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KINETIC AND MECHANISM OF OXIDATION OF ZINC (II) METAL COMPLEX BY POTASSIUM PERMANGANATE

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ABSTRACT

The Kinetic of oxidation of Iron Zinc (II) derived from 8-hydroxy quinoline and salicylaldehyde by potassium permanganate has been studied in the presence of acidic medium. The reaction is first order with respect to $KMnO_4$ as well as Metal complex concentration. The reaction rate has been determined at different temperature and different thermodynamic parameters have been calculated which shows that the reaction rate increase with increase in temperature. With increase in the concentration of acid the reaction rate increases. A suitable mechanism has been proposed.

KEYWORDS: Kinetics, Mechanism, Oxidation, Zinc (II) Metal Complex, potassium permanganate, thermodynamic parameters, etc.

INTRODUCTION

Oxidation of organic compounds for a long time has been used for many useful ends (Lichtenthaler and Mondel, 1997). Oxidation occurs under different conditions of pH[1], temperature and ionic strength giving products that depend on the reaction conditions. In spite of these, much works are yet to be done on catalytic oxidation. There are of course limited information on oxidation of metal complexes.[2] The present work seek to study the kinetics of oxidation of Zinc (II) metal complex derived from 8-hydroxy quinoline and salicylaldehyde by potassium permanganate in the presence of acidic medium.[3]

Potassium permanganate is extensively used as an oxidizing agent for numerous organic molecules in various media. The oxidation reaction mechanisms by permanganate governed by pH of the medium. Among six oxidation states of Mn (II) to Mn (VII), permanganate Mn (VII) is found to be the most powerful oxidation state in both acid and alkaline media. By using permanganate as oxidizing agent, it is understandable that the Mn (VII) in permanganate is reduced to a variety of oxidation states in acidic, alkaline and neutral media.[4,5,6]

To the best of our knowledge, there are no reports on the kinetics and mechanism of oxidation of Zinc (II) metal complex.This motivates us to investigate the kinetics and mechanism of oxidation Zinc (II) metal complex with permanganate ion in acidic medium. The objectives of the present study aimed to shed more light and establish the most favourable conditions affecting oxidation of such noteworthy compound and to elucidate a plausible oxidation reaction mechanism.

MATERIAL AND METHOD

Chemical which are used in this experiment are highly purified and AR grade, the solutions were used in this study were prepared by using distilled acetic acid[7] and double distilled water. Solution of Zinc (II) metal complex were prepared by using double distilled water and this solution was used for kinetic studies. The reaction was carried out in glass stoppered Pyrex boiling tube. The Kinetics of reaction was followed in the temperature range 30°C to 50°C.

Kinetic Measurement

The kinetic of reaction were measured by using double beam spectrophotometer model No AU2100 of Systronic Company which is having inbuilt software. The Kinetic of reaction were measured at 520nm wavelength up to the 80% completion of reaction.

Stoichiometry of reaction

The Stoichiometry of the reaction were determined by conveying out several sets of experimental with varying amount of oxidising agent potassium permanganate over Zn (II) metal complex in acetic acid using in H_2SO_4. The remaining potassium permanganate was then analysed spectrophotometrically the result indicates that 1 mole of Zn (II) metal complex react with 1 mole of potassium permanganate.

Product Analysis

Product analysis has been done by chemical test. Solution of each complex after oxidation reaction has been used for the analysis of product. In this it is found that after oxidation reaction M^{2+} is converted in M^{3+}.[8,9,10]

Zinc complex on oxidation with potassium permanganate in acid medium gets oxidized to form product. Which can be confirmed by passing H_2S as through the product solution. It gives white precipitate of ZnS which is insoluble in excess H_2S, in acetic acid, in solutions of caustic alkalis, but dissolves in dilute mineral acids.[11]

$$[Zn(II)(C_9H_6ON)(C_7H_5O_2)(H_2O)]Cl_2 + MnO_4^- + H^+$$

$$\downarrow$$

$$[Zn(II)(C_9H_6ON)(C_7H_5O_2)\ (OH^-)]\ Cl_2 + H^+$$

Product

$$\downarrow H_2S \text{ gas}$$

$$ZnS\downarrow + C_9H_6ON + C_7H_5O_2 + 2H_2O + 2HCl$$

White ppt.

RESULT AND DISCUSSION

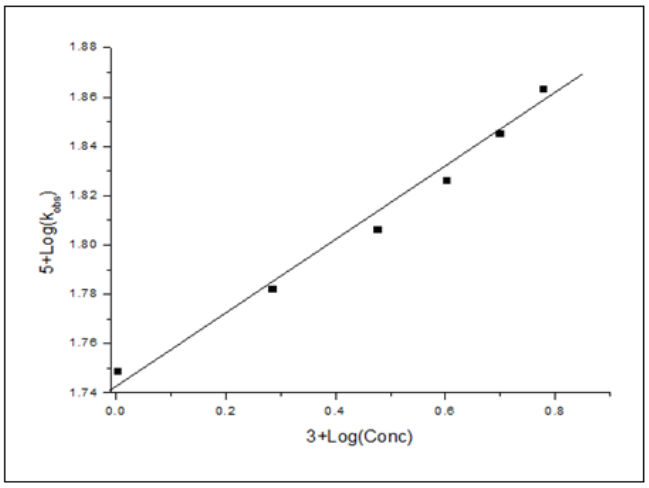
The results of various parameters is given in tabular form and presented with graphs.

1) Effect of variation of concentration of Zn (II) metal complex

The oxidation of Zn (II) metal complex with potassium permanganate in acetic acid in presence of sulphuric acid. By keeping constant concentration of potassium permanganate and $H_2SO_4$and by changing the concentration of Zn (II) metal complex increases the rate of reaction (Table-1) the plot of log of k_{obs} versus log concentration of Zn (II) metal complex for different initial concentration of metal complex is linear with unit slop, which shows that the first order dependence of rate of reaction on Zn (II) metal complex.[12]

Table. 1: Effect of variation of concentration of Zn (II) metal complex.

[Zinc complex]	Rate K_{obs}
$1x10^{-3}$	0.00057
$2 x10^{-3}$	0.0006
$3 x10^{-3}$	0.00064
$4 x10^{-3}$	0.00067
$5 x10^{-3}$	0.0007
$6 x10^{-3}$	0.00073
$7 x10^{-3}$	0.00084

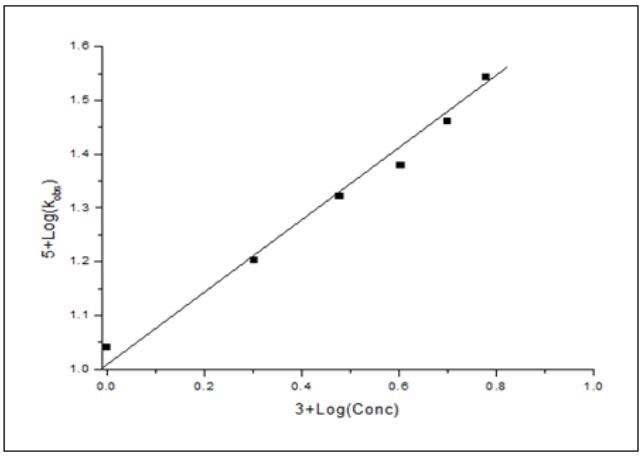


2) Effect of varying oxidising agent potassium permanganate

In this parameter studying the effect of variation of oxidising agent potassium permanganate on oxidation reaction of Zn (II) metal complex by keeping constant concentration of Zn (II) metal complex and concentration of H_2SO_4. The Concentration of oxidising agent increases, decreases the rate of reaction Table – 2 the plot of 1/log K_{obs} verses log [$KMnO_4$] for different initial concentration of [$KMnO_4$] is linear with unit slop presents the first order dependence of rate on [$KMnO_4$].[13]

Table. 2: Effect of variation of concentration of potassium permanganate.

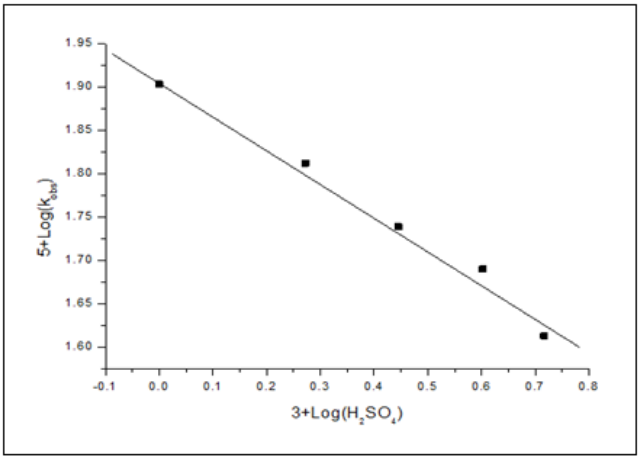
[$KMnO_4$]	Rate K_{obs}
$1x10^{-4}$	0.00011
$2 x10^{-4}$	0.00016
$3 x10^{-4}$	0.00021
$4 x10^{-4}$	0.00024
$5 x10^{-4}$	0.00029
$6 x10^{-4}$	0.00035
$7 x10^{-4}$	0.00021



3) Effect of variation of concentration of sulphuric acid: In this factor there is study of variation of concentration of sulphuric acid on oxidation of Zn (II) metal complex. By keeping constant concentration of oxidising agent and substrate changing the [H_2SO_4] we find that the rate increases with increase in [H_2SO_4] Table – 3 and plot of log k Vs log [H^+] was linear with a unit slop indicating first order reaction on [H^+].[14] Fig – 3.

Table. 3: Effect of variation of concentration of sulphuric acid.

$[H_2SO_4]$	Rate K_{obs}
0.001	0.00018
0.002	0.00019
0.003	0.00040
0.004	0.00049
0.005	0.00059
0.006	0.00069
0.007	0.00080



4) Effect of salts on reaction rate

The effect of salts on the reaction rate was studied by adding various concentration by salt. By keeping constant concentration by oxidising agent substrate and acid. It was observed that the rate of oxidation was not altered by the addition of salts.[15]

Table. 4: Effect of salts on reaction rate.

[KBr]	Rate K_{obs}
$1x10^{-2}$	0.00086
$2\ x10^{-2}$	0.00078
$3\ x10^{-2}$	0.00069
$4\ x10^{-2}$	0.00074
$5\ x10^{-2}$	0.00071
$6\ x10^{-2}$	0.00077
$7\ x10^{-2}$	0.00077

5) Effect of Temperature

The study of effect of temperature on rate of oxidation of Zn (II) metal complex by potassium permanganate has been studied at different temperature by keeping all other factors constant concentration with changing temperature from 303K to 323K. The rate constants are given in Table-5 as the temperature increases the values by rate constant also increases that shows rate of reaction depends of temperature the Arrhenius plot 10gk Vs. 1/T were found to be linear fig – 4.[16] The activation energy (Ea) were calculated from the clop of the plots from this values the thermodynamic parameters $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$ was calculated Table – 6.

Table. 5: Effect of Temperature.

Temperature (K)	Rate K_{obs}
293	0.0007
298	0.0008
303	0.001
308	0.00107
313	0.00114
318	0.0012
323	0.0012

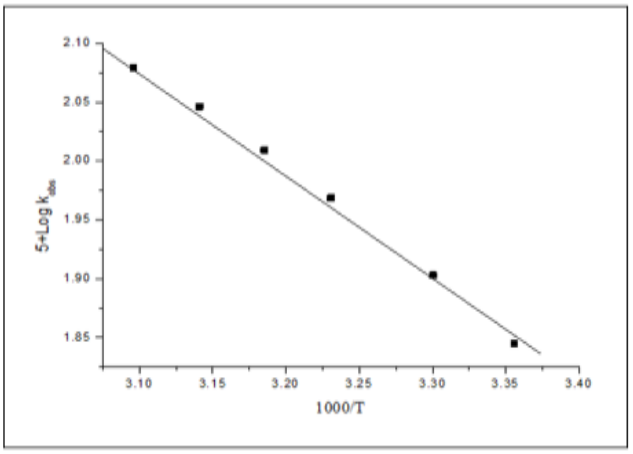


Table. 6.

Ea	21470.81
ΔH	18951.37
ΔS	-241.87
ΔG	92237.61

CONCLUSION

The oxidation of Zn (II) metal increases in acetic acid in acid medium shows that the oxidation of Zn (II) metal complex of potassium permanganate is in presence of acidic medium with effect of oxidising agent, substrate an acid and temperature the reaction is first order dependence. The addition of salt does not alter the rate of oxidation reaction. The mechanism of the reaction were given with the activation parameters the negative value of $\Delta S^{\#}$ provides support to the formation of rigid transition state. The overall mechanistic sequence described here is constituent with product and mechanistic study.

- Mechanism of oxidation of Zn (II) metal complex by potassium permanganate.

$$H^{+} + Mno_4^{-} \longrightarrow HMnO_4$$

This point has been also confirmed by previous researchers. Hence Mn (VII) could be considered as the reactive specie and this probably exists to a certain extent as $HMnO_4$. As the concentration is increased the formation of $HMnO_4$is favoured and hence increases the oxidation may be assumed to be taking place by Mn (VII) in the form of either MnO_4 or $HMnO_4$ or both depending on the acid concentration. The linear plot of log k Vs log (H_2SO_4) and log k Vs. Ho indicates that the reactions are acid catalysed, but none of the above plots gives an ideal slope for unity.

Derivation of Rate Law

Based on the results of kinetic and proposed mechanism, the following rate expression can be derived by applying steady state approximation.

$$[MnO_4] + H^+ \underset{}{\overset{k_1}{\rightleftharpoons}} HMnO_4$$

$$\text{Zinc Metal Complex} + HMnO_4 \overset{k_2}{\rightleftharpoons} C \text{ (Intermediate Complex)}$$

$$C \xrightarrow{k} \text{Product}$$

$$[MnO_4\text{-}] = [MnO_4\text{-}] + [HMnO_4]$$

$$= [MnO_4^-] + k_1\,[MnO_4^-]\,[H^+]$$

$$= [MnO_4^-] + 1 + k_1\,[H^+]$$

$$\text{Rate} = \frac{kk_2[MnO_4^-]\,[\text{Zn M.C.}]}{1 + k_1\,[H^+]}$$

$$\frac{\text{Rate}}{[MnO_4]\,[\text{Zn M.C.}]} = \frac{kk_2}{1 + k_1\,[H^+]}$$

$$K_{obs} = \frac{kk_2}{1 + k_1\,[H^+]}$$

$$\frac{1}{K_{obs}} = \frac{1}{kk_2} + \frac{k_1\,[H^+]}{kk_2}$$

The rate law can be expressed by following equation

$$\frac{-d[Mn(VII)]}{dt} = k[\text{Zn M.C.}][MnO_4]_{Total}$$

Where, Zn M.C. = Zinc Metal Complex

This type of hydride ion transfer process has been proposed in the oxidation of aldehyde, formic acid, ethers, alcohols, etc. by permanganate in moderately concentrated acid solutions.[17,18]

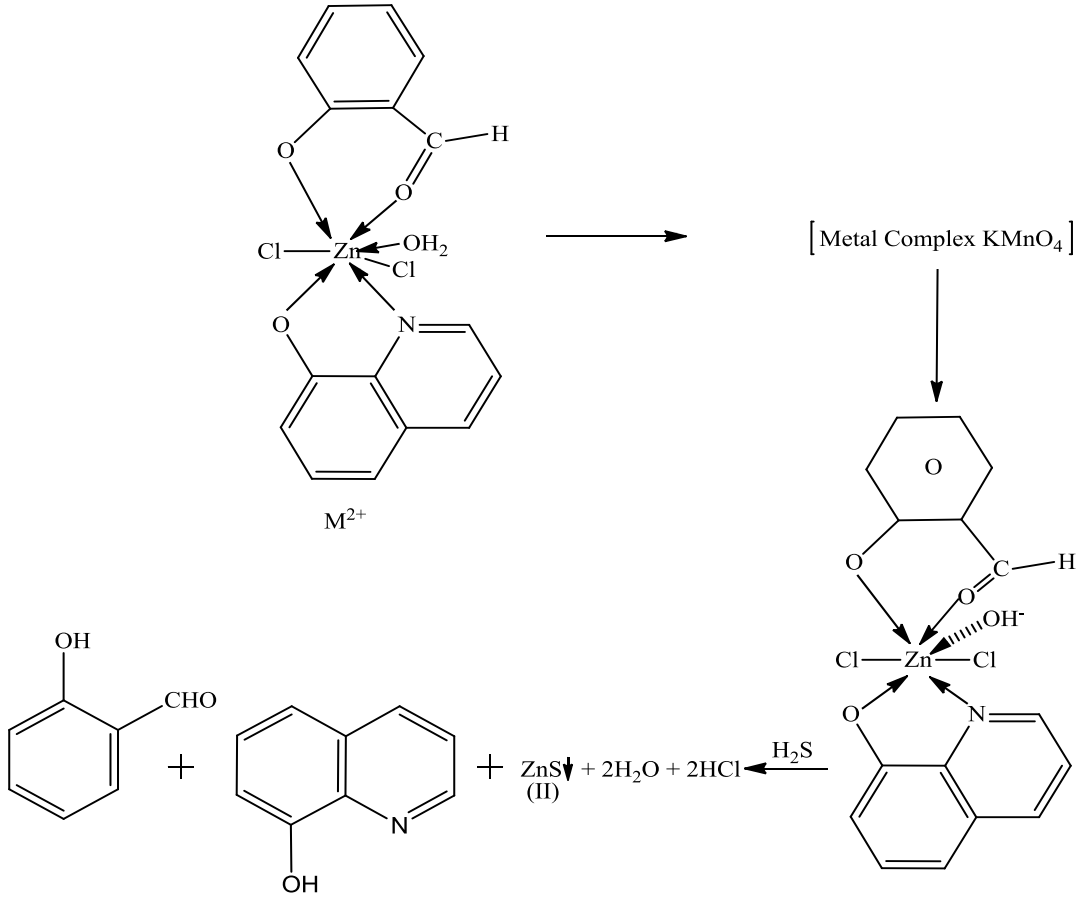
Mechanism of oxidation of Zinc metal complexes

$$MnO_4^- + H^+ \longrightarrow HMnO_4$$

$$[Zn(II)(C_9H_6ON)(H_2O)(C_7H_5O_2)]\,Cl_2 + KMnO_4$$

$$\downarrow$$

$$[Zn(II)(C_9H_6ON)(C_7H_5O_2)(OH^-)]\,Cl_2$$



Compound (III) being highly unstable disproportionate to give acid and the corresponding aldehyde. The rate law can be expressed by equation (1).

$$\frac{-d[Mn(VII)]}{dt} = k\,(\text{Zinc Metal Complex})\;\;[MnO_4]_{\text{Total}}$$

This type of hydride ion transfer process has been proposed in the oxidation of aldehyde, formic acid, ethers, alcohols etc. by permanganate in moderately concentrated acid solutions.[20]

The effect of temperature on reaction rate was studied which shows the increase in reaction rate with increase in temperature (Table 4 and 5).

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