Manganese(III) Oxidation of L-Serine in Aqueous Sulfuric Acid Medium: Kinetics and Mechanism

S. CHANDRAJU,[1] K. S. RANGAPPA,[1] N. M. MADE GOWDA[2]

[1]*Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore-570 006, India*
[2]*Department of Chemistry, Western Illinois University, 1 University Circle, Macomb, Illinois 61455*

Received 29 April 1998; accepted 11 March 1999

ABSTRACT: Kinetics and mechanism of oxidation of L-serine by manganese(III) ions have been studied in aqueous sulfuric acid medium at 323 K. Manganese(III) sulfate was prepared by an electrolytic oxidation of manganous sulfate in aqueous sulfuric acid. The dependencies of the reaction rate are: an unusual one and a half-order on [Mn(III)], first-order on [ser], an inverse first-order on [H$^+$], and an inverse fractional-order on [Mn(II)]. Effects of complexing agents and varying solvent composition were studied. Solvent isotope studies in D_2O medium were made. The dependence of the reaction rate on temperature was studied and activation parameters were computed from Arrhenius-Eyring plots. A mechanism consistent with the observed kinetic data has been proposed and discussed. © 1999 John Wiley & Sons, Inc. Int J Chem Kinet 31: 525–530, 1999

INTRODUCTION

Oxidations of organic substrates by manganese(III) are of special importance due to their biological relevance [1,2]. The reports on the kinetics of oxidation of various substrates by manganese(III) [3–12] include reactions in perchlorate, sulfate, acetate, and pyrophosphate media.

Amino acids serve an important function in our biological systems and play a significant role in metabolism. In continuation of our interest in oxidation of organic substrates by Mn(III) [13–18], we have undertaken the present work. We here report the kinetics and mechanism of oxidation of L-serine by manganese(III) in aqueous sulfuric acid medium.

EXPERIMENTAL

Solution of manganese(III) sulfate was prepared by the electrolytic oxidation of 0.200 M manganese(II) sulfate in 1.50 M H_2SO_4 in an electrochemical cell [8]. Only a fraction of manganese(II) could be converted into manganese(III) owing to low solubility of manganese(III). Furthermore, manganese(III) is always associated with a large excess of manganese(II) to suppress the disproportionation as shown below.

$$2\text{Mn(III)}_{(aq)} \rightleftharpoons \text{Mn(II)}_{(aq)} + \text{Mn(IV)}_{(aq)} \qquad (1)$$

Chromatographically pure sample of L-serine (Sisco Research Laboratories, India) was further assayed for amino acid content by standard methods [19]. Freshly prepared aqueous solutions were used throughout the experiments. Ionic strength of the medium was adjusted by $NaClO_4$. Triply distilled water was employed for preparing experimental solutions.

Correspondence to: K. S. Rangappa or N. M. Made Gowda

CCC 0538-8066/99/080525-06

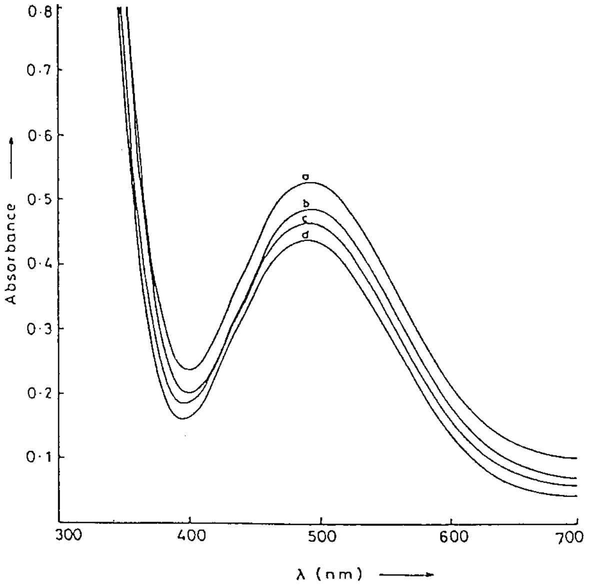


Figure 1 Absorption spectra of 4.00×10^{-3} mol dm^{-3} manganese(III) in H_2SO_4. $[H^+]$(mol dm^{-3}):1.20(a), 1.62(b), 2.04(c), 2.50(d).

Regression analyses of experimental data were carried out on a scientific calculator SHARP EL-506G DAL.

Preliminary Studies

The absorption spectra of manganese(III) sulfate solution were recorded on a Beckman DU-6 UV-visible spectrophotometer. The maximum absorption (λ_{max}) occurs at 490 nm. The molar absorptivity (ε) at 190 nm depended on pH of the solution (ε ranged from 131–111 L mol^{-1} cm^{-1} at $[H^+] = 1.28–2.98$ mol dm^{-3}, Fig. 1).

The formal redox potential (E′o) of Mn(III)-Mn(II) couple is a measure of the oxidizing power of the oxidant. Different but known amounts of manganese(III) were anodically generated in a given volume of aqueous sulfuric acid and the electrode potential was measured each time.

The potential measurements were also made at various concentrations of sulfuric acid and in the presence of added anions, HSO_4^- and ClO_4^-, and complexing agents, $P_2O_7^{4-}$ F^-, and Cl^-. A plot of the potential vs. log[Mn(III)]/[Mn(II)] gave a straight line with a slope of 0.0593 V for one-electron transfer systems at 298 K.

Kinetics Measurements

Mixtures of solutions containing excess (8.00×10^{-2} mol dm^{-3}) of serine over Mn(III) (4.00 mol dm^{-3}), sulfuric acid, sodium perchlorate (to maintain the total ionic strength constant), manganese(II) and water (to keep the total volume constant) were taken in stoppered boiling tubes. Each mixture was thermally equilibrated in a water bath. To this solution was added an aliquot of pre-equilibrated manganese(III) sulfate stock solution to give a known overall concentration. The progress of the reaction was monitored for two half-lives by withdrawing aliquots at regular time intervals and iodometrically determining the unreacted manganese(III) concentration in each aliquot using starch indicator near the end point. The rate constants, k_{obs}, calculated by the graphical method were reproducible within ±3% error.

Reaction Stoichiometry and Product Analysis

The following stoichiometry was observed, with $[Mn(III)] > [ser]$:

$$2\,Mn(III) + RCH(NH_2)COOH + H_2O \longrightarrow 2\,Mn(II) + RCHO + NH_4^+ + CO_2 + H^+ \quad \text{where } R = -CH_2OH. \qquad (2)$$

The aldehyde was quantified through its 2,4-dinitrophenyl hydrazone derivative. The I.R. spectral data of the hydrazone derivative supported its characterization. Ammonium ion and CO_2 were detected by the conventional tests.

Test for Free Radicals

The reaction mixture initiated polymerization of olefinic monomers, acrylonitrile and methyl methacrylate, indicating an in situ formation of free radicals. Proper control experiments were also performed.

RESULTS AND DISCUSSION

Dependence of the Rate on [Mn(III)] and [ser]

Kinetic runs were performed by varying concentrations of Mn(III) at constant temperature, [Mn(II)], [ser], $[H^+]$, and ionic strength. Plots of log [Mn(III)] vs. time, $[Mn(III)]^{1/2}$ vs time, and [Mn(III)] vs time were all nonlinear, while $1/[Mn(III)]^{1/2}$ vs time plots were linear even beyond 75% of the reaction indicating that one-and-a-half order with respect to [Mn(III)] exists (Fig. 2). Further, the values of k_{obs} were repro-

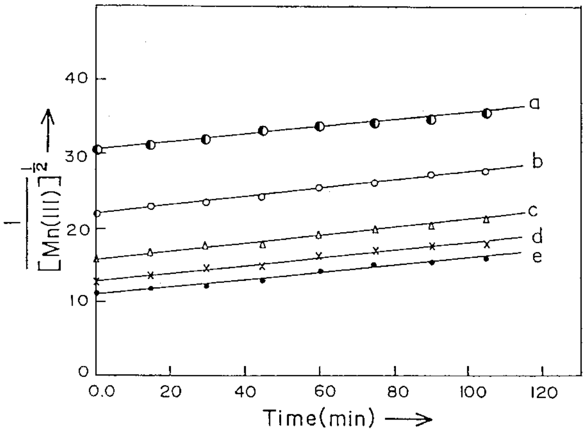


Figure 2 Plots of $1/[Mn(III)]^{1/2}$ vs time: $[Ser]_o = 8.00 \times 10^{-2}$ mol dm^{-3}; [Mn(II)] = 0.126 mol dm^{-3}; $[H_2SO_4]$ = 1.50 mol dm^{-3}; Temp. = 323 K, and 10^3 $[Mn(III)]_O$ (mol dm^{-3}) = 1.00(a), 2.00(b), 4.00(c), 6.00(d), 8.00(e).

ducible within ±0.1% error (Table I). Reactions were carried out keeping all experimental conditions constant and by varying [ser]. Plot of log *k* vs log [ser] gave a straight line with unit slope indicating the first order with respect to serine.

Table I Pseudo One-and-a-Half-Order Rate Constants (k_{obs}) for the Oxidation of Serine by Manganese(III) Sulfate at 323 K, $[H_2SO_4]$ = 1.50 mol dm^{-3}, I = 6.24 mol dm^{-3}

10^3 $[Mn(III)]_O$ (mol dm^{-3})	$10^2[ser]_O$ (mol dm^{-3})	$10[Mn(II)]_O$ (mol dm^{-3})	10^3k_{obs} ($dm^{3/2}$ $mol^{-1/2}$ s^{-1})
1.00	8.00	1.26	6.60
2.00	8.00	1.26	6.56
4.00	8.00	1.26	6.56
6.00	8.00	1.26	6.52
8.00	8.00	1.26	6.50
10.0	8.00	1.26	6.54
12.0	8.00	1.26	6.52
4.00	4.00	1.26	3.07
4.00	6.00	1.26	4.68
4.00	8.00	1.26	6.56
4.00	10.0	1.26	8.71
4.00	12.0	1.26	10.23
4.00	14.0	1.26	12.30
4.00	16.0	1.26	15.49
4.00	8.00	0.520	13.18
4.00	8.00	0.820	9.55
4.00	8.00	1.26	6.56
4.00	8.00	1.72	5.13
4.00	8.00	2.26	4.27
4.00	8.00	2.78	3.51
4.00	8.00	3.34	3.09

Table II Effect of $[H^+]$ on the Rate of Oxidation of Serine by Manganese(III) Sulfate at 323 K
$[Mn(III)]_O = 4.00 \times 10^{-3}$ mol dm^{-3}; I = 6.24 mol dm^{-3}
$[Ser]_O = 8.00 \times 10^{-2}$ mol dm^{-3}; $[Mn(II)]_O$ = 0.126 mol dm^{-3}

$[H_2SO_4]$ (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	10^3 k_{obs} ($dm^{3/2}$ $mol^{-1/2}$ s^{-1})
1.50	1.62	6.56
2.00	2.08	5.25
2.50	2.50	4.17
3.00	2.96	3.63
3.50	3.50	3.14
4.00	4.00	2.70

Dependence of the Rate on $[H^+]$

Kinetic measurements were made in H_2SO_4-$NaHSO_4$ solutions of different $[H^+]$. The effect $[H^+]$ was evaluated using a standard curve [20] of $[H_2SO_4]$ vs $[H^+]$. The rate decreased with an increase in $[H^+]$ (Table II) and a plot of log k_{obs} vs log $[H^+]$ was linear with a negative slope (Fig. 3) indicating an inverse first-order dependence on $[H^+]$.

Dependence of the Rate on [Mn(II)] and Added Salts

An increase in $[Mn(II)]_O$, decreased the rate (Table I). A plot of log k_{obs} vs log $[Mn(II)]_O$ gave a straight line with a negative slope representing an inverse-frac-

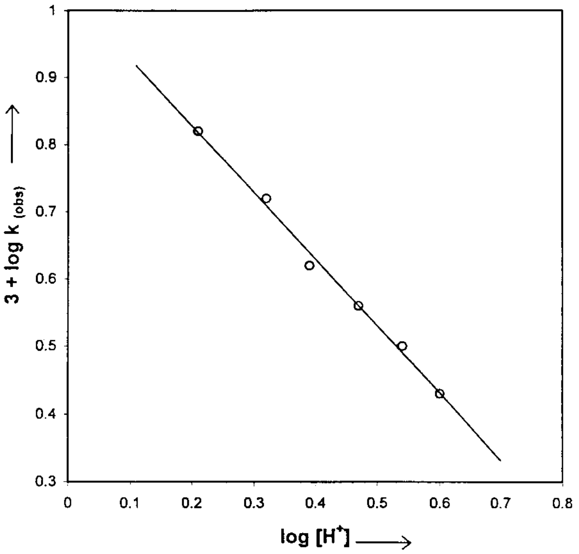


Figure 3 Plot of log $k_{(obs)}$ vs log $[H^+]$: $[Mn(III)]_O$ = 4.00×10^{-3} mol dm^{-3}; $[Ser]_O = 8.00 \times 10^{-2}$ mol dm−3; $[Mn(II)]_O$ = 0.126 mol dm^{-3}; I = 6.24 mol dm^{-3}; T = 323 K.

Table III Effect of Complexing Agents on the Rate of Oxidation of Serine by Manganese(III) Sulfate at 323 K (Other conditions are as in Table II)

10^2 [Cl^-] (mol dm^{-3})	10^3 k_{obs} ($dm^{3/2}$ $mol^{-1/2}$ s^{-1})	10^2 [F^-] (mol dm^{-3})	10^3 k_{obs} ($dm^{3/2}$ $mol^{-1/2}$ s^{-1})	10^2[$P_2O_7^{4-}$] (mol dm^{-3})	10^3 k_{obs} ($dm^{3/2}$ $mol^{-1/2}$ s^{-1})
—	6.56	—	6.56	—	6.56
0.50	6.24	0.5	6.26	0.50	4.96
1.0	5.98	1.0	6.02	1.0	4.18
1.5	5.46	1.5	5.82	1.5	3.46

[SO_4^{2-}] (mol dm^{-3})	10^3 k_{obs} ($dm^{3/2}$ $mol^{-1/2}$ s^{-1})	10[HSO_4^-] (mol dm^{-3})	10^3 k_{obs} ($dm^{3/2}$ $mol^{-1/2}$ s^{-1})
—	6.56	—	6.56
0.50	6.48	0.50	6.42
1.0	6.39	1.0	6.35
1.5	6.20	1.5	6.21

tional order (-0.78) with respect to [Mn(II)]. The effect of complexing agents such as $P_2O_7^{4-}$, F^-, Cl^-, SO_4^{2-} and HSO_4^- on the rate of oxidation was investigated (Table III). The rate decreased with increasing concentration of $P_2O_7^{4-}$, F^- and Cl^- while HSO_4^- and SO_4^{2-} had a negligible effect on the rate.

Addition of sodium pyrophosphate, sodium fluoride and sodium chloride lower the redox potential of Mn(III)-Mn(II) couple. This may be attributed to the displacement of coordinated SO_4^{2-} ligand leading to the establishment of a new Mn(III)-Mn(II) couple with $P_2O_7^{4-}$, F^-, or Cl^- as ligands.

Dependence of the Rate on Dielectric Constant of Solvent and Ionic Strength

The dielectric constant (or permittivity, D) of solvent medium was altered by the addition of HOAc to the reaction mixture (0–15% v/v). The rate decreased with increase in HOAc content of solvent (Table IV) and a plot of log k_{obs} vs 1/D was linear with a negative slope ($r = 0.998$). The reaction was studied at varying ionic strength. The rate decreased with increase in ionic strength, indicating a negative salt effect (Table IV).

Table IV Effect of Dielectric Constant of Solvent and Ionic Strength on the Rate of Oxidation of Serine by Manganese(III) in Sulfate Medium (Other conditions are as in Table II)

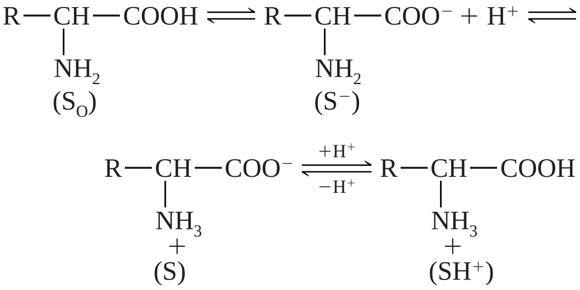
% of HOAc (v/v)	10^3 k_{obs} ($dm^{3/2}$ $mol^{-1/2}$ s^{-1})	I (mol dm^{-3})	10^3 k_{obs} ($dm^{3/2}$ $mol^{-1/2}$ s^{-1})
—	6.56	6.00	6.97
5.0	5.81	6.24	6.56
10.0	5.24	6.50	6.21
15.0	4.94	7.00	4.82
		7.50	4.23

Dependence of the Rate on Temperature

The reaction was studied at different temperatures (313–328K) (Table V) and the activation parameters were computed from Arrhenius-Eyring plots (Table VI).

The Mn(III)-ser reaction stoichiometry of 2 : 1 was observed as in eq. (2).

Amino acids are known to exist in the following equilibria depending upon acidity or basicity of the solution:



$$\underset{(S_O)}{R-\underset{NH_2}{\underset{|}{CH}}-COOH} \rightleftharpoons \underset{(S^-)}{R-\underset{NH_2}{\underset{|}{CH}}-COO^-} + H^+ \rightleftharpoons$$

$$\underset{(S)}{R-\underset{\underset{+}{NH_3}}{\underset{|}{CH}}-COO^-} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} \underset{(SH^+)}{R-\underset{\underset{+}{NH_3}}{\underset{|}{CH}}-COOH}$$

where S is a dipolar/zwitter ion of the amino acid.

Table V Pseudo One-and-a-Half-Order Rate Constants (k_{obs}) for the Oxidation of Serine by Manganese(III) Sulfate at Different Temperatures (Other conditions are as in Table II)

T (K)	10^3 k_{obs} ($dm^{3/2}$ $mol^{-1/2}$ s^{-1})
313	1.82
318	3.55
323	6.56
328	12.88

Table VI Comparison of Kinetic Data and Activation Parameters for the Oxidation of Serine by Manganese(III) in Acetate, Pyrophosphate and Sulfate Media

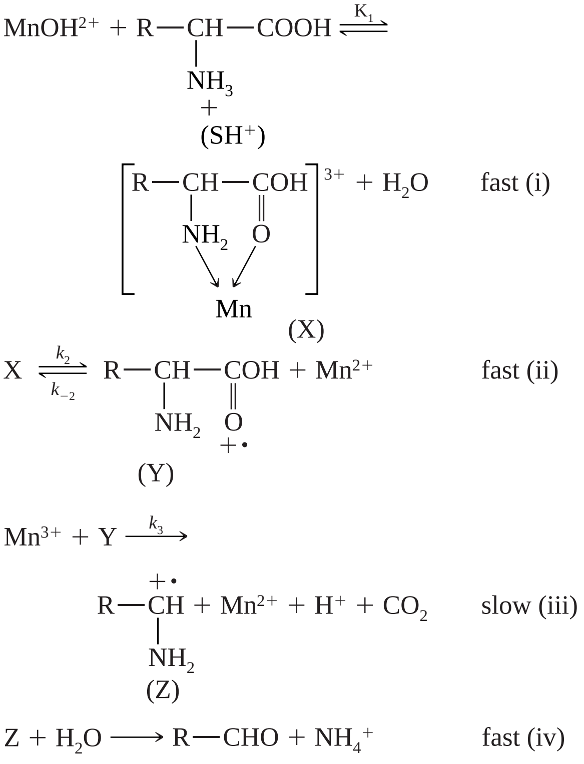
Medium Studied	Observed order [Mn(III)]	[ser]	[Mn(II)]	[H$^+$]	Ref
HOAc	0.5	1	0	−0.46	13
Pyrophosphate	1.0	1	−0.77	0.90	13
H_2SO_4	1.5	1	−1.74	−1.07	This work

	logA	E_a (kJ mol^{-1})	ΔH‡ (kJ mol^{-1})	ΔS‡ (JK^{-1} mol^{-1})	ΔG‡ (kJ mol^{-1})	Ref
HOAc	7.9	81.2	61.1	−156.2	111.7	13
Pyrophosphate	4.4	59.8	60.9	−158.0	112.7	13
H_2SO_4	15.1	107.2	103.4	−24.7	111.4	This work

It has been assumed that Mn(III) species present in aqueous sulfuric acid medium are Mn^{3+}(aq), $Mn(OH)^{2+}$(aq), and $MnSO_4^+$(aq), due to the existence of the following equilibrium:

$$MnOH^{2+}(aq) + HSO_4^-(aq) \rightleftharpoons MnSO_4{}^+_{(aq)} + H_2O \quad (4)$$

Since the effect of HSO_4^- on the reaction is negligible, Mn^{3+}(aq) and $Mn(OH)^{2+}_{(aq)}$ species become important, as reported for many Mn(III) reactions [6–10,12]. In view of this, the proposed mechanism is shown in Scheme I.



Scheme I

Here, R = $-CH_2OH$, SH^+ is protonated serine, X is a metal-serine intermediate and Y and Z are transient free radical cationic species.

Based on the slow step in Scheme I, the overall rate of oxidation of serine is given by

$$\text{rate} = -d[\mathrm{Mn(III)}]/dt = k_3[\mathrm{Mn}^{3+}][\mathrm{Y}] \quad (5)$$

Substitution for [X], from equilibrium (i) in the steady state equation for [Y] leads to eq. (6).

$$[\mathrm{Y}] = K_1k_2[\mathrm{Mn}^{3+}][\mathrm{SH}^+]/[\mathrm{H}^+]\{k_{-2}[\mathrm{Mn}^{2+}] + k_3[\mathrm{Mn}^{3+}]\} \quad (6)$$

Substitution for [Y] in Equation (5) leads to the following rate law:

$$\text{rate} = K_1k_2k_3[\mathrm{Mn(III)}]^2[\mathrm{ser}]/[\mathrm{H}^+]\{k_{-2}[\mathrm{Mn(II)}] + k_3[\mathrm{Mn(III)}]\} \quad (7)$$

The rate law is consistent with the observed kinetic data: first-order in [ser], one-and-a-half-order in [Mn(III)], a negative first-order in [H$^+$], and a negative fractional-order in [Mn(II)].

The reaction rate in D_2O medium usually decreases in acid inhibiting reactions. It is well known that D_3O^+ ion [16] is a stronger acid than H_3O^+ ion by a factor of 2–3. The present observations substantiate this view and also indicate a fast pre-equilibrium proton transfer [21]. The rate constant k_{H2O} was 6.56 × 10^{-3} s^{-1} while k_{D2O} was 4.24 × 10^{-3} s^{-1} leading to the solvent isotope effect, k_{H2O}/k_{D2O} = 1.55 and justifying the proposed mechanism.

It is observed that the addition of complexing anions such as $P_2O_7^{4-}$, Cl^-, and F^- decreased the rate of reaction by decreasing the redox potential. This may be attributed to the displacement of the coordinated ligand by the anion leading to the establishment of a new Mn(III)-Mn(II) couple. The HSO_4^- and SO_4^{2-} ions had a negligible effect on the redox potential and on the reaction rate.

It is seen from Table VI, highly negative values of ΔS‡ in the case of acetate and pyrophosphate media indicated the formation of a more rigid transition state while the relatively higher $\Delta S^{\ddagger}$ value in sulfuric acid medium indicated a moderately rigid transition state.

Spectral Evidence for Mn(III)-Serine Complex Formation in Solution

The UV-Vis spectrum of pure manganese(III) has λ_{max} at 490 nm. When serine is mixed with manganese(III), the maximum shifts to 482 nm, suggesting the complex formation between manganese(III) and serine.

CONCLUSIONS

The kinetic data of the oxidation of L-serine by Mn(III) species in different media are summarized in Table VI. It is found that the kinetic orders with respect to [Mn(III)] vary: an half-order in acetate, a first-order in pyrophosphate, and one-and-a-half-order in sulfate media, respectively. This indicates that different species of Mn(III), $Mn(OAc)_4^-$, $Mn(H_2P_2O_7)_3^{3-}$ and $MnOH^{2+}$ are the species present in acetate, pyrophosphate, and sulfate media, respectively. The order in [ser] is generally one in all cases. The dependencies on [Mn(II)] are: an inverse fractional order each in pyrophosphate and sulfate media and a zero-order in acetate medium. The other features include the varying dependence on $[H^+]$: inverse fractional-order in acetate, an inverse first-order in sulfate and a fractional-order in pyrophosphate medium.

One of the authors (SC) is grateful to the management, Bharathi Education Trust, Bharathi Nagar, for permission to work in the Department of Chemistry, University of Mysore, Manasagangotri, Mysore, India.

BIBLIOGRAPHY

1. Boucher, J. Coord Chem Rev 1969, 7, 289.
2. Calvin, M. Rev Pure Appl Chem 1965, 15, 1.
3. Ramakrishnan, K.; Shankaran, K. R.; Srinivasan, V. S. Indian J Chem 1990, 29A, 843.
4. Bhat, K. I.; Sherigara, B. S. Transition Met Chem 1994, 19, 178.
5. Bhat, K. I.; Sherigara, B. S.; Pinto, I. Indian J Chem 1994, 33A, 42.
6. Beg. M. A.; Kamaluddin. Acta Chimica 1975, 86, 3625.
7. Varadarajan, R.; Joseph, M. Indian J Chem 1980, 19A, 1977.
8. Pinto, I.; Sherigara, B. S.; Udupa, H. V. K. Bull Chem Soc Jpn 1990, 63, 3625.
9. Kamaluddin. Indian J Chem 1980, 19A, 431.
10. Ramachandran, M. S.; Vivekanandan, T. S.; Khadar, S. S. Indian J Chem 1984, 23A, 379.
11. Sherigara, B. S.; Bhat, K. I.; Pinto, I. Amino Acids 1995, 8, 291.
12. Sherigara, B. S.; Bhat, K. I.; Pinto, I.; Made Gowda, N. M. Int J Chem Kinet 1995, 27, 675.
13. Chandraju, S.; Sherigara, B. S.; Made Gowda, N. M. Int J Chem Kinet 1994, 26, 1105.
14. Rangappa, K. S.; Chandraju, S.; Mahadevappa, D. S. Transition Met Chem 1996, 21, 519.
15. Chandraju, S.; Rangappa, K. S.; Mahadevappa, D. S. Proc Natl Acad Sci India 1996, 66A, 235.
16. Chandraju, S.; Mahadevappa, D. S.; Rangappa, K. S. Indian J Chem 1997, 36A, 974.
17. Chandraju, S.; Mahadevappa, D. S.; Rangappa, K. S.; Made Gowda, N. M. Synth React Inorg Met-Org Chem 1997, 28(9), 1329.
18. Rangappa, K. S.; Chandraju, S.; Made Gowda, N. M. Int J Chem Kinet 1998, 30, 7.
19. Vogel, A. I. Qualitative Organic Analysis; Longman and Green: London, 1958; p 708.
20. Kemp, T. J.; Waters, J. J Chem Soc 1996, 336.
21. Collins, C. J.; Bowman, N. S. Isotopic Effects in Chemical Reactions; Van Nostrand: New York, 1970; p 267.