

KINETICS OF THE OXIDATION OF 2-MERCAPTobenZOIC ACID BY DI- μ -TETRAKIS(1,10-PHENANTHROLINE)-DIMANGANESE (III,IV) PERCHLORATE IN ACID MEDIUM

Y. N. LOHDIP and J. E. IYUN

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ABSTRACT

The kinetics of the oxidation of 2-mercaptobenzoic acid di- μ -tetrakis(1,10-phenanthroline)-dimanganese(III,IV) perchlorate in acid medium was investigated. The order of the reaction was found to be one in both the oxidant and reductant. The reaction was catalysed by hydrogen ion and the dependence is of the form; $k_2 = a + b[H^+]$. The rate was found to increase with decrease in the dielectric constant of the medium but was not affected by changes in the ionic strength of the medium. The reaction did not induce polymerization of acrylamide and the presence of NO_3^- or $HCOO^-$ had no effect on the rate. A plausible mechanism involving proton coupled electron transfer has been proposed.

Key words: Kinetics, oxidation, 2-mercaptobenzoic acid, di- μ -tetrakis(1,10-phenanthroline)-dimanganese(III,IV)

INTRODUCTION

Interest in the chemistry of multinuclear manganese complexes is on the increase as evident from the large volume of recent literature (Reddy et al., 1994, Arulsamy et al., 1994; Jeffery et al., 1994; Qi et al., 1995; Goodson et al., 1992; Vincent et al., 1993; Dave and Czernuzewicz 1994; Tanabe and Lippard 1995; Lohdip and Iyun 1998). This area of study holds interesting prospects because oxo-bridged manganese complexes have been found to be relevant in redox activities in biosystems and are also useful in catalysis and in molecular electronics (Babcock, 1987). Recently, the redox reactions of $[L_2MnO_2MnL_2](ClO_4)_3$ (where L = 2,2'-bipyridyl or phenanthroline) with hydroxy acids and thiols (Iyun et al., 1997), $H_2C_2O_4$ (Lohdip et al., 1998) and methionine (Lohdip and Iyun 1998) have been investigated. In continuation of these efforts, we now describe the reduction of di- μ -tetrakis(1,10-phenanthroline)-dimanganese(III,IV) perchlorate (hereafter referred to as $Mn^{III}O_2Mn^{IV}$) by 2-mercaptobenzoic acid.

EXPERIMENTAL

Materials and reagents

All reagents were of analytical or reagent grades and were used without further purification. The complex $[(phen)_2Mn^{III}O_2Mn^{IV}(phen)_2](ClO_4)_3$ was prepared

and characterized as described by Cooper and Calvin (1977). 2-Mercaptobenzoic acid ($C_6H_4COOH.SH$) (hereafter referred to as RSH, (R = C_6H_4COOH)) was dissolved in 50% ethanol- H_2O mixture and standardized gravimetrically.

Stoichiometric studies

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method.

Solutions containing a known concentration of $Mn^{III}O_2Mn^{IV}$ and varying concentrations of RSH were reacted at $[H^+] = 0.05 \text{ mol dm}^{-3}$ and $I = 0.50 \text{ mol dm}^{-3}$ (NaCl) and the absorbances were measured at 555 nm after the reactions had reached completion. A plot of absorbance versus $[RSH]/[Mn^{III}O_2Mn^{IV}]$ was made and from which the stoichiometry was evaluated.

Kinetic studies

All kinetic runs were performed under pseudo-first-order conditions with the concentration of $Mn^{III}O_2Mn^{IV}$ at least 10 fold in excess over that of RSH. The rate of reaction was monitored by following the rate of decrease in the absorbance of the mixture at 555 nm on a solid state photometer (Trojanowicz et al., 1988; Lohdip 1997). Pseudo-first-order rate constants were obtained from logarithmic plots of absorbance differences against time. The

temperature was maintained constant at $29.0 \pm 0.1^\circ\text{C}$, $[\text{H}^+] = 0.05 \text{ mol dm}^{-3}$ and $I = 0.5 \text{ mol dm}^{-3}$ (NaClO_4), unless otherwise stated. The effect of acidity on the rate of reaction was investigated by varying the concentration of HCl ($0.02 - 0.15 \text{ mol dm}^{-3}$) at $[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}] = 3.58 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{RSH}] = 0.53 \times 10^{-5} \text{ mol dm}^{-3}$ and $I = 0.50 \text{ mol dm}^{-3}$ (NaCl).

Product analysis

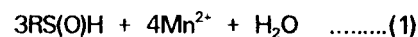
The product analysis was carried out by reacting $3.58 \times 10^{-4} \text{ mol dm}^{-3} \text{ Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$ and $0.53 \times 10^{-4} \text{ mol dm}^{-3} \text{ RSH}$ at $[\text{H}^+] = 0.05 \text{ mol dm}^{-3}$ and $I = 0.50 \text{ mol dm}^{-3}$ (NaCl). The reaction mixture was allowed to stand until the reaction had reached completion. Thereafter, a portion of the mixture was treated with methyl phenyl ether (anisole) in cold concentrated H_2SO_4 . A blue colour was produced indicating the presence of a sulphoxide (Vishnoi 1979). To the remaining portion, $0.4 \text{ mol dm}^{-3} \text{ NaHCO}_3$ (1 Q cm^3) was added and the solution stirred vigorously, followed by dropwise addition of benzoyl chloride solution until precipitation was complete. The melting point of the

benzoyl chloride derivative of the sulphoxide was found to be 116°C . Mn^{2+} was qualitatively identified using indole (Lohdip and Iyun 1998; Lohdip et al., 1998; Arabel et al., 1997).

RESULTS AND DISCUSSION

Stoichiometry

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



This 2 : 3 stoichiometry is similar to the ones reported earlier between this oxidant and $\text{H}_2\text{C}_2\text{O}_4$ (Lohdip et al., 1998) and methionine (Lohdip and Iyun, 1998) and other systems, which is in line with the $2e^-$ exchange proposed for these reductants (Ghosh et al., 1994; Arabel et al., 1997).

Kinetics

Under pseudo-first order conditions employed for this reaction, plots of $\log(A_0$

Table 1: Second order rate constants for the oxidation of 2-mercaptobenzoic acid by $\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}$; $[\text{Mn}^{\text{III}}\text{O}_2\text{Mn}^{\text{IV}}] = 3.58 \times 10^{-4} \text{ mol dm}^{-3}$, $\lambda = 555 \text{ nm}$.

$10^5[\text{RSH}]$, mol dm^{-3}	Temp, $^\circ\text{C}$	$10^2[\text{H}^+]$, mol dm^{-3}	I , $\text{mol dm}^{-3}(\text{NaCl})$	k_2 , $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
0.6	29.0	5.0	0.5	3.50
0.8	29.0	5.0	0.5	3.38
1.1	29.0	5.0	0.5	3.27
1.6	29.0	5.0	0.5	3.38
2.1	29.0	5.0	0.5	3.43
3.2	29.0	5.0	0.5	3.41
4.2	29.0	5.0	0.5	3.55
5.3	29.0	5.0	0.5	3.42
6.3	29.0	5.0	0.5	3.67
7.5	29.0	5.0	0.5	3.40
5.3	29.0	1.0	0.5	3.19
5.3	29.0	2.0	0.5	3.39
5.3	29.0	7.0	0.5	3.66
5.3	29.0	10.0	0.5	4.15
5.3	29.0	12.0	0.5	4.76
5.3	29.0	15.0	0.5	5.62
5.3	29.0	5.0	0.1	3.59
5.3	29.0	5.0	0.2	3.45
5.3	29.0	5.0	0.7	3.68
5.3	29.0	5.0	1.0	3.76
5.3	29.0	5.0	1.2	3.81
5.3	29.0	5.0	1.5	3.77
5.3	20.0	5.0	0.5	1.91
5.3	24.0	5.0	0.5	2.74
5.3	34.0	5.0	0.5	4.38
5.3	40.0	5.0	0.5	5.38

Table 2: Effect of $1/D$ on the pseudo-first-order rate constants k_{obs} for the oxidation of 2-mercaptobenzoic acid by $Mn^{III}O_2Mn^{IV}$; $[Mn^{III}O_2Mn^{IV}] = 3.58 \times 10^{-4} \text{ mol dm}^{-3}$, $[RSH] = 5.3 \times 10^{-5} \text{ mol dm}^{-3}$, $[H^+] = 0.05 \text{ mol dm}^{-3}$, $I = 0.50 \text{ mol dm}^{-3}$, $T = 29^\circ\text{C}$, $\lambda = 555 \text{ nm}$.

$10^{-2}/D$	1.32	1.37	1.42	1.48	1.54	1.61	1.76
$10^4 k_{obs} \text{ s}^{-1}$	2.30	2.35	2.38	2.45	2.52	2.56	2.67

- A_t) versus time were linear to more than 85% of the extent of reaction, indicating that the reaction is first order in $[RSH]$ (where A_0 and A_t are absorbances at time zero and t respectively). The slope (1.02) of log-log plot of k_{obs} versus $[RSH]$ signified first order in $[RSH]$. The values of the second order rate constants ($k_2 = k_{obs}/[RSH]$) were fairly constant (Table 1.), indicating that the reaction is also first order in $[Mn^{III}O_2Mn^{IV}]$, and giving second order overall. The rate equation for the reaction can therefore be represented by equation (2).

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

$$k_2 = 3.44 \pm 0.11 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The results from the acid dependence study (Table 1.) suggest that the rate constant varies directly with increase in $[H^+]$. A least squares plot of k_2 versus $[H^+]$ was linear ($r = 0.95$) with a positive intercept, so that the relationship can be given by equation (3).

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

$$a = 1.49 \times 10^{-4} \text{ s}^{-1} \text{ and}$$

$$b = 8.62 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The observed acid catalysis may well be due to the successive protonation/hydration of the dimer (Chaudhuri et. al., 1995).

Changes in ionic strength of the medium did not affect the rate of the reaction (Table 1). This is in line with the fact that one of the reacting species (unprotonated 2-mercaptobenzoic acid) is neutral. However, the rate was found to be enhanced as a function of $1/D$ (Table 2.), (D = dielectric constant of the reaction medium). Because of the neutral nature of the reactive 2-mercaptobenzoic acid specie, this dependence can not be explained in terms of primary salt effect, but in terms of the solvation process. As the polarity of the medium decreases (as it becomes less aqueous), the efficiency of electron transfer

is no longer solely dependent on the rearrangement of the solvated molecules. Instead, the activation energy becomes a function of both the reorientation of the solvated molecules around the reactants and the deformation of the encounter species (Sonoyama et. al., 1995; Dash et. al., 1995). The addition of the organic solvent tends to reduce the hydrogen-bonding between H_2O molecules and the MnO_2Mn moiety. This makes the MnO_2Mn moiety relatively free as the quantity of the co-solvent increases leading to increase in the rate of the reaction.

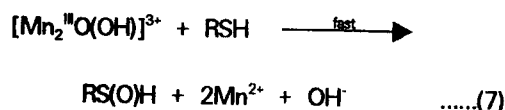
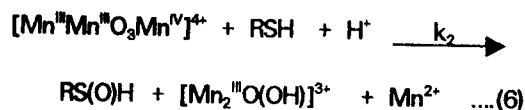
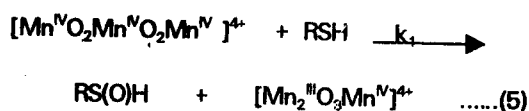
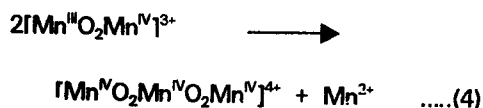
The addition of a solution of acrylamide to the partially reacted mixture did not give any gel in the presence of excess methanol, indicative of the probable absence of free radicals in the reaction medium. The absence of a free radical intermediate was also observed for the oxidation of methionine (Lohdip and Iyun 1998; Olatunji and Ayoko 1988; Lawal 1997), even though its presence has been observed in the reactions of some thiols (Ayoko and Olatunji 1983).

The results of the spectroscopic studies indicate no significant shifts from the characteristic absorption bands of $Mn^{III}O_2Mn^{IV}$ (525, 555 and 648 nm). This is suggestive of the absence of the formation of an intermediate complex in the reaction or that such intermediate has a small formation constant. This observation was also reported for $Mn^{III}O_2Mn^{IV}/H_2C_2O_4$ (Lohdip et. al., 1998) and $Mn^{III}O_2Mn^{IV}$ /methionine (Lohdip and Iyun 1998) systems. The addition of $HCOO^-$ and NO_3^- did not alter the rate of the reaction. The absence of anion catalysis indicates that outer sphere electron transfer may not be important in this reaction. The rates of oxidation were determined at different temperatures while the activation parameters evaluated as $E_a = 39.60 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 36.76 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -386.99 \text{ J K}^{-1} \text{ mol}^{-1}$ at 29°C .

Mechanism

As observed earlier (Lohdip and Iyun 1998; Ghosh et al., 1994), under the acid condition used for the stoichiometric and kinetic studies, the dimer $Mn^{III}O_2Mn^{IV}$ undergoes disproportionation to give the trimer $Mn^{IV}O_2Mn^{IV}O_2Mn^{IV}$ and Mn^{2+} . On the basis of experimental observations, scheme 1. is proposed as the mechanism for the reaction.

Scheme 1.



Scheme 1. leads to equation (9)

$$\frac{3}{2} \frac{d[\text{oxidan}]}{dt} = \{k_1 + k_2[H^+]\} [\text{oxidan}][\text{reductant}] \quad \dots(9)$$

Equation (9) is comparable to equation (3) with

$$k_1 = a \text{ and } k_2 = b.$$

Scheme 1. is in line with earlier proposals (Lohdip and Iyun 1998; Lohdip et al., 1997; Satsangi et al., 1995) that the reduction of $[Mn^{III}O_2Mn^{IV}]^{3+}$ proceeds through $1^+/2e^-$ path in the following sequence;



(Satsangi et al., 1995; Lohdip and Iyun 1998).

The interpretation of the results of this

investigation can be summarised as follows;

- i. The absence of spectrophotometric evidence suggests that a precursor complex is not formed prior to electron transfer and that the redox reaction most probably occurs by the outer sphere path.
- ii. The Michaelis-Menten plot of $1/k_{\text{obs}}$ versus $1/[RSH]$ was linear with an insignificant positive intercept, indicating the absence of a pre-association step. This absence of kinetic evidence for the formation of a precursor complex is also in favour of the outer sphere mechanism.
- iii. The absence of anion catalysis is not unexpected. As suggested earlier (Lohdip and Iyun 1998), the simultaneous involvement of 3 species in a proton coupled electron transfer (PCET) process causes a steric effect. This effect would not encourage the participation of any added ion in the reaction so that the presence of $HCOO^-$ or NO_2^- had no effect on the rate of the reaction. The neutral nature of the reductant may also be responsible for the absence of anion catalysis.
- iv. The absence of induced polymerization when the acrylamide monomer was added to the reaction mixture is not in support of a $1e^-$ redox process (Satsangi et al., 1995) which is supposed to involve free radicals. We therefore propose that the oxidation proceeds through $2H^+/2e^-$ path as indicated earlier (Lohdip and Iyun 1998; Arabel et al., 1997). In addition, $[Mn^{III}O_2Mn^{IV}]^{3+}$ contains a protonable moiety, a necessary condition for the occurrence of PCET.
- v. In line with arguments presented earlier (Lohdip and Iyun 1998; Lohdip et al., 1998; Arabel et al., 1997), and those in (i) - (iv) above, we believe that the PCET pathway is the most probable mechanism for the title reaction.

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