Decomposition of hydrogen peroxide in presence of mixed ligand cobalt (II) and nickel (II) complexes as catalysts

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The decomposition of hydrogen peroxide catalyzed by mixed ligand cobalt (II) and nickel (II) complexes as heterogeneous catalysts and adsorbate on alumina has been investigated by measuring the evolution of oxygen at different time intervals between 35-60°C. The effect of variation in the concentration of hydrogen peroxide and in the quantity of catalysts on the extent of disproportionation has also been studied. Enhanced activity has been observed in presence of alumina-adsorbed complexes. The reaction rate is found to increase with increase in temperature and quantity of the catalyst. The effect of stereochemical aspects of the complexes on the kinetics of decomposition of hydrogen peroxide has also been studied. Various thermodynamic parameters have been calculated. A probable reaction mechanism has been suggested and the results have been interpreted on the basis of formation of a surface-active intermediate and its subsequent interaction with hydrogen peroxide.

Keywords: Cobalt, Nickel, Decomposition, Hydrogen peroxide

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Introduction

The decomposition of hydrogen peroxide in presence of metal ions as homogeneous catalysts is very slow but it is fast when these ions are used along with small amounts of alumina. Fast decomposition of hydrogen peroxide has wide applications in rocket propellants, fuel cells, bleaching etc, where it is used as a source of oxygen. Many transition metal complexes are more effective catalysts. When complexes are affixed to various supports, there is enhancement of the catalytic activity. The present study reports the heterogeneous and heterogenized homogeneous catalysis in decomposition of hydrogen peroxide using mixed ligand cobalt (II) and nickel (II) complexes as catalysts, prepared by using CoCl₂·6H₂O/NiCl₂·6H₂O, 8-hydroxyquinoline and a N-O donor amino acid, phenylalanine in 1:1:1 proportion.

Experimental Details

All the chemicals used were of analytical grade.

Preparation of Catalysts and Supported Catalyst

Mixed ligand cobalt (II) and nickel (II) complexes were prepared by using 8-hydroxyquinoline as primary ligand and a N-O donor amino acid, phenylalanine, as secondary ligand. These complexes were used as heterogeneous catalysts. To a blue coloured ethanolic solution (10 cm³) of 1 M CoCl₂·6H₂O/1 M NiCl₂·6H₂O, an ethanolic solution (10 cm³) of 1 M 8-hydroxyquinoline was added. Mixture, which turned green after stirring and keeping in boiling water bath for 10 min, was added with aqueous solution (10 cm³) of 1 M phenylalanine. The mixture (1:1:1 molar proportion) was heated again in boiling water bath for 5 min. Resultant light green coloured solid was filtered and washed with ice-cold water, followed by ice-cold ethanol. Mixed ligand complexes thus prepared were dried under vacuum.

A sample of chromatographic grade alumina, to be used as adsorbent, was washed repeatedly with boiling distilled water, dried for 6 h and sieved to 100-120 (BSS) mesh and finally activated at 150 °C for 24 h. A weighed quantity of alumina thus processed was kept in contact with a measured volume of a solution of cobalt (II)/nickel (II) complex in dimethyl formamide in a glass stoppered bottle at room temperature for 24 h with intermittent shaking at definite intervals. It was filtered, washed repeatedly with distilled water and alcohol for complete removal of the adhering complex and dried at 100 °C for about 2 h. The amount of cobalt/nickel, and hence that of
the complex in the heterogenized catalyst, was determined using Atomic Absorption Spectrophotometer. The desired concentration of hydrogen peroxide was obtained by successive dilution from the stalk solution, which was standardized by titration against standard KMnO₄ solution from time to time.

**Kinetic Measurements**

Kinetic activity of the catalysts in H₂O₂ decomposition was evaluated by the rate of O₂ production using gasometric technique. Gasometric assembly (Fig. 1) consists of a gas burette (A) connected to the thistle funnel (B) by a rubber tube (C), and to the closed reaction vessel (D) by a PVC tubing (H). A reaction vessel is kept into the trough (E) placed on a hot plate with magnetic stirrer (F). A thermometer (G) inserted in the vessel records the temperature. Using the thistle funnel, water was introduced in the burette and adjusted to zero level. A weighed quantity of the catalyst was injected into a thermostatic reaction vessel, containing 10 cm³ of H₂O₂ (5 vol). The displacement of water from the burette due to the evolution of O₂ was monitored for a given temperature at atmospheric pressure.

Experiments were carried out at three different temperatures (T) between 35-60 °C. The effect of varying amount of catalyst was studied at a constant concentration of H₂O₂ at 55 °C. The specific reaction rates k were evaluated from the plot of log (a-x) against time t, where a and x are the volumes of oxygen evolved after completion of decomposition and at any time t, respectively.

The log k values were plotted against 1/T (Arrhenius plot). The slope of the straight line obtained is -E/2.303R. Thus, the activation energy (E) was calculated from slope. The changes in the enthalpy of activation (∆H°), entropy of activation (∆S°) and free energy of activation (∆G°) were calculated by using Eq. 1, 2 and 3, respectively.

\[
\Delta H^° = E - RT \\
\frac{RT}{k} = \frac{e^{\Delta S^°/R}}{N} \cdot e^{-\Delta H^°/RT} \\
\Delta G^° = \Delta H^° - T\Delta S^°
\]

where, N is Avogadro’s number and h is Plank’s constant.

**Results and Discussion**

**Characterization of the Complexes**

Both the complexes were found to be non-electrolytic, non-hygroscopic stable solids. Magnetic studies indicate tetrahedral geometry for Co (II) complex and octahedral geometry for Ni (II) complex, confirmed by crystal field transitions shown by the electronic spectra (Figs 2 & 3). IR spectra show bonding of the metal ion through N/O and O of the two ligands and presence of a water of crystallization (Fig. 4).

**Mixed Ligand Complexes as Heterogeneous Catalysts**

Cobalt (II) ions as chloride solutions show very low catalytic activity with respect to the decomposition of H₂O₂. However, in presence of Co(II) in the heterogeneous phase, the catalytic disproportionation is enhanced considerably. Complexation and heterogenization of Co(II) have an enhanced effect on the decomposition of H₂O₂ (Table 1).

The plot of log (a-x) versus t, for the complex, [Co(Q)(Phe)]·H₂O, is linear (Fig. 5) indicating that the decomposition of H₂O₂ in the presence of catalyst follows first order kinetics. Keeping the quantity of
catalyst and H\(_2\)O constant, \(k\) increased (Table 1) with increase in temperature (35-60\(^\circ\)C). Keeping the quantity of H\(_2\)O\(_2\) and the temperature constant, \(k\) increased (Table 2) with increase in the quantity of the catalyst (10-50 mg). The plot of log \(k\) versus log \([\text{[Co(Q)(Phe)]H}_2\text{O}}\) is linear with a slope of 0.85, indicating that the order of the disproportionation reaction is nearly unity (Fig. 6).

The Co(II) complex is suggested to have tetrahedral geometry on the basis of room temperature magnetic susceptibility and spectral studies. On the other hand, octahedral geometry is suggested for the Ni (II) complex, where 5\(^{th}\) and 6\(^{th}\) coordination sites being satisfied by linkage to oxygen atoms of the neighbouring molecules. Generally, tetrahedral complexes react more rapidly than six coordinated complexes as former undergoes associative mechanism favoured by high positive charge on the metal ion while in later, the enthalpy of activation is highly influenced by dissociative mechanism, which is common with octahedral complexes of 3d metal ions.\(^{11}\) The complex with Co (II) is found to show higher \(k\) values as compared to complex with Ni (II).

\[\Delta H^\circ\] values are closer to \(E\) values in accordance with absolute reaction rate theory for solution\(^{12}\). The values of \(\Delta S^\circ\) were found to be negative in both the cases indicating that molecules in transition state are more ordered than the reactants in ground state. \(\Delta G^\circ\) was found to be higher in both the cases and not much difference was found in both the systems suggesting no significant effect of arrangement of molecules in transition state on these values. The catalytic nature of the reaction was confirmed by recovering the complexes unchanged, both in amount and
composition, at the end of the reaction. The FTIR spectra of the complexes recorded before and after the reaction are almost identical indicating that these catalysts do not suffer any irreversible, compositional or structural change.

**Mixed Ligand Complexes as Heterogenized Catalysts**

With alumina, the volume of oxygen evolved was negligible. Complexes used as catalysts showed less activity as compared to the complexes adsorbed on alumina. Keeping the quantity of catalyst (0.5 g) and H₂O₂ (10 ml) constant, k increased (Table 3) with increase in the temperature (35-55°C). The plot of log (a-x) versus t (Fig. 7) is linear indicating that the decomposition of H₂O₂ in the presence of catalyst proceeds in a first order manner. Keeping the quantity of H₂O₂ and the temperature constant, k increased (Table 4) with increase in the quantity of the catalyst (1.5-6.2 ×10⁻³ g).

<table>
<thead>
<tr>
<th>Compound b</th>
<th>T °C</th>
<th>k × 10⁻² min⁻¹</th>
<th>E kJ.mol⁻¹</th>
<th>ΔH° kJ.mol⁻¹</th>
<th>ΔS° J.K⁻¹.mol⁻¹</th>
<th>ΔG° kJ.mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(Q)(Phe)]·H₂O</td>
<td>35</td>
<td>0.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>3.07</td>
<td>51.05</td>
<td>48.37</td>
<td>-152.17</td>
<td>97.52</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>3.63</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(Q)(Phe)]·H₂O</td>
<td>35</td>
<td>0.39</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>0.73</td>
<td>30.31</td>
<td>27.63</td>
<td>-226.91</td>
<td>100.92</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Amount of catalyst: 0.040 g; volume of H₂O₂: 10.0 cm³ (~5 vol)
b where Q and Phe represent the deprotonated 8-hydroxyquinoline and phenylalanine, respectively.

Fig. 4 — Structures of (A) Co(II) complex and (B) Ni(II) complex catalyzed by [Co(Q)(Phe)]·H₂O at three different temperatures (I) 35 °C, (II) 55 °C and (III) 60 °C

![Fig. 4](image_url)
**Fig. 6 — Plot of log $k$ vs log {amount of [Co(Q)(Phe)]·H$_2$O}**

**Table 2 — Influence of the amount of catalyst on the decomposition of hydrogen peroxide by representative compound [Co(Q)(Phe)]·H$_2$O**

<table>
<thead>
<tr>
<th>Amount of catalyst (g)</th>
<th>Specific reaction rate, $k$ min$^{-1}$</th>
<th>Order of reaction with respect to catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.050</td>
<td>0.039</td>
<td></td>
</tr>
<tr>
<td>0.040</td>
<td>0.034</td>
<td></td>
</tr>
<tr>
<td>0.030</td>
<td>0.029</td>
<td>0.85</td>
</tr>
<tr>
<td>0.020</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>0.010</td>
<td>0.021</td>
<td></td>
</tr>
</tbody>
</table>

*Temperature: 55 °C; volume of hydrogen peroxide: 10.0 cm$^3$ (∼5 vol)

**Table 3 — Decomposition of hydrogen peroxide by heterogenized homogeneous catalysts**

<table>
<thead>
<tr>
<th>Compound (adsorbed on alumina)</th>
<th>$T$ °C</th>
<th>$k \times 10^2$ min$^{-1}$</th>
<th>$E$ kJ.mol$^{-1}$</th>
<th>$\Delta H^\circ$ kJ.mol$^{-1}$</th>
<th>$\Delta S^\circ$ J.K$^{-1}$.mol$^{-1}$</th>
<th>$\Delta G^\circ$ kJ.mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(Q)(Phe)]·H$_2$O</td>
<td>35</td>
<td>0.60</td>
<td>47.86</td>
<td>45.18</td>
<td>-148.62</td>
<td>93.18</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>14.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>18.42</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(Q)(Phe)]·H$_2$O</td>
<td>55</td>
<td>0.92</td>
<td>25.52</td>
<td>22.84</td>
<td>-239.58</td>
<td>100.22</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Amount of catalyst: 0.5 g; volume of H$_2$O$_2$: 10.0 cm$^3$ (∼5 vol)

**Fig. 7 — Kinetics of decomposition of hydrogen peroxide (5 vol) catalyzed by [Co(Q)(Phe)]·H$_2$O adsorbed on alumina at three different temperatures (I) 35 °C, (II) 55 °C and (III) 60 °C**

**Table 4 — Influence of the amount of catalyst on the decomposition of hydrogen peroxide by [Co(Q)(Phe)]·H$_2$O adsorbed on alumina**

<table>
<thead>
<tr>
<th>Amount of [Co(Q)(Phe)]·H$_2$O on surface (g x 10$^{-3}$)</th>
<th>Specific reaction rate, $k$ min$^{-1}$</th>
<th>Order of reaction with respect to catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.525</td>
<td>0.0325</td>
<td></td>
</tr>
<tr>
<td>2.300</td>
<td>0.0497</td>
<td></td>
</tr>
<tr>
<td>3.600</td>
<td>0.0789</td>
<td>1.0</td>
</tr>
<tr>
<td>5.020</td>
<td>0.1089</td>
<td></td>
</tr>
<tr>
<td>6.232</td>
<td>0.1527</td>
<td></td>
</tr>
</tbody>
</table>

*Temperature: 55 °C; volume of hydrogen peroxide: 10.0 cm$^3$ (∼5 vol)
The plot of \( \log k \) versus \( \log \{[\text{Co(Q)(Phe)}] \cdot \text{H}_2\text{O adsorbed on alumina}\} \) is linear with a slope of 1.0, indicating that the order of the disproportion reaction with respect to quantity of catalyst is unity (Fig. 8). The plot of \( 1/k \) versus \( 1/\{[\text{Co(Q)(Phe)}] \cdot \text{H}_2\text{O}\} \) (Fig. 9) and similar plot of \( 1/k \) versus \( 1/\{[\text{Co(Q)(Phe)}] \cdot \text{H}_2\text{O adsorbed on alumina}\} \) (Fig. 10) passes through the origin with a break in linearity. This is indicative of formation of an activated complex involving catalyst-H$_2$O$_2$ species$^3$, as the plot indicates, at a certain concentration of the catalyst the rate of the reaction increases sharply, due to the formation of the intermediate.

At this stage, colour of the surface adsorbed complex changed from light yellow to light brownish due to the formation of activated complex on the surface of alumina through the interaction of H$_2$O$_2$ and mixed ligand complex. The colour persists as long as any residual H$_2$O$_2$ remains undecomposed. On completion of decomposition, the original colour returns. When alumina or mixed ligand complex is used as a heterogeneous catalyst, no colour change is observed. This is further indicative of the formation of the activated complex. Thus, an active complex formed on the surface of alumina is responsible for the fast decomposition of H$_2$O$_2$.

Efforts made to detach the active complex from the catalyst surface were unsuccessful due to its unstable nature. The surface-active complex, recovered during the reaction after washing$^{13}$, was however found to decolorize a dilute solution of potassium.
permanganate. This indicates the formation of [M^II(Q)(Phe)-peroxo] species. The formation of peroxo species in the decomposition of H$_2$O$_2$ under the catalytic action of metal complex has also been reported$^{14-17}$. Heterogenized Co (II) and Ni (II) catalysts when reused for the decomposition studies retain most of their activity, indicating the stability of heterogenized metal chelates and no leaching of the metal ions$^{18}$.

Based on the experimental observations, the following reaction mechanism may be suggested and may involve the initial steps of interaction of the surface complex with H$_2$O$_2$ or OOH$^-$ ion:

$$\text{alumina-[M}^{\text{II}}(\text{Q})(\text{Phe})] + \text{H}_2\text{O}_2 \rightarrow \text{alumina-[M}^{\text{II}}(\text{Q})(\text{Phe})(\text{H}_2\text{O}_2)]$$  \hspace{1cm} (4)

where M$^{\text{II}}$ is Co$^{\text{II}}$/Ni$^{\text{II}}$. In the second step, H$_2$O$_2$ is deprotonated:

$$\text{alumina-[M}^{\text{II}}(\text{Q})(\text{Phe})(\text{H}_2\text{O}_2)] \rightarrow \text{alumina-[M}^{\text{II}}(\text{Q})(\text{Phe})(\text{OOH}^-)] + \text{H}^+$$  \hspace{1cm} (5)

Alternatively, the initial reaction may proceed by formation of OOH$^-$ ion$^{19}$.

$$\text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{OOH}^-$$  \hspace{1cm} (6)

$$\text{alumina-[M}^{\text{II}}(\text{Q})(\text{Phe})] + \text{OOH}^- \rightarrow \text{alumina-[M}^{\text{II}}(\text{Q})(\text{Phe})(\text{OOH}^-)]$$  \hspace{1cm} (7)

The catalytic action in the decomposition of H$_2$O$_2$ may be attributed to the interaction of another molecule of H$_2$O$_2$ as:

$$\text{alumina-[M}^{\text{II}}(\text{Q})(\text{Phe})(\text{OOH}^-)] + \text{H}_2\text{O}_2 \rightarrow \text{alumina-[M}^{\text{II}}(\text{Q})(\text{Phe})][\text{H}_2\text{O}_2]$$  \hspace{1cm} (8)

The above mechanisms are in accord with the results of Sigel & Pastermack$^{20}$ pertaining to catalase like activity of Co$^{\text{III}}$-hematoporphyrin in the decomposition of H$_2$O$_2$, where, in the first step, H$_2$O$_2$ is coordinated with the catalyst and in the next step it is deprotonated.

Thus, from the above observations, the rate law may be written as:

$$\frac{d[\text{O}_2]}{dt} = k \text{ [catalyst][H}_2\text{O}_2]^2$$  \hspace{1cm} (9)

Since the concentration of H$_2$O$_2$ is in large excess compared to the quantity of [M$^{\text{II}}(\text{Q})(\text{Phe})]$ present on the surface, it may be considered to be constant$^{14}$. Thus Eq. 9 may be reduced to:

$$\frac{d[\text{O}_2]}{dt} = k \text{ [catalyst]}$$  \hspace{1cm} (10)

Eq. 10 indicates that the decomposition process would be affected by variation in the quantity of the catalyst present on the surface. This is in agreement with the experimental results; an increasing $k$ value has been observed on increasing the quantity of the catalyst in the disproportionation of H$_2$O$_2$.

Conclusions

The mixed ligand complexes act as catalysts in the decomposition of H$_2$O$_2$. The reaction proceeds through the formation of activated complex/transition state. The complexation and heterogenization of Co(II)/Ni(II) have an enhanced effect on the catalytic decomposition of H$_2$O$_2$ especially at higher temperatures. The effect of change of metal ion during complexation interestingly affects the rate of the reaction when it has been observed that octahedral Ni(II) complex shows lower $k$ value as compared to tetrahedral Co(II) complex. Co(II) complex is catalytically more active than the Ni(II) complex. The mixed ligand Co(II)/Ni(II) complexes adsorbed on alumina (heterogenized catalysts) are better catalysts as compared to non-adsorbed complexes (heterogeneous catalysts). This may be due to the increase in the concentration of adsorbed reactant molecules on the surface of the catalyst, which according to law of mass action, enhances the rate of the reaction.

References


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