

# Mechanism of Iodate Oxidation by Methylthionium Chloride in Acidic Medium

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## Authors' contributions

This work was carried out in collaboration between both authors. Author UPE performed the statistical analysis and wrote the first draft of the manuscript. Authors OAB and UPE managed the analyses of the study. Author UPE managed the literature searches. Both authors read and approved the final manuscript.

## Article Information

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## ABSTRACT

The mechanism of iodate oxidation by methylthionium chloride in acidic medium was investigated at 29±1°C. The oxidation reaction is first order in both oxidant and reductant. The rate of reaction was unaffected by increase in ionic strength, dielectric constant, added cations and anion. The reaction rate showed positive acid dependence and obeys the rate law of

$$-\frac{d[\text{MB}]}{dt} = a + b[\text{H}^+][\text{MB}]$$

where  $a = 1.19 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $b = 0.628 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 29±1°C,  $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$ ,  $1.0 \text{ mol dm}^{-3}$  ( $\text{NaClO}_4$ ) ionic strength and  $\lambda_{\text{max}} = 663 \text{ nm}$ . Investigation of spectroscopic test did not indicate the formation of intermediate complex during the course of the reaction. In line with the data obtained, plausible mechanism in favour of outer-sphere mechanism has been proposed.

**Keywords:** Mechainsm; methylthionium chloride; iodate ion.

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## 1. INTRODUCTION

Methylthionium chloride (herein referred to as MB) is a water-soluble cationic dye molecule which is easily reduced to the colourless hydrogenated molecule known as leuco-methylthionium chloride, by a variety of reductants [1]. MB and its one and two-electron reduced forms have been studied as important species in the MB/HS, MB/O<sub>2</sub> oscillating reaction system [1]. It was reported that MB also improves hypoxia and hyper dynamic circulation in liver cirrhosis and treats severe hepatopulmonary syndrome [2]. It has been found to improve hypotension associated with various clinical states [3]. Furthermore, MB also helps to improve blood pressure and cardiac function during septic shock [4].

Iodate ion is a reductant that is predominantly used as a dough conditioner [5] and is also added to lotions and ointments as an antiseptic and deodorant, as source for iodine. It is also used as an ingredient in baby formula milk [6].

In spite of these numerous uses of MB and iodate ion, little has been done on its kinetics and mechanism and as such has prompt this research work.

## 2. EXPERIMENTAL

### 2.1 Stoichiometry

The concentration of methylthionium chloride was kept constant at  $1 \times 10^{-4}$  mol dm<sup>-3</sup> while that of the iodate ion was varied from 1.0 -  $7.0 \times 10^{-3}$  mol dm<sup>-3</sup>,  $[H^+] = 1.0 \times 10^{-1}$  and at ionic strength of 1.0 mol dm<sup>-3</sup> (NaClO<sub>4</sub>),  $\lambda_{max} = 663$  nm and  $29 \pm 1^\circ C$  in order to determine the stoichiometry of the reaction using the mole ratio method.

A plot of absorbance was made against the mole ratio of the reactions and the stoichiometry was

evaluated from the point of inflection after the reaction had gone to completion as indicated by a constant value in the absorbance over a period of 24 hrs.

### 2.1.1 Kinetics and order of reactions

The reaction was monitored as it progresses by following the decrease in absorbance of the MB at  $\lambda_{max}$  663 nm using the UV/Vis Spectrumlab 752s spectrophotometer. All kinetic runs were made under pseudo-first order conditions with  $[IO_3^-]$  in at least 5 folds excess over  $[MB]$ , while the ionic strength was maintained at 1.0 mol dm<sup>-3</sup> (NaClO<sub>4</sub>) and  $[H^+] = 1.0 \times 10^{-1}$  at  $29 \pm 1^\circ C$ . "The results are presented in Table 1"

Plots of  $\log (A_t - A_\infty)$  (where  $A_t$  and  $A_\infty$  are the absorbance at time  $t$  and at the end of the reaction respectively) against time were carried out (Fig. "1".) from which pseudo-first order rate constants ( $k_0$ ) were determined. Second order rate constants ( $k_2$ ) were obtained from the relation:  $k_2 = k_0/[IO_3^-]$ . A plot of  $\log k_0$  vs  $\log [IO_3^-]$  was also made (Fig 2) to determine the order of reaction.

### 2.1.2 Effect of acid dependent

The acid dependent rate constant was investigated in the range of  $0.2 - 1.6 \times 10^{-1}$  mol dm<sup>-3</sup> (HClO<sub>4</sub>) while the concentrations of other reactants were kept constant. The results are presented in Table 2. A plot of  $k_2$  vs  $[H^+]$  was also made (Fig. 3).

### 2.1.3 Effect of ionic strength

The effect of ionic strength on the rate of the reaction was investigated in the range of 0.2 - 1.6 mol dm<sup>-3</sup> (NaClO<sub>4</sub>) while the concentrations of other reactants were kept constant. The results are presented in Table 3.

**Table 1. Pseudo-first rate constant and second order rate constant for the reaction of methylthionium chloride and iodate ion at  $29 \pm 1^\circ C$ ,  $\lambda_{max} = 663$  nm,  $[MB] = 1 \times 10^{-4}$  mol dm<sup>-3</sup>,  $[H^+] = 1 \times 10^{-1}$  mol dm<sup>-3</sup>**

$10^3 [IO_3^-], \text{mol dm}^{-3}$	$[NaClO_4] \text{mol dm}^{-3}$	$[H^+] = 1.0 \times 10^{-1} \text{mol dm}^{-3}$	$10^3 k_0 \text{s}^{-1}$	$k_2 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
2.0	1.0	1.0	3.64	1.82
3.0	1.0	1.0	5.46	1.82
4.0	1.0	1.0	7.01	1.75
5.0	1.0	1.0	8.80	1.76
6.0	1.0	1.0	10.59	1.77
7.0	1.0	1.0	12.68	1.81

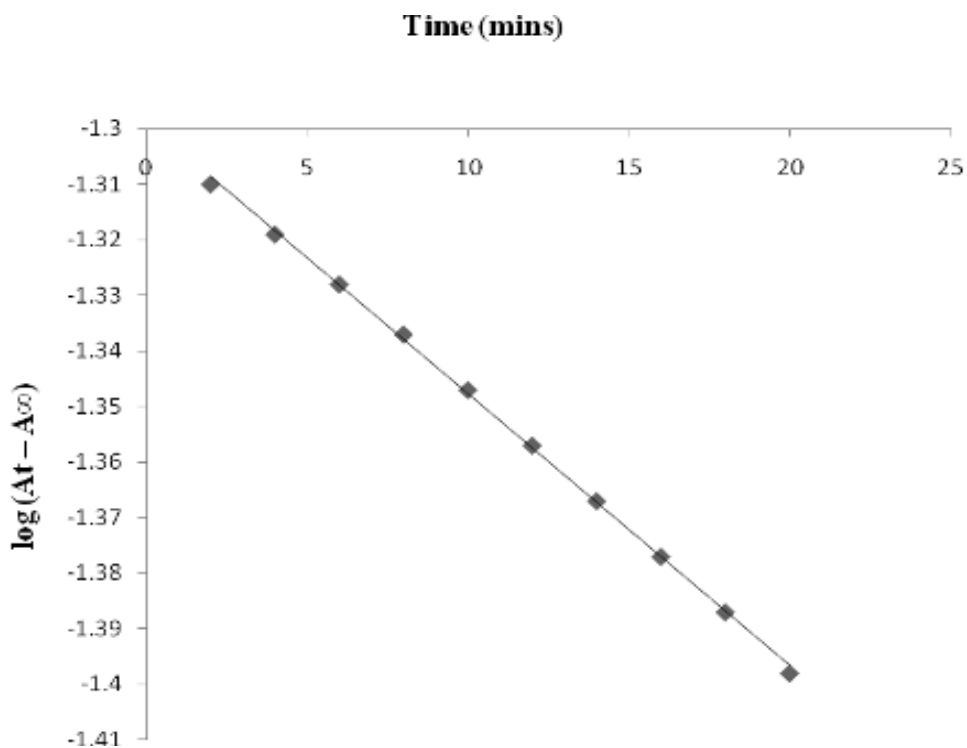


Fig. 1. A typical pseudo-first order plot for the reaction of methylthionium chloride with iodate ion. [MB] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [H<sup>+</sup>] =  $1.0 \times 10^{-1}$  mol dm<sup>-3</sup>,  $\mu$  = 1.0 mol dm<sup>-3</sup> and T =  $29 \pm 1^\circ\text{C}$  and  $\lambda_{\text{max}}$  = 663 nm

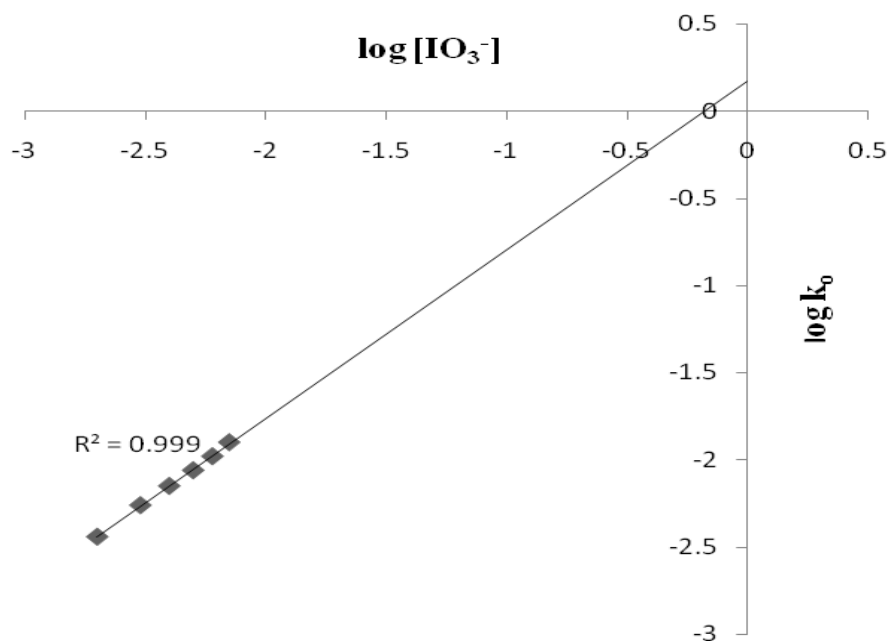
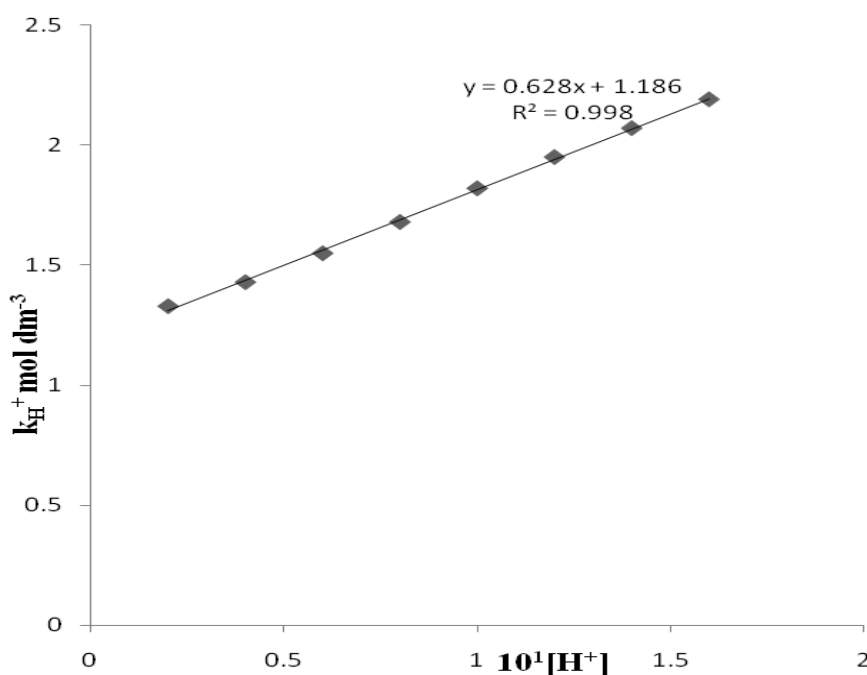


Fig. 2. Plot of log k<sub>o</sub> vs [IO<sub>3</sub><sup>-</sup>] for the reaction of methylthionium chloride and iodate ion. [MB] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [H<sup>+</sup>] =  $1.0 \times 10^{-1}$  mol dm<sup>-3</sup>,  $\mu$  = 1.0 mol dm<sup>-3</sup> and  $29 \pm 1^\circ\text{C}$  and  $\lambda_{\text{max}}$  = 663 nm

**Table 2. Hydrogen ion rate constant and second order rate constant for the reaction of methylthionium chloride and iodate ion. [MB] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [IO<sub>3</sub><sup>-</sup>] =  $3.0 \times 10^{-3}$  mol dm<sup>-3</sup>, [H<sup>+</sup>] =  $1.0 \times 10^{-1}$  mol dm<sup>-3</sup>,  $\mu$  =  $1.0$  mol dm<sup>-3</sup> and  $29 \pm 1^\circ\text{C}$  and  $\lambda_{\text{max}} = 663$  nm**

$10^3$ [IO <sub>3</sub> <sup>-</sup> ] mol dm <sup>-3</sup>	I (NaClO <sub>4</sub> ) mol dm <sup>-3</sup>	$10^3$ [H <sup>+</sup> ] mol dm <sup>-3</sup>	$10^3$ k <sub>o</sub> s <sup>-1</sup>	k <sub>2</sub> dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
3.0	1.0	0.2	3.98	1.33
3.0	1.0	0.4	4.30	1.43
3.0	1.0	0.6	4.66	1.55
3.0	1.0	0.8	5.04	1.68
3.0	1.0	1.0	5.46	1.82
3.0	1.0	1.2	5.84	1.95
3.0	1.0	1.4	6.21	2.07
3.0	1.0	1.6	6.57	2.19



**Fig. 3. Plot of k<sub>H<sup>+</sup></sub> vs [H<sup>+</sup>] for the reaction of methylthionium chloride and iodate ion. [MB] =  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>, [IO<sub>3</sub><sup>-</sup>] =  $3.0 \times 10^{-3}$  mol dm<sup>-3</sup>, [H<sup>+</sup>] =  $1.0 \times 10^{-1}$  mol dm<sup>-3</sup>,  $\mu$  =  $1.0$  mol dm<sup>-3</sup> and  $29 \pm 1^\circ\text{C}$  and  $\lambda_{\text{max}} = 663$  nm**

**Table 3. Ionic strength rate constant and second order rate constant for the reaction of methylthionium chloride and iodate ion at  $29 \pm 1^\circ\text{C}$ ,  $\lambda_{\text{max}} = 663$  nm, [MB] =  $1 \times 10^{-4}$  mol dm<sup>-3</sup>**

$10^3$ [IO <sub>3</sub> <sup>-</sup> ] mol dm <sup>-3</sup>	I (NaClO <sub>4</sub> ) mol dm <sup>-3</sup>	$\sqrt{\mu}$	$10^1$ [H <sup>+</sup> ] mol dm <sup>-3</sup>	$10^3$ k <sub>o</sub> s <sup>-1</sup>	k <sub>2</sub> dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
3.0	0.2	0.45	1.0	5.48	1.83
3.0	0.4	0.63	1.0	5.47	1.82
3.0	0.6	0.77	1.0	5.46	1.82
3.0	0.8	0.89	1.0	5.48	1.83
3.0	1.0	1.00	1.0	5.47	1.82
3.0	1.2	1.10	1.0	5.47	1.82
3.0	1.4	1.18	1.0	5.48	1.83
3.0	1.6	1.26	1.0	5.46	1.82

### 2.1.4 Effect of dielectric constant

The effect of medium dielectric constant, D, on the rate of reaction was investigated by using binary mixture of water and acetone in the range of 0.2-1.4%. "The results are presented in "Table 4".

### 2.1.5 Effect of added ions

The effect of added cations where investigated using  $Mg^{2+}$  and  $Ca^{2+}$  in the range  $0.2 - 1.4 \times 10^{-3}$  mol  $dm^{-3}$  and anion  $CH_3COO^-$  in the range of  $0.2 - 1.4 \times 10^{-3}$  at constant concentration of  $[MB] = 1 \times 10^{-4}$  mol  $dm^{-3}$ ,  $[IO_3^-] = 3.0 \times 10^{-3}$  mol  $dm^{-3}$ ,  $[H^+] = 1.0 \times 10^{-1}$  mol  $dm^{-3}$ ,  $\mu = 1.0$  mol  $dm^{-3}$  ( $NaClO_4$ ). "The results are presented in Table 5".

### 2.1.6 Test for intermediate complex formation

- The partially reacted mixtures were made to run at five minutes intervals after the commencement of the reaction over the

range 550 - 700 nm to check if there is a shift in the  $\lambda_{max}$  from 663 nm. A similar run was made for each reactant separately in each case.

- The Michaelis-Menten's plot of  $1/k_o$  vs  $1/[IO_3^-]$  was made Fig. 4.

### 2.1.7 Test for free radical

A solution of 2 ml of acrylamide was added to the partially oxidized reaction mixture of methylthionium chloride and iodate ion in excess methanol and to each of the reactant separately at  $[MB] = 1 \times 10^{-4}$  mol  $dm^{-3}$ ,  $[IO_3^-] = 3.0 \times 10^{-3}$  mol  $dm^{-3}$ ,  $[H^+] = 1.0 \times 10^{-1}$  mol  $dm^{-3}$ ,  $\mu = 1.0$  mol  $dm^{-3}$ .

### 2.1.8 Product analysis

The reaction mixtures were analyzed for the type of product(s) present after the completion of the reaction. Qualitative analysis was carried out on the mixtures using starch solution.

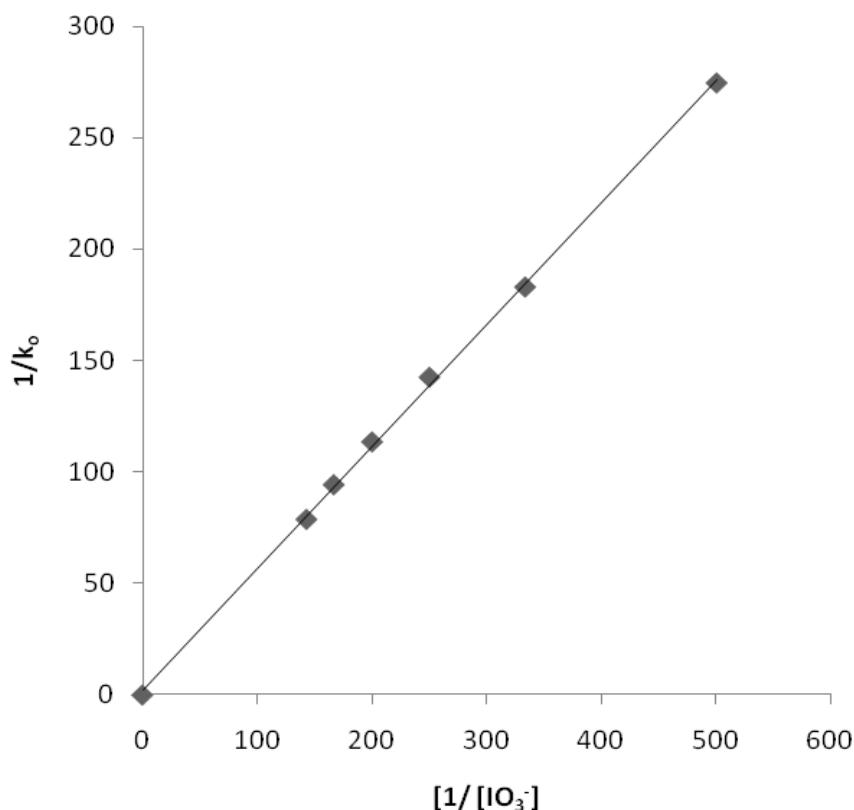


Fig. 4. Michaelis-Menten's Plot of  $1/k_o$  vs  $1/[IO_3^-]$ .  $[MB] = 1.0 \times 10^{-4}$  mol  $dm^{-3}$ .  $[H^+] = 1.0 \times 10^{-1}$  mol  $dm^{-1}$ ,  $\mu = 1.0$  mol  $dm^{-3}$  and  $29 \pm 1^\circ C$  and  $\lambda_{max} = 663$  nm

**Table 4. Effect of changes in total dielectric constant [MB] = 1.0x10<sup>-4</sup> mol dm<sup>-3</sup>, [IO<sub>3</sub><sup>-</sup>] = 3.0x10<sup>-3</sup> mol dm<sup>-3</sup>, λ<sub>max</sub> = 663 nm**

D	1/D	10 <sup>3</sup> k <sub>o</sub> s <sup>-1</sup>	k <sub>2</sub> dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
0.2	5.0	6.66	2.22
0.4	2.5	6.67	2.22
0.6	1.67	6.67	2.22
0.8	1.25	6.67	2.22
1.0	1.00	6.67	2.22
1.2	0.83	6.68	2.23
1.4	0.71	6.68	2.23

**Table 5. Effect of added anion and cations [MB] = 1.0x10<sup>-4</sup> mol dm<sup>-3</sup>, [IO<sub>3</sub><sup>-</sup>] = 3.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 1.0x10<sup>-1</sup> mol dm<sup>-3</sup> and λ<sub>max</sub> = 663 nm**

Concentration	10 <sup>3</sup> k <sub>o</sub> s <sup>-1</sup>	k <sub>2</sub> dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
<b>10<sup>3</sup>[CH<sub>3</sub>COO<sup>-</sup>]</b>		
0.2	4.15	1.38
0.4	4.15	1.38
0.6	4.14	1.38
0.8	4.14	1.38
1.0	4.15	1.38
1.2	4.15	1.38
1.4	4.15	1.38
<b>10<sup>3</sup>[Ca<sup>2+</sup>]</b>		
0.2	4.61	1.54
0.4	4.61	1.54
0.6	4.61	1.54
0.8	4.65	1.54
1.0	4.65	1.55
1.2	4.65	1.55
1.4	4.65	1.55
<b>10<sup>3</sup>[Mg<sup>2+</sup>]</b>		
0.2	5.93	1.98
0.4	4.38	1.46
0.6	3.68	1.23
0.8	2.76	0.92
1.0	2.53	0.84
1.2	2.32	0.77
1.4	2.26	0.75

### 3. RESULTS AND DISCUSSION

The stoichiometric study indicated that one mole of MB was completely consumed by one mole of IO<sub>3</sub><sup>-</sup>. This is consistent with what has been reported for the reactions of MB/mercaptoacetic acid by [7] and MB/L- ascorbic acid by [8] and MB/thiosulphate ion by [9]. Iodate has also been reported to have a 1: 1 by [10] for the reaction between MB and thiosulphate; Fe(CN)<sub>6</sub><sup>4-</sup>/IO<sub>3</sub><sup>-</sup> by [11]; Fe(II)/IO<sub>3</sub><sup>-</sup> by [12] respectively. The rate equation can be given as:



where

MW = reduced form of MB

#### 3.1 Kinetics and Order of Reaction

A pseudo-first order plot of log (A<sub>t</sub> – A<sub>∞</sub>) versus time was made and was found to be linear to about 80% of the reaction. This suggests that the reaction is first order in [MB] (Fig. 1). The order of one in the oxidant concentration in this reaction is consistent with what was reported for similar reactions of MB/ascorbic acid by [13] and MB/S<sub>2</sub>O<sub>5</sub><sup>2-</sup> by [14] respectively.

Plot of log k<sub>o</sub> versus log [IO<sub>3</sub><sup>-</sup>] was linear with a slope of 0.966 and an order of 1.00 from the relation k<sub>2</sub> = k<sub>o</sub>/[IO<sub>3</sub><sup>-</sup>]<sup>n</sup> indicating that the reaction is also first order with respect to [IO<sub>3</sub><sup>-</sup>] (Fig. 2). A similar order has been reported by [15] for the reaction between MB/thiosulphate; Fe(CN)<sub>6</sub><sup>4-</sup>/IO<sub>3</sub><sup>-</sup> by [11] and Fe(II)/IO<sub>3</sub><sup>-</sup> by [12]. The overall order is therefore second order for both MB and [IO<sub>3</sub><sup>-</sup>]. Thus, the rate equation for the reaction can be represented as:

$$-\frac{d[\text{MB}]}{dt} = k_2[\text{MB}][\text{IO}_3^-] \quad (2)$$

at [H<sup>+</sup>] = 1.0x10<sup>-1</sup> mol dm<sup>-3</sup> and T = 29±1°C, and k<sub>2</sub> = 1.79 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>

##### 3.1.1 Effect of [H<sup>+</sup>]

The rate constant of the reaction was found to increase slightly with increase in hydrogen ion concentration. This acid catalysis may be due to the successive protonation of MB according to [15] and this seems to agree with similar findings reported for the reduction of MB/bromate ion by [16]; MB/β-mercaptoethanol by [7]; MB/thiosulphate ion by [9]; MB /thiourea and permanganate ion [17,18] respectively. The rate of the reaction was varied in the acid range of 0.2 ≤ [H<sup>+</sup>] ≤ 1.6x10<sup>-1</sup> concentration (Table 2). The plot of k<sub>H</sub><sup>+</sup> versus [H<sup>+</sup>] was linear with a positive intercept on the y- axis. The intercept obtained from the plot of k<sub>H</sub><sup>+</sup> vs [H<sup>+</sup>] is an indication that the reaction occurred via acid-dependent and acid-independent pathways. The acid influenced rate equation can be given as:

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

where

$$a = 1.19 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}, b = 0.628 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

### 3.1.2 Effect of changes in ionic strength

Variation of ionic strength of the reaction mixture using  $\text{NaClO}_4$  did not have any effect on the rate of reaction (Table 3). Similar results have been reported by [19] saying that such observation is a common feature of reactions occurring between ion and neutral species where the product of charges is zero at the transition state.

### 3.2 Effect of Total Dielectric Constant

The effect of changing dielectric constant was studied by using a binary solvent mixture of water and acetone (20 %). It was found that as the concentration of acetone increased, the reaction rate was unaffected. This is in line with the plausible formation of ion-pair prior to electron transfer as earlier stated.

#### 3.2.1 Effect of added ions

The rate constant was found to be unaffected by the presence of  $\text{CH}_3\text{COO}^-$  (anion) as shown in Table 5. The presence of  $\text{Ca}^{2+}$  did not also affect the rate of reaction as the concentration of  $\text{Ca}^{2+}$  increased; however, the presence of  $\text{Mg}^{2+}$  however decreased the rate constant due to ion pair formation prior to electron transfer, Table 5. The lack of catalysis by the added  $\text{Ca}^{2+}$  is in line with the formation of ion-pair prior to electron transfer. Since the ion-pair complex does not possess a formal charge, interaction with added cation will be unlikely [20].

#### 3.2.2 Product analysis

The presence of iodine was identified qualitatively by adding starch solution to the colourless solution which gave a blue black colour indicating the presence of iodine.

#### 3.2.3 Free radicals

Addition of a solution of acrylamide to the partially reacted mixture did not give a gel even in the presence of excess methanol, indicating the probable absence of free radicals in the course of the reaction.

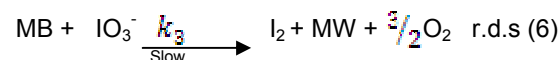
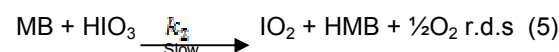
#### 3.2.4 Spectroscopic test for intermediate complex formation

Michealis Menten's plot of  $1/k_o$  vs  $1/[\text{IO}_3^-]$  gave a straight line which passed through the origin

(Fig 4). This suggests absence of intermediate complex formation prior to redox reaction. In addition, the results of the spectroscopic studies indicate no significant shifts from the absorption maxima of 663 nm. This suggests the absence of the formation of an intermediate complex in the reaction. Similar observation was reported for [18,21] and for MB/ $\text{S}_2\text{O}_5^{2-}$  by [14].

### 3.3 Reaction Mechanism

The results from the experimental data indicated that neutral specie reacted with an ion in the transition state and as such a plausible mechanism is proposed as follows:



From equation 4

$$[\text{HIO}_3] = K_1[\text{IO}_3^-][\text{H}^+] \quad (7)$$

Equations 5 and 6 are the rate determining steps, therefore:

$$\text{Rate} = k_2[\text{MB}][\text{HIO}_3] + k_3[\text{MB}][\text{IO}_3^-] \quad (8)$$

Substituting equation 7 into 8

$$\text{Rate} = k_2 K_1[\text{MB}][\text{IO}_3^-][\text{H}^+] + k_3[\text{MB}][\text{IO}_3^-] \quad (9)$$

$$\text{Rate} = k_2 + k_3 K_1[\text{H}^+][\text{MB}][\text{IO}_3^-] \quad (10)$$

Equation 10 is similar to equation 3

where

$$k_2 = 'a' = 1.19 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ and } k_3 K_1 = 'b' = 0.628 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The points below were considered in order to assign a plausible mechanism:

Plot of  $1/k_o$  vs  $1/[\text{IO}_3^-]$  was linear without an intercept indicating the absence of intermediate complex formation. This suggests the outer-sphere mechanism [22].

Due to absence of free radicals in the reaction mixture, it also suggests an outer-sphere mechanism [23].

The absence of a shift in the  $\lambda_{\max}$  from 663 nm in the electronic spectra suggests that a precursor complex is probably not formed prior to electron transfer and that the redox reaction most probably occurs by the outer-sphere mechanism.

#### 4. CONCLUSION

In conclusion, the stoichiometry showed a mole ratio of 1: 1 for MB/ $\text{IO}_3^-$ , a first order with respect to MB/ $\text{IO}_3^-$  and an overall order of 2. Furthermore, based on the plot of  $1/k_o$  vs  $1/[\text{IO}_3^-]$ , absence of an intermediate complex formation and lack of shift in the  $\lambda_{\max}$  from 663 nm gives an evidence that the reaction follows an outer-sphere mechanistic pathway.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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