

## KINETICS AND MECHANISM OF THE REDUCTION OF DI- $\mu$ -OXO-TETRAKIS-(1,10-PHENANTHROLINE)DIMANGANESE(III,IV) PERCHLORATE BY ASCORBIC ACID IN ACID MEDIUM

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### ABSTRACT

The kinetics of the reduction of di- $\mu$ -oxo-tetrakis(1,10-phenanthroline)dimanganese(III,IV) perchlorate, ( $Mn^{III}O_2Mn^{IV}$ ) by ascorbic acid, ( $H_2A$ ) in acid medium has been investigated. The reaction was found to exhibit second order kinetics, with first order each in  $[Mn^{III}O_2Mn^{IV}]$  and  $[H_2A]$ . The reaction had an inverse dependence in hydrogen ion concentration, and so the general rate law is suggested as follows:

$$-\frac{3}{2} \frac{d[Mn^{III}O_2Mn^{IV}]}{dt} = \{a + b[H^+]^{-1}\} [Mn^{III}O_2Mn^{IV}] [H_2A]$$

Where  $a = 1.50 \times 10^{-4} s^{-1}$  and  $b = 7.94 \times 10^{-4} dm^3 mol^{-1} s^{-1}$  respectively. The rate was found to increase with increase in the dielectric constant and decrease with increase in ionic strength of the reaction medium. The presence of  $CH_3COO^-$ ,  $NO_3^-$  and  $K^+$  is independent of the rate constant while the reaction has no effect on the polymerization of acrylamide. A mechanism which is consistent with the proton coupled electron transfer, has been proposed herein.

### INTRODUCTION

The chemistry of multinuclear manganese complexes has attracted a lot of attention recently because of their roles as synthetic models for the active sites of manganese containing metalloproteins [1-3]. Their relevance in redox activities in biosystems, such as manganese containing superoxide dimutase, pseudo-catalase reductase and in photosynthetic splitting of water is also of interest [4-6]. These complexes have also been identified to be useful in catalysis and in molecular electronics [7-8]. The redox reactions of the mixed valence complexes  $[L_2Mn^{III}O_2Mn^{IV}L_2](ClO_4)_3$  (where  $L = 2,2'$ -bipyridyl or 1,10-phenanthroline), with  $Co(bpy)_3^{2+}$  [9-10],  $NO_3^-$  [11] and  $\alpha$ -hydroxyacids [12] have been reported. As part of our own contribution towards the proper understanding of the redox processes of these manganese complexes, we have studied and reported the results of their reactions with  $H_2C_2O_4$  [13] methionine [14]  $SCN^-$  and 2-mercaptobenzoic acid [15-16]. In this paper, we report the results of the reduction of di- $\mu$ -oxo-tetrakis (1,10-phenanthroline)dimanganese (III,IV) perchlorate. (referred to in the text as  $Mn^{III}O_2Mn^{IV}$ ) by ascorbic acid ( $H_2A$ ).

### EXPERIMENTAL

#### Materials

The complex  $[(phen)_2Mn^{III}O_2Mn^{IV}(phen)_2](ClO_4)_3$

was prepared and characterized as described by Cooper and Calvin [17].  $0.0175 \text{ moldm}^{-3}$  of  $Mn(Ac)_2 \cdot 4H_2O$  in water was added to  $0.0525 \text{ moldm}^{-3}$  of 1,10-phenanthroline in acetone, followed by addition of  $1.0 \text{ mldm}^{-3}$  acetate buffer and the pH adjusted to 4.5. After the mixture was cooled to  $0^\circ C$  in a water bath,  $0.0075 \text{ moldm}^{-3}$  of  $KMnO_4$  was added dropwise with stirring. The resulting solution was filtered and conc.  $NaClO_4$  solution was added to precipitate the product. The product was collected on a medium frit and washed with ethanol and then diethyl ether. The complex was recrystallised at room temperature using Dowex AG1-X8 in nitrate form.

All other chemicals and reagents were Analar grade and were used as supplied.

#### Stoichiometric studies

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. Solutions containing known concentration of  $Mn^{III}O_2Mn^{IV}$  and varying concentrations of  $H_2A$  were reacted at  $[H^+] = 0.05 \text{ mol dm}^{-3}$  and  $I = 0.50 \text{ mol dm}^{-3}$  ( $NaCl$ ). The absorbances were measured at 680nm on Jenway 6300 spectrophotometer, after the completion of the reaction. The stoichiometry was evaluated from a plot of absorbance versus the ratio  $[H_2A]/[Mn^{III}O_2Mn^{IV}]$ .

#### Kinetic studies

All kinetic runs were performed under pseudo-

first order conditions. The rate of reaction was monitored by measuring the decrease in absorbance at 680nm on Jenway 6300 spectrophotometer. Pseudo-first order rate constants were obtained from logarithmic plots of absorbance differences against time. The temperature was maintained constant at  $28.5 \pm 1.0^\circ\text{C}$  with  $[\text{H}^+] = 0.05 \text{ mol dm}^{-3}$  and  $I = 0.5 \text{ mol dm}^{-3}$  (NaCl), unless otherwise stated.

## RESULTS AND DISCUSSION

### Stoichiometry

The results of the spectrophotometric titration indicated a 2 : 3 stoichiometry and the overall reaction is given by equation (1).



The symbol A is the dehydroascorbic acid.

This stoichiometry is similar to the ones reported for the reaction of  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$  with  $\text{H}_2\text{C}_2\text{O}_4$ , methionine and 2-mercaptobenzoic acid [13-15] and for other systems [10-12]. This is in line with a  $2e^-$  transfer process proposed for this system cited.

### Order of reaction

Pseudo-first order plots of  $\log (A_0 - A_t)$  versus time (where  $A_0$  and  $A_t$  are absorbances at time zero and  $t$  respectively at  $\lambda_{\text{max}} = 680 \text{ nm}$ ), were linear to more than 80% of the extent of reaction, indicating that the reaction is first order in  $[\text{H}_2\text{A}]$ . A plot of  $\log k_{\text{obs}}$  versus  $\log [\text{H}_2\text{A}]$  (Fig. 1) gave a slope 0.98, which is in support of first order in  $[\text{H}_2\text{A}]$ . The values of the second order rate constants calculated from  $k_2 = k_{\text{obs}}/[\text{H}_2\text{A}]$ , were found to be fairly constant (Table 1), indicating that the reaction is also first order in  $[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}]$ , giving an overall second order. The rate equation for the reaction can therefore be represented by equation (2).

$$-\frac{3}{2} \frac{d[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}]}{dt} = k_2[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}][\text{H}_2\text{A}] \quad (2)$$

$$k_2 = (1.10 \pm 0.07) \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \text{ at } 28.5 \pm 1.0^\circ\text{C}.$$

Second order kinetics has also been observed for the reduction of  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$  by other reductants [10-15].

The results from the acid dependence study (Table 1) indicate that the rate constant varies inversely with increase in  $[\text{H}^+]$ . A least squares plot of  $k_2$  versus  $[\text{H}^+]^{-1}$  was linear ( $r = 0.90$ ) so that the rate equation can be given by equation (3).

$$\frac{3}{2} \frac{d[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}]}{dt} = \{a + b[\text{H}^+]^{-1}\}[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}][\text{H}_2\text{A}] \quad (3)$$

$$a = 1.50 \times 10^{-4} \text{ s}^{-1} \text{ and } b = 7.94 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ at}$$

$28.5 \pm 1.0^\circ\text{C}$

The inverse acid dependence on the rate of the reaction is in agreement with earlier reports on the oxidation of  $\text{H}_2\text{A}$  [18-20], which is attributed to the deprotonation of  $\text{H}_2\text{A}$  prior to electron transfer. However, the reduction of  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$  has been reported to be catalysed by acid [11], which is due to the successive protonation and hydration of the dimer.

Changes in the ionic strength of the reaction medium had a negative effect on the rate of the reaction. This implies that the reaction path involves oppositely charged partners [12,21-22]. This is supported by the observed positive primary salt effect [23-24], as evident from the enhanced rate as a function of  $1/D$  (Table 2, where  $D =$  dielectric constant of the reaction medium). Addition of  $\text{CH}_3\text{COO}^-$ ,  $\text{NO}_3^-$  and  $\text{K}^+$  did not affect the rate of reaction. The absence of cation and anion catalysis in this reaction indicates that probably the reaction did not proceed through the outer sphere mechanism [14-15,25-26].

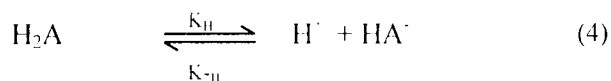
The addition of a solution of acrylamide to a partially reacted mixture did not give any gel in the presence of excess methanol. This is indicative of the probable absence of free radicals in the reaction. The absence of free radicals has also been observed for the reduction of  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$  by reductants like methionine,  $\text{H}_2\text{C}_2\text{O}_4$ , 2-mercaptobenzoic acid and  $\text{SCN}^-$  [13-16,27-28].

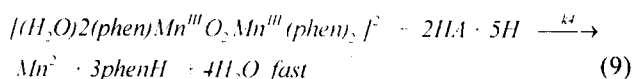
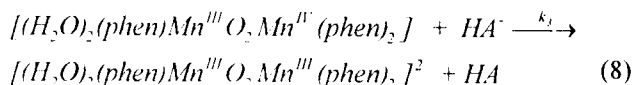
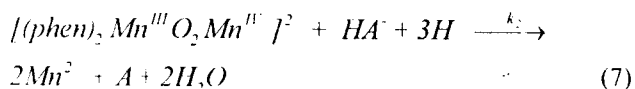
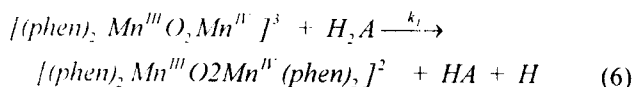
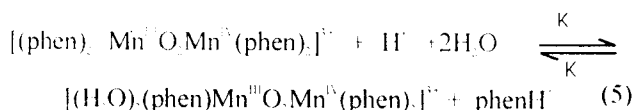
A plot of  $1/k_{\text{obs}}$  versus  $1/[\text{H}_2\text{A}]$  (Fig. 2), gave a linear relationship with an insignificant intercept, which suggests the probable absence of intermediate complex in the reaction or if an intermediate complex is formed, it may have a small formation constant. This observation has also been reported for the reduction of  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$  by  $\text{H}_2\text{C}_2\text{O}_4$ , methionine,

2-mercaptobenzoic acid and  $\text{SCN}^-$  [13-16]. This evidence is not in support of the inner sphere mechanism.

### Mechanism

Earlier reports indicate that the dimer,  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$  undergoes successive protonation and hydration during its reduction while  $\text{H}_2\text{A}$  undergoes deprotonation prior to electron transfer [10-11,19-20]. Drawing analogy from these reports and from the stoichiometric and kinetic studies of the title reaction, the following scheme (1) is proposed as the mechanism for the reduction of  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$  by  $\text{H}_2\text{A}$ .





**Scheme (1)**

Applying the steady state conditions to Scheme (1) leads to rate equation (10).

$$\text{Rate} = \{k_1 + k_3k_D\}[H^+]^{-1}\{[Mn^{III}O_2Mn^{IV}][H_2A] \quad (10)$$

Equation (10) is similar to the experimental rate law (3), where  $a = k_1$  and  $b = k_3k_D$ .

This mechanism is similar to those proposed for the reduction of  $Mn^{III}O_2Mn^{IV}$  by  $\alpha$ -hydroxyacids,  $H_2C_2O_4$  and  $SCN^-$  [12-13,16].

The most probable pathway can be proposed for this reaction by considering the following points:

Anion and cation catalysis is known to be characteristic of the outer sphere mechanism [29-30], therefore the absence of anion and cation catalysis in

**Table 2: Dielectric Constant Dependent Rate Constants for the Reduction of  $Mn^{III}O_2Mn^{IV}$  by Ascorbic Acid ( $H_2A$ )**

$[Mn^{III}O_2Mn^{IV}] = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[H_2A] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[H^+] = 0.05 \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$  (NaCl),  $T = 28.5 \pm 1.0^\circ\text{C}$  and  $l = 680 \text{ nm}$

$10^2 1/D$	11.0	6.5	4.8	4.1	3.8	2.4
$10^4 k_0, s^{-1}$	4.33	3.53	3.26	2.98	2.92	2.64

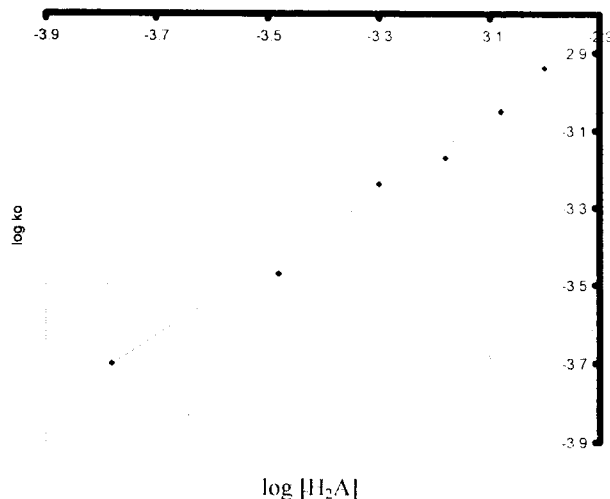


Figure 1: Plot of  $\log k_0$  versus  $\log [H_2A]$  for the reduction of  $Mn^{III}O_2Mn^{IV}$  by ascorbic acid ( $H_2A$ )

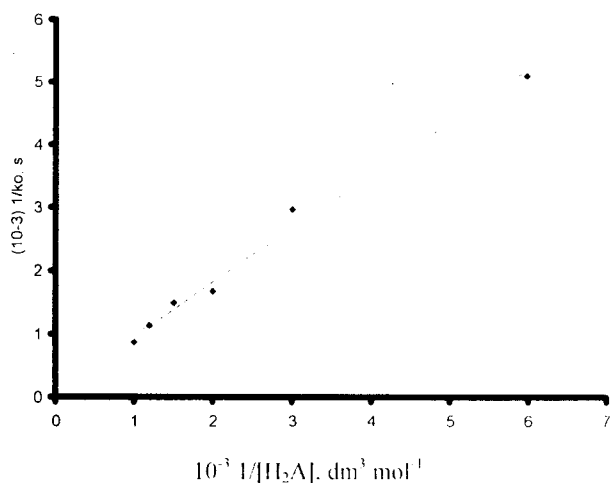


Figure 2: Plot of  $1/k_0$  versus  $1/[H_2A]$  for the reduction of  $Mn^{III}O_2Mn^{IV}$  by ascorbic acid ( $H_2A$ )

this system is not in support of simple outer sphere mechanism.

The Michealis-Menton plot of  $1/k_{obs}$  versus  $1/[H_2A]$  with an insignificant positive intercept, implies that an activated complex was probably not formed in the reaction. This evidence is not in support of the inner sphere mechanism. In addition,

**Table 1. Second Order Rate Constants for the Reduction of  $Mn^{III}O_2Mn^{IV}$  by Ascorbic Acid ( $H_2A$ )**

$[Mn^{III}O_2Mn^{IV}] = 8.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $T = 28.5 \pm 1.0^\circ\text{C}$  and  $l = 680 \text{ nm}$

$10^4 [H_2A], \text{ mol dm}^{-3}$	$10^2 [H^+], \text{ mol dm}^{-3}$	$I, \text{ mol dm}^{-3}$ (NaCl)	$k_2, \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
1.67	5.0	0.5	1.17
3.33	5.0	0.5	1.02
5.00	5.0	0.5	1.16
6.67	5.0	0.5	1.02
8.33	5.0	0.5	1.06
10.00	5.0	0.5	1.16
5.00	1.0	0.5	1.68
5.00	2.0	0.5	1.41
5.00	7.0	0.5	0.74
5.00	10.0	0.5	0.68
5.00	15.0	0.5	0.49
5.00	5.0	0.3	1.22
5.00	5.0	0.4	1.80
5.00	5.0	0.7	1.06
5.00	5.0	1.0	0.90

the absence of any effect of a radical scavenger on the reaction implies that free radicals were probably not involved in the process.

The oxidation of  $H_2A$  by  $Ru_2O^+$  has been reported to be complicated by proton transfer [22]. This implies that protons are also transferred during the electron transfer reaction, so that the reduction of  $Mn^{III}O_2Mn^{IV}$  in our title reaction most probably involves the transfer of both protons and electrons.

From the points raised in (a) – (c) above and earlier reports [12,14,16], the reduction of  $Mn^{III}O_2Mn^{IV}$  by  $H_2A$  most probably occurs by the proton couple electron transfer (PCET) pathway. This is further supported by the fact that  $Mn^{III}O_2Mn^{IV}$  has a protonable moiety and  $H_2A$  has acidic protons, which are necessary conditions for the occurrence of the proton coupled electron transfer pathway and so this pathway is hereby proposed for the title reaction.

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