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Kinetics of Acidic Mn(VII) Oxidation of Acetaldehyde in Aqueous and 5% Ethanol-Water Solvents

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ABSTRACT

Kinetics of acidic Mn(VII) oxidation of acetaldehyde in aqueous and 5% ethanol-water solvents were studied via pseudo-first order condition at λ_{\max} 525nm. The reaction showed a first order dependence with respect to acetaldehyde concentration, [Mn(VII)], fractional order to [H⁺] and independent on the ionic strength of the solution. Michaelis-Menten plot showed the existence of an intermediate complex and dependence on hydrogen ion is in the form $k_{\text{obs}} = a + b[\text{H}^+]$. However, oxidation reaction is generally faster in non-aqueous solvent than in aqueous solvent. Product analysis revealed the presence of carboxylic acid and stoichiometric study suggests the consumption of 2 moles of MnO₄⁻ by 3 moles of acetaldehyde in both solvents. Thermodynamic parameters of activation were obtained from Arrhenius and Eyring's equations. A plausible associative mechanism in agreement with kinetic and spectroscopic results was proposed.

Keyword: Potassium permanganate, Acetaldehyde(A), Hydrated acetaldehyde(HA), sulphuric acid, potassium nitrate, Ionic strength(I) and activation parameters.

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Introduction

Aldehydes are very reactive organic compounds. They exist as aliphatic or aromatic aldehydes. Acetaldehyde is one of the most important aldehydes which occurs in nature and is manufactured commercially in the industry and used as a common electrophile precursor^{1,2}. It is toxic when applied for a long period as acute exposure can lead to eye and skin irritation³. It can also damage DNA and cause abnormal muscle development as it binds to protein^{4,5}. There are several investigations on the oxidation of aldehydes using various oxidants.⁶⁻¹³ However, there are few reports on the kinetics of acetaldehyde oxidation.¹⁴⁻¹⁶ Literature survey revealed no report on the kinetics of acetaldehyde oxidation by KMnO_4 . Therefore, this research is aimed at investigating the kinetics of the oxidation of acetaldehyde by acidic KMnO_4 in aqueous and ethanol-water mixture media with the view to ascertaining the mechanism of the reaction, activation parameters and ionic strength effect on the reaction.

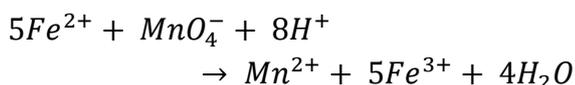
Experimental

Material

Analar grade KMnO_4 , Sulphuric acid, Potassium nitrate, Ethanol, Acetaldehyde and $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ were used.

Standardization of potassium permanganate solution

Stock solution of potassium permanganate was standardized in acidified ferrous ammonium sulfate solution.¹⁷



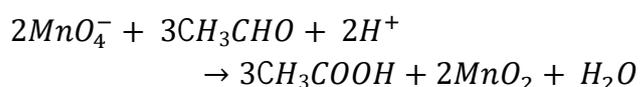
Kinetic Procedure

The kinetic study was investigated using a double beam UV-1800 Shimadzu Spectrophotometer provided with a thermostated cell interfaced to a computer. The kinetic runs were undertaken via pseudo-first order kinetics by maintaining a large excess ($\times 10$ or greater) of Acetaldehyde concentration

to potassium permanganate concentration. Appropriate quantities of reaction components in the order: Acetaldehyde, potassium nitrate, Sodium hydroxide and Potassium permanganate were taken from the stock solutions into the cuvette. A decrease in absorbance of KMnO_4 with time was measured at 525 nm. Pseudo-first order rate constants (k_{obs}) were obtained from the slope of the plot of $\ln A$ versus time.

Stoichiometry

The stoichiometry of the oxidation reaction was determined via spectroscopic titration. The absorbance at infinite time of solutions containing various concentrations of Acetaldehyde in the range 1.00×10^{-3} – $8.00 \times 10^{-3} \text{ mol dm}^{-3}$, a fixed $[\text{KMnO}_4]_0$, $[\text{H}^+]$, $[\text{KNO}_3]_0$ at 5.00×10^{-5} , 1.33×10^{-3} and 0.05 mol dm^{-3} respectively were measured. Hence, from the plot of Absorbance versus $[\text{CH}_3\text{CHO}]$ curve, the result showed that 3 moles of Acetaldehyde reacted with 2 moles of KMnO_4 .



Product Analysis

FTIR Spectroscopic study was carried out on the product of the oxidation reaction. The major oxidation product was identified as carboxylic acid due to the presence of OH stretching (strongly H-bonded) at $3400\text{--}2400 \text{ cm}^{-1}$, C-O broad band stretching at $1730\text{--}1700 \text{ cm}^{-1}$ and C-O stretching between 1320 cm^{-1} and 1210 cm^{-1} .

Induced polymerization of acrylonitrile

Polymerization test using acrylonitrile showed the absence of free radicals as the addition of acrylonitrile did not have any effect on the reaction mixture.

Results and Discussion

Rate dependence on $[\text{KMnO}_4]$

The effect of potassium permanganate concentration on the observed rate constant was investigated by studying reaction mixtures containing $[\text{KMnO}_4]_0$ in the range 1.00×10^{-5} –

$7.00 \times 10^{-5} \text{ mol dm}^{-3}$, fixed concentrations of Acetaldehyde and H_2SO_4 at 3.00×10^{-3} and $1.33 \times 10^{-3} \text{ mol dm}^{-3}$ respectively and maintaining ionic strength at 0.05 mol dm^{-3} at 298K. There was an increase in the pseudo-first order observed rate constant (k_{obs}) with

increase in $[\text{KMnO}_4]$ in both solvents as shown in Table 1. Consequently, the slope of the plot of $\ln k_{\text{obs}}$ versus $\ln[\text{KMnO}_4]$ gave 1, indicating a first order dependence on $[\text{KMnO}_4]$ in both solvents.

Table 1: Effect of $[\text{KMnO}_4]$

$10^5[\text{KMnO}_4]/\text{M}$	$10^5 k_{\text{obs}}/\text{s}^{-1}$	
	Aqueous solvent	5% Ethanol-Water solvent
1.00	0.36	0.54
2.00	0.67	0.87
3.00	0.87	1.50
4.00	1.31	1.75
5.00	1.59	2.32
6.00	1.71	2.68
7.00	1.93	3.15

[ACET] $3.00 \times 10^{-3}\text{M}$ $[\text{H}^+]$ $1.33 \times 10^{-3}\text{M}$ $I=0.05\text{M}$ $T=298\text{K}$

Rate dependence on $[\text{CH}_3\text{CHO}]$

The rate dependence as a function of $[\text{CH}_3\text{CHO}]$ was monitored with reaction mixtures containing $[\text{CH}_3\text{CHO}]_0$ in the range 1.00×10^{-3} - $8.00 \times 10^{-3} \text{ mol dm}^{-3}$, fixed concentrations of KMnO_4 and H_2SO_4 at $5.00 \times 10^{-5} \text{ mol dm}^{-3}$ and $1.33 \times 10^{-3} \text{ mol dm}^{-3}$ respectively and the ionic strength was fixed at 0.05 mol dm^{-3} . While the temperature of the

reaction mixtures was maintained at 298K. Consequently, increase in the pseudo-first order rate constant (k_{obs}) with increase in $[\text{CH}_3\text{CHO}]$ was observed (Table 2) and the presence of an intermediate complex was suggested from the Michaelis-Menten plot (Fig.1). The reaction showed a first order dependence with respect to $[\text{CH}_3\text{CHO}]$.

Table 2: Effect of $[\text{CH}_3\text{CHO}]$

$10^3[\text{CH}_3\text{CHO}]/\text{M}$	$10^5 k_{\text{obs}}/\text{s}^{-1}$	
	Aqueous solvent	5% Ethanol-Water solvent
1.00	0.48	0.75
1.67	0.73	1.18
2.33	1.01	1.62
3.00	1.39	2.03
4.00	1.70	2.48
4.33	1.88	2.79
5.00	2.23	2.98
6.00	2.67	3.45
7.00	2.98	4.11
8.00	3.32	4.67

$[\text{Mn}^{7+}]$ $5.00 \times 10^{-5}\text{M}$ $[\text{H}^+]$ $1.33 \times 10^{-3}\text{M}$ $I=0.005\text{M}$ $T=298\text{K}$

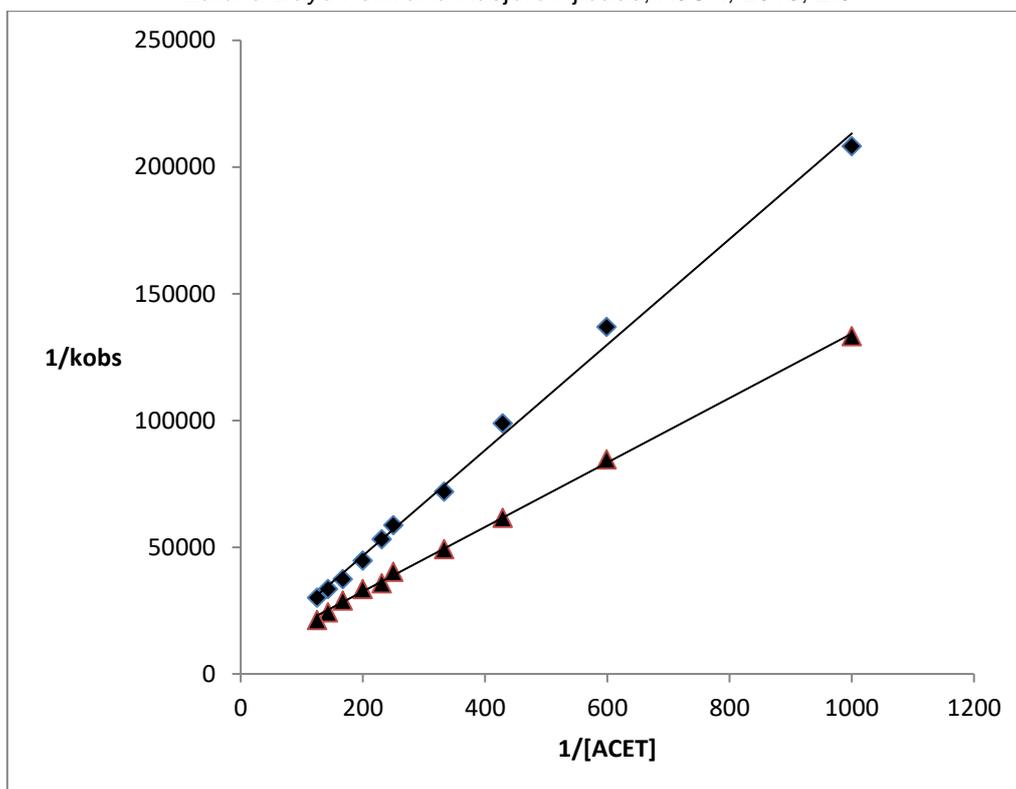


Fig. 1: Michaelis-Menten plot (■ Aqueous ▲ 5% Ethanol –Water solvent)

Rate dependence on [H⁺]

The effect of [H⁺] on the oxidation reaction was determined using reaction mixtures with varying concentrations of H₂SO₄ at 7.00 × 10⁻⁴- 4.33 × 10⁻³ mol dm⁻³ at fixed [KMnO₄]₀, [CH₃CHO] and ionic strength at 5.00 × 10⁻⁵, 2.00 × 10⁻³ and 0.05 mol dm⁻³ respectively at 298K. Increase in

[H⁺] resulted to an increase in the pseudo-first order rate constant (k_{obs}) and dependence on hydrogen ion is in the form k_{obs} = a + b[H⁺] as shown in Fig.2. The reaction is fractional order with respect to [H⁺] from the slope of the plot of ln k_{obs} versus ln [H⁺].

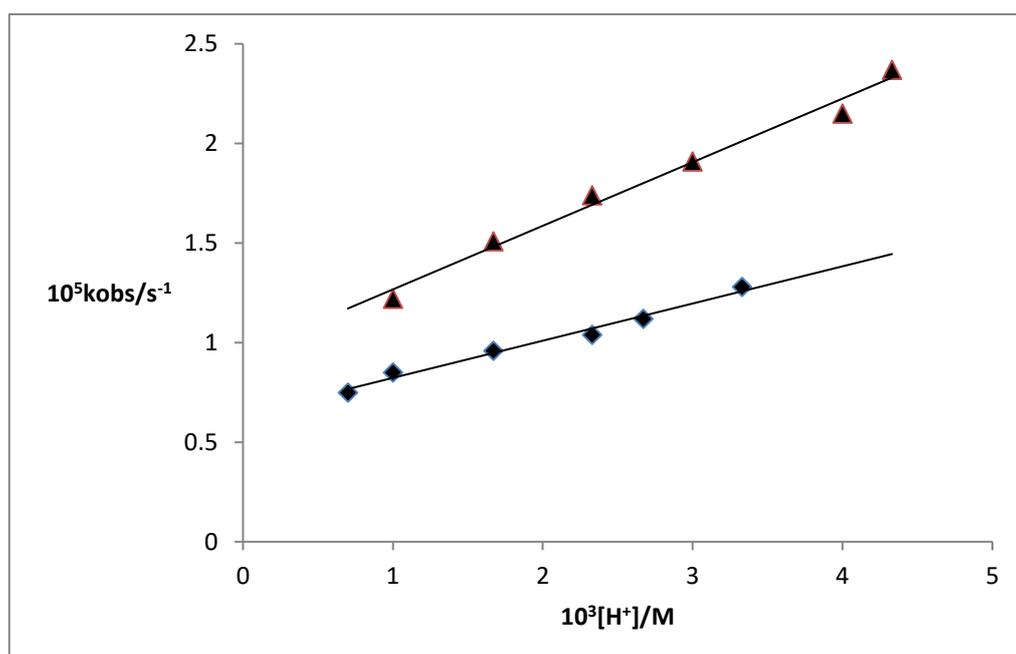
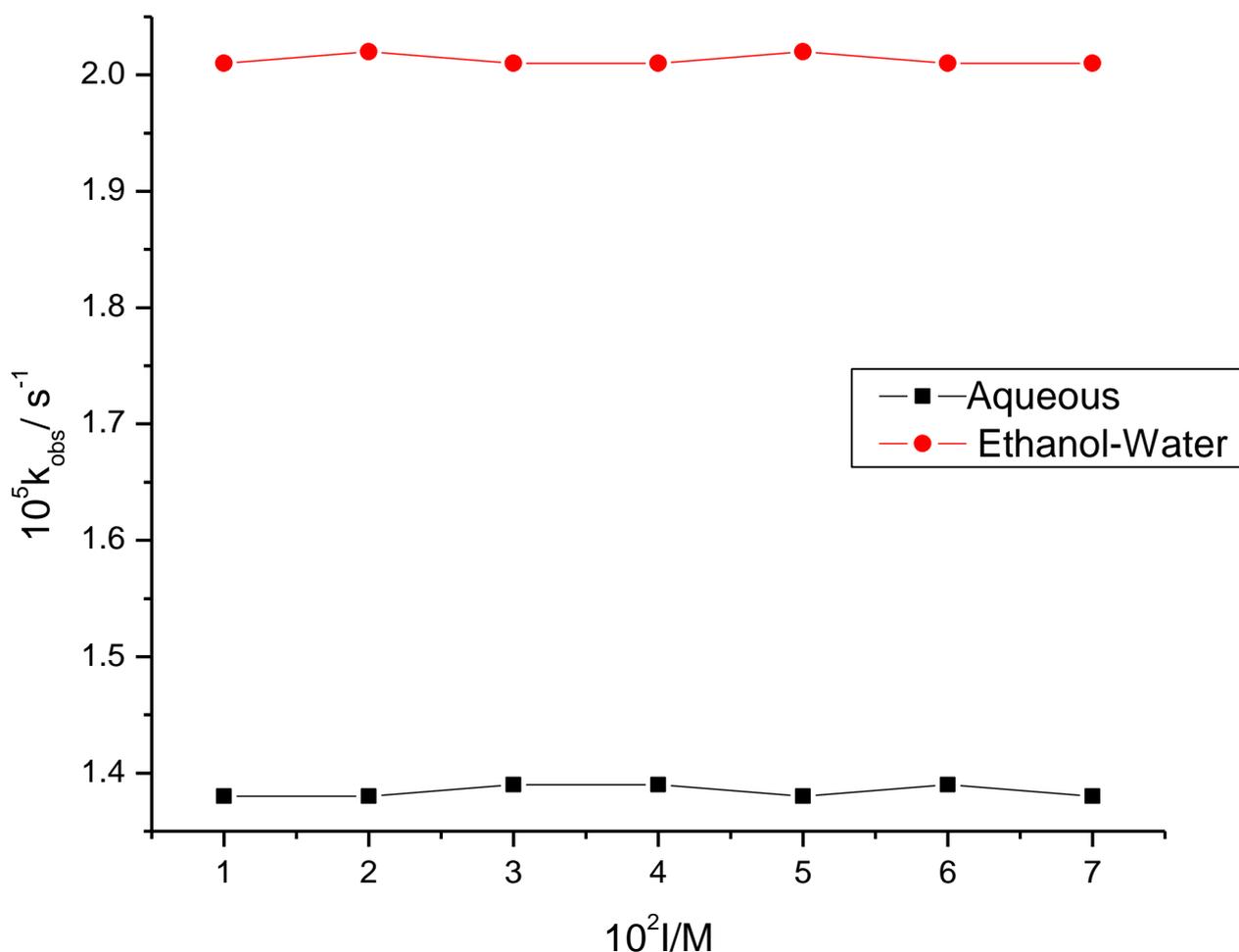


Fig.2: Plot of k_{obs} versus [H⁺](■ Aqueous ▲ 5% Ethanol-Water solvent)

Rate dependence on ionic strength

The effect of ionic strength on the oxidation reaction was monitored using reaction mixtures at varied ionic strength in the range 1.00×10^{-2} – 7.00×10^{-2} mol dm⁻³ and at fixed $[\text{KMnO}_4]_0$, $[\text{CH}_3\text{CHO}]_0$ and $[\text{H}^+]_0$ at 5.00×10^{-5} , 3.00×10^{-3}

and 1.33×10^{-3} mol dm⁻³ respectively at 298K. The reaction is independent on the ionic strength of the reaction mixtures as shown in Fig.3. Plot of $\log k_{\text{obs}}$ versus \sqrt{I} gave a straight line with zero slope, suggesting the presence of a neutral molecule in the rate determining step.



Rate dependence on Temperature

Temperature effect on the observed rate constant was determined by varying the temperature of the reaction mixtures in the range 298-308K at fixed $[\text{KMnO}_4]_0$ 5.00×10^{-5} , $[\text{CH}_3\text{CHO}]_0$ 2.00×10^{-3} , $[\text{H}^+]_0$ 1.33×10^{-3} and ionic strength at 0.05 mol dm⁻³. The activation energy (E_a) and other activation parameters (ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger) for the reaction as shown in Table 4 were obtained from Eyring's equations below .

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^\ddagger}{RT} + \ln\left(\frac{k'}{h}\right) + \left(\frac{\Delta S^\ddagger}{R}\right) \ln\left(\frac{k'}{h}\right)$$

$$= 23.76$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

K = Rate constant

 ΔG^\ddagger = Free Gibb's energy of activation

T= Temperature

R= Molar gas constant

 ΔH^\ddagger = Enthalpy of activation k^{\ddagger} = Boltzmann's constant ΔS^\ddagger = Entropy of activation

h= Plank's constant

Table 4; Activation parameters

CH ₃ CHO	Ea(kJ mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (kJK ⁻¹ mol ⁻¹)	ΔG^\ddagger (kJmol ⁻¹)
Aqueous	59.21	56.99	-0.15	101.69
5%Ethanol-Water	35.30	32.96	-0.23	101.50

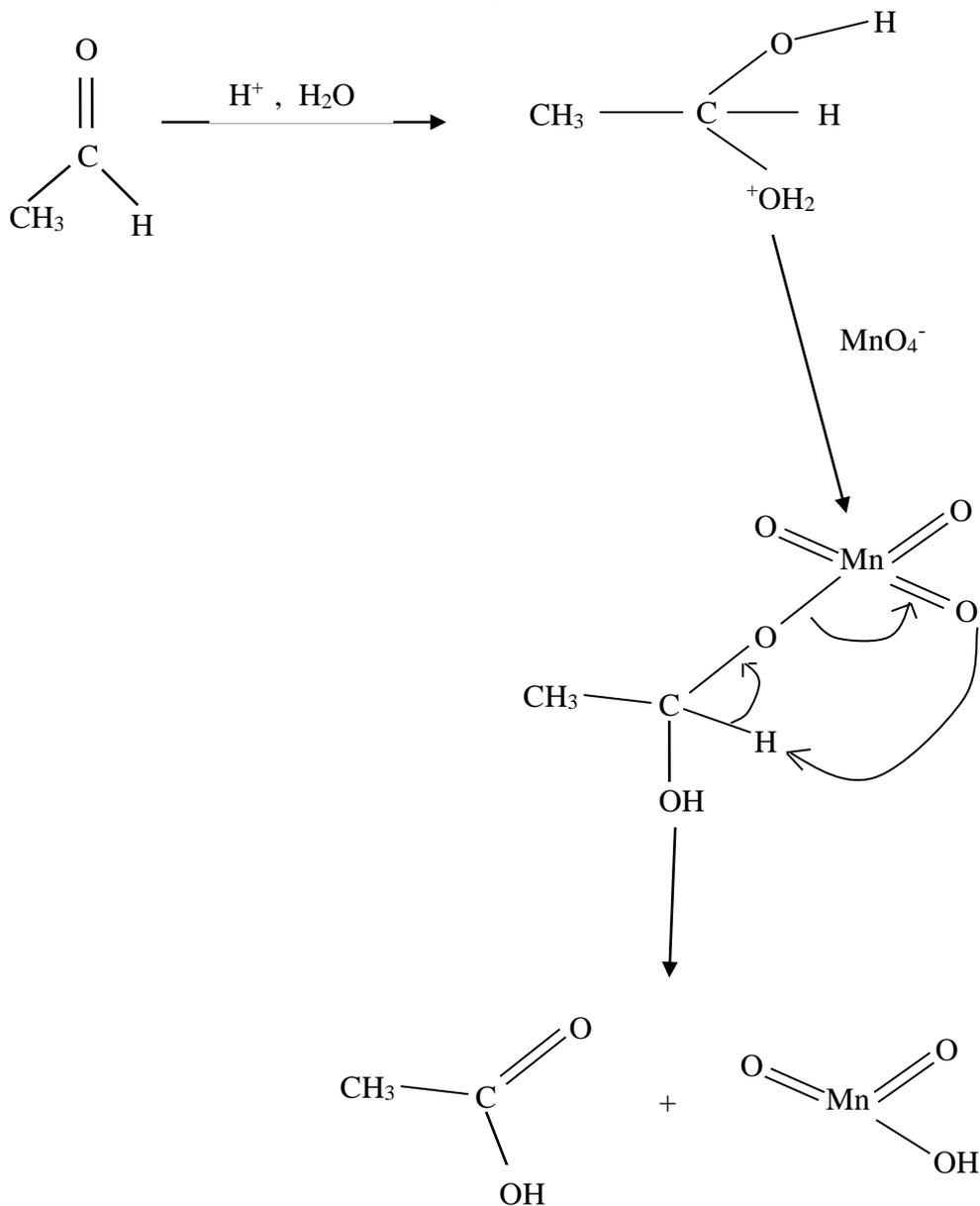
Discussion

Generally, the rate of reaction is faster in the non-aqueous solvent than in aqueous solvent. Which of course implies that the carbocation in the aldehyde is more susceptible to attack by MnO₄⁻ in non-aqueous solvent than in the aqueous solvent due to decrease in the dielectric constant of the reaction medium. The oxidation reaction studied in 5% Ethanol-Water mixture and aqueous solvents showed that reaction rate increases with decrease in dielectric constant of medium, suggesting that, polar solvents may require higher reaction time for oxidation reaction. Increase in the observed rate constant with decrease in dielectric constant of the medium implies an interaction between a dipole and a positive ion and also indicates the probable involvement of a protonated Mn⁷⁺ specie in the presence of acid in the rate determining step. The rate of reaction increased with increase in temperature and the reaction were characterized by negative entropy of activation, which suggests the solvent molecules strongly surrounds the ions, which led to loss of entropy and the effect is more pronounced in non- aqueous solvents.

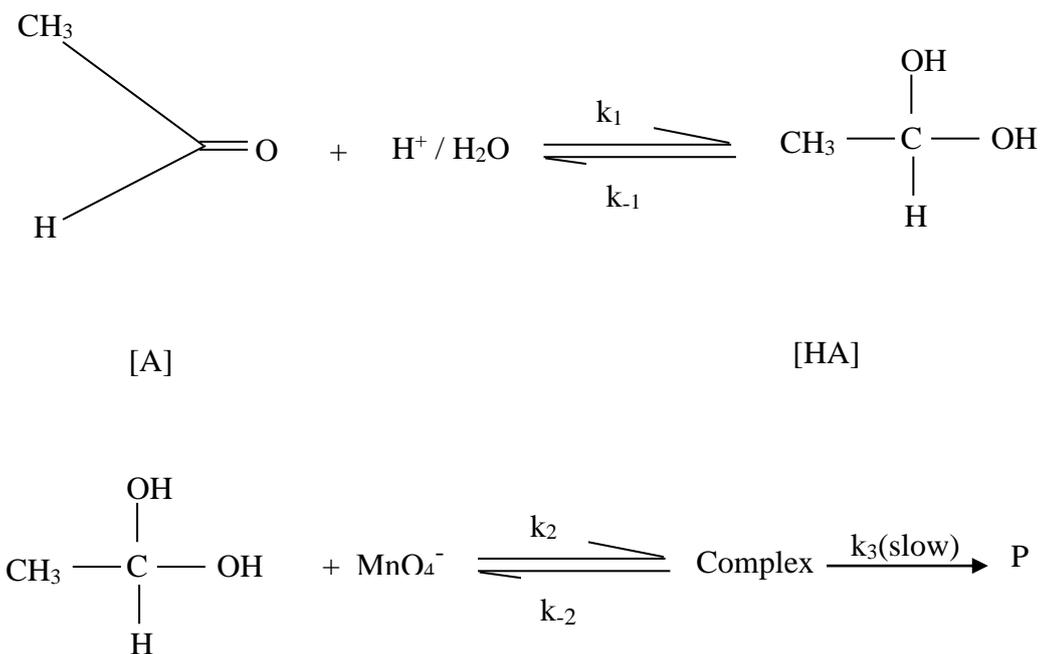
Negative ΔS^\ddagger also suggests an associative mechanism and polymerization test revealed the absence of free radicals. This indicates that one-electron oxidation leading to the formation of free-radicals can be ruled out. The reaction was independent on ionic strength of the reaction mixture, indicating the presence of a neutral molecule in the rate determining step. The same values of ΔG^\ddagger for reaction in both solvents, suggests same mechanism for the oxidation reaction. Product analysis revealed the presence of acetic acid and the Michaelis-Menten plot showed the existence of an intermediate complex.

Mechanism

The acetaldehyde is attacked by acid to produce acidified hydrated acetaldehyde, which in turn was oxidized by MnO₄⁻ to form a complex, which decomposed to form the product. The proposed mechanism is however, supported by the observed negative entropy of activation. The two ends becomes highly solvated as the charge separation takes place in the transition state. Which of course leads to an immobilization of a large number of solvent molecules as shown by the loss of entropy.



The below mechanism is hereby proposed based on the kinetic and spectroscopic results



Where,

[A] = Concentration of acetaldehyde

[HA]= Concentration of acidified hydrated acetaldehyde

The rate law obtained using steady state approximation is:

$$\text{Rate} = \frac{k_1 k_2 k_3 [A][H^+][MnO_4^-]}{(k_{-2} + k_3)}$$

$$\text{Rate} = K_1 k [A][H^+][MnO_4^-] \quad \text{where,}$$

$$K_1 = \frac{k_1}{k_{-1}} ; \quad k = \frac{k_2 k_3}{(k_{-2} + k_3)}$$

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