

Kinetic Approach To The Mechanism Of P-Bis(Dimethylamino)-Phenothiazin-5-ium Chloride Sulphate Ion In Acidic Medium

Babatunde OA, Umoru, Patricia Ese

ABSTRACT: The kinetics and mechanism of p-Bis(dimethylamino)-phenothiazin-5-ium chloride by sulphate ion has been investigated in perchloric acid. The progress of the reactions was monitored by observing the decrease in absorbance of the oxidant at λ_{\max} of 663 nm UV/Vis Spectrumlab 752s spectrophotometer. The results showed a stoichiometry of 1:2, first-order dependence in both oxidant and reductant. The second order rate equation at constant temperature is therefore given as:

$$-d[\text{MB}]/dt = k_2[\text{MB}][\text{SO}_4^{2-}]$$

where $k_2 = 4.86 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$

A positive primary salt effect was observed and an increase in the concentration of hydrogen ion as well dielectric constant increased the rate of reaction. Added ions did not show any effect on the rate of reaction. The result of spectroscopic and kinetic investigation did not indicate intermediate complex formation in the course of the reaction. A plausible mechanism for the reaction has been proposed in line with the outer-sphere reaction pathway.

Key words: kinetics, reaction mechanism, stoichiometry, sulphate ion and methylene blue.

Introduction

Sulphate ion is a very weak oxidizing agent which has found use as an algacide in therapeutic bath and as counter ion for some cationic drugs. The sulfate ion can act as a ligand attaching either by one oxygen (monodentate) or by two oxygens as either a chelate or a bridge [1]. Sulfates are widely used industrially for making plaster, detergent and surfactant found in many personal care products (soaps, shampoos, toothpaste etc.), lead-acid battery and as algacide. p-Bis(dimethylamino)-phenothiazin-5-ium chloride, is a cationic thiazine dye showing deep blue colour in the oxidized state. It is an electron donor or acceptor and a free radical scavenger. It is clinically used to identify anatomic and pathologic structures to treat methemoglobinemia. It is used to treat ich and as a pathological stain. Furthermore, it is observed to improve hypotension associated with various clinical states [2] and also results in transient and reproducible improvement in blood pressure and cardiac function in septic shock. It is an electron donor or acceptor and free radical scavenger. It is clinically used to identify anatomic and pathologic structures to treat methemoglobinemia. It is also used as a bacteriological stain in fresh frozen plasma, oxidation-reduction indicator as well.

It is also used as a pathological stain, as a diagnostic aid in the detection of the premature rupture of fetal membranes and to identify separate amniotic sacs in multiple pregnancies [3]. Due to the vital importance of methylene blue as a biological dye, it is important that the kinetics and mechanism of its reaction with sulphate ion be investigated to afford more application of both methylene blue and sulphate ion.

Material and Methods

p-Bis(dimethylamino)-phenothiazin-5-ium chloride (herein referred to as methylene blue; MB) was purchased from Aldrich Chemical company. MB was used without further purification. All other solutions were of analytical grade and prepared with distilled water. The solutions prepared were wrapped with aluminum foil to prevent photochemical decomposition. Investigation of the effect of hydrogen ion on the rate of reaction was done using perchloric acid while sodium perchlorate was used to maintain a constant ionic strength at 1.0 mol dm^{-3} . Spectrophotometer (UV/Vis Spectrumlab 752s) was used to monitor changes in absorbance of reactions.

Stoichiometry

Spectrophotometric titration was used to determine the stoichiometry of the reaction using the mole ratio method as reported by [4]. Constant concentration of oxidant was made at $1 \times 10^{-5} \text{ mol dm}^{-3}$ MB while that of the SO_4^{2-} was varied from 1.0×10^{-5} - $6.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-2}$, ionic strength of 1.0 mol dm^{-3} (NaClO_4), $\lambda_{\max} = 663 \text{ nm}$ and $T = 29 \pm 1^\circ\text{C}$. The reaction was allowed to continue at the stated temperature and the absorbance of the reaction mixture was measured at maximum wavelength of 663 nm after the reaction had gone to completion as indicated by no further change in the absorbance reading over a period of 24 hrs. A plot of absorbance against concentration of SO_4^{2-} was made and the mole ratio was evaluated from the point of inflection.

- Babatunde OA and Umoru PE
- Department of Chemistry Nigerian Defence Academy, Kaduna, Nigeria
- Corresponding Author: patriciaumoru@yahoo.com

Kinetics and Order of Reactions

All kinetic runs were performed under pseudo-first order conditions with the concentration of SO_4^{2-} at least 20 fold excess over MB, while the ionic strength was maintained at 1.0 mol dm^{-3} (NaClO_4), $[\text{H}^+] = 1.0 \times 10^{-2}$ at $29 \pm 1^\circ\text{C}$. The progress of the reactions was monitored by observing the decrease in absorbance of the oxidant at λ_{max} of 663 nm UV/Vis Spectrumlab 752s spectrophotometer. Plot of $\log(A_t - A_\infty)$ against time (where A_t and A_∞ are the absorbance at the end of the reaction and at time t respectively) were made from which pseudo-first order rate constants (k_1) were determined (Fig 1). A plot of $\log k_1$ vs $\log [\text{SO}_4^{2-}]$ was also made (Fig 2). Second order rate constants (k_2) were obtained from k_1 as $k_2 = k_1 / [\text{SO}_4^{2-}]$.

Effect of Hydrogen Ion Concentration

The influence of acid on the rate of the reaction was studied in the range of $0.5 \times 10^{-2} \text{ mol dm}^{-3}$ to $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ (HClO_4), while the concentrations of the MB, SO_4^{2-} and I were kept constant. The results are presented in Table 1. A plot of k_1 vs $[\text{H}^+]$ was also made (Fig 3).

Effect of Ionic Strength

The effect of ionic strength on the rate of the reaction was studied in the range of $0.5 - 3.0 \text{ mol dm}^{-3}$ (NaClO_4) while the concentrations of other reactants were kept constant. A plot of $\log k_1$ vs \sqrt{I} is shown in Figure 4.

Effect of Dielectric Constant

The effect of medium dielectric constant, D , on the rate of reaction was investigated by using 20% mixture of water and acetone.

Effect of Added ions

The rates of the reactions were investigated for the effect of added cations (Mg^{2+} and Li^{2+}) in the range $(0.2 - 1.6) \times 10^{-1} \text{ mol dm}^{-3}$ and anion (CH_3OOH^-) in the range $(0.2 - 1.6) \times 10^{-1}$ (Table 2) at constant concentration of $[\text{MB}] = 1 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{SO}_4^{2-}] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ and $I = 1.0 \text{ mol dm}^{-3}$ (NaClO_4).

Test for Intermediate Complex Formation

(a) Spectrophotometric Test

This test is usually carried out in order to find out if any determinable intermediate complex was formed during the reaction between the MB and SO_4^{2-} . The electronic spectra of the reaction mixtures were recorded at 5 minutes intervals after the commencement of the reaction over the range of 550-700 nm. A similar run was made for each reactant separately. The result obtained was corroborated by plotting inverse of (k_1) against inverse of molar concentration of SO_4^{2-} . The Michaelis-Menten's plot is shown in (fig 5).

Test for Free Radical

About 2 g of acrylamide was dissolved in distilled water and was added to the partially oxidized reaction mixture of MB and SO_4^{2-} in excess of methanol and to each of the reactant separately at stated condition in Table 1.

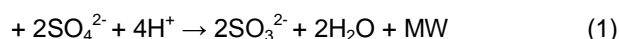
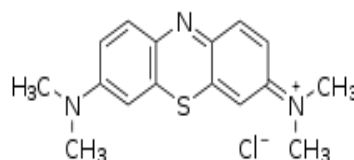
Product Analysis

The reaction mixture was analyzed for the type of product(s) present at the completion of the reaction. Sulphite ion was tested qualitatively by mixtures BaCl_2/HCl respectively and HNO_3 was finally added as a confirmatory test.

Results and Discussion

Stoichiometric investigation showed that one mole of MB is consumed by two mole of SO_4^{2-} .

The overall rate equation can therefore be represented as:



where MW is methylene white (reduced form of methylene blue).

Kinetics and order of reaction

Pseudo-first order plots of $\log(A_t - A_\infty)$ versus time were linear to about 90% of the reaction suggesting a first order dependence of rate on $[\text{MB}]$ (fig 1). Plot of $\log k_1$ (where k_1 pseudo-first order rate constant) versus $\log [\text{SO}_4^{2-}]$ at constant $[\text{H}^+]$ was linear with a slope of 1.01 indicating an order of 1.00 from the relation $k_2 = k_1 / [\text{SO}_4^{2-}]^n$ showing that the reaction is first order with respect to the concentration of (SO_4^{2-}) (fig 3). A similar order has been reported for the reaction by [5]. The overall order is therefore second order for both MB and $[\text{SO}_4^{2-}]$. Thus, the rate equation for the reaction is:

$$-d/dt[\text{MB}] = k_2[\text{MB}][\text{SO}_4^{2-}] \quad (2)$$

at $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ and $T = 29 \pm 1^\circ\text{C}$ and $k_2 = 4.86 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$

Table 1: Pseudo-First Rate Constant and Second Order Rate Constant for the Reaction of Methylene Blue and Sulphate Ion at $29 \pm 1^\circ\text{C}$, $\lambda_{\text{max}} = 663 \text{ nm}$, $[\text{SO}_4^{2-}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{MB}] = 1 \times 10^{-5} \text{ mol dm}^{-3}$ and $[\text{H}^+] = 1 \times 10^{-2} \text{ mol dm}^{-3}$

10^3 [SO ₄ ²⁻] mol dm ⁻³	I (NaClO ₄) mol dm ⁻³	10^2 [H ⁺] mol dm ⁻³	10^3 k ₁ min ⁻¹	k ₂ dm ³ mol ⁻¹ min ⁻¹
2.0	1.0	1.0	9.81	4.91
3.0	1.0	1.0	14.55	4.85
4.0	1.0	1.0	19.55	4.89
5.0	1.0	1.0	24.37	4.87
6.0	1.0	1.0	29.11	4.85
7.0	1.0	1.0	34.13	4.88
8.0	1.0	1.0	42.90	4.94
9.0	1.0	1.0	47.74	4.77
10.0	1.0	1.0	47.74	4.77
3.0	1.0	0.5	11.84	3.99
3.0	1.0	1.0	14.60	4.87
3.0	1.0	1.5	16.54	5.51
3.0	1.0	2.0	17.04	6.68
3.0	1.0	2.5	20.90	7.44
3.0	1.0	3.0	22.97	8.99
3.0	0.5	1.0	12.85	4.28
3.0	1.0	1.0	14.58	4.86
3.0	1.5	1.0	15.96	5.32
3.0	2.0	1.0	17.31	5.77
3.0	2.5	1.0	20.44	6.81
3.0	3.0	1.0	22.78	7.

Time (mins)

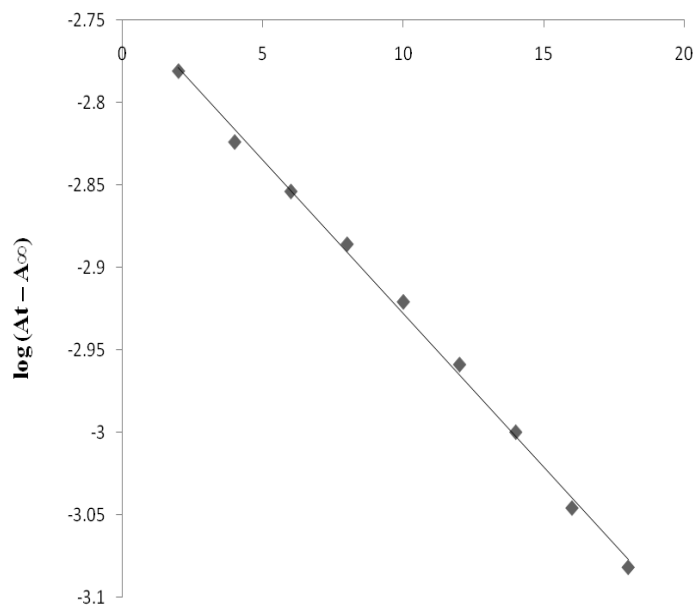


Fig 1: A Typical Pseudo-first Order Plot for the Reaction of Methylene Blue with Sulphate Ion. $[\text{MB}] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{SO}_4^{2-}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$ and $T = 29 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 663 \text{ nm}$.

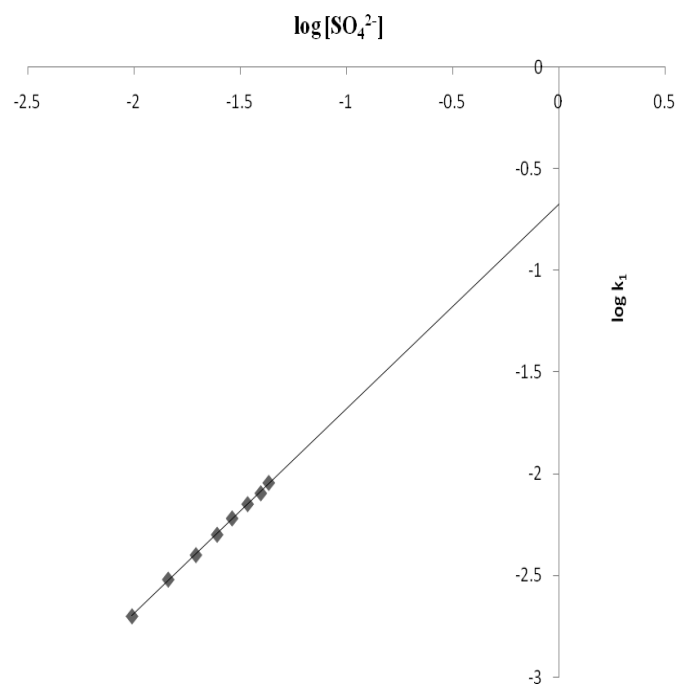


Fig 2: Plot of $\log k_1$ vs $\log [\text{SO}_4^{2-}]$ for the Reaction of Methylene Blue and Sulphate Ion. $[\text{MB}] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{SO}_4^{2-}] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$ and $T = 29 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 663 \text{ nm}$.

The order of reaction with respect to the oxidant and reductant concentrations in this reaction is one respectively. The overall order is therefore second order. The second order rate equation at constant temperature is therefore given as:

$$-d[\text{MB}]/dt = k_2[\text{MB}][\text{SO}_4^{2-}] \quad (2)$$

where $k_2 = 4.86 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$

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

The studies on the effect of acid on the reaction rates were found to increase with increase in hydrogen ion concentration in the range of $0.5 \times 10^{-2} \leq [\text{H}^+] \leq 3.0 \times 10^{-2}$ (Table 1). Plots of k_{H^+} versus $[\text{H}^+]$ (acid dependant rate constant) (Fig. 4) was linear with a slope of 2.55×10^{-2} and a positive intercept of 1.60 on the y-axis. This implies that both the protonated and the unprotonated species are reactive. Similar report for the reduction of MB by bromate ion; ethylenediamine tetracetatocobaltate (II) ion, metabisulphite and β -mercaptoethanol have been observed by [6], [7], [4], [8], respectively. The acid dependent rate equation is given as:

$$k_{\text{H}^+} = (a + b)[\text{H}^+][\text{MB}][\text{SO}_4^{2-}] \quad \text{--- (3)}$$

where $a = 1.60 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $b = 2.55 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$

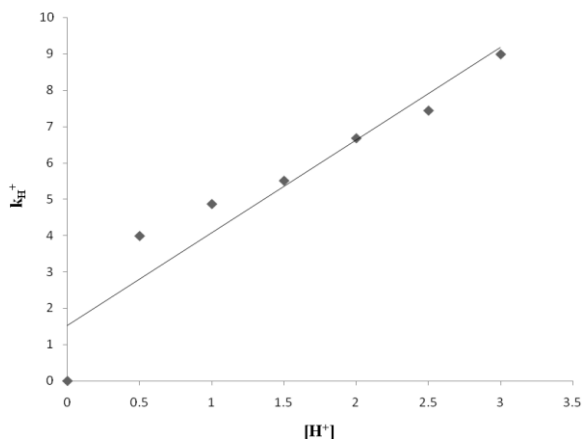


Figure 3: Plot of k_{H^+} vs $[H^+]$ for the Reaction of Methylene Blue and Sulphate Ion. $[MB] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[SO_4^{2-}] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[H^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$ and $T = 29 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 663 \text{ nm}$.

Effect of changes in Ionic Strength

A positive primary salt effect was observed in the redox reaction as the rate of reaction was found to increase with increase in ionic strength of the reaction medium from $0.5 \leq I \leq 3.0 \text{ mol dm}^{-3}$. The plot of $\log k_1$ against \sqrt{I} gave a straight line with a positive slope of 0.24 (Figure 5). The observed slope of less than one could be due to formation of ion – pair during the reaction. The positive Bronsted – Debye salt effect observed, suggests an interaction of species carrying same charge signs in the activated complex and such interaction usually accelerates reaction by increase in ionic strength, this is because of favorable interactions of the activated complex with the denser ionic environment [9]. Similar results were obtained for MB/S₂O₅²⁻ by [4] MB /thiourea as reported by [10].

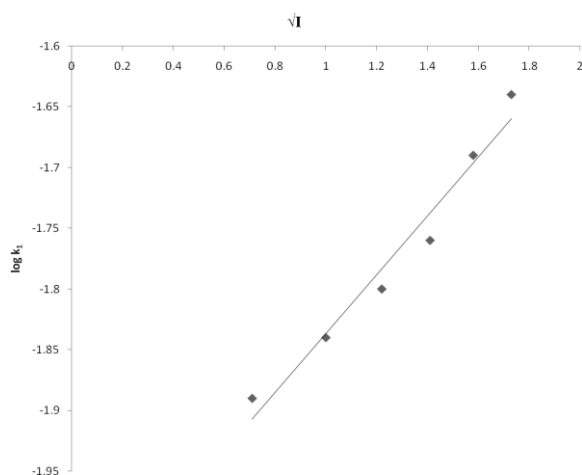


Figure 4: Plot of $\log k_1$ vs \sqrt{I} for the Reaction of Methylene Blue and Sulphate Ion. $[MB] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[SO_4^{2-}] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[H^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$ and $T = 29 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 663 \text{ nm}$.

Effect of Total Dielectric Constant

The reaction rate increased as the concentration of acetone increased. A similar result has been reported for the reaction of MB/S₂O₅²⁻ by [4].

Table 2: Effect of Changes in Total Dielectric Constant

$[MB] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[SO_4^{2-}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[H^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$, $T = 29 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 663 \text{ nm}$

D	1/D	$10^3 k_1 \text{ min}^{-1}$	$k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$
0.5	2.0	1.11	3.70
1.0	1.0	1.70	5.67
1.5	0.67	1.92	6.40
2.0	0.5	2.03	6.76
2.5	0.4	2.07	6.93
3.0	0.33	2.33	7.78

Effect of Added Ions

Added ions did not show any effect on the rate of reaction, although, [11], [12], [13] reported that added ions are expected to catalyze reactions occurring by the outer-sphere mechanism and lack of catalysis could be indicative of inner-sphere mechanism. The lack of catalysis as observed with the added anions and cation is in line with the formation of ion-pairs prior to electron transfer. Since the ion-pair complex does not possess a formal charge, interaction with added ions will not be very plausible hence the reaction is likely to follow inner- sphere pathway [14].

Table 3: Effect of Added Cation

$[MB] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[SO_4^{2-}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[H^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$, $T = 29 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 663 \text{ nm}$.

X	$10^3 k_1 \text{ min}^{-1}$	$10 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$
0.5	4.61	1.53
1.0	4.61	1.53
1.5	4.61	1.53
2.0	4.61	1.53
2.5	4.61	1.53
3.0	4.61	1.53

Product Analysis

On addition of acidified BaCl₂ to the complete reaction mixture, a white precipitate was obtained which disappeared on the addition of dilute HNO₃ indicating the presence of SO₃²⁻ as the product of the reaction. Furthermore, a colourless solution was obtained at the completion of the reaction and showed no absorption peak at maximum wavelength of 663 nm using UV-Visible spectra indicating the destruction of the quinoid group.

Free Radicals

Solution of 2 g acrylamide added to the partially reacted mixture did not form a gel even 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 semi-quinone radical which is difficult to observe experimentally [15].

Spectroscopic Test for Intermediate Complex Formation

The plot of $1/k_1$ vs $1/[\text{SO}_4^{2-}]$ 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 $\lambda_{\text{max}} = 663$ nm. This suggests the absence of the formation of an intermediate complex in the reaction. This is in good agreement with the results obtained by other workers [16], [17], [4] respectively as reported for MB/1-methyl-2-thiourea, MB/ MnO_4 and MB/ $\text{S}_2\text{O}_5^{2-}$.

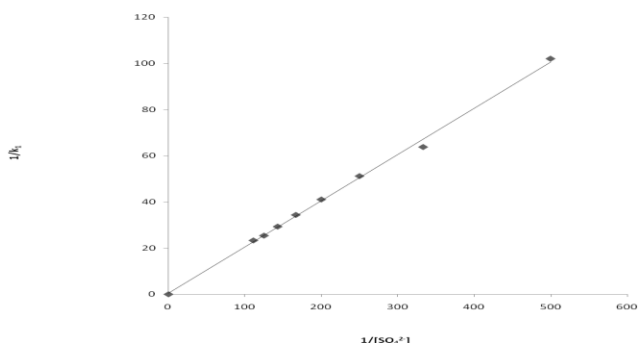
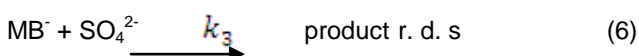
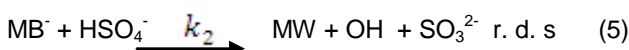
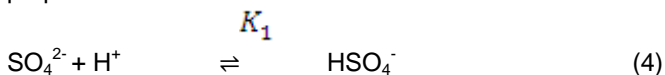


Figure 5: Michaelis-Menten's Plot of $1/k_1$ vs $1/[\text{SO}_4^{2-}]$, $[\text{MB}] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{SO}_4^{2-}] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$, $l = 1.0 \text{ mol dm}^{-3}$ and $T = 29 \pm 1^\circ\text{C}$ and $\lambda_{\text{max}} = 663 \text{ nm}$.

Reaction Mechanism

Based on the above findings the reaction mechanism is proposed as follows:



From equation 4

$$K_1 = \frac{[\text{HSO}_4^-]}{[\text{H}^+][\text{SO}_4^{2-}]} \quad (7)$$

$$[\text{HSO}_4^-] = K_1 [\text{SO}_4^{2-}][\text{H}^+] \quad (8)$$

Therefore:

$$\text{Rate} = k_2[\text{MB}^-][\text{HSO}_4^-] + k_3[\text{MB}^-][\text{SO}_4^{2-}] \quad (9)$$

$$\text{Putting equation 8 into 9} \\ \text{Rate} = k_2 K_1 [\text{MB}^-][\text{SO}_4^{2-}][\text{H}^+] + k_3[\text{MB}^-][\text{SO}_4^{2-}] \quad (10)$$

$$\text{Rate} = k_3 + k_2 K_1 [\text{H}^+][\text{MB}^-][\text{SO}_4^{2-}] \quad (11)$$

Equation 11 is similar to equation 3

where $k_3 = 'a' = 1.60 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ and $k_2 K_1 = 'b' = 2.55 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$

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

Absence of shift in λ_{max} from 663 nm in the spectroscopic runs is an evidence that shows absence of intermediate complex formation prior to electron transfer and that the redox reaction most probably occurred by the outer-sphere mechanism. The Michaelis- Menten's plot of $1/k_1$ vs $1/[\text{SO}_4^{2-}]$ was linear without an intercept indicating the absence of intermediate complex formation. This suggests an outer-sphere mechanism according to [12], [18]. Absence of free radicals in the reaction mixture suggests an outer-sphere mechanism [19]. From the results obtained above, one is able to conclude that the reaction of methylene blue with sulphate ion most probably occurred by the outer-sphere mechanism.

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