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Kinetic and mechanistic studies of the oxidation of naphthalene by potassium permanganate in aqueous acetic medium

P. Rajendran[1], P. Bashpa[2], K. Bijudas[2*]
[1] Department of Chemistry, Government Victoria College, Palakkad, Kerala, India.
[2] Department of Chemistry, N.S.S. College, Manjeri, Malappuram, Kerala, India.
***Corresponding author: E-Mail: bijudask@gmail.com**

ABSTRACT

Kinetic and mechanistic investigations on the oxidation of naphthalene by permanganate in aqueous acetic acid medium with mineral acid were reported. The product, phthalic acid was identified by melting point determination and infra red spectral analysis. The reaction showed first order kinetics with respect to the concentrations of the oxidant, substrate and added acid. The effect of dielectric constant of the solvent indicated the possible interaction between an ion and a dipole or between two dipoles. The added salt had no influence on rate of reaction and negates the possible interaction between two charged species. Various thermodynamic factors like enthalpy of activation, entropy of activation and free energy are determined and a mechanism in accordance with the observations was suggested.

KEY WORDS: Naphthalene, Potassium Permanganate, Oxidation, Kinetics, Mechanism.

1. INTRODUCTION

Many industrially significant organic compounds are produced by the use of suitable oxidizing agents. The conversion of organic compounds from one functional group to another usually involves a gain of oxygen or loss of hydrogen. Various oxidants are used in which permanganate (Lee, 1980; Wiberg, 1965; Rajendran, 2003), dichromate (Sharma, 2013; Dey, 1990; Basheer, 2007; Bijudas, 2004; 2014; 2016), Hypochlorite (Bijudas, 2015; Stephen, 1982; Hill, 1984) and bromate (Paakkonen, 2010; Hu, 2013) are quite common in many oxidation reactions. The present investigation is intended to study the kinetics of naphthalene oxidation in aqueous acetic acid medium using potassium permanganate and to propose a mechanism in accordance with the obtained results. We have carried out experiments to bring out the stoichiometry of the reaction, isolation of product and its characterisation, effect of oxidant and substrate concentration on reaction rate, effect of dielectric constant of the medium and effect of acid and added salt on reaction rate. The reaction was done at different desired temperatures to determine the thermodynamic variables such as energy of activation (Ea), enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$) and free energy of activation ($\Delta G^{\#}$).

2. EXPERIMENTAL

Acetic acid (Merck, India) was purified by refluxing with potassium dichromate for five hours and distilled (Perrin, 1966; Vogel, 1967). Analar grade naphthalene and potassium permanganate were used as available in all the experiments. All other chemicals used were of A.R. quality and doubly distilled water was employed in the entire work.

The reaction stoichiometry was studied with excess concentration of permanganate ion with that of naphthalene. A reaction mixture which contains known concentration of naphthalene and permanganate ion in 50% acetic acid-water containing 0.2 mol dm^{-3} H_2SO_4 was refluxed in a round bottom flask for about three hours for the completion of the reaction. Aliquots of the reaction mixture were taken out and the concentration of remaining permanganate was estimated spectrophotometrically. From the concentration of remaining permanganate ion, the stoichiometry of the oxidation was determined.

The product of oxidation was analysed by refluxing the reaction mixture containing excess potassium permanganate over naphthalene in 50% aqueous acetic acid and sulphuric acid (0.2 mol dm^{-3}). Unreacted permanganate was declourised on the addition of sodium bisulphate and suspended manganese dioxide particles were removed by filtration. The solution was extracted (three times) with ether and the organic layer was collected and treated with 10% sodium bicarbonate solution. The aqueous layer was collected and treated with conc. HCl. The crystalline precipitate formed was filtered, dried and the obtained product after purification is charecterised by melting point determination and infra red spectral analysis.

Kinetic investigations were carried out at various desired temperatures in a thermostat with an accuracy of $\pm 0.1^{\circ}$ C. A known concentration of permanganate in 50:50 (v/v) aqueous acetic acid containing 0.2 mol dm^{-3} H_2SO_4 is equilibrated at the desired temperature. The reaction is initiated by rapid addition of required volume of previously thermostated naphthalene solution in glacial acetic acid. The reactants were shaken well and aliquots were taken out at regular intervals of time and the unreacted permanganate concentration was determined by UV- Visible spectrophotometer. Pseoudo first order condition of the reaction was maintained by keeping [naphthalene] >> [permanganate]. The kinetic investigations were repeated and pseudo first order rate constants, k_{obs} were determined from the linear least square plots of log [permanganate] versus time.

3. RESULTS AND DISCUSSION

The stoichiometry of the oxidation under the condition [permanganate] >> [naphthalene] was seemed to be in the ratio, one molecule of naphthalene is equivalent to four molecules of permanganate. The product, formed was identified as phthalic acid from the melting point and infra red spectral analysis. The recrystallised sample of product obtained was characterized by its melting point (193 ± 2ºC). This obtained melting point was in concordance with that of pure sample and proved that the formed product may be phthalic acid. The IR spectrum was recorded in the form of KBr pellets by using Jasco FT-IR 4100 spectrophotometer (Japan) and is shown in Figure.1.

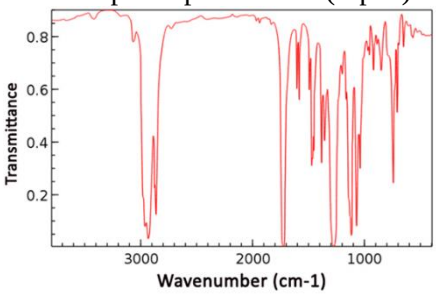


Figure.1. Infrared spectrum of the product.

The infra red spectrum showed sharp peaks at 1720 cm^{-1} (C=O stretching), 2970 cm^{-1} (O-H stretching), 2850 cm^{-1} (C-H stretching). Presence of these peaks supports the formation of phthalic acid as the product. Moreover, the obtained infra red spectrum on comparison with that of pure phthalic acid gave excellent similarities.

The oxidation reaction was done with different initial concentrations of permanganate and naphthalene in 50% aqueous acetic acid medium containing 0.2 mol dm^{-3} H_2SO_4 at 302.5 K. The effect of [oxidant] and [substrate] on oxidation is given in table.1. The logarithmic plot of [permanganate] versus time was found to be linear at various concentrations of permanganate and these results prove the first order dependence of the reaction with respect to the permanganate concentration. This was further proved from the constant values of specific rates (k_{obs}) for the different concentrations of permanganate for a given concentration of naphthalene. The effect of naphthalene concentration on reaction rate was followed by taking different initial substrate concentrations and the observed rate constant increased with concentration of naphthalene in a linear fashion. Moreover, the second order rate constants (k_2), were found to be constant which indicates the first order dependence of the reaction with respect to the naphthalene concentration. The first order dependence on the concentration of naphthalene was further confirmed by the plot of log k_{obs} versus log [naphthalene] which is linear with a unit slope.

Table.1. Effect of [oxidant] and [substrate] on the rate of oxidation of naphthalene

Temperature - 302.5 K		Medium - 50% aq. HOAc (v/v)	
[Permanganate] x 10^3 (mol dm^{-3})	**[Naphthalene] x 10^2 (mol dm^{-3})**	**k_{obs} x 10^3 (s^{-1})**	**k_2 x 10^3 (dm^3 mol^{-1} s^{-1})**
0.5	2.0	1.57	78.50
1.0	2.0	1.56	78.00
1.5	2.0	1.57	78.50
2.0	2.0	1.56	78.00
1.0	1.0	0.80	80.00
1.0	2.0	1.56	78.00
1.0	3.0	2.37	79.00
1.0	4.0	3.18	79.50

The influence of dielectric constant of the medium on naphthalene oxidation was carried under pseudo first order condition, by changing the acetic acid percentage and is given in table.2. The reaction rate is found to increase with the decrease in dielectric constant of the medium. The plot of log k_2 versus 1/D, where D is the dielectric constant is found to be linear with a negative slope and is in accordance with Amis equation (Amis, 1966).

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

[Permanganate] x 10^3 = 1.0 mol dm^{-3} Temperature - 302.5 K		[Naphthalene] x 10^2 = 2.0 mol dm^{-3}	
Acetic acid: water	**Dielectric constant**	**k_{obs} x 10^3 (s^{-1})**	**k_2 x 10^3 (dm^3 mol^{-1} s^{-1})**
40 : 60	47	1.2	60.00
50: 50	39.8	1.56	78.00
60 : 40	32	2.55	127.5
70 : 30	24.5	5.26	263.2

The effect of salt on the reaction rate was done at 302.5 K and is given in table 3. The added salt did not affect the reaction rate and this ruled out the possible interaction between two charged species in the rate determining step. Hence the reaction may be between a dipole and a charged particle or between two dipoles.

Table.3. Effect of [salt] on the rate of oxidation of naphthalene
[Permanganate] x 10^3 = 1.0 mol dm^{-3} [Naphthalene] x 10^2 = 2.0 mol dm^{-3}
Temperature - 302.5 K Medium - 50% 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})
5	1.31	65.50
10	1.32	66.00
20	1.31	65.50
30	1.31	65.50

The effect of mineral acid concentration on reaction rate was done at 302.5 K and is shown in table.4. The rate of reaction increased with increase in acid concentration and the effect of $[H^+]$ on rate is found to be linear with a unit order.

Table.4. Effect of [acid] on the rate of oxidation of naphthalene
[Permanganate] x 10^3 = 1.0 mol dm^{-3} [Naphthalene] x 10^2 = 2.0 mol dm^{-3}
Temperature - 302.5 K Medium - 50% 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	0.71	35.50
2	1.56	78.00
3	1.83	91.5
4	2.24	112.0

The effect of temperature on rate of oxidation of naphthalene was studied in the temperature range 297.5 K to 308 K. The values of various thermodynamic factors were calculated and are given in Table 5.

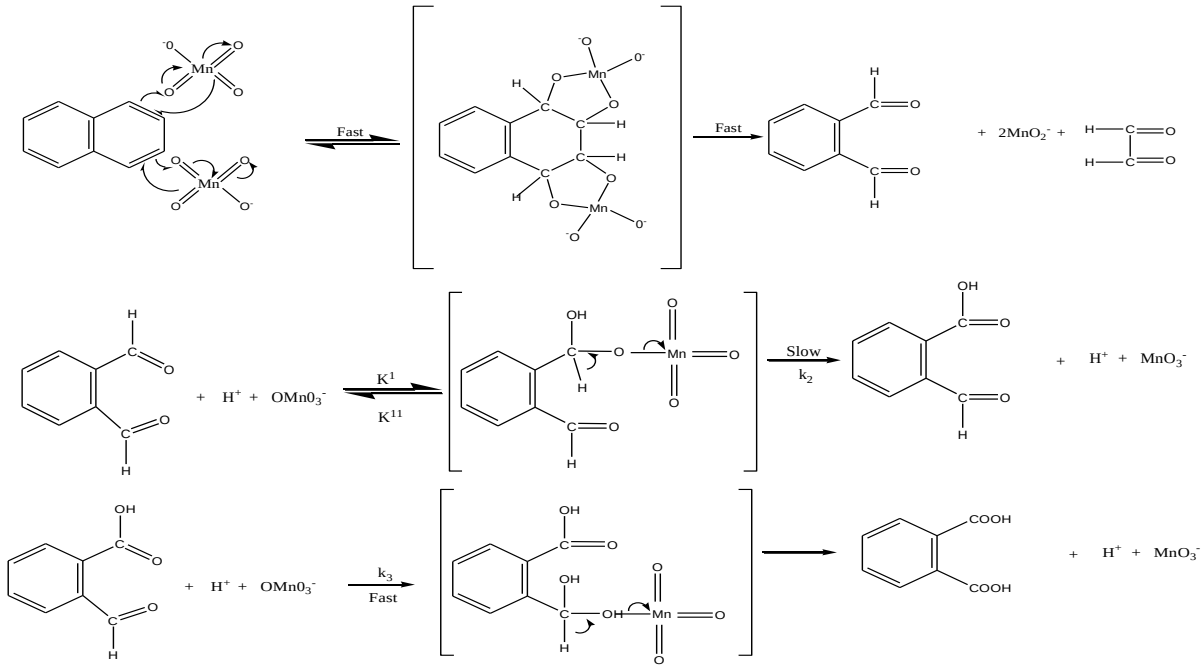
Table.5. Activation parameters for the oxidation of naphthalene
Medium - 50% aq. HOAc Temperature - 302.5 K

Substrate	k_2x10^3 (dm^3mol^{-1} s^{-1})	Ea (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (JK^1 mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
Naphthalene	78.00	86.53	85.01	13.85	80.81

The product of oxidation of naphthalene by permanganate ion in 50% aqueous acetic acid medium was ascertained to be phthalic acid and stoichiometry was determined as 1:4 to naphthalene: permanganate. The reaction showed first order kinetics with [oxidant] and [substrate]. The Line Weaver Burk plot gave no intercept which rules out the presence of long lived intermediate. The positive entropy of activation indicates that there is not so much surrendering of disorder when the reactants are converted to transition state and predicts its loose nature. The order of the reaction with [acid] is found to be unity and is due to protonation. The influence of dielectric constant of the solvent shows the possible interaction between an ion and a dipole or between two dipoles. Since the transition state is less polar than the reactants, the reaction may be between a neutral molecule and an anion. The rate acceleration with increase in dielectric constant of the solvent shows that, the reaction is between an ion and a neutral molecule. According to Eyring and Laidler, the reaction rate increases with decrease in dielectric constant of the medium in the case of a reaction between a neutral molecule and an ion as the transition state is larger than the reactant. Another possibility may be that, the reaction between naphthalene and permanganate ion gives a transition state which is less polar than the reactants. Since the oxidation is acid catalysed, an increase in acetic acid percentage increases $[H^+]$ ions which in turn increases the reaction rate. The added salt had no influence on the rate of reaction and thus rules out the possibility between two charged species.

Based upon the above results a suitable mechanism for the oxidation of naphthalene can be suggested as follows. At first two MnO_4^- ions attacks naphthalene double bond by pericyclic addition (2+4) to form a permanganate complex by fast equilibrium. This complex undergo fast decomposition with the formation of unstable 1, 2-dialdehyde benzene, glyoxal and MnO_2^-. This fast decomposition is followed by another fast equilibrium of the formation of a permanganate complex between unstable 1, 2-dibenzaldehyde, MnO_4^- and H^+. This permanganate complex undergoes the rate determining slow decomposition involving C-H bond breakage (hydride ion transfer) forming phthalic acid and Mn (V). The unstable Mn (III) and Mn (V) undergo disproportionation to give stable Mn (IV) and Mn (VII) as the final byproducts. The decomposition of the first permanganate complex cannot be the rate determining step as its formation involves two permanganate ion and due to the observations that the order obtained with respect to [permanganate] is one and also first order dependence with $[H^+]$. Hence the decomposition of second

permanganate complex, whose formation involves the above observations is the rate determining step and is given in scheme.1.



Scheme 1. Mechanism of the oxidation of naphthalene

$$2\,Mn\,(III) \rightarrow Mn\,(II) + Mn\,(IV)$$

$$3\,Mn\,(V) \rightarrow 2\,Mn\,(IV) + Mn\,(VII)$$

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

$$\text{Rate} = \frac{-d[MnO_4^-]}{dt} = k_2\,[\text{Permanganate complex}] = Kk_2[C_{10}H_8][MnO_4^-][H^+]$$

4. CONCLUSION

The acid catalysed oxidation of naphthalene by permanganate occurred smoothly in aqueous acetic acid medium with appreciable rate. Naphthalene was oxidized first to 1, 2-dibenzaldehyde and finally to phthalic acid. Thus kinetic studies of this type can be extended to study the oxidation reactions of other substrates and to deduce the mechanism of such oxidation reactions.

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