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Mechanistic study of oxidation of Copper Complex (II) derived from 8-hydroxy quinoline and salicylaldehyde in acid medium

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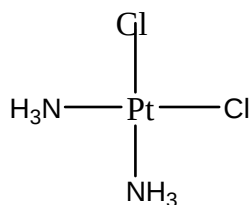
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Abstract: The kinetic of oxidation of Copper Complex (II) derived from 8-hydroxy quinoline and salicylaldehyde by potassium permanganate has been studied in the presence of acidic medium. The reaction is first order with respect to KMnO_4 and metal complex concentration. The reaction rate has been determined at different temperature and different thermodynamic parameters have been calculated which shows that with increase in temperature reaction rate increases. With increase in the concentration of acid the reaction rate increase. 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. The metal containing compounds have been used not only as biological probes but also diagnostic and therapeutic pharmaceuticals. The mechanism of action of platinum anticancer drugs, gold antiaztaratic agent and technetium radio pharmaceutical some currently active topic of investigation in bioinorganic chemistry. The study of naturally occurring inorganic elements in biology, i.e. when compound or complex containing biologically active metal known as bioinorganic chemistry. Today however inorganic chemistry is beginning to have a major impact on modern medicine there important inorganic pharmaceuticals are cisplatin as an anticancer drug.



cisplatin

Quranofin an oral rheumatoid arthritis drug and cardiolyte a heart imaging agent. In bioinorganic compounds the kinetic aspects are very good. The water exchange rates for many essential metal ions. $\text{M}-\text{OH}_2$ bonds are very labile breaking and reforming as fast as billion times per second. The labilities of metal-ligand bonds for the metal complexes. In general ligand exchange rates are faster for the less highly charged M^{+2} than for highly M^{+3} metal ions. The fast metal-ligand exchange rates of first row transition metal ions such as Fe^{+2} , Cr^{+3} , Co^{+3}

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 spectrophotometer. The reaction was followed upto 70 to 85% completion and the product was identified complex containing acid as well as aldehyde group. Complex containing acid and aldehyde functional group by were detected by 2, 4 DNP tests ¹⁶. The complex containing aldehydes and acid 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 system¹².

III. Results and discussion

Under the kinetic conditions Copper Complex (II) derived from 8-hydroxy quinoline and salicylaldehyde > [KMnO₄] in 3.25M H₂SO₄. The plot of log absorbance (O.D.) Vs time were linear indicating the first order dependence of rate on [KMnO₄]. (Fig has not shown) Oxidation of Copper Complex (II) derived from 8-hydroxy quinoline and salicylaldehyde depends on the concentration of potassium permanganate. This was also confirmed by verifying [KMnO₄] which did not show any change in Pseudo First order constant (k¹) value (Table No.1). The reaction was also found to be first order in Copper Complex (II) derived from 8-hydroxy quinoline and salicylaldehyde (Table 2). The rate of reaction increases with increases in [H₂SO₄]. (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 ΔH[#], ΔS[#], ΔG[#], E, ΔE and A i.e. frequency factor were studied.

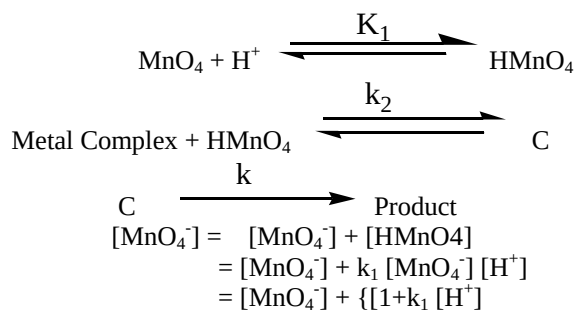
The negative values of entropy of activation shows that the intermediate transition state is rigid the relatively small values of ΔH and ΔS are consistent with the reaction generally proceeds through highly ionized transition state¹⁷.



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 HMnO₄.

As the acid concentration is increased the formation of HMnO₄ is favoured and hence increases the oxidation may be assumed to be taking place by Mn (VII) in the form of either MnO₄⁻ or HMnO₄ or both depending on the acid concentration. The linear plot of log k Vs log [H₂SO₄] 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 3.2x10⁻⁵liter mol⁻¹ sec⁻¹ under identical condition, from this it is

IV Derivation of Rate Law



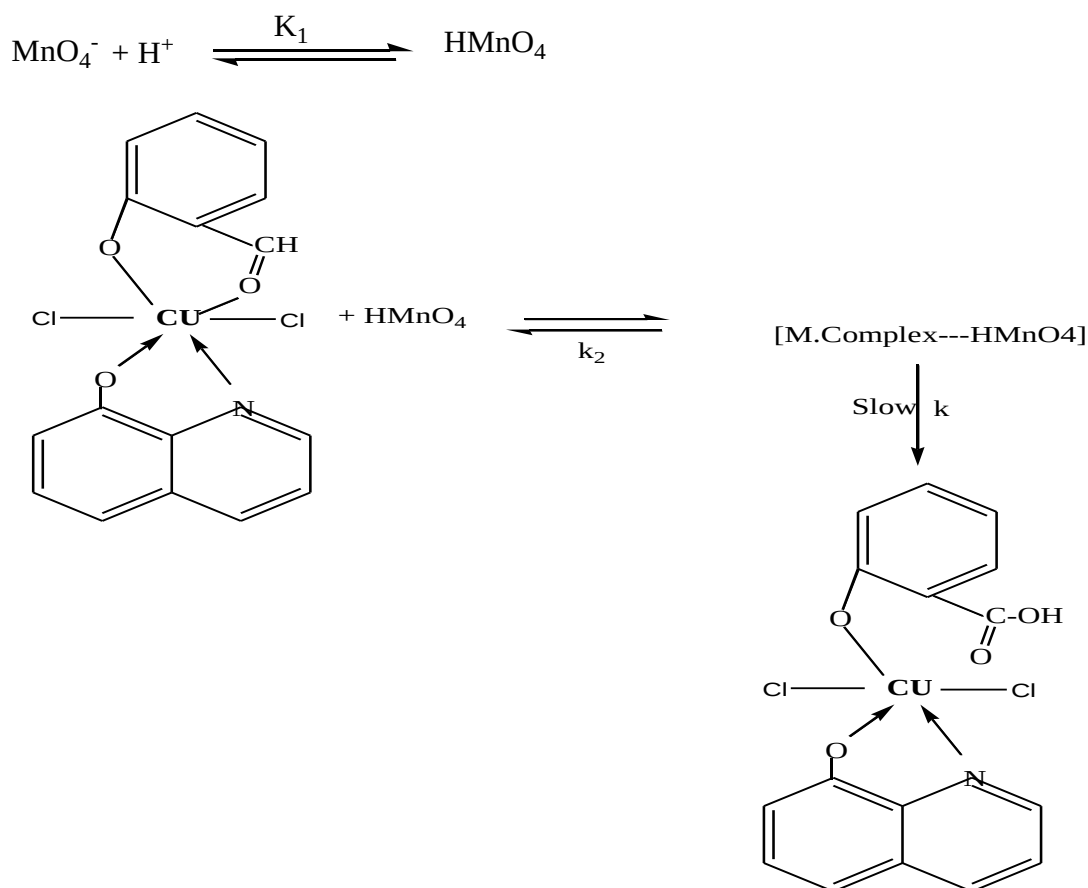
$$\text{Rate} = \frac{k k_2 [\text{MnO}_4^-] [\text{metal complex}]}{1 + k_1 [\text{H}^+]}$$

$$\frac{\text{Rate}}{[\text{MnO}_4^-] [\text{M.Complex}]} = \frac{KK_2}{1+K_1 [\text{H}^+]}$$

$$K_{\text{obs}} = \frac{KK_2}{1+K_1 [\text{H}^+]}$$

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

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)

$$\frac{-d[\text{Mn(VII)}]}{dt} = k (\text{Metal Complex}) [\text{MnO}_4]_{\text{Total}} \quad \text{----- (1)}$$

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 solutions¹⁸.

The effect of temperature on reaction rate was studied which shows the increase in reaction rate with increase in temperature (table 2 and 3).

Table 1: Effect of variation of Oxidant (KMnO₄)
[Copper metal complex] = 4.7×10^{-2} , Temperature: 30°C, λ_{Max} = 520 nm

Sr.No.	[Oxidant] $\times 10^3$ mol dm ⁻³	K _{Obs} $\times 10^2$ min. ⁻¹
I	3.002	0.7812
II	3.322	0.8614
III	3.421	0.9212
IV	3.482	1.0080
V	4.020	0.0840
VI	4.060	0.0960

Table 2: Effect of variation of Copper metal complex
[KMnO₄] = 4.7×10^{-3} , Temperature: 30°C, λ_{Max} = 520 nm

Sr.No.	[Metal complex] $\times 10^{-2}$	Log [Sub]	$K_{\text{Obs}} \times 10^2 \text{ min}^{-1}$	Log K^1
I	3.012	-2.4420	0.5162	-3.4612
II	3.256	-2.4021	0.6112	-3.6132
III	3.346	-2.3622	0.6812	-3.7012
IV	3.828	-2.3216	0.7218	-3.7818
V	4.120	-2.2926	0.7819	-3.8216
VI	4.560	-2.3462	0.8825	-3.9214

Table 3: Effect of Variation of Concentration of Acid [H₂SO₄]
(KMnO₄) = 4.7×10^{-3} M, [H₂SO₄] = 0.857M, Temperature = 30°C, λ_{Max} 520nm

Sr.No.	[H ₂ SO ₄]	Log [acid]	Log a_w	Ho	$K \times 10^{-2}/\text{min}$	logk	Ho+Log K
I	0.439	1.6424	-	-	0.5051	-3.7201	-3.7201
II	0.857	1.932	0.010	0.06	0.6198	-3.7891	-3.8491
III	1.25	0.096	0.14	0.07	0.6462	-3.8012	-3.8712
IV	1.63	0.212	0.18	0.08	0.9081	-3.9016	-3.9816
V	2.00	0.301	0.24	0.45	1.016	-2.012	-2.462
VI	2.34	0.369	0.36	0.62	1.012	-2.035	-2.655

Table 4: Effect of variation of temperature on reaction rate
[KMnO₄] = 4.7×10^{-4} M, (Copper metal complex) = 4.7×10^{-3} M

Temp	$1/T \times 10^{-3}$	$K \times 10^{-2}/\text{min}$	Log k	A	$E_{\text{j/mole}}$	$\Delta H \text{ J/mole}$	$\Delta G \text{ J/mole}$	$\Delta S \text{ J/mole}$
283	3.53×10^{-3}	0.5034	-3.7106	7.98×10^{-3}	14210	11862.41	24001.00	39.02
293	3.41×10^{-3}	0.561	-3.7212	5.82×10^{-3}	14210	11621.44	24640	40.36
303	3.30×10^{-3}	0.681	-3.7826	6.9×10^{-3}	14210	11582.02	24867	421.6
313	3.19×10^{-3}	0.880	-2.18	7.8×10^{-3}	14210	11461.12	25213	42.98
323	3.09×10^{-3}	0.601	-3.41	8.12×10^{-3}	14210	11442.36	26618	43.96
333	3.00×10^{-3}	0.6612	-3.65	8.768×10^{-3}	14210	11422.38	27125	44.12

A probable mechanism (scheme -1) in which MnO₄⁻ or HMnO₄ 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 Copper 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⁻.

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