

Kinetics of Ag^+ Catalyzed Oxidation of Mn(II) to Mn(III) in $\text{K}_6 [\text{Si Mn W}_{11}\text{O}_{40}\text{H}_2]$ with Peroxydisulfate Ion

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Summary: Mn(II) in the heteropoly ion $[\text{Si Mn W}_{11}\text{O}_{40}\text{H}_2]^{6-}$ was oxidised to Mn(III) by $\text{S}_2\text{O}_8^{2-}$ using Ag^+ as catalyst and the pseudo first order kinetics of this oxidation was studied spectrophotometrically at 35°C, ionic strength 0.2 maintained by Na_2SO_4 and pH 5.0. The reaction rates were found to be independent of heteropoly ion concentration and shows first order dependence on Ag^+ and $\text{S}_2\text{O}_8^{2-}$ concentrations, suggesting oxidation of Ag^+ as rate determining step.

Introduction

Mn(II) has been reported to be oxidised to Mn(III) in several heteropoly ions containing Mn(II) using peroxydisulphate ion as oxidising agent [1,2]. However the reaction takes place only at elevated temperatures, i.e., 45°C or more and even at boiling point it takes a while to complete. Ag^+ ions have been reported to catalyze the oxidation of many substrates where peroxydisulphate ion is used as oxidising agent [3-9].

Purpose of this study was to study the effect of the presence of Ag^+ ions on the kinetics of oxidation of Mn(II) in $\text{K}_6 [\text{Si Mn W}_{11}\text{O}_{40}\text{H}_2]$ with peroxydisulphate ion.

Experimental

Potassium 11-tungstomangano(II)silicate was prepared as described elsewhere, a sample was oxidised to Mn(III) heteropoly ion and the spectra of the compounds was found to be in full agreement with the reported spectra [1,2].

AgNO_3 , Na_2SO_4 and $\text{Na}_2\text{S}_2\text{O}_8$ of pure quality supplied by Merck and Riedel-de Haen were used.

A series of solutions containing $2 \times 10^{-2}\text{M}$ of peroxydisulphate ion, $2 \times 10^{-3}\text{M}$ of Mn(II) heteropoly ion and Ag^+ , varying from $3 \times 10^{-4}\text{M}$ to $1 \times 10^{-3}\text{M}$, were prepared.

In second set of solutions Ag^+ concentrations was kept at $3 \times 10^{-4}\text{M}$, Mn(II) heteropoly ion $2 \times 10^{-3}\text{M}$ and concentration of peroxydisulphate was varied from 2×10^{-2} to $5 \times 10^{-2}\text{M}$.

Similarly in the third set Mn(II) heteropoly ion concentration was varied from 3×10^{-3} to $6 \times 10^{-3}\text{M}$, while the concentration of peroxydisulphate ion was $5 \times 10^{-2}\text{M}$ and Ag^+ was kept at $2 \times 10^{-4}\text{M}$ concentration.

The ionic strength of all of these solutions was kept at 0.2 maintained by Na_2SO_4 and pH was adjusted to 5.0. For pseudo first order kinetic measurements all experiments were run in duplicates and triplicates. Temperature was kept at 35°C, being maintained by Thermomix 1440, with variation within $\pm 0.1^\circ\text{C}$, in a water bath. The change in O.D. were measured at 500 n.m. using Bausch and Lomb Spectronic 21 spectrophotometer. The results were occasionally cross checked on Beckman 600 spectrophotometer. At 500 n.m., Mn(III) heteropoly ion has molar absorptivity of $350 \text{ l. mole}^{-1} \text{ cm}^{-1}$ while that of Mn(II) heteropoly is negligible (Figure 1). The pseudo first order reaction rates were obtained by plots of $\ln [A_\infty - A_t]$ against time. A typical set of results and the corresponding plot is given in Table 1 and Figure 2. Linear regressions, slopes and standard deviations were calculated using standard programs on IBM computer.

Results and Discussion

The values of K_{obs} , obtained from the plot of $\ln [A_\infty - A_t]$ against time for each set of solutions, are tabulated in Table-2. It was observed that the values of K_{obs} show a linear relationship to the concentration of Ag^+ and peroxydisulphate ion but turn out to be independent of the concentration of

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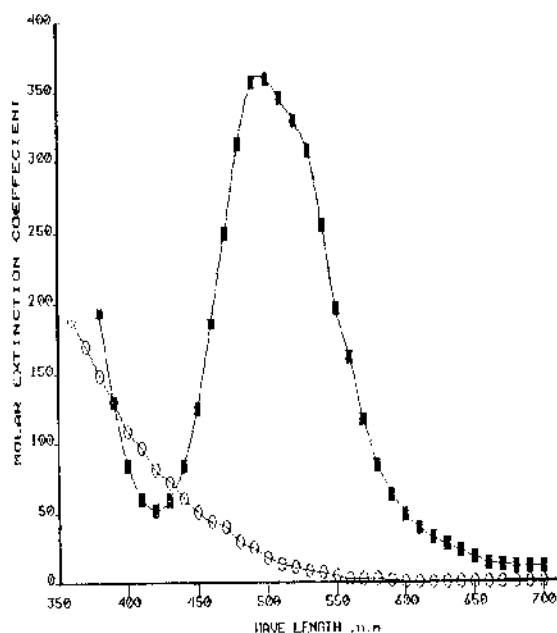


Fig. 1: Spectra of 11-tungstomangano silicate containing Mn^{II} (—○—○—) & Mn^{III} (—■—■—) ions.

Table-1: Absorbance of $Mn(II)$ at various time intervals in the reaction mixtures

The following were the reaction parameters:

$[Mn(II) \text{ Heteropoly ion}] = 2 \times 10^{-3} M$	Temperature = $35^\circ C$
$[Ag^+]_0 = 3 \times 10^{-4} M$	$\mu = 0.2$ in Na_2SO_4
$[S_2O_8^{2-}] = 2 \times 10^{-2} M$	pH = 5.0, A = 0.7

Time, s	A_t	$[A_t - A_\infty]$	$\ln [A_t - A_\infty]$
600	0.060	0.640	-0.446
1200	0.080	0.619	-0.479
1800	0.107	0.592	-0.524
2400	0.130	0.569	-0.563
3000	0.148	0.551	-0.595
3600	0.173	0.526	-0.642
4200	0.193	0.506	-0.680
4800	0.214	0.485	-0.722
5400	0.236	0.463	-0.769
6000	0.259	0.440	-0.820
6600	0.279	0.420	-0.867
7200	0.309	0.390	-0.941
7800	0.318	0.381	-0.964
8400	0.337	0.362	-1.014
9000	0.361	0.338	-1.083
9600	0.376	0.323	-1.129

heteropoly ion. It was also observed that at $35^\circ C$ $Mn(II)$ in heteropoly ion is practically not oxidized to $Mn(III)$ in absence of Ag^+ ions.

These observations lead to two possible mechanisms. In mechanism one, Ag^+ is first oxidized, probably to Ag^{2+} , by peroxydisulphate

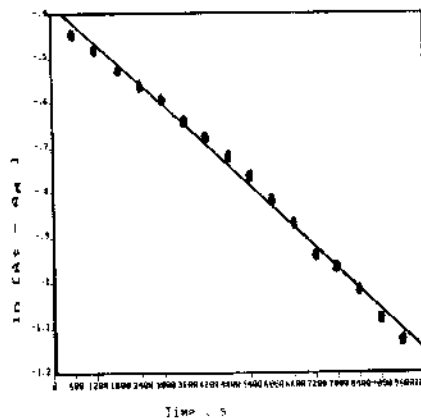


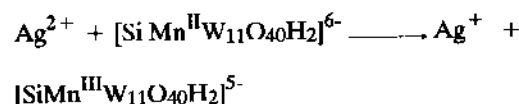
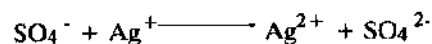
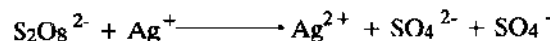
Fig.2: Plot of $\ln [A_t - A_\infty]$ Vs Time for data in Table 1. The slope obtained was $7.62 \times 10^{-5} \pm 2.1 \times 10^{-6}$

For each column of the values, one reagent mentioned in the preceding column was varied keeping the other two constant.

$[Ag^+] M$	Kobs. $M.s^{-1}$	$[S_2O_8^{2-}] M$	Kobs. $M \text{ sec}^{-1}$
3.0×10^{-4}	$7.62 \times 10^{-5} \pm 2.5 \times 10^{-7}$	2.5×10^{-2}	$6.398 \times 10^{-4} \pm 1.2 \times 10^{-7}$
4.0×10^{-4}	$1.18 \times 10^{-5} \pm 9.4 \times 10^{-6}$	3.0×10^{-2}	$8.442 \times 10^{-4} \pm 1.2 \times 10^{-7}$
5.0×10^{-4}	$1.447 \times 10^{-5} \pm 6.0 \times 10^{-6}$	3.5×10^{-2}	$1.118 \times 10^{-3} \pm 4.6 \times 10^{-6}$
6.0×10^{-4}	$1.723 \times 10^{-5} \pm 3.6 \times 10^{-6}$	4.0×10^{-2}	$1.339 \times 10^{-3} \pm 6.1 \times 10^{-6}$
7.0×10^{-4}	$2.014 \times 10^{-5} \pm 1.9 \times 10^{-6}$	4.5×10^{-2}	$1.535 \times 10^{-3} \pm 3.6 \times 10^{-6}$
7.5×10^{-4}	$2.142 \times 10^{-5} \pm 5.4 \times 10^{-6}$	5.0×10^{-2}	$1.806 \times 10^{-3} \pm 2.9 \times 10^{-6}$
8.0×10^{-4}	$2.438 \times 10^{-5} \pm 6.1 \times 10^{-6}$		
9.0×10^{-4}	$2.63 \times 10^{-5} \pm 3.4 \times 10^{-6}$		
9.5×10^{-4}	$2.774 \times 10^{-5} \pm 5 \times 10^{-6}$		

* Ag^+ varied when $[S_2O_8^{2-}]$ was $2 \times 10^{-2} M$ and $[Mn^{2+}]$ was $2 \times 10^{-3} M$.
** $S_2O_8^{2-}$ varied when $[Ag^+]$ was $3 \times 10^{-4} M$ and $[Mn^{2+}]$ was $2 \times 10^{-3} M$.

ion and Ag^{2+} oxidizes $Mn(II)$ to $Mn(III)$ in the heteropoly ion. The oxidation of Ag^+ as rate determining step has been reported in several studies [4,6,7,10-13].



Since $S_2O_8^{2-}$ is in large excess in all experiments and Ag^+ converts slowly into Ag^{2+} but reduces back very quickly, their concentrations can be assumed to be practically unaltered and hence,

$$K_{obs} = k [Ag^+] [S_2O_8^{2-}]$$

A plot of K_{obs} Vs $[Ag^+]$ for data in set one yields a straight line the slope of which would be $k [S_2O_8^{2-}]$, (Fig. 3). Since $[S_2O_8^{2-}]$ was kept at 2

$\times 10^{-2} M$, k was calculated to be $15.15 M^{-1} sec^{-1} \pm 0.05 M^{-1} sec^{-1}$. Similarly a plot of K_{obs} . Vs $[S_2O_8^{2-}]$ for set 2 yields a straight line with slope being equal to $k [Ag^+]$, (Fig. 4). Here again k was found to be $15.15 \pm 0.05 M^{-1} sec^{-1}$, since $[Ag^+]$ was $3 \times 10^{-4} M$ in all solutions. The values of k obtained from these plots are in good agreement, strongly supporting the suggested mechanism.

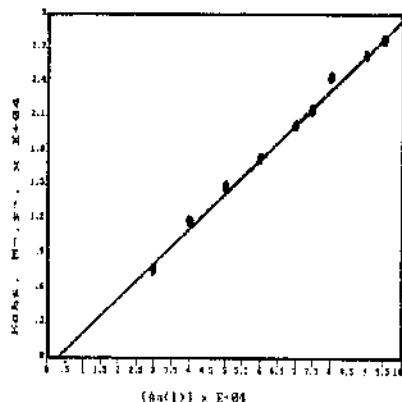


Fig. 3: Plot of K_{obs} . Vs $[Ag^+]$ for the data in Table 2. The slope obtained was $0.303 \pm 1.2 \times 10^{-5}$.

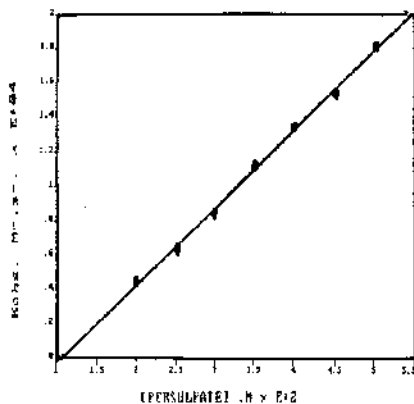
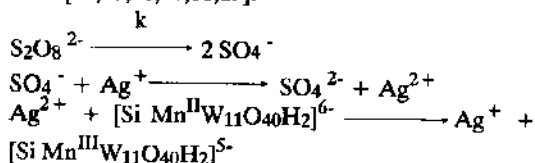


Fig.4: Plot of K_{obs} . Vs $[S_2O_8^{2-}]$ for data in Table 2. The slope obtained was $4.546 \times 10^{-3} \pm 8.9 \times 10^{-6}$.

The second possible mechanism requires formation of SO_4^- ion radical by homolytic decomposition of $S_2O_8^{2-}$, as intermediate, reported in several reactions where this oxidizing agent was used [14,15,16,17,18,19].



Here, Rate = $k [SO_4^-] [Ag^+]$
 and $[SO_4^-] = k^{1/2} [S_2O_8^{2-}]^{1/2}$
 Hence $K_{obs.} = k' [S_2O_8^{2-}]^{1/2} [Ag^+]$
 Since $k' = k.K^{1/2}$

For this mechanism also the plots of $K_{obs.}$ and Ag^+ would yield a straight line but the slope would be $k' [S_2O_8^{2-}]^{1/2}$ for first set of experiments. However in this case plots of $K_{obs.}$ vs $[S_2O_8^{2-}]^{1/2}$ would give a straight line graph for the second set of experiments.

Since the plots of $K_{obs.}$ vs $[S_2O_8^{2-}]$ and not $K_{obs.}$ vs $[S_2O_8^{2-}]^{1/2}$ yields a straight line curve the second mechanism is less likely compared to the first.

From the preceding discussion it can be concluded that for the system under consideration the reaction rates depend only on the concentration of Ag^+ and $S_2O_8^{2-}$, proceeds presumably by the oxidation of Ag^+ to Ag^{2+} by $S_2O_8^{2-}$ ions and not through SO_4^- ion radical. Further studies including a wide range of concentrations, at various temperature, pH values, ionic strengths etc. are being pursued in order to fully understand this system.

References

1. S. A. Malik and T. J. R. Weakley, *J.Chem.Soc.*, A 2647 (1968).
2. S. A. Malik, T.J.R. Weakley, Claude, M. Tourne and Gilbert F.Tourne, *J.Inorg.Nucl. Chem.*, 32, 3875 (1970).
3. D.M. Yost, *J.Am.Chem.Soc.*, 48, 152 (1926).
4. J.D. Miller, *J.Chem.Soc.*, 2348 (1969).
5. M. Andersen, J.O. Edwards, Sr. A.A. Green and Sr. M.D. Wiswell, *Inorg.Chem.Acta.*, 3, 665 (1969).
6. S.P. Srinvastava, V.K. Gupta, R.G.Sharma and B.P. Singh, *Ind.J.Chem.*, 20A, 1221 (1981).
7. M.B. Hogale, M.H. Jagdal and B.P. Nikam, *J.Indian Chem.Soc.*, 63(10), 932 (1986).
8. A.S. Readdy and J.N. Reddy, *Ind.J.Chem.*, 20A, 608 (1981).
9. M. Cyfert, *Inorg.Chem.Acta.*, 73, 135 (1983).
10. R.C. Thompson, *Inorg.Chem.*, 20, 1005 (1981).
11. G.L. Angrawal, *Z.Phys.Chem.(Lepipzig)* 265(4), 691 (1984).
12. M.B. Hogale and M.H. Jagdal *Acta.Cienc.Indica [Ser] Chem.*, 10(3) 129, (1984).

13. S. K. Gupta and S.C. Saksena, *J.Indian. Chem.Soc.*, **64**(3), 154 (1987).
14. D.A. House, *Chem.Rev.*, **62**, 185 (1962).
15. D.E. Pennington and A. Haim, *J.Amer.Chem.Soc.*, **90**, 3700 (1968).
16. F. Secco and Celsi, *J.Chem.Soc.,A* 1092 (1971).
17. W.K. Wilmarth and A. Haim, 1962. In "Peroxide Reduction Mechanism" ed. J.O. Edwards, eds.) Wiley Interscience New York, p. 175.
18. S.P. Srivastava, V.K. Gupta, R.G. Sharma, K.P. Singh, *React. Kinet.Catal.Lett.*, **24**(1-2), 167 (1984).
19. N. Patil, S.G. Sankpal and M.H. Jagdal, *J. Shivaji Univ. Sci.*, **19**, 35 (1979) (Pub. 1983) *Chem. Abs.* 101:210329u.