

# 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:

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

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 studied<sup>1-9</sup> 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  $S_N2$  mechanism. But in many cases base-hydrolysis data can be explained almost equally well by  $S_N1CB$  and  $S_N2$  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)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> by *o*-phenanthroline in water-ethanol mixture.

## Materials and Methods

*cis*-[Co(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub> was prepared by the method of Sargeson<sup>10</sup>. After its reaction with *o*-phenanthroline the product, [Co(en)<sub>2</sub>(*o*-phen)](NO<sub>3</sub>)<sub>3</sub> 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**—Temperature-equilibrated 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)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> and [Co(en)<sub>2</sub>(*o*-phenanthroline)]<sup>3+</sup>. Solution of *cis*-[Co(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub> (I) exhibits absorption maxima at 495 nm (log  $\epsilon$  1.89) and 360 nm (log  $\epsilon$  1.80). Solution of [Co(en)<sub>2</sub>(*o*-phen)](NO<sub>3</sub>)<sub>3</sub> (II) exhibits absorption maxima at

470 (log  $\epsilon$  2.00) and 352 nm (log  $\epsilon$  2.87). These values are comparable to those given in the literature<sup>11,12</sup>.

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  $D_\infty$  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)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub>, 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  $0.78 \times 10^{-5}$ ,  $0.79 \times 10^{-5}$ ,  $0.77 \times 10^{-5}$  and  $0.78 \times 10^{-5}$  sec<sup>-1</sup> 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 HNO<sub>3</sub>. In 30% ethanol as the medium, the values of pseudo-first order rate constant  $k$  at 70° and 0.11M ionic strength are  $5.73 \times 10^{-5}$ ,  $6.14 \times 10^{-5}$ ,  $5.68 \times 10^{-5}$ ,  $5.63 \times 10^{-5}$ ,  $5.91 \times 10^{-5}$  and  $5.98 \times 10^{-5}$  sec<sup>-1</sup> 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

