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Kinetics of the reduction of di-μ- oxo–tetrakis (1,10-phenan- throline)-dimanganese (III, IV) perchlorate by thiosulphate ions in acid medium

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ABSTRACT

The kinetics of reduction of di-μ- oxo –tetrakis (1,10-phenanthroline) – dimanganese (III, IV) perchlorate ($Mn^{III}O_2Mn^{IV}$) by thiosulphate ions in acid medium has been investigated. The reduction is first order in both oxidant and reductant.

The reaction obeys the rate expression

$$-\frac{3}{8}\frac{d[Mn^{III}O_2Mn^{IV}]^{3+}}{dt} = (a+b)[H^+][Mn^{III}O_2Mn^{IV}]$$

Where a =7.01 x 10^{-3} mol $dm^{-3}s^{-1}$ b = 0.92 x 10^{-3} mol dm^{-3} s^{-1} at 28.0 $\pm 1^0$C, $[H^+]$ =2x10^{-3}mol dm^{-3} and λ_{max} = 580nm.

The rate of reduction increased with increase in ionic strength and dielectric constant. It is unaffected by cationic and anionic species. There is no evidence for the formation of an intermediate complex of significant stability. Free radicals were found to be present in this reaction. The results obtained support the proton coupled electron transfer (PCET) pathway and is hereby proposed for the reaction.

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INTRODUCTION

Reactions of high valent manganese ions has witnessed intense research efforts in the past decade due to the important roles this element plays in biological processes [1-4], which utilise redox-active manganese centres. Such enzymes include, manganese catalyse, ribonucleotide reductase and photosynthetic water oxidizing catalyst photosystem II (Ps II).

Reports [5,6] show that Ps II is unique among all these redox-active manganese enzymes in that no other transition metal has been found to function in place of manganese in the water oxidation reaction catalysed by Ps II during photosynthesis.

Some of the reduction reactions reported include that of di-μ-oxo-tetrakis (1,10-phenanthroline) manganese (III,IV) perchlorate by DL – Methionine [5] and thiocyanate [6].

The motivation for this work is due to the important roles Mn element plays in biological processes. It is our hope that this study will complement the much needed kinetic information relating to the processes of reduction of this manganese complexes in the biological system.

EXPERIMENTAL

Materials and reagents

The materials were of analytical grades and were used without further purification. The complex $[(Phen)_2Mn^{III}O_2Mn^{IV}(Phen)_2].(ClO_4)_3$ was prepared and characterised as described by Cooper and Calvin [7].

Sodium thiosulphate (BDH) was standardized gravimetrically with potassium iodate [8]. Sodium nitrate was used to maintain the ionic strength constant at 0.5 mol dm^{-3} while nitric acid was used to investigate the effect of hydrogen ions on the rate of the reaction. All other chemicals were used as supplied.

Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. Solutions containing known concentrations of

$Mn^{III}O_2Mn^{IV}$ and varying concentrations of $S_2O_3^{2-}$ (0.5 – 4.0 x 10^{-3} mol dm^{-3}) were reacted at $[H^+]=2x10^{-3}$ mol dm^{-3}, I=0.5mol dm^{-3}($NaNO_3$), λ_{max} = 580nm and T =28 $\underline{+}1^oC$.

The absorbance of the reaction mixture was measured until the completion of the reaction was indicated by a constant absorbance value over a period of two days. A plot of absorbance versus $[S_2O_3^{2-}]$ was made from which the stoichiometry was determined.

Kinetics studies

All rate measurements were made using Corning Spectrophotometer Model 2 having ascertained that neither Mn complex or $S_2O_3^{2-}$ or any of the reactants absorb significantly at λ_{max} = 580nm. The reaction rates were monitored at this wavelength as reflected by decrease in absorbance of the reaction mixture.

All kinetic runs were monitored under pseudo-first order conditions with the concentration of the thio- sulphate at least 20 times greater than that of the $[Mn^{III}O_2Mn^{IV}]$ complex by following the rate of change of absorbance of the reaction mixture at λ_{max} 580nm.

The pseudo–first order rate constants were obtained from the slope of the plots of log (At – A_0) versus time (where A_t and A_0 are the absorbances of reaction mixtures at time t and time zero respectively. The temperature was kept constant at 28 $\underline{+}1$ °C for runs $[H^+]$ = $2x10^{-3}$ mol dm^{-3}, I = 0.5 mol dm^{-3} ($NaNO_3$) unless otherwise stated.

RESULTS AND DISCUSSION

Stoichiometry

The stoichiometry of the reaction between the $[Mn^{III}O_2Mn^{IV}]$ Complex and thiosulphate ion was found to be in the ratio of 8:3, the overall reaction is given by equation 1.

$$8[Mn^{III}O_2Mn^{IV}]^{3+} + 3S_2O_3^{2-} + 2H^+ \rightarrow 16Mn^{2+} + 6SO_4^{2-} + H_2O \quad .... (1)$$

Product analysis

The products of the reaction were qualitatively identified. The SO_4^{2-} ions was identified by production of white precipitate on addition of dilute HCl and $BaCl_2$ to the reacted mixture.

Mn^{2+} ions gave a white precipitate when treated with indole [5,9,10].

Kinetics

The pseudo-first order plot of log (A_t – A∞) versus time were linear to greater than 75% completion of the reaction. This suggests that there is no product inhibition and that the reaction is first order in $[Mn^{III}O_2Mn^{IV}]$. The slope of 0.97 obtained from log k_o vs log $[S_2O_3^{2-}]$ suggesting that the reaction is also first order in $[S_2O_3^{2-}]$ at $[H^+]$ = $2x10^{-3}$ mol $dm^{-3.}$ The values of second order rate constant k_2 which was determined as $\frac{k_o}{[S_2O_3^{2-}]}$ were fairly constant (Table 1) which further suggests that the reaction is also first order with respect to $[S_2O_3^{2-}]$.

The reaction is therefore second order overall and the rate law for the reaction can be written as

$$-\frac{3}{8}\frac{d}{dt} Mn^{III}O_2Mn^{IV}] = k_2[Mn^{III}O_2Mn^{IV3+}][S_2O_3^{2-}] .... (2)$$

Acid dependence

In the range of 0.5 – 50.0 x 10^{-2} mol^{-2} of the acid, k_2 versus $[H^+]$ was linear with a slope of 0.58x 10^{-5} s^{-1} and intercept of $7.67x10^{-5}$ mol $dm^{-3}s^{-1.}$ (Fig 2.) . Hence the acid dependence of the rate constant for the reaction could be given as:

$$k_2 = a + b[H^+] \text{ --------------------- } (3)$$

and the rate of the reaction as

$$-\frac{3}{8}\frac{d}{dt}[Mn^{III}O_2 Mn^{IV}]^{3+} = (a + b[H^+])[Mn^{III}O_2 Mn^{IV}][S_2O_3^{2-}]$$

Where a = 7.01 x 10^{-3} mol dm^{-3} s^{-1} and b = 0.92 x 10^{-3} mol dm^{-3} s^{-1}

From the result, it is propose that the observed acid catalysis may be due to the successive protonation of the complex [13] and this seems to agree with similar findings reported for $Mn^{III}O_2Mn^{IV}$ complex reduction by DL-Methionine [5] and thiocyanate [6].

Effect of added species

The effect of K^+, Mn^{2+}, CH_3COO^- ions on the rate of the reaction was also investigated. The results are presented in Table 2, which shows that both anion and cation studied do not catalyse the reaction. The absence of cation and anion catalysis indicates that the outersphere electron transfer mechanism may not be significant in this reaction.

Table 1: **Second order rate contants for the reduction of Mn^{III} O_2Mn^{IV} by thiosulphate ions**

[Mn^{III} O_2Mn^{IV}] = 5.46 x10^{-3} mol dm^{-3}, T = 28 ± 1^0C, λ_{max}= 580nm

10^2 [$S_2O_3^{2-}$] mol dm^{-3}	10^3 [H^+] mol dm^{-3}	I,($NaNO_3$) mol dm^{-3}	10^3k_o s^{-1}	k_2 mol dm^{-3} s^{-1}
1.82	2.0	0.5	1.63	8.97
2.73	2.0	0.5	2.40	8.78
3.64	2.0	0.5	3.26	8.97
4.55	2.0	0.5	4.17	9.17
5.46	2.0	0.5	5.14	9.42
6.37	2.0	0.5	5.81	9.13
7.28	2.0	0.5	6.72	9.23
8.19	2.0	0.5	7.52	9.18
9.10	2.0	0.5	8.45	9.30
4.55	2.0	0.2	2.50	5.48
4.55	2.0	0.4	3.60	7.92
4.55	2.0	0.6	4.80	10.53
4.55	2.0	0.8	6.14	13.35
4.55	2.0	1.0	7.68	16.87
4.55	2.0	1.2	8.19	18.00
4.55	0.5	0.5	2.67	5.85
4.55	1.0	0.5	3.71	8.15
4.55	2.0	0.5	4.17	9.17
4.55	5.0	0.5	5.46	12.00
4.55	10.0	0.5	7.31	16.07
4.55	20.0	0.5	10.96	24.10
4.55	30.0	0.5	15.95	35.05
4.55	40.0	0.5	21.00	46.15
4.55	50.0	0.5	24. 14	53.00

Table 2: Effect of added species on the rate constants for the reaction between $Mn^{III}O_2Mn^{IV}$ and $S_2O_3^2$

[Mn^{III} O_2Mn^{IV}]$^{3+}$ = 5.46 X 10^{-3}mol dm^{-3}, [H^+] = 2x 10^{-3}mol dm^{-3}

[$S_2O_3^{2-}$] = 4.55 x 10^{-2}mol dm^{-3}, I= 0.50 mol dm^{-3} ($NaNO_3$)T = 28 ± 1 °C λ_{ma} = 580 nm.

X	10^2[x],mol dm^{-3}	10^3k_o s^{-1}	k_2 mol dm^{-3} s^{-1}
Mn^{2+}	2.0	3.86	8.58
	6.0	3.97	8.72
	12.0	4.22	9.28
	16.0	4.03	8.87
	20.0	4.22	9.26
K^+	2.0	3.97	8.72
	6.0	4.13	9.07
	12.0	4.07	8.95
	16.0	4.22	9.28
	20.0	4.10	9.00
CH_3COO^-	2.0	4.03	8.87
	6.0	4.22	9.28
	12.0	4.16	9.13
	16.0	3.99	8.77
	20.0	4.22	9.28

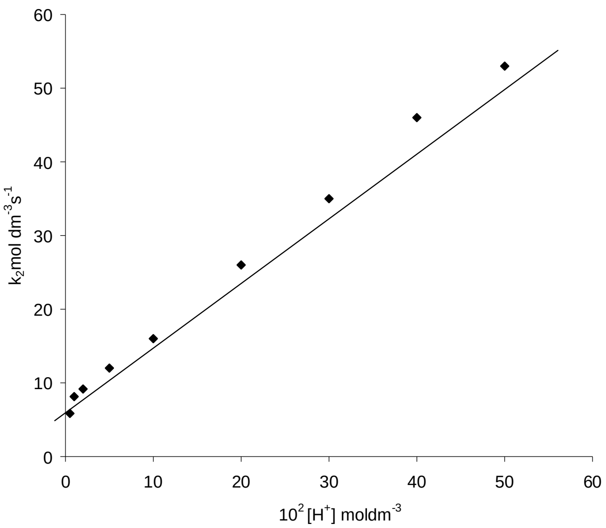

Figure 1: Plot of k_2 vs [H^+] for the redox reaction of $Mn^{III}O_2Mn^{IV}$ and thiosulphate ions

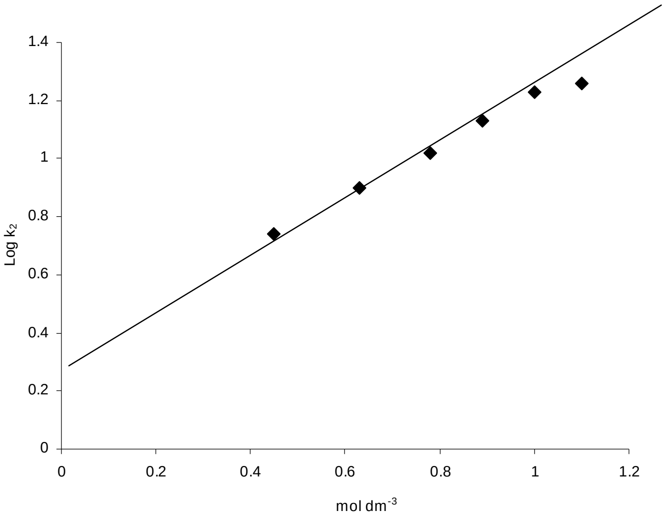

Figure 2: Plot of Log k_2 vs I for the redox reaction of $Mn^{III}O_2Mn^{IV}$ and thiosulphate ions

Effect of ionic strength

The effect of ionic strength changes on the rate of reaction was studied over the range of (0.2 – 1.2) mol dm^{-3} using $NaNO_3$ while keeping all other conditions constant. The results presented in Table 1, show that the rate constant increases with increase in ionic strength suggesting a positive Bronsted – Debye salt effect [10,11]. Plot of log k_2 versus $\sqrt{I}$ for the reaction gave a slope of 0.89 also suggesting positive salt effect. (Fig 2)

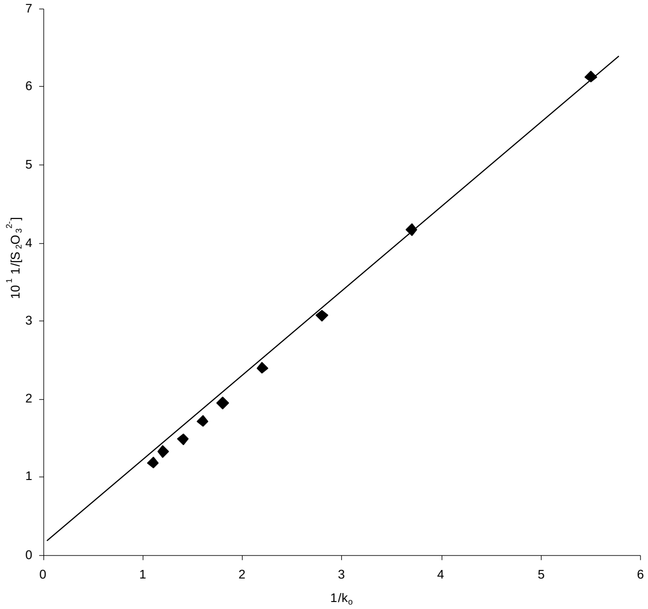

Figure 3: Michaelis-Mentens plot for the redox reaction of $Mn^{III}O_2Mn^{IV}$ and thiosuphate

Test for free radicals

Addition of acrylamide to the partially oxidized reaction mixture of $Mn^{III}O_2Mn^{IV}$ and $S_2O_3^{2-}$ at [H^+] =$2x10^{-3}$ mol dm^{-3} and I= 0.5mol dm^{-3} showed gel formation on addition of excess methanol to the reaction mixture. Therefore free radicals may have been produced as intermediate in the reaction [12].

Test for formation of intermediate complex

The results of the spectroscopic studies indicate no significant shifts from the absorption maxima of λ_{max} = 580nm. This suggests the absence of the formation of an intermediate complex in the reaction. Alternatively, if any such intermediate was formed, it must have a small formation constant. This observation has been reported for the reaction of this complex with methionine [5] and thiocyanate [6] respectively.

Effect of changes in the dielectric constant

The effect of dielectric constant (D) of the reaction medium on the rate of reactions was studied by varying ethanol/water mixtures in the ratio of 10-40% while keeping all other conditions constant. The rate of the reaction is enhanced as a function of 1/D.

Reaction mechanism

Under the experimental condition employed in this investigation, 8 moles of $[Mn^{III}O_2Mn^{IV}]$ react completely with 3 moles of $S_2O_3^{2-}$. The 8 moles of $[Mn^{III}O_2Mn^{IV}]$ undergoes dispropotionation to give 4 moles of trimer $Mn^{IV}O_2Mn^{IV}O_2Mn^{IV}$ and 4 moles of Mn^{2+} respectively [9,12]. Based on this, the following mechanism is proposed:

$$8[Mn^{III}O_2Mn^{IV}]^{3+} \rightarrow 4[Mn^{IV}O_2Mn^{IV}O_2Mn^{IV}]^{4+} + 4Mn^{2+}$$

$$4[Mn^{IV}O_2Mn^{IV}O_2Mn^{IV}]^{4+} + 2S_2O_3^{2-} \rightarrow 4[Mn_2^{IV}O_3Mn^{IV}]^{4+} + SO_3^{2-} + 2SO_2$$

$$4[Mn_2^{III}O_3Mn^{IV}O_2Mn^{IV}]^{4+} + 2SO_3^{2-} + 4H^+ \rightarrow 4Mn^{2+} + 2SO_4^{2-} 4[Mn_2O(OH)]^{3+} + O_2$$

$$4[Mn_2O(OH)]^{3+} + S_2O_3^{2-} + 2H^+ \rightarrow 8Mn^{2+} + 2SO_4^{2-} + 3H_2O$$

$$2SO_2 + O_2 \rightarrow 2SO_3^{2-}$$

$$2SO_3^{2-} + 2H_2O \rightarrow 2SO_4^{2-} + 4H^+ + 4e^-$$

The scheme proposed above is also in line with earlier reports [5,14] that the reduction of $[Mn^{III}O_2Mn^{IV}]^{+3}$ proceed in the following sequence

$$Mn^{IV} \rightarrow Mn^{IV}Mn_2^{III} \rightarrow Mn^{III}Mn^{II} \rightarrow Mn^{II} \quad [10]$$

The pathway to this reaction can be assessed as follows:

(a) Absence of spectroscopic evidence suggest that a precursor complex is probably not formed prior to the act of electron transfer and that the electron transfer may occur by the outer sphere path.

(b) Michaelis- Menten's Plot of $\frac{1}{k_o}$ verses $\frac{1}{[S_2O_3]}$ was found to be linear without positive intercept suggesting the absence of a pre-association step. This also favours an outer sphere mechanisms (Fig. 3).

(c). (a) and (b) above point to an outer sphere mechanism [12], however, absence of anion catalysis of this reaction may be due to the steric effect caused by the 3 participating species in the proton coupled electron transfer [14,15] (PCET) process.

(d) The oxidant $[MnO_2Mn^{IV}]^{3+}$ contains a protonable moiety and capable of accepting electron which is a necessary conduction for the occurrence of PCET.

The experimental results of this investigation and those from earlier studies [5,14,15] show that high valent oxo-manganese complexes have similar properties as photosystem II and therefore can serve as active sites for oxidation of water in plant.

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REFERENCES

1. B.C. Dare, and Czernuzewicz, R.C. (1994) *New. J. Chem.*, **18**, 149.
2. Tanasse ,T, and Lippard S.J. (1995). *Inorg Chem.*, **34**, 4682.
3. J.B Vincent, H.L. Isai, A.G Black, S. Wang, P.W.D Boyd, K. Folting, J.C., Huffman, E.B. Lobkovkg, D.N. Endickson, and G. J. Christian (1993). *Am Chem. Soc.*, **115**, 12353.
4. P.A Goodson, D.J. Hodgson, J. Glerup, K. Micheleson, and H. Weitie (1992). *Chim. Acta*, **197**, 141.
5. Y N. Lohdip and J.F. Iyun, (1998). *Bull. Chem. Soc. Ethiop.*, **12** (2), 113-119.
6. Y. N. Lohdip, and Iyun, J.F. (2003). *Global Jour. of Pure and Applied Sc.*, **9** (1) 105-112.
7. S R Cooper and M.J. Calvin (1977). *Am. Chem. Soc.*, **99** (20), 6623 – 6630.
8. J. Bassett, R C. Denney, G.H. Jeffery, and J. Mendhan, (1989). Vogel's *Textbook of Quantitative Inorganic Analysis*. 4th edition Longman, London. pp 375 –376.
9. M.C. Ghosh, J.W. Reed, R.N, Bose and E.S. Gould, (1994). *Inorg. Chem.*, **33**,73.
10. R. Mancharda, H.H. Thorp, G.N. Brudvig. and R.A. Crabtree (1992). *Inorg. Chem.*, **30**,494.
11. T.J Praystas and N.J.Sutin (1973). *Am. Chem. Soc.*, **95**, 5545.
12. R. Manchanda, H.H. Thorp, G.W. Bruduig and R. Crabtree (1992). *Inorg. Chem.*, **31**, 4041.
13. S. Chaudhuri, S. Mukhopadhyay and R.J. Banerjee, (1995). *Chem. Soc.* (Dalton. Trans), 621.
14. J.F Iyun, G.A Ayoko and Y.N Lohdip (1997). Exploratory Kinetics studies of the reduction of High-valent oxo-manganese complexes as model for multinuclear redox active manganese Enzymes. *Paper presented at 20th Annual Conference of the Chemical Society of Nigeria, Kaduna, Nigeria*.
15. K.R. Reddy V.M Rajasekharam, S. Padhye, F Daham, and J.P. Tuchagues, (1994). *Inorg. Chem.*, **33** (3), 428-433.