Kinetics of Substitution of Aquo Ligands from cis-Diaquobis(ethylenediamine)Co(III) Ion by o-Phenanthroline in Water-Ethanol Mixture

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The kinetics of substitution of aquo ligands from cis-diaquobis(ethylenediamine)Co(III) ion by o-phenanthroline in water-ethanol mixture has been studied spectrophotometrically. The following rate law has been established:

 $Rate = [Co(en)_2(H_2O)_2^{3+}]\{k_1 + k_2 [o-phenanthroline]\}$

The reaction for the substitution is found to be nearly pH-independent throughout the pH range 4.60-6.22. The rate constant is almost independent of pH and the ionic strength. Activation parameters for two different reaction paths (S_N1 and S_N2) have been calculated and probable mechanism has been suggested.

THE kinetics data on the much studied¹⁻⁹ ligand substitution reactions like acid hydrolysis, base hydrolysis and anation reaction in the case of octahedral complexes of Co(III) show that such reactions proceed through a $S_N 2$ mechanism. But in many cases base-hydrolysis data can be explained almost equally well by $S_N 1CB$ and $S_N 2$ mechanisms. Thus, the ligand substitution reactions in the case of octahedral complexes of Co(III) do not follow any single mechanism and the reaction path depends on the nature of the complex as well as the incoming ligand. This prompted us to study the kinetics of substitution of aquo ligands from $cis[Co(en)_2(H_2O)_2]^{s+}$ by o-phenanthroline in waterethanol mixture.

Materials and Methods

cis-[Co(en)₂(H₂O)₂](NO₃)₈ was prepared by the method of Sargeson¹⁰. After its reaction with ophenanthroline the product, [Co(en)₂(o-phen)](NO₃)₈ was separated from the reaction mixture by crystallization and analysed. Chemicals of AR quality were used in all the experiments. Solutions of o-phenanthroline and complex, of desired concentration, were prepared by dissolving the calculated amounts in 30% ethanol. The pH values of the reaction mixtures were adjusted with nitric acid. The rate constants were reproducible by $\pm 3\%$.

Procedure for the kinetic study — Temperatureequilibrated solutions of o-phenanthroline and the complex (I), of desired concentration, were mixed in the reaction vessel and the course of reaction followed by measuring the optical density (Hilger UVISPEK spectrophotometer) at 470 nm, where a substantial difference exists in the spectra of the complexes $[Co(en)_2(H_2O)_2]^{3+}$ and $[Co(en)_2(o-phenan$ $throline)]^{3+}$. Solution of cis- $[Co(en)_2(H_2O)_2](NO_3)_3$ (I) exhibits absorption maxima at 495 nm $(\log \epsilon 1.89)$ and 360 nm $(\log \epsilon 1.80)$. Solution of $[Co(en)_2(o$ $phen)](NO_3)_3$ (II) exhibits absorption maxima at 470 (log ϵ 2.00) and 352 nm (log ϵ 2.87). These values are comparable to those given in the literature^{11,12}.

The pseudo-first order rate constants for the substitution reaction were obtained by plotting $\log D_{\infty} - D_0 / D_{\infty} - D_t$ against time, where D_0 , D_t and D_{∞} are the optical density values in the beginning, after time t and at infinite time respectively.

Results and Discussion

Effect of varying [complex (I)] on the rate constant — In the first set of experiments the concentration of $[Co(en)_2(H_2O)_2](NO_3)_3$, complex (I), was varied in the range 0.005-0.012M at a fixed concentration (0.1M) of o-phenanthroline. In these experiments the ionic strength (0.082M) and pH (5.7) remained constant. k values were found to be 0.78×10^{-5} , 0.79×10^{-5} , 0.77×10^{-5} and 0.78×10^{-5} sec⁻¹ at [complex (I)] of 0.005, 0.008, 0.010 and 0.012M respectively at a temperature of 60° and in 30% ethanol medium. The rate of the reaction is first order with respect to the complex (I), i.e.

$$\frac{d[\text{complex (II)}]}{dt} = k \text{ [complex (I)]}$$

Effect of varying pH on the rate constant — Concentration of the complex (I) and o-phenanthroline were kept constant at 0.005M and 0.15M respectively and the pH was varied by varying the concentration of HNO₃. In 30% ethanol as the medium, the values of pseudo-first order rate constant k at 70° and 0.11M ionic strength are 5.73 $\times 10^{-5}$, 6.14×10^{-5} , 5.68×10^{-5} , 5.63×10^{-5} , 5.91×10^{-5} and 5.98×10^{-5} sec⁻¹ at pH 4.60, 4.88, 5.40, 5.90, 5.94 and 6.22 respectively. The rate constant in this case is almost independent of pH.

Effect of varying [o-phenanthroline] on the rate constant — The concentration of o-phenanthroline was varied in the range 0.05-0.20M at a fixed concentration of the aquo complex (0.005M). In these experiments the ionic strength was kept constant at 0.04M. The results are presented in Table 1. A plot of k versus concentration of o-phenanthroline is linear with an intercept according to the following rate law.

$$\frac{d[\text{complex (II)}]}{dt} = \begin{bmatrix} k_1 + k_2 \text{ (o-phenanthroline)} \end{bmatrix} \\ \times [\text{complex (I)}] \\ = k \text{ [complex (I)]}$$

 k_1 and k_2 were estimated from the intercept and slope of the linear plot. The values of k_1 are 0.41×10^{-5} , 0.70×10-5 and 1.30×10-5 sec-1 at 60°, 65° and 70° respectively while those of k_2 are 5.33×10^{-5} , 14.40×10^{-5} and $29.00 \times 10^{-5}M^{-1}$ sec⁻¹ respectively at 60°, 65° and 70°.

Effect of varying ionic strength - In these experiments concentration of o-phenanthroline and the complex (I) were kept constant at 0.15 and 0.005Mrespectively and the ionic strength was varied by the addition of desired amount of KNO's. It has been observed that the rate is independent of ionic strength.

The above results suggest that the reaction proceeds through both S_N1 and S_N2 paths. Each path can be represented as follows:

S_N1 Path:

$$cis-[Co(en)_{2}(H_{2}O)_{2}]^{3+} \xrightarrow{k_{1}, \text{ slow}} [Co(en)_{2}(H_{2}O)]^{3+} \xrightarrow{H_{2}O} \downarrow fast, +o-phen \\ \downarrow fast, +o-phen \\ H_{2}O + [Co(en)_{2}(o-phen)]^{3+}$$

S_N2 Path:

 k_2 , slow cis-[Co(en)2(H2O)2]8++o-phen---->

> $[Co(en)_2(H_2O)_2(o-phen)]^{3+}$ fast

 $[Co(en)_{o}(o-phen)]^{3+} + 2H_{o}O$

Scheme 1

TABLE 1 - VARIATION OF RATE CONSTANT k with CONCENTRATION OF [0-PHENANTHROLINE] AT DIFFERENT TEMPERATURES

[o-Phenan- throline] (M)	₽H	$k \times 10^{5}$ (sec ⁻¹) at		
		60°	65°	70°
0.05	5.1	0.68	1.34	2.56
0.10	5.7	0.78	1.91	3.84
0.15	5.9	1.28	2.90	5.63
0.20	6.1	Į ∙52	3.71	7.16

The activation parameters corresponding to the two paths have been calculated and found to be: $S_{N}1 \ (\Delta H_{1}^{\ddagger} = 31.1 \pm 0.5 \text{ kcal mole}^{-1}; \Delta S_{1}^{\ddagger} = 10 \pm 1 \text{ e.u.});$ $S_N^2 (\Delta H_2^{\ddagger} = 36.6 \pm 0.5 \text{ kcal mole}^{-1}; \Delta S_2^{\ddagger} = 27 \pm 1 \text{ e.u.}).$

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