THERMODYNAMICS OF THE HOMOGENOUS OXYGENATION OF CYCLOHEXENE BY MOLECULAR OXYGEN CATALYZED BY THE TERNARY Ru (III)-SCHIFF BASE IMIDAZOLE COMPLEXES

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The homogeneous oxygenation of cyclohexene by molecular oxygen catalyzed by [Ru\textsuperscript{III} (Salen)(Im) Cl] 1 and [Ru\textsuperscript{III} (Saloph) (Im) Cl] 2 (Salen = bis (salicylaldehyde) ethylenediimine, Saloph = bis(salicylaldehyde-o-phenylenediimine) was investigated in the temperature range 288–318 K, μ = 0.1 M KCl in 50% dioxan-water mixture. The rate of oxidation of cyclohexene by molecular oxygen was found to be first order with respect to the substrate, catalyst and dioxygen concentrations. Based on the kinetics data, suitable mechanisms were proposed for the oxygenation of cyclohexene catalyzed by 1 and 2. The oxygenation of cyclohexene catalyzed by 1 gave 74% of the allylic oxidation product 2-cyclohexen-1-one and 25% cyclohexene oxide, whereas catalysis by 2 afforded 90% of cyclohexene oxide and 6% 2-cyclohexene-1-one.

Thermodynamic parameters corresponding to the formation of various intermediates such as Ru(IV)-superoxo species (κ\textsubscript{1}); mixed ligand Ru(IV)-superoxo-olefin complexes (κ\textsubscript{2}) and the activation parameters for the rate determining oxygen atom transfer (κ) to the substrate were evaluated. The difference in the reactions of 1 and 2 towards the oxygenation of cyclohexene has been attributed to the difference in the activation of dioxygen and olefin by the two complexes.

Key Words: Catalysis by Ru\textsuperscript{III}-Schiff Base Complexes; Oxygen Transfer Reactions

INTRODUCTION

Dioxygen carriers are important from an industrial viewpoint as a potential attraction for the separation of oxygen and nitrogen.\textsuperscript{1,2} The Co(II) Schiff base chelate that has been studied most extensively in regard to oxygen carrying properties is bis(salicylaldehyde)ethylenediiminatecobalt(II) referred to as salco-

Salcoine undergoes gradual decomposition upon repeated dioxygen recycling.\textsuperscript{4} The Co(II) chelate of bis(3-fluorosalicylaldehyde)ethylenediimine (fluomine) shows the best performance so far in not undergoing any structural changes up to as many as 4000 operations of oxygenation and deoxygenation.\textsuperscript{5,6} An important additional factor that contributes towards the capability of Co(II) Schiff base complexes in dioxygen complex formation and its reversibility is the presence...
of an aromatic axial base in the coordination sphere of Co(II).\textsuperscript{7-9} The resulting complexes depending on the basicity of the axial base have a wide variation in dioxygen affinity. Very recently, the dioxygen affinities of Co(II) Schiff base complexes in the presence of a variety of aromatic axial bases are reported.\textsuperscript{9}

We have earlier reported the dioxygen affinities of Ru(III) complex of \textit{bis-} (salicylaldehyde)-$o$-phenylenediimine (saloph) with a variety of axial bases such as imidazole, 2-methylimidazole and pyridine and studied their catalytic properties in the oxygenation of cyclohexene.\textsuperscript{10} Since Ru(III)-dioxygen complexes are more robust as compared to cobalt complexes, an understanding of the thermodynamics and activation parameters of oxygenation of the complexes and catalysis, respectively, will lead to a better understanding of the design of a Ru(III) catalyst for reversible oxygenation and homogeneous catalysis. The present paper deals with the thermodynamics of the oxygenation of Ru(III)-Salen-imidazole and Ru(III)-Saloph-imidazole complexes and the activation parameters of the catalysis of these complexes in the oxygenation of cyclohexene by molecular oxygen. These parameters give an insight into the nature of the active intermediate involved in the oxygen atom transfer reaction catalyzed by Ru(III) complexes.

**Materials and Methods**

The synthesis of Ru(III)-salen-imidazole \textsuperscript{1} and Ru(III)-salophimidazole \textsuperscript{2} and their characterization have been described in an earlier communication.\textsuperscript{11}

The catalytic activity of the dioxygen complexes of \textsuperscript{1} and \textsuperscript{2} were investigated for the oxidation of cyclohexene by molecular oxygen in solution in the temperature range 288–318 K, $\mu = 0.1M$ KCl in 50\% dioxan-water mixture. As described earlier\textsuperscript{11,12} the kinetics of the oxygenation of cyclohexene was followed by measuring the oxygen absorption of the substrate with the help of a manometric set-up attached to a closed thermostatic cell. The product cyclohexene oxide formed in these studies was analyzed on a Shimadzu Gas Chromatograph GC-9A equipped with a CR3A Chromatopac and FDD-1A using a stainless steel column made of carbowax mesh ANAKROM on TCD. H$_2$ gas was used as a carrier. The product was identified by comparing the Chromatograms with those of the authentic sample.

**Results**

The rate of oxygenation of cyclohexene by O$_2$ catalyzed by the superoxo complexes of \textsuperscript{1} and \textsuperscript{2} at a constant catalyst concentration shows a first order dependence with respect to cyclohexene concentration in the range of the catalyst-substrate ratio of 1:10 to 1:100 at all the temperatures studied (Table 1).

Kinetics of the oxidation of cyclohexene at different dioxygen concentrations was studied by varying the partial pressure of O$_2$ (0.2 to 1.0atm) at constant catalyst (1 \times 10^{-3}M) and substrate (0.1M), concentrations at different temperatures stated earlier. The data shows a first order dependence of the rate of oxidation of cyclohexene on oxygen partial pressure.
Based on the kinetic studies of the oxygenation of cyclohexene by complexes 1 and 2 and the products of oxygenation, 2-cyclohexene-1-one and cyclohexene oxide, the mechanism proposed for the oxygenation of cyclohexene is depicted in Scheme 1 (A) for complex 1 and Scheme 1 (B) for complex 2, respectively.

In the proposed mechanism in Scheme 1 (A) complex 1 activates molecular oxygen in a pre-equilibrium step \( K_1 \) to form a superoxo complex of Ru(IV) which reacts in another pre-equilibrium step with a molecule of the olefin to form a ternary Ru (IV)-olefin-superoxo complex \( K_2 \). The rate determining step \( k \) for the reaction is the concerted hydride absorption from the \( \beta \)-position of the substrate in the ternary complex to form the allylic oxidation product, 2-cyclohexene-1-one and the catalyst.

In Scheme 1(B), the first two steps viz. the formation of the Ru(IV) superoxo complex \( K_1 \) and the ternary Ru (IV)-superoxo-olefin complex \( K_2 \) are identical to Scheme 1(A). The rate determining step of the reaction however, involves an oxygen atom transfer to the olefin in the ternary complex with the formation of the epoxide and a Ru\(^V\) = O oxo intermediate which reacts in a fast step with another molecule of the olefin to form the epoxide and the Ru(III) catalyst.

Assuming a steady state concentration of the dioxygen intermediate, the rate equations for the epoxidation of the olefin may be expressed as:

\[
\frac{d [O_2]}{dr} = \frac{kK_1K_2 [C]_r [S] [O_2]}{1 + K_1 [O_2] + K_1 K_2 [O_2] [S]} \quad \ldots (1)
\]

where \( (C)_r = \) total catalyst concentration

\([S] = \) substrate concentration

\([O_2] = \) partial pressure of \( O_2 \).

Rearranging the above rate expression, the final rate law assumes the following form:

\[
\frac{[C]_r}{rate} = \frac{1}{[S]} \left( \frac{1}{kK_2} + \frac{1}{kK_1K_2 [O_2]} \right) + \frac{1}{k} \quad \ldots (2)
\]
The equilibrium constants $K_1$ for the superoxo complexes $1a$ and $2a$ determined directly from equilibrium $O_2$ absorption method as described by Martell et al. By substituting the value of $K_1$ in rate equation (2), the value for $K_2$ and $k$ were obtained by slope and intercept method. The values are tabulated in Table I.

The thermodynamic parameters corresponding to $K_1$ and $K_2$ were calculated from the slopes of $\log K_1$ or $K_2$ vs $1/T$ using Vant Hoff's equation and are tabulated in Table II.

The Gibbs free energy $\Delta G^\circ$ and the entropy of formation $\Delta S^\circ$ of the complexes were calculated from the following equations:

$$\Delta G^\circ = -2.303 \text{ RT} \log K$$

... (3)

and

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

... (4)
Table II

Thermodynamic parameters for the formation of superoxo complex corresponding to $K_1$ and the olefin complex corresponding to $K_2$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$K_1$</th>
<th>$K_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H^\circ$</td>
<td>$\Delta S^\circ$</td>
</tr>
<tr>
<td></td>
<td>(kcal mol$^{-1}$)</td>
<td>(e.u.)</td>
</tr>
<tr>
<td>[Ru(Salen) (Im)Cl]</td>
<td>-19.36</td>
<td>-50.8</td>
</tr>
<tr>
<td>[Ru(Saloph) (Im)Cl]</td>
<td>-18.3</td>
<td>-47.1</td>
</tr>
</tbody>
</table>

* $\Delta S^\circ$ is calculated at 298 °K.

The activation parameters $E_a$ were calculated from the slope of Arrhenius plots i.e. log $k$ (rate constant) vs 1/T. The parameters $\Delta H^\ne$ and $\Delta S^\ne$ were calculated from the slope and intercept of the Eyring equation (5).

$$-\log \left( \frac{k h}{k^* T} \right) = \frac{\Delta H^\ne}{4.6 T} - \frac{\Delta S^\ne}{4.6} \quad \ldots \quad (5)$$

where $k =$ rate constant; $h =$ Planck's constant; $k^* =$ Boltzman constant and $T =$ absolute temperature. The activation parameters are tabulated in Table III.

Table III

Activation parameters for the homogeneous oxidation of cyclohexene

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$E_a$</th>
<th>$\Delta H^\ne$</th>
<th>$\Delta S^\ne$</th>
<th>$\Delta G^\ne^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(kcal mol$^{-1}$)</td>
<td>(kcal mol$^{-1}$)</td>
<td>(e.u.)</td>
<td>(kcal mol$^{-1}$)</td>
</tr>
<tr>
<td>[Ru(Salen) (Im)Cl]</td>
<td>7.6 ± 0.3</td>
<td>7.1 ± 0.2</td>
<td>-40.5 ± 1.5</td>
<td>19.5 ± 0.8</td>
</tr>
<tr>
<td>[Ru(Saloph) (Im)Cl]</td>
<td>7.3 ± 0.5</td>
<td>6.4 ± 0.3</td>
<td>-43.7 ± 2.2</td>
<td>20.0 ± 1.0</td>
</tr>
</tbody>
</table>

* $\Delta G^\ne$ calculated at 308 °K.

Discussion

From the stability data in Table I, it is obvious that the superoxo complex of $\mathbf{1}$ is slightly more stable than that of $\mathbf{2}$. The enthalpies and entropies corresponding to the oxygenation equilibrium $K_1$ are given in Table II. The enthalpy for the formation of the superoxo complex of $\mathbf{1}$ is more exothermic than that for $\mathbf{2}$. Since the axial base imidazole is the same in both the complexes the difference seems to originate in the nature of the Schiff base coordinated to Ru(III). Since saloph has an aromatic ring, one expects some delocalization of the negative charge on the ring with a consequent decrease of charge density on the metal ion as compared to salen. The same behaviour was reported$^{14}$ for Co(II)-porphyrin-imidazole complexes which exhibit less exothermic enthalpy of oxygenation as compared to Co(II)-Schiff base-imidazole complexes because of a greater spread of charge density on
the former complexes. The entropies and enthalpies of the oxygenation of Ru(III)-Schiff base-imidazole complexes are in line with the thermodynamic values reported for the analogous complexes of Co(II)-Schiff bases in the literature.\textsuperscript{9,14} The highly negative entropies in the case of Ru(III)-Schiff base complexes may be attributed to the loss of the translational, vibrational and rotational degrees of freedom of dioxygen on coordination to the metal ion.\textsuperscript{9}

The olefin complexes of 2 are more stable than those of 1 (Table I). These (Table II) have more positive enthalpies and entropies reflecting a lower stability of the olefin complexes when coordinated to the final Ru(IV) centre.

The activation parameters corresponding to the oxygenation of cyclohexene catalyzed by 1 and 2 are given in Table III. The highly negative entropies of activation for the oxygenation of cyclohexene catalyzed by complexes 1 or 2 support the mechanism depicted in Scheme 1, where the Ru(III)-Schiff base catalyst brings molecular oxygen and the olefin closer within the coordination sphere of the metal ion facilitating the formation of the products. A highly negative entropy was also reported\textsuperscript{15} for the Ru(III)-EDTA catalyzed oxidation of cyclohexene to cyclohexanol in the presence of the micellar system CTAB which helps in bringing together the reactant and facilitates oxygen atom insertion to the C-H bond. The enthalpies of activation are endothermic in line with the cleavage of O-O bond in the transition state for the formation of products in both the routes of Scheme I.

The difference in the reactivities of complexes 1 and 2 in catalyzing allylic oxidation versus oxygen atom insertion in the olefin can be sought in the difference in the enthalpies of the superoxo complex formation in 1 and 2 which gives the degree of the negative charge transfer to dioxygen in the complexes. Because of a more exothermic value of enthalpy of superoxo formation, complex 1 has a higher negative charge on the superoxo group as compared to complex 2 which facilitates a heterolytic cleavage of the O-O bond in 1. This fact couples with a greater charge density transfer to the olefin in complex 1 as compared to complex 2 facilitates the \(\beta\)-hydride abstraction in 1 resulting in the formation of 75% of the allylic oxidation product, 2-cyclohexene-1-one.

In complex 2 the charge density on coordinated superoxo group is less than that of 1. In order to facilitate a heterolytic cleavage of O-O bond for the oxygen atom transfer to the olefin, the metal ion undergoes further oxidation to the Ru(V) = O \(\alpha\)xo species. This conclusion is further supported by the fact that in the absence of the olefin the superoxo complex 2 undergoes a facile transformation to Ru(V) = O-saloph-imidazole species which was isolated and characterized.\textsuperscript{12}

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