
Mechanism of Thiosulphate Oxidation by Di- μ -Oxo-Tetrakis (2, 2'- bipyridine) - Dimanganese (III, IV) Perchlorate in Acidic Medium

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Abstract: The mechanism of the oxidation of di- μ -oxo-tetrakis(2,2' - bipyridine)-dimanganese (III,IV) perchlorate (herein referred to as $[(bipy)_2 Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ with $S_2O_3^{2-}$ was studied at constant concentration of $[(bipy)_2 Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ at $6 \times 10^{-4} \text{ mol dm}^{-3}$, ionic strength of 0.5 mol dm^{-3} , $[H^+] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ and $\lambda_{max} = 683 \text{ nm}$. The stoichiometry of 1: 3 was observed for the system. The order of reaction is first order in the oxidant and reductant, giving an overall second order rate constant. Acid dependence rate constant on oxidant were positive for the system. The acid dependent rate equation is given as: $k_H^+ = (a + b [H^+])[(bipy)_2 Mn^{III}O_2Mn^{IV}(bipy)_2][S_2O_3^{2-}]$. Negative salt effect was observed for the system. The results of spectroscopic and kinetic investigation did not indicate intermediate complex formation in the course of the reaction and acrylamide addition did not indicate gel formation. Based on the results obtained, a plausible mechanism for the reaction has been proposed in line with Proton Coupled Electron Transfer (PCET) reaction pathways.

Keywords: Mechainsm, Thiosulphate Ion, Di- μ -Oxo-Tetrakis (2,2'- bipyridine)-Dimanganese (III,IV) Perchlorate.

INTRODUCTION

Thiosulphate ion is a water soluble salt and reducing agent that reacts with oxidizing agents. It occurs naturally and is produced by certain biochemical processes. Although its exact mechanism of action is unknown, thiosulphate likely provides an exogenous source of sulphur, it is not only non-toxic, it is also life giving. When drops of thiosulphate and fulvic acid is added to plants, they grow and bloom quickly and beautifully. It was observed that fulvic acid alone doesn't work well without the presence of thiosulphate^[1]. The chemistry of Di-oxo-bridged manganese complexes has generated great interest of recent. The ligands, 1, 10-phenanthroline (phen) and 2, 2'-bipyridine (bipy) are strong field bidentate ligands that form very stable chelates with many first row transition metals^[2]. Artificial photosynthesis is an attempt to design a molecular or supra-molecular system that mimics the aspects of photosynthetic natural energy conversion, in order to produce electricity or storable energy such as hydrogen or methane^[3].^[4] reported that one of the most important reactions in biology is photosynthesis, which is completely dependent on manganese. It is the star player in the reaction centre of photosystem II involve in water oxidation. Without manganese, there would be no oxidation of water and there would be little oxygen in the atmosphere. To construct an artificial system that mimics these electron transfer reactions, 2, 2' bipyridine - dimanganese (III, IV) complex was synthesized and characterized in this work according to^[5] method. Due to these numerous importance of manganese in photosynthesis and thiosulphate ion, the synthesis, characterization and mechanistic investigation of the mixed-valence dimanganese complexes containing 2, 2'-bipyridine as ligands has been reacted with $S_2O_3^{2-}$ and the results reported accordingly.

EXPERIMENTAL

Stoichiometric Investigation

The stoichiometries of the reactions were determined by spectrophotometric titration, using the mole ratio method^[6]. The concentration of $[(\text{bipy})_2\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}(\text{bipy})_2]^{3+}$ was kept constant while that of the reductants $\text{S}_2\text{O}_3^{2-}$ was varied at constant $[\text{H}^+]$ and ionic strength. The reacting mixtures were allowed to stand for 24 hours until the reaction has gone to completion, when the absorbance had attained a steady value. The final absorbances were taken at 683 nm. Plot of absorbances versus concentration of the $\text{S}_2\text{O}_3^{2-}$ was drawn (Fig 3.1) from which the stoichiometry was evaluated.

Kinetics and Order of Reactions

The progress of the reaction was monitored using a UV/Vis Spectrumlab 752s. The rate of depletion in the concentration of $\text{S}_2\text{O}_3^{2-}$ was followed by monitoring the decrease in the absorbance of manganese complex at 683 nm. All kinetic measurements were performed under pseudo-first order condition with the concentration of the manganese complex kept constant and that of $\text{S}_2\text{O}_3^{2-}$ maintained at least 40 - folds excess over that of $[(\text{bipy})_2\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}(\text{bipy})_2]^{3+}$ and the concentrations of $[(\text{bipy})_2\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}(\text{bipy})_2]^{3+} = 6 \times 10^{-4} \text{ mol/dm}^3$, ionic strength = 0.5 mol/dm^3 , $[\text{H}^+] = 1 \times 10^{-3} \text{ mol/dm}^3$, temperature = $29 \pm 1 \text{ }^\circ\text{C}$ and $\lambda_{\text{max}} = 683 \text{ nm}$. Plot of $\log (A_t - A_\infty)$ against time (where A_t and A_∞ are the absorbances at time t and at the end of the reaction respectively) was made from which pseudo-first order rate constants (k_1) were evaluated (Fig. 3.2). Second order rate constants (k_2) were obtained as $k_2 = k_1/[\text{S}_2\text{O}_3^{2-}]$.

Effect of Change in Hydrogen Ion Concentration on Reaction Rate

The effect of change in hydrogen ion concentration on the rate of the reaction was studied by keeping the concentration of all other parameters constant while that of hydrochloric acid was varied as stated above. Graphs of k_2 versus $[\text{H}^+]$ were plotted accordingly.

Effect of Change In Ionic Strength on Reaction Rate

The influence of ionic strength on the rate of the reaction was studied by keeping the concentration of all other parameters constant as stated above while that of the sodium chloride was varied at $I = 0.1 - 1.4 \text{ mol dm}^{-3}$. Graphs of $\log k_2$ versus \sqrt{I} was plotted accordingly.

Effect of Change in Dielectric Constant on Rate Of Reaction

The effect of changes in the dielectric constant of the reaction medium on the reaction rate was investigated by varying the amount of acetone at 10 % V/V water/acetone mixture while keeping all other parameters constant as stated above.

Effect of Added Ions on Rate of Reaction

The effect of added ions on the reaction rate was studied by adding appropriate amount of ions (CH_3COO^- , NO_3^- and Mg^{2+}) at $0.5 - 3.5 \times 10^{-3} \text{ mol dm}^{-3}$.

Test for Intermediate Complex

- Spectroscopic Test: The electronic spectrum of the reaction mixture was run after every five minutes interval after the commencement of the reaction. These were compared with the spectra of the complex alone over a wavelength range of 500 - 800 nm.
- Michaelis-Mentens plots of $1/k_1$ versus $1/[\text{S}_2\text{O}_3^{2-}]$ was made.

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Test For Free Radicals

A solution of about 2 ml of acrylamide was added to the partially oxidized reaction mixture containing various concentrations of oxidants, reductants and hydrogen ion, followed by large excess of methanol to initiate free radical polymerization. Acrylamide was also added to each of the reactants separately to serve as control.

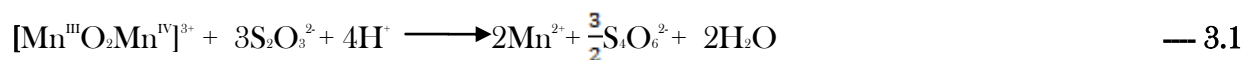
Products Analysis

After the completion of the reactions which was identified by colourless solution and constant absorbance value, qualitative analysis was carried out by the addition of appropriate reagents to identify the presence of the reaction product(s). FeCl_3 was used to identify $\text{S}_2\text{O}_6^{2-}$ as one product and Mn^{2+} as another product by addition of H_2SO_4 , KIO_4 and gentle heat for the reaction system.

RESULTS AND DISCUSSION

Stoichiometry Studies

A mole ratio of 1:3 was observed from the titration curve (Fig. 3.1). Based on the stoichiometry observed, the overall equation for the redox reaction can be represented by the following equation:



However, a mole ratio of 2: 6 and 8: 3 were reported by ^[7] for $[\text{Mn}_3^{\text{IV}}(\mu\text{-O})_4(\text{H}_2\text{O})_2]^{4+}/\text{S}_2\text{O}_3^{2-}$ system and ^[8] for the reaction of $[(\text{phen})_2\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}(\text{phen})_2]/\text{S}_2\text{O}_3^{2-}$ system respectively.

Kinetics Investigation

The kinetics investigation indicated an order of one with respect to $[(\text{bipy})_2\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}(\text{bipy})_2]^{3+}$ from the plot of $\log(A_\infty - A_t)$ versus time which was linear over 80 % extent of the reaction (Fig. 3.2). The values of the second order rate constant k_2 were fairly constant indicating a first order with respect to the $[\text{S}_2\text{O}_3^{2-}]$ (Tables 3.1). The rate law for the reaction can be represented as follows at $[(\text{bipy})_2\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}(\text{bipy})_2]^{3+} = 6 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 683 \text{ nm}$ and $T = 29 \pm 1^\circ\text{C}$.

$$-\frac{1}{3} \frac{d}{dt} [(\text{bipy})_2\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}(\text{bipy})_2] = k_2 [(\text{bipy})_2\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}(\text{bipy})_2] [\text{S}_2\text{O}_3^{2-}] \quad \text{--- 3.2}$$

where $k_2 = 21.33 \pm 0.22 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

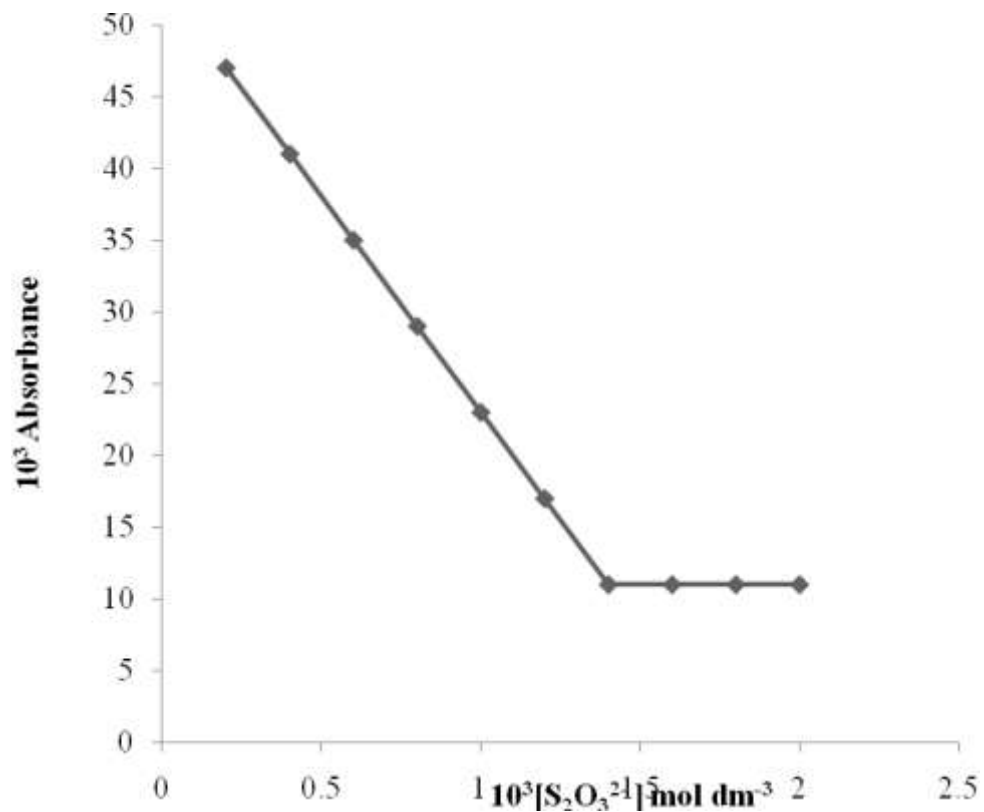


Figure 3.1: Plot of Absorbance versus $[S_2O_3^{2-}]$ for the determination of the Stoichiometry of the $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{8+}/S_2O_3^{2-}$ System.

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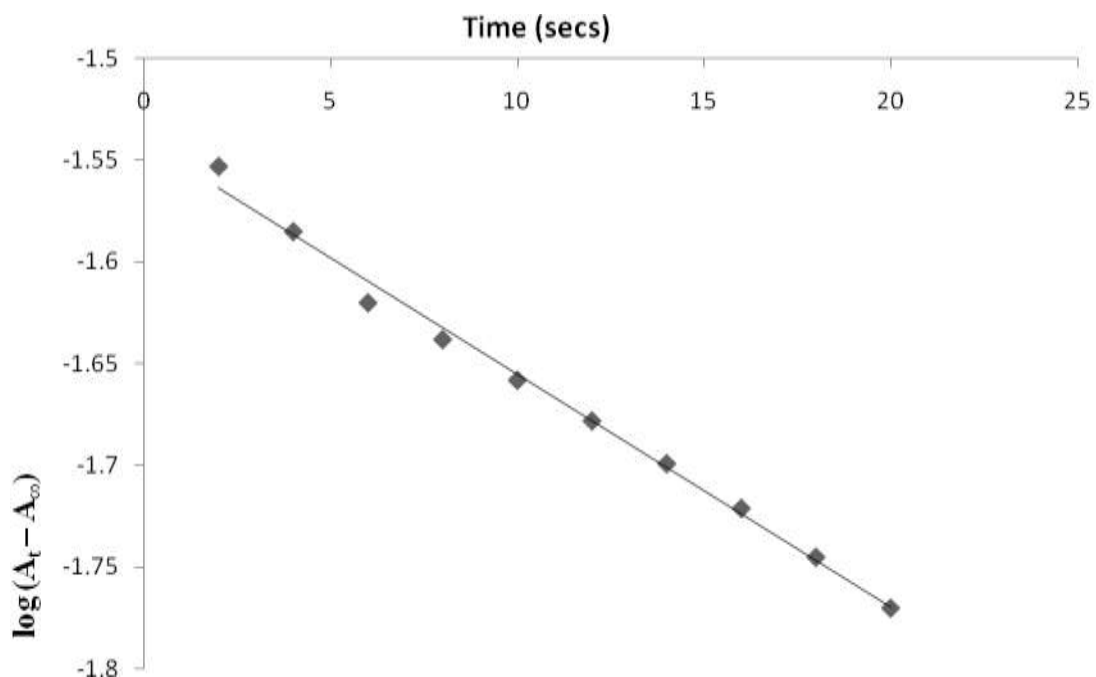


Figure 3.2: Typical pseudo-first Order plot $[(\text{bipy})_2\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}(\text{bipy})_2]^{3+} = 6 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_3^{2-}] = 7.2 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 683 \text{ nm}$ and $T = 29 \pm 1^\circ\text{C}$.

Effect of Hydrogen Ion on Rate of Reaction

Investigation of the effect of $[\text{H}^+]$ in the range of $(0.2 - 1.6) \times 10^{-3}$ indicated that the rate constant increased as the concentration of HCl increased (Table 3.1). This result is in good agreement with the reports^[8] for the reduction of $[(\text{phen})_4\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}]^{3+}$ by $\text{S}_2\text{O}_3^{2-}$; ^[7] for the reduction of $[(\text{phen})_4\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}]^{3+}$ by $\text{S}_2\text{O}_3^{2-}$ and ^[9] for the reduction of $[(\text{bipy})_2\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}(\text{bipy})_2]^{3+}$ by NO_2^- . It has also been reported by ^[10] that thiosulphate can act as a reductant in acidic solution. Graph of k_{H^+} versus $[\text{H}^+]$ (acid dependant rate constant) (Fig. 3.4) was linear with a slope of $1.28 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and an intercept of $0.093 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

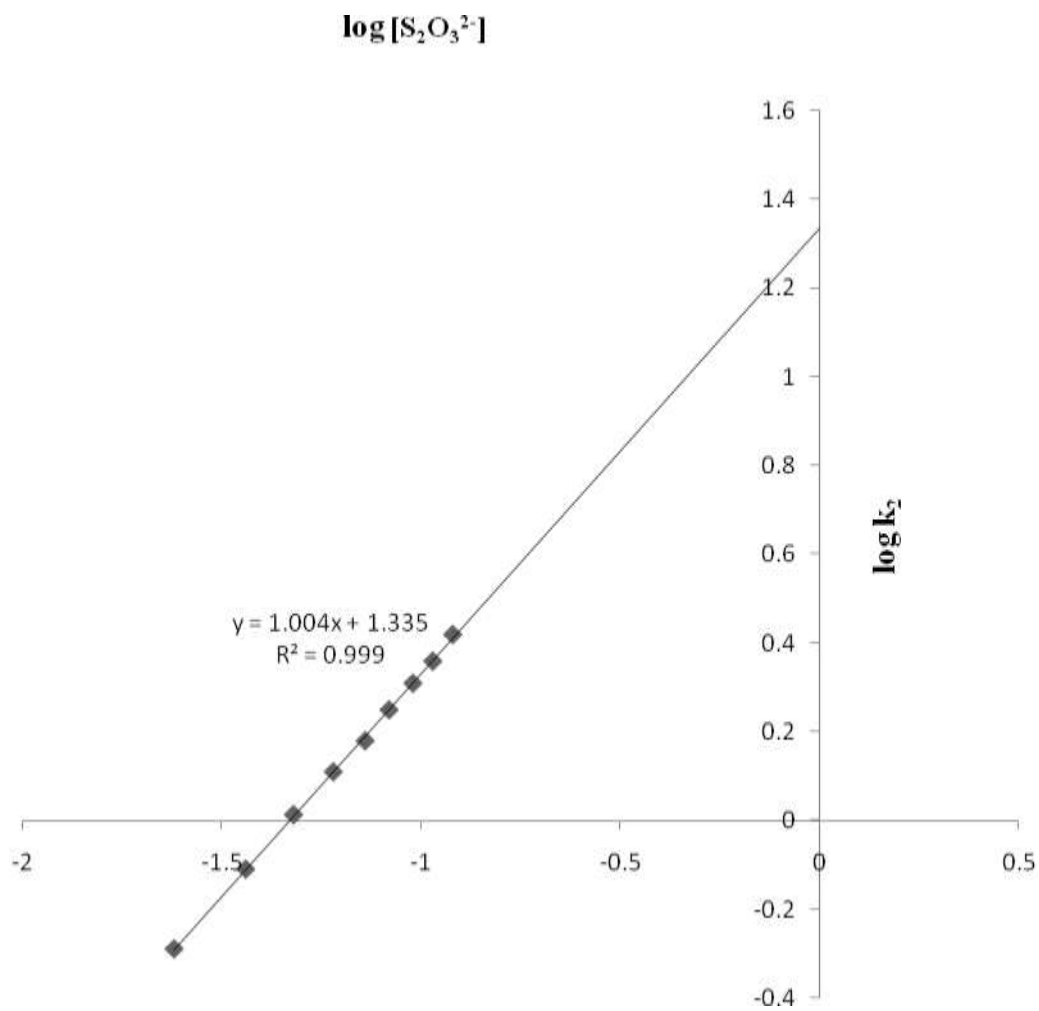


Figure 3.3: Graph of log k₁ vs log [S₂O₃²⁻], [(bipy)₂Mn^{III}O₂Mn^{IV}(bipy)₂]³⁺ = 6 x 10⁻⁴, [H⁺] = 1 x 10⁻³, I = 0.5 mol dm⁻³, λ_{max} = 683 nm and T = 29 ± 1°C.

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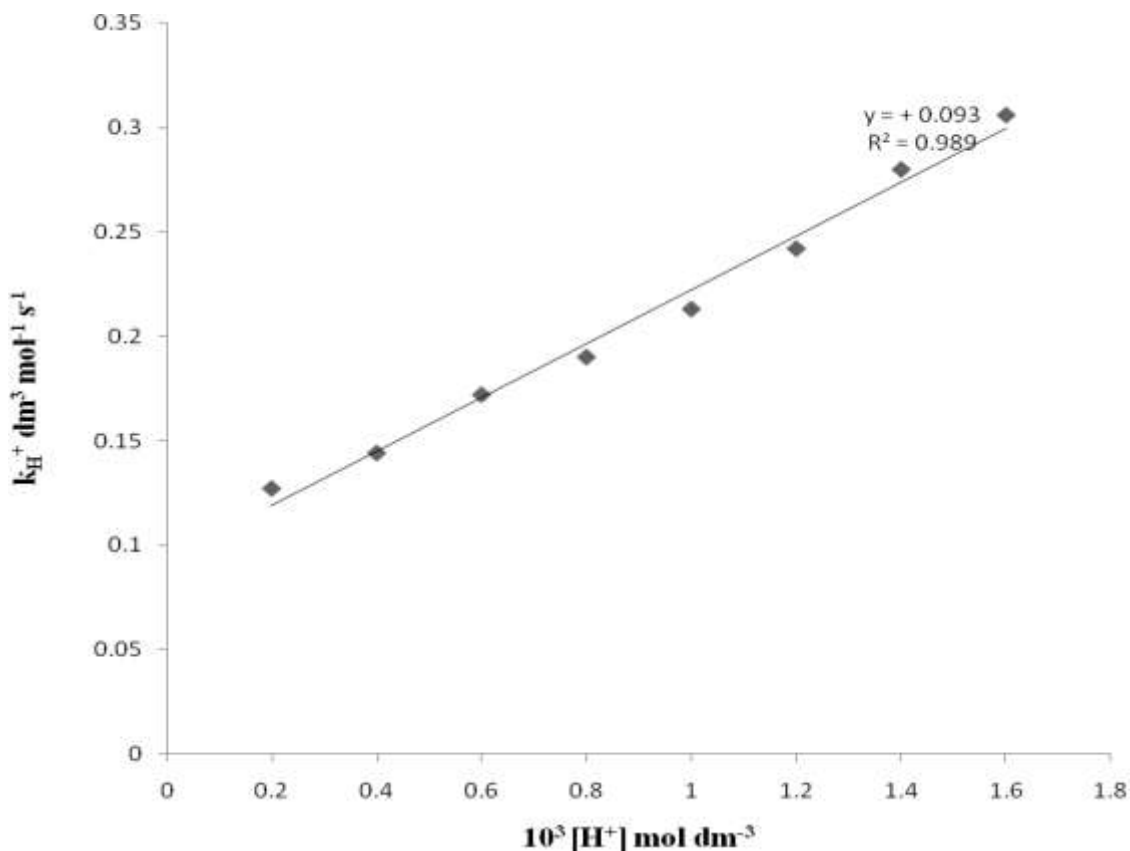


Figure 3.4: Graph of k_2 versus k_H^+ at $[(\text{bipy})_2\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}(\text{bipy})_2]^{3+} = 6 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.2 - 1.6 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_3^{2-}] = 6 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 683 \text{ nm}$ and $T = 29 \pm 1^\circ\text{C}$.

Effect of Ionic Strength on the Rate of Reaction

The rate constant was found to decrease with increase in I suggesting a negative salt effect (Table 3.5). This observation suggests that the activated complex is formed from two ions of unlike charges. This result is in good agreement with the reports of ^[11, 12, 13] for the reactions of diaquotetrakis(2, 2' - bipyridine) - μ - oxodiruthenium(III)/ascorbic acid. Graphs of $\log k_2$ versus \sqrt{I} was linear with a slope of -0.197 showing a negative salt effect (Fig. 3.4).

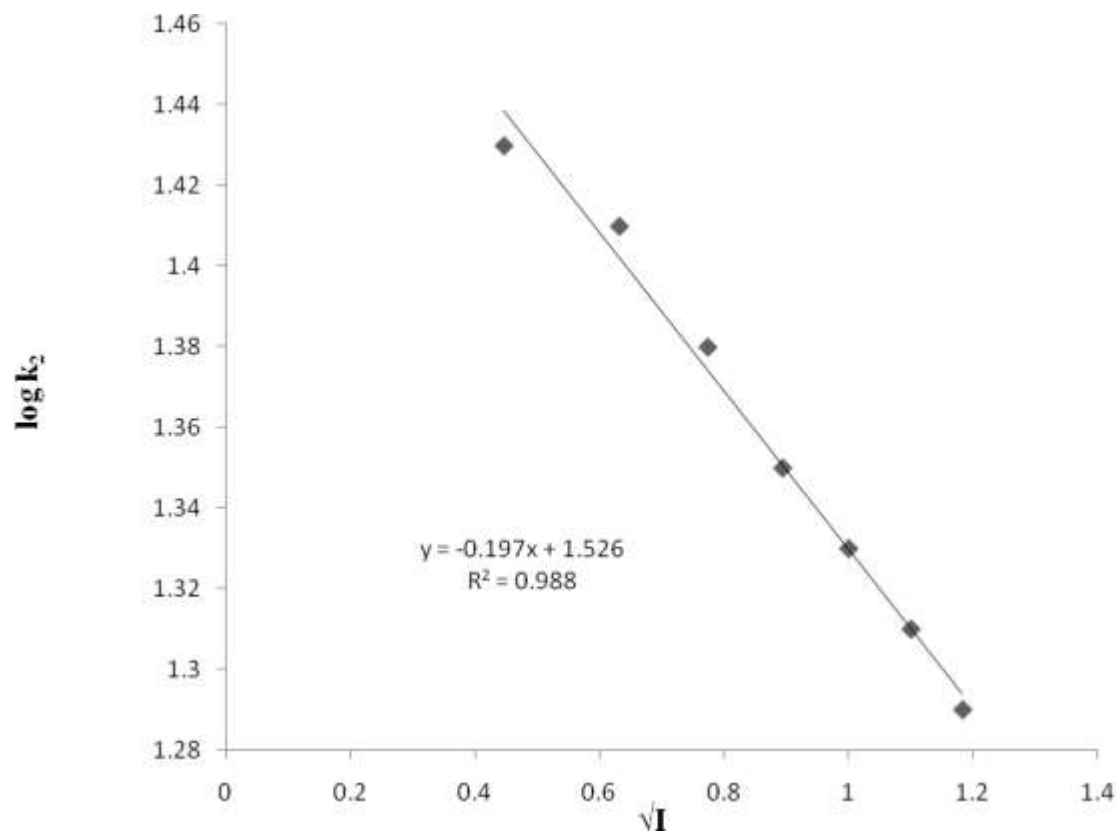


Figure 3.5: Graph of $\log k_2$ versus \sqrt{I} , $[(\text{bipy})_2\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}(\text{bipy})_2]^{3+} = 6 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{S}_2\text{O}_8^{2-}] = 6 \times 10^{-2} \text{ mol dm}^{-3}$, $\text{H}^+ = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.2 - 1.4 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 683 \text{ nm}$ and $T = 29 \pm 1^\circ\text{C}$.

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Table 3.1: Pseudo-first Order And Second Order Rate Constant for the Reaction of $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ by $S_2O_3^{2-}$, $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+} = 6 \times 10^{-4} \text{ mol dm}^{-3}$, I $[NaCl] = 0.5 \text{ mol dm}^{-3}$, $[H^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ and at $29 \pm 1 \text{ }^\circ\text{C}$ and $\lambda_{max} = 683 \text{ nm}$

$10^2 [S_2O_3^{2-}] \text{ mol dm}^{-3}$	$[H^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$	I = 0.5 mol dm ⁻³	$10^1 k_1 \text{ s}^{-1}$	$k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
2.4	1.0	0.5	5.09	21.21
3.6	1.0	0.5	7.76	21.56
4.8	1.0	0.5	10.30	21.46
6.0	1.0	0.5	12.76	21.26
7.2	1.0	0.5	15.46	21.48
8.4	1.0	0.5	17.80	21.19
9.6	1.0	0.5	20.35	21.19
10.8	1.0	0.5	22.66	20.98
12.0	1.0	0.5	26.02	21.68
6.0	0.2	0.5	7.64	12.73
6.0	0.4	0.5	8.61	14.35
6.0	0.6	0.5	10.30	17.16
6.0	0.8	0.5	11.40	19.00
6.0	1.0	0.5	12.76	21.26
6.0	1.2	0.5	14.50	24.17
6.0	1.4	0.5	16.82	28.03
6.0	1.6	0.5	18.35	30.58
6.0	1.0	0.2	16.22	27.04
6.0	1.0	0.4	15.31	25.51
6.0	1.0	0.6	14.29	23.81
6.0	1.0	0.8	13.40	22.33
6.0	1.0	1.0	12.77	21.28
6.0	1.0	1.2	12.26	20.43
6.0	1.0	1.4	11.58	19.30

Table 3.2: Effect of Dielectric Constant (D) and Added Cations and Anions for $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}/S_2O_8^{2-}$ at 29 ± 1 °C, I [NaCl] = 0.5 mol dm⁻³, $[S_2O_8^{2-}] = 6.0 \times 10^{-3}$ mol dm⁻³, $[H^+] = 1.0 \times 10^{-3}$ mol dm⁻³ and $\lambda_{max} = 683$ nm

Dielectric const. (D) and Added Ions (X)	10^3 [Ion] mol dm ⁻³	$10^{-1} k_1$ s ⁻¹	k_2 dm ³ mol ⁻¹ s ⁻¹
D	0.5	1.28	2.13
	1.0	1.21	2.02
	1.5	1.19	1.98
	2.0	1.15	1.92
	2.5	1.11	1.85
	3.0	1.02	1.70
HCOO ⁻	0.5	1.28	2.13
	1.0	1.28	2.13
	1.5	1.28	2.13
	2.0	1.28	2.13
	2.5	1.28	2.13
	3.0	1.28	2.13
NO ₃ ⁻	0.5	1.28	2.13
	1.0	1.28	2.13
	1.5	1.28	2.13
	2.0	1.28	2.13
	2.5	1.28	2.13
	3.0	1.28	2.13
Mg ²⁺	0.5	1.28	2.13
	1.0	1.28	2.13
	1.5	1.28	2.13
	2.0	1.28	2.13
	2.5	1.28	2.13
	3.0	1.28	2.13

Effect of 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 of reaction decreased (Table 3.2).

Effect of Added Cation and Anions

The addition of anions and cation (NO₃⁻, HCOO⁻ and Mg²⁺) did not have an effect on the rate constant (Table 3.2). This is consistent with the report of ^[14] for the reaction of $[(bipy)Mn^{III}O_2Mn^{IV}(bipy)]^{3+}/SCN^-$. The lack of catalysis by the added anions and cation is in line with the formation of ion-pair prior to electron transfer.

Test for 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 reaction mechanism.

Spectroscopic Test for Intermediate Complex Formation

The plot of $1/k_1$ vs $1/[S_2O_8^{2-}]$ gave a straight line which passed through the origin (Fig. 3.6). This suggests absence of intermediate complex formation prior to redox reaction. This result is also consistent with the results of ^[6] for the reaction between $[(phen)_4Mn^{III}O_2Mn^{IV}]^{3+}/S_2O_8^{2-}$. The results of

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the spectroscopic studies indicate no significant shifts from the absorption maxima of 683 nm. This further suggests the absence of the formation of an intermediate complex in the reaction.

Product Analysis

After the completion of the reaction indicated by a colourless solution Mn^{2+} was confirmed as one of the products identified by a pink solution^[15]. Furthermore, on addition of $FeCl_3$ to the complete reaction mixture, a purple colour appeared which disappeared after few second indicating the presence of $S_4O_6^{2-}$ as another product of the reaction. $S_4O_6^{2-}$ and Mn^{2+} were also reported by^[7] as products for the reaction between $[Mn_3^{IV}(\mu-O)_4(H_2O)_2]^{4+}/S_2O_3^{2-}$.^[10] also reported $S_4O_6^{2-}$ as product for the reaction of thiosulphate. However,^[6] reported SO_4^{2-} as the product of analysis for the above reaction system. A Proton Coupled Electron Transfer was proposed for the mechanism of reaction which is also consistent with what was proposed by^[6] for the reaction between $[(phen)_2Mn^{III}O_2Mn^{IV}(phen)_2]/S_2O_3^{2-}$ system.

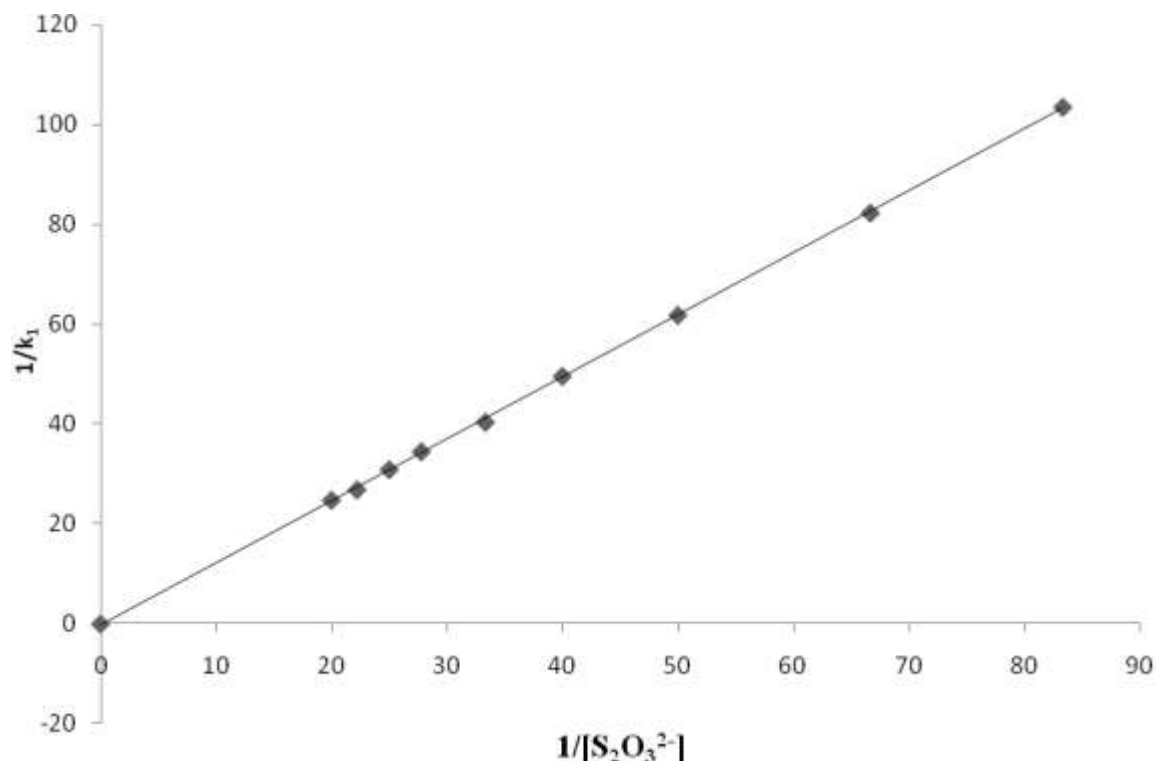
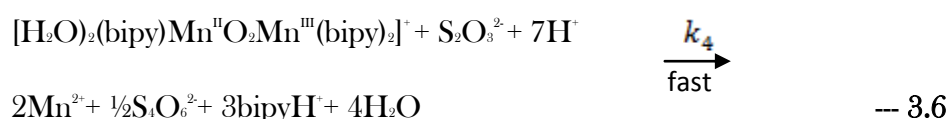
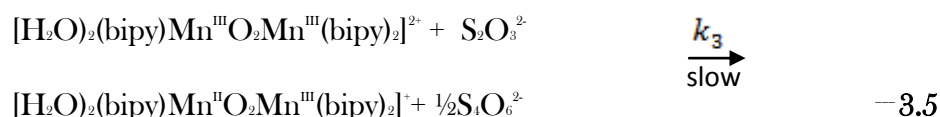
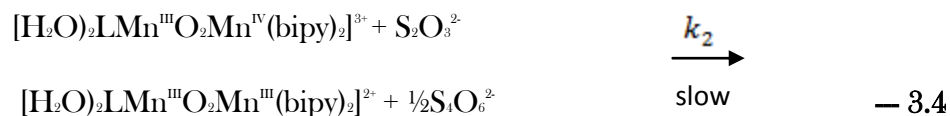
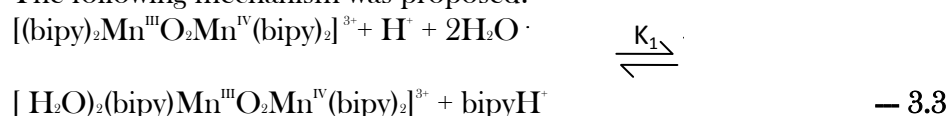


Figure 3.6: Graph of $1/[S_2O_3^{2-}]$ vs $1/k_1[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+} = 6 \times 10^{-4} \text{ mol dm}^{-3}$, $[S_2O_3^{2-}] = 6 \times 10^{-2} \text{ mol dm}^{-3}$, $H^+ = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$, $\lambda_{max} = 683 \text{ nm}$ and $T = 29 \pm 1^\circ\text{C}$.

The following mechanism was proposed:



CONCLUSION

Mechanism and oxidation of thiosulphate by di- μ -oxo-tetrakis (2, 2'- bipyridine)-dimanganese (III, IV) perchlorate showed that the reaction was catalyzed by acid showing two pathways, acid-dependent and acid-independent pathways. Spectroscopic investigations did not indicate intermediate complex formation. Furthermore, addition of acrylamide solution did not give a gel formation and added cation and anions did not catalyze the reaction system as such the reaction has been proposed to proceed via Proton Coupled Electron Transfer reaction pathways.

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