

Kinetic And Mechanism of Oxidation of Cobalt Metal Complex By Acidic Potassium Permanganate

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ABSTRACT: The Kinetic of oxidation of Cobalt derived from 8-hydroxy quinolone and salicylaldehyde by potassium permanganate has been studied in the presence of acidic medium. The overall reaction is first order with respect to $KMnO_4$, Substrate acid and temperature. No effect of salts has been found suitable mechanism is given.

Keywords: Kinetics, Mechanism, Oxidation, Cobalt Metal Complex, potassium permanganate, thermodynamic parameters, etc.

I. INTRODUCTION

Chemistry of drugs attracts many researchers because of its application in medicinal study¹. Metal complexes play a vital role in nature, they have been extensively used in clinical application as enzyme inhibitor. Because of its wide applications in drugs chemistry we have decided to go for oxidation of metal complexes^{2,3}.

Chemical Kinetics of the substance is exactly how reactant set changed over into things furthermore of all physical and compound strategies which happen in midst obviously of reaction part of reaction gives clear photograph of sanctioned complex. Potassium permanganate is very good and strong as well as mild oxidizing agent⁴ because of its easy availability and easy handling and it is available in various oxidation state by using potassium permanganate oxidation of various organic compounds^{5,6,7} has been studied but literature survey shows that very little work is found on oxidation of metal complexes by potassium permanganate^{8,9}.

II. 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^{10,11} and double distilled water. Solution of Cobalt 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^oc to 50^oc.

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 envying out several sets of experimental with varying amount of oxidising agent potassium permanganate over Cobaltmetal complex in acetic acid using in H_2SO_4 . The remaining potassium permanganate was then analysed spectrophotometrically the result indicates that 1 mole of Cobaltmetal complex react with 1 mole of potassium permanganate.

Product Analysis:

In a typical experiment a mixture of Cobaltmetal complex and potassium permanganate was made up to 50 ml with acetic acid in presence of HCl (0.8 ml). The mixture is kept in dark for 12 hours until completion of oxidation reaction¹². It was then treated over night with an excess (125ml) freshly prepared and saturated solution of and standard solution of 2, 4 dinitrophenylhydrazine in 2M HCl. The precipitated 2, 4 dinitrophenylhydrazine (DNP) was collected by filtration, dried, recrystallized from ethanol and weighed. The product was found identical melting point with authentic sample of DNP¹³, the yield was 80%.

III. RESULT AND DISCUSSION

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

1) Effect of variation of concentration of Ni (II)metal complex:-

The oxidation of Cobaltmetal complex with potassium permanganate in acetic acid in presence of sulphuric acid. By keeping constant concentration of potassium permanganate and H₂SO₄ and by changing the concentration of Cobaltmetal complex increases the rate of reaction (Table-1) the plot of log of k_{obs} versus log concentration of Cobaltmetal 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 Cobaltmetal complex¹⁴.

Concentration	Rate K _{obs}
0.001	0.00027
0.002	0.00027
0.003	0.00035
0.004	0.00032
0.005	0.00037
0.006	0.00039
0.007	0.00035

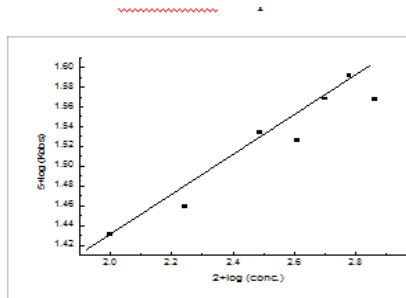


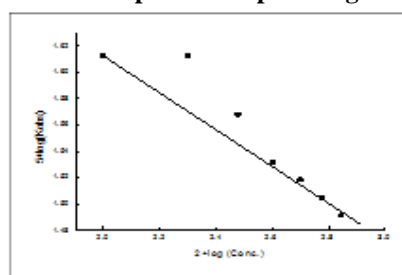
Table-1: Effect of variation of concentration of Cobaltmetal complex.

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 Cobaltmetal complex by keeping constant concentration of Cobaltmetal complex and concentration of H₂SO₄. The Concentration of oxidising agent increases, decreases the rate of reaction Table – 2 the plot of 1/log K_{obs} versus log [KMnO₄] for different initial concentration of [KMnO₄] is linear with unit slop presents the first order dependence of rate on [KMnO₄].

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

Concentration	Rate K _{obs}
0.001	0.00041
0.002	0.00041
0.003	0.00037
0.004	0.00034
0.005	0.00033
0.006	0.00032
0.007	0.00031

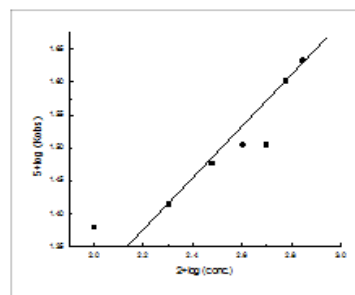


3) Effect of variation of concentration of sulphuric acid:-

In this factor there is study of variation of concentration of sulphuric acid on oxidation of Cobaltmetal complex. By keeping constant concentration of oxidising agent and substrate changing the [H₂SO₄] we find that the rate increases with increase in [H₂SO₄] Table – 3 and plot of log k Vs log [H₂SO₄] was linear with a unit slop indicating first order reaction on [H₂SO₄]. Fig – 3.

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

Concentration	Rate K _{obs}
0.001	0.00024
0.002	0.00026
0.003	0.0003
0.004	0.00032
0.005	0.00032
0.006	0.0004
0.007	0.00043



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.

Table-4: Effect of salts on reaction rate

Concentration	Rate K_{obs}
1	0.00025
2	0.00028
3	0.00027
4	0.00038
5	0.00036
6	0.0003
7	0.0003

5) Effect of Temperature:-

The study of effect of temperature on rate of oxidation of Cobaltmetal 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 Arhenious plot $\log k$ Vs. $1/T$ were found to be linear fig – 4. The activation energy (E_a) were calculated from the clop of the plots from this values the thermodynamic parameters $\Delta H^\ddagger, \Delta S^\ddagger, \Delta G^\ddagger$ was calculated Table – 6.

Table-5: Effect of Temperature

Concentration	Rate K_{obs}
293	0.00023
298	0.00039
303	0.00036
308	0.00033
313	0.00033
318	0.00026
323	0.00027

Table –6:

E_a	33079.03
ΔH^\ddagger	30559.58
ΔS^\ddagger	-213.92
ΔG^\ddagger	95378.75

IV. CONCLUSION

The oxidation of Cobalt metal increases in acetic acid in acid medium shows that the oxidation of Cobalt 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 ΔS^\ddagger provides support to the formation of rigid transition state^{15, 16}. The overall mechanistic sequence described here is constituent with product and mechanistic study.

- Mechanism of oxidation of Cobalt metal complex by potassium permanganate.

This point has

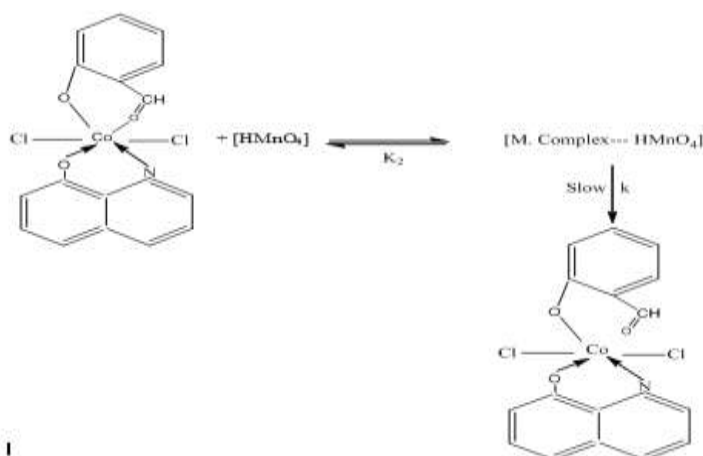
been also confirmed by previous researchers. Hence Mn (VII) could be considered as the reactive specie and this probably exists to a certain extent as $HMnO_4$.

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. H_0 indicates that the reactions are acid catalysed, but none of the above plots gives and Ideal slope for unity.

Derivation of Rate Law

$$\begin{aligned}
 [\text{MnO}_4] &= [\text{MnO}_4^-] + [\text{HMnO}_4] \\
 &= [\text{MnO}_4^-] + k_1 [\text{MnO}_4^-] [\text{H}^+] \\
 &= [\text{MnO}_4^-] + [1+k_1[\text{H}^+]] \\
 \text{Rate} &= \frac{k_2 [\text{MnO}_4^-] [\text{Metal Complex}]}{1+k_1[\text{H}^+]} \\
 \frac{\text{Rate}}{[\text{MnO}_4^-][\text{M, Complex}]} &= \frac{K_2}{1+k_1[\text{H}^+]} \\
 K_{\text{obs}} &= \frac{k_2}{1+k_1[\text{H}^+]} \\
 \frac{1}{K_{\text{obs}} K_2} &= \frac{1}{K_2} + \frac{k_1[\text{H}^+]}{K_2}
 \end{aligned}$$

Mechanism of oxidation of metal complexes:-



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

$$\frac{-d[\text{Mn(VII)}]}{Dt} = k (\text{Metal Complex}) [\text{MnO}_4]_{\text{Total}}$$

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. The effect of temperature on reaction rate was studied which shows the increase in reaction rate with increase in temperature (Table 5 and 6).

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