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Oxidation of Methionine by Colloidal MnO_2 in Aqueous and Micellar Media: A Kinetic Study

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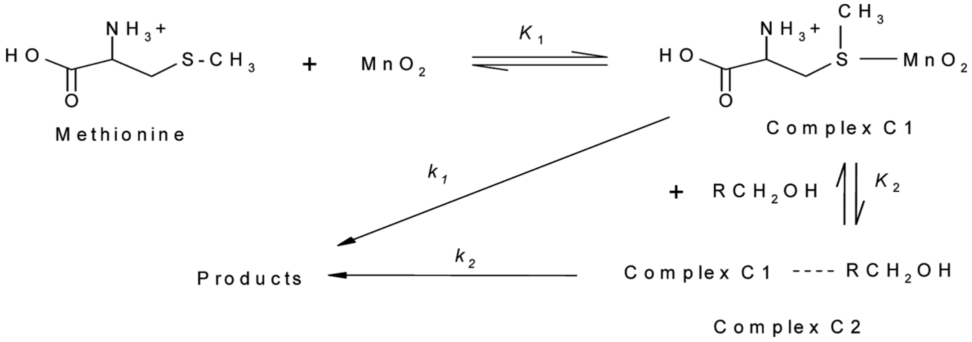
GRAPHICAL ABSTRACT



The oxidation of methionine by freshly prepared colloidal manganese dioxide in aqueous as well as micellar media was studied spectrophotometrically at 35°C. The reaction between methionine and MnO_2 in both media exhibits 1:1 stoichiometry (methionine:MnO_2). The oxidation reaction is first order with regard to the MnO_2 concentration, but is fractional-order in the methionine concentration and $HClO_4$ concentrations. A catalytic effect of nonionic surfactant TX-100 on the rate of oxidation was observed and reaction rate was found to be proportional to $\{k' + k''[\text{TX-100}]\}$, where k' and k'' are the rate constants in absence and presence of surfactant, respectively. The use of surfactant micelles is highlighted as, in favorable cases; the micelles help the redox reactions by bringing the reactants in a close proximity through hydrogen bonding. The oxidation reaction in aqueous and micellar media is shown to proceed via methionine–MnO_2 and methionine–MnO_2–TX-100 complexes, respectively, which decomposes slowly in a rate determining step to give methionine sulfoxide as the product. A suitable mechanism is proposed for these observations.

Keywords Manganese dioxide, methionine, micellar catalysis, oxidation, surfactant

1. INTRODUCTION

Manganese oxides exhibit considerable activity in oxidation–reduction reactions due to the presence of manganese ions with different oxidation states. Unfortunately, it has been shown that manganese oxides are insoluble.[1,2] In the literature, the active MnO_2 has been described as an effective oxidant for a variety of organic compounds under solvent-free and heterogeneous conditions.[3] Perez-Benito et al.[4] found quantitatively that water-soluble colloidal manganese dioxide can be prepared from reduction of aqueous potassium permanganate by sodium thiosulfate under neutral condition. Water-soluble colloidal MnO_2 has the advantage over water-insoluble forms that conventional ultraviolet-visible (UV-vis) spectrophotometers can be used to monitor reactions with organic and inorganic reductants.[5,6]

The kinetic investigations on the oxidation of amino acids become important because of their biological significance and selectivity toward the oxidants. A precise understanding of the mechanism of such biological redox reactions is important as it helps in the synthesis of specific reaction products. Methionine is a sulfur-containing essential α-amino acid which is not synthesized in the body and must be supplemented through the food. It contributes to supply mineral sulfur improving tone and pliability of the skin, conditioning the hair and strengthening nails,

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and protecting the cells from airborne pollutants. Methionine has three possible coordination sites: at the N-, O-, and S-centers[12–17] in which S-center is most reactive group because it has been established that the Sulfur is the most susceptible to transfer electrons to the oxidizing agents. In our previous studies, the $–NH_3$ and $–COOH$ groups cleavage products of the oxidation of amino acids by colloidal manganese dioxide have been reported.[7–11] The reactions of water-soluble colloidal MnO_2 with sulfur containing organic reductants,[18,19] have been investigated for several reasons. In methionine (2-amino-4-(methyl thio) butanoic acid), the reactive site is partially blocked by a methyl group, and it is, therefore, of interest to study the effect of this on the reactivity of methionine.

Generally, the surfactants bear diphilic moieties, that is, hydrophobic and hydrophilic groups. When the surfactants as solutes are taken into aqueous solution, due to the hydrophobic interaction, the solute particles have a tendency to aggregate spontaneously to form thermodynamically stable bigger particles of colloidal dimension. In micellar solutions, reactions can be both accelerated and inhibited compared to that in pure water.[20,21] A micelle offers several binding sites for relatively polar molecules. These include the hydrophobic core and hydrophobic binding sites located in the Stern region. The latter region is particularly flexible in binding molecules as it contains the highly hydrophilic surfactant headgroups and hydrophobic domains due to back folding of the surfactant tails[22,23] as well as water molecules. Quite large enhancements of reaction rate have been observed in micellar systems and have been explained by two processes: a) the micelle solubilizes both reactants in same micellar volume, thereby increasing their local concentrations, and hence increasing the reaction rate; b) the micelle–water interface can exhibit unique properties which influence a reaction. For example, the local electric field at the surface of ionic micelles can be as large as 10^6 V/cm.[24] Such a field could influence the transition state of a reaction and lead to an increased rate of reaction. The micellar effects on the kinetics of organic reactions have so far been extensively studied, relatively little attention has been paid to inorganic reactions. As far as we know, no kinetic investigation has been carried out regarding the oxidation of methionine by colloidal MnO_2 in presence of micellar aggregates.

The kinetics of the oxidation reaction between methionine and colloidal manganese dioxide in aqueous perchloric acid solution were studied in the absence and presence of nonionic surfactant (TX-100) in order to gain a better understanding of their oxidizing properties. The aim of this work is to examine the effects of nonionic surfactant at various concentrations on the reaction rate involving methionine and colloidal MnO_2 as reactants.

2. EXPERIMENTAL

2.1. Materials

All chemicals were of an analytical grade reagents. Methionine (99%, Fluka, china), potassium permanganate (98.5%, E. Merck, SA), sodium thiosulfate (99%, E. Merck, SA), Perchloric acid (70%, ACE, Glenvista) and poly (oxyethylene)-*t*-octylphenyl ether, surfactant (TX-100) (99%, Sigma, USA) were used as received without further purification. Ultra-pure water was used for the preparation of all reagents solutions. Permanganate solutions were stored in a dark glass bottle and standardized by titration against oxalate.

2.2. Preparation of Colloidal Manganese Dioxide

The colloidal MnO_2 was prepared as follows: 0.0158 g of $KMnO_4$ was dissolved in 150 ml of ultra-pure water, and the mixture was fleetly stirred for 2 hours. 0.0931 g of sodium thiosulfate dissolved in 50 ml of ultra-pure water was added to the permanganate solution at room temperature. The color of the solution changed rapidly from purple to yellow-brown (indicating the onset formation of MnO_2) and finally dark brown. The resulting solution was perfectly transparent and was very stable over extended periods of several months. The colloidal manganese dioxide was electrochemically inactive but showed a large absorption band covering the whole visible region of the spectrum with absorbance uniformly increasing with decreasing wavelength with a maximum at 360 nm (Figure 1). Prior to the kinetic studies, Beer's law was verified and the extinction coefficient was found to be $\varepsilon_{360nm} = 10113 \pm 100\,mol^{-1}\,dm^3\,cm^{-1}$. It was also verified that there was negligible

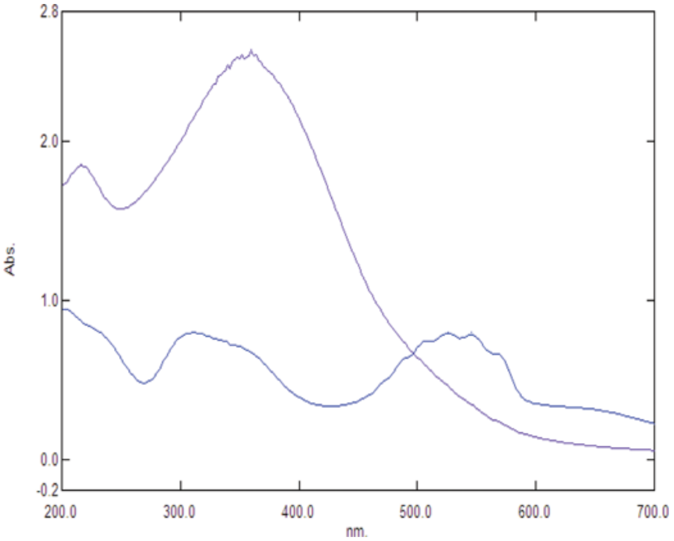


FIG. 1. Absorption spectra of $KMnO_4$ and of the reaction product of $KMnO_4$ and $Na_2S_2O_3$ (MnO_2). (Figure available in color online.)

interference from other species present in the reaction mixture at this wavelength.

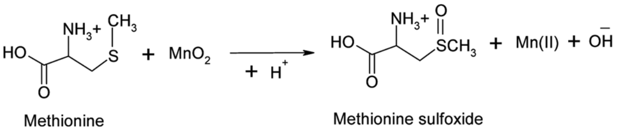
3. RESULTS AND DISCUSSION

3.1. Kinetic Measurements

The kinetic measurements were performed using a UV-1800 Shimadzu UV-vis spectrophotometer. The kinetics was followed under pseudo-first-order conditions where [Methionine] >> [MnO_2] at 35 ± 0.1°C, unless specified. The reaction was initiated by mixing MnO_2 and methionine solutions acidified using concentration of $HClO_4$. The reaction progress was followed spectrophotometrically at 360 nm by monitoring the decrease in absorbance of MnO_2. The values of rate constants (k_{obs} or k_ψ, s^{-1}—where k_{obs} refers to rate constant in aqueous medium whereas k_ψ refers to rate constant in micellar medium) were estimated from the slope of log(absorbance) versus time plots. Because $HClO_4$ is a strong oxidant, some blank experiments were performed by mixing all the reactants without manganese oxide. The experiments done without MnO_2 were longer than those done in the presence of MnO_2. No methionine oxidation products were observed in these experiments. A set of reaction was also carried out by replacing methionine with glycine under the same experimental condition. The UV-absorbance showed no decay of colloidal MnO_2, indicating that there was no reaction that took place with glycine. These results are interesting but not surprising because the reactivity of S-bonded reductants is higher in comparison to N- and O-bonded. These observations undoubtedly show that the –SCH_3 group of methionine is responsible for the reduction of colloidal MnO_2. The effect of dissolved oxygen on the reaction rate was checked by preparing the reaction mixture and following the reaction in N_2-atmosphere. No significance difference between the results obtained under N_2 and in the presence of air was observed.

3.2. Stoichiometry and Product Analysis

Different sets of reaction mixtures containing molar excesses of MnO_2-to-methionine, in the presence of constant amount of $HClO_4$, were kept for 12 hours in a closed vessel under an inert atmosphere. The remaining (unreacted) MnO_2 concentration was estimated spectrophotometrically at 360 nm. The results indicate 1:1 stoichiometry as shown in (1).



[1]

For the oxidation product of methionine, the reaction mixture containing methionine (=5.0 × 10^{-3} mol dm^{-3}) and colloidal MnO_2 (=4.0 × 10^{-4} mol dm^{-3}) was heated at 45°C for 3 hours. The oxidized reaction mixture was treated with sodium bicarbonate solution, followed by benzoyl chloride. This resulted in the formation of precipitate of *N*-benzoyl methionine sulfoxide, which was confirmed using a literature reported method.[25] CO_2 and NH_3 were not detected as the oxidation products of methionine.

3.3. Effect of [Methionine]

The dependence of the rate constant on [Methionine] was determined by carrying out the kinetic experiments at different concentrations of methionine keeping the [MnO_2] = 8.0 × 10^{-5} mol dm^{-3}, [$HClO_4$] = 2.0 × 10^{-4} mol dm^{-3}, [TX-100] = 0 and 4.0 × 10^{-4} mol dm^{-3} and temperature = 35°C constant. The rate constant (k_{obs} and k_ψ) values obtained from the slope of log(absorbance) versus time plots are summarized in Table 1. The observation is that rate constant increases with increase in methionine concentrations. This can be seen in the plots of rate constant versus [Methionine] which are nonlinear passing through the origin (Figure 2A). The linear plots shown in Figure 2B being a plot of between log(rate constant) versus log[Methionine] yield slopes equal to 0.34 (r = 0.9887) and 0.41 (r = 0.9924) for k_{obs} and k_ψ, respectively, indicating that the rate law is a fractional-order in [Methionine] in absence and presence of

TABLE 1

Effects of [Methionine], [MnO_2] and [$HClO_4$] on the oxidation of methionine by MnO_2 in absence and presence of TX-100 (4.0 × 10^{-4} mol dm^{-3}) at 35°C

10^3 [Methionine] (mol dm^{-3})	10^5 [MnO_2] (mol dm^{-3})	10^4 [$HClO_4$] (mol dm^{-3})	10^4 k_{obs} (s^{-1})	10^4 k_ψ (s^{-1})
1.0	8.0	2.0	4.76	7.89
2.0			6.35	11.58
3.0			7.20	15.25
4.0			8.18	17.02
5.0			8.30	18.5
6.0			8.60	19.3
2.0	4.0	2.0	9.03	18.93
	8.0		6.35	11.58
	12.0		4.29	7.33
	16.0		4.02	6.81
	20.0		3.96	6.52
	24.0		3.90	6.50
2.0	8.0	1.0	4.53	8.48
		2.0	6.35	11.58
		3.0	7.74	15.55
		4.0	8.48	17.54
		5.0	9.19	19.61
		6.0	9.66	20.91

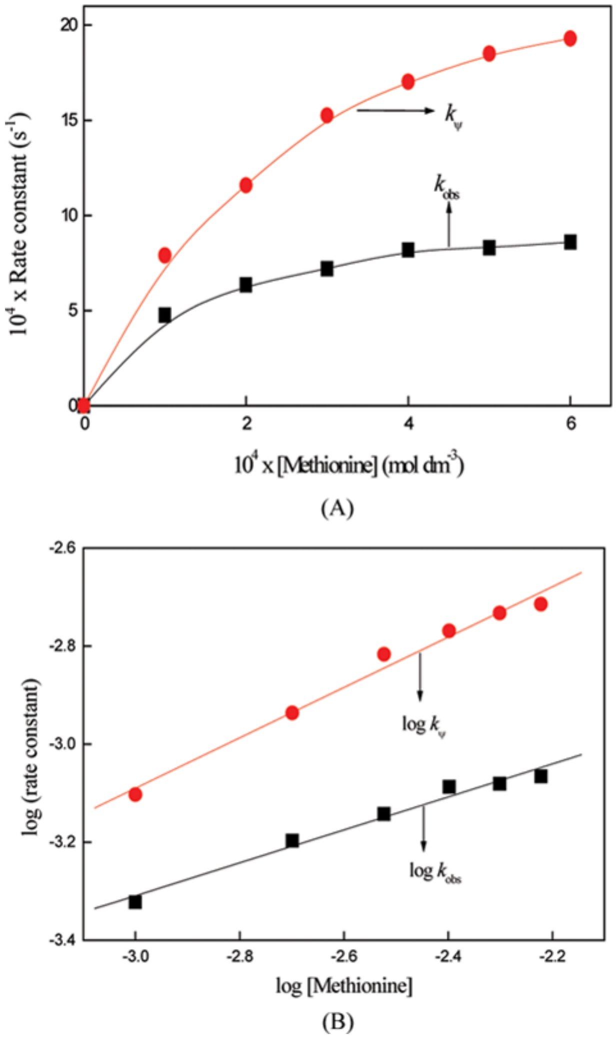


FIG. 2. A) Effect of [Methionine] on the rate constant for the oxidation of methionine by colloidal MnO_2 in absence and presence of TX-100. B) Double logarithm plots of rate constant and [Methionine]. *Reaction conditions*: $[MnO_2] = 8.0 \times 10^{-5}$ mol dm^{-3}, $[HClO_4] = 2.0 \times 10^{-4}$ mol dm^{-3}, $[TX\text{-}100] = 4.0 \times 10^{-4}$ mol dm^{-3}, temperature = 35°C. (Figure available in color online.)

surfactant (TX-100). On the other hand, the plots of 1/(rate constant) versus 1/[Methionine] are linear with positive intercepts on the y-axis (Figure 3), satisfying the Michaelis–Menten[26]/Langmuir–Hinshelwood[27,28] reciprocal relationship (a kinetic proof for the formation of complexes C1 (methionine-MnO_2) and C2 (methionine-MnO_2-(TX-100)) by adsorption of methionine and surfactant (TX-100) on the surface of the colloidal MnO_2 particles).

3.4. Effect of [Mno_2]

To see the effect of [MnO_2] on the reaction rate, the reaction was carried out at different initial concentrations of MnO_2 ranging from 4.0×10^{-5} to 24.0×10^{-5} mol dm^{-3}. The concentrations of methionine ($= 2.0 \times 10^{-3}$ mol dm^{-3}), $HClO_4$ ($= 2.0 \times 10^{-4}$ mol dm^{-3}), (TX-100) ($= 0$ and 4.0×10^{-4} mol dm^{-3}), and temperature (35°C) were kept constant. The pseudo-first-order rate constants (k_{obs} and k_ψ), obtained at different [MnO_2], are recorded in Table 1. The result shows that the rate constant decreases with increasing [MnO_2]. The decrease in rate constant may be due to the flocculation of the colloidal MnO_2 particles.[5,6]

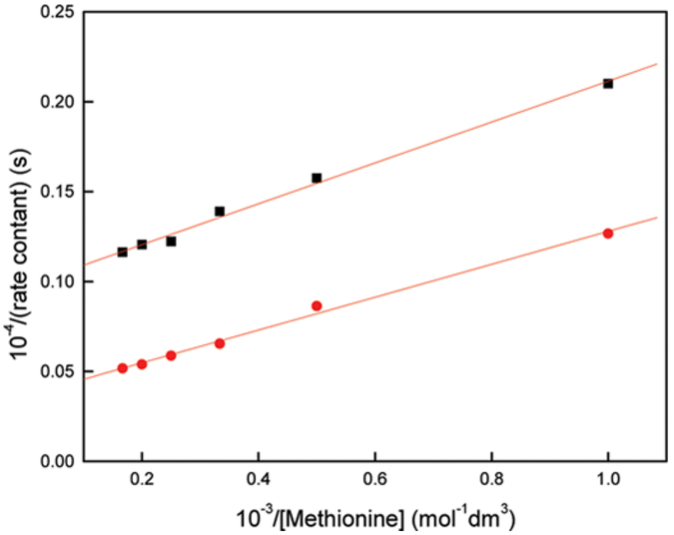


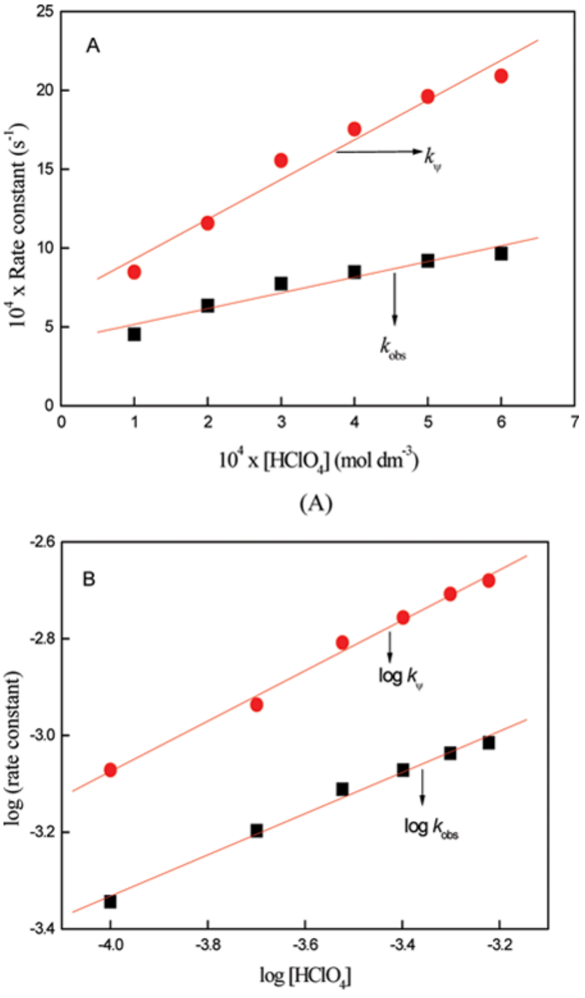
FIG. 3. Plot of 1/(rate constant) versus 1/[Methionine] for the oxidation of methionine by colloidal MnO_2. *Reaction conditions:* $[MnO_2] = 8.0 \times 10^{-5}$ mol dm^{-3}, $[HClO_4] = 2.0 \times 10^{-4}$ mol dm^{-3}, $[TX\text{-}100] = 0$ and 4.0×10^{-4} mol dm^{-3}, and temperature = 35°C. (Figure available in color online.)

3.5. Effect of [$HClO_4$]

The concentration of $HClO_4$ was varied from 1.0×10^{-4} to 6.0×10^{-4} mol dm^{-3} keeping all other concentrations and experimental conditions constant. The dependence of rates of the reaction on hydrogen ion concentration in both aqueous as well as micellar media are shown in Table 1. The plots of rate constant against [$HClO_4$] were found to be linear (Figure 4A) and the order in its concentration were found to be 0.43 (r = 0.995) and 0.52 (0.996) respectively, as found from the slopes of the plots of log(rate constant) against log[$HClO_4$] in Figure 4B, an indication of fractional-order dependence on [$HClO_4$] in both aqueous as well as micellar media.

3.6. Effect of Surfactant (TX-100)

To see the role of nonionic surfactant (TX-100) on the reaction rate, a series of kinetic runs were carried out with varied concentrations of surfactant from 2.0×10^{-4} to 20.0×10^{-4} mol dm^{-3} at constant [Methionine] ($= 2.0 \times 10^{-3}$ mol dm^{-3}), [MnO_2] ($= 8.0 \times 10^{-5}$ mol dm^{-3}), [$HClO_4$] ($= 2.0 \times 10^{-4}$ mol dm^{-3}), and temperature (=35°C). The



(A)

(B)

FIG. 4. A) Effect of [$HClO_4$] on the rate constant for the oxidation of methionine by colloidal MnO_2 in absence and presence of TX-100. B) Double logarithm plots of rate constant and [$HClO_4$]. *Reaction conditions*: [MnO_2] = 8.0×10^{-5} mol dm^{-3}, [Methionine] = 2.0×10^{-3} mol dm^{-3}, [TX-100] = 4.0×10^{-4} mol dm^{-3}, temperature = 35°C. (Figure available in color online.)

TABLE 2
Effects of [TX-100] on the oxidation of methionine by MnO_2

10^4 [TX-100] (mol dm^{-3})	10^4 k_ψ (s^{-1})
0.0	6.35
2.0	8.76
4.0	11.58
8.0	11.94
12.0	12.65
16.0	12.75
20.0	13.23

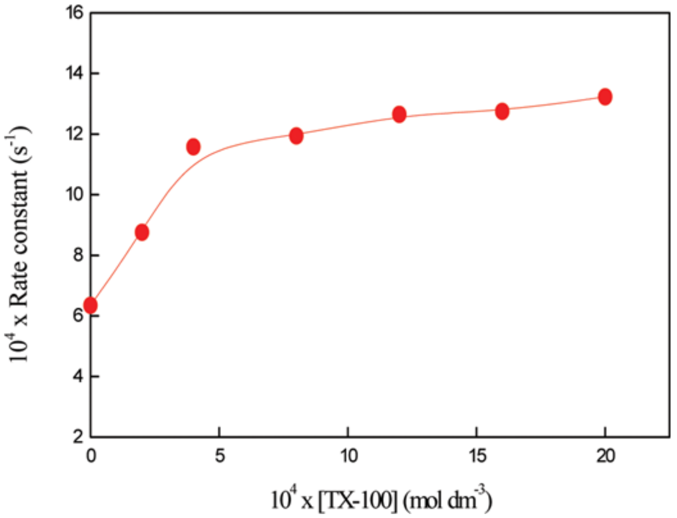


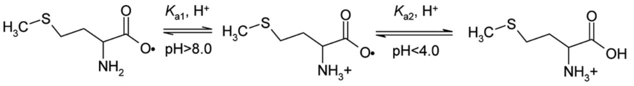
FIG. 5. Effect of [TX-100] on the rate constant for the oxidation of methionine by colloidal MnO_2. *Reaction conditions*: [MnO_2] = 8.0×10^{-5} mol dm^{-3}, [Methionine] = 2.0×10^{-3} mol dm^{-3}, [$HClO_4$] = 2.0×10^{-4} mol dm^{-3}, temperature = 35°C. (Figure available in color online.)

reaction was found to be accelerated by (TX-100) with the rate constant increasing as TX-100 concentration increased reaching a plateau at higher concentration. These are shown in Table 2 and Figure 5.

The presence of (TX-100) molecules on the interfacial region provides possible an additional attractive interaction for the methionine molecules. The most important effect of TX-100 molecules on the surface of colloidal MnO_2 may be is to increase the formation of hydrogen-bonded complexes with methionine molecules. Due to presence of a number of donor groups in one TX-100 molecule, multiple H-bonding may take place and the number of bound reactant molecules increase. The hydrogen bonding between MnO_2 sols and hydrophilic part (polar ethylene oxide) of the TX-100 cannot be ruled out either (let us call it adsorption). Therefore, the associated MnO_2 and methionine with TX-100 through hydrogen bonding seems to be responsible of facilitating the reaction. This is likely the role TX-100 is playing towards the observed catalysis. The surfactant thus, helps in bringing the reactants together into a small volume, which orients in a manner suitable for the redox reaction to take place followed by rearrangement of TX-100 molecules.

4. MECHANISM

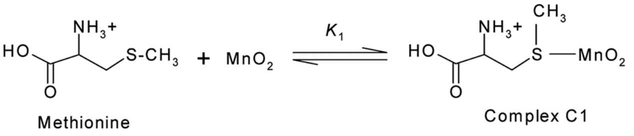
The effect of hydrogen ion concentration on the reaction was investigated so as to know the probable prior protonation equilibria of either the oxidant or the substrate and to identify the active reactant species. The pK_a values of the methionine are 2.22, 9.27, corresponding to the protonation of carboxylic acid and amino groups respectively. In acidic medium, the carboxylic acid group remains un-dissociated and the amino group is also protonated bellow pH 4 as shown in Equation (2). Therefore, under the present reaction conditions methionine exists completely in the $(CH_3)SCH_2CH_2CH(NH_3^-)COOH$ form.



[2]

On the basis of the above results and discussion, the mechanism of the oxidation of methionine by colloidal MnO_2 can be explained by Equations (3)–(6).

4.1. In Aqueous Medium



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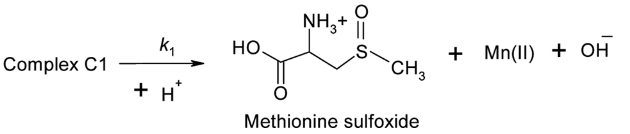
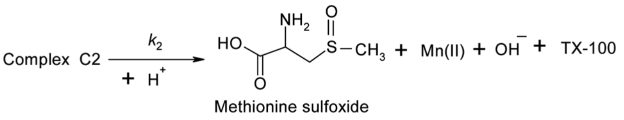


[4]

4.2. In Micellar Medium

$$\underset{}{\text{Complex C1}} + \underset{\text{TX-100}}{RCH_2OH} \xrightleftharpoons{K_2} \underset{\text{Complex C2}}{\text{Complex C1}\cdots HOCH_2R} \qquad [5]$$



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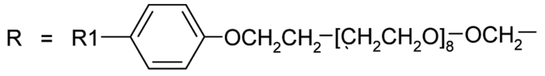

(R1 = 1,1,3,3, Tetramethyl butyl)

Equation (3) represents the formation of complex C1 between the substrate (methionine) and the oxidant (MnO_2) through electrophilic attack of the oxidant on the nucleophilic sulfur atom of methionine. Equation (5) also represents the formation of complex C2 by adsorption of TX-100 molecule on the surface of the complex C1 (methionine-MnO_2) through hydrogen bonding. Equations (4) and (6) are respective rate determining steps. In the light of previous results,[7-9] we assume that complexes C1 and C2 decompose in a one-step, two-electron oxidation–reduction mechanism to methionine sulfoxide and Mn(II).

According to Equations (4) and (6), the rate of disappearance of manganese dioxide may be given as:

$$\upsilon = \frac{d[MnO_2]}{dt} = k_1[C1] + k_2[C2] \qquad [7]$$

The concentration of the intermediates C1 and C2 is given by

$$[C1] = K_1[\text{Methionine}][MnO_2] \qquad [8]$$

And

$$\begin{aligned} [C2] &= K_2[C1][\text{TX-100}] \\ [C2] &= K_1K_2[\text{Methionine}][MnO_2][\text{TX-100}] \end{aligned} \qquad [9]$$

Therefore, the rate law in Equation (7) may be written as

$$\upsilon = \frac{d[MnO_2]}{dt} = [\text{Methionine}][MnO_2] \{k_1K_1 + k_2K_1K_2[\text{TX-100}]\} \qquad [10]$$

According to Equation (10), at lower concentration of surfactant the rate is proportional to $\{k' + k''[\text{TX-100}]\}$, where $k' = k_1K_1$ and $k'' = k_2\ K_1K_2$, are the rate constants in absence and presence of surfactant, respectively.

The total concentration of MnO_2, at any time is given as,

$$[MnO_2]_T = [MnO_2] + [C1] + [C2] \qquad [11]$$

On substituting the values of [C1] and [C2] in Equation (11) and solving it, the value of $[MnO_2]$ in terms of $[MnO_2]_T$ may be expressed as,

$$[MnO_2] = \frac{[MnO_2]_T}{1 + (K_1 + K_1K_2[\text{TX-100}])[\text{Methionine}]} \qquad [12]$$

Therefore, the rate law in (10) becomes

$$\upsilon = \frac{d[MnO_2]}{dt} = \frac{(k_1K_1 + k_2K_1K_2[\text{TX-100}])[\text{Methionine}][MnO_2]_T}{1 + (K_1 + K_1K_2[\text{TX-100}])[\text{Methionine}]} \qquad [13]$$

Under the experimental condition ($[\text{TX-100}] = 4.0 \times 10^{-4}$ mol dm^{-3}), the contribution of aqueous medium can be neglected. Thus, Equation 13 is reduced as Equation 14.

$$\upsilon = \frac{k_2K_1K_2[\text{TX-100}][\text{Methionine}][MnO_2]_T}{1 + K_1K_2[\text{TX-100}][\text{Methionine}]} \qquad [14]$$

$$k_\psi = \frac{\upsilon}{[\mathrm{MnO_2}]_\mathrm{T}} = \frac{k_2 K_1 K_2[\text{TX-100}][\text{Methionine}]}{1 + K_1 K_2[\text{TX-100}][\text{Methionine}]} \quad [15]$$

On rearrangement, Equation 15 can be written as:

$$\frac{1}{k_\psi} = \frac{1}{k_2 K_1 K_2[\text{TX-100}][\text{Methionine}]}\frac{1}{k_2} \quad [16]$$

A plot of k_ψ^{-1} versus $[\text{Methionine}]^{-1}$ should accordingly be linear with a positive intercept ($1/k_2$) on the Y-axis and a positive slope ($1/\ k_2K_1K_2[\text{TX-100}]$). This has been found to be so as shown in Figure 3.

5. CONCLUSION

The study presents a kinetic study of the oxidation of Methionine by MnO_2 in aqueous perchloric acid solution using nonionic surfactant TX-100 as a catalyst. The analysis of the kinetic data suggested that the rate-determining step takes place on the manganese dioxide surface. Both reactants need to be adsorbed onto the surface of the catalyst in order to react. The mechanism of the oxidation of methionine is same in both aqueous as well as surfactant media. The mechanism found for colloidal MnO_2 particles is hence dependent by the surface of the particles.

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