Oxidation of Lactic Acid by Water Soluble (Colloidal) Manganese Dioxide

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ABSTRACT: Spectrophotometric method has been used to characterize water-soluble colloidal manganese dioxide obtained by the redox reaction between sodium thiosulphate and potassium permanganate in neutral aqueous medium which shows a single peak in the visible region with $\lambda_{max} = 425$ nm. The kinetics of the oxidation of lactic acid by colloidal manganese dioxide (oxidant) has been investigated spectrophotometrically under pseudo-first-order conditions of excess lactic acid. The rate of the noncatalytic reaction pathway was slow which increased with increasing lactic acid concentration. The reaction was first-order with respect to [oxidant] as well as [lactic acid]. In presence of manganase(II) and fluoride ions, the noncatalytic path disappeared completely while the oxidation rate of autocatalytic path increased and decreased, respectively with increasing [Mn(II)] and [F$^-$]. A mechanistic scheme in conformity with the observed kinetics has been proposed with the rate-law:

$$\nu = \frac{-d[\text{MnO}_2]}{dt} = \frac{k_1 k_2 [\text{MnO}_2][\text{H}^+][\text{lactic acid}]_T}{([\text{H}^+] + K_a)(k_{-1} + k_2)}$$

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INTRODUCTION

It is well established that manganese dioxide acts as an oxidizing agent for both organic [1] and inorganic compounds [2,3], but, due to solubility problem under normal conditions, its use is limited [4]. Active forms of manganese dioxide have earlier been obtained by redox reaction of permanganate with hydrogen peroxide [5] and manganese(II) ion [6]. Perez-Benito et al. [7] reported a method for the preparation of water-soluble colloidal manganese dioxide by the redox reaction between permanganate and sodium thiosulphate under neutral conditions for the first time. The water-soluble form of colloidal manganese dioxide presents the advantage over water-insoluble form of possessing a larger specific surface.

The kinetic aspects of the colloidal manganese dioxide have been studied with formic and oxalic acids [8,9]. However, the details of lactic acid oxidation by colloidal manganese dioxide are yet unknown although the permanganate/lactic acid reaction has been studied in acidic solutions [10]. The process of the preparation of colloidal manganese dioxide by permanganate/sodium thiosulphate system is not available with sufficient details to describe the reaction under all conditions. Therefore, the results presented here supplement the previous studies of this system

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and contribute to the elucidation of the mechanism of oxidation of lactic acid by the water-soluble colloidal manganese dioxide.

EXPERIMENTAL

Materials

Lactic acid, sodium thiosulphate, $KMnO_4$, and H_2SO_4 were commercial products of highest purity and were used as supplied. Stock solutions of all the reagents were freshly prepared in Pyrex glass double-distilled water. The $KMnO_4$ solution was frequently restandardized and stored in amber coloured bottle in a refrigerator.

Kinetic Measurements

Requisite amounts of each reagent were pipetted out into two-necked reaction flasks and the contents were thermally equilibrated at the desired temperature in a constant temperature paraffin oil bath of $\pm 0.1°C$ accuracy. The reaction was initiated by adding lactic acid as the last component and the rate of the disappearance of colloidal MnO_2 was followed spectrophotometrically by monitoring the decay of absorbance of colloidal MnO_2 ($\lambda_{max} = 425$ nm) at regular time intervals. Neither lactic acid nor products showed any absorbance at this wavelength. Other experimental procedure details are described elsewhere [11–14]. All the kinetic runs were carried out for a period of more than 80% completion with lactic acid in excess in order to work under pseudo-first-order conditions. Observed pseudo-first-order rate constants (k_{obs}, s^{-1}) were obtained from the slopes of $\log(A)_{425}$ versus time plots (average correlation coefficient = 0.997). The experimental second-order rate constants (k^{II}, mol^{-1} dm^3 s^{-1}) were calculated from the relationship: $k^{II} = k_{obs}/$[lactic acid].

RESULTS AND DISCUSSION

Preparation and Characterization of Colloidal Manganese Dioxide

It is well known that the spectrum of acidified permanganate solution possesses an absorption band located at $\lambda_{max} = 525$ nm (Fig. 1, –■–) in the visible range. It is observed that the spectrum of permanganate changes by the addition of $Na_2S_2O_3$ solution. The band at 525 nm gradually disappears with increase in [$Na_2S_2O_3$] and a new band begins to appear at
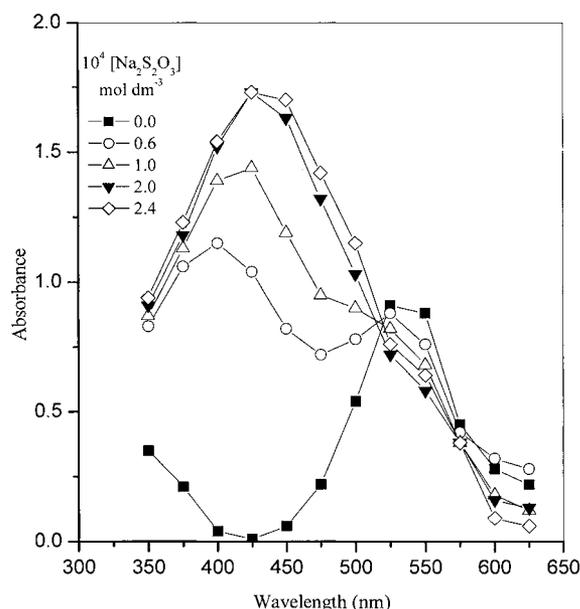
Figure 1 UV–visible spectra of the mixtures containing a fixed amount of $KMnO_4$ (=4.0×10^{-4} mol dm^{-3}) and varying amounts of $Na_2S_2O_3$ at 30°C.

400 nm (Fig. 1). At lower [$Na_2S_2O_3$] (≤ 0.6 mol dm^{-3}), the mixture showed two bands at 400 and 525 nm (Fig. 1, –○–). At higher [$Na_2S_2O_3$] ($\geq 2.0 \times 10^{-4}$ mol dm^{-3}), the mixture showed only one broad band covering the whole visible region of the spectrum with $\lambda_{max} = 425$ nm (Fig. 1, –▼–, –◇–). The concentration of $Na_2S_2O_3$ needed to stabilize the new peak was 2.4×10^{-4} mol dm^{-3}. It was also observed that at higher [$Na_2S_2O_3$] ($\geq 2.5 \times 10^{-4}$ mol dm^{-3}), the mixture turned turbid due to the precipitation of manganese dioxide. Thus, we conclude that the new stabilized spectrum (Fig. 1, –◇–) is that of water-soluble colloidal manganese dioxide. The new oxidizing solution (i.e., the water soluble colloidal manganese dioxide) was, therefore, prepared by addition of $Na_2S_2O_3$ (1.0 cm^3, 0.01 mol dm^{-3}) to a permanganate solution (2.0 cm^3, 0.01 mol dm^{-3}) diluted to 50 cm^3 with water. The resulting solution was dark brown and perfectly transparent and stable for several weeks. Figure 2 clearly indicates the effect of [$Na_2S_2O_3$] on the absorbance of colloidal manganese dioxide at 425 nm. In order to confirm the fulfillment of Beer's law, a calibration graph was constructed between $(A)_{425}$ and concentration of colloidal MnO_2. The law is obeyed for the concentration range used in the present investigations.

The reaction equation has earlier been found to be

$$8MnO_4^- + 3S_2O_3^{2-} + 2H^+$$
$$= 8MnO_2 + 6SO_4^{2-} + H_2O \qquad (1)$$
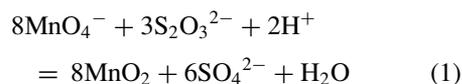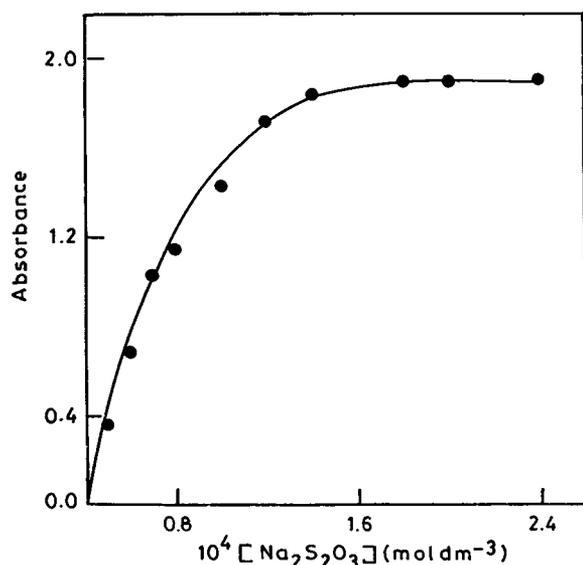
Figure 2   Effect of [Na$_2$S$_2$O$_3$] on the absorbance (425 nm) of water soluble colloidal MnO$_2$. Reaction conditions: [KMnO$_4$]= 4.0×10^{-4} mol dm^{-3}, temp. = 30°C.

Effect of [H$_2$SO$_4$] on Permanganate Spectrum in Presence of Na$_2$S$_2$O$_3$

Figure 3 shows the effect of [H$_2$SO$_4$] on the absorbance of KMnO$_4$ (=4.0×10^{-4} mol dm^{-3}) and its reduction product (colloidal MnO$_2$). At lower [H$_2$SO$_4$]
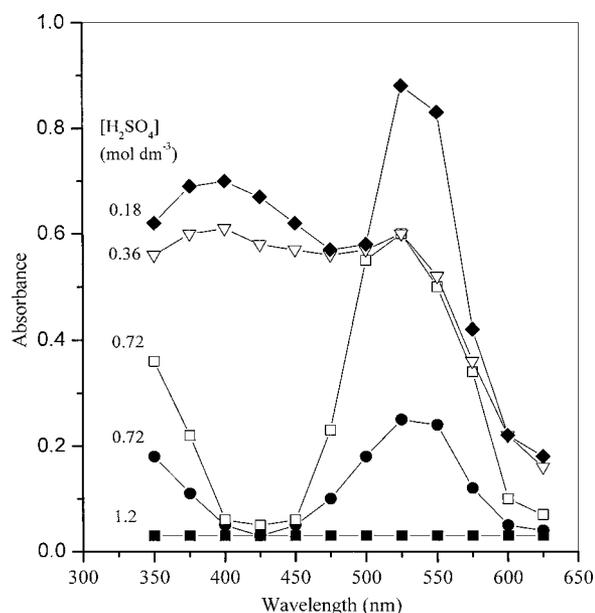
Figure 3   Effect of [H$_2$SO$_4$] on the UV–visible spectra of the mixtures containing fixed amounts of KMnO$_4$ (=4.0×10^{-4} mol dm^{-3}) and Na$_2$S$_2$O$_3$ (=2.0×10^{-4} mol dm^{-3}) at 30°C, except in (-□-) where [Na$_2$S$_2$O$_3$] = 0.0 mol dm^{-3}.

(0.18 mol dm^{-3}), the reaction mixture shows two peaks with λ_{max} = 400 (colloidal MnO$_2$) and 525 nm (MnO$_4^-$) but at higher [H$_2$SO$_4$] (1.2 mol dm^{-3}), there is no peak in the visible region. The unstability of colloidal MnO$_2$ in the presence of H$_2$SO$_4$ is probably due to the excess of sodium thiosulphate under acidic pH as an oxidant (similarly to MnO$_4^-$) with the formation of Mn(II). Since the MnO$_4^-$:S$_2$O$_3^{2-}$ molar ratio is 2:1 in our experiments and on the basis of the reaction Eq. (1) the S$_2$O$_3^{2-}$ has been present in excess. This excess can, therefore, react with the MnO$_2$ formed after acidification (the oxidation ability of both MnO$_4^-$ and MnO$_2$ depends on pH and it is increasing with decreasing pH, since the value of [H$^+$] is increased in the Nernst formula). The results indicate that amounts of both MnO$_4^-$ and colloidal MnO$_2$ are simultaneously decreasing with increasing acidity of the medium. The reactivity of MnO$_2$, however, seems larger toward the thiosulphate ion than the reactivity of the MnO$_4^-$ because decrease of MnO$_2$ was observed at lower [H$_2$SO$_4$] than the decrease of the MnO$_4^-$ content. These results are in agreement with the observations of other investigators [15]. Thus, the water-soluble colloidal MnO$_2$ can exist in neutral aqueous medium.[*]

Kinetics of Lactic Acid Oxidation by Colloidal MnO$_2$

Under the experimental conditions of (colloidal) [MnO$_2$] = 2.0×10^{-4} mol dm^{-3} and [lactic acid]$_T$ in the range 0.03–0.6 mol dm^{-3}, Fig. 4 shows examples of some of the kinetic curves from which the rate constants for the oxidation were obtained. As the plots of log(absorbance) versus time deviate from linearity, it is clear that the oxidation kinetics proceed in two stages [16], i.e., initial slow stage followed by a relatively faster step. The time at which the deviation commenced was found to decrease with an increase in [lactic acid]$_T$ (the noncatalytic path even disappeared completely at higher [lactic acid]$_T$, Table I).

In a set of experiments the reaction was studied as a function of colloidal MnO$_2$ concentration between 2.0×10^{-4} and 10.0×10^{-4} mol dm^{-3} at constant ionic strength (0.5 mol dm^{-3} NaClO$_4$), [lactic acid]$_T$ (0.06 mol dm^{-3}), and temperature (30°C). Independence of the rate constants over the range of concentration used (Table I) is in agreement with a first-order dependence on [MnO$_2$], i.e.,

$$\nu = -d\,[MnO_2]/dt = k_{obs}[MnO_2] \qquad (2)$$
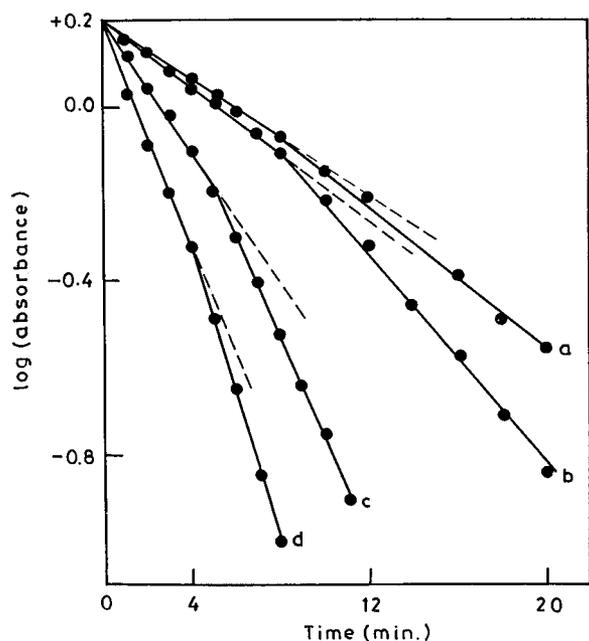
Figure 4   Plots of log(absorbance)$_{425}$ versus time for the oxidation of lactic acid by colloidal MnO$_2$. Reaction conditions: [lactic acid] = 1.2 (a); 3.0 (b); 18.0 (c); and 30.0 × 10^{-2} mol dm^{-3} (d), [MnO$_2$] = 2.0 × 10^{-4} mol dm^{-3}, [NaClO$_4$] = 0.5 mol dm^{-3}, temp. = 30°C.

In the second set of experiments, the effect of [lactic acid] on the reaction rate was studied at constant ionic strength, (colloidal)[MnO$_2$], and temperature. A variation of the [lactic acid]$_T$ (0.03–0.60 mol dm^{-3})

increased the oxidation rate (Table I). These results are also shown graphically in Fig. 5. The plot of k_{obs1} versus [lactic acid]$_T$ is a straight line whereas a log–log plot was linear with slope = 0.94. The reaction is, therefore, first-order with respect to [lactic acid]$_T$. The plot of k_{obs1} versus [lactic acid] shows a positive intercept (extrapolation until zero concentration of reductant) on the y-axis (Fig. 5). It should, however, be zero at [lactic acid] = 0.0 mol dm^{-3} (see Eq. (11)). Inspection of the figure brings to light that the aqueous solution of colloidal MnO$_2$ is unstable possibly due to its reduction to some extent [9].

In order to confirm/gain insight into the autocatalytic pathway (Fig. 4), the effect of manganese(II) (a reduction product of colloidal MnO$_2$, vide infra) was studied. The k_{obs2}, obtained as a function of [Mn(II)] at constant [lactic acid] (0.13 mol dm^{-3}), (colloidal)[MnO$_2$] (8.0 × 10^{-5} mol dm^{-3}), and temperature (30°C), was found to increase with increasing [Mn(II)] (Table II). The results are also shown in Fig. 6 as k_{obs2} − [Mn(II)] profile which indicates sigmoid dependence of k_{obs2} on [Mn(II)]. It was also noticed that the extent of the noncatalytic reaction pathway disappeared completely even at as low as [Mn(II)] = 1.0 × 10^{-4} mol dm^{-3}. Our results seem to indicate that Mn(II) is the active autocatalyst (the Mn(II) formed as reaction product contributes to accelerate the oxidation of lactic acid by colloidal MnO$_2$).

It is well known that fluoride ions form complexes with Mn(III) and Mn(IV) [9]. To substantiate the

Table I   Effect of Colloidal MnO$_2$ and Lactic Acid Concentrations on the pseudo-First-Order Rate Constants (k_{obs1}, k_{obs2}) of Lactic Acid Oxidation by Colloidal MnO$_2$[a]

10^5 [MnO$_2$][b] (mol dm^{-3})	[Lactic Acid]$_T$ (mol dm^{-3})	10^3 k_{obs1} (s^{-1})	10^3 k_{obs2} (s^{-1})
2.0	0.06	1.7	2.3
3.0		1.8	2.3
6.0		1.7	2.1
7.0		1.6	2.2
10.0		1.8	2.4
2.0	0.03	1.3	1.6
	0.06	1.7	2.3
	0.12	2.6	3.3
	0.18	3.6	4.4
	0.24	4.2	5.4
	0.30	5.1	6.1
	0.40	Not observed	7.8
	0.50	Not observed	9.5
	0.60	Not observed	11.1

[a] [NaClO$_4$] = 0.5 mol dm^{-3}, temp. = 30°C.

[b] As there exists the possibility of flocculation of colloidal MnO$_2$, the effect was seen in presence of gum arabic, which is well known stabilizing agent of the oxidant in solution [8].

Table II Effect of Different Variable Concentrations on the Pseudo-First-Order Rate Constants (k_{obs1}, k_{obs2}) of Lactic Acid Oxidation by Colloidal MnO_2 (8.0×10^{-5} mol dm^{-3}) at 30°C

10^4 [Mn(II)] (mol dm^{-3})	10^4 [F$^-$] (mol dm^{-3})	[Lactic Acid] (mol dm^{-3})	Noncatalytic 10^3 k_{obs1} (s^{-1})	Autocatalytic 10^3 k_{obs2} (s^{-1})
0.0	0.0	0.13	1.9	2.6
1.0	0.0	0.13	Not observed	2.5
2.0	0.0	0.13	Not observed	2.8
6.0	0.0	0.13	Not observed	2.9
10.0	0.0	0.13	Not observed	3.0
14.0	0.0	0.13	Not observed	3.6
20.0	0.0	0.13	Not observed	4.4
30.0	0.0	0.13	Not observed	4.6
0.0	2.0	0.13	Not observed	1.7
0.0	6.0	0.13	Not observed	1.8
0.0	10.0	0.13	Not observed	1.7
0.0	14.0	0.13	Not observed	1.6
0.0	20.0	0.13	Not observed	1.4
0.0	30.0	0.13	Not observed	1.5
0.0	40.0	0.13	Not observed	1.3

formation of Mn(III) during the oxidation of lactic acid by colloidal MnO_2, different amounts of sodium fluoride were added to the reaction mixture. As NaF decreased the rate (Table II), the noncatalytic reaction pathway also disappeared. This indicates that Mn(III) may also be the reactive species in the autocatalytic path.

On the basis of above results and previous observations [8,9], the following two mechanisms can be proposed:
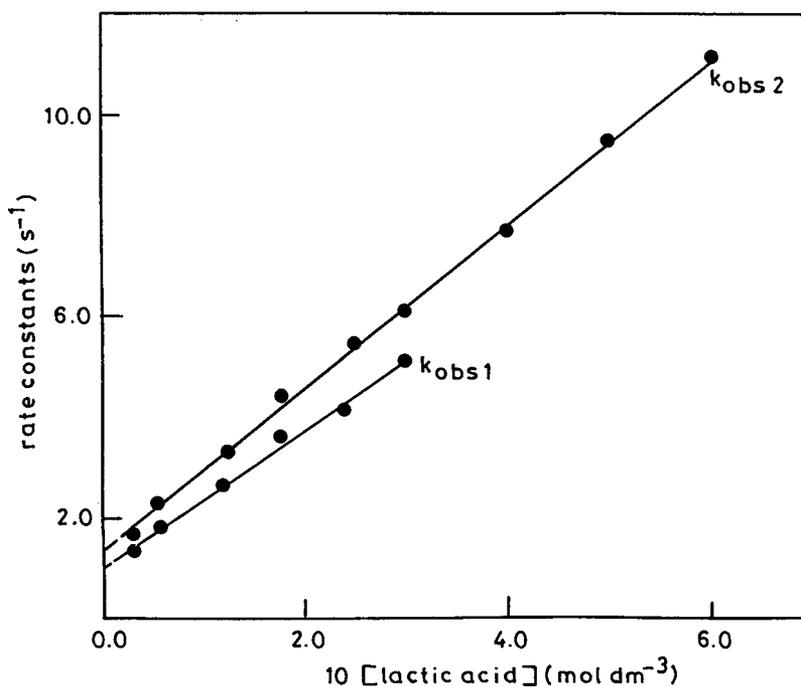
Figure 5 Effect of [lactic acid] on the pseudo-first-order rate constants for the oxidation of lactic acid by colloidal MnO_2. Reaction conditions: [MnO_2] = 2.0×10^{-4} mol dm^{-3}, [$NaClO_4$] = 0.5 mol dm^{-3}, temp. = 30°C.

(i) Non-catalytic reaction pathway:

$$CH_3-\underset{\underset{OH}{|}}{CH}-COOH \xrightleftharpoons{K_a} CH_3-\underset{\underset{OH}{|}}{CH}-COO^- + H^+ \;(K_a = 8.4 \times 10^{-4} \,[17]) \quad (3)$$

(HA)   (A⁻)

$$(MnO_2)_n + CH_3-\underset{\underset{OH}{|}}{CH}-COOH \xrightleftharpoons[k_{-1}]{k_1} (MnO_2)_n-CH_3\underset{\underset{OH}{|}}{C}HCOOH \quad (4)$$

C1

$$C1 \xrightarrow{k_2} (MnO_2)_{n-1} + Mn^{2+} + CH_3-\underset{\underset{O}{\|}}{C}-COOH + 2OH^- \quad (5)$$
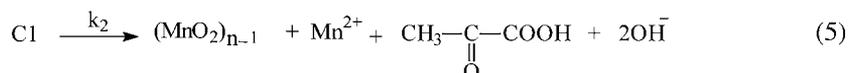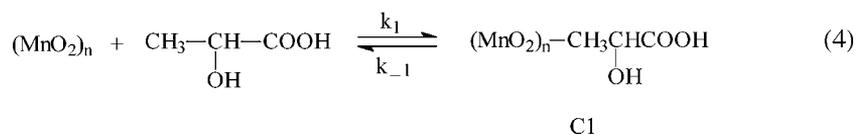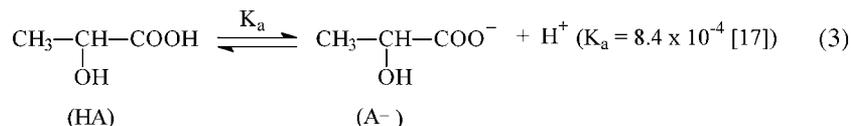
Scheme 1

(ii) Auto-catalytic reaction pathway:

$$(MnO_2)_{\overline{n}}-CH_3\underset{\underset{OH}{|}}{C}HCOOH + Mn^{2+} \xrightleftharpoons{fast} (MnO_2)_{\overline{n}}-CH_3\underset{\underset{OH}{|}}{C}HCOOH\text{-}\text{-}\text{-}Mn]^+ + H^+ \quad (6)$$

C1   C2

$$C2 \xrightarrow{slow} (MnO_2)_{n-1} + CH_3-\underset{\underset{O}{\|}}{C}-COOH + Mn(III) \quad (7)$$

$$(MnO_2)_n + Mn^{2+} \rightleftharpoons 2\,Mn(III) \quad (8)$$

$$Mn(III) + CH_3\underset{\underset{OH}{|}}{C}HCOOH \xrightarrow{fast} Mn(II) + CH_3\underset{\underset{O}{\|}}{C}COOH \quad (9)$$
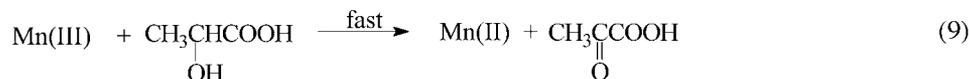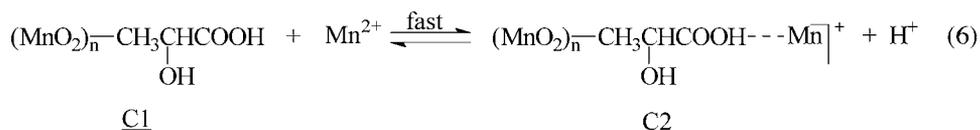
Scheme 2

In Scheme 1, $(MnO_2)_n$ stands for the colloidal manganese dioxide and Eq. (4) represents the adsorption of lactic acid on the surface of the colloidal particles to give complex C1. We assume that C1 decomposes in a one-step, two electron oxidation–reduction mechanism directly to Mn(II) and pyruvic acid (Eq. (5), the rate determining step). According to the proposed mechanism, the noncatalytic reaction pathway should be of first-order in both oxidant and reductant. Therefore, the total reaction rate law is given by Eqs. (10) and (11)

$$\nu = \frac{-d[MnO_2]}{dt} = \frac{k_1 k_2[MnO_2][H^+][\text{lactic acid}]_T}{([H^+] + K_a)(k_{-1} + k_2)} \quad (10)$$

$$k_{obs1} = \frac{k_1 k_2[H^+][\text{lactic acid}]_T}{([H^+] + K_a)(k_{-1} + k_2)} \quad (11)$$

Equation (11), explains the first-order dependence on $[\text{lactic acid}]_T$ at constant $[H^+]$ (Fig. 5).

In Scheme 2, reaction (6) represents formation of another complex (C2) with colloidal MnO_2-lactic acid complex (C1) and manganese(II). The equilibrium between Mn(II) and C1 is fast. Equation (7) is the rate determining step of autocatalytic pathway to yield Mn(III) as an intermediate. The reduction of colloidal MnO_2 by Mn(II) has also been reported by Perez-Benito [18]. The reaction product is Mn(III) which may be in equilibrium with its reactants, Eq. (8). Therefore, Mn(III) would also participate in the reaction as an autocatalyst. In presence of large amount of lactic acid, the equilibrium (Eq. (8)) shifts to forward direction. Ultimately, the intermediate (Mn(III)) immediately gets converted into the stable products (Eq. (9)). This mechanism is in agreement with the results of Perez-Benito
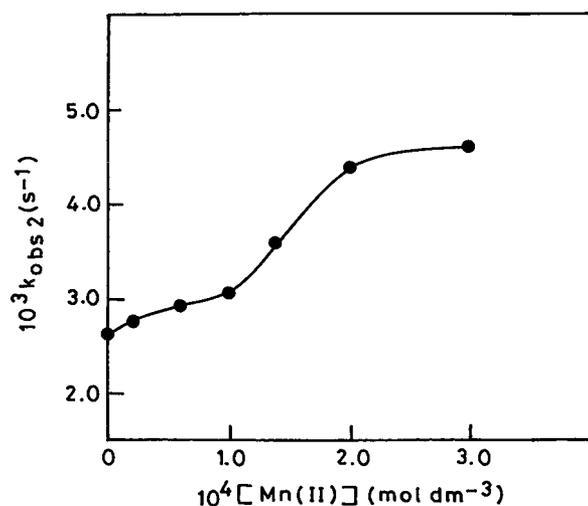
Figure 6 Effect of [Mn(II)] on the k_{obs2} for the oxidation of lactic acid by colloidal MnO_2. Reaction conditions were the same as in Fig. 5.

et al. [8,9,18] and conforms to that of Pare et al. [16].

The kinetics of the Mn(IV) reduction by Mn(II) was also studied spectrophotometrically to decide the role of Mn(II) under the similar experimental conditions. The results are given in Table III which suggest that the reactivity of Mn(II) is ca. 10-fold slower than lactic acid. The effect of addition of Mn(II) shows conclusively that colloidal MnO_2 is the main reactive oxidizing species in the noncatalytic reaction pathway. Firstly, the disappearance of this path in presence of Mn(II) indicates that the effective concentration of colloidal MnO_2 decreases by the addition of Mn(II) (Eq. (8)). Secondly, the rate of the auto-catalysis increase in presence of added Mn(II) indicates that Mn(II) is the principal reactive species of the auto-catalytic path. Our results seem to suggest that there is a competition between Mn(II) and lactic acid to react with colloidal MnO_2. The reactivity of lactic

acid toward colloidal MnO_2 is higher in comparison to Mn(II) [19]. Therefore, the participation of the colloidal MnO_2-Mn(II) reaction (Eq. (8)) in the autocatalytic pathway can be ruled out or might be of minor significance.

The probability of the direct reaction between Mn(IV) and Mn(II) to yield Mn(III) without the participation of lactic acid can not be ruled out either (Eq. (8)); the participation of Mn(III) as an intermediate is well known [20–22]). Disappearance of the noncatalytic reaction pathway in the presence of very low added Mn(II) adequately accounts for the critical concentration of Mn(III). Though Mn(III) is not stable (it immediately disproportionates, Eq. (8), reverse direction), the effect of F^- on the rate constants (Table II) suggests formation of Mn(III) as an intermediate in view of the strong complexation of Mn(III) by F^- compared to MnO_2 [23,24]. However, despite our attempt to monitor Mn(III) at 470 nm (characteristic of Mn(III) [25]), we failed to detect any build-up of Mn(III) during the course of the reaction.

Comparison of the second-order rate constants (k^{II}) with those of other oxidants involving the same reductant (lactic acid) (Table IV) shows that the reactivity/oxidation ability of colloidal MnO_2 is much higher in comparison to $KMnO_4$, $K_2Cr_2O_7$, $S_2O_8^{2-}$, or chloramine T but lower than Mn(III) (*caution*: one should keep in mind the reaction conditions! pH, temperature, etc.).

Table III The Pseudo-First-Order Rate Constants (k_{obs3}) of the Reduction of Colloidal MnO_2 (8.0×10^{-5} mol dm^{-3}) by Manganese(II) in Absence of Lactic Acid at 30°C

10^4 [Mn(II)] (mol dm^{-3})	$10^4 \, k_{obs3}$ (s^{-1})
2.0	0.7
3.0	1.5
6.0	1.0
10.0	1.5
20.0	1.5

Table IV Comparison Between the Second-Order Rate Constants (k^{II}) for the Oxidation of Lactic Acid by Different Oxidants

Oxidant	Temperature (°C)	$10^2 \, k^{II}$ (mol^{-1} dm^3 s^{-1})	Remark
$KMnO_4$	25	398.0	a
$K_2Cr_2O_7$	35	1.6	b
$S_2O_8^{2-}$	55	1.3	c
Manganse(III)	26	32.4	d
Chloramine T	45	0.1	e
Colloidal MnO_2	30	2.1	f

^{a} [$KMnO_4$] $= 2.1 \times 10^{-4}$ mol dm^{-3}, [lactic acid] $= 3.1 \times 10^{-3}$ mol dm^{-3}, [H_2SO_4] $= 2.0$ mol dm^{-3}; Ref. [10].
^{b} [$K_2Cr_2O_7$] $= 4.9 \times 10^{-4}$ mol dm^{-3}, [lactic acid] $= 4.0 \times 10^{-3}$ mol dm^{-3}, [$HClO_4$] $= 0.5$ mol dm^{-3}; Ref. [26].
^{c} [$S_2O_8^{2-}$] $= 3.0 \times 10^{-2}$ mol dm^{-3}, [lactic acid] $= 2.0 \times 10^{-2}$ mol dm^{-3}, [$CuSO_4$] $= 1.0 \times 10^{-4}$ mol dm^{-3}; Ref. [27].
^{d} [Mn(III)] $= 4.0 \times 10^{-4}$ mol dm^{-3}, [lactic acid] $= 2.0 \times 10^{-3}$ mol dm^{-3}, [H_2SO_4] $= 2.0$ mol dm^{-3}; Ref. [10].
^{e} [Chloramine T] $= 4.0 \times 10^{-3}$ mol dm^{-3}, [lactic acid] $= 5.0 \times 10^{-2}$ mol dm^{-3}, [$CuSO_4$] $= 4.0 \times 10^{-5}$ mol dm^{-3}, [OH^-] $= 0.5$ mol dm^{-3}; Ref. [28].
^{f} [MnO_2] $= 2.0 \times 10^{-4}$ mol dm^{-3}, [lactic acid] $= 12.0 \times 10^{-2}$ mol dm^{-3}, pH ≈ 3.0; present work.

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