

Mechanism of the reduction of 3,7-bis(dimethylamino)phenothionium chloride by metabisulphite ion in acidic medium

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ABSTRACT

The stoichiometry, mechanism of the reduction of 3, 7-Bis(dimethylamino) phenothionium chloride known as methylene blue (here in referred to as MB) with metabisulphite ion in acidic medium have been investigated under pseudo-first order conditions at $25 \pm 1^\circ\text{C}$, $[\text{H}^+] = 1 \times 10^{-1} \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$ (NaClO_4) and $\lambda_{\text{max}} = 663 \text{ nm}$. The stoichiometry is 1:3 and the kinetic studies indicated first order dependence in both MB and metabisulphite ion. The rate equation has been proposed as:

$$-d/dt [\text{MB}] = k_2[\text{MB}][\text{S}_2\text{O}_5^{2-}] \text{ Where } k_2 = 2.06 \times 10^{-1} \text{ mol dm}^{-3} \text{ s}^{-1}$$

The rate of reaction was enhanced by increase in hydrogen ion giving the dependence of several order rate constant on $[\text{H}^+]$ as $k_2 = a + b[\text{H}^+]$ and ionic strength in the reaction. Results from spectroscopic investigation and Michaelis-Menten's plot showed no evidence of the formation of an intermediate complex. The mechanism of the reaction is therefore discussed in terms of outer-sphere mechanism.

Keywords: 3, 7-Bis(dimethylamino) phenothionium chloride, Metabisulphite, Mechanism; Reduction.

INTRODUCTION

3, 7-Bis(dimethylamino) phenothionium chloride also known as methylene blue is a water soluble polyaromatic cationic redox dye, is widely used as a dye in biology for staining procedures to examine RNA or DNA [1]. It is also widely used in medicine for the treatment of malaria [2], cancer [3]. In chemistry, it is used as a redox indicator for the analysis of sulphide in soil and is easily reduced by various reducing agents to the colourless hydrogenated molecule, leucomethylene blue (LMB). These processes have found application in numerous inventions like data recording holographic industries, optical data storage, food and pharmaceutical industries and checking for the purity of milk. [4, 5].

Metabisulphite is a good reducing agent often used as a preservative and antioxidant in food [6]. Metabisulphite ions are the primary ingredients in campden tablets, used for wine and beer making to inhibit the growth of wild yeasts, bacteria, and fungi [7]. It is used in the manufacturing of some drugs and is also used in the textile industry for dyeing. Redox reaction of MB by permanganate ion, thiourea and hydrogen peroxide has earlier been reported by [8, 9, 10] respectively.

Knowledge of the kinetics of MB is very important in order to gain access to the mechanistic pathway of its reactions most especially in medicine for the treatment of some diseases. This work therefore is aimed at studying

the mechanism of the reduction of MB by metabisulphite ion. This is with a view to throwing more light on the mechanistic pathway of the reduction of this important dye.

MATERIALS AND METHODS

Material and Reagents

MB was obtained from Aldrich Chemical Company while all other reagents used were of BDH (analar grade). MB was used without further purification. Standard solution of dye, $S_2O_5^{2-}$ and all other salts were prepared with distilled water. The prepared solutions were wrapped with aluminum foil to avoid photochemical decomposition. Perchloric acid was used to investigate the effect of hydrogen ion on the rate while sodium perchlorate was used to maintain a constant ionic strength at 1.0 mol dm^{-3} . UV/Vis Spectrumlab 752s spectrophotometer was used to monitor changes in absorbance of reactions.

Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method [11]. The concentration of MB was kept constant at $3 \times 10^{-5} \text{ mol dm}^{-3}$ while that of the metabisulphite ions was varied from $(1.0 - 6.0) \times 10^{-4} \text{ mol dm}^{-3}$, $[H^+]$ at $1.0 \times 10^{-1} \text{ mol dm}^{-3}$, at ionic strength of 1.0 mol dm^{-3} ($NaClO_4$), $\lambda_{\text{max}} = 663 \text{ nm}$ and $T = 25 \pm 1^\circ\text{C}$.

The absorbance of the reaction mixture was measured at λ_{max} of 663 nm after the reaction had gone to completion as indicated by a constant reading in the absorbance over a period of 24 hrs. A plot of absorbance against the mole ratio of the reactants was made and the stoichiometry was evaluated from the point of inflection (fig 1).

Kinetics and Order of Reactions

All the rate measurements were made using UV/Vis Spectrumlab 752s spectrophotometer. The progress of the reactions was monitored by following the decrease in absorbance of the MB at λ_{max} 663 nm. All kinetic runs were made under pseudo-first order conditions with $[S_2O_5^{2-}]$ in at least 20 fold excess over $[MB]$, at $I = 1.0 \text{ mol dm}^{-3}$ ($NaClO_4$) and $[H^+] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$, at $25 \pm 1^\circ\text{C}$.

Plot of $\log (A_t - A_\infty)$ against time (where A_∞ and A_t are the absorbances at the end of the reaction and at time t respectively) were made from which pseudo-first order rate constants (k_0) were determined (fig 2). Second order rate constants (k_2) were obtained as $k_2 = k_0/[S_2O_5^{2-}]^0$. A plot of $\log k_0$ vs $\log [S_2O_5^{2-}]$ was also made (fig 3).

Effect of Hydrogen Ion

The effect of hydrogen ion on the rate of the reaction was investigated in the range of $(0.5 - 4.0) \times 10^{-1} \text{ mol dm}^{-3}$ ($HClO_4$) 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 4).

Effect of Ionic Strength

The effect of ionic strength on the rate of the reaction was investigated in the range of $0.5 - 4.0 \text{ mol dm}^{-3}$ ($NaClO_4$) while the concentrations of other reactants were kept constant. The results are presented in Table 3. A plot of $\log k_0$ vs \sqrt{I} was also made (fig 5).

Effect of Dielectric Constant

The effect of medium dielectric constant, D , on the rate of reaction was investigated by using 10% mixture of water and acetone, Table 4.

Effect of added ions

At constant concentration of $[MB] = 1 \times 10^{-5} \text{ mol dm}^{-3}$, $[S_2O_5^{2-}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $[H^+] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$ ($NaClO_4$), the effect of added cation (Ca^{2+}) on the rates of the reactions was investigated in the range $(0.2 - 1.6) \times 10^{-3} \text{ mol dm}^{-3}$ Table 5.

Test for Intermediate Complex Formation

a) The electronic spectra of the partially reacted reaction mixtures were recorded at five minutes intervals after the commencement of the reaction over the range of 550-700 nm. A similar run was made for the reactants separately in each case.

b) The Michaelis-Menten's plot of $1/k_o$ vs $1/[S_2O_5^{2-}]$ was made (fig 6).

Test for free radical

About 2 g of acrylamide was added to the partially oxidized reaction mixture of methylene blue and metabisulphite ions in excess methanol and to each of the reactant separately at stated condition in Table 1.

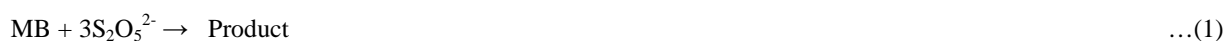
Product Analysis

At completion of the reaction, the reaction mixture was analyzed for the type of products found. SO_4^- was tested for as product. SO_4^- was tested qualitatively by mixtures of $BaCl_2/HCl$.

RESULTS AND DISCUSSION

Stoichiometry

Stoichiometric studies indicated that 3 moles of $S_2O_5^{2-}$ reacted completely with one mole of MB (Fig 1). This gives the overall equation of the reaction to be



Different stoichiometry has been reported for reactions of MB with different reductants. A stoichiometry of 1: 1 was reported for MB/thiourea by [8]; $[Fe_2(bpy)_4O]Cl_4/S_2O_5^{2-}$ by [12]; 1:2 for MB/ MnO_4^- by [9], 1:2 for MB/ $Fe(CN)_4^-$ by [13]. In this study the stoichiometry was observed to be in the ratio of 1:3 for MB/ $S_2O_5^{2-}$ (fig.1).

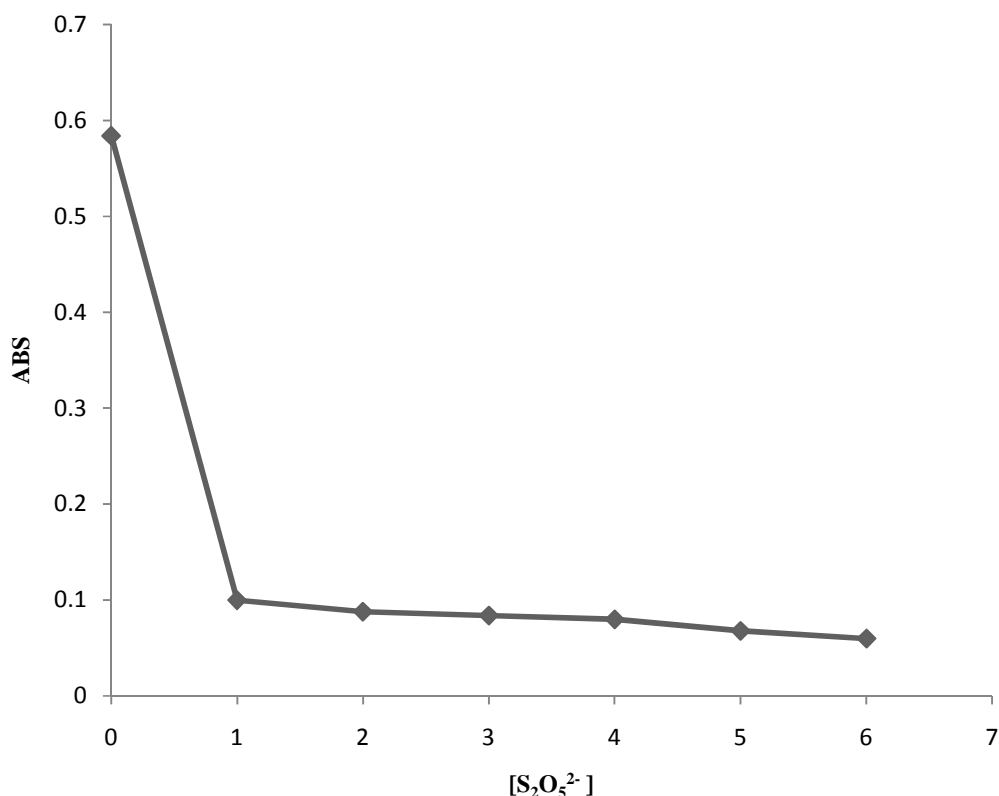


Figure 1: Stoichiometry Plot for the Reduction of MB with $S_2O_5^{2-}$. $T = 25 \pm 1^\circ C$, $\lambda_{max} = 663 \text{ nm}$

Kinetics and order of reaction

Plots of pseudo-first order of $\log(A_t - A_\infty)$ versus time were linear to about 80% of the reaction. This suggests that the reaction is first order in [MB] (fig.2). Plot of $\log k_o$ (where k_o pseudo-first order rate constant) versus $\log [S_2O_5^{2-}]$ was linear with a slope of 0.87 indicating that the reaction is first order with respect to $[S_2O_5^{2-}]$ (fig 3). A similar

order has been reported by [14]. The overall order is therefore second order for both MB and $[S_2O_5^{2-}]$. Thus, the rate equation for the reaction is

$$-d/dt[MB] = k_2[MB][S_2O_5^{2-}] \quad \dots\dots(2)$$

at $[H^+] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$ and $T = 25 \pm 1^\circ\text{C}$, and $k_2 = 2.06 \times 10^{-1} \text{ mol dm}^{-3} \text{ s}^{-1}$

Table 1: Pseudo-First rate constant and second order rate constant for the MB and $S_2O_5^{2-}$ at $25 \pm 1^\circ\text{C}$, $\lambda_{\text{max}} = 663 \text{ nm}$, $[MB] = 1 \times 10^{-5} \text{ mol dm}^{-3}$

| $10^3 [S_2O_5^{2-}] \text{ mol dm}^{-3}$ | $I (\text{NaClO}_4) \text{ mol dm}^{-3}$ | $10^1 [H^+] \text{ mol dm}^{-3}$ | $10^3 k_0 \text{ s}^{-1}$ | $10^1 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |
|--|--|----------------------------------|---------------------------|---|
| 20 | 1.0 | 1.0 | 4.49 | 2.25 |
| 30 | 1.0 | 1.0 | 6.56 | 2.19 |
| 40 | 1.0 | 1.0 | 8.38 | 2.10 |
| 50 | 1.0 | 1.0 | 9.78 | 1.96 |
| 60 | 1.0 | 1.0 | 12.32 | 2.05 |
| 70 | 1.0 | 1.0 | 13.75 | 1.96 |
| 80 | 1.0 | 1.0 | 15.23 | 1.90 |

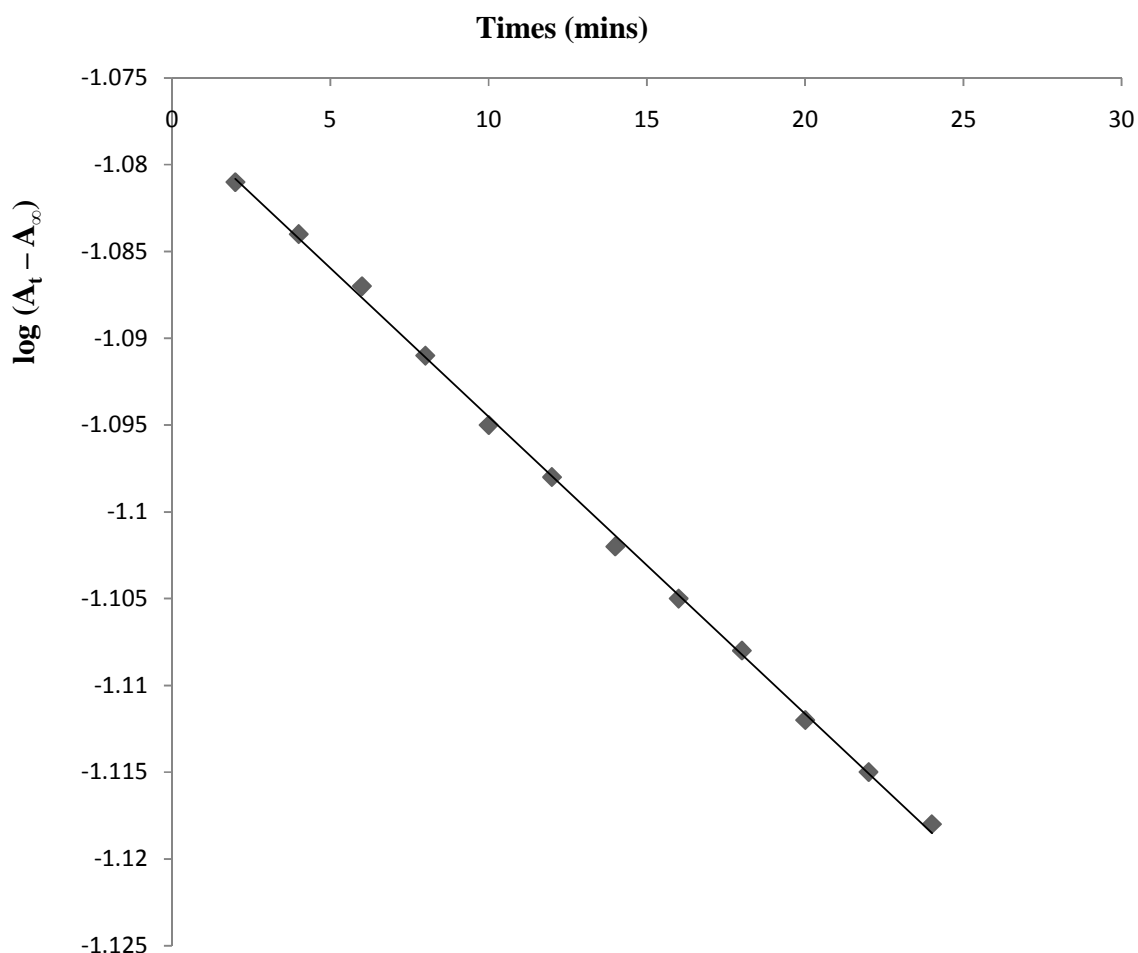


Figure 2: Typical Pseudo-first Order Plot for the Reaction of MB with $S_2O_5^{2-}$. $[MB] = 1 \times 10^{-5} \text{ mol dm}^{-3}$, $[S_2O_5^{2-}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 25 \pm 1^\circ\text{C}$, $\lambda_{\text{max}} = 663 \text{ nm}$

The order of one in the oxidant concentration in this reaction is consistent with what was reported for similar reactions of MB/ferrocyanide; sulphide ion and ascorbic acid [13, 15 and 16].

Table 2: Hydrogen ion rate constant and second order rate constant for the reaction of MB and $S_2O_5^{2-}$. [MB] = 1×10^{-5} mol dm $^{-3}$ [S $_2O_5^{2-}$] = 1×10^{-5} mol dm $^{-3}$ T = $25 \pm 1^\circ$ C, λ_{max} = 663 nm

| $10^5 [S_2O_5^{2-}]$ mol dm $^{-3}$ | I (NaClO $_4$) mol dm $^{-3}$ | $10^1 [H^+]$ mol dm $^{-3}$ | $10^3 k_0$ s $^{-1}$ | k_2 dm 3 mol $^{-1}$ s $^{-1}$ |
|-------------------------------------|--------------------------------|-----------------------------|----------------------|-------------------------------------|
| 20 | 1.0 | 0.5 | 0.83 | 4.15 |
| 20 | 1.0 | 1.0 | 1.23 | 6.15 |
| 20 | 1.0 | 1.5 | 1.38 | 6.90 |
| 20 | 1.0 | 2.0 | 1.46 | 7.30 |
| 20 | 1.0 | 2.5 | 2.30 | 11.50 |
| 20 | 1.0 | 3.0 | 2.37 | 11.85 |
| 20 | 1.0 | 3.5 | 4.21 | 21.05 |
| 20 | 1.0 | 4.0 | 5.30 | 26.50 |

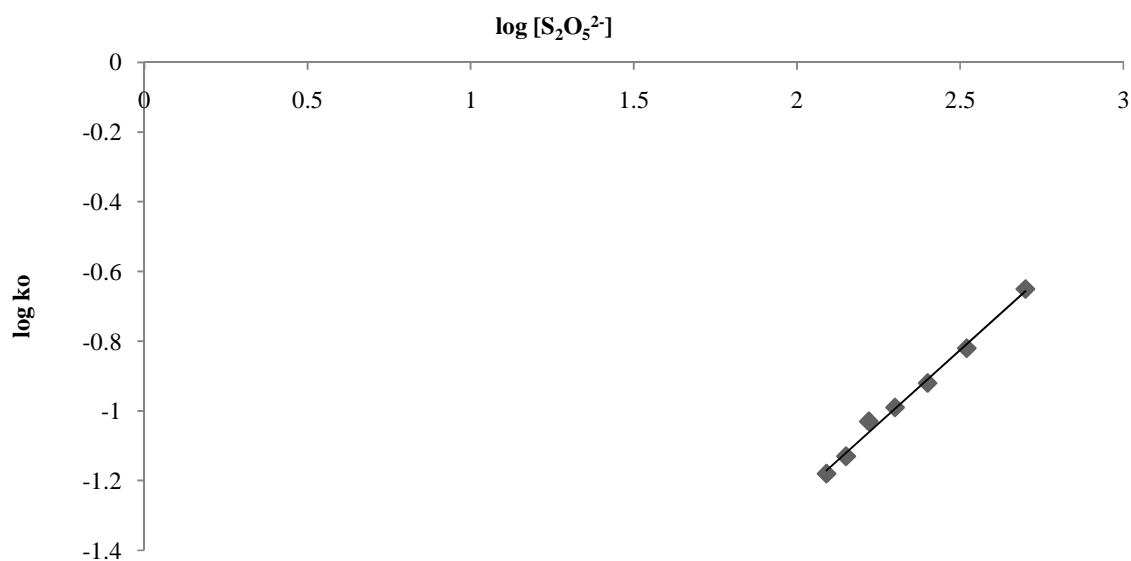


Figure 3: Plot of $\log k_0$ vs $[S_2O_5^{2-}]$ for the Reaction of MB with $S_2O_5^{2-}$.

Effect of $[H^+]$

The result on Table 2 shows that the rate constant of the reaction increased with increase in hydrogen ion concentration in the range of $(0.5-4.0) \times 10^{-1}$. Plots of k_H^+ versus $[H^+]$ (acid dependant rate constant) (Fig. 4) was linear with a slope of 4.82×10^{-1} and an intercept of 1.95×10^{-1} . The acid dependent rate equations for the reaction can be represented by equation 3,

$$k_H^+ = (a + b)[H^+][MB][S_2O_5^{2-}] \quad \dots (3)$$

where $a = 1.95 \times 10^{-1}$ mol dm $^{-3}$ s $^{-1}$, $b = 4.82 \times 10^{-1}$ mol dm $^{-3}$ s $^{-1}$

Equation 3 suggests that the reaction occurred via both acid-dependent and acid-independent pathways. Similar report for the reduction of MB by bromate ion; ethylenediamine tetracetatocobaltate (II) ion and β -mercaptoethanol have been observed by [17, 18, 19] respectively but different from the findings reported for the reduction of metabisulphate by 1, 2 benzenediol [20] and $Fe_2(bpy)_4O]Cl_4/S_2O_5^{2-}$ [12] where the rate of reactions is independent on $[H^+]$.

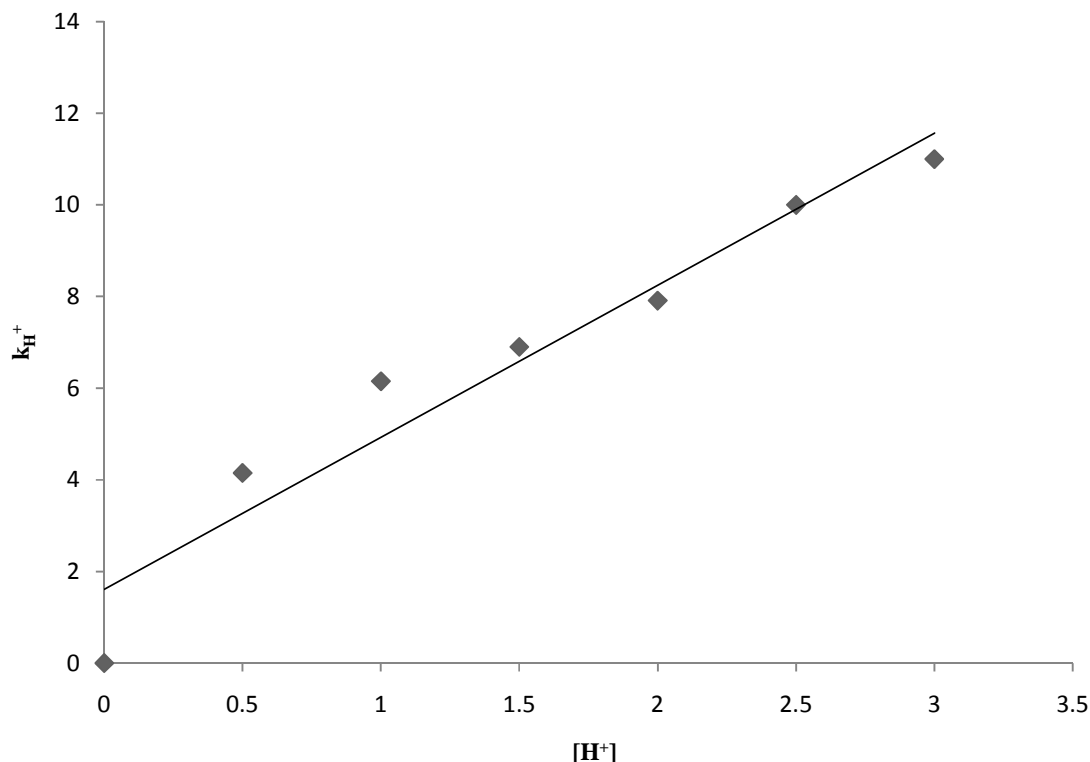


Figure 4: Plot of $\log k_{H^+}$ vs $[H^+]$ for the Reaction of MB and $S_2O_5^{2-}$

Effect of changes in Ionic Strength

The result in Table 3 shows that the rate of the reaction increased with increase in ionic strength suggesting a positive Bronsted – Debye salt effect. This observation suggests that the activated complex is formed from two ions of like charges [21]. A plot of k_o vs \sqrt{I} gave a linear graph with a slope of 0.76 showing positive effect as shown in Fig 5. This suggests that the product of the charges on the reactants in the activated complex is positive [22, 23].

Table 3: Ionic Strength rate constant and second order rate constant for the reaction of MB and $S_2O_5^{2-}$. $[MB] = 1 \times 10^{-5} \text{ mol dm}^{-3}$ $[S_2O_5^{2-}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ $T = 25 \pm 1^\circ\text{C}$, $\lambda_{\text{max}} = 663 \text{ nm}$

| $10^5 [S_2O_5^{2-}] \text{ mol dm}^{-3}$ | $I (\text{NaClO}_4) \text{ mol dm}^{-3}$ | \sqrt{I} | $10^1 [H^+] \text{ mol dm}^{-3}$ | $10^3 k_o \text{ s}^{-1}$ | $k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |
|--|--|------------|----------------------------------|---------------------------|--|
| 20 | 0.5 | 0.71 | 1.0 | 0.70 | 3.50 |
| 20 | 1.0 | 1.00 | 1.0 | 1.32 | 6.60 |
| 20 | 1.5 | 1.22 | 1.0 | 3.03 | 15.15 |
| 20 | 2.0 | 1.41 | 1.0 | 3.32 | 16.60 |
| 20 | 2.5 | 1.58 | 1.0 | 5.34 | 26.70 |
| 20 | 3.0 | 1.73 | 1.0 | 5.46 | 27.30 |
| 20 | 3.5 | 1.87 | 1.0 | 6.38 | 31.90 |
| 20 | 4.0 | 2.00 | 1.0 | 6.53 | 32.65 |

Effect of Total Dielectric Constant

The effect of changing dielectric constant was studied by using a binary solvent mixture of water and acetone (10%). It was found that as the concentration of acetone increased, the rate reaction also increased. This observation is different from that reported for the reaction of MB/1-methyl-2-thioureae in which an increase in the concentration of acetone decreased the rate of reaction [24].

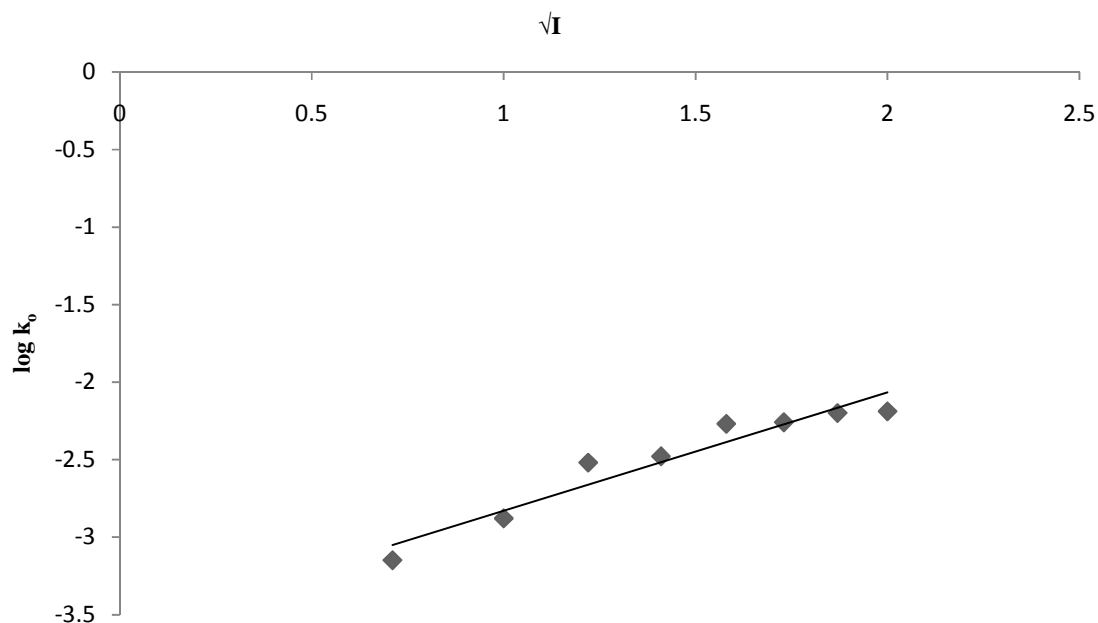


Figure 5: Plot of $\log k_0$ vs \sqrt{I} for the Reaction of MB and $S_2O_5^{2-}$ [$S_2O_5^{2-}$] = 1×10^{-3} mol dm $^{-3}$, T = $25 \pm 1^\circ\text{C}$, $\lambda_{\text{max}} = 663$ nm

Table 4: Effect of Changes in Total Dielectric Constant [MB] = 1.0×10^{-5} mol dm $^{-3}$, [$S_2O_5^{2-}$] = 1.0×10^{-3} mol dm $^{-3}$, $\lambda_{\text{max}} = 663$ nm

| D | I/D | $10^3 k_2 \text{ s}^{-1}$ | $k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |
|-----|------|---------------------------|--|
| 0.2 | 5.0 | 0.007 | 0.03 |
| 0.4 | 2.5 | 0.05 | 0.23 |
| 0.6 | 1.67 | 0.08 | 0.38 |
| 0.8 | 1.25 | 1.00 | 0.50 |
| 1.0 | 1.00 | 1.18 | 0.59 |
| 1.2 | 0.83 | 2.30 | 1.15 |
| 1.4 | 0.71 | 2.36 | 1.23 |

Effect of Added Cation

The presence of Ca^{2+} did not affect the rate constant. The lack of catalysis by the added cation 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 (Iyun *et al.*, 1995).

Table 5: Effect of Added Cation [MB] = 1.0×10^{-5} mol dm $^{-3}$, [$S_2O_5^{2-}$] = 1.0×10^{-3} mol dm $^{-3}$, $\text{CaCl}_2 = 1.0 \times 10^{-3}$, $\lambda_{\text{max}} = 663$ nm

| X | $10^3 k_2 \text{ s}^{-1}$ | $10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |
|-----|---------------------------|---|
| 0.2 | 0.38 | 0.19 |
| 0.4 | 0.15 | 7.68 |
| 0.6 | 7.68 | 3.84 |
| 0.8 | 7.68 | 3.84 |
| 1.0 | 7.68 | 3.84 |
| 1.2 | 0.15 | 3.84 |
| 1.4 | 0.15 | 7.68 |
| 1.6 | 0.38 | 0.19 |

Product Analysis

After the completion of the reaction, a colourless solution was obtained and the UV visible spectra of the product showed no absorption peak at λ_{max} of 663 nm. This indicates the destruction of the quinoid (chromophore) group. Furthermore, on addition of acidified BaCl_2 to the complete reaction mixture, a white precipitate was obtained indicating the presence of SO_4^{2-} as the product of the reaction.

Free Radicals

Addition of a solution of acrylamide to partially reacted mixture did not give a gel in the presence of excess methanol, indicating the probable absence of free radicals in the reaction mechanism. However, there is also the probability of the formation of semiquinone radical which is difficult to observe experimentally [25].

Spectroscopic Test for Intermediate Complex Formation

The plot of $1/k_0$ vs $1/[S_2O_5^{2-}]$ gave a straight line which passed through the origin (Fig 6). 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 $\lambda_{\max} = 663$ nm. This further suggests the absence of the formation of an intermediate complex in the reaction. Similar observation was reported for MB by MnO_4^- and 1-methyl-2-thiourea by [9, 24].

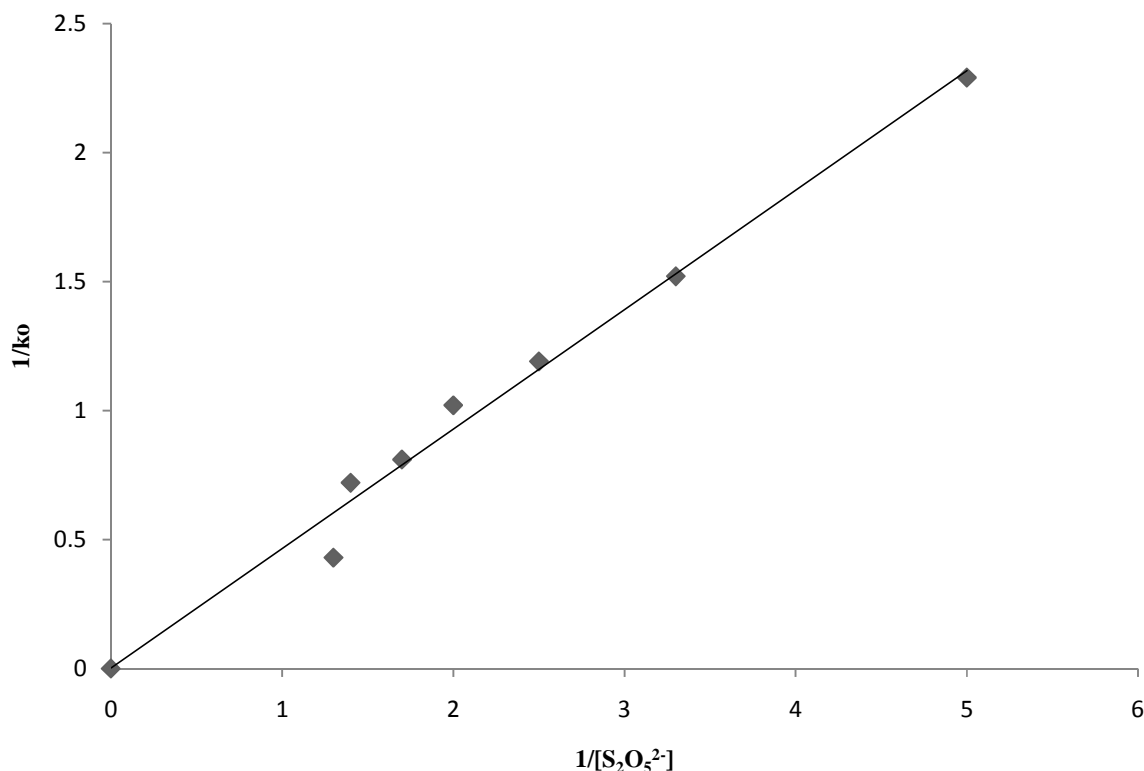


Figure 6: Michaelis-Menten's Plot of $1/k_0$ vs $1/[S_2O_5^{2-}]$. $[S_2O_5^{2-}] = 1 \times 10^{-5} \text{ mol dm}^{-3}$ $T = 25 \pm 1^\circ\text{C}$, $\lambda_{\max} = 663 \text{ nm}$

Mechanism of Reaction

[26, 27] reported that redox reactions of many oxy-anions are strongly acid dependent and as such it is reasonable to postulate that $S_2O_5^{2-}$ is protonated in a fast step to give $HS_2O_5^-$ which then reacts with MB in a slow step to give the products. Also, the intercept obtained for the plot of k_2 versus $[H^+]$ indicates that the unprotonated $S_2O_5^{2-}$ also reacts with MB to form the products. Therefore, taking recourse to the experimental data, the following mechanistic steps have been postulated for the reaction:



$$\text{Rate} = k_2[MB][HS_2O_5^-] + k_3[MB][S_2O_5^{2-}] \quad \dots\dots 7$$

From equation 5.

$$[\text{HS}_2\text{O}_5^-] = K_1[\text{S}_2\text{O}_5^{2-}][\text{H}^+] \quad \dots\dots 8$$

Putting equation 8 into 7,

$$\text{Rate} = k_2K_1[\text{MB}][\text{S}_2\text{O}_5^{2-}][\text{H}^+] + k_3[\text{MB}][\text{S}_2\text{O} \quad \dots\dots 9$$

$$\text{Rate} = k_3 + k_2K_1 [\text{H}^+][\text{MB}][\text{S}_2\text{O}_5^{2-}] \quad \dots\dots 10$$

Equation 10 is similar to equation 3

where $k_3 = 'a' = 1.95 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_2K_1 = 'b' = 4.82 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

In trying to assign mechanistic pathway for this reaction, the following points are considered:

The Michaelis- Menten plot of $1/k_0$ vs $1/[\text{S}_2\text{O}_5^{2-}]$ was linear without an intercept indicating the absence of intermediate complex formation. This suggests the outer-sphere mechanism [28].

Absence of free radicals in the reaction mixture suggests the contribution of outersphere mechanism [29].

Absence of spectrophotometric evidence of intermediate complex formation 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.

CONCLUSION

From the points above, one is able to conclude that the reaction of MB with metabisulphite ion most probably occurred by the outer-sphere mechanism.

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