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Oxidation of mandelic acid by alkaline potassium permanganate. A kinetic study

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ABSTRACT: The kinetics of the oxidation of mandelic acid (MA) by permanganate in aqueous alkaline medium at a constant ionic strength of 1.0 mol dm^{-3} were studied spectrophotometrically. The reaction shows first-order kinetics in [permanganate ion] and fractional order dependences in [MA] and [alkali]. Addition of products, manganate and aldehyde have no significant effect on the reaction rate. An increase in ionic strength and a decrease in dielectric constant of the medium increase the rate. The oxidation process in alkaline medium under the conditions employed in the present investigation proceeds first by formation of an alkali permanganate complex, which combines with mandelic acid to form another complex. The latter decomposes slowly followed by a fast reaction between the free radical of mandelic acid and another molecule of permanganate to give products. The reaction constants involved in the mechanism were derived. There is good agreement between the observed and calculated rate constants under different experimental conditions. The reaction was studied at different temperatures and activation parameters were computed with respect to the slow step of the proposed mechanism. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: mandelic acid; alkaline permanganate; oxidation; kinetics

INTRODUCTION

Oxidation by permanganate ion has extensive applications in organic syntheses,[1–7] especially since the advent of phase-transfer catalysis,[3,4,6] which permits the use of solvents such as methylene chloride and benzene. Kinetic studies are important sources of mechanistic information on the reactions, as demonstrated by results referring to unsaturated acids in both aqueous[1,3–7] and non-aqueous media.[8]

The manganese chemistry involved in these multi-step redox reactions is an important source of information as the manganese intermediates are relatively easy to identify when they have sufficiently long lifetimes and the oxidation states of the intermediates permit useful conclusions as to the possible reaction mechanisms, including the nature of intermediates.

$$\mathrm{Mn(VII)} + \mathrm{S} \xrightarrow{k_1'} \mathrm{Mn(VI)} + \mathrm{S}^{\cdot}$$

$$\mathrm{Mn(VII)} + \mathrm{S}^{\cdot} \xrightarrow{k_2'} \mathrm{Mn(VI)} + \text{products}$$

where S = substrate and $k_2' \gg k_1'$

Scheme 1

In strongly alkaline medium, the stable reduction product[9] of permanganate ion is manganate ion, MnO_4^{2-}. No mechanistic information is available which would permit one to distinguish between a direct one-electron reduction to Mn (VI) (Scheme 1), or prior formation of hypomanganate in a two-electron step followed by a fast reaction (Scheme 2).

$$\mathrm{Mn(VII)} + \mathrm{S} \xrightarrow{k_3'} \mathrm{Mn(V)} + \text{products}$$

$$\mathrm{Mn(VII)} + \mathrm{Mn(V)} \xrightarrow{k_4'} 2\mathrm{Mn(VI)}$$

where S = substrate and $k_4' \gg k_3'$

Scheme 2

Mandelic acid is used in the form of its salts as a bacteriostatic agent for genitourinary tract infections. It has been oxidized by different oxidants in aqueous alkaline medium[10] and its oxidation by permanganate in acid medium has been reported.[11] Different workers have reported different products[12] for the oxidation of mandelic acid. Although some work on the oxidation of organic[13] and inorganic[14] substrates by permanganate in aqueous alkaline medium has been carried out, there is no report in the literature on the oxidation of mandelic acid in such media. This work was carried out on such a reaction in order to elucidate the redox chemistry of permanganate in alkaline media.

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EXPERIMENTAL

Materials. Stock solutions of mandelic acid (Mallinkrodt) and potassium permanganate (BDH) were prepared by dissolving the appropriate amounts of samples in doubly distilled water. The stock solution of permanganate was standardized against oxalic acid.[15] Potassium manganate solution was prepared as described by Carrington and Symons[16] as follows: a solution of potassium permanganate was heated to boiling above 120 °C in 8.0 mol dm^{-3} potassium hydroxide solution until a green colour was produced. The solid potassium manganate formed on cooling was recrystallized from the same solvent. Using the required amount of recrystallized sample, a stock solution of potassium manganate was prepared in aqueous potassium hydroxide. The solution was standardized by measuring the absorbance using a Hitachi Model 150-20 spectrophotometer with a 1 cm cell at 608 nm ($\varepsilon = 1530 \pm 20$ dm^3 mol^{-1} cm^{-1}).

All other reagents were of analytical grade and their solutions were prepared by dissolving the requisite amounts of the samples in doubly distilled conductivity water. NaOH and $NaClO_4$ were used to provide the required alkalinity and to maintain the ionic strength, respectively.

Kinetic measurements. All kinetic measurements were performed under pseudo-first-order conditions with mandelic acid in at least a 10-fold excess over permanganate ion at a constant ionic strength of 1.0 mol dm^{-3}. The reaction was initiated by mixing previously thermostated solutions of MnO_4^- and mandelic acid which also contained the necessary quantities of NaOH and $NaClO_4$ to maintain the required alkalinity and ionic strength, respectively. The temperature was maintained at 26 ± 0.1 °C. The course of the reaction was followed by monitoring the decrease in the absorbance of MnO_4^- in a 1 cm quartz cell of a Hitachi model 150-20 spectrophotometer at its absorption maximum of 526 nm as a function of time. Earlier it was verified that there is negligible interference from other reagents at this wavelength. The application of Beer's law to permanganate at 526 nm had earlier been verified, giving $\varepsilon = 2083 \pm 50$ dm^3 mol^{-1} cm^{-1} (literature $\varepsilon = 2200$ dm^3 mol^{-1} cm^{-1}). The first-order rate constants $k_{(obs)}$ were evaluated by plots of log[permanganate] versus time. The first-order plots in almost all cases were linear up to 80% of the reaction and the $k_{(obs)}$ values were reproducible to within ±5%.

In the course of the measurements, the colour of the solution changed from violet to blue and further to green. The spectrum of the green solution was identical with that of MnO_4^{2-}. It is probable that the blue colour originated from the violet of permanganate and the green from manganate, excluding the accumulation of hypomanganate.

The effect of dissolved oxygen on the rate of reaction was checked by preparing the reaction mixture and following the reaction in an atmosphere of nitrogen. No significant difference between the results obtained under nitrogen and in presence of air was observed. In view of the ubiquitous contamination of basic solutions by carbonate, the effect of carbonate on the reaction was also studied. Added carbonate had no effect on the reaction rate. However, fresh solutions were used when conducting the experiments.

Stoichiometry and product analysis. The reaction mixture containing excess permanganate over mandelic acid was mixed in the presence of 0.50 mol dm^{-3} NaOH adjusted to a constant ionic strength of 1.0 mol dm^{-3}. When the reaction time had elapsed, solid KI was added, followed by acidification with 10% H_2SO_4. Then remaining permanganate was titrated against standard sodium thiosulphate.[13] The results indicated that 2 mol of MnO_4^- consumed 1 mol of mandelic acid according to the equation

$$C_6H_5CH(OH)COOH + 2MnO_4^- + 2OH^- \longrightarrow C_6H_5CHO + CO_2 + 2MnO_4^{2-} + 2H_2O \quad (1)$$

The main oxidation products were identified as an aldehyde[17] (by a spot test) and manganate. The presence of benzaldehyde as an oxidation product was also confirmed by preparing its 2,4-dinitrophenylhydrazone derivative and comparing its melting point with that of an authentic sample. Such products were also obtained in previous work.[18]

It was further observed that the aldehyde does not undergo further oxidation under the present kinetic conditions.

RESULTS

Reaction order

The reaction orders were determined from the slopes of log $k_{(obs)}$ versus log(concentration) plots by varying the concentration of oxidant, reductant and alkali in turn, while keeping the others constant.

Effect of oxidant and substrate

The potassium permanganate concentration was varied in the range 9.0×10^{-5}–9.0×10^{-4} mol dm^{-3} and the linearity of plots of log[MnO_4^-] versus time indicated a reaction order in [MnO_4^-] of unity. This was also confirmed by varying the [MnO_4^-], which did not show any change in pseudo-first-order rate constants $k_{(obs)}$ (Table 1). The substrate, mandelic acid concentration was varied in the range 9.0×10^{-4}–9.0×10^{-3} mol dm^{-3} at 26 °C keeping all other reactant concentrations and

Table 1. Effect of [MA], [MnO_4^-] and [OH^-] on the oxidation of mandelic acid by permanganate in aqueous alkaline medium at 26 °C ($I = 1.0$ mol dm^{-3})

[MA] × 10^3 (mol dm^{-3})	[MnO_4^- × 10^4 (mol dm^{-3})	[OH^-] (mol dm^{-3})	$k_{(obs)} \times 10^3$ (s^{-1})	
			Experimental	Calculated
0.9	3.0	0.5	0.90	0.86
2.0	3.0	0.5	1.74	1.71
3.0	3.0	0.5	2.25	2.34
5.0	3.0	0.5	3.24	3.33
9.0	3.0	0.5	5.81	4.63
3.0	0.9	0.5	2.20	2.34
3.0	2.0	0.5	2.25	2.34
3.0	3.0	0.5	2.23	2.34
3.0	7.0	0.5	2.26	2.34
3.0	9.0	0.5	2.22	2.34
3.0	3.0	0.1	0.85	0.89
3.0	3.0	0.3	1.70	1.60
3.0	3.0	0.5	2.25	2.34
3.0	3.0	0.7	2.70	2.66
3.0	3.0	1.0	3.15	2.85

conditions constant (Table 1). The reaction order in [mandelic acid] was found to be less than unity (Table 1).

Effect of alkali

The effect of alkali on the reaction was studied at constant concentrations of mandelic acid and potassium permanganate and keeping a constant ionic strength of 1.0 mol dm^{-3} at 26 °C. The rate constants increased with increase in [alkali] (Table 1).

Effect of ionic strength

The effect of ionic strength was studied by varying the sodium perchlorate concentration in the reaction medium. The ionic strength of the reaction medium was varied from 0.5 to 2.0 mol dm^{-3} at constant concentrations of permanganate, mandelic acid and alkali. It was found that the rate constant increased with increasing concentration of $NaClO_4$ and the plot of $\log k_{(obs)}$ versus $I^{1/2}$ was linear with a positive slope (Fig. 1).

Effect of solvent polarity

The relative permittivity (ε_T) effect was studied by varying the *tert*-butyl alcohol–water content in the reaction mixture with all other conditions being maintained constant. Attempts to measure the relative permittivities failed. However, they were computed from the values of pure liquids as in earlier work.[19] There was no reaction of the solvent with the oxidant under the experimental conditions used. The rate constant, $k_{(obs)}$, increased with decrease in the dielectric constant of the medium. The plot of $\log k_{(obs)}$ versus $1/\varepsilon_T$ was linear (Fig. 1).

Effect of initially added products

The initially added products such as manganate and aldehyde did not have any significant effect on the rate of the reaction.

Test for free radicals

The reaction mixture was kept for 1 h with acrylonitrile scavenger in an inert atmosphere. On diluting with methanol, the formation of a precipitate indicates free radical intervention in the reaction.

Effect of temperature

The rate constants, k, of the slow step of Scheme 3 were obtained from the intercepts of the plots of $1/k_{(obs)}$ versus 1/[MA] at different temperatures and used to calculate the activation parameters (Table 2). The values of k were $(0.90 \pm 0.04) \times 10^{-2}$, $(1.67 \pm 0.08) \times 10^{-2}$ and $(2.85 \pm 0.14) \times 10^{-2}$ s^{-1} at 26, 31 and 36 °C, respectively.

DISCUSSION

The permanganate ion, MnO_4^-, is a powerful oxidant in aqueous alkaline medium. As it exhibits a multitude of oxidation states, the stoichiometric results and pH of the reaction media play an important role. Under the present experimental conditions at pH > 12, the reduction

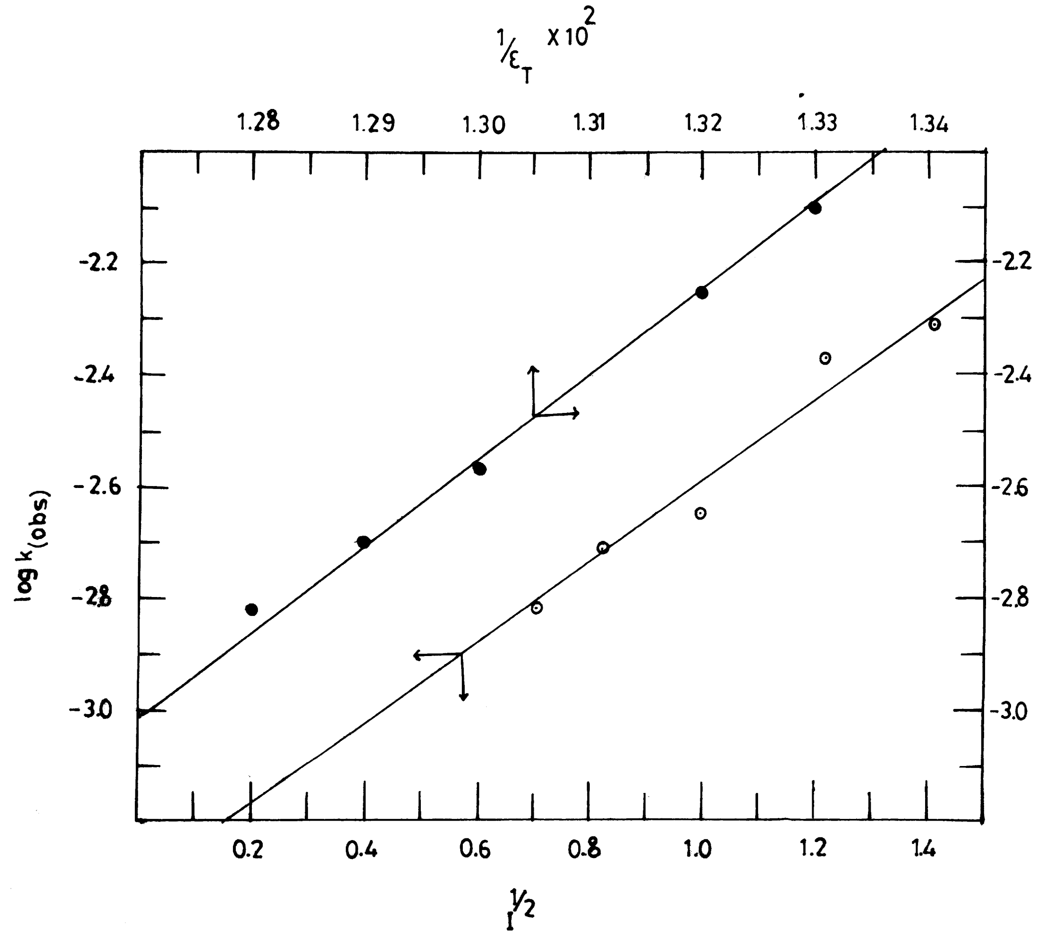


Figure 1. Plots of log $k_{(obs)}$ versus $I^{1/2}$ and versus $1/\varepsilon_T$

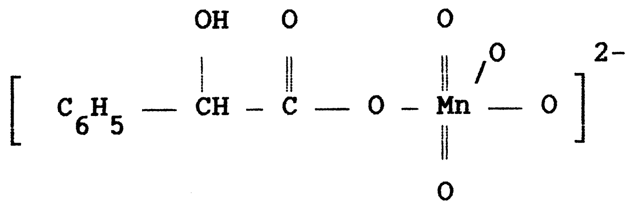
product of Mn(VII), i.e. Mn(VI), is stable and further reduction of Mn(VI) might be stopped.[14] Diode-array rapid scan spectrophotometric studies have shown that at pH > 12, the product of Mn(VII) is Mn(VI) and no further reduction was observed as reported by Simandi *et al.*[14a] However, on prolonged standing Mn(VI) is slowly reduced to Mn(IV) under our experimental conditions.

The reaction between mandelic acid and permanganate in alkaline medium has a stoichiometry of 1:2 with a fractional order dependence on both alkali and mandelic acid concentrations and a first-order dependence on permanganate concentration. No effect of the products was observed. The results suggest that first the alkali combines with permanganate to give an alkali–permanganate complex,[20] which then reacts with the substrate, mandelic acid, to give another complex. The latter complex decomposes in a slow step to give a free radical derived from decarboxylated mandelic acid, which further reacts with another molecule of permanganate in a fast step to yield the products (Scheme 3).

Table 2. Thermodynamic activation parameters for the oxidation of mandelic acid by alkaline permanganate activation parameters with respect to the slow step of Scheme 3

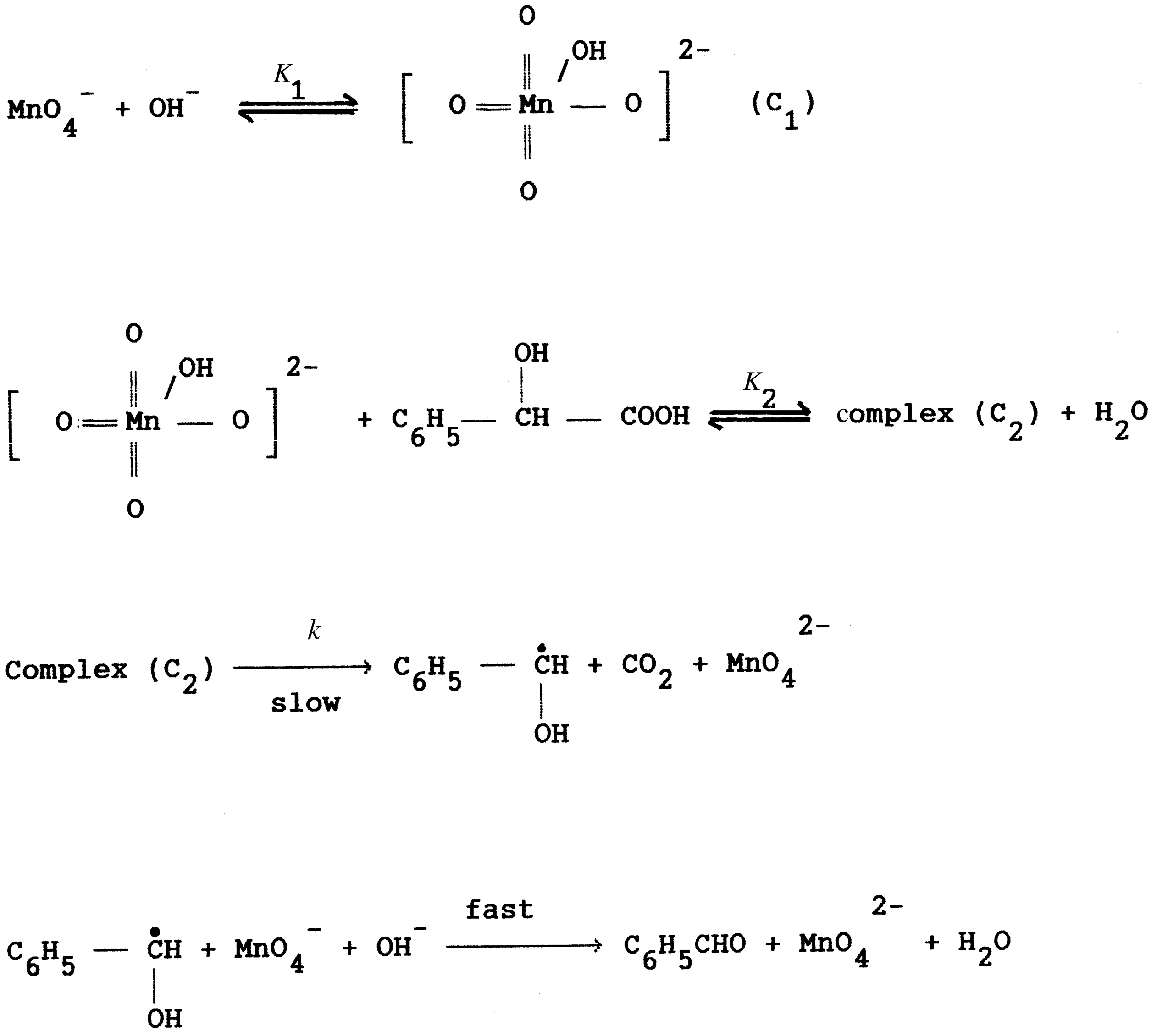
Parameter	Value
E_a	65.5 ± 3.5 kJ mol^{-1}
Log*A*	9.5 ± 0.5
$\Delta S^{\neq}$	-72 ± 3 J K^{-1} mol^{-1}
$\Delta H^{\neq}$	63 ± 3 kJ mol^{-1}
$\Delta G^{\neq}$	85.5 ± 4.0 kJ mol^{-1}

The probable structure of the complex (C_2) is



$$\left[C_6H_5 - \overset{\overset{OH}{|}}{CH} - \overset{\overset{O}{\|}}{C} - O - \underset{\underset{O}{\|}}{\overset{\overset{O}{\|}\;\,^{O}_{/}}{Mn}} - O \right]^{2-}$$

Attempts to obtain the UV–visible spectral evidence for the complex formation failed. However, the interaction might be feeble and such complex formation between a substrate and an oxidant have been observed in other studies.[21] The formation of the complex is proved kinetically, i.e. by the non-zero intercept of the plot of



Scheme 3

$1/k_{(obs)}$ vs 1/[MA]. Since Scheme 3 is in accordance with the generally well accepted principle of non-complementary oxidations taking place in sequences of one-electron steps, the reaction between the substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility (see below). This type of radical intermediate has also been observed in earlier work[22] on the alkaline permanganate oxidation of various organic substrates.

Scheme 3 leads to the following rate law:

$$\text{rate} = -\frac{\mathrm{d}[\mathrm{MnO}_4^-]}{\mathrm{d}t} = \frac{kK_1K_2[\mathrm{MA}][\mathrm{MnO}_4^-][\mathrm{OH}^-]}{(1+K_1[\mathrm{OH}^-]+K_1K_2[\mathrm{MA}][\mathrm{OH}^-])} \times \frac{1}{(1+K_1K_2[\mathrm{MnO}_4^-][\mathrm{OH}^-])(1+K_1[\mathrm{MnO}_4^-]+K_1K_2[\mathrm{MA}][\mathrm{MnO}_4^-])} \tag{2}$$

The terms $(1+K_1\ K_2\ [\mathrm{MnO}_4^-]\ [\mathrm{OH}^-])$ and $(1+K_1\ [\mathrm{MnO}_4^-]+K_1\ K_2\ [\mathrm{MA}]\ [\mathrm{MnO}_4^-])$ in the denominator of Eqn (2) approximate to unity in view of the low concentration of MnO_4^- used. Therefore, Eqn (2) becomes

$$\text{rate} = -\frac{\mathrm{d}[\mathrm{MnO}_4^-]}{\mathrm{d}t} = \frac{kK_1K_2[\mathrm{MA}][\mathrm{MnO}_4^-][\mathrm{OH}^-]}{1+K_1[\mathrm{OH}^-]+K_1K_2[\mathrm{MA}]\ [\mathrm{OH}^-]} \tag{3}$$

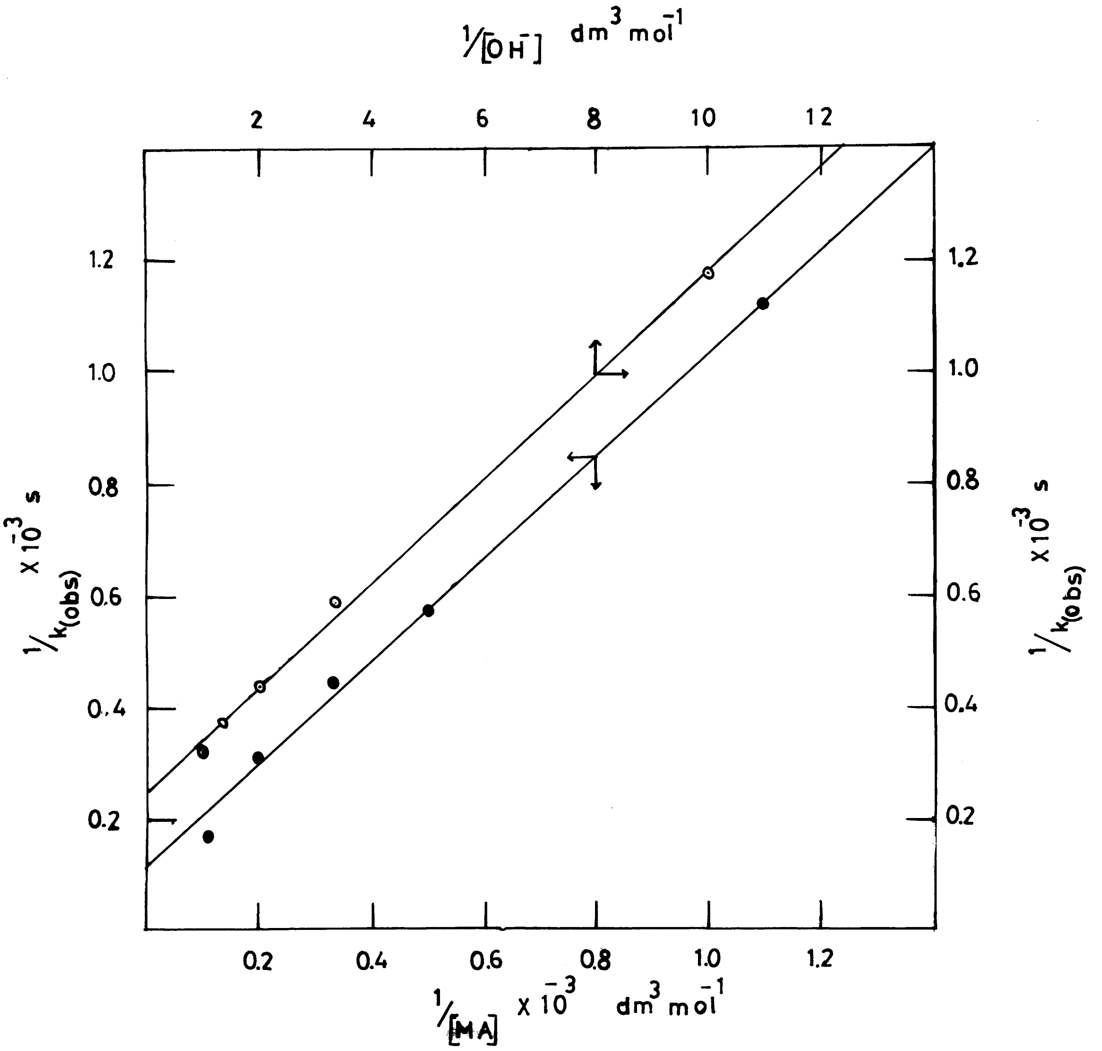


Figure 2. Plots of $1/k_{(\mathrm{obs})}$ versus 1/[MA] and versus 1/[OH$^-$]. Conditions as in Table 1

or

$$\frac{\text{rate}}{[\mathrm{MnO}_4^-]} = k_{(\mathrm{obs})} = \frac{kK_1K_2[\mathrm{MA}]\ [\mathrm{OH}^-]}{1 + K_1[\mathrm{OH}^-] + K_1K_2[\mathrm{MA}]\ [\mathrm{OH}^-]} \tag{4}$$

Equation (4) can be rearranged to the following form, which is used for verification of the rate law:

$$\frac{1}{k_{(\mathrm{obs})}} = \frac{1}{kK_1K_2\ [\mathrm{MA}]\ [\mathrm{OH}^-]} + \frac{1}{kK_2\ [\mathrm{MA}]} + \frac{1}{k} \tag{5}$$

According to Eqn (5), the plots of $1/k_{(\mathrm{obs})}$ vs 1/[MA] and $1/k_{(\mathrm{obs})}$ vs 1/[OH$^-$] should be linear, as verified in Fig. 2. The slopes and intercepts of such plots lead to values of k, K_1 and K_2 at 26 °C of $(0.9 \pm 0.04) \times 10^{-2}$ s^{-1}, 1.6 ± 0.08 dm^3 mol^{-1} and 265 ± 13 dm^3 mol^{-1}, respectively. Using these values, rate constants under different experimental conditions were calculated and compared with experimental data (Table 1). There is reasonable agreement between them, which supports Scheme 3.

The effect of increasing ionic strength on the rate qualitatively explains the reaction between the same charged ions as shown in Scheme 3. The effect of solvent on the reaction kinetics has been described in detail in the older literature.[23–28] For the limiting case of a zero angle approach between two dipoles or an ion–dipole system, Amis[27] has shown that a plot log $k_{(\mathrm{obs})}$ versus $1/\varepsilon_T$ gives a straight line with a negative slope for a reaction between a negative ion and a dipole or two dipoles, and with a positive slope for a positive ion and dipole interaction. In the present study, an increase in rate with decrease in the dielectric constant of the medium was observed, which cannot be explained by Amis theory,[27] as the presence of a positive ion is unlikely in the alkaline medium employed. Applying the Born equation, Laidler and Eyring derived the equation

$$\ln k = \ln k_0 + \frac{N\ Z^2\ e^2}{2\ D\ R\ T}\left(\frac{1}{r} - \frac{1}{r^*}\right) \tag{6}$$

where k_0 is the rate constant in a medium of infinite dielectric constant and r and r^* refer to the radius of the reacting species and activated complex, respectively. It can be seen from Eqn (6) that the rate should be greater in a medium of lower dielectric constant when $r^* > r$. There is a possibility of intramolecular hydrogen bonding that could stabilize the transition state, increasing the size of activated complex by attracting solvent molecules due to solvation effect. The fairly high positive values of $\Delta H^{\neq}$ and $\Delta G^{\neq}$ (Table 2) also indicate that the transition state is highly solvated, which results in an increase in the size of transition state. It is likely that $r^* > r$ for mandelic acid, thus explaining the experimental observations. Hence one can expect intramolecular hydrogen bonding in mandelic acid since it contains OH and COOH groups on the same carbon atom. Such hydrogen bonding is common for molecules having COOH and NH_2, COOH and OH groups, etc., either on the adjacent carbon atom or on the same carbon atom of the molecule as found[29] in simple amino acids.

The moderate values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were both favourable for electron transfer processes. The value of $\Delta H^{\neq}$ was due to release of energy of solution changes in the transition state. The negative values of $\Delta S^{\neq}$ within the range for radical reactions have been ascribed[30] to the nature of electron pairing and electron unpairing processes, and to the loss of degrees of freedom, formerly available to the reactions on the formation of a rigid transition state. It is also interesting that the oxidant species [MnO_4^-] required a pH > 12, below which the system becomes disturbed and the reaction will proceed further to give a reduced product of the oxidant as Mn(IV), which slowly develops yellow turbidity. Hence it becomes apparent that in carrying out this reaction the role of pH in the reaction medium is crucial. It is also noteworthy that under the conditions studied, the reaction occurs in two successive one-electron reductions (Scheme 3) rather than two-electron reduction in a single step (Scheme 2).

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