Research Article

OXIDATIVE MECHANISM OF OXIDATION OF CHROMIUM (II) METAL COMPLEX IN ACID MEDIUM

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ABSTRACT
The Kinetic of oxidation of Iron Chromium (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 and Chromium (II) Metal Complex.

INTRODUCTION
Chromium has frequently and extensively been employed as an oxidizing agent both for preparative as well as analytical methods in Chemistry.[1] Chromic acid, aqueous dichromate, chromyl chloride, chromyl acetate and other substituted chromates have been employed in oxidation of organic as well as inorganic compounds in aqueous acid and alkaline media.[2, 3] It is the reason for which the chemists in general and kinetics in particular are attracted to know more about such an interesting chemistry of this reagent.[4]
To understand the mechanistic aspect of reduction of Cr (II) to Cr (III), several kinetics studies of chromic acid reduction of different types of organic substrates have been carried out by different workers. In general, the oxidation of Chromium is assumed to occur via the initial formation of an intermediate complex.[5] In acidic solution an intermediate may decompose by an acid catalyzed pathway. The mechanism path of this reduction depends upon the nature of oxidant and reaction condition. This paper discusses the importance of oxidation process.[6]
In this paper efforts have been made to determine the kinetic orders with respect to each reactant and to prepare a suitable reaction path for the oxidation of 8-hydroxy quinoline and salicylaldehyde.

MATERIAL AND METHODS
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 Chromium (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 Cr (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 Cr (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]
Acidified metal complex solution was used to this one drop of saturated $KHSO_4$ solution and one drop of $AgNO_3$ solution used. This mixture solution kept 3minute and 1% alcoholic dyphenyl carbozide solution added this produces red coloured solution this confirms the presence of Cr^{3+} in the complex. [11]

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

1) Effect of variation of concentration of Cr (II) metal complex
The oxidation of Cr (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 Cr (II) metal complex increases the rate of reaction (Table-1) the plot of log of k_{obs} versus log concentration of Cr (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 Cr (II) metal complex. [12]

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

| [Chromium complex]	Rate K_{obs}
0.001	0.00086
0.002	0.00088
0.003	0.0009
0.004	0.00091
0.005	0.00092
0.006	0.00093
0.007	0.00095
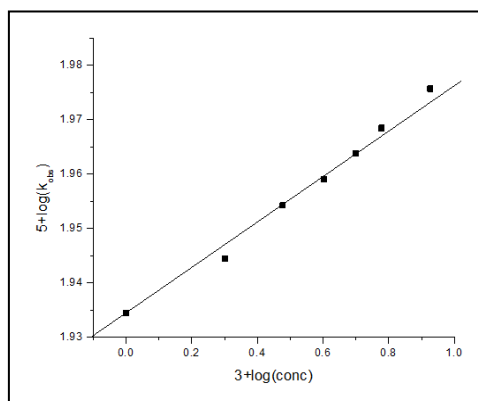
2) Effect of varying oxidising agent potassium permanganate
In this parameter studying the effect of variation of oxidising agent potassium permanganate on oxidation reaction of Cr (II) metal complex by keeping constant concentration of Cr (II) metal complex and concentration of H_2SO_4. The Concentration 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}	0.00073
2 x10^{-4}	0.00078
3 x10^{-4}	0.00083
4 x10^{-4}	0.00089
5 x10^{-4}	0.00091
6 x10^{-4}	0.00095
7 x10^{-4}	0.00019
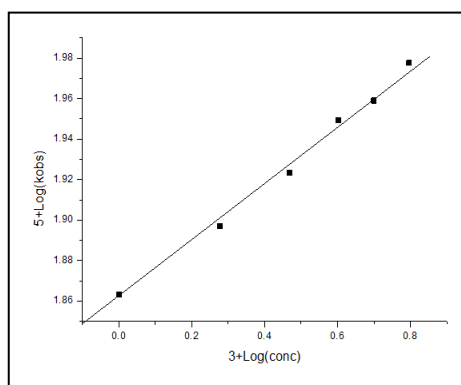
3) Effect of variation of concentration of sulphuric acid

In this factor there is study of variation of concentration of sulphuric acid on oxidation of Cr (II) metal complex. By keeping constant concentration of oxidising agent and substrate changing the [H$_2$SO$_4$] we find that the rate increases with increase in [H$_2$SO$_4$] 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$_2$SO$_4$]	Rate K$_{obs}$
0.001	0.00059
0.002	0.00063
0.003	0.00068
0.004	0.00074
0.005	0.00078
0.006	0.00082
0.007	0.00093

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}	0.00024
2 x10^{-2}	0.0003
3 x10^{-2}	0.00034
4 x10^{-2}	0.00026
5 x10^{-2}	0.0003
6 x10^{-2}	0.00023
7 x10^{-2}	0.00024

5) Effect of Temperature

The study of effect of temperature on rate of oxidation of Cr (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	0.00033
298	0.00037
303	0.00040
308	0.00043
313	0.00046
318	0.00046
323	0.00046
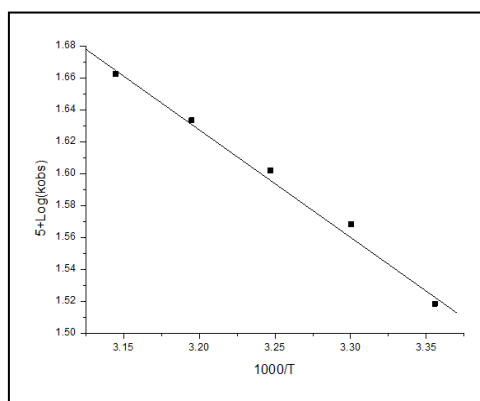
Table 6:

Ea	11853.18
ΔH	9250.59
ΔS	-281.54
ΔG	97373.53

CONCLUSION

The oxidation of Cr (II) metal increases in acetic acid in acid medium shows that the oxidation of Cr (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 Cr (II) metal complex by potassium permanganate

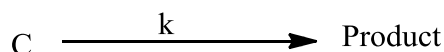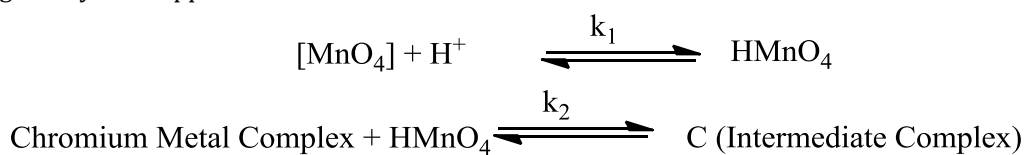$$H^{+} + Mno_4^{-} \longrightarrow HMnO_4$$
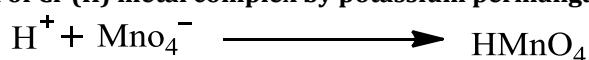
This point has been also confirmed by previous researchers. Hence Mn (VII) could be considered as the reactive specie and this probably exists to a certain extent as $HMnO_4$.

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.

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

$$Chromium\ Metal\ Complex + HMnO_4 \underset{}{\overset{k_2}{\rightleftharpoons}} C\ (Intermediate\ Complex)$$

$$C \xrightarrow{k} Product$$

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

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

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

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

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

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

$$\frac{1}{K_{obs}} = \frac{1}{kk_2} + \frac{k_1\ [H^+]}{kk_2}$$
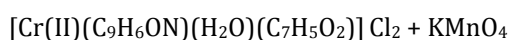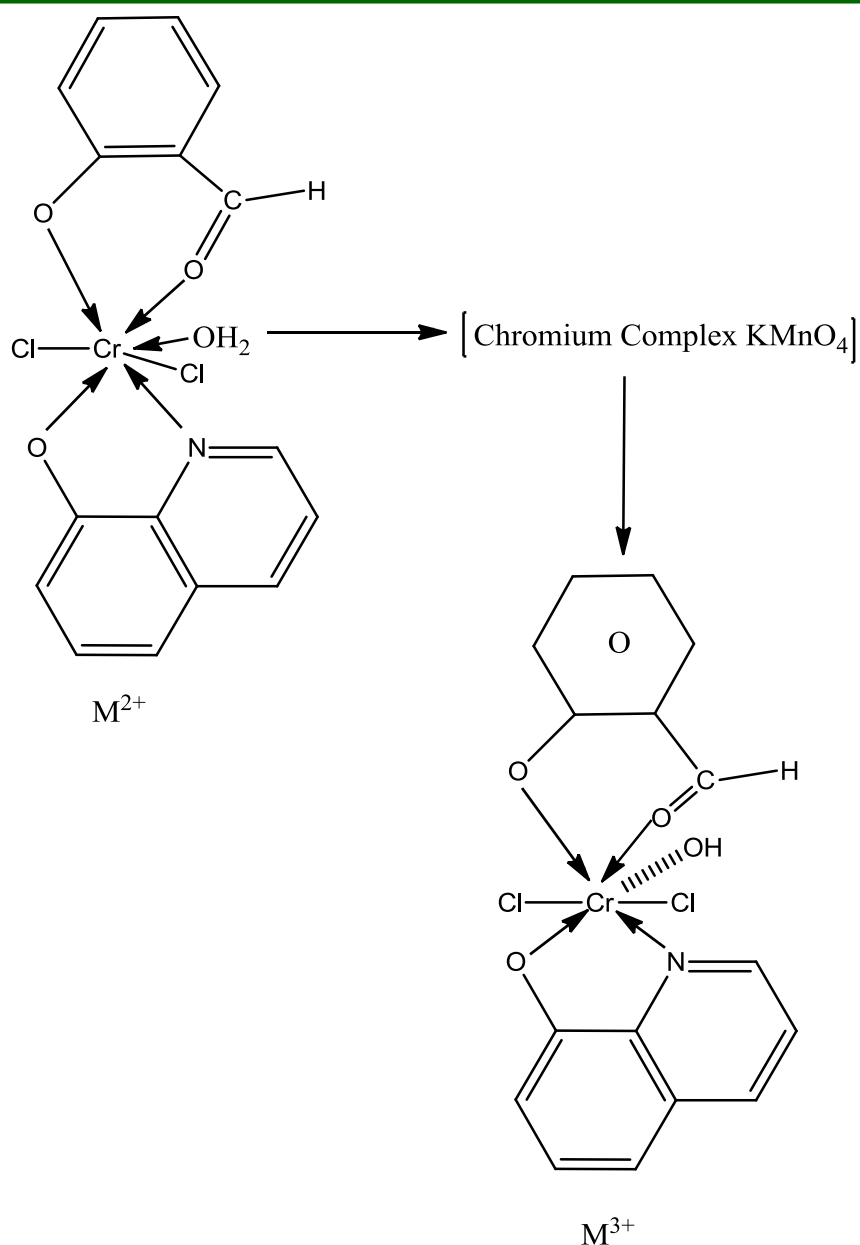
The rate law can be expressed by following equation

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

Where, Cr M.C. = Chromium 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 Chromium metal complex

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

$$\downarrow$$

$$[Cr(III)(C_6H_6ON)(C_7H_5O_2)]\ OHCl_2$$

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

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

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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