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PHYSICAL CHEMISTRY | RESEARCH ARTICLE

Free-radical-induced oxidative degradation of antibacterial drug, methylparaben by permanganate in alkaline medium: A kinetic and mechanistic approach

Girish G. Ariga¹, Sharanappa T. Nandibewoor¹ and Shivamurti A. Chimatadar^{1*}

Abstract: The kinetics of oxidation of an antibacterial drug, methylparaben by permanganate in alkaline medium at a constant ionic strength of 0.80 mol dm⁻³ was studied spectrophotometrically at 25°C. The stoichiometric ratio between permanganate and methylparaben was found to be 2:1 in alkaline medium. The main products were identified by NMR, IR, and GC-MS spectral studies. The reaction showed first-order kinetics in permanganate, fractional order in methylparaben, and OH⁻ concentrations under the experimental conditions. Ionic strength and dielectric constant did not affect the rate of reaction. The added products did not have any significant effect on the rate of reaction. Based on the rate experimental results, a suitable mechanism is proposed. Investigations at different temperatures allowed the determination of the activation parameters with respect to the slow step of the proposed mechanism. The reaction constants involved in the mechanism were



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PUBLIC INTEREST STATEMENT

The title of the paper includes kinetic study of oxidation of methylparaben by Mn(VII) in alkaline medium. Methylparaben is used as an antibacterial preservation, cosmetic and anti-fungal agent. The present study deals with free radical induced oxidative degradation and investigate the redox chemistry of [Mn(VII)] in alkaline medium and to compute the thermodynamic quantities of various steps involved in the mechanism to those derived on the basis of kinetic and mechanistic results.

evaluated. The results of this study provide fundamental mechanistic parameters and degradation efficiencies of drug by advanced oxidation processes.

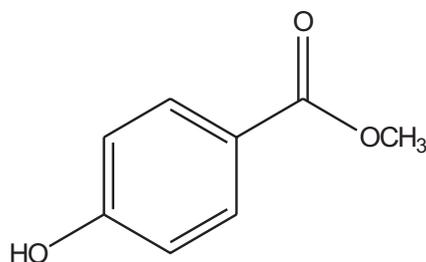
Subjects: Bioscience; Food Science & Technology; Physical Sciences

Keywords: permanganate; methylparaben; alkali; kinetics; oxidation

1. Introduction

Bioinorganic chemistry constitutes the discipline at the interface of the more classical areas of inorganic chemistry and biology. The metal containing compounds has not only been used as biological probes, but also diagnostic and therapeutic pharmaceuticals. The kinetic study also helps us to study the factors like temperature, pressure, substrate concentration, oxidant concentration, composition of the reaction mixture and catalyst which influence the rate of reaction. The permanganate ion (MnO_4^-) can oxidize a great variety of substances and it finds extensive applications in organic synthesis (Lee, 1980; Lee, Lee, & Brown, 1987; Simandi, Jaky, & Schelly, 1984; Wiberg, 1965). The updated literature survey shows that considerable amount of work has been done on the oxidation of organic compounds by potassium permanganate in alkaline media (John & Kee, 1984; Teresa, Maria, & Michal, 1992). The permanganate ion has a tetrahedral geometry with extensive pi-bonding and stable in neutral or slightly alkaline media (Jaky & Simandi, 1981). Manganese (VII) is reduced to Mn(VI) during oxidation processes in basic medium. Permanganate is a versatile oxidizing agent and is used for studying the oxidation kinetics of many organic and inorganic substrates. The mechanisms for different organic substrates suggested by various authors are not similar, indicating that a variety of mechanisms are possible, depending upon the nature of the reactive manganese species, the reaction environment, and the nature of the substrate (Cotton & Wilkinson, 1980).

Methylparaben (Methyl 4-hydroxybenzoate), has been widely used as antimicrobial preservative agents in foods, beverages, drugs, anti-fungal agent, and cosmetics for more than 50 years due to their broad antimicrobial spectrum (Soni, Burdock, Greenberg, & Taylor, 2001). Parabens are found naturally in plant sources like grapefruit seed extract (Von, Schluter, Pflugel, Lindequist, & Julich, 1999). All commercially used parabens are synthetically produced, although some are identical to those found in nature. Acute toxicity studies in animals indicate that methylparaben is practically non-toxic by both oral and parenteral routes. The chemical structure of methylparaben is given below:



Methyl 4-hydroxybenzoate

Metal ions/complexes play a dominant role in synthetic organic chemistry as they have the potential to oxidize a wide variety of organic compounds. Although considerable work has been done on the oxidation of organic compounds by KMnO_4 , very little attention has been paid to the kinetics of oxidation of esters. In view of pharmaceutical importance of methylparaben, the reaction between methylparaben and KMnO_4 in alkali medium is reported in the present work.

2. Experimental

2.1. Materials and reagents

All chemicals used were of analytical reagent grade and double distilled water was used throughout the work. Potassium permanganate, methylparaben, (99.5%) was purchased from Himedia Pvt. Ltd. The purity of the drug was checked by comparing its GC-MS spectrum with literature. The permanganate stock solution was obtained by dissolving potassium permanganate in double distilled water and standardized by titrating against oxalic acid (Jeffery, Bassett, Mendham, & Denney, 1989). The manganese (VI) solution was made by dissolving potassium manganate (K_2MnO_4) (AR) in water. KOH (S D Fine-Chem Limited) solution was used to provide required alkalinity and KNO_3 solution was used to maintain required ionic strength in the reaction medium.

2.2. Instruments used

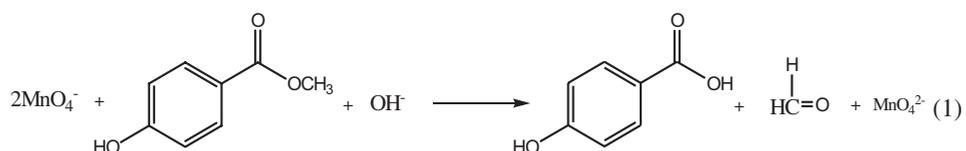
- (1) For kinetic measurements, Peltier Accessory (temperature control) attached to Varian CARY 50 Bio UV-Visible spectrophotometer (Varian, Victoria-3170, Australia) connected to a rapid kinetic accessory (HI-TECH SFA-12, UK) was used.
- (2) For product analysis, a QP-2010S Shimadzu gas chromatograph mass spectrometer, Nicolet 5700-FT-IR spectrometer (Thermo, USA), 500 MHz 1H NMR spectrophotometer (Bruker, Switzerland), Thermo Finnigan FLASH EA112. CHNS analyses were used.
- (3) For pH measurements, ELICO pH meter model Li 120 was used.

2.3. Kinetic studies

The oxidation of methylparaben by permanganate was followed under pseudo-first-order conditions where [methylparaben] was excess over [permanganate] at $25 \pm 0.1^\circ C$. The reaction was initiated by mixing the required quantities of previously thermostatted solutions of methylparaben and permanganate, which also contained constant concentrations of KOH and KNO_3 to maintain the required alkalinity and ionic strength. The progress of the reaction was followed by measuring the absorbance of unreacted permanganate in the reaction mixture present in 1 cm cell in a thermostatted compartment of a Varian CARY 50 Bio UV-vis-spectrophotometer at 526 nm. It was verified that other constituents of the reaction mixture do not absorb significantly at this wavelength. The application of Beer's law to permanganate concentration at 526 nm had been verified and the molar extinction coefficient was found to be $\epsilon = 2224 \pm 100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The reaction was followed more than three half lives. The plots were linear over 70% completion of the reaction. The first-order rate constants, k_{obs} were obtained from the plots of $\log(\text{concentration})$ vs. time and are reproducible within $\pm 5\%$ (Table 1).

2.4. Stoichiometry and product analysis

The reaction mixtures containing excess concentrations of MnO_4^- to methylparaben in the presence of constant amounts of alkali and ionic strength were kept in an inert atmosphere. The unreacted concentration of Mn(VII) is determined spectrophotometrically at 526 nm. Stoichiometry was found to be 2:1, two moles of permanganate consume one mole of methylparaben as shown in Equation (1)



The reaction mixture in the stoichiometric ratio, under stirred condition, was allowed to react in alkaline media separately for 24 h at room temperature. After completion of the reaction, the reaction mixture was neutralized with acid and extracted with ethyl acetate. The obtained products were

Table 1. Effect of variation of permanganate, methylparaben, and OH⁻ concentrations on the oxidation of methylparaben by permanganate in alkaline solution at 25°C and I = 0.80 mol dm⁻³

[MnO ₄ ⁻] × 10 ⁴ (mol dm ⁻³)	[MP] × 10 ³ (mol dm ⁻³)	[OH ⁻] (mol dm ⁻³)	k _{obs} × 10 ³ (s ⁻¹)
0.50	5.0	0.3	1.12
1.0	5.0	0.3	1.10
2.0	5.0	0.3	1.11
3.0	5.0	0.3	1.12
4.0	5.0	0.3	1.12
5.0	5.0	0.3	1.10
2.0	0.5	0.3	0.20
2.0	1.0	0.3	0.36
2.0	2.0	0.3	0.61
2.0	3.0	0.3	0.81
2.0	4.0	0.3	0.98
2.0	5.0	0.3	1.11
5.0	5.0	0.1	0.72
5.0	5.0	0.3	1.11
5.0	5.0	0.5	1.44
5.0	5.0	0.8	1.72
5.0	5.0	1.0	1.85

separated by column chromatography and were characterized by NMR, IR, CHN, and GC-MS spectral analysis. The confirmed oxidation products were 4-hydroxybenzoic acid, formaldehyde, and Mn(VI).

Figure 1. NMR-spectrum of the product 4-hydroxybenzoic acid.

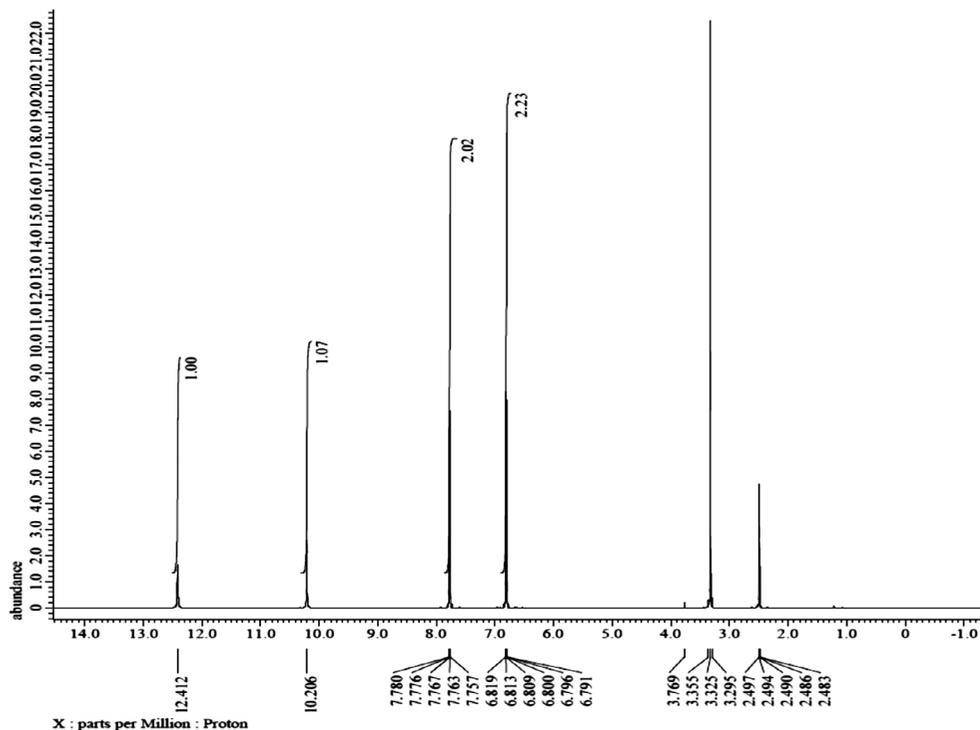
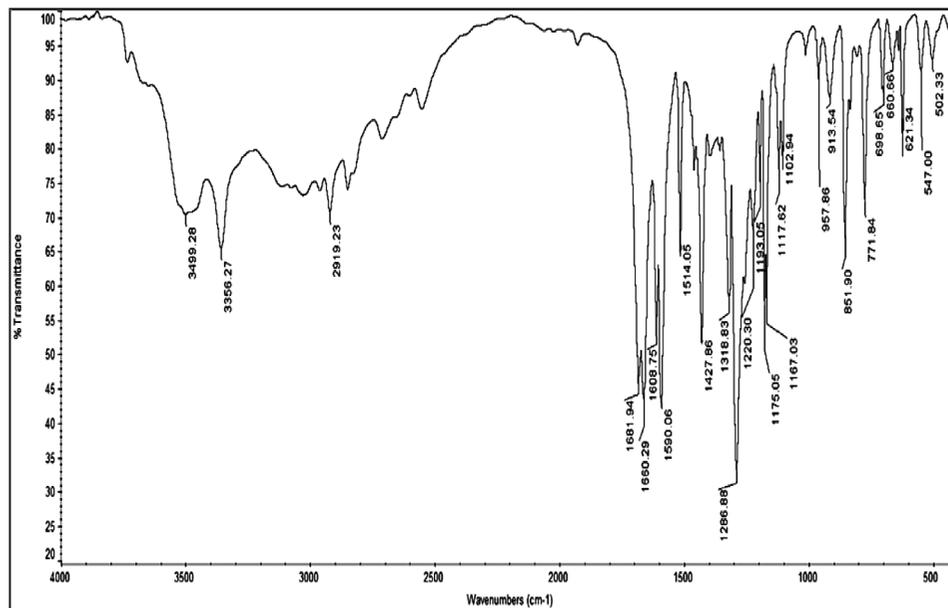


Figure 2. IR-spectrum of the product 4-hydroxybenzoic acid.

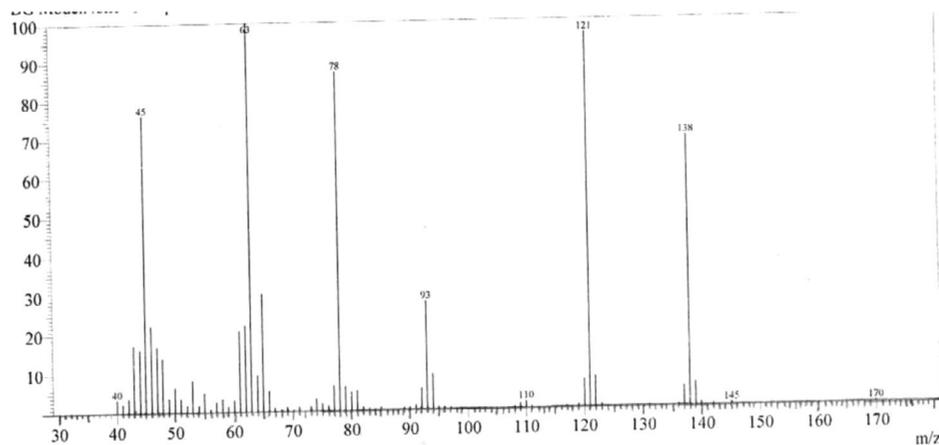


2.4.1. Spectroscopic Characterization of the Product 4-Hydroxybenzoic acid

Elemental analysis calculated for $C_7H_6O_3$ (mol. wt = 138.12); C = 12.0107; H = 1.00794; O = 15.9994. Found: C, 84.07; H, 6.18; O, 48.27. Melting for 4-hydroxybenzoic acid is 213°C (Lit. mp. 214.5°C). 1H NMR (500 MHz, DMSO, at 25°C); δ = 7.780 to 7.757 (d, 2H, Ar-H), δ = 6.819 to 6.791 (d, 2H, Ar-H), 10.206 (s, 1H, -OH), 12.412 (s, 1H, -COOH) ppm (Figure 1). IR spectrum showed an acidic C=O stretching peak at ν = 1681 cm^{-1} , phenolic -OH stretching peak at ν = 1590 cm^{-1} , and carboxylic acid peak ν = 3446 cm^{-1} (Figure 2). The EI spectrum showed an M^+ ion peak at 138 amu clearly confirming 4-hydroxybenzoic acid (Figure 3).

The product formaldehyde confirmed by spot test (Feigl, 2012). A drop of test solution is mixed with 2 cm^3 sulfuric acid in a test tube, a little chromotropic acid is added, and the test tube was heated for 10 min in a water bath at 60°C. A bright violet color appears indicating the presence of formaldehyde.

Figure 3. GC-MS spectrum of 4-hydroxybenzoic acid with its molecular ion peak at 138 amu.



3. Results

3.1. Reaction orders

The oxidation of methylparaben by potassium permanganate in alkaline medium, proceed with measurable rates. Hence, the reaction orders have been determined from the slopes of $\log k_{\text{obs}}$ vs. \log (concentration) plots by varying the concentrations of methylparaben and alkali in turn while keeping others constant.

3.2. Effect of permanganate concentration

Permanganate concentration was varied in the range of 0.50×10^{-4} to 5.0×10^{-4} mol dm⁻³ and the linearity of the plots of \log (concentration) vs. time up to 70% completion of the reaction indicates a reaction order of unity in $[\text{MnO}_4^-]$. This is also confirmed by varying of $[\text{MnO}_4^-]$, which did not result in any change in the pseudo-first-order rate constants (Table 1).

3.3. Effect of methylparaben concentration

The effect of methylparaben was studied in the range of 0.50×10^{-3} to 5.0×10^{-3} mol dm⁻³ at 25°C and at constant concentrations of MnO_4^- , OH^- and ionic strength. The rate of the reaction increased with increase in concentration of methylparaben (Table 1). The order with respect to concentration of MP was obtained from the plot of $\log k_{\text{obs}}$ vs. \log [MP] and was found to be less than unit order (0.76).

3.4. Effect of alkali concentration

The effect of alkali concentration was studied in the range of 0.10 to 1.0 mol dm⁻³ at 25°C and at constant concentrations of MnO_4^- , MP, and ionic strength. The rate of the reaction increased with an increase in the concentration of alkali concentration (Table 1). The order with respect to OH^- concentration was obtained from the plot of $\log k_{\text{obs}}$ vs. \log $[\text{OH}^-]$, and was found to be less than unit order (0.41).

3.5. Effect of ionic strength (I) and dielectric constant

The effect of ionic strength (*I*) was studied by varying the concentration of KNO_3 in the range of 0.1–1.0 at 25°C and at constant concentrations of MnO_4^- , MP, and OH^- . The dielectric constant of the medium (*D*) was studied by varying the t-butyl alcohol-water percentage (v/v) in the range of 0–25%. The ionic strength and dielectric constant did not have any significant effect on the rate of reaction.

3.6. Effect of initially added products

The initially added products, *p*-hydroxy benzoic acid and Mn(VI) (as K_2MnO_4) did not have any significant effect on the rate of reaction.

3.7. Polymerization study

To the reaction mixture a known quantity of $\text{CH}_2=\text{CHCN}$ scavenger (Moelwyn-Hughes, 1947), had been added initially, was kept in an inert atmosphere for 2 h. On diluting the reaction mixture with methanol, precipitate appears in the reaction mixture, indicating the presence of free radical in the reaction.

The observed experimental results lead to the following rate law:

$$\text{Rate} = k[\text{MnO}_4^-]^{1.0}[\text{MEP}]^{0.76}[\text{OH}^-]^{0.41}$$

3.8. Effect of temperature (T)

The kinetics was studied at four different temperatures, 15, 25, 35, and 45°C, under varying concentrations of methylparaben and alkali, keeping other conditions constant. The rate increased with increase in temperature. The rate constant (*k*) of the slow step of Scheme 1 were obtained from the slopes and intercepts of $1/k_{\text{obs}}$ vs. $1/[\text{MP}]$, (Figure 4(a)) and $1/k_{\text{obs}}$ vs. $1/[\text{OH}^-]$, (Figure 4(b)) plots at four

Figure 4. Verification of rate law (6), in the form of an Equation (7), for the oxidation of methylparaben by permanganate in alkaline medium.

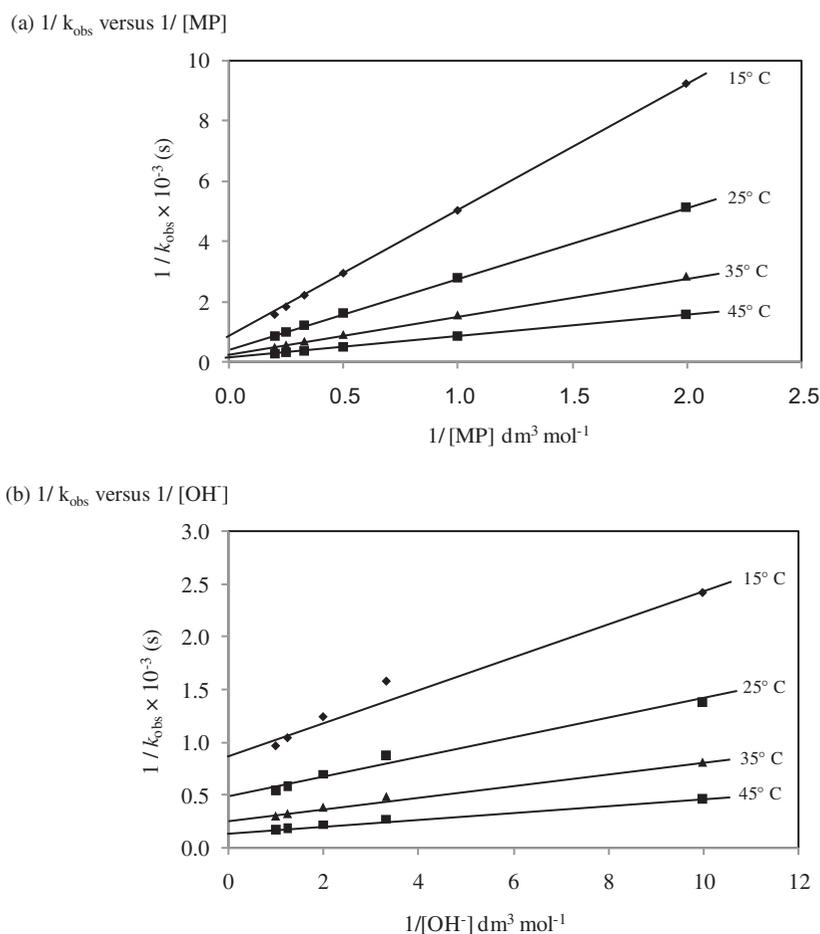


Table 2. Activation parameters and thermodynamic quantities for the oxidation of methylparaben by permanganate in aqueous basic medium with respect to the slow step of Scheme 1

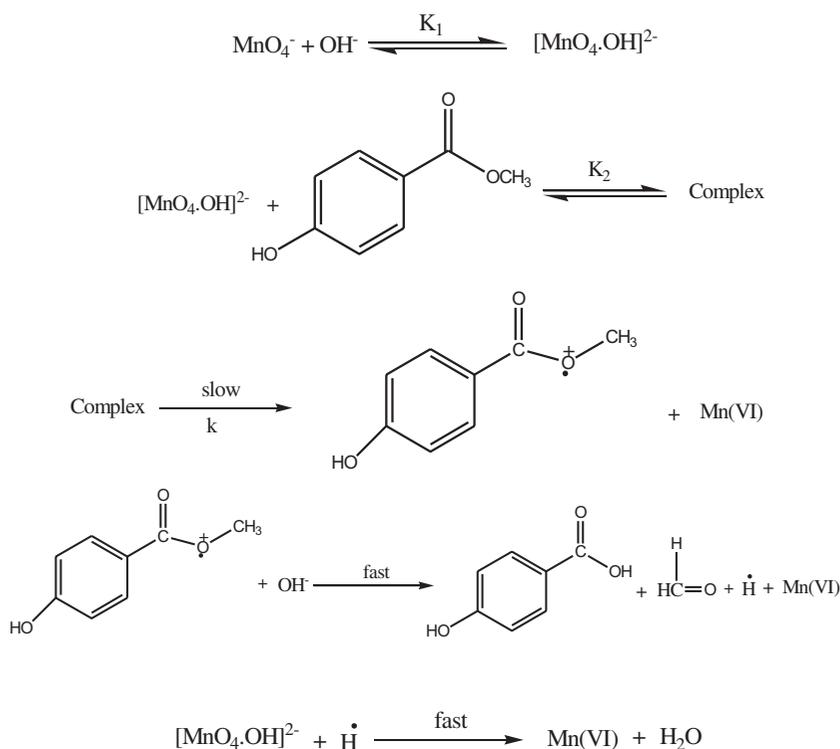
(A) Effect of temperature and activation parameters			
Temperature (K)	$k \times 10^3$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	Parameters	Values
288	1.28	E_a (kJ mol^{-1})	45 ± 3
298	2.29	ΔH^\ddagger (kJ mol^{-1})	42 ± 3
308	4.15	ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$)	-154 ± 5
318	7.44	ΔG^\ddagger (kJ mol^{-1})	88 ± 4
		log A	5.2 ± 0.02
(B) Effect of temperature on K_1 and K_2			
Temperature (K)	$K_1 \times 10^{-3}$ ($\text{dm}^3 \text{mol}^{-1}$)	$K_2 \times 10^{-3}$ ($\text{dm}^3 \text{mol}^{-1}$)	
288	7.99	1.27	
298	6.43	1.45	
308	4.39	1.97	
318	3.13	2.63	
(C) Thermodynamic quantities for first (K_1) and second (K_2) equilibrium steps of Scheme 1			
Thermodynamic quantities	K_1	K_2	
ΔH (kJ mol^{-1})	-24	19	
ΔS ($\text{J K}^{-1} \text{mol}^{-1}$)	-86	125	
ΔG (kJ mol^{-1})	1.7	-19	

different temperatures (Table 2). The energy of activation corresponding to these rate constants was evaluated from the Arrhenius plot of $\log k$ vs. $1/T$ and from which other activation parameters were obtained (Table 2).

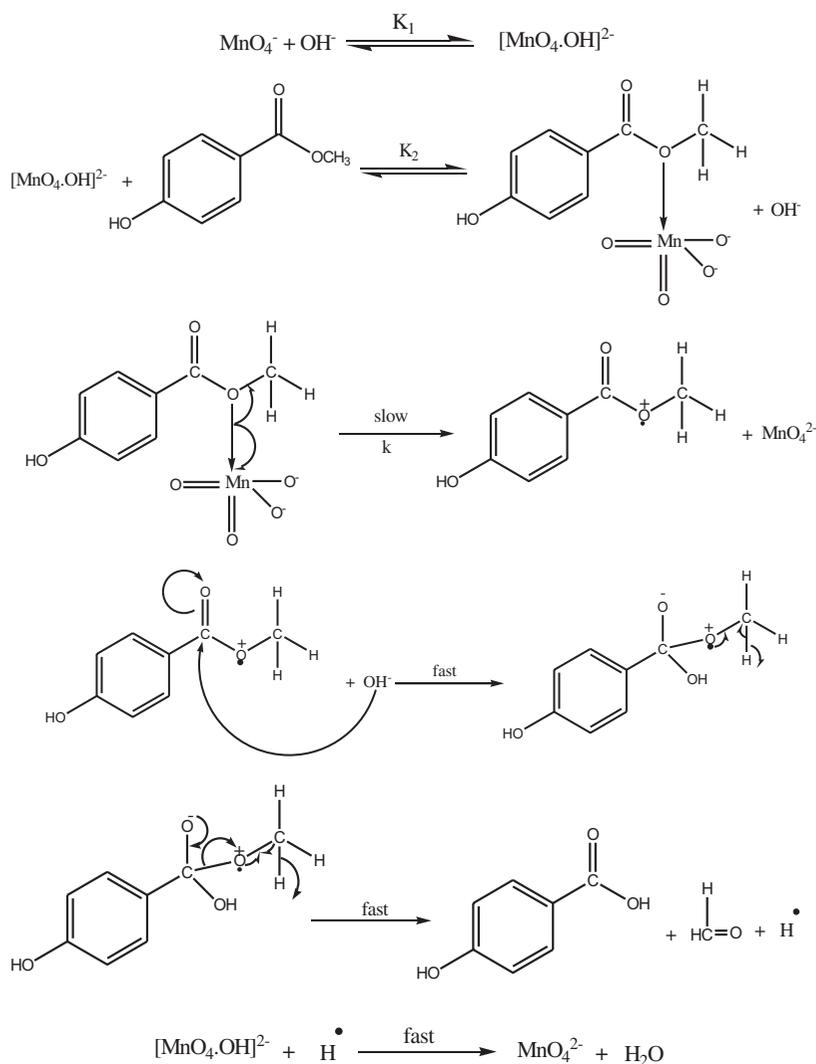
4. Discussion

The reaction between permanganate and methylparaben in alkaline medium has the stoichiometry 2:1 (MnO_4^- :MP) with a unit order dependence on $[\text{MnO}_4^-]$ and less than unit order in $[\text{MP}]$, and $[\text{OH}^-]$. No effects of added products were observed. Under these prevailing experimental conditions, the further reduction of MnO_4^{2-} might be stopped (Sukalyan, Sabita, & Bijay, 2009). The active species of MnO_4^- , $[\text{MnO}_4\cdot\text{OH}]^{2-}$, reacts with methylparaben in the second equilibrium step to form a complex, that then decomposes in a slow step to form of methylparaben cation free radical intermediate. In the fast step this free radical intermediate react with alkali to form the product, *p*-hydroxybenzoic acid, formaldehyde, MnO_4^{2-} with liberation of H^\cdot . Such type of formation of free radicals is evidenced (Laszlo, Erzsebet, Dajkaa, D'Angelantoniob, & Salvatore, 2001; Stephen, Thomas, William, & Julie, 2007; Wolf & Chrita, 1999) by pulse radiolysis work on similar compounds. The attacks of hydroxyl radical in pulse radiolysis (Wolf & Chrita, 1999) studies are different from MnO_4^- ion of methylparaben. The products which are confirmed by NMR, GC-MS, and IR studies indicate that phenolic group of the benzene do not involve in the oxidation. In the further fast step another mole of $[\text{MnO}_4\cdot\text{OH}]^{2-}$ reacts with hydrogen radical to form reduced product of Mn(VI) and H_2O . The mechanism satisfies the stoichiometric observation. A reasonable mechanism is proposed in Scheme 1.

Scheme 1. Mechanism for the oxidation of methylparaben by permanganate in aqueous alkaline medium.



Detailed mechanism of Scheme 1.



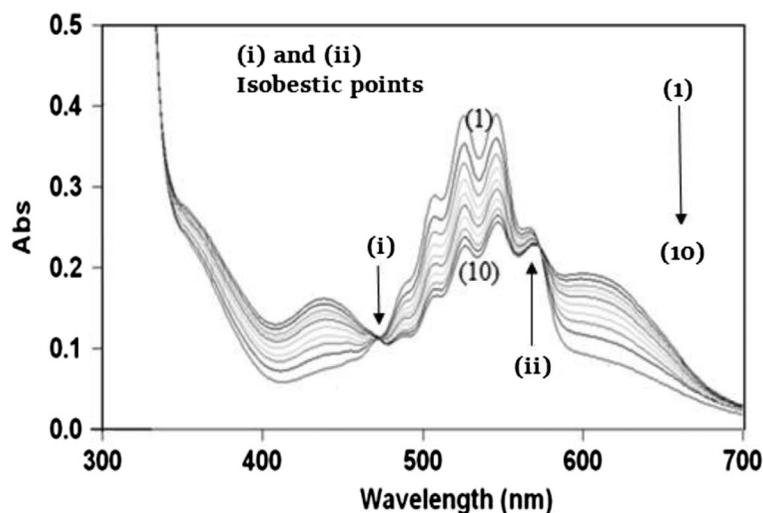
In alkaline medium permanganate(VII) undergo oxidation to form Mn(VI) (Timmanagoudar, Hiremath, & Nandibewoor, 1997). During this study, color of the solution changes from violet to blue, and then to green. The spectrum of green solution obtained during the oxidation of methylparaben by permanganate is identical to that of MnO_4^{2-} . It is probable that blue color originated from the violet of permanganate and green from manganate excluding the accumulation of hypomanganate. The spectral changes during the reaction are shown in Figure 5. It is evident from the figure that the concentration of MnO_4^- decreases at 526 nm and increases at 603 and 453 nm, 2 isobestic points are observed at 603 and 453 nm, due to Mn(VI) (Simandi, Jaky, Savage, & Schelly, 1985). The results suggest the formation of a complex (Manmeet, Faqeer, & Zaheer, 2007) between the methylparaben and permanganate.

From the above mechanism the following rate law (6) can be derived as follows:

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k K_1 K_2 [\text{MnO}_4^-]_f [\text{MP}]_f [\text{OH}^-]_f$$

Figure 5. Spectral changes during the oxidation of methylparaben by permanganate in alkaline solution at 25°C.

Notes: Conditions
 $[\text{MnO}_4^-] = 2.0 \times 10^{-4}$,
 $[\text{MP}] = 5.0 \times 10^{-3}$, $[\text{OH}^-] = 0.3$,
 and $I = 0.80 \text{ mol dm}^{-3}$.



The total $[\text{MnO}_4^-]$ can be written as

$$[\text{MnO}_4^-]_t = [\text{MnO}_4^-]_f + [\text{MnO}_4 \cdot \text{OH}^-] + [\text{Complex}] = [\text{MnO}_4^-]_f + K_1[\text{MnO}_4^-]_f[\text{OH}^-]_f + K_1 K_2[\text{MnO}_4^-]_f[\text{OH}^-]_f[\text{MP}] = [\text{MnO}_4^-]_f \{ 1 + K_1[\text{OH}^-] + K_1 K_2[\text{OH}^-][\text{MP}] \}$$

$$[\text{MnO}_4^-]_t = \frac{[\text{MnO}_4^-]_t}{1 + K_1[\text{OH}^-] + K_1 K_2[\text{OH}^-][\text{MP}]} \quad (3)$$

where t and f stands for total and free concentration of manganese (VII).

Similarly, total $[\text{OH}^-]$ can be calculated as,

$$[\text{OH}^-]_t = [\text{OH}^-]_f + [\text{MnO}_4 \cdot \text{OH}]^{2-} + [\text{Complex}]$$

$$[\text{OH}^-]_f = \frac{[\text{OH}^-]_t}{1 + K_1[\text{OH}^-] + K_1 K_2[\text{MnO}_4^-][\text{MP}]}$$

In view of the low concentration of MnO_4^- and MP used in the experiment, the term $K_1[\text{OH}^-]$ and $1 + K_1 K_2[\text{MnO}_4^-][\text{MP}]$ can be neglected in comparison with unity

$$[\text{OH}^-]_f = [\text{OH}^-]_t \quad (4)$$

Similarly,

$$[\text{MP}]_f = [\text{MP}]_t \quad (5)$$

Substituting Equations (3), (4), and (5) in Equation (2) and omitting the subscripts we get,

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = \frac{k K_1 K_2[\text{OH}^-][\text{MP}]}{1 + K_1[\text{OH}^-] + K_1 K_2[\text{MnO}_4^-][\text{MP}]} \quad (6)$$

or

$$\frac{\text{Rate}}{[\text{MnO}_4^-]} = k_{\text{obs}} = \frac{k K_1 K_2[\text{MnO}_4^-][\text{OH}^-][\text{MP}]}{1 + K_1[\text{OH}^-] + K_1 K_2[\text{MnO}_4^-][\text{MP}]} \quad (6)$$

The rate law (6), can be rearranged to Equation (7), which is suitable for verification.

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k K_1 K_2 [\text{OH}^-] [\text{MP}]} + \frac{1}{k K_2 [\text{MP}]} + \frac{1}{k} \quad (7)$$

According to Equation 7, plots of $1/k_{\text{obs}}$ vs. $1/[\text{MP}]$ and $1/k_{\text{obs}}$ vs. $1/[\text{OH}^-]$ should be linear and are found to be so (Figure 4(a and b)). The formation of the complex was also proved kinetically by the non-zero intercept of the plot of $1/k_{\text{obs}}$ vs. $1/[\text{MP}]$ (Michaelis–Menten plot). The value of K_1 (6.43×10^{-1}) is in agreement with the literature (Naik, Chimatadar, & Nandibewoor, 2009). The thermodynamic quantities for the first and second equilibrium steps of Scheme 1 can be evaluated as follows. The $[\text{MP}]$ and $[\text{OH}^-]$ (as in Table 1) were varied at four different temperatures. From the slopes and intercepts of plots, $1/[\text{MP}]$ vs. $1/k_{\text{obs}}$ and $1/[\text{OH}^-]$ vs. $1/k_{\text{obs}}$, the values of K_1 , K_2 , and k were calculated at different temperatures and the values are given in Table 2. The obtained kinetic constants k , K_1 and K_2 are in good agreement with the literature value (Hegde, Shetti, & Nandibewoor, 2009; Naik et al., 2009; Panari & Nandibewoor, 1999; Veeresh, Lamani, & Nandibewoor, 2009) given in SI Table 2. van't Hoff's plots were made for variation of K_1 and K_2 with temperature ($\log K_1$ vs. $1/T$ and $\log K_2$ vs. $1/T$). The enthalpy of reaction ΔH , the entropy of reaction ΔS , and free energy of reaction ΔG , were calculated. These values are given in Table 2. The large negative values of ΔS^\ddagger ($-154 \text{ JK}^{-1} \text{ mol}^{-1}$) suggest the formation of a rigid transition state which is more ordered than the reactants with reduction of the degrees of freedom of the molecules involved (Rafat, 2002). The energy of activation, E_a , enthalpy of activation, and higher rate constant for the slow step indicate that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observation (Reuben, Simoyi, Irving, & Kenneth, 1986). The effect of ionic strength and dielectric constant of the medium on the rate explain qualitatively the reaction between neutral and charged species, as seen in the rate-determining step of Scheme 1.

4.1. Chemical oxygen demand study

COD is the measure of the amount of oxygen required for complete oxidation of the organic matter present in a sample of reaction mixture. Oxygen demand is determined by measuring the amount of oxidant consumed using titrimetric methods (Wayne, 1997). The objective of this study is to investigate the chemical oxygen demand (COD) degradation kinetics (Lucjan, Marzenna, & Artur, 2010). Reaction mixtures were prepared by the double distilled water, which is engaged to determine the COD in present work $\{[\text{MnO}_4^-] = 2 \times 10^{-4}$, $[\text{MP}] = 5 \times 10^{-3}$, $[\text{OH}^-] = 0.3$, $I = 0.8 \text{ mol dm}^{-3}\}$. The first order plot of $\log [\text{COD}]$ vs. time is shown in SI Figure 1 (SI Table 1) and observed rate constant is $6.88 \times 10^{-3} \text{ h}^{-1}$.

5. Conclusions

The most interesting feature of this study is the reactivity of methylparaben with MnO_4^- in aqueous alkaline medium, $[\text{MnO}_4 \cdot \text{OH}]^{2-}$ is considered as active species. A free radical mechanism is proposed. Rate constant of slow step and other equilibrium constants of different steps, involved in the mechanism were evaluated and activation parameters with respect to slow step of reaction were also calculated. The overall mechanistic sequence described here is consistent with product studies, mechanistic and kinetic studies.

Supplementary material

Supplementary material for this article can be accessed here <http://dx.doi.org/10.1080/23312009.2015.1134992>.

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