

# Kinetic Approach to the mechanism of Oxidation of Hexamethylpararosaniline Chloride (Crystal Violet) by Periodate Ion in Acidic Medium

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**Abstract**— The kinetics of oxidation of hexamethylpararosaniline chloride (hereafter referred to as CV) by periodate ion have been studied in aqueous hydrochloric acid medium under pseudo-first order conditions of excess  $[\text{IO}_4^-]$  at  $28 \pm 1^\circ\text{C}$ ,  $[\text{H}^+] = 5.00 \times 10^{-2} \text{ mol dm}^{-3}$ , and ionic strength,  $I = 0.5 \text{ mol dm}^{-3}(\text{NaCl})$ . The stoichiometry of the reaction was found to be 1:2 mole ratio of CV to  $\text{IO}_4^-$  ions. The redox reaction follows first order with respect to the reductant  $[\text{CV}^+]$  and zero order with respect to the oxidant  $[\text{IO}_4^-]$  at constant hydrogen ion concentration. The rate of reaction increased with increase in hydrogen ion concentration. The overall reaction conforms to the rate law

$$-\frac{d[\text{CV}^+]}{dt} = (e + f [\text{H}^+])[\text{CV}^+]$$

$$e = 1.4916 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1} \text{ and } f = 1.8 \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

Variation of dielectric constant of the medium has no effect on the rate of reaction, addition of anions and cations ( $\text{X} = \text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) to the reaction mixture has no effect on the rate of reaction. Spectroscopic test showed evidence of intermediate complex of significant stability. Free radical polymerization test showed no free radicals. A plausible mechanism which accommodates all the experimental data was proposed.

**Key words**— Kinetics, mechanism, oxidation, periodate, hexamethylpararosaline chloride, dielectric constant, Spectroscopic test, Intermediate complex, Free radical.

## 1 INTRODUCTION

Crystal violet (Gentian violet) with a molecular formula of  $\text{C}_{25}\text{H}_{30}\text{N}_3\text{Cl}$  is a triphenyl methane dye, that is antimicrobial [1]. It is very important in biological stains for the study of bacteria and related microorganisms. The dye is also used as a constituent of culture media, as indicator and for laboratory diagnosis of disease [2]. The kinetic studies of the reaction of crystal violet ( $\text{CV}^+$ ) with chlorate and oxone has been reported [3,4].

Periodate has been used extensively in oxidations of organic as well as inorganic compounds [5,6]. Kinetics and mechanisms of the oxidation of periodate ion with various dyes has been studied by various researchers [5-11]. In this paper, we present our findings on the oxidation of crystal violet with periodate ion with the aim of providing insight into the mechanistic data to help gain a deeper insight into the nature of both the reactants.

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## 2 EXPERIMENTAL

All the reagents used were Analar grade. Crystal violet and periodate ion were used without further purifications. Sodium chloride (M&B) was used to maintain the ionic strength of the reaction medium. Hydrochloric acid was standardized titrimetrically using sodium bicarbonate. All other reagents were used as supplied.

## 3 STOICHIOMETRY

The stoichiometry of the reaction was determined using spectrophotometric titration, by the mole ratio method. Reaction mixtures containing fixed amount of  $[\text{CV}^+]$  and varied amount of  $[\text{IO}_4^-]$  were allowed to stand for 24 hours after which the excess  $[\text{CV}^+]$  was determined by measuring the absorbances of the solutions at 585 nm wavelength until a steady value was attained, the stoichiometry was evaluated from the plot of absorbance against  $[\text{CV}^+]/[\text{IO}_4^-]$ .

## 4 KINETIC MEASUREMENT

The progress of the reaction was monitored under pseudo-first order condition with the  $[\text{IO}_4^-]$  in at least 10-fold excess of  $[\text{CV}^+]$ , by following the decrease in the concentration of  $\text{CV}^+$  at 585 nm,  $[\text{H}^+] = 5.00 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1^\circ\text{C}$ .

The pseudo-first order plot of  $\log (A_t - A_\infty)$  versus time,  $t$  were linear to about 90% extent of the reaction ( $A_t$  and  $A_\infty$  are the absorbance at time  $t$  and at the end of the reaction respectively) and from the slope of the plots, the pseudo-first order rate constant ( $k_1$ ) was determined. The second order constant ( $k_2$ ) was obtained from the relation:

$$k_2 = k_1 / [IO_4^-]$$

#### 4.1 Effect of $[H^+]$ on the reaction rate

The effect of  $[H^+]$  on the rate of reaction was studied in the range  $0.02 \leq [H^+] \leq 0.14 \text{ mol dm}^{-3}$  while concentration of CV and  $IO_4^-$  ions were kept constant at  $1.0 \times 10^{-5}$  and  $5.00 \times 10^{-2} \text{ mol dm}^{-3}$  respectively at  $28 \pm 1^\circ \text{C}$  and  $I = 0.50 \text{ mol dm}^{-3}$ .

#### 4.2 Effect of Ionic Strength

The effect of ionic strength on the rate of the reaction was investigated in the range  $0.3 - 1.0 \text{ mol dm}^{-3}$ , while the concentrations of other reactant at  $28 \pm 1^\circ \text{C}$ . The results are presented in Table 1.

#### 4.3 Effect of Added Cation and Anion

The effect of added cation and anion were investigated for  $[X] = 1.0 \times 10^{-3} - 1.0 \times 10^{-2} \text{ mol dm}^{-3}$  ( $X = \text{HCOO}^-, \text{CH}_3\text{COO}^-, \text{Ca}^{2+}, \text{Mg}^{2+}$ ) and the concentration of all other reactants were kept constant at  $28 \pm 1^\circ \text{C}$  and the ionic strength was maintained constant at  $I = 0.50 \text{ mol dm}^{-3}$ .

#### 4.4 Test for Free Radicals

Acrylamide solution was added to the partially oxidized reaction mixture of CV and  $IO_4^-$  ions in a large excess of methanol and to each of the reactants separately.

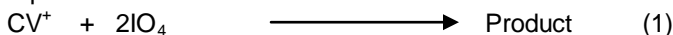
#### 4.5 Test for Intermediate Complex

The electronic spectra of the reaction mixture were obtained after two minutes of the commencement of the reaction, over the wavelength range of  $500 - 700 \text{ nm}$ . This was compared with the spectra of the dye alone within the same range.

### 5 RESULTS AND DISCUSSION

#### 5.1 Stoichiometry and Product Analysis

From the stoichiometric studies, the mole ratio of the reaction was found to be 1:2; this indicates that for every mole of  $CV^+$ , two moles of  $IO_4^-$  is being oxidized. This is conforms to the equation:



Similar stoichiometry has been reported for the reduction of tetraoxoiodate(VII) by  $n$ -(2-hydroxy)ethylenediamminetriacetocobalt (II) ion and the oxidation of azide by periodate ion in acidic medium respectively

[7, 5, 12]. Product analysis was carried out by reacting equimolar amount of the dye and the periodate at  $[H^+] = 5.00 \times 10^{-2} \text{ mol dm}^{-3}$  and  $I = 0.5 \text{ mol dm}^{-3}$  (NaCl) after the completion of the reaction, a colorless solution was obtained and UV visible spectra of the product showed no absorption peak at  $\lambda_{\text{max}} 585 \text{ nm}$ . This indicates the destruction of the quinoid structure that gives the dye color.

Qualitative test for iodate ion was carried out. Iodate ion was identified by the positive starch-indicator test for liberated  $I_2$  when KI was added to the reaction mixture.

#### 5.2 Kinetics

The pseudo first order plot of  $\log (A_t - A_\infty)$  versus time,  $t$  for these reactions were linear to about 90% extent of the reaction (Fig 1). This indicates that the reaction is first-order with respect to  $[CV^+]$  at constant  $[H^+]$ . But the rate of the reaction was found not to vary with the concentration of the  $IO_4^-$ . Thus the reaction was found to be zero order in  $[IO_4^-]$ , there was no enhancement of the rate even at high  $[IO_4^-] \geq 12 \times 10^{-2} \text{ mol dm}^{-3}$ , but it was still zero order. The  $k_1$  for the system was found not to vary. The rate equation for the reaction can be written as:

$$-\frac{d[CV^+]}{dt} = k_1[CV^+] \quad (2)$$

$$\text{where } k_1 = 6.89 \text{ s}^{-1}$$

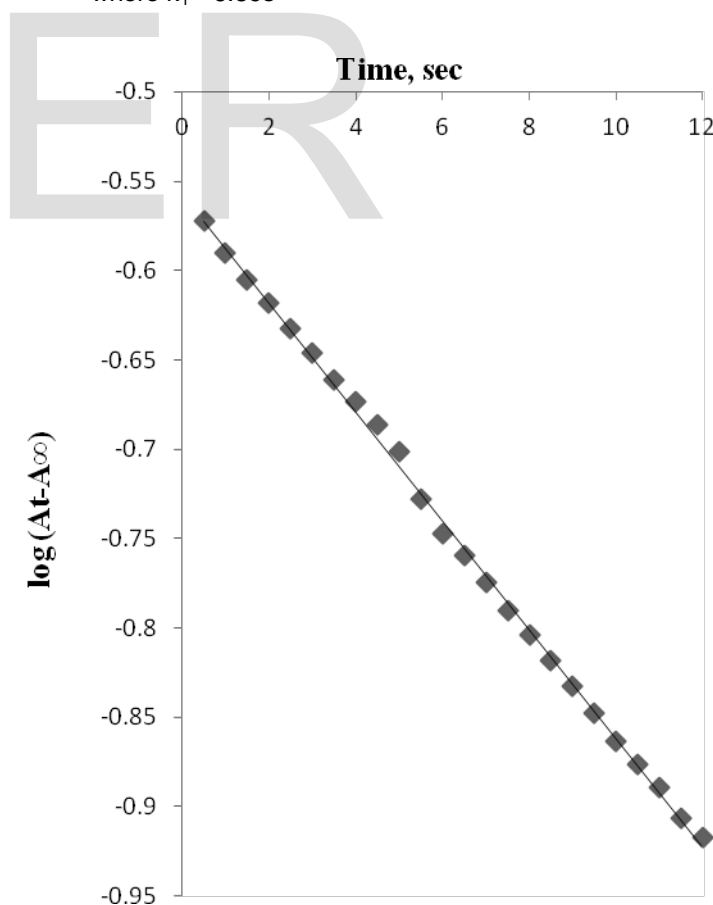


Fig. 1 Typical pseudo-first order plot for the redox reaction of crystal violet with periodate ions at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[IO_4^-] = 2 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[H^+] = 5.0 \times 10^{-2} \text{ mol}$

$\text{dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

6.00	5.00	0.60	8.66
6.00	5.00	0.70	12.51
6.00	5.00	0.80	15.96

Similar first order kinetics has been reported for the oxidation of triphenylmethane dye by periodate ion [13]. First order dependence of rate on each of the reactants is the most commonly encountered behavior in reaction of periodate ion [14, 9, 10].

### 5.3 Effect of $[\text{H}^+]$

The rate of the reaction were found to increase with increase in concentration of hydrogen ions in the range of  $(2-14) \times 10^{-2}$ ,  $\text{mol dm}^{-3}$  (Table 1). Plot of  $k_1$  versus  $[\text{H}^+]$  was also linear with positive intercept, therefore the acid dependent rate constant  $k_H$  is given by

$$k_H = e + f[\text{H}^+] \quad (3)$$

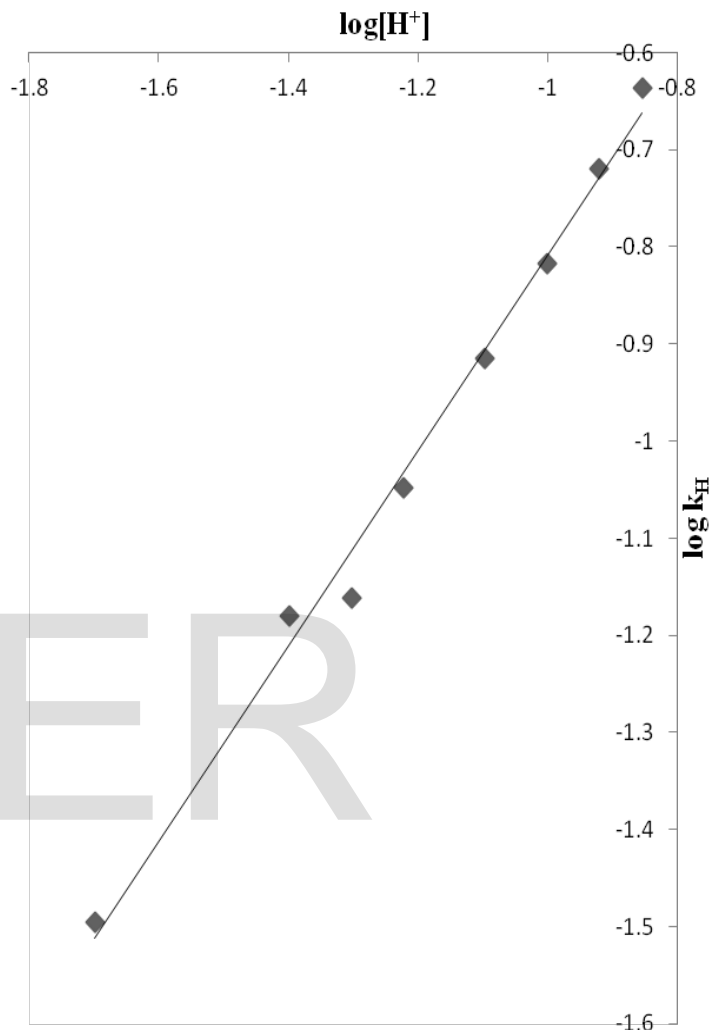
Substituting equation 3 in equation 2, the rate equation for the reaction can now be written as:

$$\frac{-d[\text{CV}^+]}{dt} = (e + f[\text{H}^+])[\text{CV}^+] \quad (4)$$

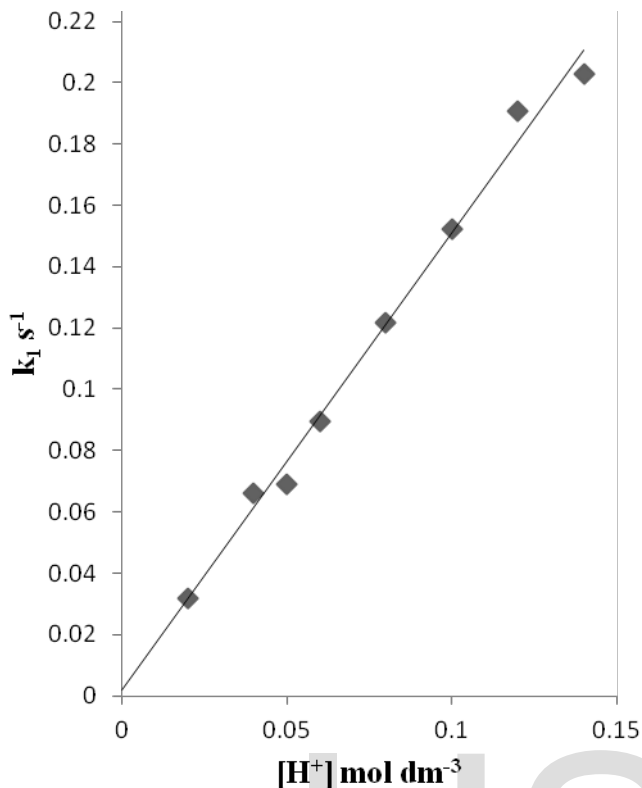
The rate constant for this reaction was found to increase with increase in  $[\text{H}^+]$ , plot of  $\log k_1$  versus  $\log [\text{H}^+]$  shows an order of one (fig. 2). Plot of  $k_1$  versus  $[\text{H}^+]$  was linear with positive intercept (fig. 3). This kind of acid dependence shows that the reaction proceeds through acid dependent and acid independent reaction pathways [16]. Similar acid dependence pathways have been reported for reactions of periodate [5, 9, 10, 16].

**Table 1: Pseudo-first order rate constants for the redox reaction of crystal violet with periodate ions in aqueous HCl medium at  $[\text{CV}^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $T = 28 \pm 1 \text{ }^\circ\text{C}$  and  $\lambda_{\text{max}} = 585 \text{ nm}$ .**

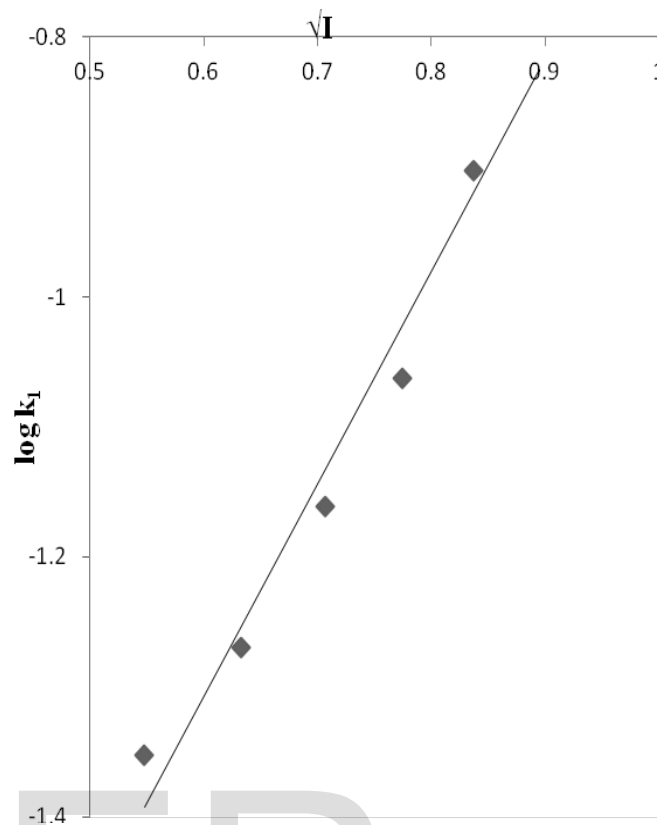
$10^3[\text{IO}_4^-]$ , mol $\text{dm}^{-3}$	$10^2[\text{H}^+]$ , mol $\text{dm}^{-3}$	$I$ , mol $\text{dm}^{-3}$	$10^2 k_1$ , $\text{s}^{-1}$
2.00	5.00	5.00	6.89
4.00	5.00	5.00	6.90
6.00	5.00	5.00	6.89
8.00	5.00	5.00	6.81
10.00	5.00	5.00	6.92
12.00	5.00	5.00	6.89
14.00	5.00	5.00	6.89
16.00	5.00	5.00	6.89
6.00	2.00	5.00	3.20
6.00	4.00	5.00	6.61
6.00	5.00	5.00	6.89
6.00	6.00	5.00	8.96
6.00	8.00	5.00	12.16
6.00	10.00	5.00	15.24
6.00	12.00	5.00	19.07
6.00	14.00	5.00	20.27
6.00	5.00	0.30	4.44
6.00	5.00	0.40	5.37
6.00	5.00	0.50	6.89



**Fig. 2 Plot of  $\log k_H$  versus  $\log [\text{H}^+]$  for the redox reaction of crystal violet with periodate ion at  $[\text{CV}^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{IO}_4^-] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$**



**Fig. 3** Plot of  $k_1$  versus  $[H^+]$  for the redox reaction of crystal violet with periodate ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[IO_4^-] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$



**Fig. 4** Plot of  $k_1$  versus  $\sqrt{I}$  for the redox reaction of crystal violet with periodate ion at  $[CV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[IO_4^-] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.50 \text{ mol dm}^{-3}$  and  $T = 28 \pm 1 \text{ }^\circ\text{C}$

#### 5.4 Effect of ionic strength and dielectric constant, D

The effect of ionic strength on the rate of reaction was investigated by varying the ionic strength of the medium within the range 0.3-1.0 mol dm<sup>-3</sup>. The rate of the reaction was found to increase with increase in ionic strength of the reaction medium (Fig 4). This result implies that the product of the charges on the activated complex is positive [17, 18]. Dielectric constant was found not to affect the rate of the reaction.

#### 5.5 Effect of added ions

Added anions and cations were observed not to catalyze the reaction. The non catalysis by these ions suggests that the reaction occur by the innersphere mechanism. Non catalysis of the reaction rate by added ions has been reported as characteristic of innersphere pathway. [18].

#### 5.6 Free Radical Test

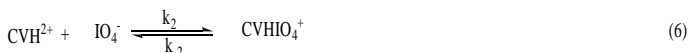
The addition of acrylamide to the partially oxidized reaction mixture followed by large excess of methanol did not lead to the formation of gelatinous precipitate. This suggests that free radicals might not likely be involved in this reaction.

#### 5.7 Test for intermediate complex formation

The results of the spectroscopic studies indicated shift in the absorption maxima,  $\lambda_{max}$  from 585-620 nm, when reactants were mixed together and the electronic spectrum was recorded after two minutes of mixing. This suggests the presence of intermediate complex during the reaction and thereby supporting the innersphere mechanism in the reaction.

## 5.8 Reaction mechanism

On the basis of the above experimental results, the following plausible mechanism is hereby proposed:



From equation 7,

$$\text{Rate} = k_3 [CVHIO_4^+] \quad (8)$$

Substitution from equation 6 leads to:

$$\begin{aligned} \text{Rate} &= \frac{k_3 k_2}{k_{-2}} [CVH^{2+}] [IO_4^-] \\ &= k_3 k_2 [CVH^{2+}] [IO_4^-] \end{aligned} \quad (9)$$

Applying steady state hypothesis to  $CVH^{2+}$  leads to:

$$[CVH^{2+}] = \frac{k_1 [CV^+] [H^+]}{k_{-1} + k_2 [IO_4^-]} \quad (10)$$

Substitution of equation 10 into 9 gives:

$$\text{Rate} = \frac{k_3 k_2 k_1 [CV^+] [H^+] [IO_4^-]}{k_{-1} + k_2 [IO_4^-]} \quad (11)$$

If  $k_2 [IO_4^-] \gg k_{-1}$ , then

$$k_{-1} + k_2 [IO_4^-] \text{ is approx. } = k_2 [IO_4^-]$$

then equation 11 becomes:

$$\begin{aligned} \text{Rate} &= \frac{k_1 k_3 k_2 [CV^+] [H^+] [IO_4^-]}{k_2 [IO_4^-]} \\ &= k_1 k_3 [CV^+] [H^+] \end{aligned} \quad (12)$$

or  $\text{Rate} = k [CV^+] [H^+]$

where  $k = e + f$  to conform to the observed rate law in equation (4)

$$e = 1.4916 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1} \text{ and } f = 1.8 \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

## 6 CONCLUSIONS

The reaction is found to be first order overall at constant  $[H^+]$ , and the proposed mechanism point to an inner sphere electron transfer process. Considering the fact that addition of added ions had no effect on the rate of reaction. When the absorbance of the reaction mixture was measured as the reaction progresses, there was shift in the  $\lambda_{\text{max}}$  from 585- 620 nm, this is an indication of the presence of intermediate complex formation which would be as a result of oxygen in  $IO_4^-$  which acts as bridging atom. These points greatly favour the inner sphere mechanistic pathway for this reaction.

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