

Ruthenium(III) catalysed oxidation of L-serine by manganese(III) - kinetics and mechanism

^aN.Baby Nirmala, ^aB.Dharma Rao, ^aP.Vani

^aDepartment of Inorganic and Analytical Chemistry, Andhra University, Visakhapatnam, Andhra Pradesh, India - 530 003

Abstract

The reaction between L-serine and manganese(III) in presence of ruthenium(III) was studied spectrophotometrically at 500 nm in sulphuric acid medium at 30 ± 0.1 °C. The orders with respect to the substrate and oxidant were found to be one in each at low [manganese(III)]. These orders were altered to two and zero respectively at high [manganese(III)] but the order in [ruthenium(III)] was found to be one and it was unchanged at low as well as at high [manganese(III)]. Ionic strength, $[H^+]$, $[HSO_4^-]$ and [manganese(II)] were found to have negligible effect on the reaction rate irrespective of the concentration of manganese(III). The activation parameters, energy of activation, E_a and the entropy of activation, ΔS^\ddagger were computed using linear least squares method and are found to be 36.18 ± 3.43 kJmol⁻¹ and -170.31 ± 11.32 JK⁻¹mol⁻¹ respectively at low manganese(III) concentration. Suitable mechanisms were proposed depending on the observed kinetics.

KEYWORDS : L-serine, Oxidation, Kinetics, Manganese(III), Ruthenium(III)

1. Introduction

Serine is an aliphatic, non-essential and a proteinogenic amino acid. It is important in metabolism in that it participates in the biosynthesis of purines and pyrimidines, and it is a precursor of several amino acids. Many kinetic and mechanistic studies were reported on the oxidation of serine with oxidants like manganese(VII)¹, chloramine-T², chromium(VI)², manganese(III)⁴⁻⁶, cerium(IV)⁷ under different conditions. Different products have been identified with different oxidants by various workers¹⁻⁷. Hence it becomes important to study the reactivity of serine towards various oxidants.

Manganese(III) is a powerful one-electron oxidant in perchloric acid, sulphuric acid, acetic acid and pyrophosphate media. The redox potential of manganese(III)-manganese(II) couple is 1.51 V⁸ in 7.5 mol dm⁻³ sulphuric acid medium and 1.56 V^{9,10} in 3.0 mol dm⁻³ perchloric acid medium.

Chandrabu *et al.*⁶ studied the oxidation of L-serine with manganese(III) in sulphuric acid medium at 50 °C. Since micro amounts of ruthenium(III) was found to catalyse the oxidation of L-serine by manganese(III) in sulphuric acid medium at 30 °C and in continuation of our studies on the oxidation of amino acids using manganese(III) as oxidant^{11,12}, we have carried out the title reaction with a view of elucidating its mechanism.

2. Experimental

A 0.5 mol dm⁻³ solution of L-serine (Himedia) was prepared in double distilled water. A 0.015 mol dm⁻³ solution of manganese(III) of 75 cm³ in 5.0 mol dm⁻³ sulphuric

acid was prepared by slowly adding 2.3 cm³ of 0.1 mol dm⁻³ KMnO₄ to an ice cold solution of 50 cm³ of 0.25 mol dm⁻³ manganese(II) sulphate and standardized by titrating against standard iron(II) solution using ferroin as indicator. A 0.01 mol dm⁻³ solution of ruthenium(III) sulphate in 0.5 mol dm⁻³ sulphuric acid was prepared from ruthenium trichloride (Johnson Mathey, London) according to Surasiti and Sandell¹³ and was standardized by the method suggested by Beamish and Vanloon¹⁴. All other chemicals used were of analytical reagent grade.

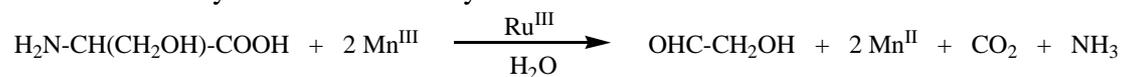
Absorption measurements were made with a Milton Roy Spectronic-1201 UV-Visible spectrophotometer with 1 cm path length silica cells. A Siskin Julabo-V constant temperature liquid circulatory bath was used as the constant temperature bath for all kinetic investigations.

Because of the considerable disproportionation of manganese(III) even in 2.0 mol dm⁻³ sulphuric acid medium, kinetic runs were always carried out in the presence of large excess of manganese(II). It was observed that the plots should not correspond to any particular order with respect to [manganese(III)], if the reaction was initiated by manganese(III). Hence, the reaction was initiated by adding requisite amount of serine solution, placed in water bath, maintained at desired temperature, to a reaction mixture containing appropriate quantities of solutions of sulphuric acid, manganese(II), manganese(III) and ruthenium(III) placed separately in the same water bath. An important feature of this reaction is the change in the orders of the substrate and the oxidant upon changing the concentration of manganese(III). The rate of oxidation was followed by monitoring the decrease in the absorbance of manganese(III) as a function of time at 500 nm, where no other species of the reaction mixture has significant absorption. The rate constants were found to be reproducible within $\pm 4\%$.

Results and Discussion

3.1 Product analysis

The reaction mixture containing 0.05 mol dm⁻³ serine, 2.0 mol dm⁻³ sulphuric acid, 0.2 mol dm⁻³ manganese(II), 2.0 x 10⁻³ or 3.5 x 10⁻³ mol dm⁻³ manganese(III) and 6.0 x 10⁻⁶ mol dm⁻³ ruthenium(III) was extracted with diethyl ether after completion of the reaction. From IR spectral studies, it was identified that 2-hydroxyethanal was the oxidation product of serine (Fig 1). In the IR spectrum, the peaks at 3451.07 cm⁻¹, 2961.56 cm⁻¹, 2855.19 cm⁻¹ and 1728.42 cm⁻¹ are corresponding to O-H(str), C-H(str), O=C-H(str) and C=O(str) frequencies respectively. On the basis of the aforesaid results, the stoichiometry of the reaction may be written as below



3.2 Test for free radicals

The test for free radicals was carried out by adding the monomer, acrylonitrile, to the reaction mixture. The negative response indicating the absence of intervention of free radicals during the course of the reaction.

3.3 Effect of [manganese(III)] on the reaction rate

In order to view the effect of [manganese(III)] on the rate of ruthenium(III) catalysed oxidation of serine, the reaction was studied at various initial concentrations of manganese(III) by varying it from 1.0 – 4.0 x 10⁻³ mol dm⁻³, keeping the other experimental conditions constant. The plots of log(absorbance) versus time were found to be linear upto 75% completion of the reaction upto the manganese(III) concentration,

$2.5 \times 10^{-3} \text{ mol dm}^{-3}$, suggesting the order with respect to [manganese(III)] was unity and the pseudo-first order rate constants, k' were evaluated from the slopes of the plots of $\log(\text{absorbance})$ versus time (Table 1). Further, it was observed that the plots of [manganese(III)] versus time were found to be linear upto 70% completion of the reaction at a [manganese(III)] of $3.0 - 4.0 \times 10^{-3} \text{ mol dm}^{-3}$ range, indicating zero order dependence on [manganese(III)] at higher concentrations of manganese(III). The pseudo-zero order rate constants were calculated from the plots of [manganese(III)] versus time and were found to remain constant at high concentrations of manganese(III) (Table 2).

3.4 Effect of [serine] on the reaction rate

To find out the dependence of [serine] on the reduction rate of manganese(III) in presence of ruthenium(III), kinetic runs were carried out at serine concentrations ranging from $3.0 - 8.0 \times 10^{-2} \text{ mol dm}^{-3}$, keeping the concentrations of all other reactants and the temperature constant at low initial concentration of manganese(III). It was found that the rate was directly proportional to the concentration of serine (Table 1). Further, the plot of k' versus [ser] was found to be a straight line passing through origin, suggesting first order dependence on [serine] (Fig. 2).

Also it was found that at high initial concentration of manganese(III), the rate was increased with increase in serine concentration (Table 2) and the order with respect to serine was found to be two from the plot of k_0 versus [ser]², which was a straight line passing through origin (Fig. 3).

3.5 Effect of [ruthenium(III)] on the reaction rate

Kinetic measurements were performed at constant [serine], $[\text{H}^+]$, $[\text{Mn}^{\text{III}}]$, $[\text{Mn}^{\text{II}}]$ and temperature to know the effect of [ruthenium(III)] on the reaction rate by varying the concentration of ruthenium(III) from $4.0 - 9.0 \times 10^{-6} \text{ mol dm}^{-3}$. It was observed that the increase in [ruthenium(III)] enhanced the rate of the reaction (Tables 1 & 2). The plots of k' versus [ruthenium(III)] (Fig. 4) and k_0 versus [ruthenium(III)] (Fig. 5) were found to be straight lines passing through origin, showing unit order dependence on the catalyst at low as well as at high initial [manganese(III)].

3.6 Effect of [manganese(II)], ionic strength, $[\text{H}^+]$ and $[\text{HSO}_4^-]$

The initially added product, manganese(II), ionic strength and $[\text{HSO}_4^-]$ did not have significant effect on the rate of the reaction. It was also found that the rate of the reaction is independent of $[\text{H}^+]$. A similar observation was made earlier in the oxidation of uronic acids by manganese(III)¹⁵.

3.7 Effect of temperature

The influence of temperature on the reaction rate was investigated at four different temperatures, 298, 303, 308 and 313 K, keeping the concentrations of all other reactants constant (Table 5). The energy of activation, E_a and the entropy of activation, ΔS^\ddagger values were computed using the linear least squares method and are found to be $36.18 \pm 3.43 \text{ kJmol}^{-1}$ and $-170.31 \pm 11.32 \text{ JK}^{-1}\text{mol}^{-1}$ respectively at low [manganese(III)].

3.8 Discussion

In sulphuric acid medium, manganese(III) is assumed to exist as Mn^{3+} , MnOH^{2+} and MnSO_4^+ . The absence of bisulphate ion effect on the rate of the reaction indicating MnSO_4^+ cannot be the reactive species of manganese(III). As the reaction rate did not

alter with $[H^+]$, it was assumed that both the species, Mn^{3+} and $MnOH^{2+}$ are considered to be the reactive species of manganese(III).

Ruthenium(III) is readily and quantitatively oxidized to ruthenium(VIII) when its aqueous solutions are mixed with excess manganese(III) solutions. This fact is also supported by the reports in the past by Bhaskara Sastry et al¹⁶ in the ruthenium(III) catalysed oxidation of tellurium(IV) by manganese(III) and by Zameela et al¹⁷ in the ruthenium(III) catalysed oxidation of selenium(IV) by manganese(III). In view of these reports, it may be regarded that ruthenium(VIII) is the reactive species of ruthenium(III) under the present experimental study.

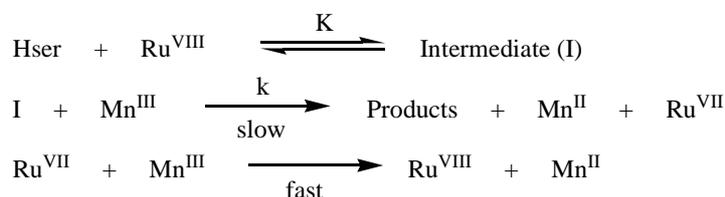
In 2.0 mol dm^{-3} sulphuric acid, serine mainly exists as protonated species, Hser, $H_3N^+-CH(CH_2OH)-COOH$.

The kinetic investigations indicated that the reaction is first order dependent on [substrate], [oxidant] and [catalyst] at low initial concentrations of manganese(III), and zero order dependent on [manganese(III)], second order dependent on [serine] and unit order dependent on [ruthenium(III)] at high initial concentrations of manganese(III). Hence, it may be concluded that the total order of the reaction was remain constant although there are changes in the orders of substrate and oxidant with an initial change in the [oxidant].

Based on these experimental observations, the following two schemes of mechanism were proposed.

Scheme I

At low initial [manganese(III)]



Where, Hser = $H_3N^+ - CH(CH_2OH) - COOH$

The above mechanism leads to the rate law,

$$\begin{aligned}
 \text{Rate} &= -\frac{d[Mn^{\text{III}}]}{dt} = k [I] [Mn^{\text{III}}] \\
 &= k K [Hser] [Ru^{\text{VIII}}] [Mn^{\text{III}}]
 \end{aligned}$$

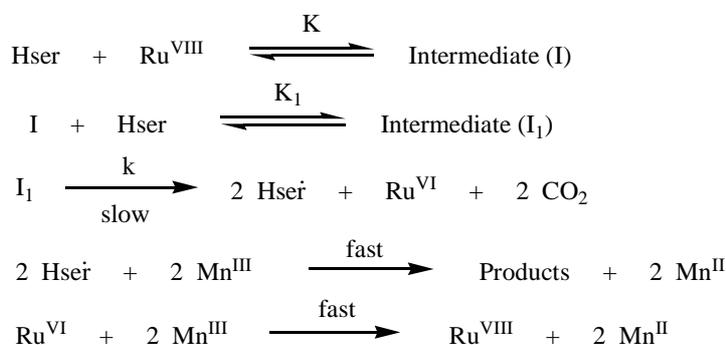
But, $[Hser] = [ser]_t$ and $[Ru^{\text{VIII}}] = [Ru^{\text{III}}]_t$

Hence, rate = $k K [ser]_t [Ru^{\text{III}}]_t [Mn^{\text{III}}]$.

The above rate equation explains the unit order in [substrate], [catalyst] and [oxidant] at low initial concentration of manganese(III).

Scheme II

At high initial [manganese(III)]



Where, $\text{Hser} = \text{H}_3\text{N}^+ - \text{CH}(\text{CH}_2\text{OH}) - \text{COOH}$

and $\text{Hser} = \text{H}_3\text{N}^+ - \dot{\text{C}}\text{H} - (\text{CH}_2\text{OH})$

From the above mechanism the rate equation can be written as

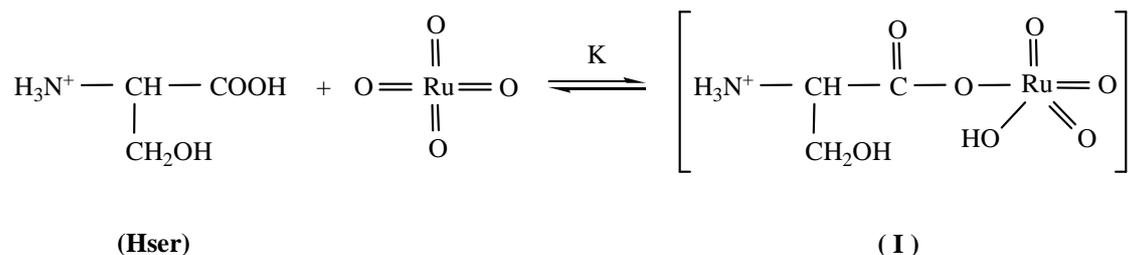
$$\begin{aligned}
 \text{Rate} &= -\frac{d[\text{Mn}^{\text{III}}]}{dt} = k [\text{I}_1] \\
 &= k K_1 [\text{I}] [\text{Hser}] \\
 &= k K K_1 [\text{Hser}]^2 [\text{Ru}^{\text{VIII}}]
 \end{aligned}$$

But, $[\text{Hser}] = [\text{ser}]_t$ and $[\text{Ru}^{\text{VIII}}] = [\text{Ru}^{\text{III}}]_t$

Hence, $\text{rate} = k K K_1 [\text{ser}]_t^2 [\text{Ru}^{\text{III}}]_t$.

The rate equation explains the second order dependence on [substrate], zero order dependence on [manganese(III)] and unit order dependence on [catalyst] at high initial concentrations of manganese(III).

Scheme I – Intimate mechanism at low initial [manganese(III)]



- In the subsequent fast steps these two react with manganese(III) to form the products and regenerating the catalyst.

4. Conclusions

In acid medium, Mn^{III} exists as Mn^{3+} and $MnOH^{2+}$ and both of them are considered to be reactive since the reaction is independent of $[H^+]$. Further, the total order of the reaction and the oxidation product, 2-hydroxyethanal, remains the same though the mechanism of oxidation differs at different concentrations of manganese(III).

5. Acknowledgements

One of the authors, N.Baby Nirmala, thanks the management of V.S.M.College, Ramachandrapuram, for the encouragement and University Grants Commission for the award of teacher fellowship under Faculty Development Programme. The other author, Mr. B.Dharma Rao expresses his grateful thanks to the UGC, New Delhi, for the award of BSR fellowship.

6. References

1. Surender Rao, V., Sethuram, B. and Navneeth Rao, T. (1979) Kinetics of Oxidation of Some Amino Acids by $KMnO_4$ in a Moderately Concentrated H_2SO_4 Medium in the Presence and Absence of Ag^+ , Int. J. Chem. Kinet, IX, pp. 165-173
2. Katgeri, S.N., Mahadevappa, D.S. and Naidu, H.M.K. (1980) Kinetics of Oxidation of α -Amino Acids by Sodium N-Chloro-4- Methylbenzene Sulphonamide in Hydrochloric Acid Medium, Indian J. Chem. 19A, pp. 29-32
3. Goswami, K.B., Chandra, G. and Srivastava, S.N. (1981) Kinetics of Chromic Acid Oxidation of Serine, Methionine and Cysteine, J. Indian Chem. Soc. Vol LVIII: pp. 252-258
4. Chandraju S, Mahadevappa DS, Rangappa KS, Made Gowda NM (1997) Anodically Generated Manganese(III) Oxidation Of L-serine and L-threonine on Aqueous Acetic Acid Medium : Kinetics And Mechanism, Synth. React. Inorg. Met.- Org. Chem. 27(9), pp. 1329-1346
5. Chandraju, S., Mahadevappa , D.S. and Rangappa, K.S. (1997) Manganese(III) Oxidation of Some Neutral Amino Acids in Pyrophosphate Medium : A Kinetic and Mechanistic Study, Indian J. Chem. 36A, pp. 974-980
6. Chandraju S, Rangappa KS, Made Gowda NM (1999) Manganese(III) Oxidation of L-serine in Aqueous Sulphuric Acid Medium : Kinetics and Mechanism, Int. J. Chem. Kinet. 31, pp. 525-530
7. Bayulken, S. and Sarac, A.S. (1998)) Kinetics and Mechanism of Oxidation of Some Amino Acids with Cerium(IV), Zeitschrift fur Physikalische Chemie. 205, pp. 181
8. Vetter, K.J. and Manecke, G. (1950) Z. Phys. Chem. (Leipzig) 195, pp. 270
9. Rossiensky, D.R. (1963) J. Chem. Soc. 11, pp. 1181
10. Diebler, H. and Sutin, N. (1964) J. Phys. Chem. 68, pp. 174-180
11. Vani P, Raja Rajeswari T, Dikshitulu LSA (1994) Kinetics and Mechanism of Oxidation of DL-Methionine by Manganese(III) in Sulphuric Acid Medium, React. Kinet. Catal. Lett. 52, pp. 175-182
12. Annapurna, N., Kalyan Kumar, A., Vani, P. and Nageswara Rao, G. (2008) Trans. Met. Chem. 33, pp. 691-696

13. Surasiti, C. and Sandell, E.B. (1960) Anal. Chim. Acta. 22, pp. 261-269
14. Beamish, F.E. and Vanloon, J.C. (1972) Recent advances in the analytical chemistry of noble metals, Pergamon Press, London, p. 465.
15. Rangappa, K.S., Anitha, N., Ayesha Nikath, M., Rai, K.M.L. and Made Gowda, N.M. (2001) Oxidation of Uronic Acids by Manganese(III) sulphate in Acid Solution: A Kinetic and Mechanistic Study, Synth. React. Inorg. Met.- Org. Chem. 31(5), pp. 713-723
16. Bhaskara Sastry, C., Zameela, M. and Dikshitulu, L.S.A. (1996) Mechanism of Ruthenium(III) catalyzed Oxidation of Tellurium(IV) by Manganese(III) – A kinetic study, Proc. Natn. Acad. Sci. 66(A), pp. 279-286
17. Zameela, M., Bhaskara Sastry, C. and Dikshitulu, L.S.A. (1998) Kinetics and Mechanism of Ruthenium(III) catalyzed Oxidation of Selenium(IV) by Manganese(III) in sulphuric acid medium, J. Indian Chem. Soc. 75, pp. 63-66

Table 1: Effect of [serine], [manganese(III)], [ruthenium(III)] on the pseudo-first order rate constant, k'

$[H^+] = 2.0 \text{ mol dm}^{-3}$; $[Mn^{II}] = 0.2 \text{ mol dm}^{-3}$; $t = 30 \pm 0.1 \text{ }^\circ\text{C}$

$[ser] \times 10^2$, mol dm^{-3}	$[Mn^{III}] \times 10^3$, mol dm^{-3}	$[Ru^{III}] \times 10^6$, mol dm^{-3}	$k' \times 10^4$, sec^{-1}
3.0	2.0	6.0	3.90
4.0	2.0	6.0	5.15
5.0	2.0	6.0	6.62
6.0	2.0	6.0	8.58
7.0	2.0	6.0	9.60
8.0	2.0	6.0	11.26
5.0	1.0	6.0	15.18
5.0	1.5	6.0	9.14
5.0	2.0	6.0	6.19
5.0	2.5	6.0	3.71
5.0	2.0	4.0	3.75
5.0	2.0	5.0	4.80
5.0	2.0	6.0	6.16
5.0	2.0	7.0	7.13
5.0	2.0	8.0	8.12
5.0	2.0	9.0	9.00

Table 2: Effect of [serine], [manganese(III)], [ruthenium(III)] on the pseudo-zero order rate constant, k_0

$[H^+] = 2.0 \text{ mol dm}^{-3}$; $[Mn^{II}] = 0.2 \text{ mol dm}^{-3}$; $t = 30 \pm 0.1 \text{ }^\circ\text{C}$

$[ser] \times 10^2$, mol dm^{-3}	$[Mn^{III}] \times 10^3$, mol dm^{-3}	$[Ru^{III}] \times 10^6$, mol dm^{-3}	$k_0 \times 10^5$, $\text{mol dm}^{-3} \text{sec}^{-1}$
3.0	3.5	6.0	1.04
4.0	3.5	6.0	1.69
5.0	3.5	6.0	2.63
6.0	3.5	6.0	4.07
7.0	3.5	6.0	5.42
8.0	3.5	6.0	7.00
5.0	3.0	6.0	2.53
5.0	3.5	6.0	2.70

5.0	4.0	6.0	2.60
5.0	3.5	4.0	1.60
5.0	3.5	5.0	2.10
5.0	3.5	6.0	2.53
5.0	3.5	7.0	2.92
5.0	3.5	8.0	3.55
5.0	3.5	9.0	4.00

Table 3: Effect of temperature on the pseudo-first order rate constant, k'
 $[\text{ser}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{Mn}^{\text{III}}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{H}^+] = 2.0 \text{ mol dm}^{-3}$;
 $[\text{Mn}^{\text{II}}] = 0.2 \text{ mol dm}^{-3}$; $[\text{Ru}^{\text{III}}] = 6.0 \times 10^{-6} \text{ mol dm}^{-3}$

Temperature	298 K	303 K	308 K	313 K
$k' \times 10^4, \text{sec}^{-1}$	4.52	6.34	8.39	10.75

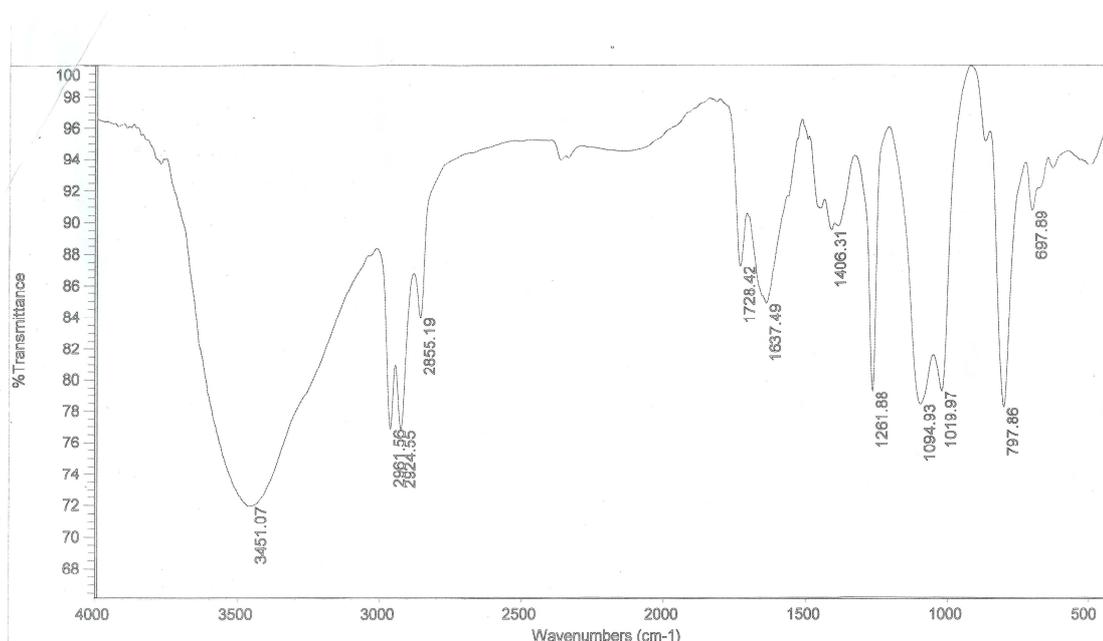


Fig.1: FT-IR spectrum of 2-hydroxyethanal

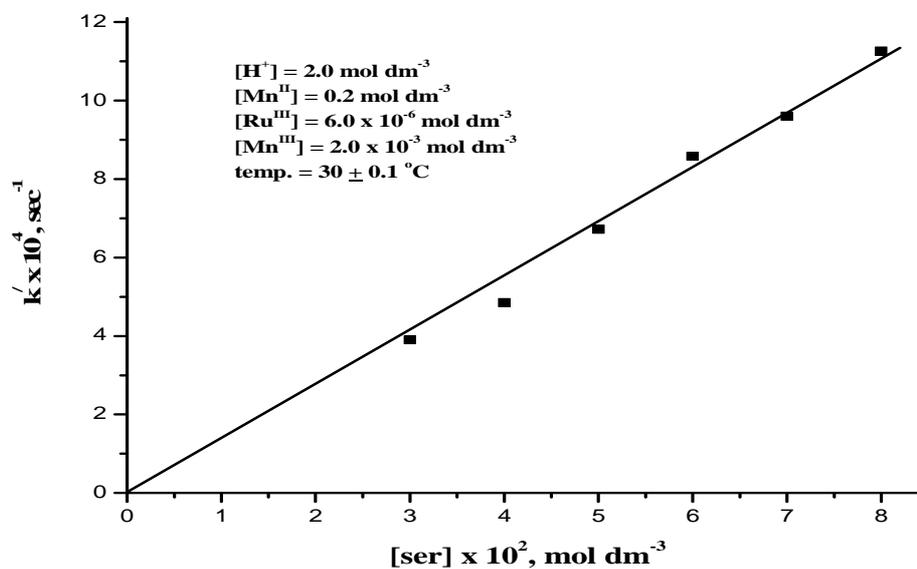


Fig.2: Order plot of serine at low [manganese(III)]

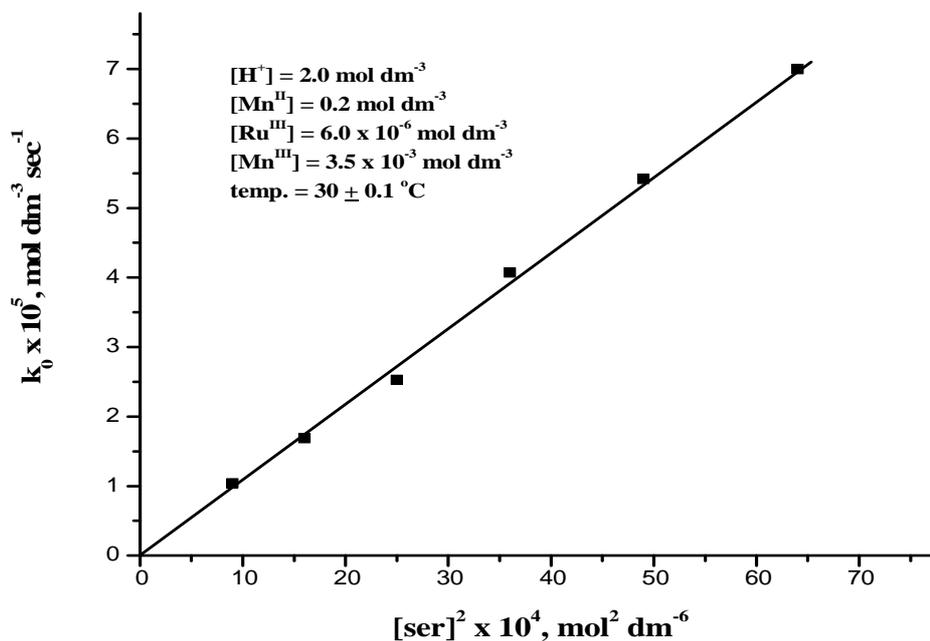


Fig.3: Order plot of serine at high [manganese(III)]

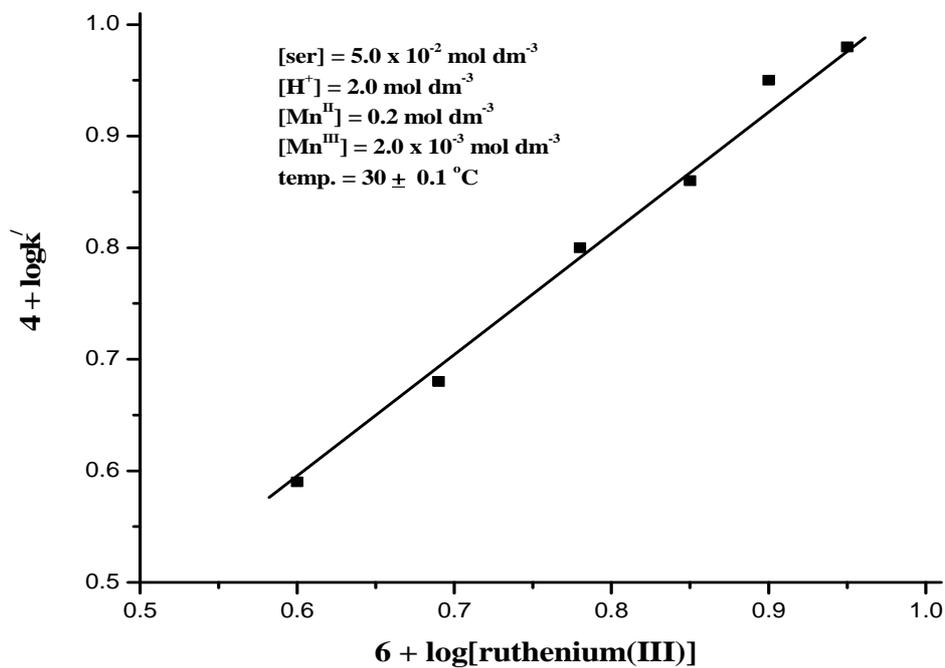


Fig.4: Plot of $\log k^1$ versus $\log[\text{ruthenium(III)}]$

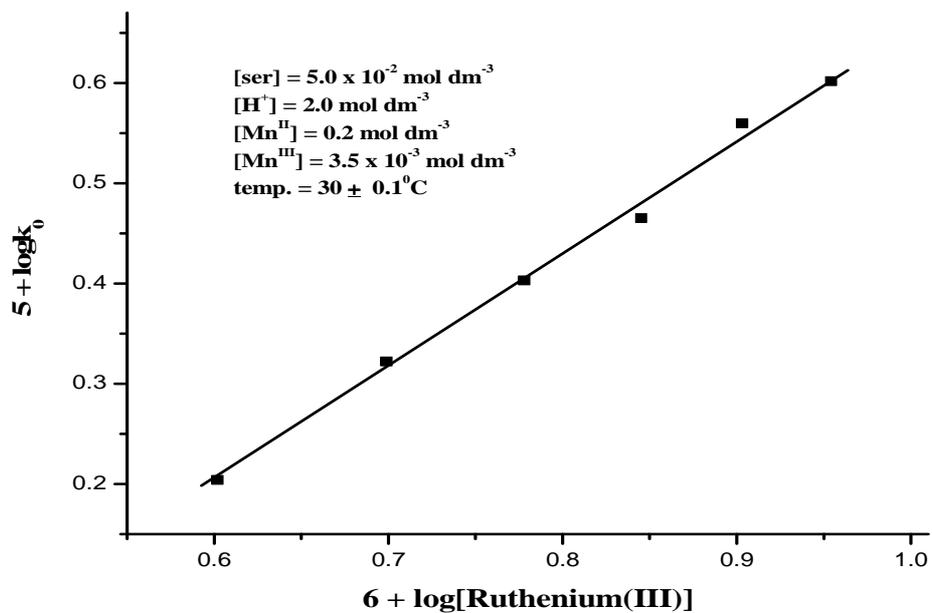


Fig.5: Plot of $\log k_0$ versus $\log[\text{Ruthenium(III)}]$