KINETIC APPROACH OF OXIDATION OF NICKEL COMPLEX (II) DERIVED FROM 3-[3-HYDROXY -PHENYLIMINO-ETHYL] -6-METHYL-PYRANE-2,4-DION LIGAND IN ACID MEDIUM

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ABSTRACT
The kinetic of oxidation of Nickel Complex (II) derived from 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyrane-2,4-dion ligand by potassium permanganate has been studied in acid medium spectrophotometrically at 520nm. The reaction is first order with respect to KMnO4 as well as Metal Complex concentration. With the increase in concentration of acid the reaction rates increase. The reaction rate has been determined at different temperature and activation parameters have been calculated. Suitable mechanism has been proposed.

Key words – Kinetics, Mechanism, 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyrane-2,4-dion ligand, Oxidation, Activation parameters, etc.

INTRODUCTION
Selective oxidation of Ni - complex derived from 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyrane-2,4-dion ligands to their corresponding aldehydes and acid is an important transformation in organic chemistry which has received the most attention over years, especially in the search of versatile and selective reagent for this purpose. KMnO4 have been used as mild and selective oxidizing reagent in synthetic organic chemistry. KMnO4 being one of the most versatile and selective available oxidizing reagent. The synthesis of newer Mn (VI) reagent for the oxidation of organic substrates continues to be interest. In recent years, significant improvements were achieved by the use of new oxidizing agents for the study of kinetics and mechanism of various organic compounds. Literature survey reveals...
that there no report is available on kinetics and mechanism of oxidation of Ni -complex derived from 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyranne-2,4-dion ligand by KMnO₄; hence we have considered it to study the kinetics and mechanism of oxidation of Ni-complex derived from 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyranne-2,4-dion ligand by KMnO₄.

PRODUCT ANALYSIS
The product analysis was carried out under kinetic conditions. In a typical experiment, Ni -complex derived from 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyranne-2,4-dion ligand (0.05 mol) and KMnO₄ (0.01) were made up to 50 ml in 20% acetic acid and kept in dark for about 24 hours to ensure the completion of the reaction. The solution was then treated with an excess of sodium bicarbonate, then 1N HCl and kept overnight in a refrigerator. The precipitated acid was filtered off, dried, weighed, recrystallized from ethanol and weighed again. The yield of acid before and after recrystallization was 1.0 g (90%) and 0.8 g (75%) respectively. The products were also characterized by TLC, IR, and NMR spectra.

KINETIC MEASUREMENTS
The reactions were followed under pseudo-first-order conditions by keeping large excess (x 10 or greater) of the Ni - complex derived from 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyrane-2,4-dion ligands over KMnO₄. The temperature was kept constant to +/- 0.1 K. The solvent was acetic acid. The reactions were followed by monitoring the decrease in the concentration of KMnO₄ spectrophotometrically at 520 nm for 80% completion of the reaction. The pseudo-first-order rate constants Kₐₙs, were evaluated from the linear (r=0.990-0.999) plots of log [KMnO₄] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within +/- 3%.

RESULT AND DISCUSSION
The results of oxidation of Ni-complex derived from 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyrane-2, 4-dion ligand by KMnO₄ are represented in table 1-7.

Effect of variation of concentration Ni - complex derived from 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyrane-2,4-dion ligand:- The oxidation of Ni - complex derived from 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyrane-2,4-dion ligand with KMnO₄ in 20% of acetic acid in presence of sulphuric acid yields corresponding acids. By keeping constant [KMnO₄] and [H₂SO₄], the increase in Ni - complex derived from 3-[3-
Hydroxy -Phenylimino-ethyl]-6-methyl-pyrane-2,4-dion ligand] increases the rate of reaction (Table-1). The plot of log of $k_{obs}$ versus log [ Ni - complex derived from 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyran-2,4-dion ligand] for different initial concentration of Ni -complex derived from 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyrane-2,4-dion ligand is linear with unit slope demonstrate the first –order dependence of rate on Ni -complex (Figure: 1).

Table 1  Effect of variation of [Ni -complex] on reaction rate

<table>
<thead>
<tr>
<th>[Ni –Comp]</th>
<th>0.01M</th>
<th>0.02M</th>
<th>0.03M</th>
<th>0.04M</th>
<th>0.05M</th>
<th>0.06M</th>
<th>0.07M</th>
<th>0.08M</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k \times 10^3$sec$^{-1}$</td>
<td>2.13</td>
<td>2.47</td>
<td>2.85</td>
<td>3.18</td>
<td>3.56</td>
<td>3.91</td>
<td>4.27</td>
<td>4.63</td>
</tr>
</tbody>
</table>

$[\text{KMnO}_4]=0.001 \text{ M}, [\text{H}_2\text{SO}_4]=0.1 \text{ N}, \text{Temperature }=303K, \text{AA }=20\% \ (v/v)$

Figure 7 Plot of 2+ Log [Ni -complex] Vs 3+Logk

Effect of variation of concentration of KMnO$_4$

At constant [Ni-complex derived from 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyran-2,4-dion ligand] and [H$_2$SO$_4$], the increase in [KMnO$_4$] increases the rate of reaction (Table-2). The plot of log $k_{obs}$ versus log [KMnO$_4$] for different initial concentration of KMnO$_4$ is linear with unit slope present the first-order dependence of rate on KMnO$_4$.

Table 2  Effect of variation of [KMnO$_4$] on reaction rate

<table>
<thead>
<tr>
<th>[KMnO$_4$] Mole</th>
<th>0.001</th>
<th>0.0015</th>
<th>0.002</th>
<th>0.0025</th>
<th>0.003</th>
<th>0.0035</th>
<th>0.004</th>
<th>0.0045</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k \times 10^3$sec$^{-1}$</td>
<td>2.13</td>
<td>2.43</td>
<td>2.75</td>
<td>3.07</td>
<td>3.37</td>
<td>3.64</td>
<td>3.96</td>
<td>4.28</td>
</tr>
</tbody>
</table>

$[\text{Ni - complex}]=0.01 \text{ M}, [\text{H}_2\text{SO}_4]=0.1 \text{ N}, \text{Temp }=303K, \text{AA }=20\% \ (v/v)$
Effect of variation of concentration of H⁺

In order to study the effect the H⁺ ion concentration on the rate of oxidation reaction of Ni-complex derived from 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyrane-2,4-dion ligand, the dependence of reaction rate has been investigated at different initial concentration of H₂SO₄. The rate of reaction increases with increase in [H₂SO₄] (Table-3). The plot of log $K_{obs}$ verses log [H+] are also straight line with slope less than unity, indicating a fractional order dependence on [H+].

### Table 3 Effect of variation of [H₂SO₄] on reaction rate

<table>
<thead>
<tr>
<th>[H₂SO₄]</th>
<th>0.1M</th>
<th>0.2M</th>
<th>0.3M</th>
<th>0.4M</th>
<th>0.5M</th>
<th>0.6M</th>
<th>0.7M</th>
<th>0.8M</th>
</tr>
</thead>
<tbody>
<tr>
<td>k $\times 10^3$ sec⁻¹</td>
<td>2.13</td>
<td>2.24</td>
<td>2.43</td>
<td>2.62</td>
<td>2.89</td>
<td>2.99</td>
<td>3.19</td>
<td>3.37</td>
</tr>
</tbody>
</table>

$[KMnO_4]= 0.001 \text{ M, } [\text{Ni-complex}] = 0.01 \text{ M, Temp. } = 303 \text{ K, AA } = 20\% (v/v)$

### Effect of ionic strength:

In the present investigation effect of salt on the rate of reaction is carried out. The salts selected are KCl, KBr, and KI. These will give effect of anion particularly halides on the rate of reaction. The divalent and trivalent cationic salt were also used such as CaCl₂, Ca(NO₃)₂, Al(NO₃)₃ and K₂SO₄. The experiments were carried out under pseudo- first- order condition. These results were used to determine first order rate constant. The rate constants for the oxidation of Ni-complex derived from 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyran-2,4-dion ligand in presence of different salt are shown in [Table 4]. From table it is clear that, the rate increases with increase in cationic charge and decreases with increase in anionic charge.

### Table 4 Effect of variation of [salts] on reaction rate

<table>
<thead>
<tr>
<th>Salts 0.1M</th>
<th>KCl</th>
<th>KBr</th>
<th>KI</th>
<th>CaCl₂</th>
<th>Ca(NO₃)₃</th>
<th>Al(NO₃)₃</th>
<th>K₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>k $\times 10^3$ sec⁻¹</td>
<td>2.04</td>
<td>2.26</td>
<td>2.26</td>
<td>2.46</td>
<td>2.57</td>
<td>2.66</td>
<td>2.53</td>
</tr>
</tbody>
</table>

$[KMnO_4]= 0.001 \text{ M, [Ni-comp]} = 0.01 \text{ M, } [\text{H}_2\text{SO}_4] = 0.1 \text{ N, Temp. } = 303 \text{ K}$

Effect of solvent composition

At fixed [Ni-complex], [KMnO₄] and [H⁺], the rate of oxidation of Ni-complex derived from 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyrane-2,4-dion ligand with KMnO₄ increases with decrease in polarity of solvent (Table 5). This is due to polar character of transition state.
as compared to the reactant. The plot of log k_{obs} verses 1/D is linear with positive slope indicating ion- dipole type of reaction [20].

**Table 5** Effect of variation of Acetic Acid % on reaction rate

<table>
<thead>
<tr>
<th>Acetic acid</th>
<th>10 %</th>
<th>20 %</th>
<th>30 %</th>
<th>40 %</th>
<th>50 %</th>
<th>60 %</th>
<th>70 %</th>
<th>80 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>k x 10^3sec^{-1}</td>
<td>2.02</td>
<td>2.13</td>
<td>2.28</td>
<td>2.46</td>
<td>2.56</td>
<td>2.68</td>
<td>2.83</td>
<td>2.97</td>
</tr>
</tbody>
</table>

[KMnO₄]= 0.001 M, [H₂SO₄] = 0.1 N, [Ni - complex] =0.01M, Temp=303 K

**Effect of temperature:** The study of effect of temperature on rate of oxidation of Ni - complex derived from 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyrane-2,4-dion ligand by KMnO₄ has been subjected to different temperature range 293K to 313K by keeping the concentration of Ni - complex and other reagent constant. Rate constants are given in [Table 6].

The plots of log of K_{obs} verses 1/T are linear (Figure: 2)

**Table 6 Effect of variation of Temperatures on reaction rate**

<table>
<thead>
<tr>
<th>Temperatures (K)</th>
<th>293</th>
<th>298</th>
<th>303</th>
<th>308</th>
<th>313</th>
<th>318</th>
</tr>
</thead>
<tbody>
<tr>
<td>k x 10^3sec^{-1}</td>
<td>1.29</td>
<td>1.70</td>
<td>2.13</td>
<td>2.53</td>
<td>2.97</td>
<td>3.39</td>
</tr>
</tbody>
</table>

[KMNO₄]= 0.001 M, [Ni - complex] = 0.01 M, [H₂SO₄] = 0.1 N, AA = 20% (v/v)

![Figure 12 Arrhenius plot of oxidation of Ni - complex](image-url)
Activation parameters are presented in [Table 7]. The negative values of entropy of activation reflect that the transition state is more rigid than initial state. The nearly constant $\Delta G$ value indicates that similar mechanism is operative for the oxidation of Ni - complex derived from 3-[3-Hydroxy -Phenylimino-ethyl]-6-methyl-pyran-2,4-dion ligand.

**Table 7 Activation Parameters**

<table>
<thead>
<tr>
<th>Activation parameters</th>
<th>$\Delta E_a$ KJ mole$^{-1}$</th>
<th>$\Delta H^#$ KJ mol$^{-1}$</th>
<th>$\Delta S^#$ JK mole$^{-1}$</th>
<th>$\Delta G^#$ KJ mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25.06</td>
<td>22.57</td>
<td>-215.64</td>
<td>88.68</td>
</tr>
</tbody>
</table>

$[KMNO_4]$= 0.001 M, $[AP]$ = 0.01 M.  $[H_2SO_4]$ = 0.1 N, Temp. =303 k,  $AA$ = 20 %

**Derivation of Rate Law**

$$\text{MnO}_4^- + H^+ \rightleftharpoons K_1 \text{HMnO}_4$$

$$\text{Metal Complex} + \text{HMnO}_4 \rightleftharpoons k_2 C$$

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

$$[\text{MnO}_4^-] = [\text{MnO}_4^-] + [\text{HMnO}_4]$$

$$= [\text{MnO}_4^-] + k_1 [\text{MnO}_4^-] [H^+]$$

$$= [\text{MnO}_4^-] + ([1+k_1 [H^+])$$

Rate $= k k_2 [\text{MnO}_4^-] [\text{metal complex}]$

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

\[
K_{obs} = \frac{K K_2}{1+K_1 [H^+]} \\
\]

**Mechanism of oxidation of metal complexes**

$$\text{MnO}_4^- + H^+ \rightleftharpoons K_1 \text{HMnO}_4$$
CONCLUSION

The rate constants of the slow step involved in the mechanism were evaluated and activation parameters were also computed. The negative value of $\Delta S^\#$ provides support to the formation of rigid transition state. The overall mechanism described here is consistent with product and kinetic studies.

ACKNOWLEDGEMENT

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REFERENCES

5. S.SheikMansoor, Asian Journal of chemistry, 22, 10, 2010, 7591-7600