전이금속 촉매작용의 산화반응과 리간드 효과

김 상 복 *
울산대학교 화학 생명과학부
(2003. 9. 28. 접수)

Transition Metal Catalysed Oxidation Reactions and Ligand Effects in Aprotic Solvents

Sang Bock, Kim*
School of Chemistry and Life Sciences, University of Ulsan, P.O. Box 18, Ulsan 680-749, Korea
(Received September 28, 2003)

요약. 코발트 산소 온반제인 N,N'-ethylenebis(3-methoxysalicylideneiminato)cobalt(II), Co(3MeOsalen)을 25℃에서 합성하였다. 이 촉매와 하이드라조벤젠의 침음 및 가시부분 광спект럼은 파장 범위 200-600 nm에서 비수용액 메탄올을 사용하여 연구하였다. 하이드라조벤젠의 산소와의 산화반응은 메탄올에서 Co(3MeOsalen) 촉매로 사용하였다. 트라이페닐포스핀(PPh3) 존재하에, 반응속도는 감소하였으며 이것은 촉매가 리간드 트라이페닐포스핀과 배위화합된 것으로 추정되며 촉매가 비활성인 Co(3MeOsalen)(PPh3)으로 되어 속도가 급격히 멀어지는 것으로 생각된다. 리간드 트라이페닐포스핀과 하이드라조벤젠의 초기산화속도는 이론속도식, Rate=k1+K1[P]+K2K3[P]2으로 측정되었다. 이것은 리간드가 메탄올 분자보다 더 중심적이고 σ-수지일 것으로 추정된다.
주제어: 리간드 효과

ABSTRACT. Cobalt oxygen carrier complex N,N'-ethylenebis(3-methoxysalicylideneiminato)cobalt(II), Co(3MeOsalen) was prepared at 25℃. UV and visible absorption spectra of the complex and hydrazobenzene were studied in non-aqueous solvent methanol in the range of wavelength 200-600 nm. The oxidation of hydrazobenzene by oxygen in non-aqueous solvent is catalysed by Co(3MeOsalen). In the presence of triphenylphosphine(PPh3), the rate decreases in methanol. This is presumably attributable to the coordination of PPh3 to the Co(3MeOsalen), resulting in the catalytically inactive compound. The initial rates of the oxidation of hydrazobenzene with the ligand triphenylphosphine were measured by the theoretical values of the rates. Rate=k1+K1[P]+K2K3[P]2. This fact would be a poorer σ-donor ligand than methanol.

Keywords: Ligand Effects,

INTRODUCTION

It has been known since the observation of Pfeiffer and his cowokers in 19331 that cobalt(II) schiff's base complexes such as Co(salen), oxygen carrier, form reversible complex with oxygen. There has been considerable recent interest in these compounds because of their relationship to the natural iron-containing oxygen carrier hemoglobin and myoglobin.2

Hemoglobin and myoglobin consists of an iron-porphyrin complex containing the heme group and imidazole group. On oxygenation the sixth coordination site of the iron accepts the dioxygen ligand. Accordingly, the ligands around the iron in oxyhemoglobin are approximately octahedral.3

Co(salen) and Co(3MeOsalen) are square planar with a low spin d^0 electron configuration, Fig. 1.
The binding of an axial, fifth ligand, e.g. triphenylphosphine(PPh₃) leads to a ground state with the unpaired electron in the dₓ² orbital. This electron configuration is a necessary prerequisite for the binding with dioxygen which is called cobalt oxygen carriers.

Cobalt(II) Schiff's base complexes with added axial ligands have been shown to catalyse the oxidation by oxygen of secondary alcohols to ketones, and of phenols to quinones. Kinetic studies have shown that in the oxidation of alcohols and phenols the transition state is a ternary complex of dioxygen, cobalt catalyst (including axial base) and substrate. Thus the reactions resemble an enzyme-catalysed process in which the two substrate, dioxygen and the organic molecule, are brought together by the catalyst.

The effects of bases coordinated trans to dioxygen have been investigated by measurement of the equilibrium constants. Pure σ-bonding can occur by interaction of metal dₓ² orbital with non-bonding electron pairs of the N-ligand (e.g. n BuNH₂). Complexes with strong σ-donor ligands in the axial position, such as primary aliphatic amines form the strongest complexes with dioxygen. This can be attributed to the more stable molecular orbital formed between the oxygen π* orbital and the cobalt dₓ² orbital when the energy of the latter is raised towards the energy of the π* orbital by the axial ligand.

π-donor ligands will enhance the bonding from cobalt to dioxygen. It follows that imidazoles, which are better π-donors than pyridines, produce an increase in the oxygen binding constants of the dioxygen complex of Co(benacen). The strength of the cobalt-oxygen bond should reflect the extent of back-donation of electron density from the filled 3dₓ₀ (or 3dᵧ₀) orbital of the cobalt atom into the π* orbital of the oxygen moiety. Therefore, a good π-donating axial ligand forces more electron density on to the cobalt and enhances the π-bonding between cobalt and oxygen. However, π-acceptor ligand (CO for instance) trans to O₂ will decrease π-electron density on the metal, resulting in a weaker Co-O₂ bond by lowering the dₓ₀, dᵧ₀ orbital. Axial ligands such as P(C₅H₅)₃, AsPh₃ and S(CH₃)₂ were considered to have not only σ-donor, but also π-acceptor properties.

In this paper we show that the oxidation of hydrazobenzene catalysed by Co(3MeOsalen) has been studied in the non-aqueous solvent methanol. When a σ- and π-donor ligand, PPh₃, was added to the reaction mixture of hydrazobenzene, the effect of added axial ligand will be enabled to be investigated.

**EXPERIMENTAL**

Co(3MeOsalen) was prepared under dry nitrogen according to the method of Diehl et al. The reaction mixture was prepared by mixing the catalyst solution, O₂ saturated methanol, and the substrate solution using a syringe. The catalyst (5.20×10⁻⁴ M) was dissolved in methanol by stirring magnetically under dry nitrogen gas. The catalyst solution was injected by syringe into a 10 ml volumetric flask and diluted with O₂ saturated methanol to 9.0 ml. The substrate hydrazobenzene (3.33×10⁻² M) was easily dissolved in the methanol after passing nitrogen gas continuously and stirring magnetically for a few minutes. The solution was moved with a syringe and put into a 10 ml volumetric flask and diluted under nitrogen to 10 ml.

The catalyst solution (9.0 ml) and substrate solution (1.0 ml) were warmed in a thermostat for about 15 minutes at 25.0 °C. The two solutions were then mixed, shaken, a portion transferred to a UV cell and the initial gradients, (dA/dt)₀, were measured in the UV-visible spectrophotometer thermostatted at 25.0 °C. The time was taken to be zero when the catalyst and substrate were mixed.

*Journal of the Korean Chemical Society*
RESULTS AND DISCUSSION

Initial rates $R_0$ were employed and calculated from the slopes of tangents at time $t=0$:

$$R_0 = 1/\Delta \Lambda_0 (d\Lambda/d\tau)_0$$

where $l$ is the path length, $\Delta \Lambda$ the difference of the extinction coefficients of product and reactants, $(d\Lambda/d\tau)_0$, initial tangents to the absorbance/time traces. The reaction was followed with Co(3MeOsalen) ($7.43 \times 10^4 \text{ M}$) and the appropriate ligand: triphenylphosphine ($1.91 \times 10^5 \text{ M}$).

When the initial rate $R_0$ is plotted against the hydrazobenzene concentration, the plots are linear. Fig. 2. We have demonstrated that the autoxidation of hydrazobenzene in anhydrous methanol was found to be first order in air or $O_2$, Table 1. The rate constants of the reaction mixture were calculated to be $3.85 \times 10^4 \text{ sec}^{-1}$ in the $O_2$ saturated methanol and $1.98 \times 10^6 \text{ sec}^{-1}$ in the air saturated methanol.

As the ligand triphenylphosphine, Table 2. the initial rate was decreased, Fig. 3, which is in good agreement with the experimental values. The destruction of catalyst system Co(3MeOsalen)(O$_2$) could be due to the catalyst becoming coordination with triphenylphosphine in both $Z$ axis sites of the catalyst. The ligand could affect dioxygen binding to the catalytic system Co(3MeOsalen)(O$_2$) as triphenylphosphine is usually considered to have not only $\sigma$-donor but also $\pi$-acceptor properties. Table 2. Triphenylphosphine is an interesting ligand as it decrease the rate of the oxidation of hydrazobenzene in methanol. This may be due to the destruction of the catalytic activity because the catalyst becoming coordinated with triphenylphosphine at both $Z$ axis sites of the complex e.g. Co(3MeOsalen)-(PPh$_3$). The second triphenylphosphine molecule may prevent oxygen binding to the complex. It seems more likely that it is due to the specific solvent effect of methanol through coordination to the cobalt catalyst.

The initial rates, $R_0$, of the oxidation of hydrazobenzene with the ligand triphenylphosphine (PPh$_3$) were measured, Table 2. As the triphenylphosphine concentrations increased, the initial rates were found to

---

**Table 1.** Effect of varying hydrazobenzene concentration, $[H_2AB]$, on the autoxidation of hydrazobenzene in $O_2$ and air saturated methanol at 25.0°C

<table>
<thead>
<tr>
<th>NO.</th>
<th>$[H_2AB]$/$10^{-3}$ M</th>
<th>$O_2$ saturated methanol</th>
<th>air saturated methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(d\Lambda/d\tau)/10^3 \text{ sec}^{-1}$</td>
<td>$R_0/10^4 \text{ M sec}^{-1}$</td>
<td>$(d\Lambda/d\tau)/10^3 \text{ sec}^{-1}$</td>
</tr>
<tr>
<td>1</td>
<td>0.102</td>
<td>0.657</td>
<td>0.0469</td>
</tr>
<tr>
<td>2</td>
<td>0.388</td>
<td>2.29</td>
<td>0.161</td>
</tr>
<tr>
<td>3</td>
<td>0.411</td>
<td>3.05</td>
<td>0.215</td>
</tr>
<tr>
<td>4</td>
<td>2.45</td>
<td>10.0</td>
<td>0.704</td>
</tr>
<tr>
<td>5</td>
<td>4.90</td>
<td>22.6</td>
<td>1.59</td>
</tr>
<tr>
<td>6</td>
<td>7.35</td>
<td>30.1</td>
<td>2.12</td>
</tr>
<tr>
<td>7</td>
<td>9.80</td>
<td>41.4</td>
<td>2.91</td>
</tr>
<tr>
<td>8</td>
<td>14.7</td>
<td>60.0</td>
<td>4.22</td>
</tr>
</tbody>
</table>

$\lambda=315 \text{ nm (} \Delta \Lambda = 1.61 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$ (NO. 1-3) and $\lambda=437 \text{ nm (} \Delta \Lambda = 5.09 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1})$ (NO. 4-8). $\Delta \Lambda_{\lambda} = 7.04 \times 10^2 \text{ M} \cdot \text{cm}$. $R_0 = \Delta \Lambda_{\lambda} (d\Lambda/d\tau)_0$.

2003, Vol. 47, No. 6
Table 2. Effect of varying triphenylphosphine concentration ([PPh₃]) on the oxidation of hydrazobenzene (H₂AB) in O₂ saturated methanol at 25 °C

<table>
<thead>
<tr>
<th>[PPh₃] 10⁻⁴ M</th>
<th>(dA/dt) 10⁻⁴ sec⁻¹</th>
<th>R₀/10⁻⁸ M·sec⁻¹</th>
<th>Rₒ/10⁻⁸ M·sec⁻¹</th>
<th>k/10⁻⁸ M⁻²·sec⁻¹</th>
<th>(k−kₒ)/10⁻⁸ M⁻²·sec⁻¹</th>
<th>[PPh₃]k−kₒ)/10⁻⁷ M⁻¹·sec⁻¹</th>
<th>k−kₒ)/10⁻⁵ M⁻¹·sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>14.2</td>
<td>9.99</td>
<td>9.99</td>
<td>11.0</td>
<td>0</td>
<td>0.909</td>
<td></td>
</tr>
<tr>
<td>0.529</td>
<td>6.25</td>
<td>4.40</td>
<td>4.32</td>
<td>4.80</td>
<td>-6.20</td>
<td>0.853</td>
<td>2.19</td>
</tr>
<tr>
<td>1.0</td>
<td>5.54</td>
<td>3.90</td>
<td>3.82</td>
<td>4.25</td>
<td>-6.75</td>
<td>1.61</td>
<td>2.36</td>
</tr>
<tr>
<td>1.6</td>
<td>4.83</td>
<td>3.40</td>
<td>3.32</td>
<td>3.69</td>
<td>-7.31</td>
<td>2.19</td>
<td>2.71</td>
</tr>
<tr>
<td>2.7</td>
<td>4.47</td>
<td>3.15</td>
<td>3.07</td>
<td>3.41</td>
<td>-7.59</td>
<td>3.56</td>
<td>2.93</td>
</tr>
<tr>
<td>3.77</td>
<td>4.26</td>
<td>3.00</td>
<td>2.92</td>
<td>3.24</td>
<td>-7.76</td>
<td>4.86</td>
<td>3.09</td>
</tr>
<tr>
<td>4.88</td>
<td>3.76</td>
<td>2.65</td>
<td>2.57</td>
<td>2.86</td>
<td>-8.14</td>
<td>5.99</td>
<td>3.49</td>
</tr>
</tbody>
</table>

Fig. 3. Plots of k against [PPh₃]. O₂ saturated methanol, 250 °C, λ=315 nm, [Co(3MeOsalen)]=4.78×10⁻⁵ M, [H₂AB]=1.95×10⁻⁴ M. Solid curve: experimental value; dotted curve: theoretical value.

When the initial rates were plotted against the triphenylphosphine concentrations, a curve was formed, Fig. 3. Theoretical values of the rates, Table 3, were calculated from Eq. 2:

\[
\text{Rate} = k = \frac{k_1 + k_x [P]}{1 + k_1 [P] + k_2 [P]^2}
\]

Where \(k = (R_0 - k[S][O_2]) / [S][O_2][C]_r\)

The rate \(k_2[S][O_2]\) is the autoxidation of hydrazobenzene whose observed value of 7.51×10⁻¹⁰ M·sec⁻¹, Fig. 2, is independent of triphenylphosphine concentration. The second term \(k_1[S][O_2][C]\) is the rate of oxidation catalysed by Co(3MeOsalen) without an axial ligand. The third term is the rate of oxidation of hydrazobenzene catalysed by Co(3MeOsalen)-(PPh₃). The fourth term \(k_2=0\) because it is assumed that the complex Co(3MeOsalen)(PPh₃) is catalytically inactive, the second triphenylphosphine molecule preventing oxygen binding to the complex. Eq. 5 is rearranged to Eq. 6.

Journal of the Korean Chemical Society
Table 3. Theoretical values of the rates calculated from Eq. 2 using the values of \(k_i\), \(k_1\), \(K_i\), and \(K\).

<table>
<thead>
<tr>
<th>[PPh] (10^{-4}) M</th>
<th>[P] (10^{-6})</th>
<th>(1+K) [P]</th>
<th>(K_iK_iP)</th>
<th>((k_i+k_iK_iP)) (10^{-3})</th>
<th>(1+K_iP+K_iK_iP)</th>
<th>(k/10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.529</td>
<td>0.279</td>
<td>3.41</td>
<td>0.0686</td>
<td>1.76</td>
<td>3.48</td>
<td>5.06</td>
</tr>
<tr>
<td>1.09</td>
<td>1.19</td>
<td>5.97</td>
<td>0.293</td>
<td>2.45</td>
<td>6.26</td>
<td>3.91</td>
</tr>
<tr>
<td>1.60</td>
<td>2.56</td>
<td>8.29</td>
<td>0.629</td>
<td>3.08</td>
<td>8.92</td>
<td>3.45</td>
</tr>
<tr>
<td>2.70</td>
<td>7.29</td>
<td>13.3</td>
<td>1.79</td>
<td>4.43</td>
<td>15.1</td>
<td>2.93</td>
</tr>
<tr>
<td>3.77</td>
<td>14.2</td>
<td>18.2</td>
<td>3.49</td>
<td>5.75</td>
<td>21.7</td>
<td>2.65</td>
</tr>
<tr>
<td>4.88</td>
<td>23.8</td>
<td>23.3</td>
<td>5.85</td>
<td>7.11</td>
<td>29.2</td>
<td>2.43</td>
</tr>
</tbody>
</table>

\[
k= (k_i+k_iK_iP)(1+K_iP+K_iK_iP)
\]

The rate of reaction \(k\) is given by Eq. 2.

The total concentration of the catalyst \([C]_t\) is given by Eq. 7.

\[
[C]_t = [C]+[CP]+[CP_2]
\]  

Substituting Eq. 3 and 4 into 7 gives:

\[
[C]_t = [C]+K_i[CP]+K_iK_i[CP_2]
\]  

Eq. 8 gives rise to

\[
[C] = \frac{[C]_t}{1+K_i[CP]+K_iK_i[CP_2]}
\]  

Substituting Eq. 9 into 6 gives Eq. 2. The constants \(k_i\), \(K_i\), and \(K\) were determined by reciprocal plots from Eq. 2, and \(k_i\) is known to be \(1.10 \times 10^6\) M\(^{-1}\) sec\(^{-1}\) when \([P]=0\), Table 2.

When \([P]\) is small, Eq. 2 reduces to Eq. 10 as \(K_i[CP] \gg K_iK_i[CP_2]\).

\[
k = \frac{k_i+k_iK_iP}{1+K_iP}
\]

Subtracting \(k_i\) from both sides,

\[
\frac{P}{k-k_i} = \frac{k_iK_i}{1+K_iP}
\]

When \(P/(k-k_i)\) is plotted against \(P\) from Eq. 10, \(K_i\) and \(k_i\) were obtained graphically, Table 2.

When \([P]\) is large, Eq. 2 reduces to Eq. 11 as \(k_i \ll k_iK_i[CP]\) and \(1 \ll K_i/P\), \(1/k\) is plotted against \(P\) from Eq. 11 and \(K_i\) was determined graphically, Table 2.

As the theoretical values of the initial rates agreed fairly well with experimental observations, Fig. 3, it is suggested that the catalyst Co(3MeOsalen) was associated with triphenylphosphine which would be a poorer \(\sigma\) donor ligand compared with methanol molecule and the reaction rate therefore decreased. The large \(K_i\) value \(K_i=4.56 \times 10^6\) dm\(^3\) mol\(^{-1}\) means that the equilibrium to Co(3MeOsalen)(PPh\(_3\)) was soon achieved and was ready to associated with triphenylphosphine and became Co(3MeOsalen)-(PPh\(_3\)) which is catalytically inactive and the rates were then expected to decrease quickly.

Acknowledgment. This work was supported in part by the grant from University of Ulsan.

REFERENCES


