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KINETICS AND MECHANISM OF THE OXIDATION OF THIOCYANATE ION BY DI-μ-OXO-TETRAKIS (1,10-PHENANTHROLINE)-DIMANGANESE (III, IV) ION IN ACID MEDIUM

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ABSTRACT

The kinetics of oxidation of thiocyanate ion by di-μ-oxo-tetrakis(1,10-phenanthroline)dimanganese(III,IV) perchlorate in acid medium has been investigated. The reaction follows first order in both the oxidant and the reductant. The reaction is catalysed by hydrogen ion and the rate dependence given as $k_2 = a + b[H^+]$. The reaction rate is not affected by changes in the ionic strength and dielectric constant of the reaction 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 (PCET) is proposed

Key words: Kinetics, mechanism, oxidation, thiocyanate, di-μ-oxo-tetrakis(1,10-phenanthroline)-dimanganese (III,IV)

INTRODUCTION

Interest in the chemistry of multinuclear manganese complexes has continued to increase (Reddy et. al., 1994; Arulsamy et. al., 1994; Jeffery et. al., 1994; Miao et. al., 1995; Goodson et. al., 1992; Vincent et. al., 1993; Dave and Czernuzewicz, 1994; Tanase and Lippard, 1995; Lohdip and Iyun, 1998, 2001). This interest is due to their relevance to redox activities in biosystems, usefulness in catalysis and molecular electronics (Babcock, 1987) Recently, we have investigated the redox reactions of the mixed valence complexes $[L_2MnO_2MnL_2]^{3+}{}_{(aq)}$. (where L = 2,2′-bipyridyl or 1,10-phenanthroline) with hydroxy acids and thiols (Iyun et. al., 1997), $H_2C_2O_4$ (Lohdip et. al., 1998), methionine (Lohdip and Iyun, 1998) and 2-mercaptobenzoic acid (Lohdip and Iyun, 2001). In continuation of our effort in this direction, we now report the results of the oxidation of SCN^- by aqueous di-μ-oxo-tetrakis(1,10-phenanthroline)-dimanganese (III,IV) perchlorate. (referred to in the text as $Mn^{III}O_2Mn^{IV}$)

EXPERIMENTAL

Materials and reagents

The materials were of 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 (1977). Sodium thiocyanate was standardized gravimetrically by oxidising it with bromine water and precipitated as barium sulphate (Bassett et. al., 1983). 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 0.50 mol dm^{-3}. 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 SCN^- (0.55 - 3.86 × 10^{-3} mol dm^{-3}) were reacted at $[H^+] = 0.05$ mol dm^{-3} and $I = 0.50$ mol dm^{-3} (NaCl). The absorbances were measured at 555 nm (on a solid state photometer, Trojanowicz et. al., 1988; Lohdip et. al., 1997), after completion of the reaction. The stoichiometry was evaluated from a plot of absorbance versus $[SCN^-]/[Mn^{III}O_2Mn^{IV}]$.

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Table 1: Second order rate constants for the oxidation of thiocyanate ion by $Mn^{III}O_2Mn^{IV}$. $[Mn^{III}O_2Mn^{IV}] = 4.403 \times 10^{-4}$ mol dm^{-3}; λ = 555 nm, T = 29.0 ± 0.1°C.

10^3 [SCN^-], mol dm^{-3}	10^2[H^+], mol dm^{-3}	I, mol dm^{-3} (NaCl)	10 k_2, dm^3 mol^{-1} s^{-1}
2.76	5.0	0.5	1.10
4.14	5.0	0.5	1.11
5.51	5.0	0.5	1.11
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

Kinetic studies

All kinetic runs were performed under pseudo-first-order conditions with the concentration of SCN^- in at least 10 fold excess over that of $Mn^{III}O_2Mn^{IV}$. The rate of reaction was monitored measuring the decrease in absorbance at 555 nm with a solid state photometer (Trojanowicz et. al., 1988; Lohdip et. al., 1997). 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 with $[H^+] = 0.05$ mol dm^{-3} and I = 0.5 mol dm^{-3} (NaCl) unless otherwise stated.

RESULTS AND DISCUSSION

Stoichiometry

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

$$[Mn^{III}O_2Mn^{IV}]^{3+} + 3SCN^- + 4H^+ \rightarrow {}^3/_2(SCN)_2 + 2Mn^{2+} + 2H_2O \qquad \ldots\ldots (1)$$

This stoichiometry is different from the one reported for most SCN^-/substrate reactions and for various $[Mn^{III}O_2Mn^{IV}]^{3+}$ reaction systems. Most reports on the oxidation of SCN^- indicate that 1 mole of SCN^- reacts with 6 moles of the oxidant yielding the reduced form of the oxidant, CN^- and SO_4^{2-} as the redox products (Stanbury et. al., 1980; Chung and Wood, 1970; Ng and Henry, 1975; Nord et. al., 1978). The oxidation of SCN^- to CN^- is suggested to pass through the intermediate species $(SCN)_2$ and $(SCN)_3^-$ (Ng and Henry, 1975; Barbosa-Filbo and Monhemius, 1994). Thiocyanogen $(SCN)_2$, is known to undergo hydrolysis in aqueous solution (Ng and Henry, 1975; Nord et. al., 1978; Olatunji and Ayoko, 1984), as in equation (2), so that CN^- and SO_4^{2} are some of the reaction products.

$$3(SCN)_2 + 4H_2O \longrightarrow CN^- + SO_4^{2} + 5SCN + 8H^+ \quad .....(2)$$

CN^- was identified by precipitating with $AgNO_3$ while SO_4^{2} was identified by the production of a white precipitate on addition of $BaCl_2$ to the reacted mixture. Mn^{2+} was detected by reaction with indole (Lohdip et. al., 1998; Arabel et. al., 1997).

Order of reaction

Kinetic measurements were made under pseudo-first-order conditions with $[Mn^{III}O_2Mn^{IV}]$ = 3.58 x 10^{-4} mol dm^{-3}, $[SCN^-]$ = (2.76 - 22.05) x 10^{-3} mol dm^{-3}, $[H^+]$ = 0.05 mol dm^{-3} and I = 0.50

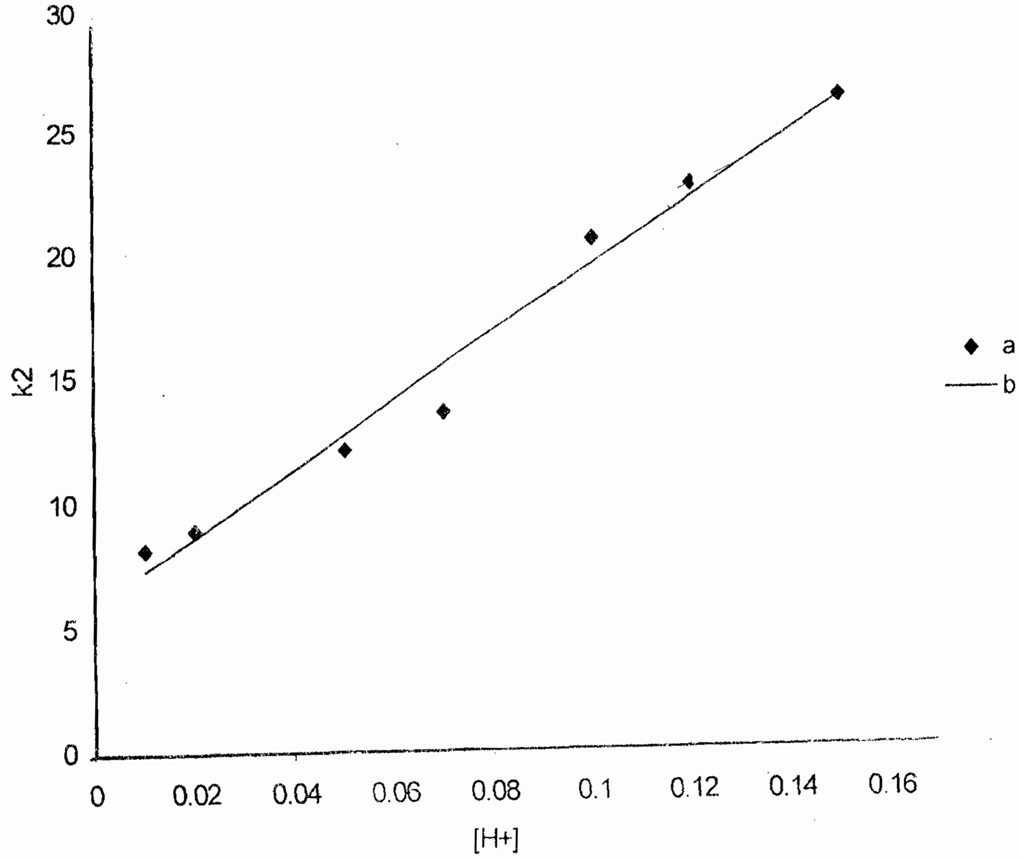

Fig. 1: Plot of k_2,($dm^3mol^{-1}s^{-1}$) Versus $[H^+]$,(mol) for the oxidation of thiocyanate ion by $Mn^{III}O_2Mn^{IV}$, (a) = experimental points, (b) = regressed line.

$[Mn^{III}O_2Mn^{IV}]$ = 3.58 x 10^{-4} mol dm^{-3}, $[SCN^-]$ = 1.01 x 10^{-2} mol dm^{-3}, I = 0.50 mol dm^{-3}, λ = 555 nm, T = 29.0 ± 0.1°C.

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

T, K	293 K	297 K	302 K	307	313
10^4 k_o, s^{-1}	7.14	9.48	12.22	14.63	18.54

*E = 36.62 kJ mol^{-1}, *$\Delta H^{\#}$ = 34.11 kJ mol^{-1}, *$\Delta S^{\#}$ = -380.23 J mol^{-1} K^{-1}
*values calculated at 302 K

$[Mn^{III}O_2Mn^{IV}]$ = 3.58 x 10^{-4} mol dm^{-3}, $[SCN^-]$ = 1.01 x 10^{-2} mol dm^{-3},
$[H^+]$ = 0.05 mol dm^{-3}, I = 0.50 mol dm^{-3}, λ = 555 nm.

mol dm^{-3} (NaCl). 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), 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 [$Mn^{III}O_2Mn^{IV}$], giving a second order reaction overall. The rate equation for the title reaction can therefore be represented by equation (4), with k_2 = (1.19 ± 0.05) x 10^{1} mol^{1} dm^{3} s^{1} at 29.0°C.

$$-3\frac{d[oxidant]}{dt} = k_2\ [Mn^{III}O_2Mn^{IV}]\ [SCN^-] \qquad ....(3)$$

Second order kinetics have also been observed for other oxidations of SCN^- (Olatunji and Ayoko, 1984; Peloso et. al, 1967a; Peloso et. al., 1967b; Davies and Watkins, 1970).

The effect of acid on the rate of reaction was investigated by varying the concentration of HCl (0.01 - 0.15 mol dm^{-3}) at [$Mn^{III}O_2Mn^{IV}$] = 3.58 x 10^{-4} mol dm^{3}, [SCN^-] = 1.01 x 10^{2} mol dm^{3} and I = 0.50 mol dm^{-3} (NaCl). The results (Table 1.) suggest that the rate constant increases with increase in [H^+]. A least squares plot of k_2 versus [H^+] (Fig.1) was linear (r = 0.99) with a positive intercept, so that the relationship can be given by equation (5), with a = 5.92 x 10^{2} mol^{1} dm^{3}s^{1} and b = 1.36 s^{-1} at 29.0°C.

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

The observed acid catalysis may be due to the successive protonation/hydration of the dimer (Chaudhuri et. al., 1995), since the rates of most of the oxidations of SCN^- have been reported to have [OH^-] dependence (Gowda and Bhat, 1988), inverse dependence on [H^+] (Ng and Henry, 1975; Davies and Watkins, 1970; Kazakov and Konovalova, 1968), or independence of acid concentration (Olatunji and Ayoko, 1984; Przystas and Sutin, 1973).

Changes in ionic strength and dielectric constant of the medium had no affect on 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. The non-dependence of 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 had no effect on the rate of the reaction.

The addition of a solution of acrylamide to a partially reacted mixture did not give any gel in the presence of excess methanol, indicating the probable absence of free radicals in the reaction. The absence of free radicals has also been observed for the oxidation of other sulphur containing species like methionine (Lohdip and Iyun, 1998; Ng and Henry, 1975; Lawal, 1997) and 2-mercaptobenzoic acid (Lohdip and Iyun, 2001).

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 $Mn^{III}O_2Mn^{IV}/H_2C_2O_4$ (Lohdip et. al., 1998), $Mn^{III}O_2Mn^{IV}$/methionine (Lohdip and Iyun, 1998) and $Mn^{III}O_2Mn^{IV}$/2-mercaptobenzoic acid (Lohdip and Iyun, 2001) systems.

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

Mechanism

As noted earlier, the observed acid catalysis in the reaction is due to the successive protonation/hydration of the dimer, $Mn^{III}O_2Mn^{IV}$ (Chaudhuri et. al., 1995). Under the acid condition used for the stoichiometric and kinetic studies, the following scheme 1 is proposed for the reaction.

$$[(phen)_2Mn^{III}O_2Mn^{IV}(phen)_2]^{3+} + H^+ + 2H_2O \overset{K_5}{\rightleftharpoons}$$

$$[(H_2O)_2(phen)Mn^{III}O_2Mn^{IV}(phen)_2]^{3+} + phenH^+ \quad \text{.........(5)}$$

$$[(H_2O)_2(phen)Mn^{III}O_2Mn^{IV}(phen)_2]^{3+} + SCN^- \xrightarrow{k_6}$$

$$[(H_2O)_2(phen)Mn^{III}O_2Mn^{III}(phen)_2]^{2+} + {}^1/_2(SCN)_2 \quad \text{..... (6)}$$

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

$$[(H_2O)_2(phen)Mn^{II}O_2Mn^{III}(phen)_2]^{+} + {}^1/_2(SCN)_2 \quad \text{..... (7)}$$

$$[(H_2O)_2(phen)Mn^{II}O_2Mn^{III}(phen)_2]^{+} + SCN^- + 7H^+ \xrightarrow{fast}$$

$$2Mn^{2+} + {}^1/_2(SCN)_2 + 3phenH^+ + 4H_2O \quad \text{......(8)}$$

Scheme 1.

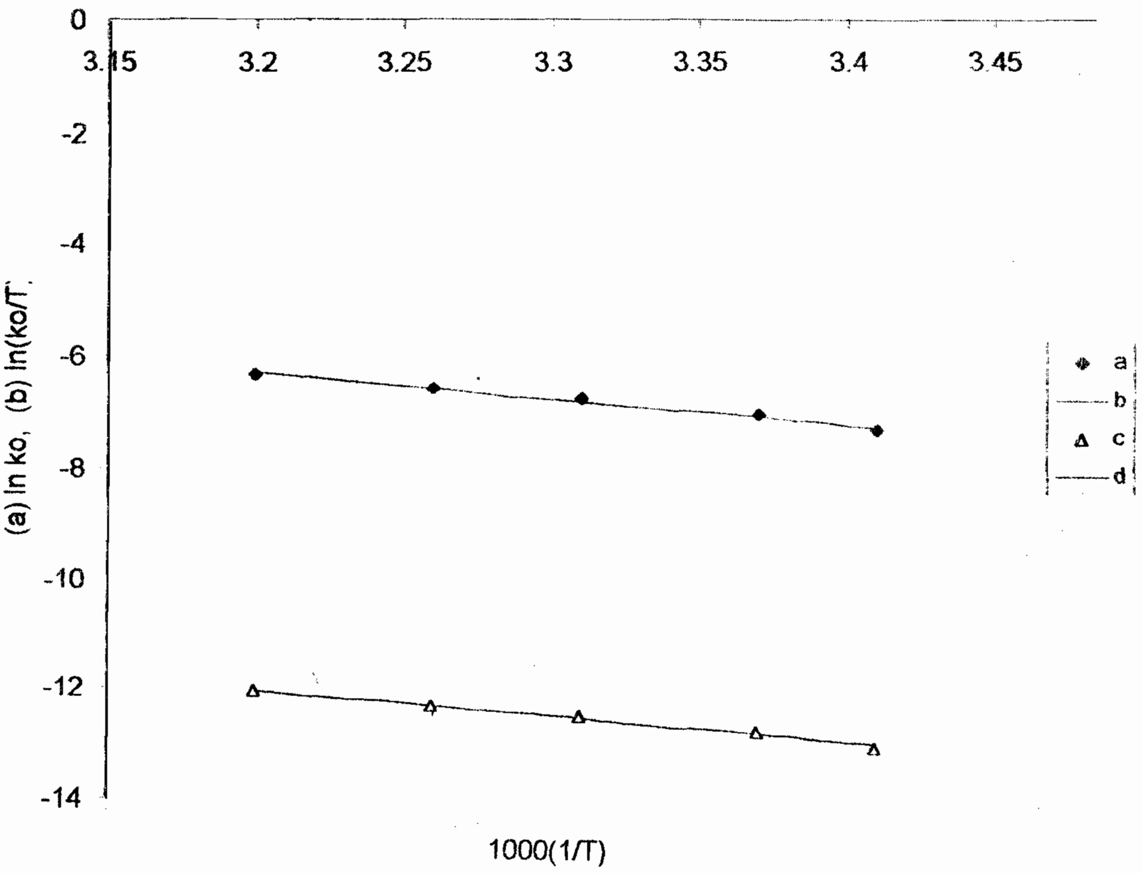

Fig. 2: Plot ln k_o Vs 1/T & ln(k_o/T) Vs 1/T for the oxidation of thiocyanate ion by $Mn^{III}O_2Mn^{IV}$.
(a) ◆ exptal points, (b) = regressed line, (c) = exptal. points, (d) = regressed line.

$[Mn^{III}O_2Mn^{IV}] = 3.58 \times 10^{-4}$ mol dm^{-3}, $[SCN^-] = 1.01 \times 10^{-2}$ mol dm^{-3},
$[H^+] = 0.05$ mol dm^{-3}, I = 0.50 mol dm^{-3}, λ = 555 nm.

Scheme 1 leads to equation (9)

[oxidant] [reductant] .... (9)

$$-3\frac{d[oxidantt]}{dt} = \{k_6 + k_7K_5[H^+]\}$$

Equation (9) is comparable to equation (3) with
$k_6 = a$ and $k_7K_5 = b$.

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 (Lohdip and Iyun, 1998, 2001), the simultaneous involvement of 3 species in a proton coupled electron transfer (PCET) process is subject to restrictions. This effect would not encourage the participation of any added ion in the reaction so that the presence of $HCOO^-$ or NO_3^- had no effect on the rate of the reaction.

The absence of induced polymerization when acrylamide was added to the reaction mixture is in support of a 2 electron ($2e^-$) redox process. We therefore propose that the oxidation proceeds through a $2H^+/2e^-$ path as indicated earlier earlier (Lohdip and Iyun, 1998, 2001; Arabel et. al., 1997; Lawal, 1997). 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 (Reddy et.al., 1994; Lohdip et. al., 1998; Lohdip and Iyun, 1998, 2001; Arabel et. al., 1997; Lawal, 1997), and those discussed above, we believe that the proton coupled electron transfer (PCET) pathway is the most probable mechanism for the reaction under investigation.

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