Kinetics of the oxidation of oxalic acid by di-μ-tetrakis(1,10-phenanthroline)-dimanganese (III,IV) perchlorate in aqueous acid medium

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The kinetics and stoichiometry of the oxidation of oxalic acid with $[(phen)_2Mn^{III}O_2Mn^{IV}(phen)_2](ClO_4)_3$ have been studied in aqueous acid medium. The reaction follows the general rate law:

$$-\frac{3}{2}\frac{d[Mn^{III}O_2Mn^{IV}]}{dt} = \{a + b[H^+]\}[Mn^{III}O_2Mn^{IV}][H_2C_2O_4]$$

with $a=0.36$ s^{-1} and $b=52.80$ M^{-1} s^{-1} at 27.0 ± 0.1°C, $[H^+]=0.05$ M and $I=0.50$ M (NaCl) and $\lambda=555$ nm. The kinetic and spectroscopic findings support the proton coupled electron transfer pathway and is hereby proposed for the title reaction.

The chemistry of multinuclear manganese complexes as synthetic models for active sites of manganese containing metalloenzymes has received considerable attention[1-4]. Of particular interest are the oxo-bridged manganese complexes due to their relevance to the redox activities in biosystems like manganese containing superoxide dimutase[5], pseudo catalase[6], reductase[7] and photosynthetic water oxidation catalyst, phososystem II (PS II)[8], usefulness in catalysis[9] and molecular electronics[10].

The reduction of bis(μ-oxo)dimanganese(III, IV) dimers by Co(byp)$_3^{2+}$ (ref. 11), hydroquinone and HSO$_3$ (ref. 12) and NO$_2$ (ref. 13) has been reported in literature. Since the reactions of the $[Mn^{III}O_2Mn^{IV}]$ moiety are of interest and relevant to photosynthetic oxygen evolution and other properties similar to those of PS II. We have chosen to study the reactions of di-μ-tetrakis(2,2'-bipyridyl)-dimanganese (III, IV) perchlorate and its 1,10-phenanthroline analogue (hereafter abbreviated as $[Mn^{III}O_2Mn^{IV}]$), with thiols and hydroxy acids[14]. In this paper, we present the results of the oxidation of oxalic acid by di-μ-tetrakis(1,10-phenanthroline)-dimanganese (III, IV) perchlorate.

Experimental

The complex $[(phen)_2Mn^{III}O_2Mn^{IV}(phen)_2](ClO_4)_2$ was prepared and characterized as described by Cooper and Calvin[15]. Oxalic acid was prepared and standardized as described elsewhere[16]. HCl (A.R.) was used to investigate the effect of hydrogen ions on the rate of the reaction while 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 using the mole ratio method. Solutions containing known concentration of $Mn^{III}O_2Mn^{IV}$ and varying concentrations of $H_2C_2O_4$ were reacted at $[H^+]=0.05$ M and $I=0.50$ M (NaCl) and the absorbances were measured at 555 nm after the completion of the reaction. A plot of absorbance versus $[H_2C_2O_4]/[Mn^{III}O_2Mn^{IV}]$ was drawn, 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 5-fold exceeding over that of $H_2C_2O_4$. 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[17,18]. Pseudo-first-order rate constants were obtained from logarithmic plots of absorbance differences against time. The temperature was maintained constant at 27.0 ± 0.1°C, $[H^+]=0.05$ M and $I=0.50$ M (NaCl), unless otherwise stated. Replicate measurements agreed within ~5%.

Results and discussion

Stoichiometry and product analysis

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

$$2 [Mn^{III}O_2Mn^{IV}]^{3+}+3H_2C_2O_4+2H^+ \rightarrow 4Mn^{2+}+6CO_2+4H_2O \qquad \ldots (1)$$
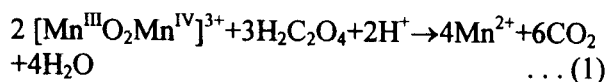
A stoichiometry of 2:3 has also been reported for hydroquinone and HSO_3 (ref. 12), NO_2 (ref. 13) and hydroxy acids[19] systems. This stoichiometry is in line with the 2 e⁻ exchange proposed for these reductants[12,13,19]. The reaction products were identified qualitatively, i.e., Mn^{2+} by indole[19] and CO_2 by lime water test.

Order of reaction

Kinetic measurements were made under pseudo-first-order conditions with $[Mn^{III}O_2Mn^{IV}]=4.403 \times10^4 M$, $[H_2C_2O_4]=1.37-9.61\times10^5 M$, $[H^+]=0.05 M$ and $I=0.50 M$ (NaCl). Under these conditions, plots of $\log(A_0-A_t)$ versus time were found to be linear to more than 75% of the extent of reaction, indicating that the reaction is first order in $[H_2C_2O_4]$ (where A_0 and A_t are the absorbances at time zero and t respectively). The slope $(0.98\approx1.0)$ of log-log plot of k_{obs} versus $[H_2C_2O_4]$ signifies first order in $[H_2C_2O_4]$. The values of the second order rate constants $(k_{obs}/[H_2C_2O_4])$ were fairly constant (Table 1), indicating that the reaction is also first order in $[Mn^{III}O_2Mn^{IV}]$, giving second order overall. The rate equation for the reaction can therefore be represented by Eqn (2).

$$-\frac{3}{2}\frac{d[Mn^{IIII}O_2Mn^{IV}]}{dt}=k_2[Mn^{III}O_2Mn^{IV}][H_2C_2O_4] \qquad \ldots (2)$$

$k_2=(2.35\pm0.15)\times10^2 M^{-1}s^{-1}$

The effect of $[H^+]$ on the reaction rate was studied by varying $[H^+]$ from 0.01 to 0.15 M employing HCl at $[Mn^{III}O_2Mn^{IV}]=4.403\times10^4M$, $[H_2C_2O_4]=6.86\times10^{-5} M$ and $I=0.50 M$ (NaCl). The values of the acid dependent rate constants are given in Table 1. A least squares plot of k_2 versus $[H^+]$ was found to be linear $(r=0.95)$ with a positive intercept, and the relationship is given by Eqn (3).

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

$a=0.36 s^{-1}$ and $b=52.80 M^{-1} s^{-1}$

However, the effect of the acid is less pronounced on the rate of reaction at $[H^+]<0.05 M$. This may be due to the slight deprotonation of $H_2C_2O_4$, which suppresses the effect of the acid at lower concentrations.

The ionic strength was varied from 0.1 to 1.5 M using NaCl and dielectric constant was varied by varying C_2H_5OH/H_2O ratios at $[Mn^{III}O_2Mn^{IV}]=4.403\times10^{-4} M$, and $[H_2C_2O_4]=6.86\times10^{-5} M$. The corresponding rate constants are given in Table 2

Table 1—Second order rate constants for the oxidation of oxalic acid by $Mn^{III}O_2Mn^{IV}$
$[Mn^{IIII}O_2Mn^{IV}]=4.403\times10^{-4} M$;
$\lambda=555$ nm

$10^5[H_2C_2O_4]$, M	Temp, °C	$10^2[H^+]$, M	I, M (NaCl)	$10^{-2}k_2$, $M^{-1} s^{-1}$
1.37	27.0	5.0	0.5	2.39
2.75	27.0	5.0	0.5	2.34
4.13	27.0	5.0	0.5	2.21
5.49	27.0	5.0	0.5	2.17
6.86	27.0	5.0	0.5	2.56
8.24	27.0	5.0	0.5	2.22
9.61	27.0	5.0	0.5	2.56
6.86	27.0	1.0	0.5	2.47
6.86	27.0	2.0	0.5	2.54
6.86	27.0	7.0	0.5	4.10
6.86	27.0	10.0	0.5	9.81
6.86	27.0	12.0	0.5	10.59
6.86	27.0	15.0	0.5	11.69
6.86	27.0	5.0	0.1	2.92
6.86	27.0	5.0	0.2	2.68
6.86	27.0	5.0	0.7	2.46
6.86	27.0	5.0	1.5	1.97
6.86	20.0	5.0	0.5	1.09
6.86	30.0	5.0	0.5	4.68
6.86	35.0	5.0	0.5	7.52

Table 2—Effect of added species on the rate constants for the reaction between $Mn^{III}O_2Mn^{IV}$ and $H_2C_2O_4$. $[Mn^{III}O_2Mn^{IV}]=4.403\times10^{-4}$ M; $[H_2C_2O_4]=1.37-9.61\times10^{-5}$ M; $[H^+]=0.05$ M; $I=0.50$ M (NaCl); Temp=27.0±0.1°C; λ=555 nm

X	$10^3[X]$	$10^5 k_{obs}$, s^{-1}	$10^{-2}k_2$ M^{-1} s^{-1}
Mn^{2+}	3.0	1.91	2.86
	6.0	1.81	2.64
	8.0	2.01	2.93
	12.0	1.48	2.16
	15.0	1.66	2.42
K^+	3.0	1.71	2.49
	6.0	1.71	2.49
	8.0	1.83	2.67
	12.0	1.83	2.67
	15.0	1.74	2.54
	20.0	1.74	2.54
NO_3^-	3.0	1.72	2.51
	6.0	1.72	2.51
	8.0	1.64	2.39
	12.0	1.93	2.81
	15.0	1.87	2.73
$HCOO^-$	3.0	1.79	2.61
	6.0	1.80	2.63
	8.0	1.81	2.63
	12.0	1.81	2.63
	20.0	1.61	2.42
	25.0	1.73	2.52

Table 3—Dependence of first-order-rate constants in the ionic strength and dielectric constant for the reaction between $Mn^{III}O_2Mn^{IV}$ and $H_2C_2O_4$. $[Mn^{III}O_2Mn^{IV}]=4.403\times10^{-4}M$; $[H_2C_2O_4]=1.37-9.61\times10^{-5}M$; $[H^+]=0.05$ M

I, M	0.1	0.2	0.5	0.7	1.5
$10^5 k_{obs}$, s^{-1}	2.00	1.84	1.76	1.69	1.35
$10^1/D^*$	1.32	1.37	1.41	1.54	1.76
$10^5 K_{obs}$, s^{-1}	1.96	2.11	4.22	5.33	7.47

*Varied using different C_2H_5OH/H_2O ratios

The effects of added species, Mn^{2+}, K^+, $HCOO^-$ and NO_3^- on the reaction rate was studied and 'it was found that they did not have any effect on the rate of reaction as reflected from the values of the rate constants (Table 3). The absence of cation and anion catalysis indicates that the outer sphere electron transfer may be unlikely.

Rate constants obtained at various temperatures are presented in Table 1. Using the temperature dependent rate constants, least squares plots of ln$k$ versus $1/T$ and ln(k/T) versus $1/T$ were obtained, from which the activation parameters were evaluated as: ΔE=98.11 kJ mol^{-1}, $\Delta H^{\#}$=96.44 kJ mol^{-1} and $\Delta S^{\#}$=−196.17 J mol^{-1} K^{-1}.

which relevant that the rates of reaction are retarded by increasing ionic strength and are enhanced as a function $1/D$ (D=dielectric constant of the reaction medium). Both these features indicate that the rate determining steps or one of the rate determining steps involves oppositely charged reacting species.

Addition of acrylamide to partially reacted mixture gave a gel in the presence of excess methanol which indicates the presence of free radicals in the reaction medium. This effect has also been reported for $CoW_{12}O_{40}^{8-}$/hydroxy acids[20] and $Mn^{III}O_2Mn^{IV}$/hydroxy acids[19] systems. However, the corresponding reaction with pyridinium chlorochromate did not proceed through a free radical intermediate[20].

The spectrum of partially reacted mixture of the redox species was taken and compared with the spectrum of $Mn^{III}O_2Mn^{IV}$. There were no significant shifts from the absorption peaks of 525 nm, 555 nm and 648 nm characteristic for $Mn^{III}O_2Mn^{IV}$. This suggests that no intermediate complex was formed prior to electron transfer, but if there was any, it must have a small formation constant.

Reaction mechanism

Based on the stoichiometry and other observations, the redox reaction is proposed to proceed by Scheme 1 (Eqns 4-10):

$$[(phen)_2Mn^{III}O_2Mn^{IV}(phen)_2]^{3+}+H^++2H_2O \overset{K_1}{\rightleftharpoons}$$
$$[(H_2O)_2(phen)Mn^{III}O_2Mn^{IV}(phen)_2]^{3+}+phenH^+ \quad \dots (4)$$

$$[(phen)_2Mn^{III}O_2Mn^{IV}(phen)_2]^{3+}+H_2C_2O_4 \overset{k_1}{\longrightarrow}$$
$$[(phen)_2Mn^{III}O_2Mn^{III}(phen)_2]^{2+}+HC_2O_4+H^+ \quad \dots (5)$$

$$[(phen)_2Mn^{III}O_2Mn^{IV}(phen)_2]^{3+}+HC_2O_4 \overset{k_2}{\longrightarrow}$$
$$[(phen)_2Mn^{III}O_2Mn^{III}(phen)_2]^{2+}+2CO_2+H^+ \quad \dots (6)$$

$$[(phen)_2Mn^{III}O_2Mn^{III}(phen)_2]^{2+}+H_2C_2O_4+6H^+ \overset{k_3}{\longrightarrow}$$
$$2Mn^++2CO_2+2H_2O+4phenH^+ \quad \dots (7)$$

$$[(H_2O)_2(phen)Mn^{III}O_2Mn^{IV}(phen)_2]^{3+}+H_2C_2O_4 \overset{k_4}{\longrightarrow}$$
$$[(H_2O)_2(phen)Mn^{III}O_2Mn^{III}(phen)_2]^{2+}+HC_2O_4+H^+ \quad \dots (8)$$

$$[(H_2O)_2(phen)Mn^{III}O_2Mn^{IV}(phen)_2]^{3+}+HC_2O_4 \overset{k_5}{\longrightarrow}$$
$$[(H_2O)_2(phen)Mn^{III}O_2Mn^{III}(phen)_2]^{2+}+2CO_2+H^+ \quad \dots (9)$$

$$[(H_2O)_2(phen)Mn^{III}O_2Mn^{IV}(phen)_2]^{3+}+H_2C_2O_4+5H^+$$
$$\overset{k_6}{\longrightarrow} 2Mn^++2CO_2+2H_2O+3phenH^+ \quad \dots (10)$$

Scheme 1

The rate expression (11) can be derived from Scheme 1.

$$-\frac{d[Mn^{III}O_2Mn^{IV}]}{dt} = \{k_1 + k_4K_1[H^+]\}[Mn^{III}O_2Mn^{IV}][H_2C_2O_4]$$
$$\dots(11)$$

Equation (11) is comparable to equation (3) with k_1=a, k_4K_1=b.

The assignment of any particular pathway to this reaction can be approached as follows:

(a) The absence of spectrophotometric evidence suggests 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) A plot of $1/k_{obs}$ versus $1/[H_2C_2O_4]$ was found to be 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 not in favour of the inner sphere mechanism.

(c) The views in (a) and (b) above, suggest an outer sphere oxidation, but the absence of anion catalysis is against this pathway. Anion catalysis has been noted to be characteristic of outer sphere reaction[21] and therefore it is not probable that this reaction can operate via the outer sphere mechanism.

(d) The above observations (a) to (c), do not require the postulation of inner sphere mechanism for this reaction. The most probable pathway is the proton coupled electron transfer (PCET). By analogy, we have drawn a correlation from earlier studies[19,22] to support this mechanism. The ratio $\dfrac{k_{H_2O}}{k_{D_2O}} = 4.3$ is large enough to account for the isotopic effect consistent with the PCET mechanism. In addition, our reactants satisfy the requirement for this pathway, i.e. $Mn^{III}O_2Mn^{IV}$ contains a protonable moiety and capable of accepting an electron and $H_2C_2O_4$ contains acidic protons, which are the necessary conditions for the occurrence of PCET.

Our findings and those from earlier studies[19,22] show that the high valent oxo-manganese complexes have similar properties as photosystem II and therefore can serve as active sites for oxidation of water in plants.

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