Europium(III) 및 Ytterbium(III) \( N,N'\)-Ethylenebis[2-(o-hydroxyphenyl)glycine] 복합체의 해리 반응속도론

목원대학교 화학과,  \(^1\)공주대학교 자연과학 화학과
(1995. 1. 11 접수)

Dissociation Kinetics of \( N,N'\)-Ethylenebis[2-(o-hydroxyphenyl)glycine] Complexes of Europium(III) and Ytterbium(III)

Ki-Young Choi\(^*\), Hyung Seung Kim, Suk Nam Choi\(^1\), and Hae Il Ryu\(^1\)

Department of Chemistry, Mokwon University, Taehyon 301-729, Korea
\(^1\)Department of Chemistry, Kongju National University, Kongju 314-701, Korea
(Received January 11, 1995)

In recent years the two phenolate-containing multidentate ligand with \( N,N'\)-ethylenebis[2-(o-hydroxyphenyl)glycine] (EHPG), an EDTA-type framework has been developed as ligand having high affinities for \( \text{Ga}^{3+}, \text{In}^{3+} \) and \( \text{Gd}^{3+} \) as well as \( \text{Fe}^{3+} \), as radiopharmaceuticals, and as magnetic resonance paramagnetic contrast imaging agents.\(^5\) Recently EHPG was also used as an active site model of the iron transport protein transferrin,\(^5\) and the stabilities of the complexes with variety of metal ions have been determined.\(^4\) Studies on the dissociation kinetics of lanthanide complexes of polyaza and polyaminopolycarboxylates demonstrated that the exchange occurs via both acid-dependent and acid-independent pathways.\(^6\) The rate-determining step in the acid-catalyzed mechanism was assigned either to slow rupture of one of the metal-carboxylate bonds following the protonation of a carboxylate group or to slow transfer of the hydronium ion from the protonated carboxyl oxygen to the neighboring nitrogen site, causing the metal nitrogen bond to break. The acid-independent mode was assumed to proceed via a binuclear intermediate, \( \text{LnYM} \), in which the lanthanide and the metal ion are bound to opposite ends of the ligand. The influence of metal ion, ligand topology, buffer anion and electrolyte on the rate and mechanism of both dissociative and associative pathways has been also reported by our and other research groups.\(^7\)\(^-\)\(^9\) However, this effect has not been studied systematically and there is no general explanation.

To further understand the factors involved in the chelating kinetics, we hereby report the result of the dissociation kinetics of Eu(III) and Yb(III) complexes of \( N,N'\)-ethylenebis[2-(o-hydroxyphenyl)glycine] (EHPG) (Chart 1).

**EXPERIMENTALS**

Stock solutions of Eu\(^{3+} \) and Yb\(^{3+} \) were prepared from \( \text{Eu}_2\text{O}_3 \) and \( \text{Yb}_2\text{O}_3 \) (Aldrich, 99.99%) and their concentrations were determined by complexometric titration using Xylenol Orange as an indicator. \( N,N'\)-ethylenebis[2-(o-hydroxyphenyl)glycine] (EHPG) was obtained from Aldrich and purified
by successive recrystallization from a hot basic solution by adding perchloric acid and cooling. The concentration of a EHPG stock solution was determined by titration against a standard Cu(CIO$_4$)$_2$ solution using murexide as an indicator. Complex solutions were made by mixing appropriate amount of lanthanide perchlorate and a slight excess of ligand. All other chemicals used were of analytical grade without further purification. Distilled water was used for all solutions.

The ionic strength of the sample solution was adjusted to 0.10 M with NaClO$_4$ and sodium acetate was used as a buffer. The pH measurements were made by a Beckman Model P 71 pH meter fitted with a Beckman combination electrode. The hydronium ion concentrations were established from the measured pH values by procedures previously reported. Kinetic measurements were carried out on a Hi-Tech stopped-flow spectrophotometer interfaced with Scientific data acquisition system. The temperature of the reaction mixture was maintained at 25.0±0.1°C with the use of a Lauda RM 6 circulatory water bath. Since the Ln (EHPG)$^-$ complexes do not show appreciable absorption in the UV or visible region, Cu$^+$ was used as a scavenger of free ligand and the reaction kinetics was followed by monitoring the growth in absorbance due to the formation of Cu(EHPG)$^{2+}$ complex at 285 nm. The concentration of the Ln (EHPG)$^-$ was 1.0×10$^{-4}$M, while that of the exchanging Cu$^{2+}$ ion was either constant at 2.0×10$^{-3}$ M or varied between 2.0×10$^{-4}$ and 2.0×10$^{-3}$ M. The reaction was studied over the pH range of 4.03−5.26.

**RESULTS AND DISCUSSION**

Since the stability constants of Ln(EHPG)$^-$ complexes are much lower than that of the corresponding Cu(EHPG)$^{2+}$ complex, the displacement of Ln$^{3+}$ ions from the Ln(EHPG)$^-$ complexes is complete in the presence of excess Cu$^{2+}$ ions

$$\text{Ln(EHPG)$^-$ + Cu$^{2+}$ → Cu(EHPG)$^{2+}$ + Ln$^{3+}$} \quad (1)$$

The experimental data show excellent pseudo-first-order reaction rates. The rate of dissociation of Ln(EHPG)$^-$ was independent of [Cu$^{2+}$], suggesting no appreciable Cu$^{2+}$ ion attack on the Ln$^{3+}$ complex. The concentration of Cu$^{2+}$ ion was varied by a factor of 10, and the observed rate constant ($k_{obs}$) values were within 5% of the average value of $k_{obs}$ at a given pH. Such independence of [Cu$^{2+}$] in the dissociation kinetics of lanthanide complexes has been observed by other workers.$^{5,7,12,13}$ Plots of $k_{obs}$ versus [H$^+$] at various acetate buffer concentrations as shown in Fig. 1 always deviated from linearity. The proton dependence upon the rate decreased reaching a saturation condition with a shift from first-to zero-order dependence. Eq. (2) accounts

$$k_{obs} = \frac{a[H^+]}{1+b[H^+]} \quad (2)$$

for the experimental behavior which reduce to zero-order dependence when 1< b[H$^+$]. The experimental data fitted with the linear functional form as shown in Fig. 2. The terms a and a/b from Eq. (3) could be obtained. In analogy with previous
Fig. 2. Plots of [H⁺]/κ₂ versus [H⁺] for the dissociation kinetics of Eu(EHPG)⁺ at different acetate buffer concentrations ([Eu(EHPG)⁺] = 1.0 × 10⁻⁴ M, [Cu⁺] = 2.0 × 10⁻³ M, T = 25.0 ± 0.1 °C, I = 0.10 M (NaClO₄); [Acetate] = 10 mM (O); 25 mM ( ); 50 mM ( ).)

Table 1. Values of κ₄ and κ₅ for dissociation reactions of Ln(EHPG)⁺ at 25.0 ± 0.1 °C and I = 0.10 M (NaClO₄)

<table>
<thead>
<tr>
<th>Ln⁺</th>
<th>10^3[OAc⁻], M</th>
<th>κ₄, s⁻¹</th>
<th>κ₅, M⁻¹s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu³⁺</td>
<td>1.0</td>
<td>5.02</td>
<td>2.73 × 10⁸</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>5.59</td>
<td>2.74 × 10⁸</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>6.60</td>
<td>2.71 × 10⁸</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>7.70</td>
<td>2.76 × 10⁸</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>8.86</td>
<td>2.69 × 10⁸</td>
</tr>
<tr>
<td>Yb³⁺</td>
<td>1.0</td>
<td>2.46 × 10⁻¹</td>
<td>5.93 × 10⁹</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>2.52 × 10⁻¹</td>
<td>6.01 × 10⁹</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>2.42 × 10⁻¹</td>
<td>5.86 × 10⁹</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>2.48 × 10⁻¹</td>
<td>5.97 × 10⁹</td>
</tr>
</tbody>
</table>

\[
\frac{[H^+]}{k_{obs}} = \frac{1}{a} + \frac{b}{a}[H^+] \quad (3)
\]

Fig. 3. Plots of κ₄ versus [OAc⁻] for the dissociation kinetics of Eu(EHPG)⁺ ([Eu(EHPG)⁺] = 1.0 × 10⁻⁴ M, [Cu⁺] = 2.0 × 10⁻³ M, T = 25.0 ± 0.1 °C, I = 0.10 M (NaClO₄)).

dependence. This fact may be attributed to the increase in coordination site of Eu³⁺ compared to that of Yb³⁺.³ The dependence of κ₄ on the acetate buffer concentration can be given by

\[
k_{obs} = k'_{d} + k_{obs}[OAc⁻] \quad (4)
\]

Fig. 3 shows that the straight line was obtained by plotting κ₄ versus [OAc⁻], which indicates a first-power dependence on acetate buffer concentration. The values of the specific rate constant (κ₄, k₄·obs, and k₅) calculated from the data are given in Table 2. The mechanism of the dissociation of Ln(EHPG)⁻ complexes seems to be similar to that of the dissociation of other polyaminopolycarboxylate complexes previously reported.³ In these mechanisms, the Ln-carboxylate bonds are rapidly formed and broken, allowing attachment of H⁺ or Cu⁺² to dissociated carboxylate. Presumably, the slow step involves the rupture of a Ln-N bond subsequent to the formation of a protonated LnLH intermediate.

The effect of the metal and ligand on the dissociation rate constant can be considered by comparing the values in Table 2 along with the other lanthanide polyaminopolycarboxylate complexes.³⁻⁷⁻¹⁹
Table 2. Rate constants for dissociation reactions of lanthanide complexes of polyaminopolycarboxylate at 25.0±
0.1°C and I = 0.10 M (NaClO₄)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$k'_2$, s⁻¹</th>
<th>$k_2$, M⁻¹s⁻¹</th>
<th>$k_n$, M⁺⁺s⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(EHPG)⁺⁻</td>
<td>(2.47±0.04)×10⁻¹</td>
<td>(4.35±0.13)×10¹</td>
<td>(2.73±0.03)×10⁶</td>
<td></td>
</tr>
<tr>
<td>Yb(EHPG)⁺⁻</td>
<td>*</td>
<td>*</td>
<td>(5.94±0.06)×10⁴</td>
<td></td>
</tr>
<tr>
<td>Eu(EDTA)⁻⁻</td>
<td>*</td>
<td>*</td>
<td>(2.28±0.05)×10²</td>
<td>17</td>
</tr>
<tr>
<td>Yb(EDTA)⁻⁻</td>
<td>*</td>
<td>*</td>
<td>7.60±0.80</td>
<td>18</td>
</tr>
<tr>
<td>Eu(ENDPDA)⁻⁻</td>
<td>(3.60±0.50)×10⁻¹</td>
<td>5.80±0.60</td>
<td>(4.26±0.10)×10⁴</td>
<td>19</td>
</tr>
</tbody>
</table>

*Not observed. In this Table $k'_2$ and $k_n$ are rate constants of acid-independent and acid-catalyzed dissociation rates of the Ln⁺⁺ complexes.

The consistent decrease in the acid-independent and acid-catalyzed dissociation rates of the Ln (EHPG)⁺⁻ complexes from Eu⁺⁺ to Yb⁺⁺ parallels the thermodynamic stability of these complexes with decreasing ionic size or increasing charge density of Ln⁺⁺ ion. This fact may be attributed to decreasing metal-nitrogen bondability. The acid-catalyzed rate constant of Eu(EHPG)⁺⁻ was found to be about two orders of magnitude larger than that for the analogous dissociation of the Eu (EDTA)⁻⁻ complex. This fact may be interpreted as reflecting the 6-membered rings for chelation of Eu⁺⁺ to an oxygen of the phenolate groups and the neighboring nitrogen in EHPG. Meanwhile, the acid-catalyzed rate of Eu(EHPG)⁺⁻ dissociates about six times faster than that of Eu(ENDPDA)⁺⁻ (ethylenedinitrilo-N,N⁺⁻)-di(3-propanoic)-N,N⁺⁻-diaacetic acid), even though EHPG as well as ENPDPA has the same 6-membered chelate ring size (O-Eu-N). This indicates that the chelate ring conformation of the 6-membered phenolate in Eu (EHPG)⁺⁻ may be somewhat different from that of Eu(ENDPDA)⁺⁻. This conformation may allow easier dissociation of one of the phenolate oxygens from the Eu⁺⁺ coordination sphere.

ACKNOWLEDGEMENT. This paper was supported by NON DIRECTED RESEARCH FUND, Korea Research Foundation, 1993.

REFERENCES