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**Kinetics and Mechanisms of the Reactions of Thiosulphato-amine Complexes of Cobalt(III). Part II. Base Hydrolysis of the Bis(ethylenediamine)thiosulphocobalt(III) Ion.**

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**Summary**

Base hydrolysis of the bis(ethylenediamine)thiosulphocobalt(III) was investigated spectrophotometrically between 35 and 65 °C and with base concentrations (NaOH) up to 2.0 mol dm$^{-3}$. The hydrolysis consists of a one-stage reaction, followed by a slow dechelation step, and then by a fast ligand loss. The reaction is base-dependent. The products of the reaction are an equilibrium mixture of cis- and trans-Coen$_2$(OH)$_2$$^2$>. Activation parameters for the reaction as determined by the Eyring equation, are $\Delta H^\circ = 77.8 \pm 4.6$ kJ mol$^{-1}$ and $\Delta S^\circ = -75 \pm 20$ JK$^{-1}$ mol$^{-1}$.

**Introduction**

The $S_2$I CB mechanism has been firmly established for the base hydrolysis of monodentate ligand cobalt(III) amine complexes$^{(1,2)}$. In recent years a number of kinetic studies on the base hydrolysis of simple oxymine chelates bis-ethylenediaminecobalt(III) complexes have appeared in the literature$^{(3-6)}$. The hydrolyzes follow various mechanistic paths, such as associative$^{(4,5)}$, dissociative$^{(6)}$ or interchange$^{(6)}$ and proceed through a two-stage reaction (except the malonato-

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Experimental

Materials

Bis(ethylenediamine)thiosulphatocobalt(III) perchlorate was obtained by the metathesis of the bromide with silver perchlorate in aqueous solution before each kinetic or spectral run. Found: Co, 13.95; N, 13.5; S, 15.5; C, 11.0; H, 5.40%; Calcd. for \([\text{Coen}_2(S_2O_3)]\text{Br} \cdot 3\text{H}_2\text{O}:\) Co, 13.88; N, 13.18; S, 15.06; C, 11.29; H, 5.18%.

Cis- and trans-Diaquabis(ethylenediamine)cobalt(III) nitrates were prepared by the literature methods. The corresponding dihydroxo-complexes were obtained in solution whenever required by the treatment of a solution of the diaqua complex with sodium hydroxide to a suitable pH (above pH 10.00). The [Coen$_2$(H$_2$O)$_2$]$(NO_3)_3$ complex was prepared by the literature methods.

A Beckman DU-2 spectrophotometer was used for all the spectrophotometric observations.

Kinetic Measurements

The kinetics of the base hydrolysis of the complex were monitored spectrophotometrically. Loss of thiosulphate was followed at 510 nm, corresponding to the absorption maxima of the complex. Kinetic runs were carried out in a Jena volumetric flask placed in a thermostat where the temperature was held to within ±0.1 °C of the desired value. In general the reactions were initiated by the addition of the requisite amount of sodium hydroxide solution to the complex solution (0.0025 mol dm$^{-3}$), both being previously thermostatted at the desired temperature which also contained the desired amount of sodium perchlorate to maintain $I = 1.0$ mol dm$^{-3}$. Aliquots were withdrawn from the reaction mixture at suitable intervals, cooled in ice-water, and transferred to the optical cell and the absorbances were then measured. Rates were evaluated from the conventional first-order plots, which were linear throughout the entire course of the reaction.

Results and Discussion

Spectra of a 2.5 x 10$^{-3}$ mol dm$^{-3}$ aqueous solution of the complex at 25 °C are shown in Figure 1 which contains spectra of the complex at different times of base hydrolysis, along with the spectrum of the cis dihydroxo-complex.

Figure 1. Base hydrolysis of bis(ethylenediamine)thiosulphatocobalt(III) perchlorate. Spectra of 2.5 x 10$^{-3}$ mol dm$^{-3}$ solution of \([\text{Coen}_2(S_2O_3)]^+\) at 25 °C. (1) Fresh aqueous solution. (2) Fresh aqueous solution (3-5 minutes aged) of complex in presence of 0.1 mol dm$^{-3}$ NaOH. (3) One day aged. (4) Three days aged. (5) Seven days aged. (6) Cis-Coen$_2$(H$_2$O)$_2$ in presence of 0.01 M NaOH, fresh aqueous solution.

One equivalent of thiosulphate was released at the end of the reaction as determined with standard iodine solution. The visible spectrum of this product was compared with the known spectra of cis- and trans-Coen$_2$(S$_2$O$_3$)(OH)$^\circ$ and did not correspond to either alone, but to an equilibrium mixture of the two. Although the absorbance of the reaction mixture decreases continuously at all wavelengths, the position of the maxima changes little (from 512 nm to 515 nm) during the hydrolysis and consequently no clear-cut isosbestic points were obtained at any stage of the reaction.

A consistent unimolecular rate plot throughout the entire reaction and the spectral change indicate that the reaction takes place in one step only. Pseudo-first order rate constants, determined from the slopes of first-order rate plots, and generally reproducible to ±2.0%, were plotted against the concentration of base. The plot is linear and passes through zero. The rate expression may then be given as:

$$-\frac{d[\text{complex}]}{dt} = k[\text{complex}][OH^-] = k_{\text{obs}}$$

The kinetic data are summarized in Table 1. A probable reaction sequence is as follows.

\[
\text{Coen}_2S_2O_3^+ + OH^- \rightarrow \text{cis-Coen}_2(S_2O_3)(OH)^0 \quad (2)
\]
\[
\text{cis-Coen}_2(S_2O_3)(OH)^0 \rightleftharpoons \text{trans-Coen}_2(S_2O_3)(OH)^0 \quad (3)
\]
\[
\text{cis- and trans-Coen}_2(S_2O_3)(OH)^0 + OH^- \rightarrow \text{cis- or trans-Coen}_2(OH)_2^+ \quad (4)
\]
\[
\text{cis-Coen}_2(OH)_2^+ \rightleftharpoons \text{trans-Coen}_2(OH)_2^+ \quad (5)
\]

Table 1. Rates of base hydrolysis (10$^5$ k$_{\text{obs}}$ s$^{-1}$) of Coen$_2$(S$_2$O$_3$)$^+$ in the presence of different amounts of sodium hydroxide. Complex 2.5 x 10$^{-3}$ mol dm$^{-3}$, I (NaClO$_4$) 1.0 mol dm$^{-3}$.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>[OH$^-$]</th>
<th>10$^5$k$_{\text{obs}}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>0.1</td>
<td>2.0</td>
</tr>
<tr>
<td>45</td>
<td>0.2</td>
<td>2.6</td>
</tr>
<tr>
<td>36</td>
<td>0.3</td>
<td>3.5</td>
</tr>
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<td>45</td>
<td>0.4</td>
<td>4.2</td>
</tr>
<tr>
<td>45</td>
<td>0.5</td>
<td>8.7</td>
</tr>
<tr>
<td>55</td>
<td>0.6</td>
<td>7.9</td>
</tr>
<tr>
<td>55</td>
<td>0.7</td>
<td>12.0</td>
</tr>
<tr>
<td>60</td>
<td>0.8</td>
<td>26.2</td>
</tr>
<tr>
<td>65</td>
<td>0.9</td>
<td>26.9</td>
</tr>
<tr>
<td>75</td>
<td>2.0</td>
<td>35.0</td>
</tr>
</tbody>
</table>

$\Delta H^\circ = 77.8 \pm 4.6$ kJ mol$^{-1}$; $\Delta S^\circ = 75 \pm 20$ J K$^{-1}$ mol$^{-1}$