Substitution Reaction of $\textit{trans}$-dichloro-$\textit{bis}$- (ethylenediamine) Cobalt (III) Chloride and Phenylalanine - A Kinetics and Mechanism Study

K. Asemave*, S. G. Yiase, S. O. Adejo, B. A. Anhwange

1 Department of Chemistry, Benue State University, P.M.B. 102119, Makurdi, Nigeria

* Author to whom correspondence should be addressed; E-Mail: kasemave@bsum.edu.ng.

Article history: Received 15 February 2012, Received in revised form 15 March 2012, Accepted 18 March 2012, Published 25 March 2012.

Abstract: The kinetics and mechanism of substitution of chloride ion in $\textit{trans}$-dichloro-$\textit{bis}$-(ethylenediamine) cobalt(III) chloride, $\{\textit{trans}-[\text{Co(en)}_2\text{Cl}_2]\text{Cl}\}$ with phenylalanine in aqueous media at ionic strength of 0.01M NaNO$_3$ is reported. Shifts in IR peaks from 1555.44 to 1571 cm$^{-1}$ and 1301.29 to 1050 cm$^{-1}$ were indicative of complexation of the phenylalanine with the complex via the carboxylate group. The reaction was monitored under pseudo first-order conditions using spectrophotometric method. The reaction followed a total order of second order kinetics; first order with respect to each of the reactants, with the rate equation; $-d[\textit{trans}-[\text{CoCl}_2\text{en}]_2]\text{Cl}]/dt = k_2[\textit{trans}-[\text{Co(en)}_2\text{Cl}_2]\text{Cl}][\text{A}]$. The value of $k_2$ was obtained as $2.97 \times 10^{-1} \pm 0.0337$ dm$^3$ mol$^{-1}$ s$^{-1}$. Values of activation parameters, $\Delta H^*$ and $\Delta S^*$ were evaluated as 96.63 kJ mol$^{-1}$, 15.71 J mol$^{-1}$ K$^{-1}$, respectively. The positive value of the entropy of activation ($\Delta S^*$) implies a dissociative mechanism for the substitution reaction.

Keywords: Kinetics, Dissociative Mechanism, Substitution reaction, phenylalanine

1. Introduction

Amino acids are important low molecular weight ligands in biological systems. It is well known that some metal ions are essential for living organisms. They play important roles in the synthesis and transport of organic molecules and in catalyzing acid-base and redox processes of biological systems. Their involvement in Cu$^{II}$ transport in blood has been reported [1, 2]. Acidic and basic amino acids can in principle bind to metal ions through the amino, carboxylate, thiol groups or guanidinium groups, respectively. However, the glycine-like coordination through the $\alpha$-amino and
α-carboxylate groups is most common among these amino acids at neutral pH [1-5]. When incorporated into proteins, the side chain carboxylate groups of the aspartyl and glutamyl residues constitute the metal binding sites, e.g. zinc enzymes such as carboxypeptidases A and B, alkaline phosphatase and in iron proteins such as hemerythrin [1]. On the other hand, the side chains of the basic amino acids are not known to be metal binding sites in proteins. They are important as a positive charge carrier [1]. Also antibacterial, anticancer and antifungal activities have been linked to amino acid complexes of Co(III) and other transition metals. The interaction between some amino acid with mercury to form complexes has been useful in the development of detoxifying agents toward mercury poisoning [6, 7]. Thus it is important to make more kinetic investigation of interactions between transition metal with amino acid. In this research work, the substitution reaction between trans-[Co(en)2(Cl)2]Cl with phenylalanine is investigated by spectrophotometric method at constant ionic strength = 0.01M NaNO₃, in aqueous media.

2. Experiments

2.1. Materials

Co(II) chloride hexahydrate (Hopkins & Williams), NaNO₃ (M & B), phenylalanine (Qualikems), ethylenediammine (Qualikems), and concentrated hydrochloric acid (M & B), were received in analytical grade and used without further purification. Distilled water was used for solution preparations. Nicolet 100-FTIR spectrophotometer was used for the product analysis. The complex trans-[CoCl₂(en)₂]Cl was prepared according to the literature [1]. The visible absorption spectrum (λ_max = 618 nm, ε_max = 37.60 M⁻¹ cm⁻¹) was in good agreement with the published spectra. The molar conductivity of the complex was obtained as 270 Ω⁻¹ cm² mol⁻¹ [5, 8].

2.2. Stoichiometry of the Reaction

Stoichiometry of reaction was determined by spectrophotometric titration using the mole ratio method. Reaction mixtures containing various concentrations of phenylalanine in the range of 2.00 × 10⁻⁴ – 6.00 × 10⁻⁴ moldm⁻³ with trans-[CoCl₂(en)₂]Cl at constant I = 0.01 moldm⁻³ (NaNO₃) were allowed to go to completion. The absorbance of the solution was measured at λ = 618nm. The equivalent points was determined from the plot of absorbance of each solution against the mole ratio, [amino acid]/[trans-[CoCl₂(en)₂]Cl} [5, 9].

2.3. Product Analysis

trans-[CoCl₂(en)₂]Cl and the amino acids were mixed respectively and allowed to stand for three hours; in order to obtained the substituted product. The substituted product collected were dried
and kept. Nicolet 100-FTIR spectrophotometer was used to ascertain the formation of the product [10 - 12].

2.4. Kinetic Studies

Stoichiometry of reactions was determined at \( \lambda = 618 \text{nm} \) by spectrophotometric titration using mole ratio method, [9]. The rate of the reaction was monitored spectrophotometrically, following the decrease in concentration of \( \text{trans}[[\text{CoCl}_2(\text{en})_2]\text{Cl} \) at 618nm. The kinetic measurements were made under pseudo-first order conditions at temperature range of 30\(^\circ\)C to 55\(^\circ\)C. The rate constant was computed from the plot of \( \ln [A_t-A_\infty]/A_0-A_\infty \) against time. Plot of \( \log k_1 \) vs. \( \log [\text{phenylalanine}] \) was obtained. Kinetic activation parameters (activation entropy and enthalpy) were obtained from Eyring’s plots, \( \ln (k/T) \) vs. \( 1/T \), [3, 13 and 14].

3. Results and Discussion

3.1. Product Analysis

The IR spectra of the phenylalanine and the substituted complex showed a shift in peaks from 1555.44 to 1571 cm\(^{-1}\), 1301.29 to 1050 cm\(^{-1}\), all indicative of complexation of the amino acid with complex, \( \text{trans}[[\text{CoCl}_2(\text{en})_2]\text{Cl} \) [10 - 12].

3.2. Stoichiometry of the Reaction

The calculation of the mole ratio at the equivalence point of the spectrophotometric titration gave the Stoichiometry of the reaction as 1:1. Similar Stoichiometry has been reported for the reaction between the complex \( \text{trans}[[\text{CoCl}_2(\text{en})_2]\text{Cl} \) and the amino acids alanine, valine and cysteine, [3, 5].

\[
\text{trans}[[\text{CoCl}_2(\text{en})_2]\text{Cl} + A \rightarrow \text{trans}[[\text{CoCl}_2(\text{en})_2]\text{Cl}; \quad A = \text{phenylanine}
\]

\( \text{trans-dichloro-bis-(ethylenediammine) cobalt(III) chloride (trans-[CoCl}_2(\text{en})_2]\text{Cl}) \)
3.3. Determination of Rate Constant and Order

The pseudo-first order plots of ln \([A_t-A_\infty]/ A_0-A_\infty\] vs. time for the reaction is linear as shown in Figure 2. The linearity of the plot is a clear indication that the reaction is first order in \emph{trans-}[CoCl}_2 (en)]_2 Cl. Table 1 summarises the values of \(k_{obs}\) and \(k_2\) of the substitution reaction of the complex with phenylalanine. A plot of log \(k_1\) vs. log [phenylanine] in Figure 3 shows also a linear relationship; with the slope of 1.00, explicitly implying that the reaction is also first order with respect to phenylanine. Hence, the reaction is second order overall, which is in agreement with other works, [3, 5, and 8]. Therefore the rate equation for the reaction is

\[
-d[\text{trans-}[\text{CoCl}_2 (\text{en})]_2 \text{Cl}]/dt = k_2[\text{trans-}[\text{Co (en)}_2\text{Cl}_2]\text{Cl}][\text{A}].
\]

The second order rate constant, \(k_2\) was then found to be \(2.97 \times 10^{-1} \pm 0.0337 \text{dm}^3\text{mol}^{-1}\text{s}^{-1}\).

Figure 2. The Pseudo First-Order Plots of \(\ln [A_t-A_\infty]/ A_0-A_\infty\) vs. Time for the Complex
Table 1. Pseudo-First Order and Second Order Rate Constant Data for the Reaction at 26 (±0.1°C)

<table>
<thead>
<tr>
<th>[NaNO₃]/10⁻³ moldm³</th>
<th>[phenylalanine]/10⁻³ moldm³</th>
<th>k₂obs/(10⁻³s⁻¹)</th>
<th>K₂/10⁻¹dm³mol⁻¹s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>9.00</td>
<td>2.50</td>
<td>2.77</td>
</tr>
<tr>
<td>3.50</td>
<td>6.00</td>
<td>1.70</td>
<td>2.83</td>
</tr>
<tr>
<td>5.00</td>
<td>4.50</td>
<td>1.40</td>
<td>3.11</td>
</tr>
<tr>
<td>6.50</td>
<td>3.00</td>
<td>0.80</td>
<td>2.66</td>
</tr>
<tr>
<td>7.50</td>
<td>2.00</td>
<td>0.70</td>
<td>3.50</td>
</tr>
</tbody>
</table>

Table 2. Temperature Dependent Pseudo First-Order Rate Constant Data for the Reaction

<table>
<thead>
<tr>
<th>Tempt. (°C)</th>
<th>K₂obs/10⁻³(s⁻¹) Phenylalanine</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>21.00</td>
</tr>
<tr>
<td>50</td>
<td>10.50</td>
</tr>
<tr>
<td>45</td>
<td>5.20</td>
</tr>
<tr>
<td>40</td>
<td>3.50</td>
</tr>
<tr>
<td>35</td>
<td>1.80</td>
</tr>
</tbody>
</table>
3.4. Temperature Dependence rates of reaction

The reaction was investigated at the temperature range 35°C and 55°C (±0.1°C). It was found that $k_{obs}$ increases with increase in temperature as presented in Table 2. Values of $\Delta H^*$ and $\Delta S^*$ were evaluated as presented in Figure 4. They are 96.63 kJmol$^{-1}$ and 15.71 Jmol$^{-1}$ K$^{-1}$ respectively. The positive value of activation entropy ($\Delta S^*$) implies dissociative mechanism for this substitution reaction, [5, 8, and 15]. Therefore the following mechanism has been proposed for the reaction;

$$\begin{align*}
\text{trans-[CoCl}_2\text{(en)}_2\text{Cl]} & \quad \text{slow} \quad \rightarrow \quad \text{trans-[CoCl(en)}_2\text{Cl}_2] \\
\text{trans-[CoCl(en)}_2\text{Cl}_2 + A & \quad \text{fast} \quad \rightarrow \quad \text{trans-[CoClA(en)}_2\text{Cl}_2]
\end{align*}$$
4. Conclusion

Kinetic and mechanistic studies of the substitution reaction of phenylanine with trans-[CoCl$_2$(en)$_2$]Cl were carried at the temperature range of 35°C to 55°C. The amino acid evidently coordinated to the Co (III) complex through the carboxylate group. Rate constant $k_2$, of the reaction was obtained as $2.97 \times 10^{-1} \pm 0.0337$ dm$^3$ mol$^{-1}$ s$^{-1}$. Enthalpy and Entropy of activation ($\Delta H^*$, $\Delta S^*$), were evaluated to be 96.63 kJmol$^{-1}$, 15.71 Jmol$^{-1}$ K$^{-1}$ respectively. From value of the activation entropy ($\Delta S^*$), the substitution reaction follows a dissociative mechanism.

5. Recommendations

Phenylalanine has substituted chloride ion in trans-dichloro-bis-(ethylenediammine)cobalt(III) chloride. Thus, it may be used as detoxifying agent towards transition metal atoms; Also the catalytic activities of Co(III) carboxylate of the phenylanine complex could be tested in organic synthesis, such as manufacturing of cyclohexanone and polymerization of butadiene rubber.

Acknowledgement

I want to appreciate the Department of Chemistry, Benue State University, Makurdi Nigeria, where this research was carried out.
References


