Br_3^-] \dots(2)$$

$$k_3 = 6.56 \pm 0.565 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

**Acid Dependence**

The acid dependence on the rate of this reaction was investigated at constant  $[CH_3CHO]$ ,  $[Br_3^-]$  and

ionic strength of  $0.5 \text{ mol dm}^{-3}$  ( $NaClO_4$ ) at  $27.0 \pm 1.0^\circ C$ . A plot of the acid dependent rate constants ( $k_H$ ) versus  $[H^+]$  was linear with a positive intercept and is shown in Figure 1. This suggests that the redox reaction occurs via two parallel pathways similar to other systems earlier investigated<sup>(9,14,20)</sup>.

Therefore, the rate equation under the experimental conditions becomes:

$$-d [CH_3CHO] / dt = \{a+b[H^+]\} [CH_3CHO]^2 [Br_3^-] \dots(3)$$

where  $a$  = intercept and  $b$  = slope.

Least square analysis of the plot of  $k_H$  versus  $[H^+]$  gave the values of  $a$  and  $b$  as follows  
 $a = 3.45 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ,  $b = 1.61 \times 10^{-2} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$   
 at  $27.0 \pm 1.0^\circ C$ ,  $\lambda_{max} = 410 \text{ nm}$ .

**Effect of added acetate ion**

The effect of added acetate ion on the rate of the reaction was studied and the results presented in Table 2. The values of the rate constants were found to decrease with increase in the concentration of the added acetate ion. A plot of  $1/k_x$  versus  $[CH_3COO^-]$  was found to be linear and fitted into equation (4)

$$1/k_x = p + q [x^-] \dots(4)$$

where  $k_x$  is acetate ion dependent rate constant,  $p$  is the intercept and  $q$  is the slope. The least square analysis of the plot gave the values of  $p$  and  $q$  as follows:

$$p = 25 \text{ mol dm}^{-3} \text{ S and } q = 1.15 \times 10^3 \text{ S}$$

**Table 1: Rate Constants for the Oxidation Reaction of Acetaldehyde with bromate ion.**

$[H^+] = 1.0 \text{ moldm}^{-3}$	$I = 0.50 \text{ mol dm}^{-3} (NaClO_4)$		
$\lambda_{max} = 410 \text{ nm}$	$Temp = 27.0 \pm 1.0^\circ C$		
$10^2 [CH_3CHO], \text{ moldm}^{-3}$	$10^2 [Br_3^-], \text{ moldm}^{-3}$		
$10^3 k_{obs}, \text{ s}^{-1}$	$k_3, \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$		
1.5	10.0	1.65	7.30
2.0	10.0	2.52	6.30
2.5	10.0	4.25	6.80
3.0	10.0	6.67	7.41
3.5	10.0	9.14	7.46
4.0	10.0	10.56	6.60
4.5	10.0	12.58	6.21
5.0	10.0	14.09	5.64
10.0	1.0	6.40	6.40
10.0	1.5	9.90	6.60
10.0	2.0	12.80	6.40
10.0	2.5	17.40	6.96
10.0	3.0	18.82	6.07
10.0	4.5	25.60	5.69

**Table 2: Acetate Ion dependent rate Constants for the Oxidation Reaction of Acetaldehyde with bromate ion.**

[H<sup>+</sup>] = 0.10 mol dm<sup>-3</sup>, [CH<sub>3</sub>CHO] = 0.035 mol dm<sup>-3</sup>  
 [BrO<sub>3</sub><sup>-</sup>] = 0.10 mol dm<sup>-3</sup>, I = 0.50 mol dm<sup>-3</sup> (NaClO<sub>4</sub>)  
 Temp = 27.0 ± 1.0°C, λ<sub>max</sub> = 410 nm.

[CH <sub>3</sub> COO <sup>-</sup> ], mol dm <sup>-3</sup>	10 <sup>3</sup> k <sub>p</sub> S <sup>-1</sup>
0.03	11.52
0.05	11.44
0.07	10.95
0.09	9.68
0.11	7.45
0.13	6.55
0.15	4.09

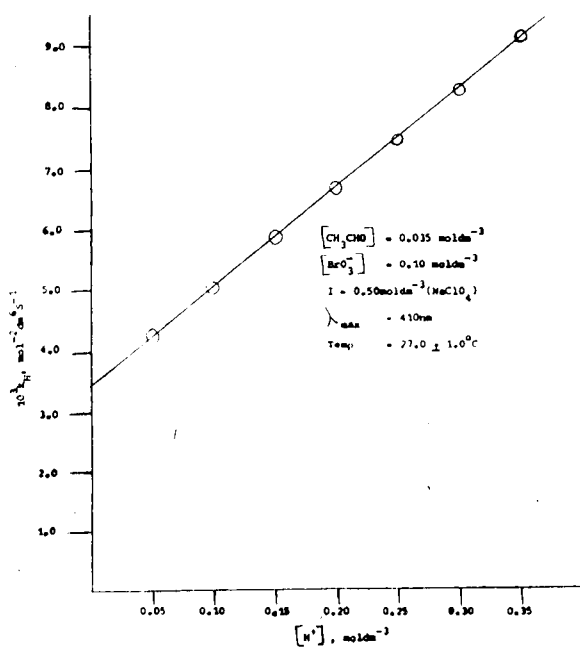


Figure 1: Plot of  $k_H$  versus  $[H^+]$  for the oxidation reaction of  $CH_3CHO$  with  $BrO_3^-$

**Discussion**

The rate of oxidation-reduction reactions of many oxyanions have been shown to strongly on acid concentration<sup>(19,20,21)</sup>. The [H<sup>+</sup>] dependence in this reaction suggests that it occurs through two pathways-involving protonated and unprotonated species of the bromate ion<sup>(14,16)</sup>. The observed increase in the rate due to increase in [H<sup>+</sup>] has also been ascribed to the substantial and rapid hydration of aliphatic aldehydes<sup>(11,20)</sup>, so that they react via the hydrate form.

Some redox reactions of bromate ion have been interpreted in terms of parallel outer and inner pathways<sup>(2,18)</sup>, with the acid dependent path occurring via the outer sphere mechanism. In some other cases, the bromate reduction of some Fe(II) complexes involve two parallel outer sphere pathways<sup>(3,89)</sup>.

The inhibition of the rate of this reaction by the presence of acetate ion tends to suggest that it occurs by the outer sphere mechanism<sup>(19,23)</sup>. The linearity of the plots of  $1/k_{obs}$  versus  $1/[CH_3CHO]^2$  and  $1/k_{obs}$  versus  $1/[BrO_3^-]$  is on support of the outer sphere pathway<sup>(24)</sup>.

However, most of the outer sphere redox reactions that have been studied show first order dependence on each of the reactant concentrations<sup>(8-15,20)</sup>, while those which have second order in one of the reactant concentrations, have been shown to occur by the inner sphere mechanism<sup>(1,25,26)</sup>. Therefore, the second order dependence on [CH<sub>3</sub>CHO] in this reaction is suggestive of the inner sphere mechanism.

For now, we are unable to assign any clear cut mechanism(s) for the title reaction. This will have to await further investigations into certain aspects like ionic strength dependence, dielectric constant dependence, effect of other added anions and activation parameters.

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