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ORIGINAL CONTRIBUTION

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Reduction of water-soluble colloidal manganese dioxide by thiourea: a kinetic and mechanistic study

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Abstract Kinetic data for the colloidal MnO_2–thiourea redox system are reported for the first time. The reduction of water-soluble colloidal MnO_2 by thiourea (sulfur containing reductant) in aqueous perchloric acid medium has shown that it proceeds in two stages, i.e., a fast stage followed by a relatively slow second stage. The log (absorbance) versus time plot deviates from linearity. The kinetics of both the stages was investigated spectrophotometrically. The first-order kinetics with respect to [thiourea] at low concentration shifts to zero-order at higher concentration. The reaction rate increases with $[HClO_4]$ and the kinetics reveals complex order dependence in $[HClO_4]$. Addition of $P_2O_7^{4-}$ and F^- in the form of $Na_4P_2O_7$ and NaF, respectively, has inhibitory effect on the reaction rate. The reaction proceeds through the fast adsorption of thiourea on the surface of the colloidal MnO_2. A mechanism involving the protonated thiourea as the reactive reductant species is proposed. The observed results are discussed in terms of Michaelis–Menten/Langmuir–Hinshelwood model. From the observed kinetic data, colloidal MnO_2–thiourea adsorption constant (K_{ad1}) and rate constant (k_1) were calculated to be 1.25×10^{10} mol^{-1} dm^3 and 3.1×10^{-4} s^{-1}, respectively. The variation of temperature does not have any effect on the reaction rate.

Keywords Colloidal MnO_2 · Kinetics · Thiourea · Oxidation · Mechanism

Introduction

A survey of literature shows that the oxidation of sulfur containing reductant by colloidal MnO_2 has not been investigated so far. Thiourea is of interest as a reducing agent because of the absence of information on S–MnO_2 adsorbed complex. The method of preparation of water-soluble colloidal manganese dioxide by potassium permanganate and sodium thiosulfate, first prepared by Perez-Benito et al. [1], reportedly follows the stoichiometry shown in Eq. 1.

$$8MnO_4^- + 3S_2O_3^{2-} + 2H^+ = 8MnO_2 + 6SO_4^{2-} + H_2O \tag{1}$$

These investigators followed spectrophotometrically the kinetics of the oxidation of two organic [2, 3] (oxalic and formic acids) and one inorganic [4] (manganese(II)) reductant. Mechanisms proposed for the oxidation of citric and malic acids [5, 6] and oxidative decomposition of D-fructose by colloidal MnO_2 suggest the formation of an adsorption complex between the oxidant and the reductant [7]. We report herein the kinetics of the reaction in the presence and absence of perchloric acid media and examine inferences drawn from the $P_2O_7^{4-}$, F^- and Mn^{2+} trapping experiments. Zero-order dependence with respect to thiourea was observed and it is of interest to compare these data with those of other reductants.

Experimental

Materials

Thiourea (99%, Merck, India) was used without further purification. The solvent water was purified by deionization followed by double distillation. A standard solution of perchloric acid (Fisher, 70% regent) was prepared and analyzed by titration against sodiumtetraborate. All the reagents (potassium permanganate, sodium thiosulfate, sodium pyrophosphate, sodium fluoride, manganese(II) chloride) used were as supplied by Merck, India and were of commercially available purity.

Kinetic measurements

The reaction was initiated by adding the required quantity of thiourea, maintained at constant temperature to the mixed solution of colloidal MnO_2 and perchloric acid maintained at the same temperature. The zero-time was taken when half of the thiourea solution was added. The rate of disappearance of MnO_2 was monitored at 375 nm using cell of path length 1 cm^3. The pseudo-first order rate constants were calculated from the slopes of plots of log (absorbance) versus time. Other details of the kinetic measurements were the same as described elsewhere [8–11].

Product analysis

The oxidation product of thiourea was confirmed as follows: a solution of thiourea (6.0×10^{-2} mol dm^{-3}) was added slowly in the acidic solution of colloidal MnO_2 (6.0×10^{-4} mol dm^3). The reaction mixture rapidly turned dark brown to colorless and 10 cm^3 ethanol was added followed by concentrated hydrochloric acid. After sometime, white crystals of dithiobis (formamidinium) were obtained. The compound was identified by the reported method [12].

Result and discussion

General considerations

When a solution containing $KMnO_4$ (5 cm^3, 20.0×10^{-2} mol dm^{-3}) in $Na_2S_2O_3$ solution (20 cm^3, 1.88×10^{-2} mol dm^{-3}) was mixed at 30 °C for 30 min; it changed from purple to dark brown. The mixture was diluted with H_2O (2 dm^3). The presence of colloidal MnO_2 particle was confirmed by Perez–Benito method. The uv-visible spectrum of the resulting MnO_2 solution exhibits one absorption maxima at 375 nm, presumably due to intraligand excitation. The intense uv-visible absorption has a tail in the visible region and this hampers assignment of the relatively weak d–d transitions to the manganese(IV) ion. Figure 1 represents the changes in the log (absorbance) of colloidal MnO_2–thiourea system with definite time intervals in perchloric acid media. It can be noted here that the absorbance of colloidal MnO_2 is 0.460 at 375 nm before the addition of thiourea and perchloric acid. As the thiourea and $HClO_4$ are added, it results in a sudden decrease in the absorbance. As the plots of log(absorbance) versus time deviate from linearity, it is clear that the reduction kinetics proceed in two stages. The time up to the linearity can be considered to be the induction period (first stage, k_{obs1}). After this point, the deviation in linear plot could be called the (second stage, k_{obs2}). It can be observed that the addition of [$HClO_4$] decreases the induction period. Further, at higher [$HClO_4$], no deviations in the plot of log (absorbance) versus time are observed. These results indicate a complex kinetic behavior of colloidal MnO_2–thiourea reaction. The colloidal MnO_2 solution is unstable in aqueous solutions of $[H^+] > 1.0\times10^{-3}$ mol dm^{-3}. It was also observed that the absorbance of the reaction mixture (colloidal MnO_2 + thiourea) changed very rapidly during the mixing of the $HClO_4$ ($>1.0\times10^{-4}$ mol dm^{-3}). Therefore, the kinetic studies were limited in the $[H^+]$ range of 0.9×10^{-5} to 7.4×10^{-5} mol dm^{-3}. $HClO_4$ was used as the acidifying agent due to the non-complexing nature of ClO_4^-.

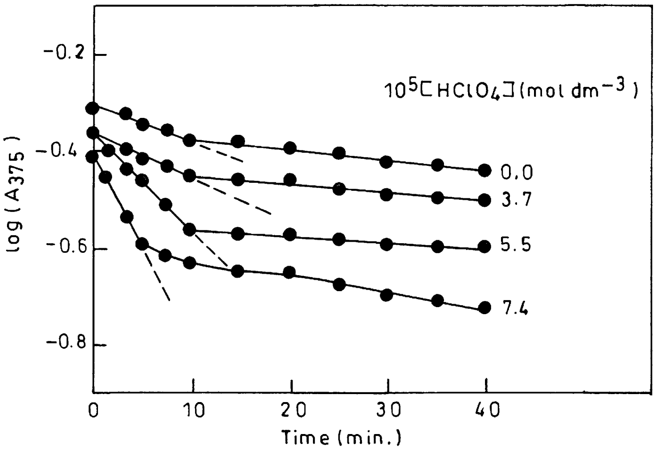


Fig. 1 Pseudo-first order plots for the reduction of colloidal MnO_2 (5.0×10^{-5} mol dm^{-3}) by thiourea (6.0×10^{-4} mol dm^{-3}) as a function of [$HClO_4$] at 40 °C

Rate dependence on colloidal [MnO_2]

In the first set of experiments, the reaction was studied as a function of [MnO_2] at constant [thiourea],

[$HClO_4$] and temperature. Variation of [MnO_2] (1.0×10^{-5} to 5.0×10^{-5} mol dm^{-3}) decreased the reaction rate (Table 1). The initial decrease in the rate constant is due to the possible coagulation of the colloidal particles. As the MnO_2 concentration increases, the rate constants become independent on the initial MnO_2 concentration [7], which is due to the fast adsorption of thiourea on the surface of colloidal MnO_2.

Rate dependence on [thiourea]

In the second set of experiments, the effect of [thiourea] was studied at constant [MnO_2] (5.0×10^{-5} mol dm^{-3}), [$HClO_4$] (3.7×10^{-5} mol dm^{-3}) and temperature (40 °C). The values of rate constant increased with increase in [thiourea] (Table 1). A plot of rate constants versus [thiourea] is nonlinear passing through the origin (Fig. 2a). However, a double logarithmic plot between k_{obs1} and [thiourea] resulted in two straight lines with slopes = 0.65 and 0.0 The reaction follows different order kinetics with respect to [thiourea]: it is fractional- and zero-order for the [thiourea] range 0.6×10^{-4} to 4.0×10^{-4} mol dm^{-3} and 6.0×10^{-4} to 40.0×10^{-4} mol dm^{-3}, respectively. On the other hand, at constant [$HClO_4$], a plot of $1/k_{obs1}$ versus 1/[thiourea] is linear with a positive intercept on the y-axis (Fig. 2b), thus satisfying the Michaelis–Menten [13]/Langmuir–Hinshelwood [14, 15] reciprocal relationship (kinetic proof for complex formation/adsorption of thiourea on the surface of the colloidal MnO_2 particle). Under pseudo-first order conditions (thiourea > MnO_2), the reaction follows zero-order kinetics with respect to [thiourea] (Tables 1 and 2). Therefore, kinetic experiments were also performed in the presence of lower concentration of thiourea (Table 1, effect of thiourea).

Rate dependence on [$HClO_4$]

The rate constant, obtained as a function of [$HClO_4$] at constant [MnO_2] (5.0×10^{-5} mol dm^{-3}), [thiourea] (6.0×10^{-4} mol dm^{-3}) and temperature (40 °C), was found to increase with increasing [$HClO_4$] (Table 1). The results are also shown in Fig. 3 as rate constant—[$HClO_4$] profile that indicates sigmoid dependence of k_{obs1} on [$HClO_4$]. It was also observed that the extent of induction period disappeared completely at higher [$HClO_4$]. The rate increases steadily with increase in [H^+], this may be due to the adsorption of hydrogen ion on the surface of the MnO_2–thiourea complex.

In order to confirm the intercept on the y-axis in the plot of rate constant versus [$HClO_4$] (Fig. 3), a series of experiments were performed in the absence of $HClO_4$ as a function of [MnO_2], [thiourea] and

Table 1 Dependence of first-order rate constants on [MnO_2], [thiourea], [$HClO_4$] and temperature for the reduction of colloidal MnO_2 by thiourea

10^5 [MnO_2] (mol dm^{-3})	10^4 [thiourea] (mol dm^{-3})	10^5 [$HClO_4$] (mol dm^{-3})	Temp (°C)	10^4 k_{obs1} (s^{-1})	10^4 k_{cal1} (s^{-1})	(k_{obs1}−k_{cal1})/k_{obs1}	10^5 k_{obs2} (s^{-1})
1.0	6.0	3.7	40	12.2			No reaction
2.0				9.2			No reaction
3.0				2.6			7.6
4.0				2.6			7.6
5.0				2.6			7.6
5.0	0.6	3.7	40	0.76	0.67	0.11	7.6
	1.0			1.1	0.97	0.11	7.6
	1.4			1.5	1.2	0.20	7.6
	2.0			1.9	1.5	0.21	7.6
	3.0			2.4	1.8	0.25	7.6
	4.0			2.6	2.0	0.23	7.6
	6.0			2.6			7.6
	10.0			2.6			7.6
	20.0			2.6			7.6
	30.0			2.6			7.6
	40.0			2.6			7.6
5.0	6.0	0.9	40	1.1			6.2
		1.8		2.3			7.6
		3.7		2.6			7.6
		4.6		3.8			8.4
		5.6		6.9			9.4
		6.5		7.6			10.0
		7.4		7.6			11.1
5.0	6.0	3.7	30	2.6			3.8
			40	2.6			7.6
			50	2.6			11.5

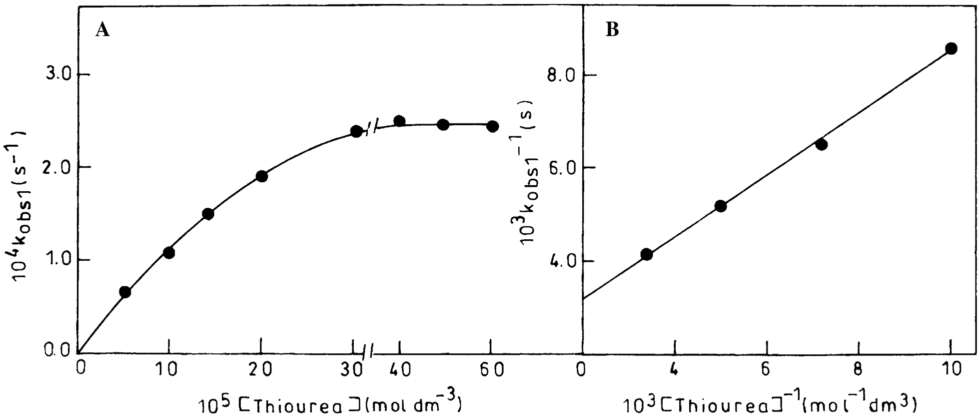


Fig. 2 Dependence of initial rate constant (k_{obs1}) on [thiourea] (**A**). *Reaction conditions*: [MnO_2] = 5×10^{-5} mol dm^{-3}, temperature = 40 °C, [$HClO_4$] = 3.7×10^{-5} mol dm^{-3}. Double reciprocal plot between k_{obs1} and [thiourea] (**B**) for the same kinetic data

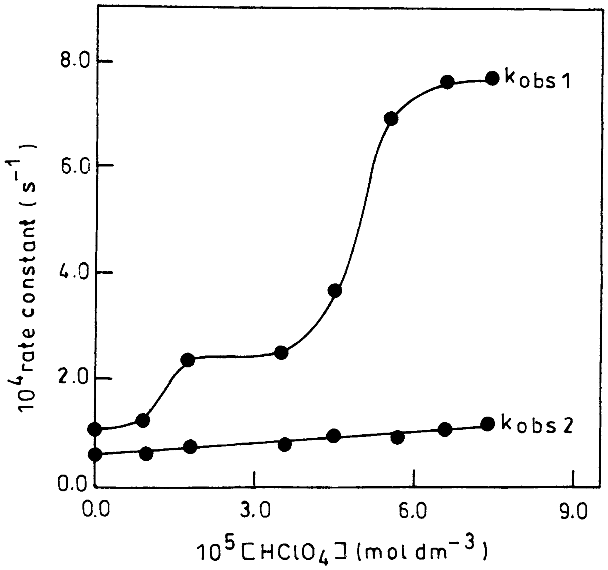
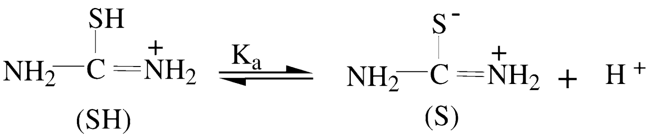


Fig. 3 Dependence of rate constant on [$HClO_4$]. *Reaction conditions*: [MnO_2] = 5.0×10^{-5} mol dm^{-3}, [thiourea] = 6.0×10^{-4} mol dm^{-3}, temperature = 40 °C

temperature. The results of these experiments are summarized in Table 2. The reaction follows zero-order kinetics with respect to [thiourea]. It was observed that the value of rate constant decreases with increase in [MnO_2]. Thus, the oxidation of thiourea by colloidal MnO_2 follows both the acid-independent and acid-dependent path.

To explain the [H^+] dependence of the reaction rate, it is necessary to consider the following equilibrium for which we can write expression (2).



$$\underset{(SH)}{NH_2{-}\overset{\overset{SH}{|}}{C}{=}\overset{+}{N}H_2} \overset{K_a}{\rightleftharpoons} \underset{(S)}{NH_2{-}\overset{\overset{S^-}{|}}{C}{=}\overset{+}{N}H_2} + H^+$$

$$pK_a = pH + \log\frac{[SH]}{[S]} \qquad (2)$$

At lower [H^+] thiourea exists mainly as S and as the [H^+] increases the percentage of protonated thiourea (SH) species increases, which in turn, increases the reaction rate.It was reported that thiourea is neutral in solution but reacts towards acids as a monoacidic base [16]. Under our experimental conditions of [H^+] (3.7×10^{-5} mol dm^{-3}), the monopositive and zwitter ionic species exist in significant concentration. The zwitter ionic species carry a negative charge, which is unfavorable for adsorption on the surface of the colloidal MnO_2 solution. On the other hand, in the presence of mineral acid, nearly every oxidizing agent gives a salt of formamidinedisulfide (oxidation product of compound containing the thiol group). This deduction is supported by the action of oxidizing agents on thiourea. The zero-order dependence and effect of temperature further suggest the fast adsorption of thiourea on MnO_2 surfaces. Thus, we may safely conclude that there is always a competition in the solution between hydrogen ion and protonated thiourea seeking the negative sites on colloidal MnO_2.

Rate dependence on temperature

The reaction was studied at three different temperatures, viz, 30, 40 and 50 °C at two different [thiourea], (1.4×10^{-4} and 6.0×10^{-4} mol dm^{-3}). It may be interesting to note that no change in the rate constant was observed with the variation of temperature (Table 1). This type of behavior of thiourea–MnO_2 redox reaction with temperature is unusual. Generally, the rate of reaction increases appreciably even with a small rise in the temperature.

Effect of added trapping agents

Pyrophosphate and fluoride ions are efficient trapping agents for Mn(III) [17–19]. Therefore, in order to con-

Table 2 Values of first-order rate constants for the reduction of colloidal MnO_2 by thiourea in the absence of $HClO_4$

10^5 [MnO_2] (mol dm^{-3})	10^4 [thiourea] (mol dm^{-3})	Temp (°C)	10^4 k_{obs1} (s^{-1})	10^5 k_{obs2} (s^{-1})
1.0	6.0	40	2.3	3.8
2.0			1.9	3.8
3.0			1.1	3.8
4.0			1.1	Not observed
5.0			1.1	Not observed
5.0	6.0	40	1.1	7.6
	10.0	1.1	7.6	
	15.0	1.1	7.6	
	20.0	1.1	7.6	
	30.0	1.3	7.6	
	40.0	1.3	7.6	
5.0	20.0	30	0.76	Not observed
		40	1.1	Not observed
		50	2.5	Not observed

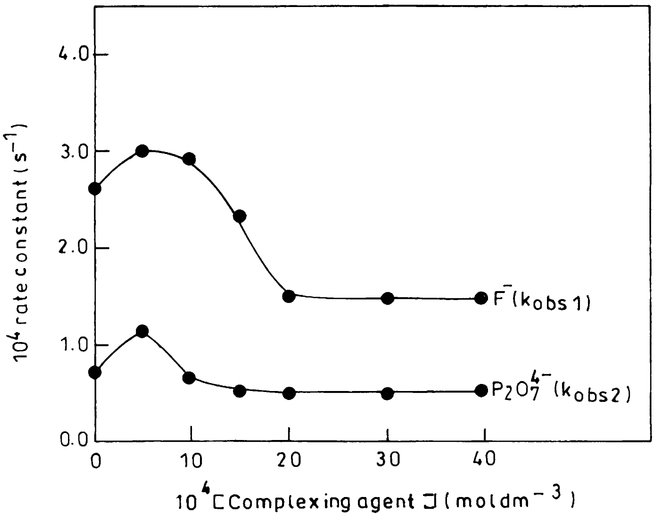


Fig. 4 Dependence of rate constant on complexing agents. *Reaction conditions*: [MnO_2] = 5.0×10^{-5} mol dm^{-3}, [thiourea] = 6.0×10^{-4} mol dm^{-3}, [$HClO_4$] = 3.7×10^{-5} mol dm^{-3}, temperature = 40 °C

firm the formation of Mn(III) during the course of reduction of colloidal MnO_2 by thiourea, a series of experiments were also performed in the presence of $P_2O_7^{4-}$ and F^- ions. Surprisingly in the presence of $P_2O_7^{4-}$, the absorbance of the reaction mixture remains unchanged up to ca. 20 min. These observations indicate that the values of k_{obs1} cannot be evaluated for this period. As the time increases, the effective concentration of Mn(III) increases, which in turn, forms complex with $P_2O_7^{4-}$. In the presence of F^-, the oxidation rate of first stage (k_{obs1}) decreases, while the second stage rate constant (k_{obs2}) is not observed (Table 2). These results are also depicted in Fig. 4 as rate constant–[complexing agent] profile. This indicates that Mn(III) is formed as an intermediate during the reduction of colloidal MnO_2 by thiourea.

Adsorption isotherms

The results of the oxidation rate of thiourea at the initial stage (ca. 20 min.) were fitted to the Langmuir–Hinshelwood expression [14, 15] as plotted in Fig. 2b (vide supra). The Langmuir–Hinshelwood kinetic rate law, which expresses the initial rate as a function of initial concentration of thiourea, is given by

$$v = \frac{kK[\text{thiourea}]}{1 + K[\text{thiourea}]} \qquad (3)$$

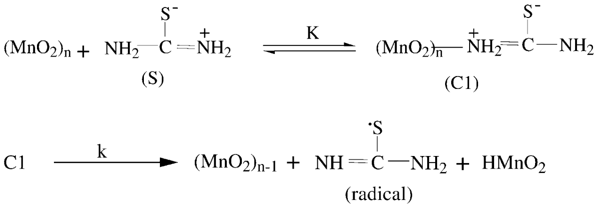
where k denotes the rate constant for the process and K is taken as the adsorption coefficient for the simple Langmuir–Hinshelwood model. The linear transform equation is

$$\frac{1}{v} = \frac{1}{kK[\text{thiourea}]} + \frac{1}{k} \qquad (4)$$

According to Eq. 4, a plot of $1/v$ versus 1/[thiourea] should be linear with a positive intercept on the y-axis ($1/k$) and a positive slope ($1/kK$).

Mechanism and rate law

The interaction of thiourea and colloidal MnO_2 is shown in Scheme 1 for acid-independent path.


(5)

(6)

$$(MnO_2)_n + \underset{(S)}{NH_2-\overset{S^-}{C}=\overset{+}{N}H_2} \overset{K}{\rightleftharpoons} \underset{(C1)}{(MnO_2)_n-\overset{+}{N}H_2=\overset{S^-}{C}-NH_2} \qquad (5)$$

$$C1 \xrightarrow{k} (MnO_2)_{n-1} + \underset{\text{(radical)}}{NH=\overset{\cdot S}{C}-NH_2} + HMnO_2 \qquad (6)$$

Scheme 1

In Scheme 1, Eq. 5 represents the fast adsorption of thiourea on the surface of the colloidal MnO_2 through the electrostatic interaction to form complex C1. We were unable to obtain any spectrophotometric evidence for C1 formation, but rate constant-thiourea profile provides the kinetic evidence for complex formation. The rate-limiting step is a one-step, one electron oxidation–reduction taking place in a C1. This reaction results in the formation of Mn (III) and a radical.

Table 3 Effect of complexing agents ($[P_2O_7^{4-}]$ and $[F^-]$) on the first-order rate constants for the reduction of colloidal MnO_2 (5.0×10^{-5} mol dm^{-3}) by thiourea (6×10^{-4} mol dm^{-3}) in the presence of $HClO_4$ (3.7×10^{-5} mol dm^{-3}) at 40 °C

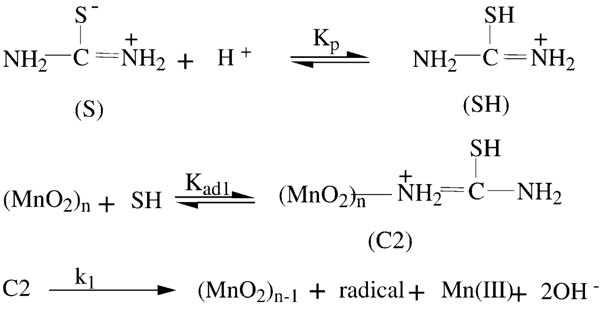
10^4 $[P_2O_7^{4-}]$ (mol dm^{-3})	10^4 $[F^-]$ (mol dm^{-3})	10^4 k_{obs1} (s^{-1})	10^5 k_{obs2} (s^{-1})
0.0	0.0	2.6	7.6
5.0	0.0	No reaction	10.0
10.0		No reaction	7.6
15.0		No reaction	6.2
20.0		No reaction	5.0
30.0		No reaction	5.0
40.0		No reaction	4.9
0.0	5.0	3.0	No reaction
	10.0	2.9	No reaction
	15.0	2.4	No reaction
	20.0	1.5	No reaction
	30.0	1.5	No reaction
	40.0	1.5	No reaction

Table 4 Values of first-order rate constants for the reduction of colloidal MnO_2 by manganese(II) in the absence and presence of thiourea (6.0×10^{-4} mol dm^{-3}) at constant $HClO_4$ (3.7×10^{-5} mol dm^{-3}) and temperature = 40 °C

10^4 [Mn(II)] (mol dm^{-3})	10^4 k_{obs1} [a] (s^{-1})	10^4 k_{obs1} [b] (s^{-1})	10^4 k_{obs2} [a] (s^{-1})	10^4 k_{obs2} [b] (s^{-1})
0.0	2.6	0.0	0.76	0.0
5.0	6.1	1.0	1.1	1.2
10.0	6.1	1.0	1.2	1.3
15.0	5.3	1.1	1.5	1.2
20.0	5.3	1.0	1.5	1.1
30.0	4.6	1.0	1.5	1.2
40.0	5.3	1.1	1.6	1.2

[a] Presence of thiourea
[b] Absence of thiourea

In the presence of $HClO_4$, Scheme 1 is, therefore, modified as follows (Scheme 2):



$$\underset{(S)}{NH_2{-}\overset{\overset{S^-}{|}}{C}{=}\overset{+}{N}H_2} + H^+ \overset{K_p}{\rightleftharpoons} \underset{(SH)}{NH_2{-}\overset{\overset{SH}{|}}{C}{=}\overset{+}{N}H_2} \tag{7}$$

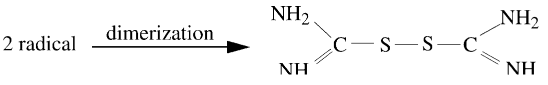
$$(MnO_2)_n + SH \overset{K_{ad1}}{\rightleftharpoons} \underset{(C2)}{(MnO_2)_n{-}\overset{+}{N}H_2{=}\overset{\overset{SH}{|}}{C}{-}NH_2} \tag{8}$$

$$C2 \xrightarrow{k_1} (MnO_2)_{n-1} + \text{radical} + Mn(III) + 2OH^- \tag{9}$$

Scheme 2

After the slow steps, the following fast reactions may also take place.

$$HMnO_2 + \text{thiourea} \xrightarrow{\text{fast}} Mn^{2+} + \text{radical} \tag{10}$$



(11)

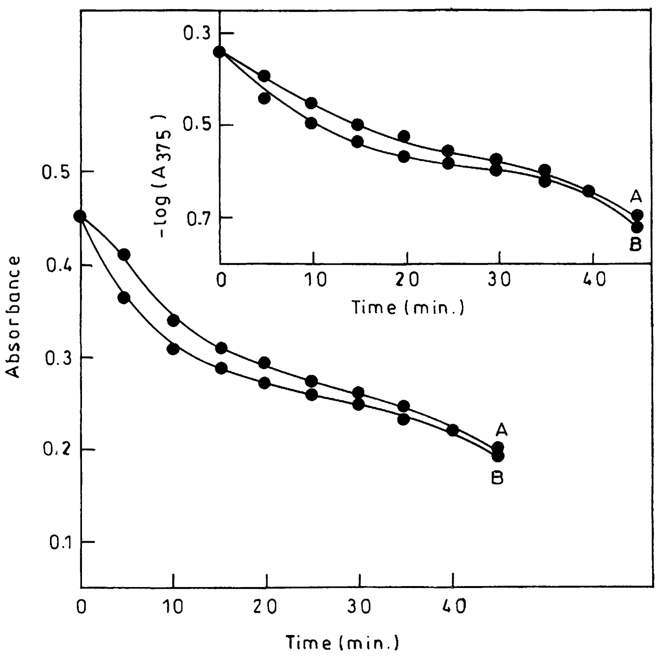


Fig. 5 Plots of absorbance versus time for two kinetic runs. Inset-plots of log (A_{375}) versus time for the same plots. *Reaction conditions*: $[MnO_2] = 5\times10^{-5}$ mol dm^{-3}, [thiourea] = 6.0×10^{-4} mol dm^{-3}, $[HClO_4] = 3.7\times10^{-5}$ mol dm^{-3}, temperature = 40 °C. [Mn(II)] = 30.0 (**a**); 10×10^{-4} mol dm^{-3} (**b**)

A rate law consistent with Scheme 2 may be expressed as Eq. 12.

$$k_{obs1} = \frac{(k_1K_{ad1}K_p[H^+])[\text{thiourea}]}{1 + K_{ad1}K_p[H^+][\text{thiourea}]} \tag{12}$$

The rate law Eq. 12 is in agreement with the observed kinetics. At lower [thiourea], Eq. 12 can be reduced to Eq. 13; whereas at higher [thiourea], Eq. 14 applies.

$$k_{obs1} = (k_1K_{ad1}K_p[H^+])[\text{thiourea}] \tag{13}$$

$$k_{obs1} = k_1 \tag{14}$$

This clearly explains the first and zero-order dependence of the reaction on [thiourea] at constant $[H^+]$ (Fig. 2). Eqs. 13 and 14 correspond to two extreme conditions for which the reaction-order should vary between unity and zero. These results are in good agreement with the Langmuir-adsorption isotherm (vide supra).Rearrangement of Eq. 12 gives:

$$\begin{gathered}\frac{1}{k_{obs1}} = \frac{1}{B_1[\text{thiourea}]} + B_2\\ B_1 = k_1K_{ad1}K_p[H^+];\quad B_2 = \frac{1}{k_1}.\end{gathered} \tag{15}$$

Thus, a plot of $1/k_{obs1}$ versus 1/[thiourea] at constant $[H^+]$ should give a straight line (Fig. 2b). The values of k_1 and K_{ad1} were calculated from the intercept and slope of the

Table 5 Comparison between the second-order rate constants (k^{II}) for the reduction of colloidal MnO_2 by different reductants

Reductant	Temperature (°C) and medium	10^2 k^{II} (mol^{-1} dm^3 s^{-1})	References
Oxalic acid	25, CH_3COOH-CH_3COONa, pH 4.6	46.0	[a]
Lactic acid	30, pH 2.0	2.1	[b]
Formic acid	25, $HClO_4$, pH 0.366	12.0	[c]
Citric acid	40, aqueous	130.6	[d]
Malic acid	40, aqueous	59.3	[e]
D-fructose	40, $HClO_4$ (3.7×10^{-4} mol dm^{-3})	12.6	[f]
Thiourea	40, $HClO_4$ (3.7×10^{-5} mol dm^{-3})	43.0	[g]

[a] $[MnO_2] = 2.0\times10^{-4}$ mol dm^{-3}, [oxalic acid] = 1×10^{-3} mol dm^{-3}, Ref. [2]

[b] $[MnO_2] = 2.0\times10^{-5}$ mol dm^{-3}, [lactic acid] = 0.12 mol dm^{-3}, Ref. [8]

[c] $[MnO_2] = 3.0\times10^{-4}$ mol dm^{-3}, [formic acid] = 0.265 mol dm^{-3}, Ref. [3]

[d] $[MnO_2] = 8.0\times10^{-5}$ mol dm^{-3}, [citric acid] = 16.0×10^{-4} mol dm^{-3}, Ref.[6].

[e] $[MnO_2] = 8.0\times10^{-5}$ mol dm^{-3}, [malic acid] = 6.0×10^{-4} mol dm^{-3}, Ref. [5]

[f] $[MnO_2] = 5.0\times10^{-5}$ mol dm^{-3}, [D-fructose] = 3.0×10^{-3} mol dm^{-3}, Ref. [7]

[g] $[MnO_2] = 5.0\times10^{-5}$ mol dm^{-3}, [thiourea] = 3.0×10^{-3} mol dm^{-3}, Ref. [present work]

Fig. 2b, and are 3.1×10^{-4} s^{-1} and 1.25×10^{10} mol^{-1} dm^3, respectively. At constant [H$^+$], it was confirmed that the redox reaction of colloidal MnO_2 and thiourea occurs in two kinetically distinguishable steps. The first, a fast formation of an adsorption complex; the second, a slower electron transfer reaction. Using the value of k_1, K_{ad1}, K_p and [H$^+$], the k_{cal1} can be generated for various kinetic runs (Table 3). This is a close agreement between k_{obs1} and k_{cal1}, which provides the supportive evidence for the proposed mechanism (Scheme 2) and confirms the validity of expression (12).

Reaction in the presence of Mn(II)

It is well known that colloidal MnO_2 is reduced to Mn(III) in the presence of Mn(II) [4, 7, 8]. Therefore, in order to gain insight into the slow-stage reaction (Fig. 1) (vide supra), the effect of externally added manganese(II) (a reaction product) was also investigated in the absence and presence of thiourea at constant $[MnO_2] = 5.0\times10^{-5}$ mol dm^{-5}, $[HClO_4] = 3.7\times10^{-5}$ mol dm^{-3} and temperature = 40 °C. Figure 5 (absorbance or log (absorbance)–time profiles) indicate the sigmoid behavior of MnO_2–thiourea redox reaction in the presence of externally added Mn(II). The values of rate constant are summarized in Table 4, which suggest that reactivity of thiourea is ca. fivefold higher than Mn(II). Interestingly; the reaction time curve is not a true path of the oxidation of thiourea. It is a mixture of the rates of oxidation of thiourea and Mn(II). Our results seem to suggest that there is a competition between thiourea and Mn(II) to adsorb on the surface of colloidal MnO_2. Due to the complicated features of the reaction, exact dependence of k_{obs1} or k_{obs2} on [thiourea] cannot be estimated in the presence of the other reductant (Mn(II)).

Reactivity of colloidal MnO_2 with other reductants

Interestingly, the reactivity of thiourea towards colloidal MnO_2 is much higher than the corresponding oxidation of many other organic substrates (Table 5). Comparison of the second-order rate constant (k^{II}) of this reaction with those of similar reactions involving the same oxidant (colloidal MnO_2) shows that the reactivity decreases in the order citric > malic > oxalic > thiourea > D-fructose ~ formic > lactic (*caution*: one should keep in mind the reactions conditions; pH, temperature, etc.). The observed results (effect of temperature and zero-order kinetics with respect to thiourea) are consistent with the postulate that the formation of an adsorption complex between the two reactants (thiourea and colloidal MnO_2) takes place. This is not very surprising judging from the fact that the presence of negative charge on the surface of colloidal MnO_2 would provide the site most susceptible to attack by the positive charge of thiourea.

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