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ORIGINAL CONTRIBUTION

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Unusual stabilization of water-soluble colloidal MnO_2 during the oxidation of paracetamol by MnO_4^-

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Abstract The kinetics of the formation and decomposition of water-soluble colloidal MnO_2 in the paracetamol–MnO_4^- redox system have been investigated spectrophotometrically in aqueous-neutral media at 30 °C. Upon mixing aqueous solutions of permanganate and paracetamol, a readily distinguishable brown color appears and then disappears slowly. Experiments have been done to confirm the nature of intermediate (Mn(IV)) formed during the reduction of permanganate by paracetamol. The stoichiometry was found to be 1:1. Formation and decomposition of water-soluble colloidal MnO_2 depend upon the experimental conditions, i.e., [paracetamol] and $[H^+]$. The effect of total $[MnO_4^-]$, [paracetamol], and $[H^+]$ on the rate of the reaction was determined. On the basis of various observations, two mechanisms are proposed: one for MnO_2 formation and the other for decomposition.

Keywords Permanganate · Paracetamol · Oxidation · Colloidal MnO_2 · Kinetics

Introduction

The oxidation of organic reductants by permanganate in aqueous media has received considerable attention [1–10]. It has become clear that when manganous and organic substrates are initially present in excess, the reaction involves two processes [11–15].

$$MnO_4^- \xrightarrow{\text{Reductant}} \text{Intermediate(s)} \quad (1)$$

$$\text{Intermediate(s)} \xrightarrow{\text{Reductant}} Mn(II) \quad (2)$$

In alkaline or weakly acidic solution, permanganate changes to Mn(IV), while in strongly acidic medium, permanganate is further reduced, forming Mn(II). It has been reported on several occasions that the intermediate (Mn(IV)) could be H_2MnO_4, H_2MnO_3, or a water-soluble colloidal MnO_2 [16–19]. The MnO_2 appears practically only after MnO_4^- has completely disappeared from the system. In the case where permanganate serves as an oxidizing agent in acid medium, the possible intermediate species are Mn(VI), Mn(V), Mn(III), and Mn(IV). On the other hand, Mn(II) (reaction product) acts as autocatalyst. Therefore, the MnO_4^- oxidations provide chemical kinetics with challenging mechanism to possibilities due to the ability of Mn to exist in a multitude of oxidation states.

Paracetamol (*N*-acetyl-*p*-aminophenol) is well known for its analgesic and antipyretic action. It is the most widely used medicine worldwide for the relief of pain associated with headache, backache, and postoperation. On the other hand, when consumed in overdose, it may cause severe hepatic toxicity or death. Several spectroscopic methods for its determination based on the oxidation have been reported [20–22]. However, the details of permanganate oxidation of paracetamol are not yet known, and no information regarding the formation of water-soluble colloidal MnO_2 (brown-yellow product) has been reported. The purpose of this article is to analyze the permanganic

Table 1 Second-order rate constant for the oxidation of paracetamol by MnO_4^- at 525 nm

$10^4[MnO_4^-]$ (mol dm^{-3})	10^4 [paracetamol] (mol dm^{-3})	10^2 [H^+] (mol dm^{-3})	k_{obs} (mol^{-1} dm^3 s^{-1})
2.0	1.0	0.0	11.4
2.4			4.7
2.8			1.8
3.0			1.1
3.2			0.7
3.4			0.6
3.0	1.0	0.0	1.1
	1.1		1.4
	1.2		1.9
	1.3		4.9
	1.4		10.5
	1.6		21.6
3.0	0.8	2.3	1.6
	1.0		9.9
	1.1		25.0
	1.2		34.2
	1.4		70.0
3.0	1.0	0.0	1.1
		0.4	4.4
		0.9	5.4
		1.3	8.8
		1.8	9.6
		2.3	9.9

oxidation of paracetamol in weak acid medium, as no references to such process have been found.

Experimental

Materials

Potassium permanganate, sodium fluoride, manganese(II) chloride (all E. Merck, India; 99 %), paracetamol (Acros; 98 %), and perchloric ($HClO_4$, Thomas Baker; 70 % reagent) were purchased and used as supplied. Aqueous solutions of all the reagents were prepared in doubly distilled, deionized and CO_2-free H_2O.

Kinetic measurements

Preliminary observations showed that the oxidation of paracetamol by permanganate is very fast at room temperature (30 °C). Due to the experimental limitations, all kinetic reactions were performed under second-order conditions. Known concentrations of both paracetamol and permanganate were placed in separate vessels, which were placed in a thermostat at desired temperature for a sufficient time to attain the temperature (±0.1). The two solutions were then mixed, and zero time was taken when half of the paracetamol had been added. The progress of the reaction was monitored spectrophotometrically by pipetting out aliquots at different time intervals and measuring the change in the absorbance of permanganate at 525 nm with the help of the Bausch & Lomb Spectronic-20D spectrophotometer. Other details of the kinetic measurements were the same as described elsewhere [23, 24].

Results and discussions

General considerations

The study of the kinetics of MnO_4^--paracetamol reaction did not give useful information under the pseudo-first-order conditions owing to the fast disappearance of purple color. The stoichiometry of the reaction as determined by spectrophotometric titrations measuring the absorbance of unreacted MnO_4^- was found to be 1:1, i.e., 1 mol of MnO_4^- reacts with 1 mol of paracetamol to give stable dark brown color (unstable in excess of [paracetamol] and in presence of [$HClO_4$]). Therefore, the choice of the best conditions for the kinetic experiments is a crucial problem that we address first. To examine the effect of variables, experiments were carried out under second-order kinetic conditions. It should also be emphasized in this study that

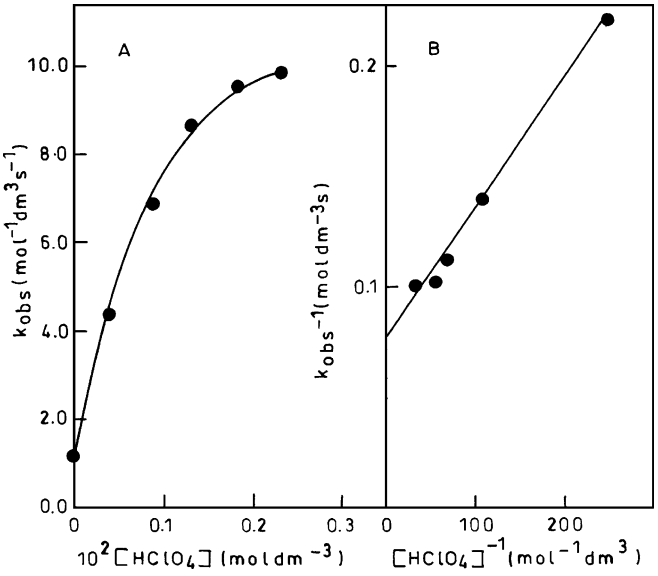


Fig. 1 Effect of [$HClO_4$] on k_{obs} for the MnO_4^- oxidation of paracetamol. [MnO_4^-] (3.0×10^{-4} mol dm^{-3}); [paracetamol], (1.0×10^{-4} mol dm^{-3}); temperature, (40 °C)

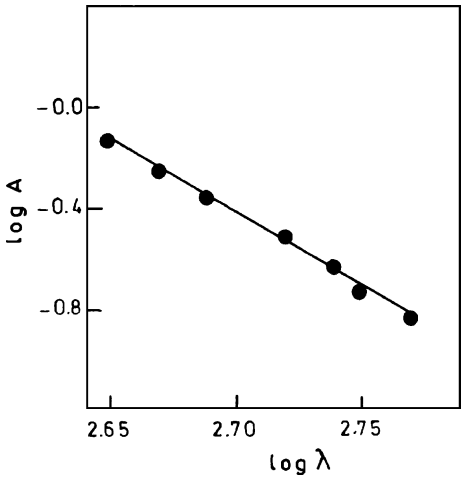


Fig. 2 Plot of log(absorbance) vs logλ for the product (MnO_2) obtained from the MnO_4^- oxidation of paracetamol. [MnO_4^-], (2.0×10^{-4} mol dm^{-3}); [paracetamol], (1.0×10^{-4} mol dm^{-3}); temperature, (40 °C). Slope=−6.2 (correlation coefficient=0.998)

reactions were studied without adding $HClO_4$. Equation 3 was used to calculate the second-order rate constant k_{obs}.

$$k_{obs} = \frac{1}{t}\left[\frac{x}{a(a-x)}\right], \quad (3)$$

where a is the initial molar concentration of MnO_4^- and x is the amount of MnO_4^- which has disappeared at time t. The value k_{obs} was determined from the gradient of $[x/a(a-x)]$ vs t plots. The kinetics of this reaction remained unaffected by increasing the ionic strength of the medium by adding neutral salt, $KClO_4$. Therefore, the ionic strength of the medium was not maintained.

Order of reaction

The effects of [MnO_4^-] [paracetamol], and the added [H^+] were studied at constant temperature (40 °C). The [MnO_4^-] varied from 2.0×10^{-4} to 3.4×10^{-4} mol dm^{-3} at constant [paracetamol] (1.0×10^{-4} mol dm^{-3}). It was observed that as the initial [MnO_4^-] increased, the values of k_{obs} decreased (Table 1). The abnormal behavior probably was due to possible flocculation of colloidal particles. It was found that the rates increased with the increase in [paracetamol]. There was no kinetic evidence for intermediate complex formation between MnO_4^- and paracetamol; if any complex is formed, its formation constant would be extremely small [25]. The observed results are summarized in Table 1. To study the effect of [H^+], the [H^+] was varied in the range of 0.4×10^{-3} to 2.3×10^{-3} mol dm^{-3} by keeping the other [reactants] constant. The rate constants increased with the increase in [H^+]. The plot yields a curve (Fig. 1a) concave in nature (facing down). The plot of k_{obs}^{-1} vs $[H^+]^{-1}$ is also linear with a positive intercept and slope (Fig. 1b). Such a plot is indicative of Michaelis–Menten behavior, which is a kinetic proof for complex formation between the reactant and the hydrogen ion. The reaction was studied at different temperatures at constant reactant concentrations. The values of rate constant were found to be 1.1, 1.7, and 2.5 mol^{-1} dm^3 s^{-1} at 40, 50, and 60 °C, respectively. The activation parameters E_a, $\Delta H^{\#}$, and $\Delta S^{\#}$ were found to be 33 and 31 kJ mol^{-1}, and −137 J K^{-1} mol^{-1}, respectively.

Characterization and identification of intermediate(s)

Preliminary observations showed that the reduction of MnO_4^- by paracetamol is very fast at room temperature (30 °C), and pink (λ_{max}=525 nm) reaction mixture becomes brown to colorless immediately. At lower [paracetamol], the brown color is stable for some time. To confirm the nature of brown color, the spectrum of the reaction mixture containing paracetamol (1.0×10^{-4} mol dm^{-3}) and MnO_4^- (2.0×10^{-4} mol dm^{-3}) was recorded at the end of the reaction. It is well known that if the brown color is due to the formation of water-soluble colloidal MnO_2 as an intermediate, the spectrum will be mainly due to the scattering of light (Rayleigh's Law, [26, 27]: $A=C/\lambda$). The plot of log$A$ vs logλ was linear with slope (−6.2) (Fig. 2). These results are in good agreement with the observations of Freeman and Kappos [26] and Mata-Perez and Perez-Benito [18] (Mn(IV) is commonly involved in the MnO_4^- oxidation of organic reductants).

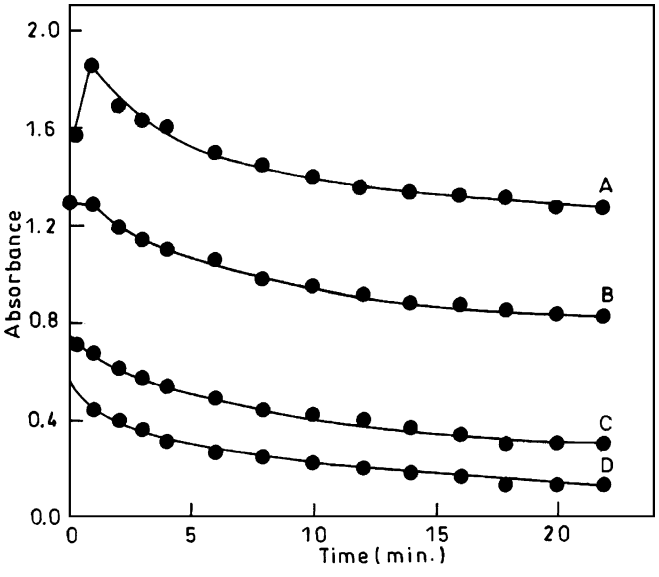


Fig. 3 Absorbance vs time plots at 420 nm for the formation and decomposition of colloidal MnO_2 at 30 °C. [paracetamol]=1.0 (**a**), 1.2 (**b**), 1.4 (**c**), and 1.6×10^{-4} mol dm^{-3} (**d**)

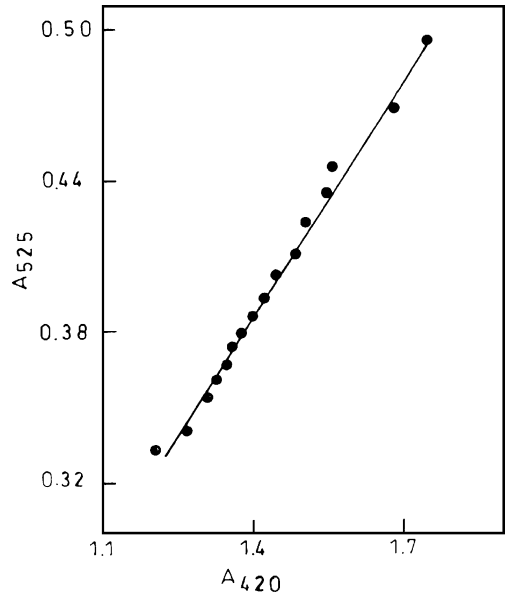


Fig. 4 Plot of absorbance at 525 nm vs absorbance at 420 nm for the MnO_4^- oxidation of paracetamol. [MnO_4^-] (3.0×10^{-4} mol dm^{-3}); [paracetamol] (1.0×10^{-4} mol dm^{-3}); temperature (40 °C)

To confirm the nature of Mn(IV) species and to calculate the second-order rate constants, some kinetic experiments were also performed by monitoring the absorbance of the reaction mixture at 420 nm (the contribution from MnO_4^- is negligible [7]). The observed results are depicted graphically in Fig. 3 as an absorbance–time profile at different [paracetamol]. At lower [paracetamol] ($\geq1.0\times10^{-4}$ mol dm^{-3}), the absorbance increases until it reaches a maximum, and then decreases with time. This behavior indicates the formation and decomposition of intermediate (colloidal MnO_2) during the course of the reaction. A quite noticeable effect can be observed for [paracetamol] $\geq1.2\times10^{-4}$ mol dm^{-3}. As can be seen from Fig. 3 (typical example), as the [paracetamol] increases, the formation of brown color is not observed. On the other hand, at higher [paracetamol] ($\geq5.0\times10^{-4}$ mol dm^{-3}), as the reaction becomes so fast, the formation and decomposition of colloidal MnO_2 are not observed. The values of the second-order rate constant for the decomposition of colloidal MnO_2 as a function of [paracetamol] are summarized in Table 2.

To further identify the formation of colloidal MnO_2 as an intermediate, the absorbance of the reaction mixture was monitored at two wavelengths (420 and 525 nm). A plot of the A_{525} vs A_{420} is expected to be linear (Fig. 4), indicating that product formation occurs at the same rate as the reaction of MnO_4^- which is converted to highly unstable Mn(VI) species that goes very rapidly to MnO_2. The

Table 2 Second-order rate constant for the reduction of colloidal MnO_2 by paracetamol at 420 nm

10^4 [paracetamol] (mol dm^{-3})	10^2 [H^+] (mol dm^{-3})	k_{obs} (mol^{-1} dm^3 s^{-1})
1.3	0.0	2.0
1.4		3.8
1.5		7.2
1.6		15.3
1.3	0.9	2.6
	1.3	3.0
	1.5	3.3
	1.8	3.6
	2.5	4.2

species which absorbs light at 420 and 525 nm is a soluble colloidal MnO_2. Thus, we may safely conclude that this available data are consistent with the formation of water-soluble colloidal MnO_2 as an intermediate during the oxidation of paracetamol by MnO_4^- in aqueous-neutral media.

It is well known that stability of colloidal MnO_2 depends strongly on the pH and nature of the reductant [28–31], and the water-soluble colloidal MnO_2 can exist in aqueous-neutral medium [32, 33]. Therefore, to gain further insight into the mechanistic aspects and the role of hydrogen ions, a series of kinetic experiments were carried out at constant [MnO_4^-] (3.0×10^{-4} mol dm^{-3}), [paracetamol] (1.0×10^{-4} mol dm^{-3}), and temperature (40 °C). The rate of formation and decomposition of colloidal MnO_2 increased with the increase in [$HClO_4$] at 420 nm (Table 2). On the other hand, at higher [$HClO_4$] (≥1.0 mol dm^{-3}), the formation and decomposition of colloidal MnO_2 were not observed. Thus, in presence of $HClO_4$, the intermediate colloidal MnO_2 is unstable and undergo acid hydrolysis.

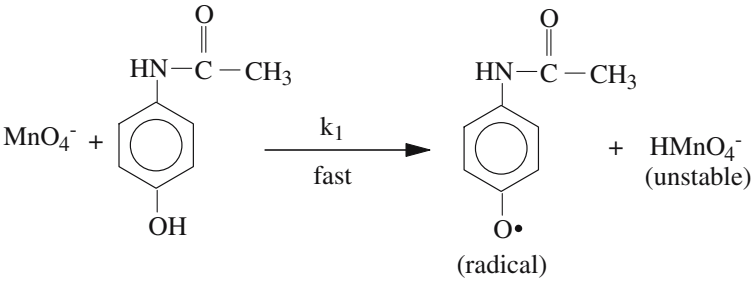
To substantiate the formation of Mn(III) at 420 nm and to clarify the role of this oxidizing species, different amounts of sodium fluoride were added to the reaction mixture. The values k_{obs} at 30 °C were 3.8, 3.4, 3.0, 2.5, and 2.1 mol^{-1} dm^3 s^{-1} at [F^-]=0.0, 0.5, 1.0, 1.5, and 2.0×10^{-3} mol dm^{-3}, respectively. Oxidation rate of paracetamol is decreased by adding F^- ions. This indicates that Mn(III) is also formed as an intermediate in the reduction of permanganate by paracetamol.

Mechanism and rate-law

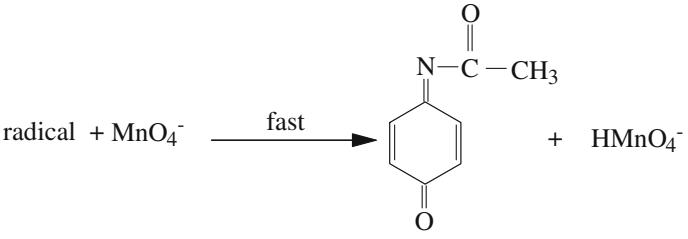
The experimental observations for the formation of colloidal MnO_2 can be explained by considering the following reaction mechanism.

Scheme 1 In presence of $HClO_4$, there is a competition between H^+ and paracetamol to react with colloidal MnO_2. Based on these findings and other results discussed earlier, the Scheme 2 mechanism is proposed

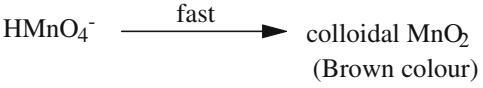
i *Acid-uncatalyzed path:*



(4)



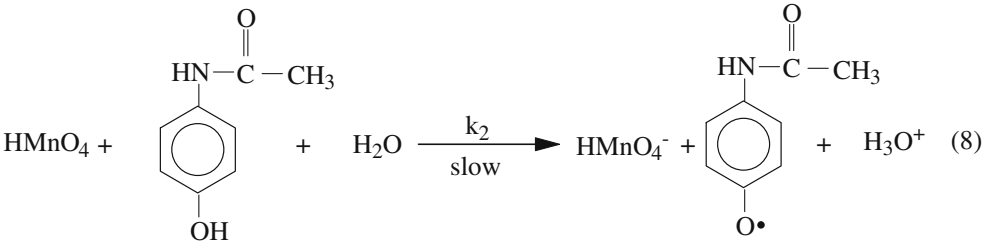
(5)



(6)

ii *Acid-catalyzed path:*

(7)



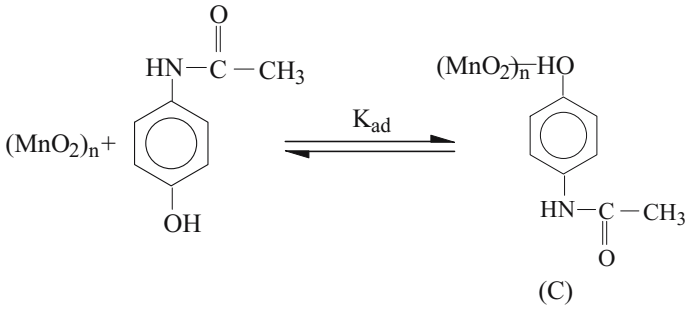
(8)

(reactions (5) and (6) then follow)

The similar mechanisms for one-step, one-electron transfer have been proposed by many researchers [25, 34, 35]. In Scheme 2, second step (Eq. 11 in Scheme 2) represents the adsorption of paracetamol on the surface of the colloidal MnO_2. The hydrogen bonding between the –OH group of paracetamol and MnO_2 is responsible for the formation of complex C. In analogy with our previous results [28, 30, 31], we assume that C decomposes by a one step, one-electron oxidation–reduction mechanism to Mn (III) and other products (Eq. 11 in Scheme 2). Mn(III) is a strong oxidant and is unstable with respect to disproportionation in the presence of large amount of paracetamol it immediately gets converted into stable products (Eq. 14 in Scheme 2).

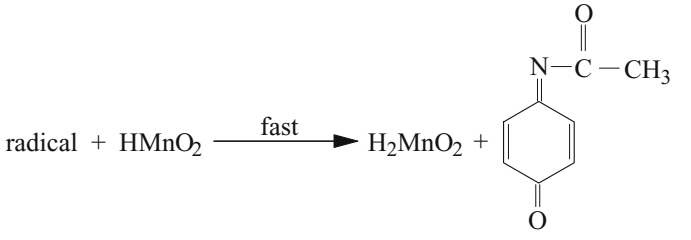
Scheme 2 Finally, by hydrolysis of the imine intermediate, the benzoquinone, ammonia, and acetic acid are obtained

$$MnO_2 + 3H^+ \xrightarrow{k_3} Mn^{2+} + H_2O + OH^- \quad (9)$$



(10)

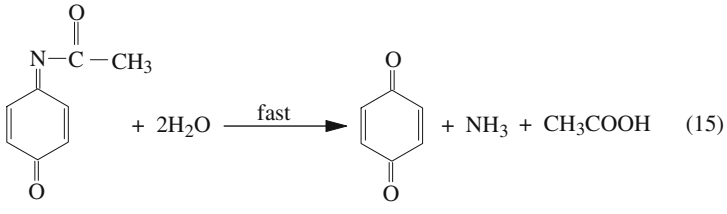
$$C \xrightarrow{k_4} (MnO_2)_{n-1} + HMnO_2 + \text{radical} \quad (11)$$



(12)

$$H_2MnO_2 + 2H^+ \xrightarrow{\text{fast}} Mn^{2+} + 2H_2O \quad (13)$$

$$Mn(III) + \text{paracetamol} \xrightarrow{\text{fast}} Mn(II) + \text{other products} \quad (14)$$



(15)

To confirm the formation of a radical, a solution of MnO_4^- (6.0×10^{-4} mol dm^{-3}) was added to a mixture of [paracetamol] (2.0×10^{-4} mol dm^{-3}) and saturated solution of mercuric(II) chloride (5 cm^3) at 30 °C. The formation of white precipitate was observed which confirms that the free radicals responsible for the reduction of Hg(II)ions were produced in this system [36]. The proposed mechanism is further supported by analysis of the products. Ammonia has been detected as ammonium ions in solution. Benzoquinone and acetic acid were also detected by the spot tests [37, 38]. Similar products using different oxidant have been also suggested by Sultan [39].

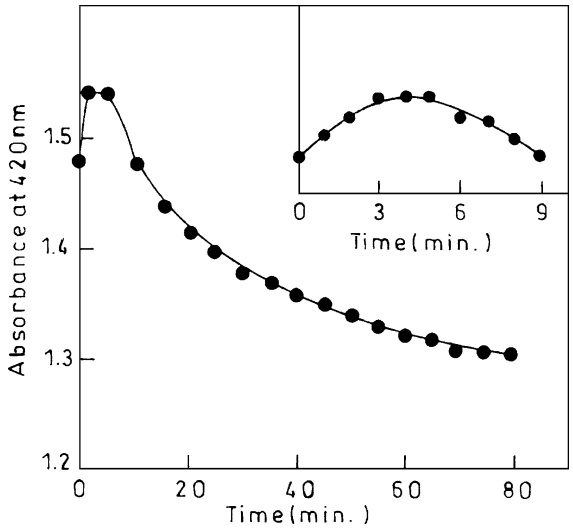


Fig. 5 Absorbances vs time plot for the formation and decomposition of colloidal MnO_2 at 30 °C. *Inset* Plot showing the formation of water-soluble colloidal MnO_2. *Reaction conditions* $[MnO_4^-]$ (= 2.3×10^{-4} mol dm^{-3}), [paracetamol] (= 6.9×10^{-5} mol dm^{-3})

According to Scheme 1, the overall reaction rate is given by Eq. 16 for the acid-uncatalyzed and acid-catalyzed paths.

$$\frac{-d[MnO_4^-]}{dt} = \left(k_1 + \frac{k_2 K_a [H^+]}{1 + K_a [H^+]}\right)[MnO_4^-][paracetamol] \quad (16)$$

The Eq. 16 is in good agreement with the observed results.

A series of experiments were also performed to observe the solid MnO_2 precipitation under various experimental conditions. These results are given in Table 3. It was observed that at specific concentrations of permanganate, paracetamol, and perchloric acid, the reaction mixture turned turbid due to the deposition of MnO_2. It was also noticed that MnO_2 deposition appeared at 30 °C after prolonged incubation. The time of deposition was also depending upon the experimental condition. Under our experimental condition, MnO_2 deposition was observed after 12 h (Fig. 5). The instability of colloidal MnO_2 in presence of $HClO_4$ or paracetamol is probably due to the excess of paracetamol under acidic pH as an oxidant with the formation of Mn(II) (Table 3). This excess can, therefore, react with the MnO_2 formed after reduction of permanganate. The results indicate that amounts of colloidal MnO_2 is simultaneously decreasing with increasing acidity of the medium and [paracetamol], respectively. The reactivity of MnO_2, however, seems larger toward the paracetamol than the reactivity of permanganate.

Table 3 Effects of $[MnO_4^-]$, [paracetamol], and $[H^+]$ on the MnO_2 deposition

$10^4[MnO_4^-]$ (mol dm^{-3})	10^5 [paracetamol] (mol dm^{-3})	10^2 $[H^+]$ (mol dm^{-3})	MnO_2^a deposition	Reaction mixture
2.3	27.9	0.0	N	Colorless
	23.2		N	Colorless
	18.6		N	Colorless
	13.9		N	Colorless
	9.3		N	Colorless
	6.9		O	Brown
	4.6		O	Brown
	2.3		O	Brown
1.8	6.9		O	Brown
2.3			O	Brown
2.7			O	Brown
3.2			O	Brown
2.3	6.9	0.4	N	Colorless
		0.9	N	Colorless
		1.3	N	Colorless
		1.8	N	Colorless

[a]Deposition test: *N* No MnO_2; *O* MnO_2 observed

Comparison with related reductant

It is interesting to note that the kinetic experiments for the oxidation of paracetamol cannot be performed under pseudo-first-order conditions, whereas for the oxidation of acetanilide, the presence of $[H^+]$ is essential. Under our experimental conditions, [permanganate] (2.0×10^{-4} mol dm^{-3}), [acetanilide] (2.0×10^{-3} mol dm^{-3}), $[HClO_4]$ (6.9×10^{-2} mol dm^{-3}), and temperature (40 °C), the oxidation rate of acetanilide is 3.4×10^{-4} s^{-1}, whereas the oxidation of paracetamol is not observable (very fast) in these conditions. Therefore, the reactivity of paracetamol and acetanilide is in the order paracetamol ≫ acetanilide. The presence of –OH group (Scheme 2) is responsible for the higher reactivity of paracetamol which easily transfers the proton to MnO_4^- leading to the formation of stable water-soluble colloidal MnO_2 as an intermediate. On the other hand, F^- ions inhibit the oxidation rate of paracetamol and have no effect on the oxidation of acetanilide. These results clearly suggest that oxidation of acetanilide and paracetamol proceeds through the different reaction path.

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