

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

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**Abstract** The kinetics of the oxidation of orange II (OR) by  $\text{ClO}_3^-$  was studied in aqueous hydrochloric acid where the ionic strength and other parameters of the reaction mixture was,  $I = 0.50 \text{ mol dm}^{-3}$  (NaCl),  $[\text{H}^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$  (HCl) and  $T = 21 \pm 1^\circ\text{C}$ . The redox reaction displayed a stoichiometry of 1:2 and obeys the rate law given as,  $-d[\text{OR}^-]/dt = b[\text{H}^+][\text{OR}^-][\text{ClO}_3^-]$ . The observed second order rate constant was found to increase with increase in hydrogen ion concentration. The rates of reaction displayed a zero salt effect and was inhibited by some added cations and anions. From the Michaelis-Menton Buck plot, there was no evidence for the formation of intermediate during the course of the reaction. Based on the results obtained, the outersphere mechanism was proposed for the reaction.

**Key Words:** Orange II, oxidation, kinetic, mechanism, chlorate ion.

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### 1.0 Introduction

Dyes are widely used in paint, leather, textile, food and other industries. Most dyes are persistent indicating that they are non-biodegradable. This makes their disposal a threat to the environment. Therefore, oxidation can reduce the dye to a form that it can be disposed safely to the environment. Most azo dyes are toxic and should be treated prior to their disposal. They are produced by coupling reaction between 2-naphthol or  $\beta$ -naphthol and diazonium compound of sulphanilic acid. It is a mono-azo acidic dye, which is soluble in water and is widely used in dyeing, tanning and paper industries (Mark *et al.*, 1978). The dye has a high photo- and thermal stability.

Chlorate is a synthetic chloroxyanion that is strongly oxidizing (Patnaik *et al.*, 1991; Villa *et al.*, 1995). Earlier studies have shown that chlorate undergoes reduction in bovine ruminal fluid (Oliver *et al.*, 2007). Chlorate,  $\text{ClO}_3^-$  (with oxidation state of +5), during its reduction to chloride,  $\text{Cl}^-$  (oxidation state of -1), intermediates such as chlorite,  $\text{ClO}_2^-$  (oxidation state of +3) and hypochlorite,  $\text{ClO}^-$  (oxidation state of +1) could be formed. Hypochlorite is not stable enough to be detected as an intermediate form, because it is an extremely strong oxidizing agent (Prakash *et al.*, 2006) but chlorate can be oxidised to the perchlorate (Munichandraiah and Sethyanarayana, 1987). It has a potential in preharvest food safety applications (Callaway *et al.*, 2002).

Oxidation of dyes has been found to be one of the best chemical methods of decolorizing aqueous system since it may be difficult to remove them by other means. Several studies have been reported on oxidation of dye as a measure of solving environmental contamination by dyes. Olajire and Olajide, (2014) used sodium sulphite to decolorize methylene blue and found that the kinetic of the decoloration process was a function of ionic strength and the presence of metal ions. Adetoro *et al.* (2014) investigated the oxidation of crystal violet in aqueous HCl and found that the kinetic rate of oxi-

dation could be represented as,  $a[H^+][CV^-][ClO_3^-]$ , which reflects a third order reaction. Adetoto *et al.* (2010) found that pyrocatechol violet in aqueous HCl was successfully oxidized by chlorine and the kinetic study was informative proposing the rate and mechanism of the oxidation process. According to Sulaiman *et al.* (2019), cyanide ion is an effective radical that is suitable for decolouration of crystal violet dye while Mohammed *et al.* (2011) acknowledge similar finding for oxidation of crystal violet by chlorate ions in aqueous media. Redox reaction aim at decolourizing indigo carmine contaminated medium was studied extensively by Edokpayi *et al.* (2011). Decolouration of aqueous medium by rosaniline using persulfate at ambient temperature was studied by Gamra (2015). The kinetic and mechanism of the reaction was also studied. Literature is scanty on the oxidation of orange II dye by chlorate. Therefore, the persistent nature of dyes and the possibility of constituting disposal threat to the environment, this present study was designed to investigate the kinetic of oxidation of orange II dye by chlorate.

## 2.0 Materials and Methods

The chemicals used were of analytical grade and were used without further purification. Standard solution of orange II (OR<sup>-</sup>) was prepared by dissolving a 0.1876 g in 250 cm<sup>3</sup> volumetric flask using distilled water. Sodium Chlorate solution was prepared by dissolving known quantities in distilled water. The stoichiometry of the reaction was determined spectrophotometrically using the mole ratio method by keeping the concentration of the dye constant at  $5.0 \times 10^{-5}$  mol dm<sup>-3</sup>,  $[H^+] = 5.0 \times 10^{-2}$  mol dm<sup>-3</sup>,  $I = 0.50$  C<sup>2</sup>mol dm<sup>-3</sup>,  $\lambda_{max} = 484$  nm,  $T = 21 \pm 1$  °C and  $[CrO_3^-] = (0.1 - 2.0) \times 10^{-4}$  mol dm<sup>-3</sup>. The stoichiometry was evaluated from the plot of

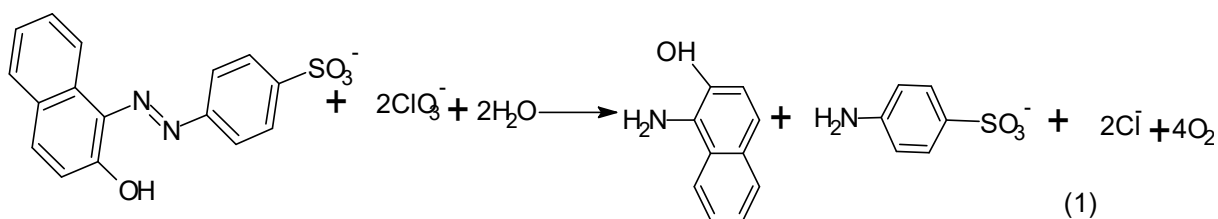
absorbance versus [reductant]/ [oxidant] after the reaction had gone to completion by the observation of a steady zero absorbance value over a period of two days.

A 6405 UV-Vis spectrophotometer was used to follow the decrease in absorbance of the dye at 484nm,  $T = 21 \pm 1$  °C,  $I = 0.5$  mol dm<sup>-3</sup> (NaCl) and  $[H^+] = 5.0 \times 10^{-2}$  mol dm<sup>-3</sup> (HCl). The kinetic experiments were conducted under pseudo – first order conditions with  $[ClO_3^-]$  in at least 10 - fold excess over orange II (OR<sup>-</sup>). 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 hydrogen ion on the rate of reaction was studied by varying  $[H^+]$  in the range  $(2.0 - 10.0) \times 10^{-2}$  mol dm<sup>-3</sup>, while  $[OR^-]$  and  $[ClO_3^-]$  were kept constant at  $21 \pm 1$  °C and  $I = 0.5$  mol dm<sup>-3</sup> (NaCl). The effect of ionic strength on the rate of the reaction was studied in the range of 0.1 - 0.6 mol dm<sup>-3</sup> (NaCl) while the concentrations of other reagents were kept constant at  $21 \pm 1$  °C. The effect of added ions on the reaction rate was observed by addition of various amounts of ions ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $SO_4^{2-}$  and  $CH_3COO^-$ ), while the concentrations of OR<sup>-</sup>, the oxidant, hydrogen ion, temperature and ionic strength of reaction medium were kept constant (Idris *et al.*, 2014).

## 3.0 Results and Discussion

The stoichiometric study showed that one mole of orange II was oxidised by two moles of  $ClO_3^-$ . Hence the overall equation for the reaction is shown in equation 1.



A similar stoichiometry has been reported for the hexamethylpararosaniline chloride (Crystal Violet) oxidation by chlorate ions in aqueous acidic medium (Mohammed *et al.*, 2011). Sulphanilic acid and

2-naphthol were confirmed as the organic products through chemical test (Stephanie, 2008).

The pseudo - first order plots of  $\log (A_t - A_\infty)$  versus time for this reaction was linear; the linearity of



these plots indicated that these reactions are first order with respect to  $[OR^-]$ . A plot of  $\log k_1$  versus  $\log [ClO_3^-]$  (Fig. 1) was linear with a slope of 1.00 showing that the reaction is also first order with respect to  $[ClO_3^-]$ . This is also supported by the constancy of  $k_2$  values as shown in Table 1.

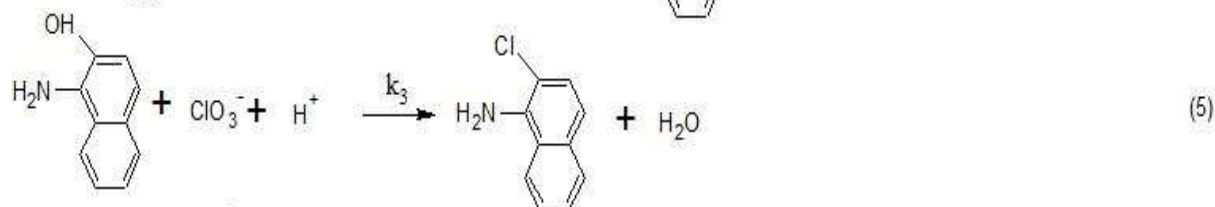
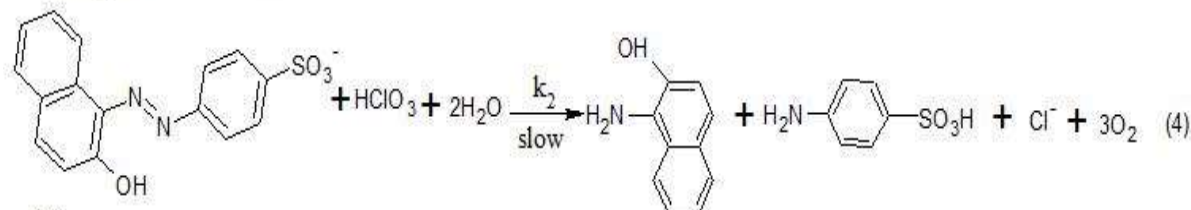
The result of the acid dependence study (Table 1) shows that the rate of reaction increases with increase in  $[H^+]$ . Plot of  $\log k_{obs}$  versus  $\log [H^+]$  gave a slope of 0.97 (Fig. 2) indicating that the reaction is first order with respect to  $[H^+]$ . Plot of  $k_2$  versus  $[H^+]$  was linear with zero intercept ( $R^2 = 0.97$ ). This showed that equilibrium between protonated and deprotonated forms of a reactant prior to the rate determining step is rapid indicating that the equilibrium constant for protonation is small and the protonation is not complete even at high acidity, in which the protonated form is only reactive species (Gupta and Gupta, 1984). The rate equation for the reaction is given by equation 2.

$$\frac{-d[OR^-]}{dt} = b[H^+][OR^-][ClO_3^-] \quad (2)$$

Variation of the ionic strength of the medium from 0.1 – 0.6 mol dm<sup>-3</sup> (NaCl) did not revealed any observable effect on the rate constants of the reaction (Table 1). This suggests the presence of neutral species in the rate determining step.

Added ions  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $CH_3COO^-$  and  $SO_4^{2-}$  inhibited the rate of the reaction, indicating that the reaction might be operating via the outer sphere mechanism. Polymerisation test to determine the participation of free radicals in the reaction was negative because no gel was formed when acrylonitrile was added to partially reacted reaction mixture with excess methanol. The result from the spectroscopic analysis indicated that the formation of an intermediate complex might be unlikely. Plot of  $1/k_1$  versus  $1/[ClO_3^-]$  gave a straight line that passed through the origin. Based on the information obtained in this system, the outersphere mechanism is favoured.

The reaction scheme proposed is shown in equations 3 – 7.



$$\text{Rate} = k_2[OR^-][HClO_3] \quad (6)$$

$$\text{Rate} = k_2K_1[OR^-][ClO_3^-][H^+] \quad (7)$$

\*\*Equation 7 is analogous to equation 2 where  $b = k_2K_1$



**Table 1: Pseudo – first order and second order rate constants for the reaction of OR<sup>-</sup> and ClO<sub>3</sub><sup>-</sup> at [OR<sup>-</sup>] = 5.0 × 10<sup>-5</sup> mol dm<sup>-3</sup>, λ = 484 nm and T = 21 ± 1°C**

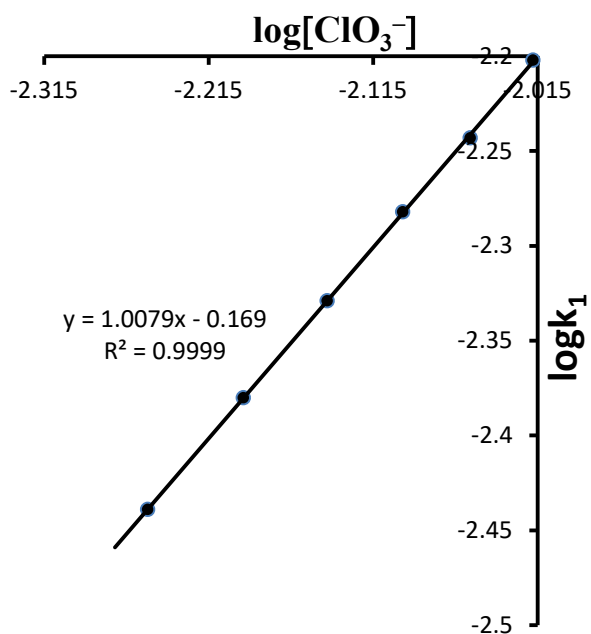
[ClO <sub>3</sub> <sup>-</sup> ] 10 <sup>3</sup> (M)	10 <sup>2</sup> [H <sup>+</sup> ] (M)	I (C <sup>2</sup> M)	K <sub>1</sub> (s <sup>-1</sup> )	K <sub>2</sub> (M <sup>-1</sup> s <sup>-1</sup> )
5.6	5.0	0.5	3.64	0.650
6.4	5.0	0.5	4.17	0.652
7.2	5.0	0.5	4.69	0.651
8.0	5.0	0.5	5.22	0.652
8.8	5.0	0.5	5.71	0.649
9.6	5.0	0.5	6.28	0.654
8.0	2.0	0.5	2.03	0.254
8.0	3.0	0.5	2.55	0.319
8.0	4.0	0.5	3.43	0.429
8.0	5.0	0.5	5.22	0.652
8.0	8.0	0.5	6.58	0.822
8.0	10.0	0.5	9.68	1.210
8.0	5.0	0.1	5.20	0.650
8.0	5.0	0.2	5.22	0.653
8.0	5.0	0.3	5.20	0.650
8.0	5.0	0.4	5.19	0.649
8.0	5.0	0.5	5.21	0.651
8.0	5.0	0.6	5.22	0.653

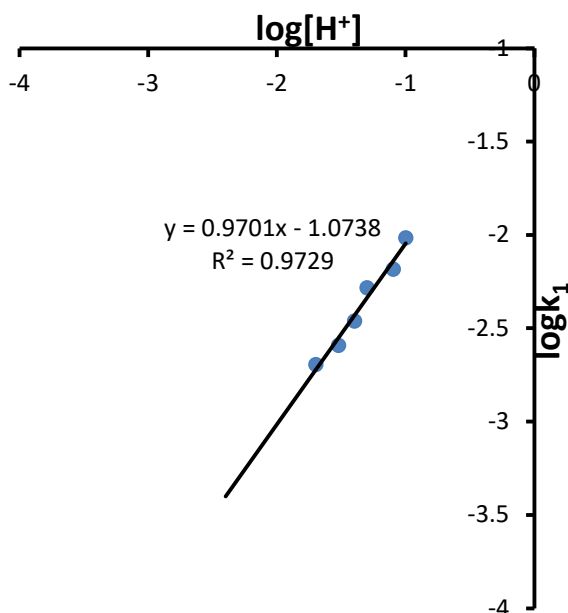
**Table 2: Rate data for the effect of added anions (CH<sub>3</sub>COO<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) on the rate of reaction of OR<sup>-</sup> and ClO<sub>3</sub><sup>-</sup> at [OR<sup>-</sup>] = 5.0 × 10<sup>-5</sup> mol dm<sup>-3</sup>, [ClO<sub>3</sub><sup>-</sup>] = 8.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 5.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>, I = 0.50 C<sup>2</sup>mol dm<sup>-3</sup>, λ = 484 nm and T = 21 ± 1 °C**

ion	10 <sup>3</sup> [ion] (M)	10 <sup>3</sup> k <sub>1</sub> (s <sup>-1</sup> )	K <sub>2</sub> (M <sup>-1</sup> s <sup>-1</sup> )
CH <sub>3</sub> COO	0.0	5.22	0.652
CH <sub>3</sub> COO <sup>-</sup>	10.0	4.74	0.593
CH <sub>3</sub> COO	20.0	4.43	0.554
CH <sub>3</sub> COO	40.0	3.37	0.421
CH <sub>3</sub> COO	60.0	3.18	0.398
CH <sub>3</sub> COO	80.0	2.92	0.365
CH <sub>3</sub> COO	100.0	1.78	0.222
SO <sub>4</sub> <sup>2-</sup>	0.0	5.21	0.651
SO <sub>4</sub> <sup>2-</sup>	10.0	4.66	0.583
SO <sub>4</sub> <sup>2-</sup>	20.0	3.80	0.475
SO <sub>4</sub> <sup>2-</sup>	40.0	2.48	0.355
SO <sub>4</sub> <sup>2-</sup>	60.0	2.12	0.265
SO <sub>4</sub> <sup>2-</sup>	80.0	1.68	0.211
SO <sub>4</sub> <sup>2-</sup>	100.0	1.32	0.165

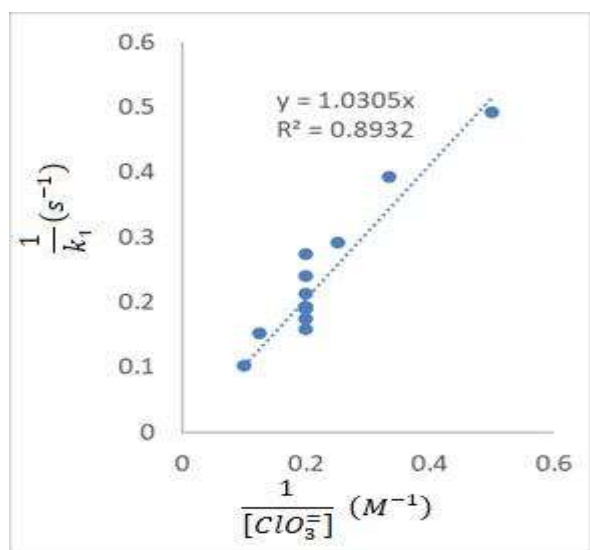
**Table 3: Rate data for the effect of added cations (Ca<sup>2+</sup> and Mg<sup>2+</sup>) on [ClO<sub>3</sub><sup>-</sup>] = the rate of reaction of OR<sup>-</sup> and ClO<sub>3</sub><sup>-</sup> at [OR<sup>-</sup>] = 5.0 × 10<sup>-5</sup> mol dm<sup>-3</sup>, 8.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 5.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>, I = 0.50 C<sup>2</sup>mol dm<sup>-3</sup>, λ = 484 nm and T = 21 ± 1 °C**

ion	10 <sup>3</sup> [ion] (M)	10 <sup>3</sup> k <sub>1</sub> (s <sup>-1</sup> )	K <sub>2</sub> (M <sup>-1</sup> s <sup>-1</sup> )
	0.0	5.22	0.653
Ca <sup>2+</sup>	10.0	4.67	0.584
Ca <sup>2+</sup>	20.0	4.38	0.547
Ca <sup>2+</sup>	40.0	3.47	0.434
Ca <sup>2+</sup>	60.0	2.88	0.360
Ca <sup>2+</sup>	80.0	2.50	0.312
Ca <sup>2+</sup>	100.0	2.24	0.280
Mg <sup>2+</sup>	0.0	5.22	0.652
Mg <sup>2+</sup>	10.0	4.96	0.620
Mg <sup>2+</sup>	20.0	4.45	0.556
Mg <sup>2+</sup>	40.0	3.33	0.416
Mg <sup>2+</sup>	60.0	3.10	0.387
Mg <sup>2+</sup>	80.0	2.82	0.353
Mg <sup>2+</sup>	100.0	2.62	0.328


**Fig.1: Plot of log k<sub>1</sub> versus log[ClO<sub>3</sub><sup>-</sup>] for the redox reaction of OR<sup>-</sup> with ClO<sub>3</sub><sup>-</sup> at [OR<sup>-</sup>] = 5.0 × 10<sup>-5</sup> mol dm<sup>-3</sup>, [ClO<sub>3</sub><sup>-</sup>] = (5.6 – 9.6) × 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 5.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>, I = 0.50 C<sup>2</sup> mol dm<sup>-3</sup>, λ = 484 nm and T = 21 ± 1°C**

**Fig. 2:** Plot of  $\log k_1$  versus  $\log[H^+]$  for the redox reaction of  $OR^-$  with  $ClO_3^-$  at  $[OR^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[ClO_3^-] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[H^+] = (2.0-10.0) \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ C}^2 \text{ mol dm}^{-3}$ ,  $\lambda = 484 \text{ nm}$  and  $T = 21 \pm 1 \text{ }^\circ\text{C}$



**Fig. 3:** Michaelis - Menten plot for the redox reaction between  $OR^-$  and  $ClO_3^-$  at  $[OR^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[ClO_3^-] = (5.6 - 9.6) \times 10^{-3} \text{ M}$ ,  $[H^+] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ C}^2 \text{ mol dm}^{-3}$ ,  $\lambda = 484 \text{ nm}$  and  $T = 21 \pm 1 \text{ }^\circ\text{C}$

#### 4.0 Conclusion

A stoichiometry of 1:2 was observed for the redox reaction between orange II and chlorate ion in aqueous acid. 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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