

**KINETICS OF THE REDUCTION OF DI- $\mu$ -OXO-TETRAKIS  
(1,10-PHENANTHROLINE)-DIMANGANESE (III,IV) PERCHLORATE  
BY DL-METHIONINE IN ACID SOLUTION**

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**ABSTRACT.** The kinetics of reduction of di- $\mu$ -oxo-tetrakis(1,10-phenanthroline)-dimanganese(III,IV) perchlorate by DL-methionine in acid solution has been studied. The data are consistent with the rate law:  $(-3/2) (d[\text{oxidant}]/dt) = (a + b [H^+]) [\text{oxidant}] [\text{reductant}]$  with  $a = 4.75 \times 10^{-5} \text{ s}^{-1}$ ,  $b = 1.55 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ ,  $E_a = 74.1 \text{ kJ mol}^{-1}$ ,  $\Delta H^\ddagger = 72.0 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -293 \text{ J K}^{-1} \text{ mol}^{-1}$  at  $I = 0.50 \text{ M NaCl}$ ,  $T = 29.0 \text{ }^\circ\text{C}$  and  $\lambda = 555 \text{ nm}$ . There is no evidence for the formation of an intermediate complex of significant stability and free radicals are unimportant in the reaction. The reduction is rationalised in terms of a proton coupled electron transfer pathway (PCET).

### INTRODUCTION

Interest in the chemistry of multinuclear manganese complexes has continued to increase as evident from the large volume of literature [1-8]. Most attention is given to the synthesis, characterization and reactions of oxo-bridged manganese complexes. This is because of their redox activities in biosystems [9-12]. They also have been shown to be useful in catalysis [13] and in molecular electronics [14]. Reduction reactions reported include those of bis( $\mu$ -oxo)dimanganese(III,IV) dimers by  $\text{Co}(\text{byp})_3^{2+}$  [15], hydroquinone and  $\text{HSO}_3^-$  [16] and  $\text{NO}_2^-$  [17]. As our contribution to this area of studies, we have reported the redox reactions of  $[\text{L}_2\text{MnO}_2\text{MnL}_2](\text{ClO}_4)_3$  (where  $\text{L} = 2,2'$ -bipyridyl or 1,10-phenanthroline) with hydroxyacids and thiols [18] and with  $\text{H}_2\text{C}_2\text{O}_4$  [19]. We now present the results of our investigation of the reduction of di- $\mu$ -oxo-tetrakis(1,10-phenanthroline)-dimanganese (III,IV) perchlorate (hereafter referred to as  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$ ) by DL-methionine (hereafter referred to as  $\text{RSCH}_3$ ;  $\text{R} = \text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ ).

### EXPERIMENTAL

**Materials and reagents.** The complex  $[(\text{phen})_2\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}(\text{phen})_2](\text{ClO}_4)_3$  was prepared and characterized as described by Cooper and Calvin [20]. DL-methionine,  $\text{RSCH}_3$  (Aldrich) was used without further purification.  $\text{HCl}$  (A.R.) was used to investigate the effect of hydrogen ions on the rate of reaction while  $\text{NaCl}$  (BDH) was employed to maintain the ionic strength constant at 0.50 M. All other chemicals were used as supplied.

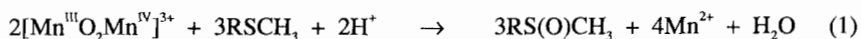
**Stoichiometric studies.** The stoichiometry of the reaction was determined by spectrophotometric titration with the mole ratio method. Solutions containing known concentration of  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$  and varying concentrations of  $\text{RSCH}_3$  were reacted at  $[H^+] = 0.05 \text{ M}$  and  $I = 0.50 \text{ M NaCl}$  and the absorbances were measured at 555 nm after the

reactions had gone to completion. A plot of absorbance versus  $[\text{RSCH}_3]/[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}]$  was made from which the stoichiometry was evaluated.

*Kinetic studies.* All kinetic runs were performed under pseudo-first-order conditions with the concentration of  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$  at least 30 times greater than that of  $\text{RSCH}_3$ . The rate of reaction was monitored by following the rate of decrease in the absorbance of  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$  at 555 nm on a solid state photometer [21,22]. Pseudo-first-order rate constants were obtained from logarithmic plots of absorbance differences against time. The temperature was maintained constant at  $29.0 \pm 0.1^\circ\text{C}$ ,  $[\text{H}^+] = 0.05 \text{ M}$  and  $\text{I} = 0.5 \text{ M NaClO}_4$ , unless otherwise stated.

## RESULTS AND DISCUSSION

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



This 2:3 stoichiometry is similar to those reported for reduction of the oxidant with  $\text{H}_2\text{C}_2\text{O}_4$  [19] and with other systems by other authors [13,16,23], in line with the 2e oxidation of these reductants.

The product analysis was carried out by reacting  $3.58 \times 10^{-4} \text{ M Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$  and  $3.98 \times 10^{-2} \text{ M RSCH}_3$  at  $[\text{H}^+] = 0.05 \text{ M}$  and  $\text{I} = 0.50 \text{ M NaCl}$ . The reaction mixture was allowed to stand until the reaction had gone to completion. Thereafter,  $0.4 \text{ M NaHCO}_3$  (10 mL) was added and the solution stirred vigorously, followed by dropwise addition of benzoyl chloride solution until precipitation was completed. The precipitate was identified as N-benzoyl methionine sulphoxide (m.p. 180-182 °C), a derivative of methionine sulphoxide [24-27].  $\text{Mn}^{2+}$  was qualitatively identified by reaction with indole [19,23].

*Kinetics.* Kinetic measurements were made under pseudo-first-order conditions with  $[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}] = 3.58 \times 10^{-4} \text{ M}$ ,  $[\text{RSCH}_3] = 3.98 \times 10^{-2} \text{ M}$ ,  $[\text{H}^+] = 0.05 \text{ M}$  and  $\text{I} = 0.50 \text{ M NaCl}$ . Under these conditions, plots of  $\log(A_0 - A_t)$  (where  $A_0$  and  $A_t$  are absorbances  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$  species at time zero and t, respectively), versus time were linear to more than 80% of the extent of reaction, indicating that the reaction is first order in  $[\text{RSCH}_3]$ . The slope (1.04) of log-log plot of  $k_{\text{obs}}$  versus  $[\text{RSCH}_3]$  signifies a first order dependence on  $[\text{RSCH}_3]$ . The values of the second order rate constants ( $k_2 = k_{\text{obs}}/[\text{RSCH}_3]$ ) were fairly constant (Table 1), indicating that the reaction is also first order in  $[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}]$  and that the reaction is second order overall, equation (2), with  $k_2 = (3.08 \pm 0.25) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  at  $29.0^\circ\text{C}$ .

$$(-3/2) (d[\text{oxidant}]/dt) = k_2 [\text{oxidant}] [\text{reductant}] \quad (2)$$

The effect of acidity on the rate of reaction was investigated by varying the concentration of HCl ( $0.02$ - $0.15 \text{ M}$ ) at  $[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}] = 3.58 \times 10^{-4} \text{ M}$ ,  $[\text{RSCH}_3] = 3.98 \times 10^{-2} \text{ M}$  and  $\text{I} = 0.50 \text{ M NaCl}$ . The results (Table 1) show that the rate constant increases

directly with increasing  $[H^+]$ . A least squares plot of  $k_2$  versus  $[H^+]$  was linear ( $r = 0.99$ ) with a positive intercept, so that the relationship is given by equation (3):

$$k_2 = a + b [H^+] \quad (3)$$

with  $a = 4.75 \times 10^{-5} \text{ s}^{-1}$  and  $b = 1.55 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  at  $T = 29.0 \text{ }^\circ\text{C}$ . The observed acid catalysis may be due to successive protonation/hydration of the dimer [17] since unprotonated methionine has been identified to be the more reactive species in most of the reactions studied [24,28].

Table 1. Second order rate constants for the reduction of  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$  by DL-methionine,  $[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}] = 4.403 \times 10^{-4} \text{ M}$ ;  $I = 0.50 \text{ M NaCl}$ ,  $T = 29.0 \text{ }^\circ\text{C}$ ;  $\lambda = 555 \text{ nm}$ .

$10^2 [\text{RSH}]$ M	$10^2 [H^+]$ M	$10^3 k_2$ $\text{M}^{-1} \text{ s}^{-1}$
1.11	5.0	3.3
1.78	5.0	2.9
2.01	5.0	2.6
2.39	5.0	3.0
3.18	5.0	3.2
3.98	5.0	3.1
4.78	5.0	3.1
5.97	5.0	3.5
3.98	2.0	2.3
3.98	7.0	3.7
3.98	10.0	5.0
3.98	12.0	5.3
3.98	15.0	7.9

Changes in ionic strength of the reaction medium had no effect on the rate of the reaction. This is because one of the reacting species (unprotonated methionine) is neutral [24,28]. However, the rate was found to be enhanced as a function of  $1/D$  (Figure 1) ( $D =$  dielectric constant of the reaction medium, varied using different ethanol/water ratios). Because of the neutral nature of the reactive methionine species, this dependence can not be explained in terms of a salt effect, but in terms of a solvation process. As the polarity of the medium decreases, the efficiency of electron transfer is no longer solely dependent on the rearrangement of the solvated molecules. Instead, the activation energy is a function of both the reorientation of the solvated molecules around the reactants and deformation of the encounter species [29].

Addition of a solution of acrylamide to partially reacted mixture did not give a gel in the presence of excess methanol, indicating the probable absence of free radicals in the reaction medium. The absence of a free radical intermediate is a common feature of methionine oxidations [26,28], even though its presence has been observed in the reactions of some thiols [30,31].

The results of the spectroscopic studies indicate no significant shifts from the absorption maxima of 525, 555, and 648 nm characteristic of  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$ . This is suggestive of 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 also been reported for the  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}/\text{H}_2\text{C}_2\text{O}_4$  system [19].

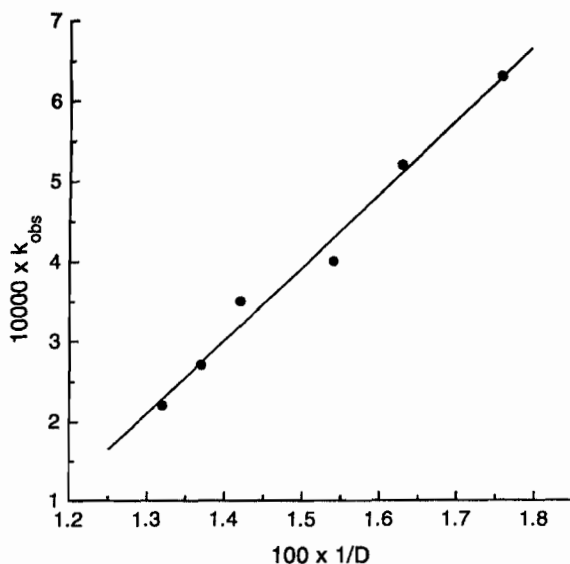


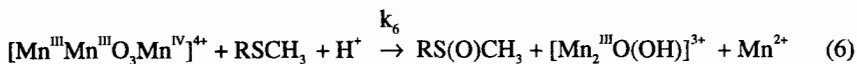
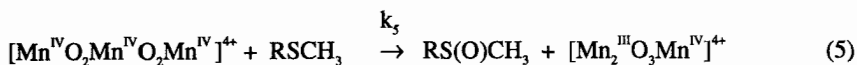
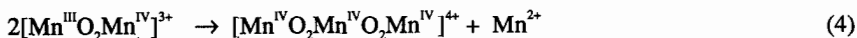
Figure 1. Plot of  $k_{\text{obs}}$  versus  $1/D$  ( $D$  was varied by varying ethanol/water ratios) for the reduction of  $[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}]$  by DL-methionine.  $[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}] = 3.58 \times 10^{-4} \text{ M}$ ;  $[\text{RSCH}_3] = 3.98 \times 10^{-2} \text{ M}$ ;  $[\text{H}^+] = 0.05 \text{ M}$ ;  $I = 0.50 \text{ M NaCl}$ ;  $T = 29.0 \text{ }^\circ\text{C}$ ;  $\lambda = 555 \text{ nm}$ .

Added  $\text{Mn}^{2+}$ ,  $\text{K}^+$ ,  $\text{HCOO}^-$  and  $\text{NO}_3^-$  had no effect on the rate of the reaction. The absence of cation and anion catalysis indicates that outer sphere electron transfer may not be important in this reaction. Rate constants were obtained at various temperatures from which plots  $\log k_o$  and  $\log (k_o/T)$  versus  $1/T$  were drawn. From linear least squares analysis of the plots, the energy of activation  $E_a$ , the enthalpy of activation  $\Delta H^\ddagger$ , and entropy of activation  $\Delta S^\ddagger$ , were calculated at  $30 \text{ }^\circ\text{C}$  to be  $74.1 \text{ kJ mol}^{-1}$ ,  $72.0 \text{ kJ mol}^{-1}$  and  $-293.0 \text{ JK}^{-1}\text{mol}^{-1}$ , respectively. The temperature dependent rate constants and the activation parameters are shown on Table 2.

Table 2. Temperature dependent rate constants and activation parameters for the reduction of  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$  by DL-methionine:  $[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}] = 3.58 \times 10^{-4} \text{ M}$ ;  $[\text{RSCH}_3] = 3.98 \times 10^{-2} \text{ M}$ ;  $[\text{H}^+] = 0.05 \text{ M}$ ;  $I = 0.50 \text{ M NaCl}$ ;  $\lambda = 555 \text{ nm}$ .

$10^3 k_2 (\text{M}^{-1}\text{s}^{-1})$					$E$ ( $\text{kJ mol}^{-1}$ )	$\Delta H^\ddagger$ ( $\text{kJ mol}^{-1}$ )	$\Delta S^\ddagger$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )
293 K	298 K	303 K	308 K	313 K			
1.13	1.86	3.49	4.93	7.49	74.1	72.0	-293

**Reaction mechanism.** Under the acid condition used for the stoichiometric and kinetic studies, the dimer  $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$  undergoes disproportionation to give the trimer  $\text{Mn}^{\text{IV}}\text{O}_2\text{Mn}^{\text{IV}}\text{O}_2\text{Mn}^{\text{IV}}$  and  $\text{Mn}^{\text{II}}$  [16,32]. Based on the stoichiometry and kinetic results, the following scheme is proposed for the reaction;



The above scheme leads to equation (9)

$$k_2 = k_5 + k_6 [\text{H}^+] \quad (9)$$

so that the rate equation can be written as

$$(-3/2) (d[\text{oxidant}]/dt) = (k_5 + k_6 [\text{H}^+]) [\text{oxidant}] [\text{reductant}] \quad (10)$$

Equation (10) is analogous with equation (3) with  $k_5 = a$  and  $k_6 = b$ .

A similar analogy has been employed [16,32] to propose that the reduction of  $[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}]^{3+}$  proceeds through a  $2\text{H}^+/2e^-$  pathway. The scheme proposed above is also consistent with the sequence:  $\text{Mn}_3^{\text{IV}} \rightarrow \text{Mn}^{\text{IV}}\text{Mn}_2^{\text{III}} \rightarrow \text{Mn}_2^{\text{III}}\text{Mn}^{\text{IV}} \rightarrow \text{Mn}_3^{\text{II}}$  [32].

The pathway for this reaction can be assessed by considering the following points:

- The absence of spectrophotometric evidence suggests that a precursor complex is probably not formed prior to electron transfer and that the redox reaction may occur by the outer sphere path.
- The Michaelis-Menten plot of  $1/k_{\text{obs}}$  versus  $1/[\text{RSCH}_3]$  was linear with an insignificant positive intercept, indicating the absence of a pre-association step. The absence of kinetic evidence for the formation of a precursor complex is not in favour of an inner sphere mechanism.
- The views in (a) and (b) above point to an outer sphere reduction. However, there is absence of anion catalysis. This is expected because of the steric effect caused by the 3 participating species in the proton coupled electron transfer (PCET) process. The neutral nature of the reductant may be another reason for the absence of anion catalysis.
- The absence of any effect of radical scavenger (acrylamide) on the reaction is not in support of a  $1e^-$  reaction that would give rise to free radicals [25]. Instead, we propose that the reduction of  $[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}]^{3+}$  proceeds through a  $2\text{H}^+/2e^-$  pathway [23,32]. In addition, the oxidant contains a protonable moiety, a necessary condition for the occurrence of PCET.
- In line with arguments presented earlier [19,23,32] and those in (a)-(d) above, we believe that the PCET pathway is the most probable mechanism that explains our experimental results. In the same manner, we surmise that the high valent oxomanganese complexes have similar properties with Photosystem II and therefore can serve as active sites for oxidation of water in plants.

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