
Biswanath Chakravarty* and Pradip Kumar Das

Department of Chemistry, University of Kalyani, Kalyani - 741235, W. B. India.

Summary

Base hydrolysis of the bis(ethylenediamine)thiosulphatothiocobalt(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- Coen₂(S₂O₃)²⁻. Activation parameters for the reaction as determined by the Eyring equation, are ΔH° = 77.8 ± 4.6 kJ mol⁻¹ and ΔS° = -75 ± 20 JK⁻¹ mol⁻¹.

Introduction

The S₄I CB mechanism has been firmly established for the base hydrolysis of monodentate ligand cobalt(III) amine complexes[2,3]. In recent years a number of kinetic studies on the base hydrolysis of simple oxoxygen chelate bis-ethylenediaminocobalt(III) complexes have appeared in the literature[4-6]. The hydrolyses follow various mechanistic paths, such as associative[3,4,5], dissociative[6] or interchange[6] and proceed through a two-stage reaction (except the malonato complex) in which the first stage is a ring opening. However, the position of bond cleavage is not the same in all these complexes.

Whereas the oxalato-complex has second-order kinetics in basic solution and ring-opening takes place by carbon-oxygen bond fission[36,37], the similar malonato-complex is different, and ring opening takes place by cobalt-oxygen bond fission only[42,43]. The carbonato-complex also undergoes cobalt-oxygen bond fission for its base-catalyzed path, but carbon-oxygen bond fission for the base-independent path[39]. The phospha-complex indicates a synchronous interchange of phospho- and hydroxide ion between the first and the second coordination spheres of the complexes[40].

All these anionic chelate complexes have cobalt-oxygen bonds at both ends. In the present paper we discuss the kinetics of the base hydrolysis of Coen₂(S₂O₃)²⁻ in which the thiosulphato-chelate is linked through two different donors, oxygen and sulphur[7]. This, as well as the known trans-labilising effect of sulphur in cobalt complexes[8-30], may influence the hydrolysis of this complex and show new mechanistic phenomena. Base hydrolysis of other cobalt(III)thiosulphato-complexes including cis- and trans-bis(ethylenediamine)dithiosulphatothiocobalt(III)[11], and pentamethylenedithiosulphatothiocobalt(III)[12] proceed primarily through an associative S₂O₂ mechanism.

* Author to whom all correspondence should be directed.

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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 [Coen₂(S₂O₃)]Br·3H₂O: 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 ca. 10.00, pH’s of the cis are 6.06 and 8.19 and of the trans are 4.45 and 7.94 at 25°C). Found: (cis complex); C, 12.2; H, 4.90; N, 25.0%; (trans complex), C, 12.25; H, 5.10; N, 24.3%; Calcd. for [Coen₂(H₂O)₂](NO₃)₃: C, 12.00; H, 5.02; N, 24.44%. Analyses were carried out by Dr. H. Malissa and G. Reuter, Microanalytisches Laboratorium, Elbach, West Germany.

All the reagents and chemicals used were either of analytical grade or purified by suitable 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 required amount of sodium perchlorate to maintain I = 1.0 mol dm⁻³. Aliquots were withdrawn from the reaction mixture at suitable intervals, cooled in iced-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.

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-Coen₂(OH)₂ 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:

\[-\frac{d[\text{complex}]}{dt} = k[\text{complex}][\text{OH}^-] = k_{\text{obs}} (1)\]

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

\[\text{Coen}_2\text{S}_2\text{O}_3^- + \text{OH}^- \rightarrow \text{cis-Coen}_2(\text{S}_2\text{O}_3)\text{(OH)}^0\] (2)

\[\text{cis-Coen}_2(\text{S}_2\text{O}_3)\text{(OH)}^0 \rightleftharpoons \text{trans-Coen}_2(\text{S}_2\text{O}_3)\text{(OH)}^0\] (3)

\[\text{cis- and trans-Coen}_2(\text{S}_2\text{O}_3)\text{(OH)}^0 + \text{OH}^- \rightarrow \text{cis- or trans-Coen}_2(\text{OH})_2^2\] (4)

\[\text{cis-Coen}_2(\text{OH})_2^2 \rightleftharpoons \text{trans-Coen}_2(\text{OH})_2^2\] (5)

Table 1. Rates of base hydrolysis (10⁵ k_{\text{obs}} s⁻¹) of Coen₂(S₂O₃)⁺ in the presence of different amounts of sodium hydroxide. Complex 2.5 x 10⁻³ mol dm⁻³, I (NaClO₄) 1.0 mol dm⁻³.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>[OH⁻]</th>
<th>10⁵k_{\text{obs}} mol⁻¹⁻¹ s⁻¹</th>
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<tr>
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</tr>
<tr>
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</tr>
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<td>7.4</td>
<td>20.5</td>
</tr>
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AH⁺ = 77.8 ± 4.6 kJ mol⁻¹; ΔS⁻ = 75 ± 20 J K⁻¹ mol⁻¹