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ORIGINAL CONTRIBUTION

A kinetic study of the oxidation of L-methionine by water soluble colloidal MnO_2

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Abstract Aqueous solution of water soluble colloidal MnO_2 was prepared by Perez-Benito method. Kinetics of L-methionine oxidation by colloidal MnO_2 in perchloric acid (0.93×10^{-4} to 3.72×10^{-4} mol dm^{-3}) has been studied spectrophotometrically. The reaction follows first-order kinetics with respect to $[H^+]$. The first-order kinetics with respect to L-methionine at low concentration shifts to zero order at higher concentration. The effects of [Mn(II)] and $[F^-]$ on the reaction rate were also determined. Manganese (II) has sigmoidal effect on the rate reaction and act as auto catalyst. The exact dependence on [Mn(II)] cannot be explained due to its oxidation by colloidal MnO_2. Methionine sulfoxide was formed as the oxidation product of L-methionine. Ammonia and carbon dioxide have not been identified as the reaction products. The mechanism with the observed kinetics has been proposed and discussed.

Keywords Methionine · Kinetics · Oxidation · Colloidal MnO_2

Introduction

Water soluble colloidal manganese dioxide was originally prepared by Perez-Benito et al. from the reduction of permanganate by sodium thiosulfate in neutral aqueous medium [1–3] and also used as an oxidant for the oxidation of formic acid [3], oxalic acid [4], and manganese (II) [5]. It has been established that water-soluble colloidal MnO_2 has the advantage over the water insoluble forms. The aqueous solution of colloidal MnO_2 is unstable in acidic medium and has found extensive use as an oxidant in the aqueous neutral medium.

The oxidation of amino acids is particularly interesting because $–NH_3$ and –COOH cleavage products have been reported [6–10]. Sulfur containing amino acids has three possible coordination sites: at the N-, O-, and S-centers [11–16]. Sulfur has been established as the most susceptible to gain electrons from the oxidizing agents. The reactions of water-soluble colloidal MnO_2 with sulfur containing organic reductants (thiourea [17], cysteine [18, 19], and glutathione [19]) have been investigated for several reasons. The –SH group was responsible for the oxidation of these reductants.

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 L-methionine. As a part of our investigations on the oxidation of N-, O-, and S-containing organic reductants [17, 19–22] by colloidal MnO_2, we report in this paper the kinetics and mechanism of colloidal MnO_2 oxidation of L-methionine in the perchloric acid medium and examine the inferences drawn from the sodium fluoride and manganese (II) trapping experiments. The colloidal MnO_2 solution undergoes acid hydrolysis or is unstable in aqueous solutions of $[H^+] > 1.0\times10^{-3}$ mol dm^{-3} [20]. Therefore, the kinetic studies were limited in $[H^+]$ range of 0.93×10^{-4} to 3.72×10^{-4} mol dm^{-3}.

Experimental

Materials

Water (deionized and free from CO_2) was used after double distillation throughout as solvent. Potassium permanganate

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(98.5%, E. Merck, India), sodium thiosulfate (98.5%, E. Merck, India), sodium fluoride, manganese(II) chloride and L-methionine (99%, E. Merck, India) were used without further purification. Perchloric acid (Fisher Scientific UK, 70% reagent) was used to maintain the desired hydrogen ion concentration.

Kinetic measurements

The oxidation of methionine by the colloidal MnO_2 was carried out under pseudo first-order conditions (L-methionine ≫ colloidal MnO_2). The reaction was initiated by adding the required amount of L-methionine to a thermally equilibrated mixture of colloidal MnO_2 containing perchloric acid and other reagents. The progress of the reaction was monitored spectrophotometrically by measuring the absorbance of remaining colloidal MnO_2 at known time intervals at 375 nm (λ_{max} for MnO_2) using a Bausch & Lomb Spectronic-20 spectrophotometer. Pseudo-first-order rate constants were determined from the plots of slope of log (absorbance) vs time. The reaction was usually followed up to 80% completion.

Product identification

For the oxidation product of L-methionine, the reaction mixture containing L-methionine (= 2.0×10^{-3} mol dm^{-3}) and colloidal MnO_2 (= 2.0×10^{-4} mol dm^{-3}) was heated at 40 °C for 2 h. 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 by the reported method [12]. CO_2 and NH_3 were not detected as the oxidation products of L-methionine.

Table 1 Values of pseudo-first-order rate constants (k_{obs}) for the oxidation of L-methionine] (=5.0×10^{-4} mol dm^{-3}) by colloidal MnO_2 in [$HClO_4$]=0.93×10^{-4} mol dm^{-3}

10^5 [MnO_2] (mol dm^{-3})	Temp. (°C)	10^5 k_{obs} (s^{-1})
3.0	30	15.3
4.0		11.5
5.0		7.6
6.0		5.6
7.0		3.8
5.0	30	7.6
	40	14.5
	50	23.0

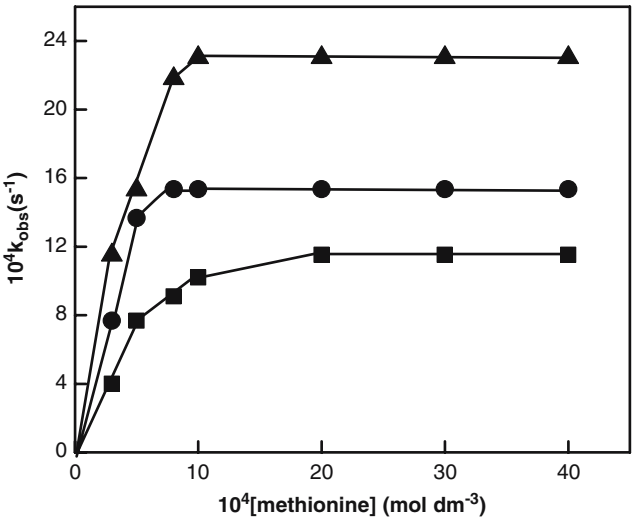


Fig. 1 Plots of k_{obs} vs [L-methionine]. Reaction conditions: [MnO_2] (=5.0×10^{-5} mol dm^{-3}); [$HClO_4$] (=0.93 [■, ●] and 1.86×10^{-4} mol dm^{-3} [▲]); temp. (=30 [■, ▲] and 40 °C [●])

Results and discussion

General considerations

Preparation and characterization of colloidal MnO_2

The water-soluble colloidal manganese dioxide was prepared by the reduction of permanganate (5.0×10^{-4} mol dm^{-3}) by $Na_2S_2O_3$ (1.88×10^{-4} mol dm^{-3}) solution. The reaction takes place in the 8:3 ratio and stock solution of colloidal manganese dioxide (5.0×10^{-4} mol dm^{-3}) was prepared [3, 4]. The resulting solution was dark brown and perfectly transparent and stable for several weeks. The absorption spectrum of the reaction mixture consists of a single broad band in the visible region. To confirm the

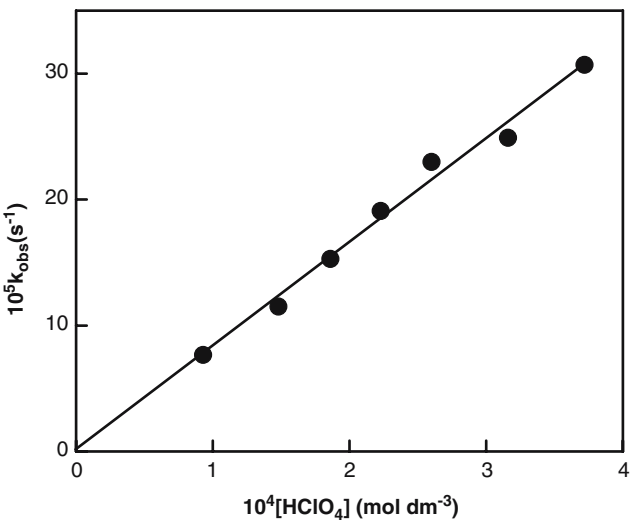


Fig. 2 Plot of k_{obs} vs [$HClO_4$]. Reaction conditions: [MnO_2] (=5.0×10^{-5} mol dm^{-3}); [L-methionine] (=5.0×10^{-4} mol dm^{-3}); temp. =30 °C

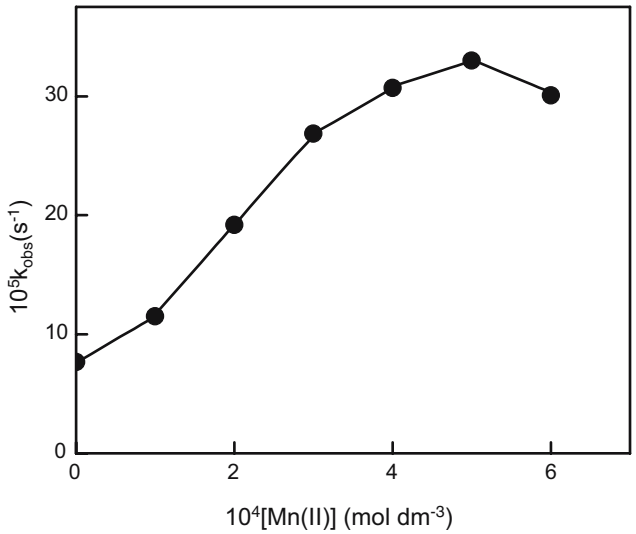


Fig. 3 Plot of k_{obs} vs [Mn(II)]. Reaction conditions: same as in Fig. 2 and [$HClO_4$] (=0.93×10^{-4} mol dm^{-3})

formation of water-soluble colloidal MnO_2, the fulfillment of the Beer–Lambert law by the resulting solution was studied. A calibration graph was constructed between absorbance (λ_{max} nm) and concentration of colloidal MnO_2. The law is obeyed for the concentration range used in the present investigations.

The effect of adding different electrolytes ($MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, $LiCl_2$, NaCl, KCl, NH_4Cl, $MnCO_3$, and Pb $(NO_3)_2$) in the transparent solution of water-soluble colloidal MnO_2 was also studied. In presence of these electrolytes, the precipitation of manganese dioxide occurs, which suggests that the soluble manganese(IV) species is present in the form of colloidal particles of manganese dioxide [2, 20].

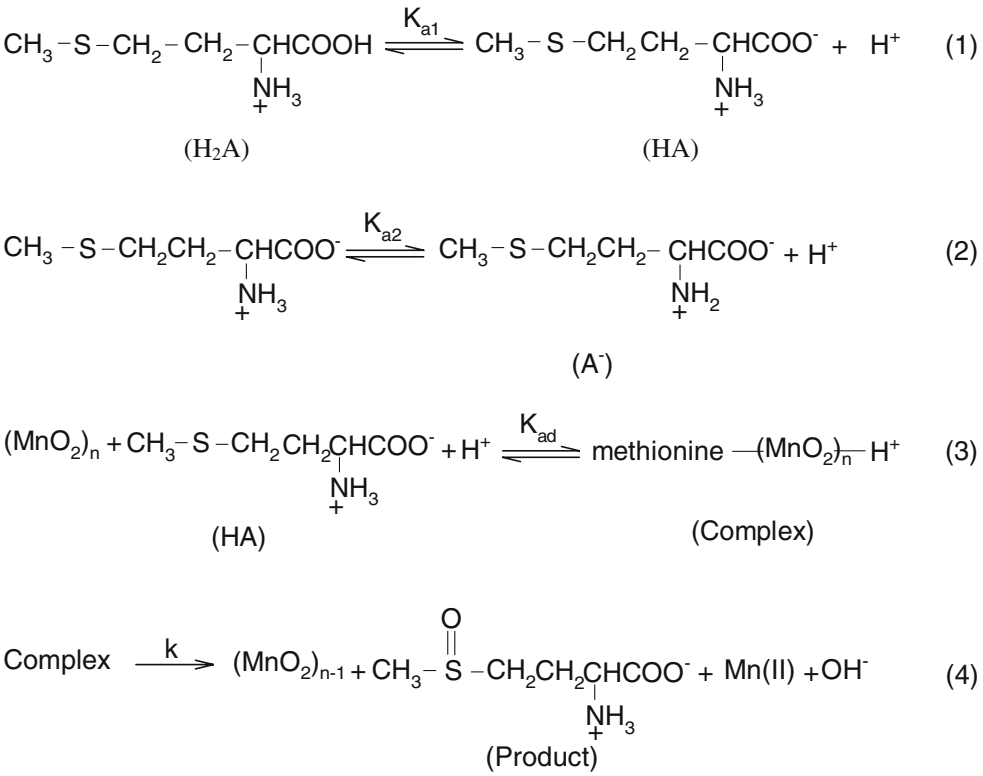
Rate dependence on [MnO_2]

The oxidation of L-methionine by colloidal MnO_2 was studied as a function of [MnO_2] between 3.0×10^{-5} and 7.0×10^{-5} mol dm^{-3} at constant [L-methionine] (= 5.0×10^{-4} mol dm^{-3}) and [$HClO_4$] (= 0.93×10^{-4} mol dm^{-3}) at 30 °C. k_{obs} values decrease with increase in [MnO_2] (Table 1). It is well established that pseudo-first-order rate constants are independent on the initial reactant concentration. The abnormal behavior (Table 1) is due to possible coagulation (flocculation) of the colloidal particles of MnO_2. This type of ambiguity has also been previously observed in many permanganate and colloidal MnO_2 reactions [10, 19, 20].

Rate dependence on [L-methionine]

A series of kinetics runs were performed within [L-methionine] (range 3.0×10^{-4}–40.0×10^{-4} mol dm^{-3}) at constant [MnO_2] (= 5.0×10^{-5} mol dm^{-3}) at two different [$HClO_4$] (= 0.93×10^{-4} mol dm^{-3} and 1.86×10^{-4} mol dm^{-3}) and temperatures 30 °C and 40 °C. The pseudo-first-order

Scheme 1 Reaction leading to the oxidation of L-methionine



rate constants are depicted graphically in (Fig. 1). The effect [L-methionine] indicates that the first-order kinetics at low L-methionine concentrations shifts to zero-order at higher concentrations (Fig. 1).

Rate dependence on [$HClO_4$]

The rate constant, obtained as a function of [$HClO_4$] at constant [L-methionine] (= 5.0×10^{-4} mol dm^{-3}) and [MnO_2] (= 5.0×10^{-5} mol dm^{-3}) at temperature 30 °C, was found to increase with the increase in [$HClO_4$]. The results are also shown in Fig. 2 as rate constant-[$HClO_4$] profile, which indicates the linear dependence of k_{obs} on [$HClO_4$]. The steady increase in the rate may be due to the adsorption of hydrogen ion on the surface of the colloidal MnO_2.

Rate dependence on temperature

To calculate the values of activation parameters, the reaction was studied at three different temperatures, viz., 30, 40, and 50 °C at constant [L-methionine] (= 5.0×10^{-4} mol dm^{-3}), [MnO_2] (=5.0×10^{-5} mol dm^{-3}), and [$HClO_4$] (=0.93×10^{-4} mol dm^{-3}). The k_{obs} was found to increase with temperature (Table 1). The values of activation parameters were evaluated as E_a=45 kJ mol^{-1}, $\Delta S^{\#}$=−175 JK^{-1} mol^{-1}, and $\Delta H^{\#}$=42 kJ mol^{-1}.

Effect of [Mn(II)] and [F^-]

To confirm the involvement of Mn(III) as an intermediate, the effect of sodium fluoride (range: 2.0×10^{-4} to $20.0\times1\ 0^{-4}$ mol dm^{-3}) was studied under the same experimental condition of [L-methionine] (=5.0×10^{-4} mol dm^{-3}), [$HClO_4$]=(0.93×10^{-4} mol dm^{-3}) and [MnO_2] (=5.0×10^{-5} mol dm^{-3}) at 30 °C. Under these conditions, the rate constants remain unaffected with increase in [F^-]. The constant values of k_{obs} with increasing [F^-] (7.5, 7.6, 7.6, 7.6, 7.6 s^{-1} at [F^-]=2.0, 4.0, 6.0, 10.0, and 20.0×10^{-4} mol dm^{-3}) indicate that Mn(III) is not formed during the course of reduction of colloidal MnO_2 by L-methionine. Thus, we may safely conclude that reduction of colloidal MnO_2 proceeds by one step, two-electrons oxidation-reduction mechanism to produce Mn(II), and methionine sulfoxide as the reaction product. To see the role of Mn(II), the effect of Mn(II) (a reduction product of MnO_2) was evaluated under the same experimental condition of [L-methionine] (=5.0×10^{-4} mol dm^{-3}), [$HClO_4$] (=0.93×10^{-4} mol dm^{-3}) and [MnO_2] (=5.0×10^{-5} mol dm^{-3}) at 30 °C.

The rate constants, obtained as a function of Mn(II), were found to increase with increase [Mn(II)]. These results are shown in (Fig. 3). The reduction of colloidal MnO_2 by Mn (II) has also been reported by several investigators [5, 20–23]. Therefore, the exact dependence of k_{obs} on externally added Mn(II) concentrations cannot be predicted. Sigmoid dependence of k_{obs} on [Mn(II)] is due to autocatalytic role of Mn(II) on the oxidation of L-methionine.

Mechanism

In the light of observed experimental data, Scheme 1 is considered to represent the most plausible mechanism of the reaction.

Under our experimental conditions ([$HClO_4$]=0.93×10^{-4} mol dm^{-3}), L-methionine exists mainly as HA (K_{a1} and K_{a2} of L-methionine are 10^{-2} and 10^{-10}, respectively). Therefore, K_{a1} and K_{a2} are not considered in the derivation of the rate equation. The rate of disappearance of colloidal MnO_2, in terms of Scheme 1, is given by

$$k_{obs} = \frac{kK_{ad}[H^+][\text{L} - \text{methionine}]}{(1 + K_{ad}[\text{L} - \text{methionine}][H^+])} \quad (5)$$

As the reaction has a strict first-order dependence in [L-methionine], it is apparent that $1 \gg K_{ad}$[L-methionine][H^+], which is consistent with the lower value of [L-methionine]. The rate law, Eq. 5, is thus reduced to Eq. 6.

$$k_{obs} = kK_{ad}[H^+][\text{L} - \text{methionine}] \quad (6)$$

Eq. 6 predicts that plot of k_{obs} vs [L-methionine] at constant [H^+] should be linear and pass through the origin (Fig. 1). At higher [L-methionine], Eq. 7 applies.

$$k_{obs} = kK_{ad}[H^+][\text{L} - \text{methionine}] \quad (7)$$

This clearly explains the zero-order dependence of reaction on [L-methionine] (Fig. 1).

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