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KINETICS AND MECHANISM OF OXIDATION OF SAFRANIN – O BY PERMANGANATE ION IN ACIDIC MEDIUM

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ABSTRACT

The kinetics and mechanism of oxidation of safranin O by permanganate ion has been investigated in aqueous hydrochloric acid medium at 303 ± 1K, I = 0.2 C^2 mol dm^{-3} (NaCl), $[H^+]$ = 2.0×10^{-5} mol dm^{-3}. The result obeys the rate law:

$$\frac{-d\,[SO^+]}{dt} = (\,a + b\,[H^+]\,)\,[SO^+]\,[MnO^-_4]$$

where a = 5.0×10^{-6}; b = 3.2×10^{-6} dm^6 mol^{-2} s^{-1}. The rate of reaction increased with increase in $[H^+]$ and displayed negative salt effect. Added cations and anions inhibited the reaction rate. The result of spectroscopic investigation did not indicate intermediate complex formation. A plausible mechanism has been proposed based on the experimental findings.

Key words: Kinetics, Mechanisms, Permanganate, Safranin-O, Dye, Oxidation, Outer -sphere.

INTRODUCTION

Permanganate ion is a strong oxidant used in analytical chemistry, in the determination of content of pharmaceutical formulation and as a disinfectant [1 - 3]. It serves as an oxidizing agent for removal of organic molecules and heavy metals from nuclear waste [4]. Its intense coloration confers on it an advantage to serve as a self - indicator [5]. It also has wide applications in the kinetics of many organic, inorganic and biological active compounds [6 - 15] The oxidizing ability of MnO_4^- is a function of the pH of the medium [3, 8].

In acidic medium, the oxidizing Mn(VII) species are $HMnO_4$, $H_2MnO_4^+$, Mn_2O_7 and MnO_3^+[16 -17]. The explanation for the positive acid dependence on the rate of MnO_4^- oxidation has been rationalized in terms of the protonation of MnO_4^- in a fast step to give $HMnO_4$, which subsequently react with the reductant in a slow step to give the products [18, 19].

Safranin- O dye (Basic red 2) here and thereafter represented as SO^+ belongs to phenazine class of dye. Among the various classes of dyes that have been investigated, the phenazine dyes have received much attention due to their importance as sensitizers in photogalvanic cells for the conversion of light to electrical energy [20 - 21] and also in connection with elucidation of photosynthetic mechanism in plants [22].

However, literature on the redox reactions of safranin – O is scanty. Hence this work is carried out in order to obtain relevant kinetic data which would give an idea on the conditions best suitable for the reactions of safranin – O and the mechanistic pathway for such reactions. It is our hope that the knowledge would be beneficial to workers in the dye industries and also those involved in its handling when used in staining and other purposes.

MATERIALS AND METHOD

Materials

Analar grade reagents were used as received without further purification. Distilled water was used to prepare all solutions. Stock solutions of safranin – O was prepared by dissolving 6.6×10^{-3}g of the dye in 25 cm^3 volumetric flask. Potassium permanganate solution was prepared by dissolving accurate quantity in 100 cm^3volumetric flask and standardized according to literature [23]. HCl was used as the acid medium and also to investigate the effect of $[H^+]$ on the rate of reaction. A stock solution of the acid was made by diluting hydrochloric acid (35.6 %, specific gravity1.18) and standardized titrimetrically. NaCl was used to maintain the ionic strength constant at 0.2 C^2 mol dm^{-3}.

Stoichiometric Studies

Spectrophotometric titration using the mole ratio method was employed in determining the stoichiometry of the reaction. The concentration of safranin – O was kept constant while that of permanganate was varied as follows: $[SO^+] = 1.0 \times 10^{-5}$ mol dm^{-3}, $[MnO_4^-] = (0.2 - 3.5) \times 10^{-5}$ mol dm^{-3}. The reaction mixtures were kept until reactions were completed as evidenced from the constancy of the measurement of absorbance (A_∞) at 520 nm using JENWAY 7513 spectrophotometer. The various absorbance values obtained ware plotted against the mole ratio of the reactants and the point of sharp inflection in the plot gave the stoichiometry of the reaction.

Kinetic measurement

The rate of reaction was studied by monitoring the decrease in absorbance of the dye using the JENWAY 7513 Spectrophotometer at 520 nm. Kinetic measurement was carried out under pseudo - first order condition with $[MnO_4^-]$ in 10 - fold excess over $[SO^+]$ as shown in Table 1. The pseudo - first order plots of log $(A_t - A_\infty)$ versus time were made. From the slope of the plot, the pseudo -first order rate constants (k_1) were determined. The second order rate constant (k_2) were obtained from

$$k_2 = \frac{k_1}{[MnO^-_4]^n}$$

Where 'n' is the order with respect to permanganate ion.

Effect of changes in $[H^+]$ on the rate of reaction

The effect of changes in $[H^+]$ on the rate of reaction was investigated by keeping $[SO^+]$ and $[MnO_4^-]$ constant, ionic strength was maintained at 0.2 C^2 mol dm^{-3} (NaCl) at 301 ± 1K .The $[H^+]$ was varied within the range of $(0.4 – 2.8)\times10^{-5}$ mol dm^{-3}, the range of stability of the dye. Variation of acid dependent rate constants with $[H^+]$ was studied by plotting k_1 against $[H^+]$.

Effects of Ionic Strength of the Reaction Medium on the Rate of Reaction

The ionic strength of the reaction mixture was varied between 0.1 – 0.7 C^2 mol dm^{-3} (NaCl) while maintaining $[SO^+] = 1.0\times 10^{-5}$ mol dm^{-3}, $[MnO_4^-] = 4.0 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-5}$ mol dm^{-3} constant at 301 ± 1K. The relationship of the reaction with changes in the ionic strength was determined by plotting log k_2 against $\sqrt{I}$.

Effect of Added Ions

Effect of added ions on the rate of reaction was investigated for NO_3^- and Mg^{2+}in the concentration range $(2.0 – 12.0) \times 10^{-3}$ while the concentration of all other reactants were kept constant; $[SO^+] = 1.0\times 10^{-5}$ mol dm^{-3}, $[MnO_4^-] = 4.0 \times10^{-4}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-5}$ mol $dm^{-3}$and I = 0.2 C^2mol dm^{-3} (NaCl).

Test for Intermediate Complex Formation

Test for the presence of stable detectable intermediate complex formed during the course of the reaction was carried out spectrophotometrically. An electronic spectrum of partially reacted mixture was recorded at various time intervals. A similar run was made for reactants separately in each case. This was carried out in order to determine whether shift in λ_{max}, or enhancement of peak resulted as the reaction progress.

Test for free radicals

Exactly 5 cm^3solution of acrylamide was added to a partially oxidized reaction mixture followed by addition of excess of methanol. Control experiment was carried out by adding acrylamide solution to the solution of SO^+ and MnO_4^- separately. Gel formation indicates presence of free radicals in the reaction mixture.

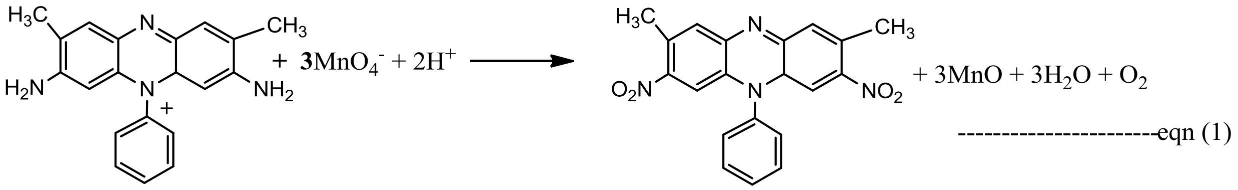
Product analysis

At the completion of the reaction, the reaction mixtures were analyzed for the type of products formed. The organic product was analyzed by FT-IR analysis, while the inorganic product was qualitatively identified to be Mn^{2+} by the addition of 1cm^3 of 6 mol dm^{-3} HNO_3 to 10 drops of the solution of the product followed by addition of some quantity of solid sodium bismuthate and stirred.

RESULTS AND DISCUSSION

Stoichiometry

Stoichiometric studies indicated that for every mole of SO^+, 3 mole of MnO_4^- was consumed as shown by the equation below:



The stoichiometry of 1: 3 is similar with what has been reported in the reaction of $MnO_4^-$with acetaldehyde [8].

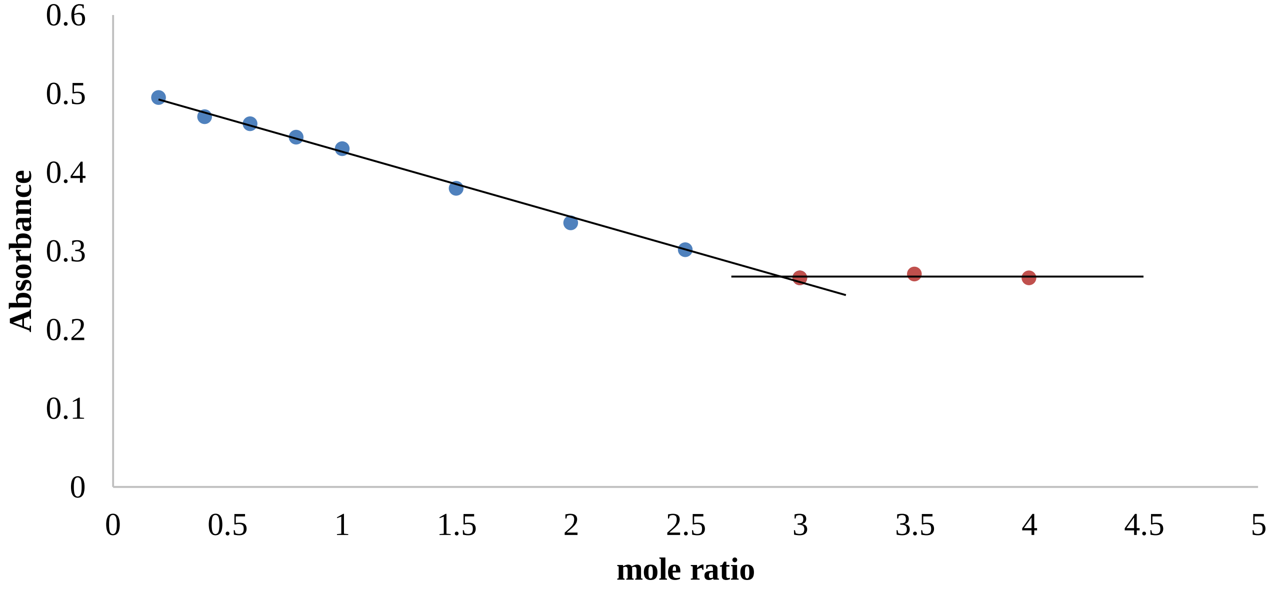


Fig 1: Plot of absorbance versus mole ratio for the determination of stoichiometry of the oxidation of SO^+byMnO_4^-at $[SO^+]$= 1.0×10^{-5} mol dm^{-3}, $[MnO_4^-]$=(0.2 - 3.5) ×10^{-5}mol dm^{-3}, $[H^+]$ = 2.0 ×10^{-5} mol dm^{-3}, I = 0.1C^2 mol dm^{-3} (NaCl), T = 302±1K and λ_{max} = 520 nm.

Order of Reaction

Kinetics studies showed the reaction to be first order dependence on each of the reactant. Plot of log A_t – A_∞ versus time were linear to about 90% of the reaction (where A_t and A_∞ are the absorbance at time t and at the end of the reaction respectively), indicating the order with respect to SO^+ to be one. A typical plot is presented in Figure 2. Pseudo - first order rate constants k_1 determined as the slope are presented in Table 1. The plot of log k_1 versus log $[MnO_4^-]$ was linear with a slope of 1.0 indicating first order dependence of the rate of reaction on $[MnO_4^-]$ (Figure 3). The second order rate constants, k_2 were found to be fairly constant (Table 1). The rate equation can be represented by equation 2, at $[H^+]$ = 2.0 × 10^{-5} mol dm^{-3}, I = 0.3 C^2 mol dm^{-3} (NaCl) and T = 301 ± 1K.

$$-\frac{d[SO^+]}{dt} = k_2 [SO^+][MnO_4^-] \qquad \text{--------------------------(2)}$$

where k_2 = 3.57 ± 0.012 dm^3 mol^{-1} s^{-1}. Similar first order dependence has been reported in the redox reactions of MnO_4- [24, 25].

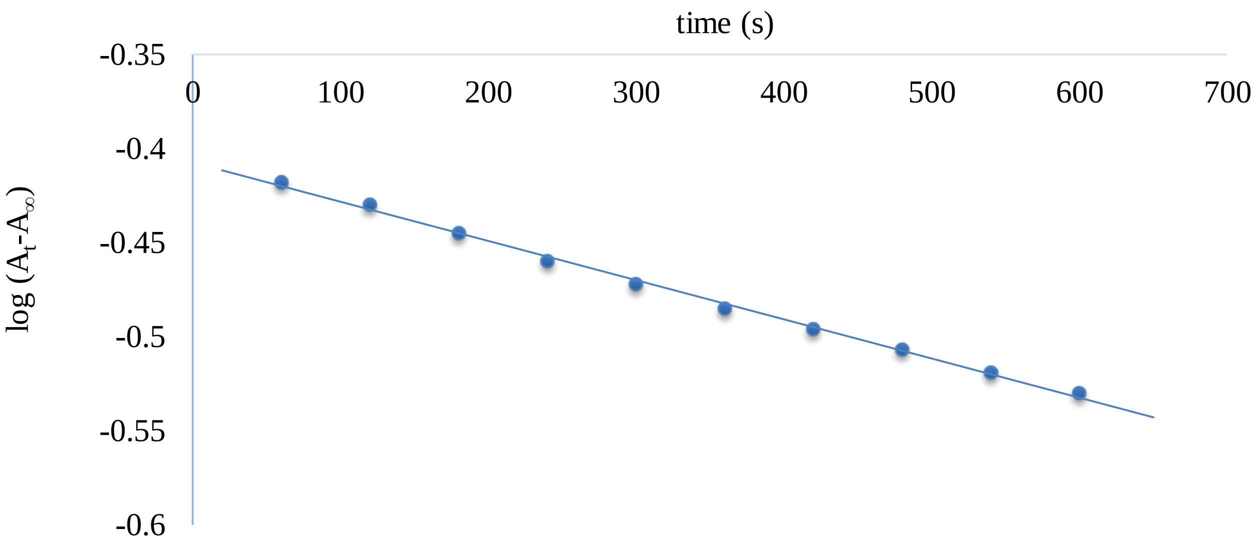


Fig. 2: Typical pseudo - first order plot for the reaction of SO^+withMnO_4^-at [SO^+] = 1.0×10^{-5}mol dm^{-3}, [MnO_4^-] = (1.0– 7.0) ×10^{-4}mol dm^{-3}, [H^+] = 2.0×10^{-5}moldm^{-3}, I= 0.2 C^2 mol dm^{-3} (NaCl), T = 303 ± 1K and λ_{max}= 520nm.

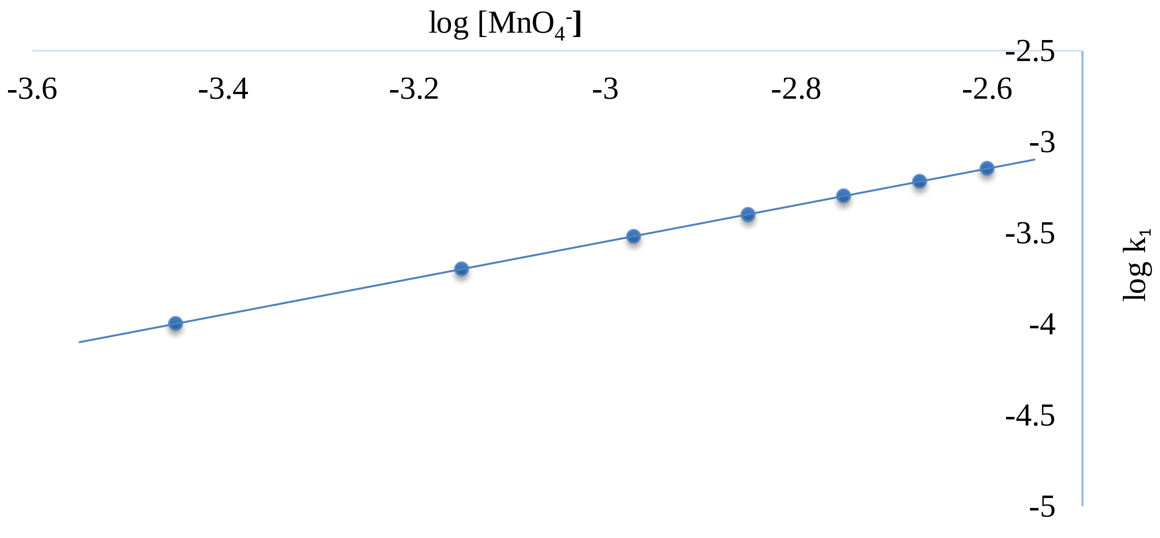


Fig. 3: Plot of logk_1 versus log [MnO_4^-] for the reaction of SO^+withMnO_4^-at[SO^+] = 1.0×10^{-5}moldm^{-3}, [MnO_4^-] = (1.0 – 7.0) ×10^{-4} mol dm^{-3}, [H^+] = 2.0 ×10^{-5} mol dm^{-3}, I = 0.2 C^2mol dm^{-3}, T= 303 ±1K, λ_{max}= 520nm.

Table 1: Pseudo - first Order and Second Order Rate Constants for the Reaction of SO^+ with MnO_4- at $[SO^+] = 1.0 \times 10^{-5}$ mol dm^{-3}, λ_{max}=520nm, T= 301 ± 1K

10^4 $[MnO_4^-]$ ($moldm^{-3}$)	10^5 $[H^+]$ (mol dm^{-3})	I(C^2mol dm^{-3})	10^4 k_1 (s^{-1})	k_2 (dm^3 mol^{-1} s^{-1})
1.0	2.0	0.2	3.56	3.56
2.0	2.0	0.2	7.11	3.56
3.0	2.0	0.2	10.77	3.59
4.0	2.0	0.2	14.26	3.56
5.0	2.0	0.2	17.87	3.57
6.0	2.0	0.2	21.44	3.57
7..0	2.0	0.2	25.03	3.58
4.0	0.4	0.2	10.03	2.51
4.0	0.8	0.2	11.22	2.80
4.0	1.2	0.2	12.93	3.23
4.0	1.6	0.2	13.18	3.30
4.0	2.0	0.2	14.18	3.55
4.0	2.4	0.2	15.35	3.84
4.0	2.8	0.2	16.37	4.09
4.0	2.0	0.1	18.71	4.68
4.0	2.0	0.2	14.19	3.55
4.0	2.0	0.3	8.48	2.12
4.0	2.0	0.4	7.46	1.86
4.0	2.0	0.5	5.81	1.45
4.0	2.0	0.6	4.74	1.19
4.0	2.0	0.7	4.32	1.08

Table 2: Rate Data for the Effects of Added Ions on the Reaction Rate of SO^+ with MnO_4^- at $[SO+] = 1.0 \times 10^{-5}$ mol dm^{-3}, $[MnO_4^-] = 4.0 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-5}$ mol dm^{-3}and I = 0.2 C^{2}mol dm^{-3} (NaCl), T= 301 ± 1K and λ_{max}= 520nm.

X	10^3 [X] mol dm^{-3}	10^4 k_1 (s^{-1})	k_2 dm^{3}mol^{-1}s^{-1}
Mg^{2+}	0.0	14.18	3.55
	2.0	14.00	3.50
	4.0	13.70	3.43
	6.0	11.66	2.91
	8.0	9.80	2.45
	10.0	8.59	2.15
	12.0	7.08	1.77
NO_3^-	0.0	14.34	3.58
	2.0	8.07	2.02
	4.0	7.61	1.90
	6.0	7.12	1.78
	8.0	6.48	1.62
	10.0	5.82	1.46
	12.0	5.48	1.37

Effect of Changes of Acid Concentration on the Rate of Reaction

The effect of $[H^+]$ on the rate of reaction is reported in Table 1. The rates were found to be first order acid dependence on $[H^+]$. The plot of k_1 versus $[H^+]$ was linear with a positive intercept (Figure 4). The acid dependence rate equation for the reaction can be represented by equation 3 where a = 5.0×10^{-6}; b = 3.2×10^{-6}dm^6 mol^{-2} s^{-1}

$$-\frac{d[SO^+]}{dt} = (a + b[H^+])[SO^+][MnO_4^-] \qquad \text{-------------------------(3)}$$

In the acid range investigated the rate of the reaction increases with increase in hydrogen ion concentration (Table 2). Similar result has been reported in the permanganate oxidation of nicotinic acid [12] and in the oxidation of indigo carmine by permanganate [25]. Equation 3 suggests that the reaction occurs via acid dependence and acid independence pathways (Figure

4). This has been explained in terms of protonation of MnO_4^- in a fast step to give $HMnO_4$, which subsequently reacts with the substrate in a slow step to give the product [18– 19, 25].

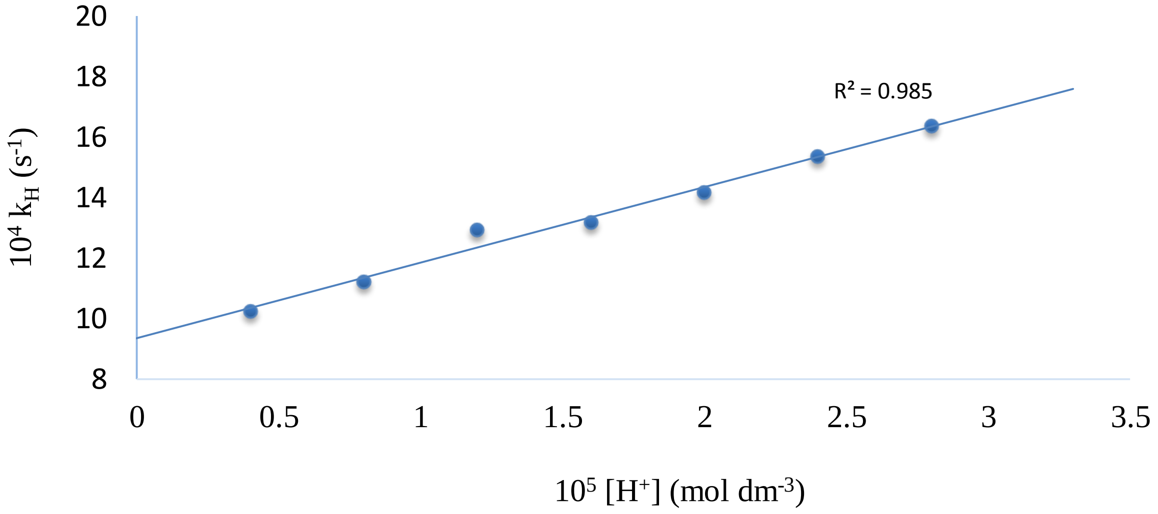


Fig. 4: Plot of $\mathbf{10^5 k_H}$ versus $[H^+]$ for the redox reaction of SO^+withnMnO_4^- at $[SO^+]=1.0\times10^{-5}$ moldm^{-3}, $[MnO_4^-] = 1.0\times10^{-4}$ mol dm^{-3}, $[H^+]= (0.4– 2.8)\times10^{-5}$ mol dm^{-3},
I= 0.2 C^2 mol dm^{-3}, T= 300± 1 K and λ_{max} = 520nm

Effect of changes in Ionic strength on the rate of reaction

The relationship of reaction rate with changes in ionic strength was determined by plotting log k_2 against $\sqrt{I}$. The plot is linear (Figure 5) with a slope of – 1.02(R^2 = 0.98). The rate of reaction was found to decrease with increase in ionic strength (Table 1). Variation in ionic strength generally resulted in primary and secondary salt effects. The primary salt effect arises on the basis of the different types of reactive species present in the rate determining step. Reactions involving a pair of ions of like charges are usually accelerated by increasing ionic strength of reaction medium.

A reverse trend is observed in the case of reactions of oppositely charged species. The result of this study revealed that reactions between ions of oppositely charge species are operative in the rate determining step. Similar result has been reported in the oxidation of nicotinic acid and malachite green by permanganate ion [12, 26].

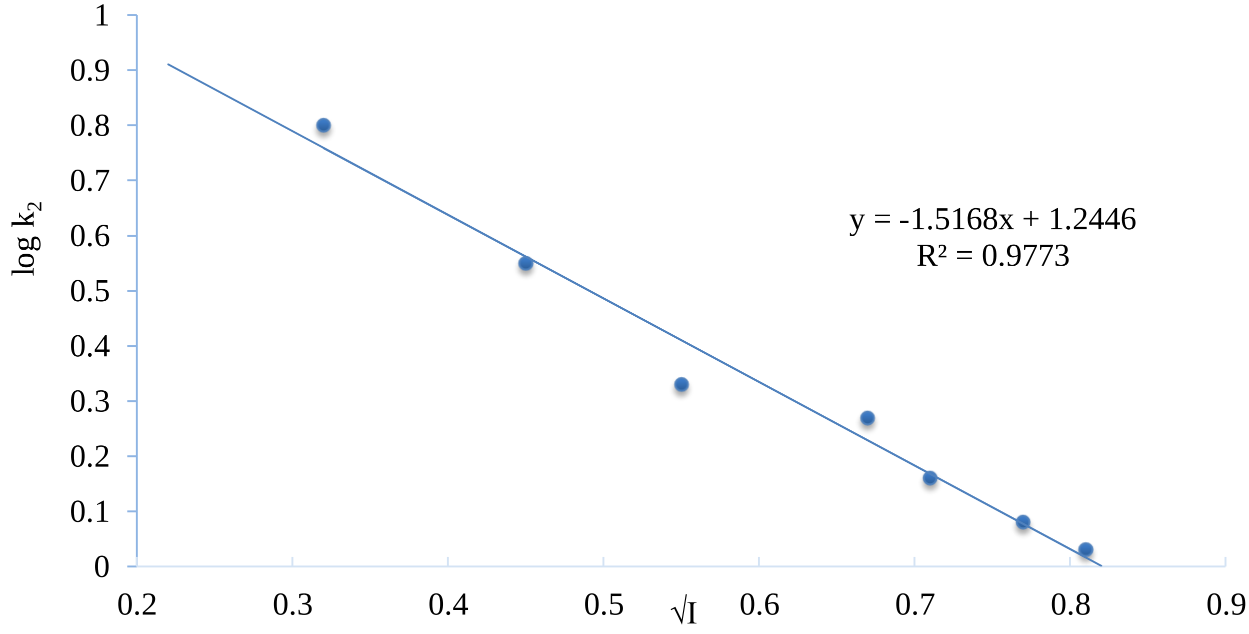


Fig. 5: Plot of log $k_2$versus √I for the redox reaction of SO^+ withMnO_4^-at $[SO^+]$ =1.0×10^{-5} mol dm^{-3},$[MnO_4^-]$ = 4.0×10^{-4} mol dm^{-3}, $[H^+]$ = 2.0×10^{-5}mol dm^{-3}, I= C^2 0.2 mol dm^{-3},

T= 300±1K and λ_{max}= 520nm.

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Effect of Added Ions on the Rate of Reaction

The rate constants were found to be inhibited by the presence of Mg^{2+} and NO_3^- ions. This inhibited effect by the ions suggests that the reaction might be operating via the outer - sphere pathway, and this is in line with earlier reports [24].

Test for Intermediate Complex Formation.

Spectroscopic test indicates no shift in λ_{max} of SO^+**.** This indicated absence of the formation of an intermediate complex, which points out to the outer - sphere mechanism. Also Michaelis - Menten plot of $1/k_1$ versus $1/[MnO_4^-]$ gave a zero intercept (Figure 6).

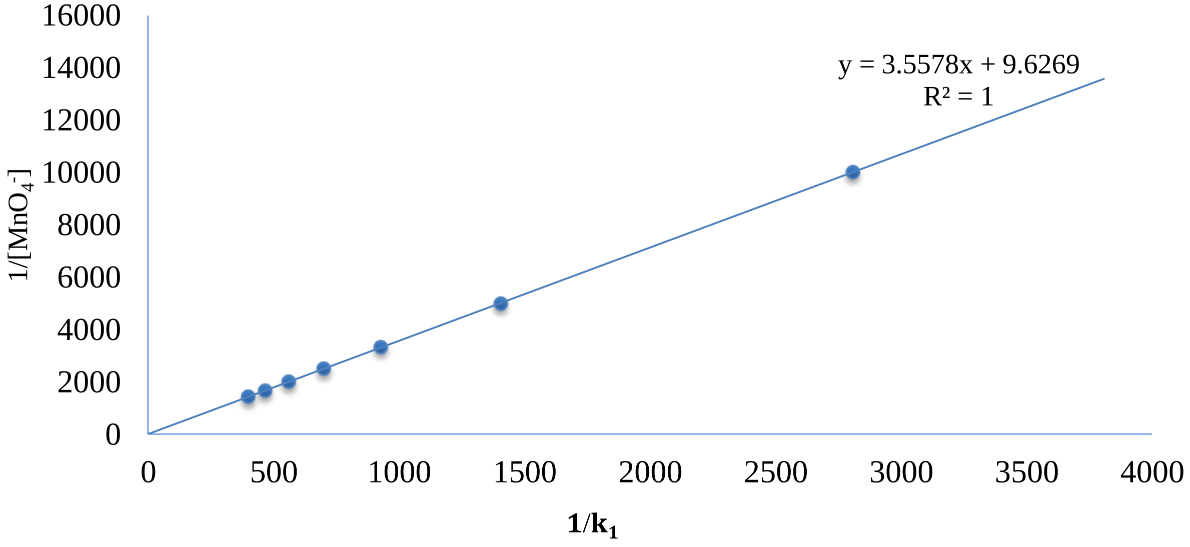


Fig.6**:** Michaeli's-Menten Plot of $\frac{1}{k1}$ versus 1/[MnO_4^-] for the reaction of SO^+withMnO$_4^-$at [SO^+] =1.0×10^{-5} mol dm^{-3}, [MnO_4^-] = 4.0×10^{-4} mol dm^{-3}, [H^+] = 2.0×10^{-5} mol dm^{-3}, I = C^{2}0.2 mol dm^{-3}, T= 300±1K and λ_{max}= 520nm.

Polymerization Test

Addition of 5 cm^3 solution of acrylamide followed by excess methanol showed gel formation. This suggests a probable presence of free radical formation during the reaction.

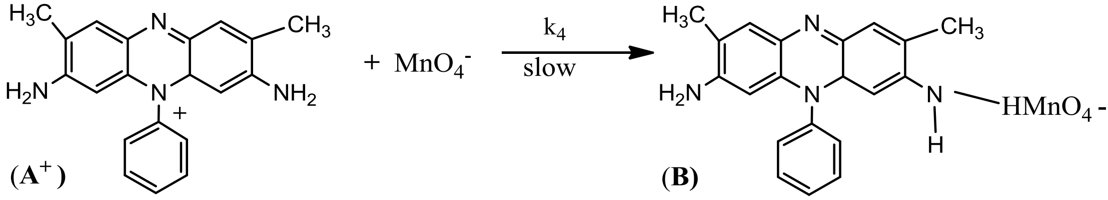
Product analysis

The organic product showed a strong signal at 1382 cm^{-1} corresponding to the N–O group with disappearance of amino group at 3295 cm^{-1} signal. Mn^{2+} was confirmed as the inorganic product.

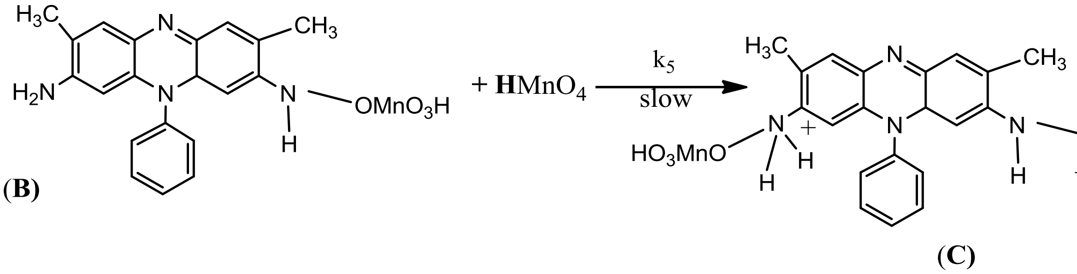
Reaction Mechanism

The inhibition of the reaction by added ions, the linearity of the Michaelis - Menten plot without intercept and the result of spectroscopic test suggest that the reaction occurs through the outer-sphere pathway. Therefore, outer–sphere mechanism is proposed for the reaction.

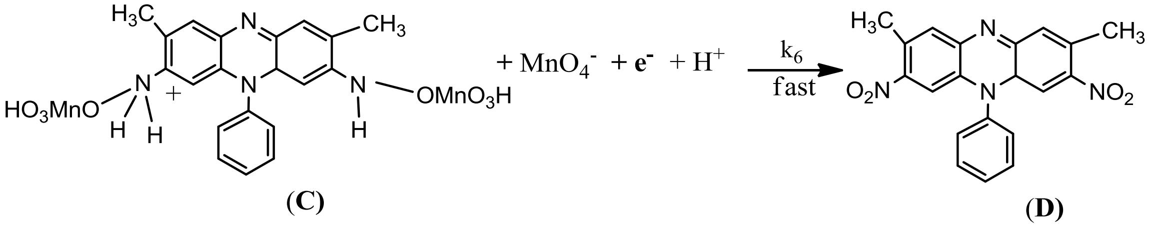
$$MnO_4^- + H^+ \underset{}{\overset{K_3}{\rightleftharpoons}} HMnO_4$$ --(4)



--------- (5)



$+ e^-$ ------ (6)



$+ 3MnO + 3H_2O + O_2$ ------------------- (7)

$$Rate = k_4 [A^+] [MnO_4^-] + k_5 [B] [HMnO_4]$$ -- (8)

$$\text{Rate} = k_4\,[A^+]\,[MnO_4^-] + k_5\,[B]\,[HMnO_4] \text{ -- } (9)$$

$$\frac{-d}{dt}[B] = k_4\,[B]\,[MnO_4^-] - k_{-4}\,[A^+] - k_5[B]\,[HMnO] = 0 \text{ --------------------------------- } (10)$$

$$k_4\,[A^+]\,[MnO_4^-] = k_{-4}\,[B] + k_5\,[B]\,[HMnO_4] \text{ --- } (11)$$

$$k_4\,[A^+]\,[MnO_4^-] = [B]\,(k_{-4} + k_5\,[HMnO_4]\,) \text{ --- } (12)$$

$$B = \frac{[k_4\,[A^+]\,[MnO_4^-]}{k_{-4} + k_5[HMnO_4]} \text{ -- } (13)$$

$$\text{Rate} = k_4[A^+]\,[MnO_4^- + \frac{k_5k_4\,[A^+]\,[MnO_4^-]\,[HMnO_4]}{k_{-4} + k_5[HMnO_4]} \text{ ------------------------------------- } (14)$$

if $k_{-4} + k_5\,[HMnO_4^-] = [MnO_4^-]$

Therefore,

$$\text{Rate} = k_4[A^+]\,[MnO_4^-] + k_5\,k_4\,[A^+]\,[HMnO_4] \text{ --------------------------------------- } (15)$$

But,

$$K_3 = \frac{[HMnO_4]}{[H^+]\,[MnO_4^-]} \text{ --- } (16)$$

$$[HMnO_4] = K_3\,[MnO_4^-]\,[H^+] \text{ -- } (17)$$

insert eqn(17) in to eqn (15) above,

$$\text{Rate} = k_4\,[A^+]\,[MnO_4^-] + K_3\,k_4\,k_5\,[A^+]\,[MnO_4^-]\,[H^+] \text{ ------------------------------ } (18)$$

$$= (\,k_4 + K_3\,k_4k_5[H^+]\,)\,[A^+]\,[MnO_4^-] \text{ --- } (19)$$

$$\text{Rate} = k_4\,[A^+]\,[MnO_4^-] + K_3\,k_4\,k_5\,[A^+]\,[MnO_4^-]\,[H^+]$$

$$= (\,k_4 + K_3\,k_4k_5[H^+]\,)\,[A^+]\,[MnO_4^-]$$

CONCLUSION

The redox reaction of safranin – O with permanganate ion in aqueous acidic medium revealed a stoichiometry of 1:3, first order with respect to [SO^+] and [MnO_4^-] respectively – second order overall. The rate of reaction increased with increase in [H^+], decreased with increase in ionic strength of the reaction medium and added ions inhibited the reaction. An intermediate complex was not detected.

Based on the findings of this study, it is evident that the reaction is probably operating through the outer-sphere mechanism.

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