Kinetic and Mechanistic Study of Oxidation of Cobalt Complex (II) Derived From 8-Hydroxy Quinoline and Salicylaldehyde in Acid Medium

Sayyed Hussain[1], Takale Surendra[1], Wankhede D. N.[2]

1- P.G. Dept. of Chemistry, Sir Sayyed College of Arts, Commerce &

Science, Aurangabad - 431001 (M.S.) India.

2- School of Chemical Sciences, S. R. T. M. University, Nanded (M.S) India.

………………………………………………………………………………………...

Abstract*: The kinetic of oxidation of Cobalt Complex (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 KMnO4 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 increases with increase in temperature. With increase in the concentration of acid the reaction rate increases. A suitable mechanism has been proposed.*

Key words *– Kinetics, Mechanism, 8-hydroxy quinoline, salicylaldehyde, Oxidation, thermodynamic parameters, etc.*

I   Introduction

Bioinorganic chemistry constitutes the discipline at the interface of the more classical areas of inorganic chemistry and biology. This has two major components: the study of naturally occurring inorganic elements in biology and the introduction of metals in to biological systems. The chemistry of life involves many elements which are essential and indispensible in biological system. The elements are classified on the basis of their action in biological system and the molecules possessing one or more metallic elements are called metallobiomolecules. The metallobiomolecules are natural products and are usually Complex co-ordination compounds. The active sites contain various biochemical process such as electron transfer binding of exogenous molecules and catalysis[1-15].

II   Material and Methods

All the chemicals used were of AR grade, specially potassium per magnate used were of AR grade and was prepared and estimated by standard method. Metal complex is used as prepared in laborites. The acetic acid were always freshly distilled before used for the kinetic measurement, permanganate and sulphuric acid solution were taken in two

different flasks and covered with black cloth and placed in a thermostat for 1 hour to attain constant temperature by both the flask. In order to prevent the hydrolysis, required volume of given metal complex was directly added to acid solution with micro pipette just before mixing it with permanganate solution. The course of reaction was followed by measuring the absorbance (optical density) of unreacted permanganate ions from time to time at 520 nm using systronics uv-visible spectrophotomer. The reaction was followed up to 70 to 85% completion and the product was identified complex containing aldehyde group. Complex containing aldehyde functional group were detected by 2, 4 DNP tests [16]. The complex containing aldehydes were obtained in 90% yield. The addition of mercuric chloride to reaction system did not induce the precipitation of mercuric chloride showing that no free radicals are formed in the system.

III   Results and discussion

Under the kinetic conditions Cobalt Complex (II) derived from 8-hydroxy quinoline and salicylaldehyde > [KMnO$_4$] in 1M H$_2$SO$_4$. The plot of log absorbance (O.D.) Vs time were linear indicating the first order dependence of rate on [KMnO$_4$). Oxidation of Cobalt Complex (II) derived from 8-hydroxy quinoline and salicylaldehyde depends on the concentration of potassium permanganate. This was also confirmed by verifying [KMnO$_4$] which did not show any change in Pseudo First order constant (k^1) value (Table No.1). The reaction was also found to be first order in Cobalt Complex (II) derived from 8-hydroxy quinoline and salicylaldehyde (Table 2). The rate of reaction increases with increases in [H$_2$SO$_4$]. (Table No.3)

The effect of temperature was also studied at different temperature like 283K, 293K, 303K, 313K, 323K and 333K. It is shown in Table No.4. It is clear that as temperature increases rate constant increases (Table No. 4). Thermodynamic parameters such as $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$, E, ΔE and A i.e. frequency factor were studied.

The negative values of entropy of activation shows that the intermediate transition state is rigid the relatively small values of ΔH and ΔS are consistent with the reaction generally proceeds through highly ionized transition state[17].
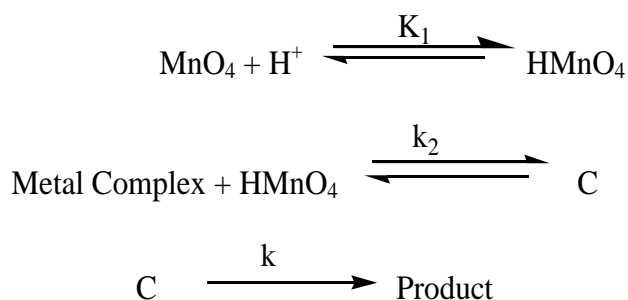
$$H^+ + MnO_4^- \longrightarrow HMnO_4$$

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 acid 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$_2$SO$_4$] and log k$^'$ Vs Ho indicates that the reactions are acid catalyzed,

but none of the above plots gives an ideal slope for unity. In view of the departure from the ideal behavior, applicability of Bunnett's hypothesis was tested. A plot of log k$^{'}$ Vs Ho was linear (fig has not shown) and the slop was found to be -2.5. This value indicates non-involvement of water molecule in the rate determining steps as per Bunnett's, while the hydrolysis rate was 3.2×10^{-5} liter mol^{-1} sec^{-1} under identical condition, from this it is
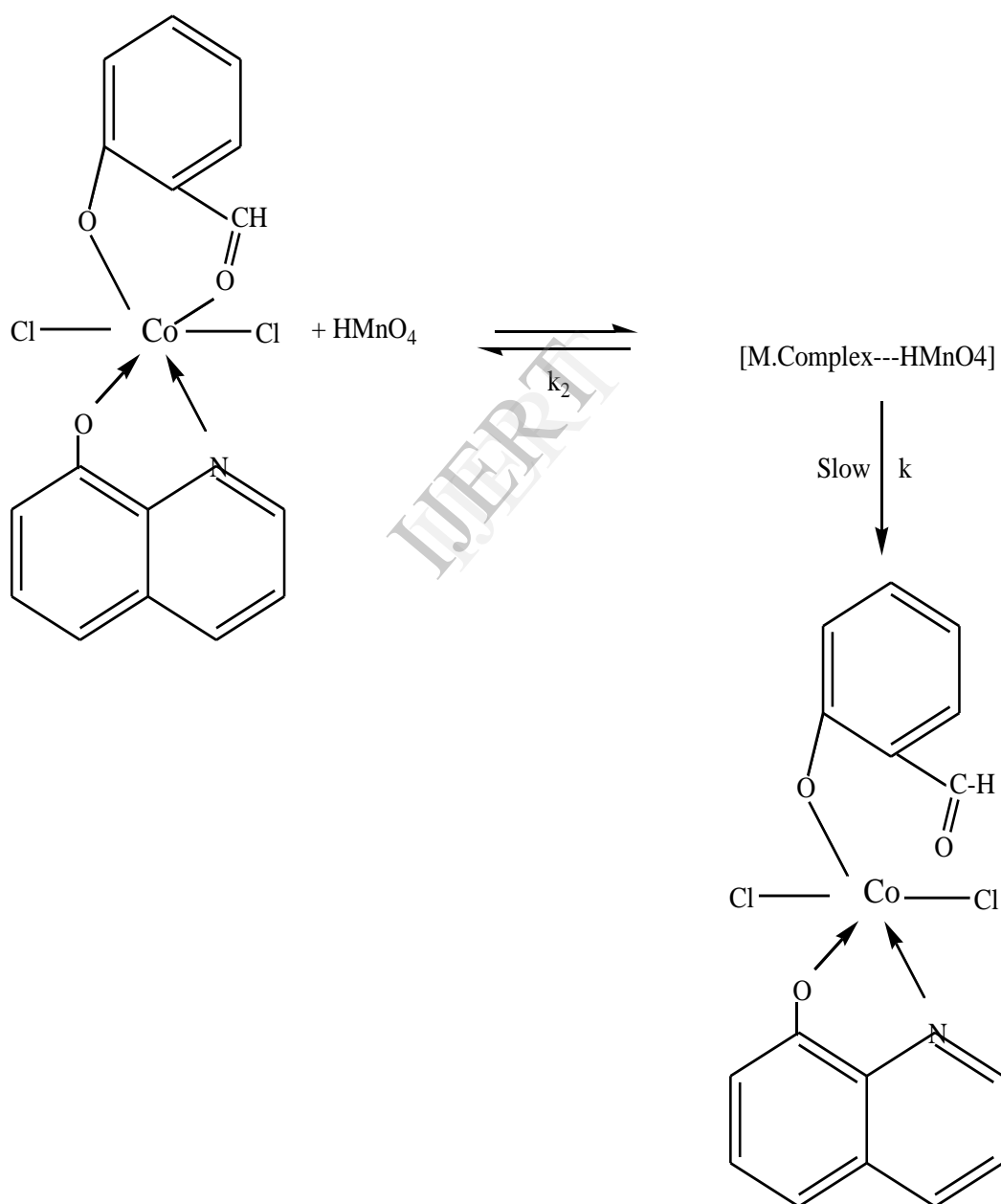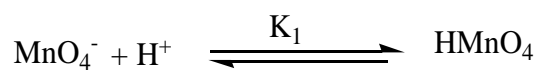
IV Derivation of Rate Law

$$MnO_4 + H^+ \underset{\longleftarrow}{\overset{K_1}{\longrightarrow}} HMnO_4$$

$$Metal\ Complex + HMnO_4 \underset{\longleftarrow}{\overset{k_2}{\longrightarrow}} C$$

$$C \xrightarrow{k} Product$$

$$[MnO_4^-] = [MnO_4^-] + [HMnO4]$$

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

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

$$Rate = \frac{k\ k_2 [MnO_4^-] [\ metal\ complex]}{1+ k_1 [H^+]}$$

$$\frac{Rate}{[MnO_4]\ [M.Complex]} = \frac{KK_2}{1+K_1 [H^+]}$$

$$Kobs = \frac{KK_2}{1+K_1 [H^+]}$$

$$\frac{1}{k_{obs}} = \frac{1}{kK_2} + \frac{k_1[H^+]}{K\ K_2}$$

Mechanism of oxidation of metal complexes:-

$$MnO_4^- + H^+ \xrightleftharpoons{K_1} HMnO_4$$

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

$$\frac{-d[Mn(VII)]}{dt} = k \text{ (Metal Complex) } [MnO4]_{Total}$$

---------- (1)

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

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

Table 1: Effect of variation of Oxidant (KMnO$_4$)

[Cobalt metal complex]= 0.01 M, [H$_2$SO$_4$] = 1M, Temp =303 k   AA = 20% (v/v)

KMno$_4$	k x 10^4 sec^{-1}
0.001M	5.98
0.0015M	7.96
0.002M	9.37
0.0025M	11.48
0.003M	13.48
0.0035M	14.36
0.004M	16.38
0.0045M	17.45

Table 2: Effect of variation of Cobalt Metal Complex

[KMnO4] = 4.7 x 10^{-3}, Temperature: 30°C, λ Max = 520 nm

[Cobalt metal complex]	k x 10^4 sec^{-1}
0.01M	2.99
0.02M	5.97
0.03M	9.36
0.04M	12.48
0.05M	14.48
0.06M	16.36
0.07M	18.38
0.08M	20.45

Table 3: Effect of Variation of Concentration of Acid [H_2SO_4]

(KMnO4) = 0.1×10^{-3}M, [H_2SO_4] = 1 M, Temperature = 30 ^{O}C, λ Max 520nm

[H_2SO_4]	k x 10^4 sec^{-1}
0.1M	2.97
0.2M	4.92
0.3M	5.38
0.4M	6.47
0.5M	7.41
0.6M	8.34
0.7M	9.36
0.8M	10.50

Table 4: Effect of variation of temperature on reaction rate

[$KMnO_4$] = 0.1×10^{-3}M, (Cobalt metal complex) = 0.1×10^{-2}M, λ Max 520nm

Temperatures(k)	k x 10^4 sec^{-1}
293	2.70
298	5.56
303	9.36
308	14.24
313	22.78

Table 5: Activation Parameters

[$KMnO_4$] = 0.1×10^{-3}M, (Cobalt metal complex) = 0.1×10^{-2}M, λ Max 520nm

Activation Parameters	
ΔE_a kJ mole^{-1}	69.92
$\Delta H^{\#}$ kJmole^{-1}	67.44
$-\Delta S^{\#}$ KJ mole^{-1}	284.65
$\Delta G\#$ KJ mole^{-1}	140.37

A probable mechanism (scheme -1) in which MnO4$^-$ or HMnO$_4$ attacks the alcohol moiety of the metal complex is considered, explaining the observed kinetic results. The rate constant value (k), due to steric effect In case of Cobalt Complex (II) derived from 8-hydroxy quinoline and salicylaldehyde and the rate of reaction is more though there is presence of electron with drawing group Cl$^-$.

V References:

1. *Neerja Gupta and Monal Singh, Essentials of bio-inorganic chemistry, 1-2, 2009.*

2. *S.Sheik Mansoor, 22, 10, 2010, 7591-7600*

3. *Firouzabadi F., Sharif, Synthesis, 1992, 999.*

4. *P. Shhaya Amutha And N. Mathiyalagan, 22, 3, 2010, 1918-1924*

5. *Panday Dinesh, Dilsha K.M., Kothari Seema, J. Indian-Chem.Soc. 2009,86, 816.*

6. *Dilsha K.M., Kothari Seema, Prog. Rec.Kinet.Mech.,2007, 32, 119.*

7. *Kothari Seema, Goyal A., Banerji K. K., J. Chem. Res. (S), 2002, 363(M), 863.*

8. *Kothari Seema, Kothari A., Banerji K. K., Indian J. Chem.2000, 39 (A), 734.*

9. *Kothari Seema, Kothari A., Banerji K. K., Oxidn. Commun. 2000,23, 93.*

10. *Subbarao P.V.Z., Phy Chem.,19 246, (1971), 352*

11. *Sayyed Hussain, et.al. IJERA 2 (1) 558-561, 2012.*

12. *Syyed Hussain, Takale Surendra, orient. J.Chem 27 (4), 1729-1734, 2011*

13. *Kinetic and mechanistic study of Oxidation of ester by K2Cr2O7, Sayyed Hussain et al, Der Chemica Sinica, 2 (1), 2011, 61-65.*

14. *Kinetic and mechanistic study of Oxidation of ester by KMnO$_4$, Sayyed Hussain et al, Asian J. Research Che, 4 (4), 2011, 607-610.*

15. *V.Surendra Rao and Workers, Ind.J.Chem. 1979,18 (A), 37.*

16. *Steward R, oxidation in organic chemistry, edit by wibera (Academic press, London) 1965, 2, 48, 57).*

17. *Mohajer D., tangetaninejad S., Tetrahrdron Lett. 1994, 35, 845.*

18. *Narayan, Kutty and M.V.Bhat, TettLett. 1979. 2121.*

19. *Banerji K.K., Indian J. Chem. 1973,11, 242.*

VI Acknowledgement