The Kinetics of the Oxidation of Thiocyanate ion by Di-μ -oxo-tetrakis (1,10-phenanthroline)-dimanganese (III,IV) perchlorate in Acid Medium

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ABSTRACT

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

INTRODUCTION

The interest in the chemistry of multinuclear managese complexes has continued to increase as evident from the number of recent reports in literature[1-9]. This interest is due to their relevance in redox acitivities in biosystem[10-13] and in molecular electronics[15]. We have recently investigated the redox reactions of $[L_2MnO_2MnL_2](ClO_4)_3$ (where L = 2,2-bipyridyl or phenanthroline) with hydroxy acids and thiols[16], $H_2C_2O_4$[17], methionine[9] and 2-mercaptobenzoic acid[18]. In continuation of our effort in this direction, we now report the results of the oxidation of SCN⁻ by Di-μ-oxo-tetrakis (1,10-phenanthroline) - dimanganese (III,IV) perchlorate.

EXPERIMENTAL

Materials and reagents: The materials were analytical or reagent grades and were used as received. The complex $[(phen)_2Mn^{III}O_2MN^{IV}(phen)_2]$ $(ClO_4)_3$ was prepared and characterized as described by Cooper and Calvin[19]. Sodium thiocyanate was standardized gravimetrically by oxidising it with bromine water and precipitated as barium sulphate[20]. HCl was used to investigate the effect of hydrogen ions on the rate of the reaction while NaCl was employed to maintain the ionic strength constant at 0.50M. 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 know concentration of $Mn^{III}O_2Mn^{IV}$ and varying concentrations of SCN⁻ (0.55 - 3.86 x 10^{-3}M) 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 [SCN]/[$Mn^{III}O_2Mn^{IV}$] was drawn, from which the stoichiometry was evaluated.

Kinetic studies

All kinetic runs were performed under pseudo-first-order conditions with the concentration of SCN⁻ at least 10 fold excess over that of $Mn^{III}O_2Mn^{IV}$. The rate of reaction was monitored following the rate of decrease in the absorbance of the mixture 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 ± 0.1°C. [H⁺] = 0.05 M and I = 0.5 M (NaCl), unless otherwise stated.

RESULTS AND DISCUSSION

Stoichiometry

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

$$[Mn^{III}O_2Mn^{IV}]^{3+} + 3SCN^- + 4H \rightarrow {}^3/_2 (SCN)_2 + 2Mn^{2+} + 2H_2O \quad .... (1)$$
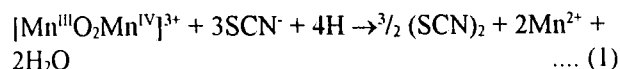
This stoichiometry is different from the one reported for most SCN⁻/substrate and for various Mn^{III}O$_2$Mn^{IV}]$^{3+}$ / substrate reaction systems. Most of the reports on the oxidation of SCN indicate that 1 mole of SCN⁻ reacts with 6 moles of the substrate yielding the reduced form of the substrates, CN⁻ and SCN⁻ and SO$_4$⁻ as the redox products[23-26]. The oxidation of SCN⁻ to CN⁻ is therefore suggested to pass through the intermediate species (SCN)$_2$ and (SCN)$_2$⁻ [25,27]. Thiocyanogen (SCN)$_2$, is known to undergo hydrolysis in aqueous solution[25,26,28], according to equation (2) so that SCN⁻ and SO$_4$⁻ are some of the reaction products.

$$3(SCN)_2 + 4H_2O \rightarrow CN^- + SO_4^- + 5SCN^- + 8H^+ .... (2)$$
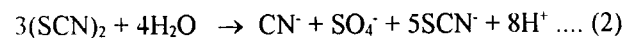
SO$_4$⁻ was identified by the production of white precipitate on addition of BaCl$_2$ to the reacted mixture. Mn^{2+} was detected by reaction with indole[17,29].

Order of reaction

Kinetic measurement were made under pseudo first order conditions with [Mn^{III}O$_2$Mn^{IV}] = 3.58 x 10⁻⁴M, [SCN⁻] = (2.76 - 22.05) x 10⁻³ M, [H⁺] = 0.05 M and I = 0.50M (NaCl). Pseudo-first order plots of log (A$_o$ - A$_t$) versus time (where A$_o$ and A$_t$ are absorbances at time zero and t respectively), were linear to more than 80% of the extent of reaction, indicating that the reaction is first order in [SCN⁻].

The slope (1.07) of log-log plot of k$_{obs}$ versus [SCN⁻] supports first order in [SCN⁻]. The values of the second order rate constants calculated from k$_2$ = k$_{obs}$/[SCN⁻], were found to be fairly constant (Table 1), indicating that the reaction is also first order in [Mn^{III}O$_2$Mn^{IV}], giving second order overall. The rate equation for the title reaction can therefore be represented by equation (3).

$$d[Mn^{III}O_2Mn^{IV}]/dt = k_2[Mn^{III}O_2Mn^{IV}][SCN^-] \quad ... (3)$$
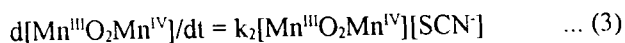
k$_2$ = (1.19± 0.05) x 10⁻¹M⁻¹s⁻¹ at 29.0°C.

Table 1. Second order rate constants for the oxidation of thiocyanate ion by Mn^{III}O$_2$Mn^{IV}.
[Mn^{III}O$_2$Mn^{IV}] = 4.403 x 10⁻⁴M; λ = 555nm, T = 29.0±.1°C

10^3[SCN⁻], mol dm⁻³	10^3[H⁺], mol dm⁻³	I, mol dm⁻³ (NaCl)	$10 k_2$, dm³ mol⁻¹s⁻¹
2.76	5.0	0.5	1.10
4.14	5.0	0.5	1.11
5.51	5.0	0.5	1.14
6.89	5.0	0.5	1.18
8.27	5.0	0.5	1.19
9.65	5.0	0.5	1.21
10.10	5.0	0.5	1.21
12.41	5.0	0.5	1.21
13.78	5.0	0.5	1.22
16.54	5.0	0.5	1.23
19.30	5.0	0.5	1.23
22.05	5.0	0.5	1.21
10.10	1.0	0.5	0.81
10.10	2.0	0.5	0.89
10.10	7.0	0.5	1.36
10.10	10.0	0.5	2.05
10.10	12.0	0.5	2.27
10.10	15.0	0.5	2.63
10.10	5.0	0.1	1.16
10.10	5.0	0.2	1.20
10.10	5.0	0.7	1.18
10.10	5.0	1.0	1.17
10.10	5.0	1.2	1.23
10.10	5.0	1.5	1.21

This characteristic second order kinetics has also been observed for other oxidation reactions of SCN⁻ [28,30-32].

The effect of acidity on the rate of reaction was investigated by varying the concentration of HCl (0.01 - 0.15 M) at [Mn^{III}O$_2$Mn^{IV}] = 3.58 x 10⁻⁴ M, [SCN⁻] = 1.01 x 10⁻²M and I = 0.50 M (NaCl). The results (Table 1.) suggest that the rate constant increases with increase in [H⁺]. A least squares plot of k$_2$ versus [H⁺] was linear (r = 0.99) with a positive intercept, so that the relationship can be given by equation (4).

$$k_2 = a + b\ [H^+] \qquad ..... (4)$$

a = 5.92 x $10^{-2}s^{-1}$ and b = 1.36 $M^{-1} s^{-1}$ at 29.0°C

The observed acid catalysis may be due to the successive protonation/hydration of the dimer[33], since the rates of most of the oxidations of SCN^- have been reported to have $[OH^-]$ dependence[34], inverse dependence on $[H^+]^{(25,32,35)}$, or independent of acid concentration[28,36].

Changes in ionic strength and dielectric constant of the medium had no affect the rate of the reaction. It is expected that the rate should vary with changes in these two parameters since the redox species are charged. Therefore, the non dependence on ionic strength and dielectric constant may only be explained in terms of the Proton Coupled Electron Transfer (PCET) process in which 3 species are simultaneously reacting in the rate determining step. The addition of $HCOO^-$ and NO_3^- also did not have any effect on the rate of the reaction.
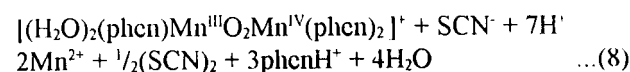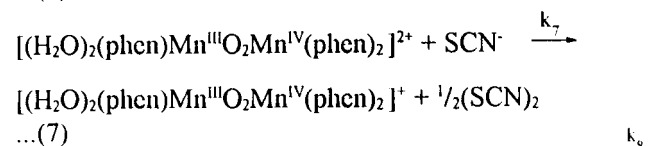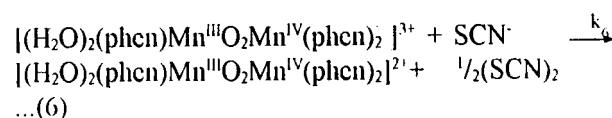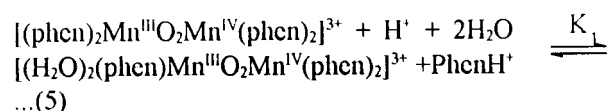
The addition of a solution of acrylamide to partially reacted mixture did not give any gel in the presence of excess methanol, indicating the probable absence of free radicals in the reaction medium. The absence of a free radical intermediate has also been observed for the oxidation of other sulphur containing species like methionine[9,25,37] and 2-mercaptobenzoic acid[18].

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 suggests the absence of the formation of an intermediate complex in the reaction or that if such intermediate is formed, it has a small formation constant. This observation has also been reported for $Mn^{III}O_2Mn^{IV}/H_2C_2O_4$[17], $Mn^{III}O_2Mn^{IV}/methionine$[9] and $Mn^{III}O_2Mn^{IV}/2$-mercaptobenzoic acid[18] systems.

Rate constants were obtained at various temperatures from which plots of log k_o and log (k_o/T) versus $^1/T$ were drawn. From linear least squares analysis of the plots, the activation parameters were calculated as $E_a = 36.62kJ\ mol^{-1}$, $\Delta H^{\#} = 34.11kJ\ mol^{-1}$ and $\Delta S^{\#} = -380.23\ J\ K^{-1}mol^{-1}$ at 29°C. The temperature-dependent rate constants and the activation parameters are shown on Table 2.

Mechansim

As noted earlier, the observed acid catalysis in the reaction is due to the successive protonation/hydration of the dimer, $Mn^{III}O_2Mn^{IV(33)}$. Under the acid condition used for the stiochiometric and kinetic studies, the following scheme 1is proposed for the reaction.

$[(phen)_2Mn^{III}O_2Mn^{IV}(phen)_2]^{3+} + H^+ + 2H_2O \xrightleftharpoons{K_1}$
$[(H_2O)_2(phen)Mn^{III}O_2Mn^{IV}(phen)_2]^{3+} + PhenH^+$ ...(5)

$[(H_2O)_2(phen)Mn^{III}O_2Mn^{IV}(phen)_2\ ]^{3+} + SCN^- \xrightarrow{k_4}$
$[(H_2O)_2(phen)Mn^{III}O_2Mn^{IV}(phen)_2]^{2+} + ^1/_2(SCN)_2$ ...(6)

$[(H_2O)_2(phen)Mn^{III}O_2Mn^{IV}(phen)_2\ ]^{2+} + SCN^- \xrightarrow{k_7}$
$[(H_2O)_2(phen)Mn^{III}O_2Mn^{IV}(phen)_2\ ]^+ + ^1/_2(SCN)_2$ ...(7)

$\xrightarrow{k_8}$

$[(H_2O)_2(phen)Mn^{III}O_2Mn^{IV}(phen)_2\ ]^+ + SCN^- + 7H^+$
$2Mn^{2+} + ^1/_2(SCN)_2 + 3phenH^+ + 4H_2O \qquad ...(8)$

Scheme 1.

Scheme 1 leads to equation (9)

$$-3\ \frac{d[oxidant]}{dt} = \{k_6 + k_7K_1[H^+]\}[oxidant]\ [reductant]$$

$$... (9)$$

Equation (9) is comparable to equation (4) with $k_6 = a$ and $k_7K_1 = b$.

Table 2. Temperature dependent rate constants and activation parameters for the oxidation of thiocyanate ion by $Mn^{III}O_2Mn^{IV}$.

$[Mn^{III}O_2Mn^{IV}]$ = 3.58 x $10^{-1}M$; $[SCN^-]$ = 1.01 x $10^{-2}M$ and I = 0.50 M (NaCl). λ = 555nm, T = 29.0±0.1°C

$10^3 k_o,\ s^{-1}$ 293K	297K	302K	307K	313K	*E (kJ mol^{-1})	*$\Delta H^{\#}$ (kJ mol^{-1})	*$\Delta S^{\#}$ (J $mol^{-1}K^{-1}$)
7.14	9.48	12.22	14.63	18.54	36.62	34.11	-380.23

The absence of spectrophotometric evidence for the formation of an intermediate 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. The Michaelis-Menten plot of $1/k_{obs}$ versus $1/[RSH]$ was linear with an insignificant positive intercept, indicating the absence of a pre-electron transfer step. This absence of kinetic evidence for the formation of a precursor complex is also in favour of the outer sphere mechanism.

The absence of anion catalysis is not unexpected. As suggested earlier[9,18], 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 absence of induced polymerization when acrylamide monomer was added to the reaction mixture is in support of a 2e redox process. We therefore propose that the oxidation proceeds through a $2H^+/2e^-$ path as indicated earlier[9,18,29,37,38]. In addition, $[Mn^{III}O_2Mn^{IV}]$ contains a protonable moiety, a necessary condition for the occurrence of PCET.

In line with arguments presented earlier[1,17,18,29,37], and those highlighted above, we believe that the PCET pathway is the most probale mechanism for the title reaction.

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