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# Kinetics and Mechanism of the Oxidation of Orange II by Bromate Ion in Aqueous Hydrochloric Acid Medium

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**Abstract:** The kinetics of the oxidation of orange II here and thereafter referred to as OII<sup>-</sup> by BrO<sub>3</sub><sup>-</sup> was studied in aqueous hydrochloric acid medium at an ionic strength of reaction medium,  $I = 0.50 \text{ mol dm}^{-3}$  (NaCl),  $[H^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$  (HCl) and  $T = 21 \pm 1^\circ\text{C}$ . The redox reaction displayed a stoichiometry of 2:1. The second order rate constant increases with increase in acid concentration. The rates of reaction displayed a positive salt effect. Added cations and anions inhibited the reaction rates. Results of the Michaelis – Menten plot gave no evidence of intermediate complex formation during the course of the reaction. Based on the results obtained, the outersphere mechanism is proposed for the reaction.

**Keywords:** Orange II, Kinetics, Mechanism, Bromate.

## 1. Introduction

Azo dyes are characterized by the presence of one or more azo group ( $-N=N-$ ) in association with two or more aromatic or heterocyclic system [1,2,3,4]. Azo dyes have been studied widely because of

their excellent thermal and optical properties in applications such as optical recording medium [5], toner [6,7], inkjet printing [5], and oil-soluble light fast dyes. Azo dye like Orange II, is used in many industries like textile, leather, plastics, paper, food and cosmetics as a colouring agent. In view of these and other applications, there is need for investigation of the kinetics and mechanism of its electron transfer reactions.

Bromate, an oxyanion, is a versatile oxidizing agent. It oxidizes and is itself reduced to bromide. Bromate ion reaction with real and synthetic gastric juices has been documented [6]. In this work, we report our finding on the oxidation of  $\text{OII}^-$  by  $\text{BrO}_3^-$  in aqueous acid medium with a view to providing sufficient information on the kinetic and mechanism of this reaction.

## 2. Materials and Methods

The chemicals used were of analytical grade and were used without further purification. Standard solution of  $\text{OII}^-$  was prepared by dissolving a 0.1876 g in 250  $\text{cm}^3$  volumetric flask using distilled water. Sodium bromate solution was prepared by dissolving known quantity in distilled water. All other reagents used were of analytical grade.

The stoichiometry of the reaction was determined spectrophotometrically using the mole ratio method by keeping the concentration of the dye constant at  $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50$ ,  $\lambda_{\text{max}} = 484 \text{ nm}$ ,  $T = 21 \pm 1^\circ\text{C}$  and  $[\text{BrO}_3^-] = (0.1 - 2.0) \times 10^{-4} \text{ mol dm}^{-3}$ . The stoichiometry was evaluated from the plot of absorbance versus [reductant]/ [oxidant] after the reaction had gone to completion by the observation of a steady zero absorbance value over a period of two days[8].

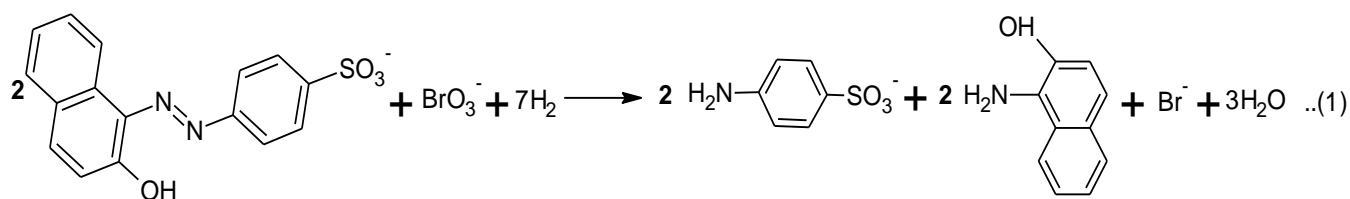
A 6405 UV-Vis spectrophotometer was used to follow the decrease in absorbance of the dye at 484nm,  $T = 21 \pm 1^\circ\text{C}$ ,  $I = 0.5 \text{ mol dm}^{-3}$  (NaCl) and  $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$  (HCl). The kinetic runs were conducted under pseudo – first order conditions with  $[\text{BrO}_3^-]$  in at least 80 - fold excess over  $[\text{OII}^-]$ . The pseudo-first order plots of  $\log (A_t - A_\infty)$  versus time, were made (where  $A_t$  and  $A_\infty$  are the absorbance at time  $t$  and at the end of the reaction respectively). From the slope of the plots, the pseudo-first order rate constant ( $k_1$ ) was determined.

The effect of acid on the rate of reaction was studied by varying  $[\text{H}^+]$  in the range  $(1.0 - 8.0) \times 10^{-2} \text{ mol dm}^{-3}$ , while  $[\text{OII}^-]$  and  $[\text{BrO}_3^-]$  were kept constant at  $21 \pm 1^\circ\text{C}$  and  $I = 0.5 \text{ mol dm}^{-3}$  (NaCl). The effect of ionic strength on the rate of the reaction was studied in the range of  $0.2 - 0.9 \text{ mol dm}^{-3}$  (NaCl) while the concentration of other reagents were kept constant at  $21 \pm 1^\circ\text{C}$ .

## 3. Results and Discussion

The result of stoichiometric studies reveals that two moles of  $\text{OII}^-$  reacted with one mole of  $\text{BrO}_3^-$ .

Hence the overall equation for the reaction is shown in equation (1).



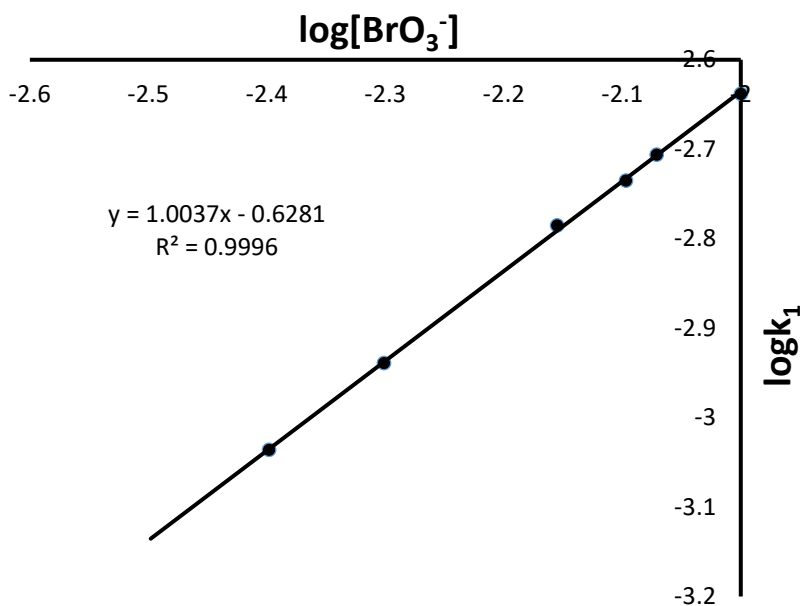
A stoichiometry of 2:3 has been reported for the oxidation of methylene blue by bromate ion [3]. The inorganic product was qualitatively confirmed to be bromide ion by adding dilute nitric acid to the reaction mixture followed by silver nitrate solution. The colour observed was pale- yellow precipitate of silver bromide.

Sulphanilic acid was confirmed as one of the organic product on addition of few drops of Conc. HCl to the reaction solution, followed by solution of sodium nitrite. This formed a diazonium ion. The reaction was carried out in an ice-bath at 3°C. On addition of the solution of 2-naphthol to the diazonium ion, an orange II dye was formed. On addition of FeCl<sub>3</sub> to the reaction solution, a faint green colour was observed. This indicates the presence of 2-naphthol [9]

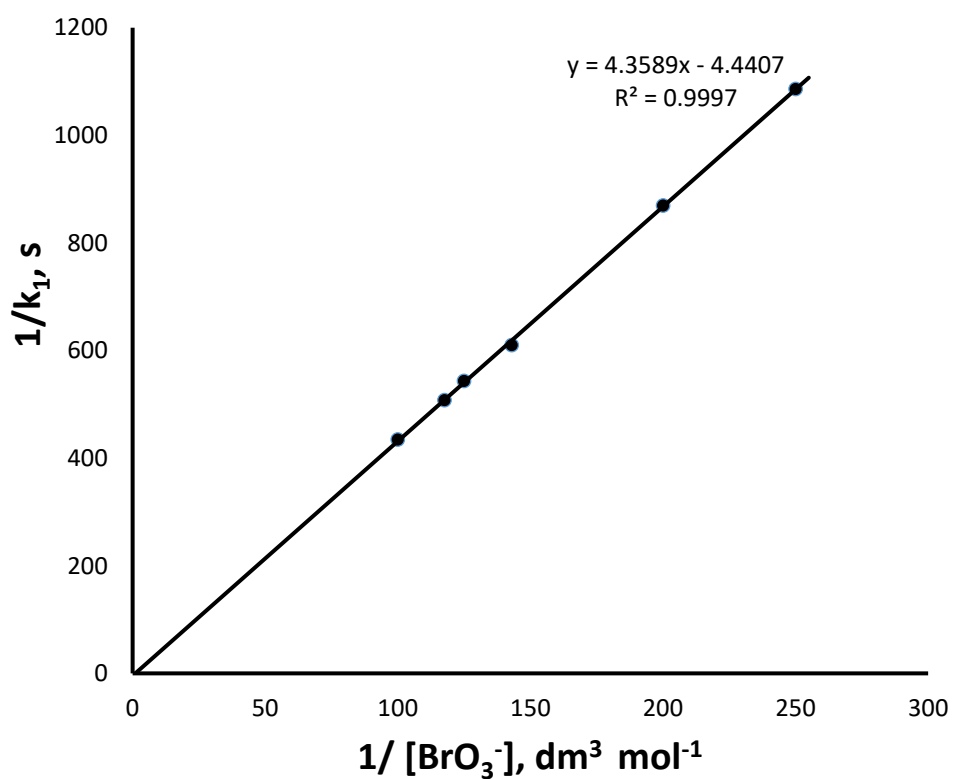
The pseudo - first order plots of  $\log (A_t - A_\infty)$  versus time for these reactions were linear. The linearity of these plots indicates that these reactions are first order with respect to [OII<sup>-</sup>]. A plot of  $\log k_1$  versus  $\log [\text{BrO}_3^-]$  was linear with a slope of one showing that the reaction is also first order with respect to  $[\text{BrO}_3^-]$  (Fig.1). This is also supported by the constancy of  $k_2$  values (Table 1) as obtained by  $k_2 = k_1/[\text{oxidant}]$ . Also, first order reaction has been reported in both oxidant and reductant in bromate oxidation of methylene blue in aqueous acidic medium [3].

Effect of changes in ionic strength of the reaction medium had no effect on the rate of the reaction. This obeyed a zero Bronsted Debye salt effect. The result in Table 1 shows that the rate of reaction increases with increase in  $[\text{H}^+]$  in the range  $1.0 \times 10^{-2} \leq [\text{H}^+] \leq 8.0 \times 10^{-2} \text{ mol dm}^{-3}$ . Plot of  $\log k_{\text{obs}}$  versus  $\log [\text{H}^+]$  gave a slope of one, indicating that the reaction is first order with respect to  $[\text{H}^+]$ . Plot of  $k_2$  versus  $[\text{H}^+]$  gave a straight line that passes through the origin.

Lack of spectroscopic evidence and results obtained from Michaelis – Menten's plot of  $1/k_1$  versus  $1/[\text{BrO}_3^-]$  (Fig. 2) suggests the absence of an intermediate in the rate determine step. Free radical test did not yield gel formation or if present it might be transient.



**Fig. 1:** Plot of  $\log k_1$  versus  $\log[\text{BrO}_3^-]$  for the redox reaction of  $\text{OI}^-$  with  $\text{BrO}_3^-$  at  $[\text{OI}^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{BrO}_3^-] = (4.0 - 10.0) \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$ ,  $\lambda = 484 \text{ nm}$  and  $T = 21 \pm 1^\circ\text{C}$



**Fig. 2:** Michaelis-Menten plot for the redox reaction between  $\text{I}^-$  and  $\text{BrO}_3^-$  at  $[\text{OI}^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{BrO}_3^-] = (4.0 - 10.0) \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$ ,  $\lambda = 484 \text{ nm}$  and  $T = 21 \pm 1^\circ\text{C}$

**Table 1:** Pseudo – first order and second order rate constants for the reaction of  $\text{OI}^-$  and  $\text{BrO}_3^-$  at  $[\text{OI}^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $\lambda = 484 \text{ nm}$  and  $T = 21 \pm 1^\circ\text{C}$ 

$10^3[\text{BrO}_3^-]$ , $\text{mol dm}^{-3}$	$10^2[\text{H}^+]$ , $\text{mol dm}^{-3}$	$10^4\text{I}$ , $\text{mol dm}^{-3}$	$10^3k_1$ , $\text{s}^{-1}$	$k_2$ , $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
4.0	5.0	5.0	0.921	0.230
5.0	5.0	5.0	1.15	0.230
7.0	5.0	5.0	1.64	0.234
8.0	5.0	5.0	1.84	0.230
8.5	5.0	5.0	1.97	0.232
10.0	5.0	5.0	2.30	0.230
5.0	1.0	5.0	0.307	0.061
5.0	2.0	5.0	0.461	0.092
5.0	3.0	5.0	0.898	0.180
5.0	4.0	5.0	1.07	0.214
5.0	5.0	5.0	1.15	0.230
5.0	6.0	5.0	1.54	0.308
5.0	8.0	5.0	2.30	0.460
5.0	5.0	2.0	1.15	0.230
5.0	5.0	3.0	1.16	0.232
5.0	5.0	4.0	1.14	0.228
5.0	5.0	5.0	1.15	0.230
5.0	5.0	6.0	1.16	0.232
5.0	5.0	8.0	1.14	0.228
5.0	5.0	9.0	1.17	0.234

**Table 2:** Rate data for the effect of added anions ( $\text{CH}_3\text{COO}^-$  and  $\text{SO}_4^{2-}$ ) on the rate of reaction of  $\text{I}^-$  and  $\text{BrO}_3^-$  at  $[\text{OI}^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{BrO}_3^-] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $\text{I} = 0.50 \text{ mol dm}^{-3}$ ,  $\lambda = 484 \text{ nm}$  and  $T = 21 \pm 1^\circ\text{C}$ 

Ion	$10^3[\text{ion}]$ , $\text{mol dm}^{-3}$	$10^3k_1$ , $\text{s}^{-1}$	$k_2$ , $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
$\text{CH}_3\text{COO}^-$	0.0	1.15	0.230
	10.0	0.921	0.184
	20.0	0.658	0.132
	40.0	0.384	0.077
	60.0	0.192	0.038
	80.0	0.115	0.023

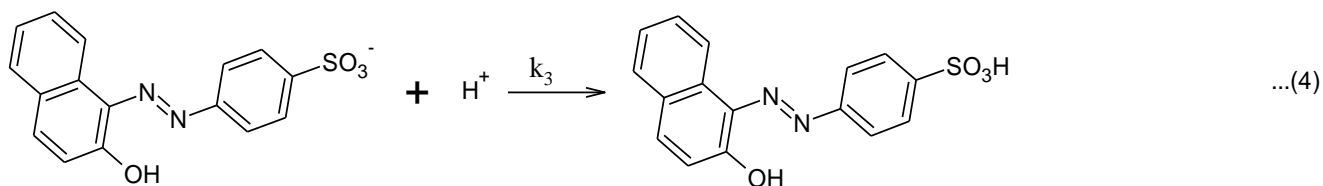
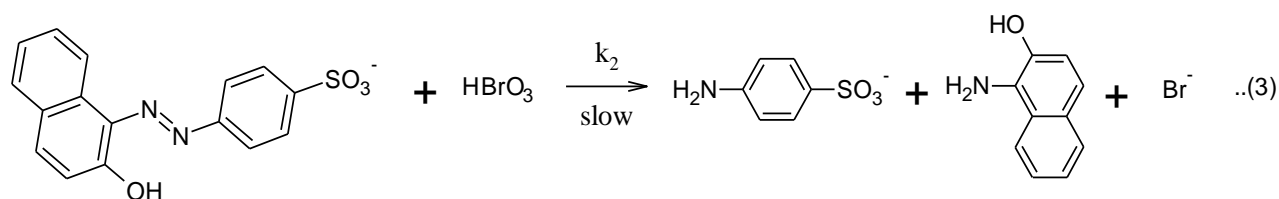
	100.0	0.092	0.018
SO <sub>4</sub> <sup>2-</sup>	0.0	1.15	0.230
	10.0	0.829	0.116
	20.0	0.640	0.128
	40.0	0.461	0.092
	60.0	0.345	0.069
	80.0	0.230	0.046
	100.0	0.115	0.023

**Table 3:** Rate data for the effect of added cations (Ca<sup>2+</sup> and Mg<sup>2+</sup>) on the rate of reaction of II<sup>-</sup> and BrO<sub>3</sub><sup>-</sup> at [OII<sup>-</sup>] =  $5.0 \times 10^{-5}$  mol dm<sup>-3</sup>, [BrO<sub>3</sub><sup>-</sup>] =  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup>, [H<sup>+</sup>] =  $5.0 \times 10^{-2}$  mol dm<sup>-3</sup>, I = 0.50 mol dm<sup>-3</sup>,  $\lambda$  = 484 nm and T = 21 ± 1 °C

Ion	10 <sup>3</sup> [ion], mol dm <sup>-3</sup>	10 <sup>3</sup> k <sub>1</sub> , s <sup>-1</sup>	k <sub>2</sub> , dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
Ca <sup>2+</sup>	0.0	1.14	0.228
	10.0	0.832	0.166
	20.0	0.712	0.142
	40.0	0.520	0.104
	60.0	0.376	0.075
	80.0	0.190	0.038
	100.0	0.122	0.024
Mg <sup>2+</sup>	0.0	1.15	0.230
	10.0	0.921	0.184
	20.0	0.691	0.138
	40.0	0.461	0.092
	60.0	0.288	0.058
	80.0	0.173	0.035
	100.0	0.115	0.023

#### 4. Reaction Scheme

On the basis of the above findings, the mechanism below is proposed for this reaction



$$\text{Rate} = K_1 k_2 [\text{Orange II}] [\text{BrO}_3^-] [\text{H}^+] \quad \dots(5)$$

## 5. Conclusion

A stoichiometry of 1:2 was obtained for the redox reaction between orange II and bromate ion in aqueous acidic medium. A first - order reaction was obtained for both reductant and oxidant. The rate of reaction increases with increase in acid concentration. Changes in ionic strength of the reaction medium had no effect on the rate of the reaction. Results of the Michaelis–Menten's plot gave no evidence of intermediate complex formation during the course of the reaction. Based on the results obtained, the outersphere mechanism is proposed for this reaction.

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