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Kinetics of Acidic Potassium Permanganate Oxidation of Formaldehyde in Aqueous and 5% Ethanol-Water Solvents.

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Abstract:

Kinetics of acidic Mn(VII) oxidation of Formaldehyde 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 formaldehyde concentration, [Mn(VII)], first order to $[H^+]$ and independent on the ionic strength of the solution. Michaelis-Menten plot showed the existence of an intermediate complex. 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 MnO_4^- by 3 moles of formaldehyde in both solvents. Thermodynamic parameters of activation were obtained from Arrhenius and Erying's equations. A plausible associative mechanism in agreement with kinetic and spectroscopic results was proposed.

Keyword: Potassium permanganate, Formaldehyde (A), Hydrated formaldehyde(HA), Sulphuric acid, potassium nitrate, Ionic strength(I) and activation parameters.

Introduction

Potassium permanganate is a strong oxidant which has been employed for the oxidation of several substrates[1-7]. Formaldehyde is the simplest aldehyde and it is an important precursor to many materials and chemical compounds[8].It forms cyclic trimer metaformaldehyde and linear polymer known as paraformaldehyde as its major derivatives and found use in the eradication of parasites[9]. Formaldehyde is a very reactive aldehyde, reports of its oxidation by some oxidants has been reported[10-19]. However, no report on formaldehyde oxidation by $KMnO_4$ have been reported. Hence, this research shall delve into the kinetics of the oxidation of formaldehyde by acidic $KMnO_4$ in both aqueous and ethanol-water solution with the view to reporting novel results on the kinetics and thermodynamics of the reaction and possibly elucidate a plausible mechanism for the reaction.

Experimental:

Materials:

All reagents used were of A.R grade. Stock solutions were prepared with doubly distilled water. The ionic strength was maintained by adding a solution of KNO_3. Kinetic data were obtained via pseudo-first order kinetics using a UV- 1800 Shimadzu Spectrophotometer fitted with a thermostated cell, interfaced to a computer.

Standardization of potassium permanganate solution

Stock solution of potassium permanganate was standardized in acidified ferrous ammonium sulfate solution[20]

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Kinetic Measurement:

Appropriate quantities in the order: Formaldehyde, potassium nitrate, sulphuric acid and $KMnO_4$ were taken from the stock solutions (kept in a water bath for 30 minutes) into a $1cm^3$ quartz cuvette, decrease in absorbance of $KMnO_4$ with time at 525nm were monitored. Consequently, pseudo-first order rate constant(k_{obs}) were obtained from the slope of the plot of In A versus time

Stoichiometry

The ratio of the number of moles of the consumption of formaldehyde to $KMnO_4$ was studied via spectroscopic titration by monitoring change In absorbance at infinite time of solutions containing various [HCHO] in the range $1.00 \times 10^{-3} – 7.33 \times 10^{-3}$ mol dm^{-3}, fixed $[KMnO4]_o$, $[H^+]_o$ and ionic strength at 5×10^{-5}, 1.33×10^{-3} and 0.05mol dm^{-3} respectively. The stoichiometry was evaluated from the plot of Absorbance versus [HCHO] curve and was 3 moles of formaldehyde consuming 2 moles of $KMnO_4$.

$$2MnO_4^- + 3HCHO + 2H^+ \rightarrow 3HCOOH + 2MnO_2 + H_2O$$

Product Analysis:

FTIR showed absorption at 3400-2400 cm^{-1}, which is indicative of the presence of OH (strongly H-bonded), 1730-1700 cm^{-1} is attributed to C=O stretching and absorption between 1320 and 1210 cm^{-1} is due to C-O of a carboxylic acid.

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 [$KMnO_4$]

At fixed [HCHO]$_o$, [H^+]$_o$ and ionic strength at 298K of the reaction mixture. Pseudo-first order rate constant increased with increase in [$KMnO_4$] as shown in Table1. The oxidation reaction is first order dependence with respect to [$KMnO_4$] as the slope of a plot of In k_{obs} versus In [$KMnO_4$] gave 1.

Table 1: Effect of [$KMnO_4$]:

10^5[$KMnO_4$]/M	$10^5k_{obs}/s^{-1}$	
	Aqueous solvent	5% Ethanol-Water solvent
1.00	0.25	0.38
2.00	0.52	0.65
3.00	0.86	1.25
4.00	1.02	1.61
5.00	1.32	1.83
6.00	1.69	2.01
7.00	2.06	2.43

[HCHO] 3.00 x 10^{-3}M [H^+] 1.33 x 10^{-3}M I=0.05M T=298K

Rate dependence on [HCHO]:

At fixed [$KMnO_4$]$_o$, [H^+]$_o$ and ionic strength at 298K. Pseudo-first order rate constant increased with increase in [HCHO] (Fig.1) and showed first order dependency. Michaelis-Menten plot of 1/k_{obs} versus 1/[HCHO] gave an intercept, suggesting the presence of an intermediate complex in the course of the reaction[21].

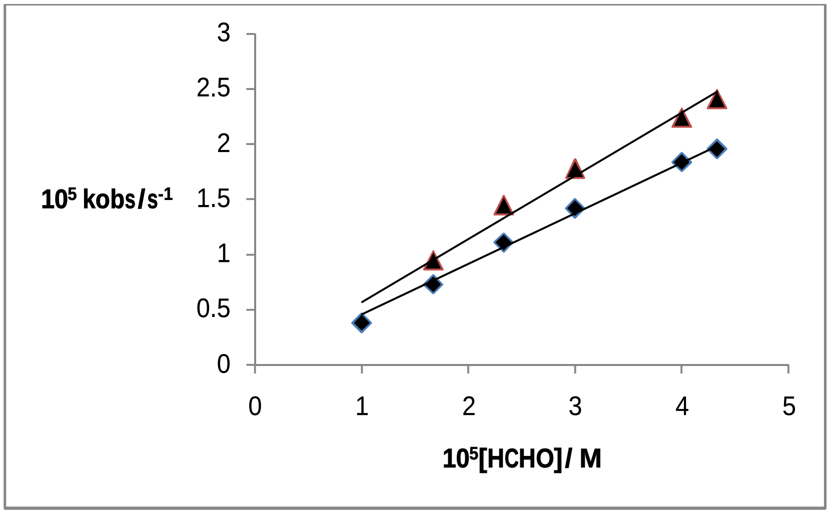


Fig. 1: Plot of k_{obs} versus [HCHO] (▲ 5% Ethanol-Water, ■ Aqueous) [Mn^{7+}] 5.00 x 10^{-5}M [H^+] 1.33 X 10^{-3}M I= 0.05M

Rate dependence on $[H^+]$:

At fixed $[KMnO_4]_o$, $[HCHO]_o$, and ionic strength of the reaction mixture at 298K. The reaction showed increase in k_{obs} with increase in H^+ (Fig.2). The slope of the plot of In k_{obs} versus In$[H^+]$ was 1, suggesting a first order dependence on $[H^+]$.

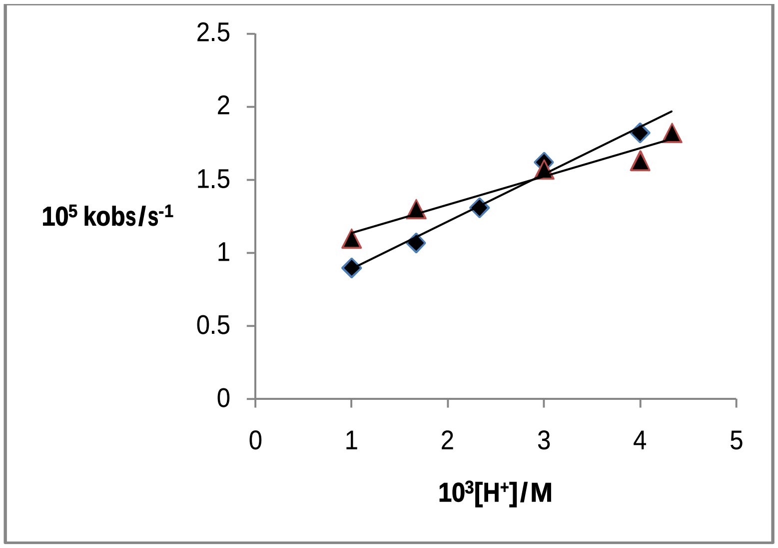


Fig. 2: Plot of k_{obs} versus $[H^+]$ (▲5% Ethanol-Water, ■ Aqueous) $[Mn^{7+}]$ 5.00 x 10^{-5}M [HCHO] 2.00 X 10^{-3}M I= 0.05M

Rate dependence on ionic strength:

At fixed [KMnO4]o, $[HCHO]_o$, $[H^+]_o$ at 298K. There was no significant change in kobs with increase in ionic strength of the reaction mixtures. Therefore, plot of log k_{obs} versus $\sqrt{I}$ gave a straight line with Z_AZ_B as zero. Thereby, revealing the presence of a neutral molecule in the rate determining step[22].

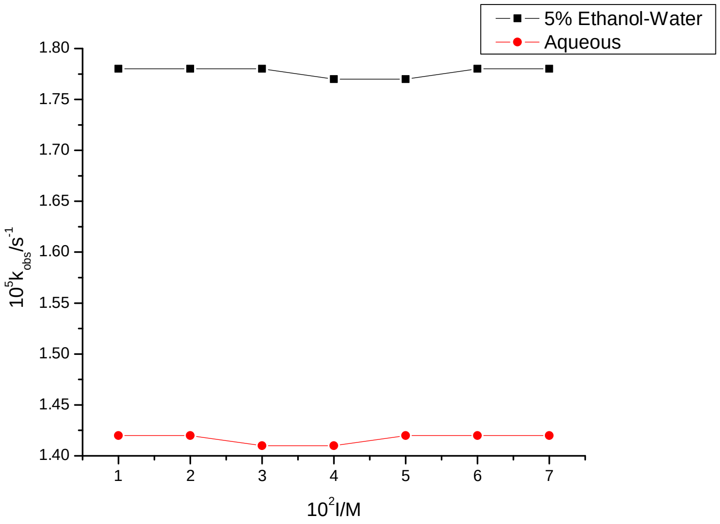


Fig. 3: Plot of Ionic strength dependence

Rate dependence on Temperature:

At fixed $[KMnO_4]_o$, $[HCHO]_o$, $[H^+]_o$ and ionic strength, kobs increased with increase in temperature . Activation energy Ea, was obtained from Arrhenius plot of In k_{obs} versus 1/T and other activation parameters like $\Delta H^\ddagger$,$\Delta S^\ddagger$ and $\Delta G^\ddagger$ were obtained from Erying's equation and represented in Table 2.

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

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^{\#}}{RT} + \ln\left(\frac{k^{/}}{h}\right) + \left(\frac{\Delta S^{\#}}{R}\right)$$

$$\ln\left(\frac{k^{/}}{h}\right) = 23.76$$

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

K = Rate constant

T= Temperature

$\Delta H^\ddagger$= Enthalpy of activation

$\Delta S^\ddagger$= Entropy of activation

$\Delta G^\ddagger$ = Free Gibb's energy of activation

R= Molar gas constant

$k^{/}$= Boltzmann's constant

h= Plank's constant

Table 2; Activation parameters:

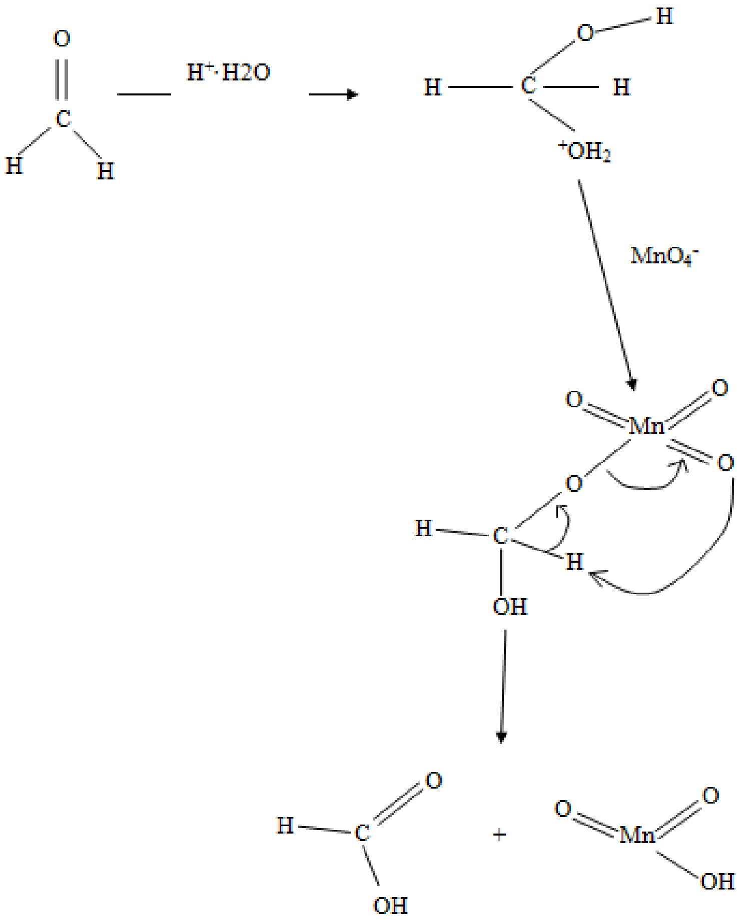
HCHO	Ea(kJ mol^{-1})	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$(kJK^{-1} mol^{-1})	$\Delta G^\ddagger$ (kJmol^{-1})
Aqueous	84.98	82.37	-0.06	100.25
5%Ethanol-Water	72.91	70.57	-0.10	100.37

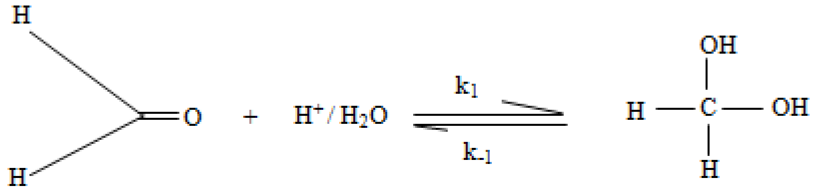
Reaction mechanism:

Mechanism for the reaction was proposed based on the kinetic and spectroscopic results which are summarized below:

1. The reaction is first order dependent with respect to each of $[KMnO_4]$, [HCHO] and $[H^+]$.
2. Michaelis-Menten plot suggests the presence of an intermediate complex.
3. Presence of a neutral molecule at the rate determining step as the reaction was dependent on ionic strength of the reaction mixtures.
4. Absence of free radicals as polymerization test was negative. Hence, one electron oxidation for the formation of free radicals can be ignored.
5. Negative $\Delta S^\ddagger$ suggests that solvent molecules are strongly oriented around the ions and possibility of an associative mechanism.
6. Same values of $\Delta G^\ddagger$ indicates similar mechanism.

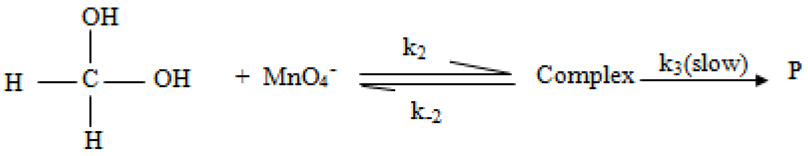
7. Increase in observed rate constant with decrease in dielectric constant of the medium implies the interaction between a dipole and a positive ion and also indicates the probable involvement of a protonated Mn^{7+} specie in the presence of acid in the rate determining step.
8. FTIR product analysis showed the presence of Formic acid.





$$H_2C{=}O + H^+/H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-OH$$

[A] [HA]



$$H-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-OH + MnO_4^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{Complex} \xrightarrow{k_3(\text{slow})} P$$

Applying steady state approximation to the above scheme

$$Rate = \frac{K_1 k_2 k_3 [A][H^+][MnO_4^-]}{(k_{-2} + k_3)}$$

$Rate = K_1 k [A][H^+][MnO_4^-]$ where, $K_1 = \frac{k_1}{k_{-1}}$; $k = \frac{k_2 k_3}{(k_{-2} + k_3)}$

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