Kinetics and mechanism of the oxidation of hypophosphorous acid by di-µ-oxotetrakis(2,2'-bipyridyl)dimanganese (III,IV) perchlorate in acid medium

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ABSTRACT

The kinetic study of the oxidation of hypophosphorous acid by di- μ -oxo-tetrakis(1,10-phenanthroline)dimanganese(III,IV) perchlorate in acid medium has been carried out at [H⁺] = 0.05 mol dm⁻³(HCl), I = 0.50 mol dm⁻³ (NaCl), T = 27.5 ± 1.0°C and λ = 680 nm. The reaction obeys the rate law:

$$-\frac{3}{2}\frac{d[Mn^{11}O_2Mn^{1V}]}{dt} = k_2[Mn^{11}O_2Mn^{1V}][H_3PO_2]$$

 $k_2 \ = \ 0.57 \ \pm \ 0.05 \ dm^3 \ mol^{\text{--}1} \ s^{\text{--}1}.$

The rate increased with increase in acid concentration and decreased with increase in the ionic strength and dielectric constant of the reaction medium. The presence of added anions and cations had no affect the rate of reaction. A plausible mechanism is proposed.

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INTRODUCTION

Multinuclear manganese complexes have been identified to play important roles in synthetic models for the active sites of manganese containing metalloproteins [1-3]. Their relevance in redox activities in biosystems like manganese containing supoxide, pseudo catalase, reductase and photosynthetic water catalyst, photosystem II (PS II) has also been highlighted [4, 5]. These complexes have also been found to be useful in catalysis and in molecular electronics [6]. It is because of the usefulness of these manganese complexes that their chemistry has attracted a lot of interest [1-3]. For example, the redox reactions mixed of the valence complexes $[L_2Mn^{III}O_2Mn^{IV}L_2](ClO_4)_3$ (where L = 2,2'-bipyridyl or 1,10-phenanthroline), with $Co(bpy)_3^{2+}$, NO_3^{-} and a-hydroxyacids have been reported by various authors [7-10]. In like manner, we have studied and reported the results of their redox reactions with $H_2C_2O_4$, methionine, SCN⁻, 2-mercaptobenzoic acid, ascorbic acid and malonic acid [11-16]. In this paper, we present the results of the oxidation of hypophosphorous acid (H_3PO_2) by di-µ-oxo-tetrakis(2,2/-bipyridyl)dimanganese (III,IV)

perchlorate (referred to in the text as $Mn^{III}O_2Mn^{IV}$).

EXPERIMENTAL

Materials

The method of Cooper and Calvin [17] was employed for the synthesis and characterization of the complex [(bpy)₂Mn^{III}O₂Mn^{IV}(bpy)₂](ClO₄)₃. The visible spectrum of the complex in aqueous bipyridyl buffer was run and the ratio of absorbances at 600 nm and 680 nm was found to be consistent with the reported value. HCl(A.R) was used to investigate the effect of hydrogen ion on the rate of reaction while NaCl (BDH) was employed to maintain a constant ionic strength of 0.50 mol dm⁻³. All other chemicals and reagents were AnalaR grade and were used as supplied.

Stoichiometric studies

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. Solutions containing known concentrations of $Mn^{III}O_2Mn^{IV}$ and varying concentrations of H_3PO_2 were reacted at [H⁺] = 0.05 mol dm⁻³(HCl) and I = 0.50 mol dm⁻³ (NaCl). The absorbances were measured at 680nm on Jenway 6300 Spectrophotometer, after the completion of the reaction indicated by constant absorbance values after repeated measurements. A plot of absorbance versus the ratio $[H_3PO_2]/[Mn^{II}O_2Mn^{IV}]$ was obtained from which the stoichiometry was calculated.

Kinetic studies

All kinetic runs were performed under pseudo-first order conditions. This was achieved by keeping the concentration of the complex constant while varying the concentration of H₃PO₂. The rate of reaction was monitored by measuring the decrease in at 680nm on Jenway absorbance 6300 Spectrophotometer. Pseudo-first order rate constants were obtained from logarithmic plots of absorbance differences against time. The temperature was maintained constant at 27.5 \pm 1.0°C with [H⁺] = 0.05 mol dm⁻³ (HCl) and I = 0.5 mol dm⁻³ (NaCl), unless otherwise stated.

RESULTS AND DISCUSSION

Stoichiometry and product analysis

$$2[Mn^{III}O_2Mn^{IV}]^{3+} + 3H_3PO_2 + 2H^+ \rightarrow 3H_3PO_2 + 4Mn^{2+} + H_2O$$
...(1)

The results of the spectrophotometric titration revealed a 2 : 3 stoichiometry as represented in equation (1)

A 2 : 3 stoichiometry has also been reported for this complex with $H_2C_2O_4$, methionine, 2-mercaptobenzoic acid, ascorbic acid and malonic acid and some other systems [8,10-15]. The reaction products were identified qualitatively i.e. Mn^{2+} by indole, and H_3PO_3 by saturated ammonium molybdate.

Order of Reaction

Under the pseudo-first order conditions, 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 the reaction. This suggests that the reaction is first order in hypophosphorous acid concentration. The least squares plot of log k_{obs} versus log [H_3PO_2] was linear with a slope of 1.07 (where k_{obs} is the pseudo-first order rate constant). This is in support of the first order rate constants (k_2) calculated from $k_2 = k_{obs}/[H_3PO_2]$, were fairly constant and are presented in Table 1. This indicates that the reaction is also first order in [$Mn^{III}O_2Mn^{IV}$], giving an overall second order. This is

$$-\frac{3}{2}\frac{d[Mn^{III}O_2Mn^{IV}]}{dt} = k_2[Mn^{III}O_2Mn^{IV}][H_3PO_2]\dots(2) \quad \text{si}$$
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to what had been reported by other authors [10,12,15,16,18,19].

The rate equation for the reaction can therefore be represented by equation (2).

$$\frac{3}{2} \frac{d[Mn^{III}O_2Mn^{IV}]}{dt} = (a + b[H^+])[Mn^{III}O_2Mn^{IV}][H_3PO_2] \dots (3)$$

k₂ = 0.57 ± 0.05 dm³ mol⁻¹ s⁻¹ at 27.5 ± 1.0 °C.

The acid dependent study shows that the rate constant increases with increase in [H⁺]. The values of the second order rate constants due to the effect of hydrogen ions, are presented in Table 1. A least squares plot of k_{obs} versus [H⁺] was linear (r = 0.96), so that the relationship can be given by equation (3).

where $a = 3.49 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $b = 5.95 \times 10^{-2} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ at $27.5 \pm 1.0 \text{ °C}$.

It has been reported that hypophosphorous acid is mostly present in the unionised form in fairly strong acid medium [20]. Therefore the observed positive acid dependence on the rate can only be explained in terms of the successive protonation and or hydration of the $[Mn^{II}O_2Mn^{IV}]$ dimer [9,11-14]

Changes in the ionic strength of the reaction medium had an inverse dependence on the rate of the reaction as shown in Table 2. This implies that the reaction involves oppositely charged partners, $Mn^{III}O_2Mn^{IV}$ species and $H_2PO_2^-$ in one of the rate determining steps [10,21,22]. This is supported by the observed negative primary salt effect [23,24], as evident from the enhanced rate as a function of ¹/D (Table 2, where D is the dielectric constant of the reaction medium). Addition of CH₃COO⁻, NO₃⁻ and K⁺ into the reaction mixture did not affect the rate of reaction, which is an indication that probably the reaction did not proceed through the outer sphere mechanism [12,13, 16,25].

The spectrum of partially reacted mixture of the redox species was taken and compared with the spectrum of $Mn^{II}O_2Mn^{IV}$. There were no significant shifts from absorption peaks of 525 nm, 555 nm and 680 nm, characteristic for $Mn^{II}O_2Mn^{IV}$. In addition, the plot of $^{1}/k_{obs}$ versus $^{1}/[H_3PO_2]$ gave a linear relationship with an insignificant negative intercept. These pieces of evidence suggest the probable absence of an intermediate complex in the reaction or if an

10 ³ [H ₃ PO ₂], mol dm ⁻³	$10^{2}[H^{+}]$, mol dm ⁻³	I, mol dm ⁻³	k ₂ , dm ³ mol ⁻¹ s ⁻¹
7.5	5.0	0.5	0.61
9.0	5.0	0.5	0.51
10.0	5.0	0.5	0.55
12.0	5.0	0.5	0.52
13.5	5.0	0.5	0.57
15.0	5.0	0.5	0.52
16.5	5.0	0.5	0.65
18.0	5.0	0.5	0.65
12.0	1.0	0.5	0.47
12.0	3.0	0.5	0.58
12.0	7.0	0.5	0.87
12.0	10.0	0.5	1.15
12.0	15.0	0.5	1.28
12.0	5.0	0.2	085
12.0	5.0	0.3	0.77
12.0	5.0	0.7	0.30
12.0	5.0	1.0	0.27
12.0	5.0	1.5	0.21

Table 1: Second order rate constants for the oxidation of hypophosphorous acid by $Mn^{III}O_2Mn^{IV}$ [$Mn^{III}O_2Mn^{IV}$] = 6.0 x 10⁻⁴ mol dm⁻³, T = 28.5 ± 1.0°C and λ = 680 nm

Table 2: Dependence of pseudo-first order rate constants on the ionic strength and dielectric constant for the oxidation of hypophosphorous acid by Mn^{III}O₂Mn^{IV}

 $[Mn^{III}O_2Mn^{IV}] = 8.0 \ x \ 10^{-4} \ mol \ dm^{-3}, \ [H_3PO_2] = \ 1.2 \ x \ 10^{-2} \ mol \ dm^{-3}, \ [H^+] = 0.05 \ mol \ dm^{-3}, \ T = 28.5 \pm 1.0^{\circ}C \ and \ \lambda = 680 \ nm$

I, mol dm ⁻³	0.2	0.3	0.5	0.7	1.0	1.5
$10^{3}k_{obs}, s^{-1}$	10.16	9.32	6.25	3.59	3.26	2.50
10 ² /D	1.2	1.6	1.7	19	2.2	2.5
$10^{3}k_{obs}, s^{-1}$	6.24	7.33	7.62	8.28	9.22	10.25

intermediate complex is formed, it may have a small formation constant, and so may not be a major part for the reaction. This evidence is not in support of the inner sphere mechanism [25,26].

Reaction Mechanism

Under the acid condition used for the stoichiometric and kinetic studies, the dimer,

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\begin{split} & [(bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{3+} + H^+_{abc} H(bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{4+} \\ & ....(4) \\ & [(bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{3+} + H_3PO_2^{-}_{abc} + [(bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{2+} + H_3PO_2^{+} \\ & ....(5) \\ & [(bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{3+} + H_3PO_2^{-+} + H_2O_2^{-}_{abc} + (bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{2+} + H_3PO_2^{+} + H_3O_2^{-}_{abc} \\ & (bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{2+} + H_3PO_2^{-+} + H_2O_2^{-}_{abc} + 4Mn^{2+} + 2H_3PO_3^{+} + 8bpyH^+ + 2H_2O_{....(7)} \\ & (H(bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{4+} + H_3PO_2^{-}_{abc} + [H(bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{3+} + H_3PO_2^{+} \\ & ....(8) \\ & (H(bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{4+} + H_3PO_2^{-}_{abc} + H_2O_2^{-}_{abc} + [H(bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{3+} + H_3PO_3^{+} + 2H_3^{-} \\ & ....(9) \\ & (2H(bpy)_2Mn^{III}O_2Mn^{IV}(bpy)_2]^{3+} + 2H_3PO_3^{-} + 10H^{+}_{abc} + 4Mn^{2+}_{abc} + 2H_3PO_3^{+} + 8bpyH^{+} + 2H_2O_{....(9)} \\ \end{array}
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 $-\frac{3}{2}\frac{d[Mn^{III}O_2Mn^{IV}]}{dt} = \{k_1 + k_4K_H[H^+]\}[Mn^{III}O_2Mn^{IV}][H_3PO_2].(11)$

Mn^{III}O₂Mn^{IV} has been reported to undergo successive protonation and hydration during its redox reactions [11-16]. It has also been reported that H₃PO₂ can ionise in aqueous solution ($k_{dissoc} = 10^{-2}$ mol dm⁻³ at 25°C), but exists predominantly in the unionised form in fairly strong acid medium [20]. Based on these and other reports, the following scheme is proposed for the title reaction:

With equation (5) and (8) as the rate determining step. Equation (11) is comparable to equation (3),

with $k_1 = a$ and $k_4 K_H = b$.

This mechanism is similar to those proposed for the oxidation of α -hydroxyacids, $H_2C_2O_4$ and SCN^- and ascorbic acid by $Mn^{III}O_2Mn^{IV}$ [10,11,14,15].

Reaction Pathway

The postulation of the pathway for the reaction can be approached as follows;

- (a) A plot of ${}^{1}/k_{obs}$ versus ${}^{1}/[H_{3}PO_{2}]$ was found to be linear with an insignificant negative intercept, indicating the absence of a pre-association step in the reaction. This absence of kinetic evidence for the formation of a precursor complex is not in support of the inner sphere mechanism.
- (b) 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 mechanism but the absence of cation and anion catalysis is against this mechanism. Anion and cation catalysis has been noted to be characteristic of the outer sphere reaction [12,27] but since this is absent, it is not probable for the title reaction to operate via this mechanism.
- (c) The above observations (a) and (b) do not support the postulation of either the inner sphere or outer sphere mechanism for the reaction. The most probable pathway is the proton coupled electron transfer (PCET). Our postulation has been based on correlation with earlier reports [10,11,15,28]. Further more, the $Mn^{III}O_2Mn^{IV}$ contains a protonable moiety and capable of accepting a electron and H₃PO₂ contains acidic protons, which are necessary conditions for the occurrence of PCET.

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