# Kinetics of Oxidation of Mn(II) in $[SiMn^{II}W_{11}O_{40}H_2]^{6-}$ To Mn(III) by Peroxydisulphate Ion

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Summary:The pseudo-first order kinetics of oxidation of Mn(II) to Mn(III) in heteropoly ion, $[SiMn^{II}W_{11}O_{40}H_2]^{6-}$, was studied at $50^{\circ}C$ using peroxydisulphate ion as an oxidizing agent. The pH was kept at 5.0 and ionic strength was 2.0 in $Na_2SO_4$. It was found that over a wide range of concentrations of $S_2O_8^{2-}$ ion the kobs varies linearly with $[S_2O_8^{2-}]^{1/2}$ rather than $[S_2O_8^{2-}]$, values suggesting that oxidation of Mn(II) is preceeded by homolytic dissociation of $S_2O_8^{2-}$ ion into $SO_4^-$ ion radicals.

## Introduction

Mn(III) compounds with few exceptions only are known to be unstable and either reduced to Mn(II) or disproportion to Mn(II) and Mn(IV) [1-3]. However Mn(III) hetropoly ions formed by oxidation of the corresponding Mn(II) containing ions are quite stable over a wide range of pH [4,5]. Kinetics of the oxidation of these heteropoly ions by peroxydisulphate ion has not been reported.

The purpose of this study was to understand the mechanism of oxidation of Mn(II) heteropoly ion $[SiMn^{II}W_{11}O_{40}H_2]^{6-}$ using peroxydisulphate ion as oxidizing agent.

## Experimental

Potassium 11-tungstomagno (II) silicate, $K_6[SiMn^{II}W_{11}O_{40}H_2]$, was prepared according to the procedure describe elsewhere [5]. The compound was heated with $Na_2S_2O_8$ excess to about 70°C and converted to Mn(III) hetropoly ion. The spectra of the oxidised and unoxidised compound perfectly matched with the one reported [5] (Fig. 1). On the basis of these spectra 500 and 550 nm were chosen as appropriate wavelengths to monitor the formation of Mn(III). A series of solutions containing $1x10^{-2}$, $2x10^{-2}$ and $3x10^{-2}$ M, Mn(II) heteropoly ion and in each case $Na_2S_2O_8$ varying from 0.01 M to 0.25M was prepared, and the formation of Mn(III) heteropoly ion was monitored at 500 and 550 nm. Each kinetic experiment was repeated several times. In each case the temperature was kept at 50°C, pH at 5.0 and ionic strength adjusted to 2.0 with $Na_2SO_4$. For each experiment
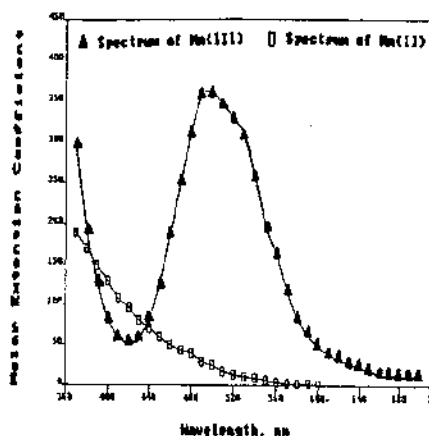


Fig.1: Spectra of $[SiMn^{II}W_{11}O_{40}H_2]^{6-}$ and $[SiMn^{II}W_{11}O_{40}H_2]^{5-}$ hetropoly ion in visible region.

fresh solution of $Na_2S_2O_8$ was used. All chemicals were of pure quality supplied by E. Merck and Riedel-De-Haen. In this study Bausch and Lomb spectronic 21 spectrophotometer, pH meter model EIL 7020 of Kent Instrumental measurement Ltd. and thermomix 1440, to maintain the temperature of water bath, was used.

Linear regression, standard deviation and slope of the kinetics plot were calculated using standard programs on $IBM^{TM}$ Personal Computer.

## Results and Discussion

The values of absorbance at 500 and 550 nm at constant time interval were obtained for solu-

Table 1:Abosrbance of $[SiMn^{III}W_{11}O_{40}H_2]^{5-}$ and ln $[A_t - A_\infty]$ data at different time intervals for initial concentration $K_6[SiMn^{II}W_{11}O_{40}H_2].16H_2O$ = 0.001M; $Na_2S_2O_8$ = 0.065M, pH = 5.0; temperature = 50°C; ionic strenght = 2.0; A at 500 nm = 0.350 and at 500 nm = 0.195.

| S.No. | Time min | At 500 nm | | | | At 550 nm | | | |
| | | Flask A | | Flask B | | Flask A | | Flask B | |
| | | $A_t$ | ln[$A_t$-A$_\infty$] | $A_t$ | ln[$A_t$-A] | $A_t$ | ln[$A_t$-A] | $A_t$ | ln[$A_t$-A] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 10 | 0.033 | -1.148 | 0.036 | -1.158 | 0.013 | -1.703 | 0.013 | -1.703 |
| 2 | 20 | 0.060 | -1.237 | 0.060 | -1.237 | 0.028 | -1.777 | 0.029 | -1.795 |
| 3 | 30 | 0.086 | -1.331 | 0.086 | -1.331 | 0.043 | -1.883 | 0.043 | -1.883 |
| 4 | 40 | 0.113 | -1.439 | 0.113 | -1.439 | 0.057 | -1.880 | 0.057 | -1.980 |
| 5 | 50 | 0.139 | -1.555 | 0.136 | -1.541 | 0.071 | -2.087 | 0.065 | -2.040 |
| 6 | 60 | 01.65 | -1.687 | 0.158 | -1.650 | 0.087 | -2.225 | 0.094 | -2.292 |
| 7 | 70 | 0.182 | -1.783 | 0.177 | -1.754 | 0.096 | -2.312 | 0.085 | -2.302 |
| 8 | 80 | 0.204 | -1.924 | 0.200 | -1.879 | 0.109 | -2.453 | 0.103 | -2.395 |
| 9 | 90 | 0.223 | -2.063 | 0.218 | -2.024 | 0.123 | -2.631 | 0.116 | -2.538 |
| 10 | 100 | 0.240 | -2.207 | 0.234 | -2.154 | 0.133 | -2.780 | 0.124 | -2.645 |
| 11 | 110 | 0.259 | -2.396 | 0.255 | -2.353 | 0.145 | -2.985 | 0.138 | -2.882 |

tions containing different concentrations of Mn(II) heteropoly ions and peroxydisulphate ions. A representative set of data is given in Table-1. Plots of ln $[A_t - A_\infty]$ vs time were drawn to obtain pseudo first order rate constant ($k_{obs}$) from this data (Fig. 2). Each experiment was carried out till atleast two half lives passed. The pseudo first order rate constants obtained at various concentration are tabulated in Table-2.
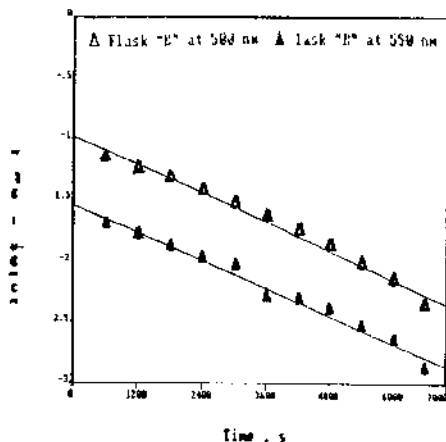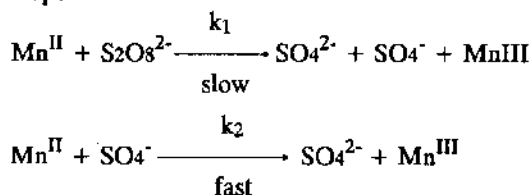


Fig.2: Plot of ln[$A_t$-A$_\infty$] vs time (in second) for data in Table-1. The value of $k_{obs}$ from this data was $1.94 \times 10^{-4} \pm 6.63 \times 10^{-6}$ sec$^{-1}$ at 500 nm and $1.87 \times 10^{-4} \pm 8.82 \times 10^{-6}$ sec$^{-1}$ at 550 nm.

Two possible mechanism have been proposed for the reaction of $S_2O_8^{2-}$ ions. According to the first mechanism $S_2O_8^{2-}$ ions oxidise the substrate

and decompose into $SO_4^{2-}$ ions and $SO_4^-$ ion radical which converts into $SO_4^{2-}$ by taking the next electron from the substrate [6-10]. Hence oxidation of Mn(II) would proceed according to the following steps.

$$Mn^{II} + S_2O_8^{2-} \xrightarrow[\text{slow}]{k_1} SO_4^{2-} + SO_4^- + MnIII$$

$$Mn^{II} + SO_4^- \xrightarrow[\text{fast}]{k_2} SO_4^{2-} + Mn^{III}$$

Here, since first reaction is the rate determining step,

$k_{obs} = k_1[S_2O_8^{2-}]$, since (MnII) < $[S_2O_8^{2-}]$

If such is the case, the plot of $k_{obs}$ against $[S_2O_8^{2-}]$ should yield a straight line with slope being equal to $k_1$.

The second possible mechanism which has been proposed by many authors in various cases require homolytic dissociation of $S_2O_8^{2-}$ ions into $SO_4^-$ ion radicals followed by oxidation of substrate and formation of $SO_4^{2-}$ ions [11-18]. It can be represented as,

$$S_2O_8^{2-} \xrightarrow{K} 2SO_4^-$$

$$SO_4^- + Mn^{II} \xrightarrow[\text{slow}]{k_1} SO_4^{2-} + Mn^{III}$$
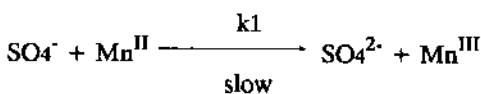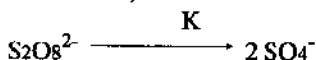
In this case,  $k_{obs} = k_1 [SO_4^-]$ ,

and since,  $[SO_4^-] = K^{1/2} [S_2O_8^{2-}]^{1/2}$ ,

or  $k_{obs} = k [S_2O_8^{2-}]^{1/2}$ , where  $k = k_1 K^{1/2}$

For this mechanism the plot of $k_{obs}$ vs $[S_2O_8^{2-}]^{1/2}$ should yield a straight line with k as, slope.

Table 2: Average values of $k_{obs}$ obtained from kinetics plots at various concentrations of S2O8²⁻ ion and [SiMn¹¹W₁₁O₃₉H₂]⁶⁻ ion at 50°C

| S.No. | [S₂O₈²⁻] | [S₂O₈²⁻]¹ᐟ² | Average values of k$_{obs}$×10⁵ mol⁻¹s⁻¹ calculated at 500 nm and 50°C Conc. of Mn(II) | | | |
|---|---|---|---|---|---|---|
| | | | 0.001 M | 0.002 M | 0.003 M | Average |
| 1 | 0.010 M | 0.100 M | 2.30 | 4.40 | 2.16 | 2.28 |
| 2 | 0.015 M | 0.122 M | 3.33 | 4.10 | 3.03 | 3.48 |
| 3 | 0.025 M | 0.158 M | 7.23 | 6.55 | 7.11 | 6.96 |
| 4 | 0.030 M | 0.173 M | 7.68 | 7.31 | - | 7.49 |
| 5 | 0.035 M | 0.187 M | 8.76 | 9.56 | 9.13 | 9.15 |
| 6 | 0.040 M | 0.200 M | 9.80 | 9.93 | - | 9.86 |
| 7 | 0.45 M | 0.212 M | 11.50 | 13.00 | 10.90 | 11.80 |
| 8 | 0.050 M | 0.223 M | 13.50 | 11.56 | - | 12.50 |
| 9 | 0.055 M | 0.234 M | - | 14.90 | 12.20 | 13.50 |
| 10 | 0.065 M | 0.254 M | 20.00 | 16.30 | 12.40 | 16.20 |
| 11 | 0.075 M | 0.273 M | 26.80 | 21.20 | 17.60 | 22.20 |
| 12 | 0.085 M | 0.291 M | 28.10 | 21.50 | 20.40 | 23.30 |
| 13 | 0.095 M | 0.308 M | - | 22.60 | 23.80 | 23.20 |

*Since maximum difference in molar extention coefficient of Mn(II) and Mn(III) heteropoly ion is at 500 nm, this wave length has been selected for calculation of rate constants.
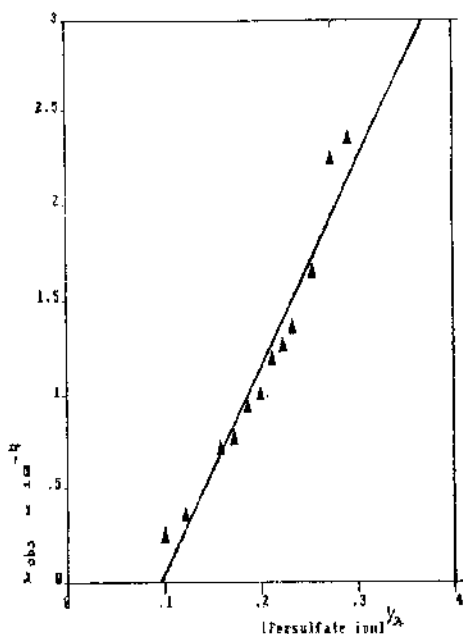


Fig.3: Plot of average $k_{obs}$ vs $[S_2O_8^{2-}]^{1/2}$ when the concentration of K₆[SiMn¹¹W₁₁O₃₉H₂].16H₂O = 0.001M; Na₂S₂O₈ = 0.065M; pH = 5.0; temperature = 50°C; ionic strenght = 2.0; A at 500 nm = 0.350 and at 550 nm = 0.195. The value of constant, k, obtained for these plots is 1.118×10⁻³ + 2.05×10⁻⁶ mole⁻¹ sec⁻¹.

The data in Table 2 used to determine the rate consta,t k, and the plot of $k_{obs}$ against $[S_2O_8^{2-}]^{1/2}$ and not kobs vs. $[S_2O_8^{2-}]$ yield a straight line graph (Fig. 3). This suggesting that the reaction proceeds through formation of SO₄⁻ ion radical generated by homolytic dissociation of S₂O₈²⁻ ions.

The effect of pH, ionic strength variation and temperature on the reaction rates of this system are under study.

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