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Kinetics and mechanism of the oxidation of p-xylene using permanganate in aqueous acetic medium.

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ABSTRACT

Kinetic studies of the acid catalysed oxidation of p-xylene by permanganate ion have been studied in acetic acid-water medium. The product of oxidation was found to be terephthalic acid which was proved by melting point determination and infra red spectral analysis. The reaction showed first order dependence on both [substrate] and [oxidant]. The influence of dielectric constant of the solvent indicated that the reaction is between an ion and a dipole or between a neutral molecule and an ion. The added salt had no effect on reaction rate and thus ruled out the possibility of interaction between two charged species. Various thermodynamic activation parameters were determined and a suitable mechanism is proposed based on the obtained results.

Keywords: p-xylene, permanganate, oxidation, kinetics, mechanism

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INTRODUCTION

Different oxidising agents are employed for the oxidation of various organic substrates to produce compounds having high commercial importance [1,2]. Primary and secondary alcohols have been oxidised in a selective manner to get corresponding aldehydes by chromate ions [3,4]. Reports on kinetic studies on oxidation of alcohols using permanganate and chromate are plenty in literature [5-10]. But reports on the use of permanganate as an oxidant for the oxidation of aromatic hydrocarbons and kinetic studies on such oxidations are scanty and hence we carried out this work [11,12].

The present paper reports the kinetics of the oxidation of p-xylene in aqueous acetic acid medium containing 0.2 mol dm^{-3} H_2SO_4 with permanganate. Stoichiometry of the reaction, product analysis, effect of [oxidant], [substrate] and [acid], effect of dielectric constant of the medium, effect of temperature on the oxidation were carried out. Thermodynamic variables like energy of activation (Ea), enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$) and free energy of activation ($\Delta G^{\#}$) were computed and a suitable mechanism is proposed based on the experimental results.

EXPERIMENTAL

Analar grade p-xylene and potassium permanganate were used as such in kinetic experiments. (Merck, India) Acetic acid was purified by refluxing with potassium dichromate for six hours and then distilled [13,14]. Doubly distilled water was used throughout the experiments.

Product analysis was carried out by stirring excess permanganate with p-xylene in 20% aqueous acetic acid and 0.2 mol dm^{-3} H_2SO_4 for about six hours at room temperature. Unreacted permanganate was decolourised by the addition of sodium bisulphate and suspended manganese dioxide particles are removed by filtration. The solution was extracted with ether three times and ether extract was collected. It is treated with 10% sodium bicarbonate solution and the aqueous layer was collected and treated with Conc. HCl. The crystalline precipitate formed is filtered, dried and characterised by melting point determination and infra red spectral analysis

Kinetic experiments were carried out at desired temperatures in a thermostat with an accuracy of $\pm$ 0.1° C by maintaining pseudo first order condition by keeping [p-xylene] >> [permanganate]. A known quantity of exactly known concentration of permanganate in 20% aqueous acetic acid with 0.2 mol dm^{-3} H_2SO_4 was equilibrated. The reaction was initiated by adding required quantity of previously thermo stated p-xylene in acetic acid to the permanganate solution. The reaction mixture was stirred well and aliquots were withdrawn at regular intervals and the concentration was determined spectrophotometrically up to 90% completion of the reaction. The experiments were repeated and pseudo first order rate constants, k_{obs} were computed from the linear least square plots of log [permanganate] versus time.

RESULTS AND DISCUSSION

The product of oxidation of p-xylene by permanganate in 20% aqueous acetic acid medium was ascertained to be terephthalic acid. The recrystallised sample of product obtained was characterised by its melting point (298 $\pm$ 2º C). This obtained melting point was in concordance with that of pure sample and proved that the formed product may be terephthalic acid. The IR spectrum was recorded from KBr pellets by using Jasco FT-IR 4100 spectrophotometer (Japan) and is shown in Figure 1.

The IR spectrum showed sharp peaks at 2920 cm^{-1} (O–H stretching), 3066 cm^{-1} (Aromatic C–H stretching), 1686 cm^{-1} (C=O stretching), 1608 cm^{-1} (C=C stretching) and 1416 cm^{-1} (C-O-H in plane bending). Presence of these peaks leads to the conclusion that the product formed may be terephthalic acid. Furthermore this spectrum was compared with the IR spectrum of pure terephthalic acid and found to have excellent similarities.

The oxidation of p-xylene was carried out with different initial [oxidant] and [substrate] in 20% aqueous acetic acid medium with 0.2 mol dm^{-3} H_2SO_4 at 302.5 K. The effect of [permanganate] and [p-xylene] on reaction is given in Table 1. The plot of log [permanganate] versus time was found to be linear at various [permanganate]. This proved that the reaction may be first order with respect to [permanganate]. This was further confirmed from the constancy in the values of specific rates (k_{obs}) for the different [permanganate] for a given [p-xylene]. The effect of [p-xylene] on the rate of oxidation was studied by taking different initial [p-xylene] and the observed rate constant increased linearly with the increase in [p-xylene]. Moreover, the second order rate constants k_2, were found to be constant indicating the first order dependence of the reaction with respect to [p-xylene]. The first order dependence on [p-xylene] was further confirmed by the plot of log k_{obs} versus log [substrate] which is linear with a slope of unity.

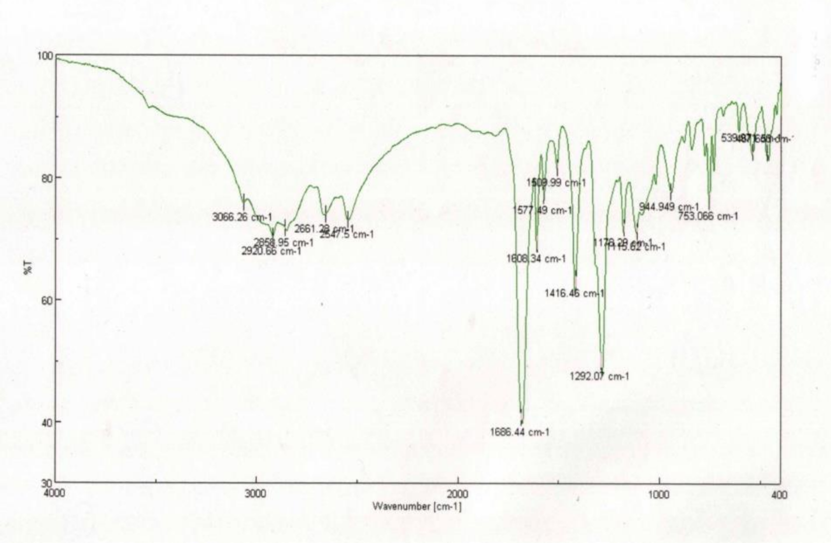


Figure 1: IR spectrum of the product

Table 1: Effect of [oxidant] and [substrate] on the rate of oxidation of p-xylene

Temperature – 302.5 K Medium - 20% aq. HOAc (v/v)

$[MnO_4^-] \times 10^3$ (mol dm^{-3})	[p-xylene] $\times 10^2$ (mol dm^{-3})	$k_{obs} \times 10^5$ (s^{-1})	$k_2 \times 10^4$ (dm^3 mol^{-1} s^{-1})
0.5	2.0	9.58	47.90
1.0	2.0	9.58	47.90
1.5	2.0	9.56	47.80
2.0	2.0	9.57	47.85
1.0	1.0	4.76	47.60
1.0	2	9.58	47.90
1.0	3	14.36	47.89
1.0	4	19.08	47.70

The effect of dielectric constant of the medium on the oxidation of p-xylene was done under pseudo first order condition, by varying the acetic acid percentage and is given in Table 2. The reaction rate increased with decrease in dielectric constant of the medium.

Table 2: Effect of dielectric constant of the medium on the rate of oxidation

$[MnO_4^-] \times 10^3$ =1.0 mol dm^{-3} [p-xylene] $\times 10^2$ = 2.0 mol dm^{-3} Temperature – 302.5 K

Acetic acid: water	Dielectric constant	$k_{obs} \times 10^5$ (s^{-1})	$k_2 \times 10^4$ (dm^3 mol^{-1} s^{-1})
20 : 80	61	9.58	47.90
40 : 60	47	17.27	86.33
60 : 40	32	25.58	127.91
80 : 20	27	32.23	161.17

Table 3: Effect of [salt] on the rate of oxidation of p-xylene [MnO_4^-] x10^3 =1.0 mol dm^{-3} [p-xylene] x10^2 = 2.0 mol dm^{-3}

Temperature - 302.5 K Medium - 20% aq. HOAc (v/v)

[KCl] x 10^2 (mol dm^{-3})	k_{obs} x 10^3 (s^{-1})	k_2 x 10^3 (dm^3 mol^{-1} s^{-1})
0	9.58	47.90
2	9.24	46.20
3	9.24	46.20
30	9.58	47.90

The effect of salt on the reaction rate was done at 302.5 K and is given in table 3. The salt effect on reaction rate is found to be negligible which rules out the interaction between charged species in the rate determining step. Hence the reaction may be between a dipole and a charged species or between two dipoles.

The effect of concentration of mineral acid on reaction rate was carried out at 302.5 K and is given in table 4. The rate of reaction is found to increase with increase in the [acid] and the effect of [acid] on reaction rate is found to be linear with order of one.

Table 4: Effect of [acid] on the rate of oxidation of p-xylene [MnO_4^-] x10^3 = 1.0 mol dm^{-3} [p-xylene] x10^2 = 2.0 mol dm^{-3}

Temperature - 302.5 K Medium - 20% aq. HOAc (v/v)

[Acid] x 10^1 (mol dm^{-3})	k_{obs} x 10^3 (s^{-1})	k_2 x 10^3 (dm^3 mol^{-1} s^{-1})
1	3.83	19.15
2	9.58	47.90
3	13.66	68.30
4	18.18	90.90

Table 5: Activation parameters for the oxidation of p-xylene

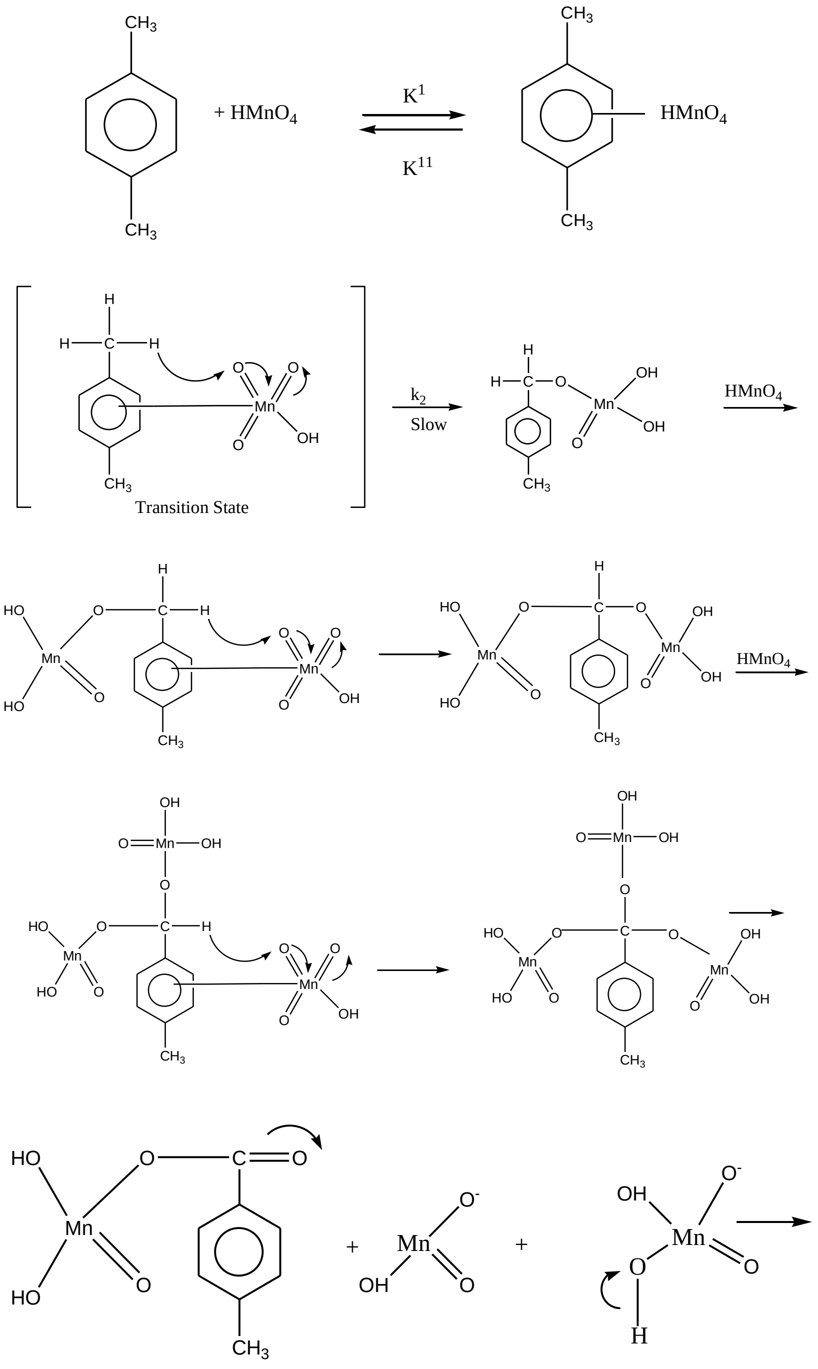
Medium - 20% aq. HOAc Temperature – 302.5 K

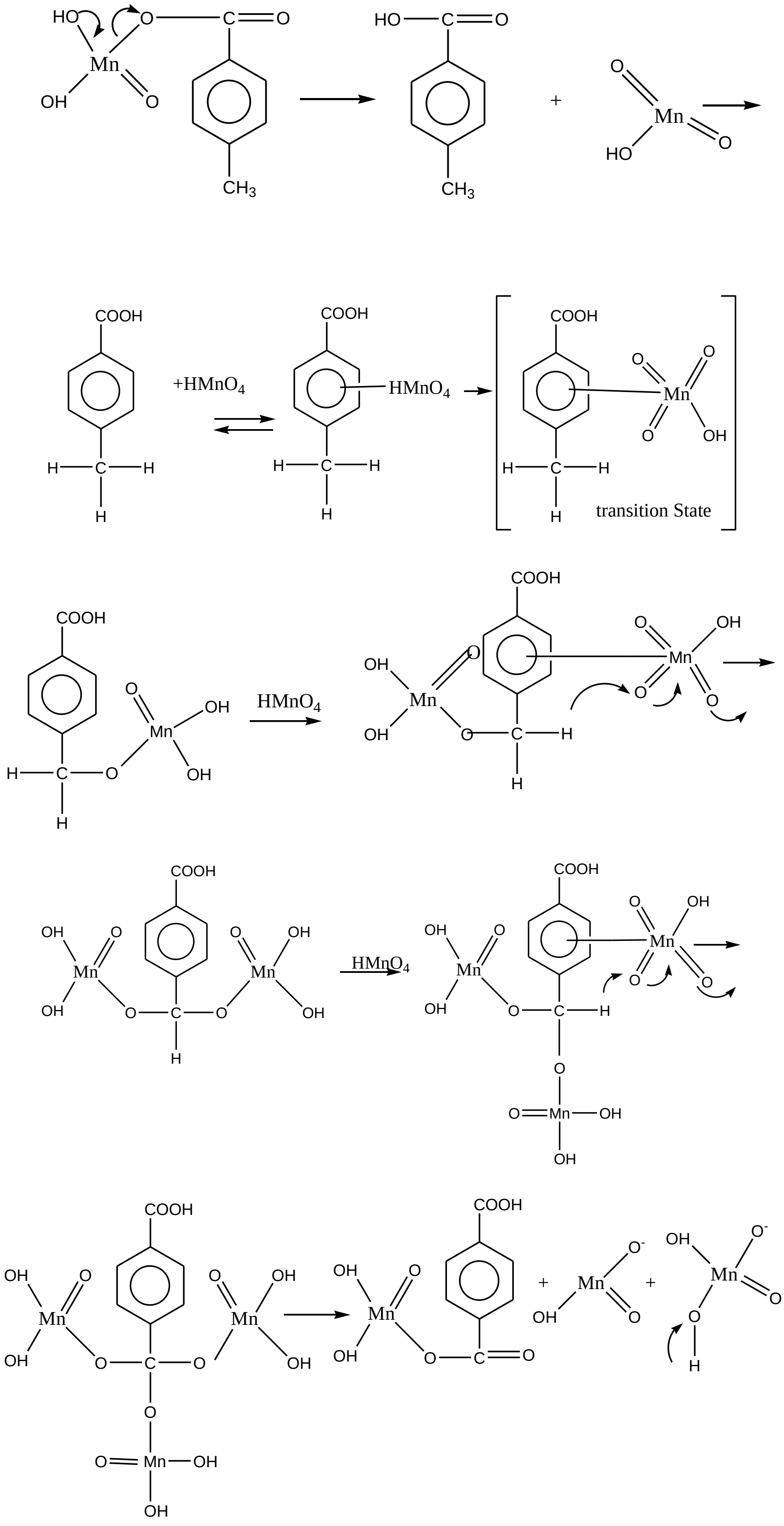
Substrate	k_2×10^4 (dm^{3}mol^{-1} s^{-1})	Ea (kJ mol^{-1})	ΔH $^{\#}$ (kJ mol^{-1})	-ΔS$^{\#}$ (JK^{1} mol^{-1})	ΔG$^{\#}$ (kJ mol^{-1})
p-xylene	47.90	68.93	67.01	67.60	87.43

The effect of temperature on the rate of oxidation of p-xylene using permanganate ion in 20% aqueous acetic acid (v/v) was studied in the temperature range 302.5 K to 314.5 K. The values of various thermodynamic parameters were calculated and presented in Table 5.

The product of oxidation of p-xylene by permanganate ion in 20% aqueous acetic acid medium was found to be terephthalic acid. The reaction showed first order dependence with respect to [oxidant], [substrate] and [acid]. The Line Weaver Burk plot with no Y-intercept showed the absence of formation of long lived intermediate. The negative value of ΔS$^{\#}$ was due to surrendering of large degree of disorder during the conversion of reactants into transition state. The influence of dielectric constant of the solvent indicated that the reaction is between an ion and a dipole or between a neutral molecule and an ion. A plot of log k_2 versus 1/D, where D is the dielectric constant of the medium is linear with a negative slope and is reported elsewhere [15]. It indicates the involvement of a negative and a neutral dipolar molecule. So the rate determining step may involve neutral p-xylene and negative charged MnO_4^- along with H^+ to form less polar larger transition state. Hence according to Eyring Laidler equation, rate increases with decrease of dielectric constant in the case of a reaction between a neutral molecule and an ion as the transition state is larger and less polar than the reactants. Added salt had no influence on the reaction rate and thus rules out the possibility of interaction between two charged species.

Based on the above experimental results a suitable mechanism for the oxidation of p-xylene by permanganate ion can be suggested as follows. At first permanganate ion is protonated to form permanganic acid. One permanganic acid then attached to the π electron cloud of the benzene ring to form a permanganate complex. Then this complex undergoes a slow rate determining decomposition to five another intermediates through a cyclic transition state which then combine with five other permanganic acid molecules in a fast step to form the final product. The decomposition of first permanganate complex may be the rate determining step and all other similar steps are seemed to be fast. It is already proved that the order of reaction is first with [permanganate] and [acid]. Hence first C-H bond cleavage of the permanganate complex which involves the above observations is the rate determining step and is given in scheme 1.

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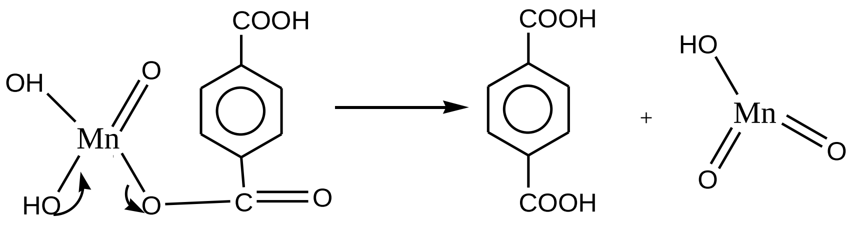

Scheme 1: Mechanism of the oxidation of p-xylene

A suitable rate expression in consistent with above mechanism can be formulated as follows:

$$\text{Rate} = \frac{-d\left[\text{MnO}_4^-\right]}{dt} = k_2\left[\text{Permanganate complex}\right]$$

$$= Kk_2\left[p-\text{xylene}\right]\left[\text{MnO}_4^-\right]\left[\text{H}^+\right]$$

CONCLUSIONS

The acid catalysed permanganate oxidation of p-xylene in aqueous acetic acid medium is studied conveniently with appreciable rate. The product obtained is terephthalic acid which is having high industrial application. Kinetic studies of this type can be extended to study the oxidation reactions of other organic compounds and mechanism of such reactions can be deduced.

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