Amino Acids (2010) 38:789–795
DOI 10.1007/s00726-009-0285-0

ORIGINAL ARTICLE

Kinetic and mechanistic study of oxidation of L-methionine by Waugh-type enneamolybdomanganate(IV) in perchloric acid

V. M. Gurame · A. R. Supale · Gavisiddappa S. Gokavi

Received: 12 October 2008 / Accepted: 24 March 2009 / Published online: 15 April 2009

Abstract The reaction between methionine and enneamolybdomanganate(IV) in perchloric acid was carried out under pseudo-first-order conditions keeping large excess of methionine. The orders in oxidant and substrate were found to be unity and 0.91, respectively. The reaction proceeds with rapid formation of complex between the reactants followed by its decomposition in a rate determining step. The accelerating effect of hydrogen ions on the reaction is due to the formation of active hexaprotonated oxidant species. The product of the reaction was found to be methionine sulfoxide. The reaction involves direct two-electron transfer step without any free radical intervention. The effect of ionic strength, solvent polarity and the activation parameters were also in support of the mechanism proposed.

Keywords Kinetics · Mechanism · Oxidation · Methionine · Waugh-type enneamolybdomanganate(IV)

Introduction

Molybdenum is found in several tissues of human body and is required for the activity of some enzymes which are involved in the catabolism of purines and sulfur containing amino acids. Methionine is a sulfur containing amino acid which is involved in the wide range of biochemical reactions. Although methionine has three co-ordinating centers, viz., O, N and S, it has been reported by McAuley and coworkers that the sulfur is more susceptible to attack by oxidants like Cr^{VI} (Olatunji and McAuley 1977; McAuley and McCann 1975). Methionine, a thioether containing amino acid behaves differently than other amino acids towards many oxidants (Sharma et al. 1996; Mahadevappa et al. 1985), due to the presence of electron rich sulfur which is easily oxidizable. Oxidations of different amino acids by manganese are of special significance because of their biological relevance (Boucher 1972). Molybdenum forms clusters with the sulfur compounds; these clusters are also important in enzyme catalysis (George et al., 2000).

Chemistry of heteropoly acids received much attention in the recent past due to their applications in biochemistry and material chemistry (Katsoulis 1998; Sadakane and Steckhan 1998). These polyoxometalate salts are used (Katsoulis 1998; Sadakane and Steckhan 1998; Weinstock 1998) as oxidants and catalysts (both redox and acid) for various organic transformations. Tunable physical properties like redox potential and acidity of transition metal substituted heteropolyoxometalates make them attractive from catalytic and electrocatalytic point of view (Kozhevnikov 1998). Most of the electron transfer reactions of polyoxometalate (POM) anions and their mechanistic studies are concentrated (Ayoko 1990; Hasure and Gokavi 2003; Saha et al. 1988; Mehrotra and Mehrotra 2003; Satpathy et al. 2006; Bhosale and Gokavi 2003, 2004a, b, 2006; Baciocchi et al. 1996a, b; Shah et al. 1999; Goyal et al. 1998; Dholia et al. 1997), on the Keggin type salts containing hetero atom in its higher oxidation state. Varieties of organic and inorganic substrates have also been oxidized (Sadakane and Steckhan 1998), by these POMs and the mechanisms generally follow outer-sphere pathway. POMs contain a hetero atom which is surrounded by number of oxoanions; thus, making the central hetero atom

---

V. M. Gurame · A. R. Supale · G. S. Gokavi (✉)
Kinetics and Catalysis Laboratory, Department of Chemistry,
Shivaji University, Kolhapur 416004, India
e-mail: gsgokavi@hotmail.com

unavailable for the inner sphere interaction with the substrate. In comparison with Keggin and Dawson type of salts, less attention is given to other type of POM anions. In continuation of our interest (Hasure and Gokavi 2003; Bhosale and Gokavi 2003, 2004a, 2004b, 2006; Gurame and Gokavi 2008), in the electron transfer reactions involving POMs, the present study of oxidation of methionine by enneamolybdomanganate(IV), a Waugh-type heteropolyacid, was carried out in perchloric acid medium. Enneamolybdomanganate(IV) contains one MnO_6 unit surrounded by nine MoO_6 octahedra. The redox potential of the Mn^{IV}/Mn^{II} couple also decreases (Dunne et al. 1992) from 1.51 to 1.035 V at pH 3.94 in presence of molybdate ions leading to the formation of POM; thus, making the Mn^{IV} ion stable in aqueous solution.

Therefore, the oxidation of methionine by enneamolybdomanganate(IV) ion was undertaken to understand the mechanism of the reaction as both the ions are prone to form complex with molybdate ion. Methionine has been oxidized by various oxidants (Gensch and Higuchi 1967; Young and Hsich 1978; Mansour 2002; Natile et al. 1975; Johnson and Read 1996), and the mechanisms generally involve formation of a complex between the two reactants. The polyoxometalates like enneamolybdomanganate(IV) are considered as outer-sphere electron transfer reagents; therefore, it would be of interest to understand the mechanism of title reaction between two redox centers interacting with molybdate ion.

Materials and methods

All the solutions were prepared in doubly distilled water. The solution of L-methionine was prepared by dissolving methionine (SD Fine) in water and standardized by reported method (Lavine 1993). The solution of sodium thiosulphate was freshly prepared every day and standardized against standard potassium dichromate solution iodometrically (Vogel 1961). Enneamolybdomangnate complex $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$ was prepared by reported method (Baker and Weakly 1966) as follows: 50 g of ammonium molybdate was dissolved in 200 ml of water and excess of hydrogen peroxide as oxidant was added to it and the resultant solution was heated to 95°C. To this hot solution, 5 g of $MnSO_4{\cdot}H_2O$ in 50 ml of water was added slowly with constant stirring. The resultant orange-red colored solution was boiled for 10 min and quickly filtered and cooled. The orange-red colored crystals were recrystalized thrice from hot (70°C) water. The solution of $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$ was standardized by treating known amount of complex solution with excess of As^{III}, and back titrating As^{III}. The oxidation state of hetero atom was also confirmed to be four, by iodometric method.

Kinetic measurements

The reaction between $[Mn^{IV}Mo_9O_{32}]^{6-}$ and methionine was studied under pseudo-first-order conditions at a constant temperature of 26.0 ± 0.1°C. The reaction was initiated by mixing the previously thermostated solutions of methionine and $[Mn^{IV}Mo_9O_{32}]^{6-}$, which also contained the required amount of perchloric acid, and doubly distilled water. The reaction was followed by determining the concentration of remaining $[Mn^{IV}Mo_9O_{32}]^{6-}$ iodometrically. The pseudo-first-order rate constants were determined from the plots of log $[Mn^{IV}Mo_9O_{32}]^{6-}$against time and the rate constants were reproducible within ±6%.

Atomic absorption analysis

The complex $(NH_4)_6[Mn^{IV}Mo_9O_{32}]{\cdot}3H_2O$, was analyzed by AAS. The solution for AAS analysis was prepared by dissolving 100 mg of recrystalized sample in double distilled water and 5 ml of this stock solution was diluted to 100 ml. The diluted solution was used for AAS analysis of Mn and Mo using Perkin–Elmer AAnalyst-300 instrument. The complex $(NH_4)_6[Mn^{IV}Mo_9O_{32}]{\cdot}3H_2O$ shows (theoretical): Mn, 3.501% (3.4493%) and Mo, 54.217% (54.2125%).

Spectrophotometric measurements and FTIR-spectral study

The visible spectra of $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$ complex, and the reaction mixture were recorded by using Elico SL-177 spectrophotometer between the wavelength region 400–650 nm. The spectrum of the reaction mixture at various time intervals is shown in Fig. 1.

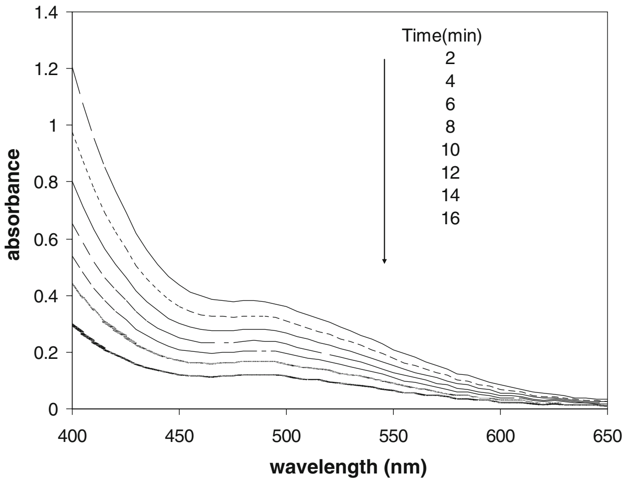


Fig. 1 The spectra of the reaction mixtures at different time intervals at 26°C $10^3[Mn^{IV}Mo_9O_{32}]^{6-} = 1.8$ mol dm^{-3}, 10^2[Methionine] = 3.0 mol dm^{-3} 10[$HClO_4$] = 3.5 mol dm^{-3}

The FTIR-Spectra of $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$ complex was taken in KBr by using Perkin–Elmer Spectrumone spectrophotometer. The complex $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$ contains Mn^{IV} as a hetero atom surrounded by octahedral groups of $MoO_6{}^{2-}$. In the IR-spectrum of Mn^{IV} complex, the peaks obtained at 3521, 933, 918 and 900 cm^{-1} corresponds to lattice water molecules (Nakamoto 1977), Mo–O stretching (Martin et al. 2004), Mn^{IV}–O stretching and tetrahedral $MoO_4{}^{2-}$ groups (Nakamoto 1977), respectively.

Test for free radicals

The reaction was also studied in presence of added acrylonitrile to understand the intervention of free radicals (Kolthoff et al. 1953; Mahesh et al. 2004), in the reaction. There was no effect of added acrylonitrile on the reaction and also no precipitate due to the polymerization of the added acrylonitrile was observed thus confirming the absence of any free radical formation in the reaction.

Results and discussion

Stoichiometry and product analysis

The stoichiometry was studied by keeping concentration of $[Mn^{IV}Mo_9O_{32}]^{6-}$ constant at 5×10^{-3} mol dm^{-3} and varying concentration of methionine from 0.5×10^{-3} to 3.0×10^{-3} mol dm^{-3}. Different reaction mixtures containing varying concentration of methionine were prepared, which also contained required amount of perchloric acid. The concentration of unreacted $[Mn^{IV}Mo_9O_{32}]^{6-}$ was determined after 24 h iodometrically as well as spectrophotometrically at 468 nm. The stoichiometry was found to be one mole of $[Mn^{IV}Mo_9O_{32}]^{6-}$ per mole of methionine. The reaction mixture containing excess of oxidant was kept undisturbed up to 24 h and the complete disappearance of amino acid was confirmed by thin layer chromatography. The product methionine sulfoxide was isolated from the reaction mixture by reported method (Natile et al. 1975). Acetone–ethanol (1:1 volume ratio) was added to the reaction mixture previously brought to pH 4 by adding sodium bicarbonate and precipitated methionine sulfoxide was identified by its melting point (Natile et al. 1975).

Reaction order

The reaction was carried out under pseudo-first-order conditions, keeping the concentration of perchloric acid constant at 0.35 mol dm^{-3} and varying either methionine from 0.01 to 0.077 mol dm^{-3} at constant $[Mn^{IV}Mo_9O_{32}]^{6-}$ (1.8×10^{-3} mol dm^{-3}) or $[Mn^{IV}Mo_9O_{32}]^{6-}$ from 2.2×10^{-4} to 1.8×10^{-3} mol dm^{-3} at constant methionine (3.0×10^{-2} mol dm^{-3}). The pseudo-first-order rate constants were found to be increased with increase in the concentration of the reductant (Table 1) and the order was found to be 0.91 as determined by log (k_{obs}) against log [methionine] plot. The order in oxidant concentration was found to be unity as the pseudo-first-order plots were found to be linear and the pseudo-first-order rate constants were fairly constant as the concentration of oxidant is varied (Table 1). Added molybdate ion over the concentration range of 0.1×10^{-2} to 1.0×10^{-2} mol dm^{-3} did not affect the rate of reaction.

Effect of hydrogen ion concentration

The effect of hydrogen ion concentration on the reaction was studied to know probable prior protonation equilibria

Table 1 Effect of concentration of methionine, perchloric acid and enneamolybdomanganate(IV) ion, on the reaction between methionine and enneamolybdomanganate(IV) at 26°C

$10^3[Mn^{IV}Mo_9O_{32}]^{6-}$ (mol dm^{-3})	$10[HClO_4]$ (mol dm^{-3})	10^2[Methionine] (mol dm^{-3})	$10^3\ k_{obs}\ s^{-1}$
0.22	3.5	3.0	1.3
0.45	3.5	3.0	1.4
0.9	3.5	3.0	1.3
1.3	3.5	3.0	1.3
1.8	3.5	3.0	1.4
1.8	3.5	1.0	0.6
1.8	3.5	2.0	1.0
1.8	3.5	3.0	1.4
1.8	3.5	5.0	2.2
1.8	3.5	7.7	3.7
1.8	0.38	3.0	0.2
1.8	0.7	3.0	0.4
1.8	1.9	3.0	0.7
1.8	3.5	3.0	1.4

of either the oxidant or the substrate and to identify the active reactant species. The concentration of H^+ ion was varied from 0.0385 to 0.35 mol dm^{-3} keeping all other concentrations constant. It was found that the reaction rate increases with the concentration of H^+ ions (Table 1) and the graph of k_{obs} against $[H^+]$ was found to be linear without intercept (Fig. 2) and the order in $[H^+]$ was found to be 0.9.

Effect of solvent polarity, ionic strength and temperature

The effects of ionic strength, solvent polarity and temperature were studied keeping concentration of $[Mn^{IV}Mo_9O_{32}]^{6-}$, methionine and perchloric acid constant at 1.8×10^{-3}, 0.03 and 0.35 mol dm^{-3}, respectively, at 26°C. Sodium perchlorate and acetonitrile were used to vary the ionic strength and solvent polarity, respectively. The rate of the reaction was found to be increased as ionic strength increases from 0.39 to 0.75 mol dm^{-3}. The rate of reaction decreases as percentage of acetonitrile increases from 0 to 57% v/v. This decrease in the rate with decrease in the dielectric constant is in conformity with Amis concept for ion–dipole interactions. The effect of temperature was studied at 15, 20, 26, 30 and 35°C and the activation parameters were determined $\Delta H^{\#} = 46.78 \pm 6$ $kJmol^{-1}$, $\Delta G^{\#} = 55.50 \pm 6$ kJ mol^{-1}, $\Delta S^{\#} = -30.18 \pm 5$ JK^{-1} mol^{-1}.

The order in methionine concentration was found to be close to unity (0.91) and the pseudo-first-order plots were linear as well as the pseudo-first-order rate constants were constant as the concentration of oxidant was increased indicating an order of unity in its concentration also. Therefore, the mechanism of the reaction involves prior interaction between the oxidant and methionine. Since, the added molybdate ion did not influence the rate of the reaction, there is no possibility of a prior equilibrium involving it. The oxidant, $[Mn^{IV}Mo_9O_{32}]^{6-}$, is a heteropolyoxometalate of Mn^{IV} and molybdate ion; the effect of added molybdate ion signifies the stability of the $[Mn^{IV}Mo_9O_{32}]^{6-}$ ion under experimental conditions of the reaction.

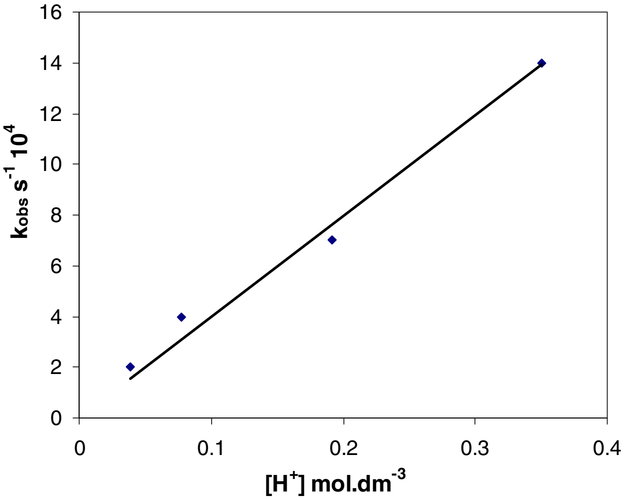


Fig. 2 Plot of k_{obs} against $[H^+]$(conditions as in Table 1)

Enneamolybdomanganate(IV) is one of the stable heteropolymolybdate containing Mn^{IV} as a hetero atom and is noncentrosymmetric. It also shows a characteristic charge transfer band at 468 nm which has been assigned to $^4A_{2g} \rightarrow {}^4T_{2g}$ transition of Mn^{IV}. This band is sensitive (Saito et al. 1997), to the changes in the electronic state of the Mn^{IV} ion and any perturbations due to interaction of MnO_6 groups with neighboring ions will result in the shift of band. The arrangements of oxygen atoms (Saito et al. 1997), around $[MnMo_9O_{32}]^{6-}$ are of two different types A and B as shown in the Fig. 3. The negative charge of the oxygen atoms at site A is greater than that of the oxygen at site B. From the spectrophotometric investigation (Saito et al. 1997), on interaction of various cations with the anion, it was concluded that metal cations will bind to site A due to their larger negative charge in comparison with that of site B. Such type of cation interaction at site A perturbs the electronic state of the central hetero atom, manganese, resulting in change of absorption spectra of the anion. In aqueous solution the UV–VIS spectrum of the

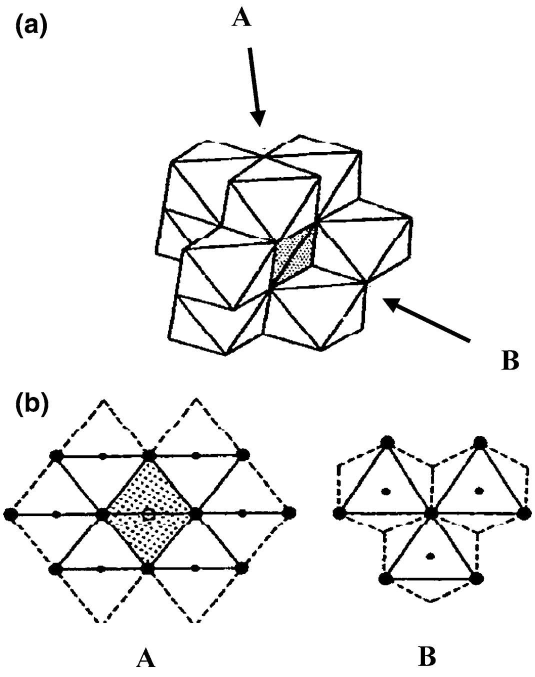
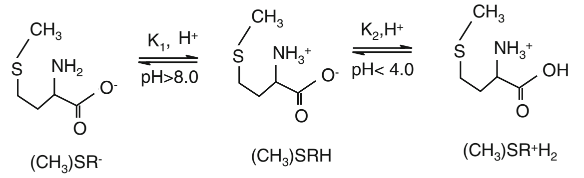


Fig. 3 Arrangements of oxygen atoms in $[MnMo_9O_{32}]^{6-}$ (from reference Saito et al., 1997). **a** Structure of the $[MnMo_9O_{32}]^{6-}$ anion. (*shaded octahedron* in **a** is MnO_6). **b** Two arrays of oxygen atoms as the potential metal binding sites. (*large solid circles* in **b** are oxygen atoms, *small solid circles* are Mo atoms and an *open circle* is a Mn atom.)

anion, $[MnMo_9O_{32}]^{6-}$, shows a peak at 468 nm and in presence of acid two isosbestic points are obtained at 435 and 520 nm due to its protonation. At high metal ion concentrations, the peak at 468 nm reappeared (Saito et al. 1997) as a result of metal ion substitution on the anion at oxygen atoms of A type. In order to understand the interaction between the methionine and $[MnMo_9O_{32}]^{6-}$, UV–VIS spectra of the reaction mixture was examined. The anion shows a characteristic peak at 468 nm in aqueous solution and in 0.35 mol dm^{-3} perchloric acid the spectrum of protonated anion contain two isosbestic points at 435 and 520 nm due to its protonation. To an acidic solution of the anion when methionine is added the reappearance of peak at 468 nm was not observed which is expected if the interaction of added methionine would have been through oxygen atoms of site A. Therefore, the methionine is interacting with the anion, $[MnMo_9O_{32}]^{6-}$, through the oxygen atoms of site B without perturbing the electronic state of MnO_6 octahedra. The spectra of the reaction mixtures at different time intervals are given in Fig. 1 which indicates the decrease in absorbance of the anion as the reaction proceeds.

The dependence of rate of the reaction on hydrogen ion concentration is shown in Table 1 and the order in its concentration was found to be 0.9 as found from the plot of log k_{obs} against log $[H^+]$ plot. The plot of k_{obs} against $[H^+]$ is also found to be linear (Fig. 2). The order of close to unity in $[H^+]$ indicates a prior protonation equilibrium. The pK_a values of the methionine are 2.22, 9.27 (Weast et al. 1986), corresponding to the protonation of amino and carboxylic acid groups. In strongly acidic medium, the carboxylic acid group remains un-dissociated and the amino group is also protonated bellow pH 4 as shown in Eq. 1. Therefore, under the present reaction conditions methionine exists completely in the $(CH_3)SR^+H_2$.



(1)

The pK_a of the anion, $[MnMo_9O_{32}]^{6-}$, is reported (Saito et al. 1997), to be around 3.0 and at pH = 2 approximately 90% of the anion is totally protonated and it is completely deprotonated at pH = 4. Therefore, at a pH bellow 2, used in the present study, the accelerating effect of hydrogen ion can be accounted due to the formation of hexaprotonated, $H_6[MnMo_9O_{32}]$, anion in a prior equilibrium between hydrogen ion and the pentaprotonated, $H_5[MnMo_9O_{32}]^-$, anion. Therefore, under the reaction conditions employed in the present study the hexaprotonated anion, $H_6[MnMo_9O_{32}]$, and the protonated methionine are the reactive species.

Under the pseudo-first-order condition, methionine is oxidized to methionine sulfoxide only. Oxidation product of methionine depends upon the oxidants, with some oxidants it is oxidized to sulfoxide stage (Gensch and Higuchi 1967; Young and Hsich 1978; Mansour 2002; Natile et al. 1975), and with certain others it is oxidized to sulfone stage (Mahadevappa et al. 1983; Wani et al. 1994). In all these reactions, electrophilic attack of oxidant take place at sulfur site due to the higher electronegativity of S rather than O and N. The stoichiometry of the reaction was found to be 1:1 in presence of excess of enneamolybdomanganate(IV) when analyzed after 24 h. The mechanism for the formation of methionine sulfoxide reaction product with the observed stoichiometry 1:1 can be represented as in Scheme 1 in terms of the active species of the reactants. The mechanism of the reaction represented in Scheme 1 involves a complex formation between the substrate and the oxidant through electrophilic attack of the oxidant on the nucleophilic sulfur atom of methionine. The product of the reaction under present conditions is methionine sulfoxide only and further oxidation does not takes to the sulfone stage even in presence of stoichiometrically excess oxidant as noticed in the product analysis. The nucleophilicity of the sulfur atom in the methionine sulfoxide decreases as it binds to an oxygen atom, thus retarding the attack of the electrophilic oxidant which prevents the further oxidation to the corresponding sulfone. The formation of polyoxometalate around a hetero atom like Mn(IV) also reduces its oxidizing capacity of form 1.51–1.03 V(Dunne et al. 1992) thus making it a mild oxidant which also

Scheme 1

$$H_5[Mn^{IV}Mo_9O_{32}]^- + H^+ \overset{K_3}{\rightleftharpoons} H_6[Mn^{IV}Mo_9O_{32}]$$

$$H_6[Mn^{IV}Mo_9O_{32}] + (CH_3)SR^+H_2 \overset{K_c}{\rightleftharpoons} \text{Complex}$$

$$\text{Complex} + H_2O \xrightarrow{k_1} (CH_3)SOR^+H_2 + H_4[Mn^{II}Mo_9O_{32}] + 4H^+$$

$$H_4[Mn^{II}Mo_9O_{32}] + 4H_2O \xrightarrow{\text{fast}} Mn^{II} + 9HMoO_4^- + 3H^+$$

renders further oxidation of the sulfoxide to the sulfone difficult. The methionine sulfoxide is also reported to be stable towards its oxidation to sulfone by stronger oxidizing agents like permanganate and Mn(IV) (Satsangi et al. 1995), also. Therefore, in view of decrease in the nucleophilicity of the sulfur atom and decrease in the oxidizing power of the oxidant the reaction stops only at methionine sulfoxide. The corresponding rate law according to Scheme 1 also considering protonation equilibrium of the oxidant and substrate is given by Eq. 2 and the corresponding pseudo-first-order rate constant k_{obs}, value by Eq. 3. Since the value of K_3 is of the order of 1.0×10^{-3} dm^3 mol^{-1}, the term containing K_3 in the denominator of Eq. 3 can be neglected and then the plot of k_{obs} against [H$^+$] will be a linear as obtained in Fig. 2 thus verifying the rate law.

$$\text{Rate} = \frac{k_1 K_c K_3 \left[\text{H}_5\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}\right]^- \left[(\text{CH}_3)_2\text{SR}^+\text{H}_2\right]\left[\text{H}^+\right]}{\left(1 + K_3[\text{H}^+]\right)} \tag{2}$$

$$k_{obs} = \frac{k_1 K_c K_3 \left[(\text{CH}_3)_2\text{SR}^+\text{H}_2\right]\left[\text{H}^+\right]}{\left(1 + K_3[\text{H}^+]\right)} \tag{3}$$

The mechanism according to Scheme 1 proceeds with the rapid formation of a complex between the methionine and $[\text{H}_6\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]$ and subsequent rate determining decomposition of complex to give methionine sulfoxide and $[\text{Mn}^{\text{II}}\text{Mo}_9\text{O}_{24}]^{10-}$. The interaction between methionine and $[\text{H}_6\text{MnMo}_9\text{O}_{32}]$ during complex formation occurs through the oxygen atoms of the site B. The reduced polyoxometalate, $[\text{Mn}^{\text{II}}\text{Mo}_9\text{O}_{24}]^{10-}$, undergoes fast decomposition to generate aqueous Mn^{2+} ion and molybdate ions. In an earlier ESR study the interaction between aqueous Mn^{2+} and molybdate ions was examined and the alteration of linewidth of the Mn^{2+} signal in presence of molybdate (Dunne et al. 1993) was found to be comparable with that in presence of acetate ions. From this result, it has been concluded that the interaction between molybdate ions and Mn^{2+} ions in aqueous solutions is weak. Therefore, the dissociation of the $[\text{Mn}^{\text{II}}\text{Mo}_9\text{O}_{24}]^{10-}$ under the present reaction conditions is considered to be fast. Acrylonitrile, free radical scavenger, did not affect the reaction rate indicates direct two-electron transfer from methionine to $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$. The effect of ionic strength and the solvent polarity on the rate qualitatively explains the reaction involves charged species. The moderate values of $\Delta H^{\#} = 46.78 \pm 6$ kJmol^{-1}, $\Delta G^{\#} = 55.50 \pm 6$ kJ mol^{-1}, $\Delta S^{\#} = -30.18 \pm 5$ JK^{-1} mol^{-1} were favorable for electron transfer processes. The negative value of $\Delta S^{\#}$, can be ascribed to the nature of electron pairing and unpairing processes and to the loss of degrees of freedom formerly available to the reactants upon the formation of transition state.

References

Ayoko GA (1990) Oxidations of hypophosphorus and arsenious acids by 12-tungstocobaltate(III) anion in aqueous solution. Transit Met Chem 15:421–424. doi:10.1007/BF01040768

Baciocchi E, Bietti M, Steenken S (1996a) Reactivity of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ with organic radicals in aqueous solution. Evidence for electron transfer mechanism. J Chem Soc Perkin Trans 2:1261–1263. doi:10.1039/p29960001261

Baciocchi E, Putignani M, Steenken S (1996b) Side-chain fragmentation of arylalkanol radical cations. Carbon–carbon and carbon–hydrogen bond cleavage and the role of α-and β-OH groups. J Am Chem Soc 118:5952–5960. doi:10.1021/ja954236s

Baker LCW, Weakly TJR (1966) The stabilities of 9-molybdomanganate (IV) ions. J Inorg Nucl Chem 28:447–454. doi:10.1016/0022-1902(66)80324-X

Bhosale BD, Gokavi GS (2003) Kinetics and mechanism of oxidation of antimony (III) by Keggin type 12-tungstocobaltate (III) in aqueous hydrochloric acid. Int J Chem Kinet 35:9–14. doi:10.1002/kin.10097

Bhosale BD, Gokavi GS (2004a) Oxidation of arsenous acid by 12-tungstocobaltate (III) catalysed by ruthenium(III) in aqueous acid medium. Inorg React Mech 5(2):79–85

Bhosale BD, Gokavi GS (2004b) Outer-sphere electron transfer from platinum(II) to Keggin-type 12-tungstocobaltate(III) in presence and absence of chloride ions. Indian J Chem A 43:799–802

Bhosale BD, Gokavi GS (2006) Kinetics and mechanism of oxidation of arsenous acid by Waugh-type enneamolybdomanganate(IV). Indian J Chem A 45:398–401

Boucher LJ (1972) Manganese porphyrin complexes. Coord Chem Rev 7:289–329. doi:10.1016/S0010-8545(00)80024-7

Dholia S, Prakash A, Mehrotra RN (1997) Kinetics of oxidation of thioacids by tetrabutylammonium-12-tungstocobaltate(III) ion in dimethyl sulphoxide medium. Indian J Chem A 36:959–963

Dunne SJ, Burns RC, Hambey TW, Lawrance GA (1992) Oxidation of manganese(II) by peroxomonosulfuric acid in aqueous solution in the presence of molybdate. Crystal-structure of the $\text{K}_6[\text{MnMo}_9\text{O}_{32}]\cdot6\text{H}_2\text{O}$ product. Aust J Chem 45:685–693

Dunne SJ, Irwin JA, Burns RC, Lawrance GA (1993) Reaction kinetics and mechanism of formation of $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ by hypochlorous acid oxidation of Mn^{2+} (aq) in the presence of molybdate. J Chem Soc Dalton Trans 18:2717–2726. doi:10.1039/dt9930002717

Gensch KH, Higuchi T (1967) Kinetic investigation of reversible reaction between methionine and iodine. Improved iodometric determination of methionine. J Pharm Sci 56:177–184. doi:10.1002/jps.2600560205

George GN, Pickering IJ, Yu EY, Prince RC, Bursakov RC, Gavel OY, Moura I, Moura JJG (2000) A novel protein-bound copper-molybdenum cluster. J Am Chem Soc 122:8321–8322. doi:10.1021/ja000955h

Goyal B, Prakash A, Mehrotra RN (1998) Kinetics and mechanism of the oxidation of thiolactic acid by 12-tungstocobaltate(III) ion in acetate buffer. Indian J Chem A 37:973–979

Gurame VM, Gokavi GS (2008) Kinetics and mechanism of oxidation of hypophosphite by enneamolybdomanganate(IV) in perchloric acid. Polyhedron 27:1905–1910. doi:10.1016/j.poly.2008.02.028

Hasure AM, Gokavi GS (2003) Ruthenium(III)-catalyzed oxidation of thallium(I) by 12-tungstocobaltate(III) in hydrochloric acid medium. React Kinet Catal L 80:59–65. doi:10.1023/A:1026024007436

Johnson MD, Read JF (1996) Kinetics and mechanism of the ferrate oxidation of thiosulfate and other sulfur-containing species. Inorg Chem 35:6795–6799. doi:10.1021/ic960480o

Katsoulis DE (1998) A survey of applications of polyoxometalates. Chem Rev 98:359–388. doi:10.1021/cr960398a

Kolthoff IM, Meehan EJ, Carr EM (1953) Mechanism of initiation of emulsion polymerization by persulfate. J Am Chem Soc 75:1439–1441. doi:10.1021/ja01102a048

Kozhevnikov IV (1998) Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions. Chem Rev 98:171–198. doi:10.1021/cr960400y

Lavine TF (1993) An iodometric determination of methionine. J Biochem 151:281–297

Mahadevappa DS, Madegowda MB, Rangappa KS (1983) Oxidimetric determination of methionine and its metal complexes with chloramine-B and dichloramine-B. Microchem J 28:235–249. doi:10.1016/0026-265X(83)90056-5

Mahadevappa DS, Ananda S, Gowda NMM (1985) Oxidation of methionine by sodium *N*-chlorotoluene-*p*-sulphonamide in aqueous solution: a kinetic study. J Chem Soc Perkin Trans 2:39–43. doi:10.1039/p29850000039

Mahesh RT, Bellakki MB, Nandibewoor ST (2004) Spectral and mechanistic study of the ruthenium (III) catalysed oxidation of gabapentin (neurontin) by heptavalent manganese: a free radical intervention. Catal Lett 97:91–98. doi:10.1023/B:CATL.0000034293.78427.8d

Mansour MA (2002) Kinetics and mechanism of chromium (VI) oxidation of L-methionine. Transit Met Chem 27:818–821. doi:10.1023/A:1021326228930

Martin C, Lamonier C, Fournier M, Mentre O, Harle V, Guillaume D, Payen E (2004) Preparation and characterization of 6-molybdocobaltate and 6- molybdoaluminate cobalt salts. Evidence of a new heteropolymolybdate structure. Inorg Chem 43:4636–4644. doi:10.1021/ic0354365

McAuley A, McCann JP (1975) Metal-ion oxidations in solution. Part XIII. The reaction of chromium (VI) with L-cysteine in perchlorate media. J Chem Soc Dalton Trans 783–790

Mehrotra M, Mehrotra RN (2003) The kinetics of the oxidation of thiourea by 12-tungstocobaltate (III) ion: evidence for anionic, neutral and protonated thiourea species in acetic-acid buffer and perchloric acid solution. J Chem Soc Dalton Trans 18:3606–3611

Nakamoto K (1977) Infrared and Raman spectra of inorganic compounds, 3rd edn. John Wiley and Sons, New York, pp 115, 226, 143

Natile G, Bordignon E, Cottalini L (1975) Chloroauric acid as oxidant. Stereospecific oxidation of methionine to methionine sulfoxide. Inorg Chem 15(1):246–248. doi:10.1021/ic50155a054

Olatunji MA, McAuley A (1977) Metal-ion oxidations in solution. Part XVIII. Characterization, rates, and mechanism of formation of the intermediates in the oxidation of thiols by chromium(VI). Can J Chem 55:3328–3334. doi:10.1139/v77-464

Sadakane M, Steckhan E (1998) Electrochemical properties of polyoxometalates as electrocatalysts. Chem Rev 98:219–238. doi:10.1021/cr960403a

Saha SK, Ghosh MC, Banerjee P (1988) Kinetics and mechanism of the alkali metal ions promoted electron transfer between 12-tungstocobaltate(III) and citric acid. Int J Chem Kinet 20:699–712. doi:10.1002/kin.550200904

Saito A, Tomari H, Choppin GR (1997) Spectrophotometric studies of metal cation interaction with nanomolybdomanganate(IV) anion, $MnMo_9O_{24}^{6-}$. Inorg Chim Acta 258:145–153. doi:10.1016/S0020-1693(96)05465-5

Satpathy PK, Dash GC, Acharya S, Mohanty P (2006) Kinetics and mechanism of oxidation of DL-methionine by Keggin-type 12-tungstocobaltate(III) in aqueous acetic acid medium. J Indian Chem Soc 83:891–894

Satsangi BK, Kothari S, Banerji KK (1995) Kinetics and mechanism of the oxidation of bis(2,2′-bipyridyl)copper(II) permanganate by DL-methionine. Transit Met Chem 20:288–290

Shah R, Prakash A, Mehrotra RN (1999) Outer-sphere mechanism of oxidation of hydrazine and hydrazinium ion by 12-tungstocobaltate(III) ion in acetate-acetic acid buffer: Marcus treatment. Indian J Chem A 38:680–685

Sharma V, Sharma PK, Banerji KK (1996) Kinetics and mechanism of the oxidation of DL-methionine by pyridinium fluorochromate. J Chem Res (S) 290–291

Vogel AI (1961) Textbook of quantitative inorganic analysis including elementary instrumental analysis, 3rd edn. Longmans, London, pp 350, 411, 810

Wani P, Raja Rajeswari T, Dikshitulu LSA (1994) Kinetics and mechanism of oxidation DL-methionine by manganese (III) in sulphuric acid medium. React Kinet Catal L 52:175–182. doi:10.1007/BF02129866

Weast RC, Astle MJ, Beyer WH (1986) Handbook of physics and chemistry, 67th edn. CRC Press, Boca Raton, pp C-699

Weinstock IA (1998) Homogeneous-phase electron-transfer reactions of polyoxometalates. Chem Rev 98:113–170. doi:10.1021/cr9703414

Young PR, Hsich H (1978) General base catalysis and evidence for a sulfurane intermediate in the iodine oxidation of methionine. J Am Chem Soc 100:7121–7122. doi:10.1021/ja00490a082