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RESEARCH ARTICLE

Kinetics and Mechanism of Substitution of Aquo – Ligands from cis-Diaquo-Bis (Ethylenediamine) Cobalt (III) ion by o-Phenylenediamine in Ethanol - Water Mixture

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Abstract

The anation kinetics and mechanism of cis$[Co(en)_2(H_2O)_2]^{3+}$ by o-phenylenediamine will be described in which the incoming ligand OPDA behaves as a neutral bidentate (N, N) donor. The anation rate has been studied as a function of substrate complex concentration, ionic strength, p^H, o-phenylenediamine, temperature and medium dielectric constant.

INTRODUCTION

In our earlier reports[1,2], the anation kinetics and mechanism of cis$[Co(en)_2(H_2O)_2]^{3+}$ was described with various incoming bidentate ligands. In the present work, the anation kinetics of o-phenylenediamine is studied and a mechanism is proposed on the basis of results obtained.

The anation rates are governed by the Equation 1.

$$\frac{d[Co\ (en)_2\ (OPDA)_2]^{3+}}{dt} = \frac{K_a\ K_E[Co\ (en)_2\ (H_2O)_2]^{3+}\ [OPDA]}{1 + K_E\ [OPDA]} \quad --(\text{Equation 1})$$

Where K_a is the anation rate constant of cis$[Co(en)_2(H_2O)_2]^{3+}$ and K_E is ion-pair equilibrium constant respectively. Increasing ionic strength increases the rate constant. The anation rate increases with the increase of p^H. Under the condition of [complex-I] < < [OPDA] the plots of $\ln (A_\infty - A_o)/ (A_\infty - A_t)$ versus time were linear, indicating first order dependence of rate in ligand. From the slopes of such plots, the pseudo-first order rate constants were evaluated at different complex-I concentration and found to be almost same. Plots of $1/K_{obs}$ versus 1/[OPDA] were linear with positive intercept at different temperatures indicating $[Co(en)_2(OPDA)]^{3+}$ (complex-II) formation. Activation parameters have been evaluated from Eyring plot. A dissociative interchanging mechanism[3-5] has been suggested, which is also supported by the decrease of reaction rate with decrease in dielectric constant (D).

EXPERIMENTAL

cis$[Co(en)_2(H_2O)_2]3NO_3$ (complex-I) was prepared and characterized as described earlier[6-8]. The product (complex-II) resulting from the reaction between substrate complex and OPDA was prepared by mixing the reactants in 1:15 ratio at 45°C for 36 hours. The spectrum with λ_{max} at 406 nm (Fig. 1) of the product complex indicates good complexation between the substrate complex and the incoming ligand. It is to be noted that λ_{max} of the substrate complex is 495 nm. The metal: ligand ratio of the product in solution was found to be 1:1 by Job's method of continuous variation.

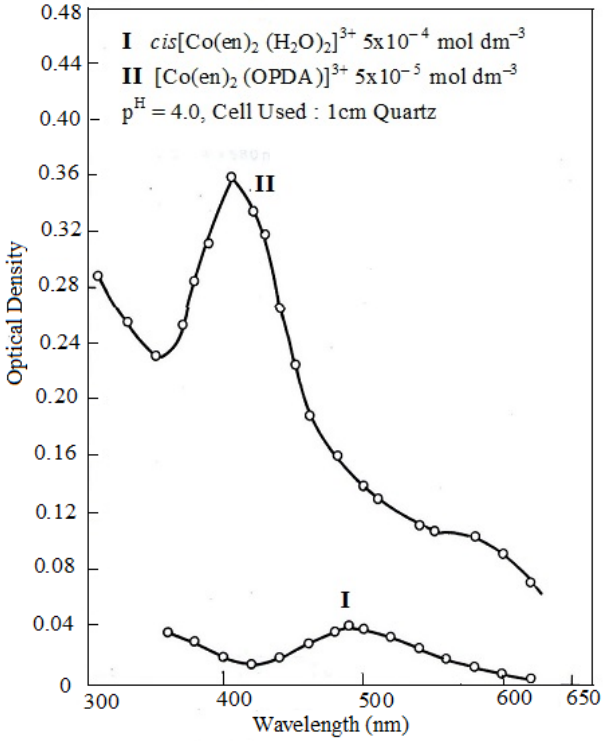


Fig. 1. Absorption Spectra

The kinetic experiments were performed using U-1000 Hitachi digital spectrophotometer and spekol Carlzeiss Jena make was used for measuring the absorbance values of the test solutions at 580 nm where a substantial difference existed in the spectra of complex-I and complex-II as shown in Fig. 1. The results were reproducible within ±3% error limits.

EFFECT OF [COMPLEX – I] VARIATION ON REACTION RATE

Five sets of experiments were carried out at 30°C in 20% (v/v) EtOH-H_2O medium, maintaining constant o-phenylenediamine (0.1 mol dm^{-3}), p^H (4.0), ionic strength (0.2 mol dm^{-3}) and varying [complex-I] from 0.005 to 0.018 mol dm^{-3}. The 10^4 K_{obs} (s^{-1}) values were found to be 2.549, 2.542, 2.550 and 2.548 at the [complex-I] $5x10^{-3}$, $8x10^{-3}$, $12x10^{-3}$, $15x10^{-3}$ and $18x10^{-3}$ respectively. These K_{obs} values are in good agreement with the first order rate law (Equation 2) with respect to the [Complex-I].

$$\frac{d[Co\ (en)_2\ (OPDA)]^{3+}}{dt} = K_{obs}\ [Co\ (en)_2\ (H_2O)_2]^{3+} -- \text{(Equation 2)}$$

EFFECT OF IONIC STRENGTH VARIATION ON REACTION RATE

At constant [Complex-I] ($5x10^{-3}$ mol dm^{-3}), o-phenylenediamine (0.2 mol dm^{-3}), p^H (4.0) and temperature (30°C), the ionic strength of the medium was varied by adding KNO_3. It is observed that K_{obs} values increases with the increase in NO_3^- concentration. The values of K_{obs} (10^4 s^{-1}) were found to be 3.87, 4.11, 4.31, 4.52 and 4.74 at different ionic strengths μ = 0.06, 0.10, 0.14, 0.18 and 0.20 mol dm^{-3} respectively in 20% (v/v) EtOH-H_2O medium. Effect of ionic strength on the rate of ionic reaction in solution can best be represented by the well known Equation 3[9].

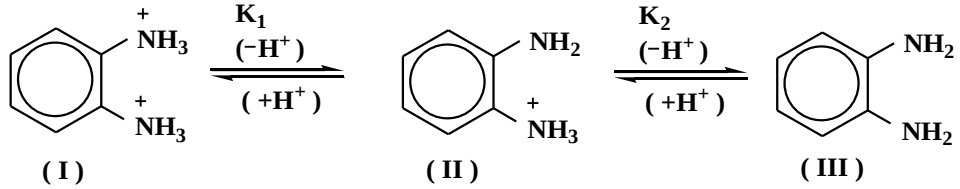
$$\log K = \log K_0 + 2Q Z_A Z_B \sqrt{\mu} \qquad -- \text{(Equation 3)}$$

Where K is the specific rate constant, K_o is the specific rate constant for infinite dilution, and Z_A and Z_B are the charges on the two reactants, at p^H (4.0), OPDA exists predominantly in neutral form. The rate of reaction between an ion and a neutral molecule in solution should have been independent of ionic strength of the medium according to Equation 3.

The increase in rate with increasing ionic strength can be explained by the fact that the reaction between cis$[Co(en)_2(H_2O)_2]^{3+}$ and o-phenylenediamine involves ion-pair formation followed by dissociative interchange in which bond breaking is significant. On the addition of excess nitrate ion, water molecules which are coordinated in ion-pairs reorient considerably around nitrate ions through hydrogen bonding. As a result NO_3^- ions facilitate the cobalt ion-water (Co–OH_2) bond fission and consequently labilization of this water molecule catalyses the entry of OPDA and thus increases the rate of reaction.

EFFECT OF p^H VARIATION ON REACTION RATE

The p^H of the reaction mixtures were varied in the range 4.0 to 6.0 at 30°C in 20% (v/v) EtOH-H_2O medium, keeping the [Complex-I], ionic strength and [OPDA] fixed at $5x10^{-3}$ mol dm^{-3}, 0.2 mol dm^{-3} and 0.1 mol dm^{-3} respectively. The 10^4 K_{obs} (s^{-1}) values were found to be 2.54, 6.57, 8.95, 13.12 and 17.18 at p^H 4.0, 4.5, 5.0, 5.5 and 6.0 respectively. The increase in rate with p^H may be attributed to acid dissociation equilibria of the reactant complex and incoming ligand. The acid dissociation equilibrium of o-phenylenediamine can be represented by Scheme 1.



Scheme - 1

Where at 25°C, the pK_1 and pK_2 values are 0.80 and 4.57 respectively[10,11]. It is obvious that the reagent o-phenylenediamine exists in a non-reactive deprotonated form below p^H 3.4 and it is unable to function as a nucleophile in the substitution reaction. At p^H 4.0 OPDA exists in a monoprotonated form and with the increase of p^H, the percentage of un-protonated o-phenylenediamine increases. The increase in the percentage of un-protonated o-phenylenediamine increases the rate of substitution reaction. But to explain the whole of p^H variation from 4.0 to 6.0, the acid dissociation equilibrium of complex-I can be represented by Equations 4 and 5.

$$cis[Co(en)_2(H_2O)_2]^{3+} \rightleftharpoons cis[Co(en)_2(H_2O)(OH)]^{2+} + H^+ \quad \text{-- Equation 4}$$

(K'_1)

$$cis[Co(en)_2(H_2O)(OH)]^{2+} \rightleftharpoons cis[Co(en)_2(OH)_2]^{+} + H^+ \quad \text{-- Equation 5}$$

(K'_2)

The pK'_1 and pK'_2 values were found to be 5.8 and 8.1 at 25°C[12]. As the p^H of the medium is increased, the percentage of dihydroxo complex increases. It is obvious that within 4.0 to 6.0 p^H range the complex exists in the diaquo or hydroxo-aquo form. The water exchange rate with hydroxo-aquo ion is about 60 times more rapid than that of diaquo species. The hydroxide ion can exert a strong electromeric effect on the adjacent water molecule by virtue of its lone-pairs, consequently an aquo molecule is labilised. Furthermore hydroxide ion is not only a strong σ bonding ligand but also a strong π donor as well which facilitates the formation of a very reactive hydroxo-intermediate of lower coordination number, which in turn increases the reaction rate hence, the rate of reaction increases with increase of p^H.

EFFECT OF [OPDA] VARIATION ON REACTION RATE

At constant [complex-I] ($5x\ 10^{-3}$ mol dm^{-3}), p^H (4.0) and ionic strength (0.2 mol dm^{-3}), the [OPDA] was varied in the range 0.05 to 0.3 mol dm^{-3} at four different temperatures in 20% (v/v) EtOH-H_2O medium. The effects of concentration on rate of the reaction are presented in **Table 1**. On observation of these results, the rate of reaction increases with increase in the concentration of o-phenylenediamine and tends to approach to a limiting value at higher [OPDA] at each temperature.

TABLE - 1: Variation of Rate Constant (K_{obs}) with [OPDA] at Different Temperatures in 20%(v/v) EtOH – H_2O Medium (p^H = 4, μ = 0.2 mol dm^{-3}, [Complex–I] = 0.005 mol dm^{-3})

[OPDA] mol dm^{-3}	10^4 K_{obs} (s^{-1})			
	30°C	35°C	40°C	45°C
0.05	–	2.656	2.923	4.808
0.10	2.549	4.850	5.784	8.928
0.15	3.674	6.748	7.536	11.249
0.20	4.750	8.319	9.058	14.513
0.25	5.513	9.452	10.384	17.018
0.30	6.402	–	–	–

The incoming ligand is neutral under the reaction conditions when the o-phenylenediamine is brought into reaction with triply charged complex ion, it occupies a site close to the complex ion replacing the solvent molecule and forming an ion-pair species rapidly. The bound ligand molecule thus occupies the site vacated by departing water molecule in a slower rate determining step. Incoming ligand concentration increases the ion-pair concentration in solution and also the rate of the reaction. The reaction mechanism can be proposed to explain the variation of rate with concentration through Equation 6 & 7.

$$cis[Co(en)_2(H_2O)_2]^{3+} + (OPDA) \underset{\text{Fast}}{\overset{K_E}{\rightleftharpoons}} cis[Co(en)_2(H_2O)_2]^{3+},\ (OPDA) \quad \text{- - Equation 6}$$

$$cis[Co(en)_2(H_2O)_2]^{3+},\ (OPDA) \underset{\text{Slow}}{\overset{K_a}{\rightleftharpoons}} cis[Co(en)_2(OPDA)]^{3+} + 2H_2O \quad \text{- - Equation 7}$$

Where K_E, K_a are ion-pair equilibrium and anation rate constants respectively. For the above mechanism, the rate at constant p^H and ionic strengths can be represented by equation 8 & 9.

$$\frac{d[Co(en)_2(OPDA)]^{3+}}{dt} = \frac{K_a K_E[Complex - I][OPDA]}{1 + K_E[OPDA]} \quad ----\text{Equation 8}$$

$$= K_{obs}\ cis[Co(en)_2(H_2O)_2]^{3+} \quad ----\text{Equation 9}$$

On the basis of reactions (Equation 6 & 7), ion-pair equilibrium can be considered. This indicates the increase in rate with increase in concentration of ligand.

$$K_{obs} = \frac{K_a K_E[OPDA]}{\{1 + K_E[OPDA]\}} \quad ----\text{Equation 10}$$

$$\frac{1}{K_{obs}} = \frac{1}{K_a} + \frac{1}{K_a K_E[OPDA]} \quad ----\text{Equation 11}$$

According to Equation 11, the plot of $1/K_{obs}$ versus 1/[OPDA] (at a constant p^H and μ) should be

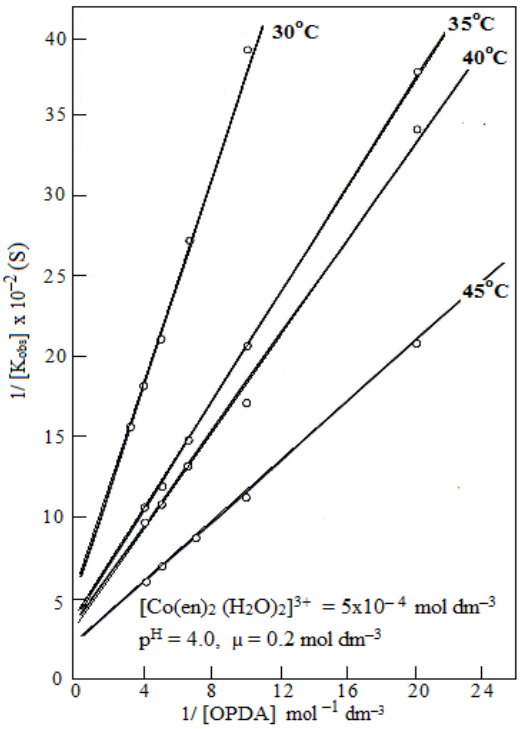


Fig. 2: Plot of $1/K_{obs}$ Vs 1/ [OPDA] at different temperatures in 20% EtOH – H_2O medium

linear with an intercept of $1/K_a$ and slope $1/K_a K_E$. Actually such straight lines were obtained at four different temperatures (**Fig. 2**). The K_a and K_E values at different temperatures are given in **Table 2**. The K_E values evaluated graphically are more or less independent of the temperature.

EFFECT OF TEMPERATURE VARIATION ON REACTION RATE

The anation reaction of complex-I by o-phenylenediamine was studied at four different temperatures (30° - 40°C) for different [OPDA] in 20% (v/v) EtOH-H_2O medium. The activation parameters were calculated using Eyring Equations.

The plot of ln $K_a^{'}$ versus 1/T gives a straight line. From the slope, enthalpy of activation (ΔH^*) (45.55 kJ mol^{-1}) and entropy of activation (ΔS^*) (– 61.84 J $mol^{-1}deg^{-1}$) were evaluated.

TABLE – 2: VALUES OF K_a AND K_E AT DIFFERENT TEMPERATURES

pH = 4, Ionic strength = 0.2 mol dm^{-3} in 20% EtOH – H_2O mixture

Temp (°C)	$\frac{1}{[OPDA]}$ $mol^{-1}dm^{-3}$	$\frac{1}{K_{obs}}$ $X10^3$ (S^{-1})	K_a $X10^2$ (S^{-1})	K_E
30	20	–	0.185	1.67
	10	3.923		
	6.67	2.722		
	5	2.104		
	4	1.814		
	3.3	1.562		

	20	3.765		
	10	2.062		
35	6.67	1.482	0.277	2.16
	5	1.202		
	4	1.058		
	20	3.421		
	10	1.729		
40	6.67	1.327	0.294	2.28
	5	1.104		
	4	0.963		
	20	2.080		
	10	1.120		
45	6.67	0.889	0.454	2.36
	5	0.689		
	4	0.587		

EFFECT OF MEDIUM DIELECTRIC CONSTANT VARIATION ON REACTION RATE

The anation reaction between complex-I and OPDA was studied in 20, 30 and 40% (v/v) EtOH-H_2O mixtures at 45°C where in each set the ligand concentration was varied from 0.05 to 0.25 mol dm^{-3} at fixed [complex-I] ($5x10^{-3}$ mol dm^{-3}), p^H (4.0) and ionic strength (0.2 mol dm^{-3}). The K_{obs} values are given in **Table 3**. It has been observed that the K_{obs} values decreases with decrease in dielectric constant of the medium. From the plot of $1/K_{obs}$ versus 1/OPDA, the K_a and K_E values were calculated for different solvent compositions (**Table 4**). It is observed that the K_a values decrease with the increase in organic component of the medium. The effect of dielectric constant on the reaction can be calculated by Laidler-Eyring equation[13] (Equation 12) that shows the effect of dielectric constant on the reaction.

$$\frac{d(\ln K_a)}{d(\frac{1}{D})} = \frac{e^2Z^2(\frac{1}{r_1} - \frac{1}{r_2})}{2KT} \qquad ----\text{Equation 12}$$

Where Z is the charge on the ion-pair, r_1 and r_2 are the effective radii of the ion-pair in the ground and activated states respectively. K is Boltzman constant, T is absolute temperature and D is

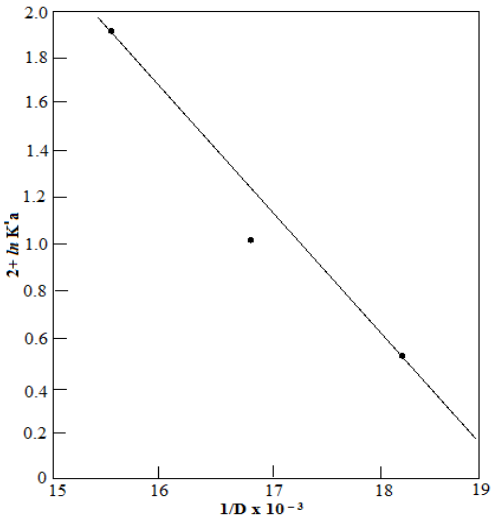


Fig. 3: Plot of $ln K_a$ Vs 1/ D at 45°C

dielectric constant. Considering the net charge of o-phenylenediamine as zero here, r_1 and r_2 are the effective radii of ion-pair and activated species respectively. In this case $r_1 > r_2$ because, in activated state one coordinate water molecule comes out from inner sphere to provide space for the incoming ligand and consequently the size of activated species is lowered. According to Equation 12, plots of ln K'_a versus 1/D should be linear with a negative slope. In practice, we have obtained a good straight line with a negative slope which confirms the dissociative interchange process (Id).

TABLE – 3: THE VALUES OF 10^4 k_{obs} (s^{-1}) FOR DIFFERENT EtOH – H_2O MIXTURES AT 45°C
p^H = 4, Ionic strength = 0.2 mol dm^{-3}, [Complex-I] = 5 x 10^{-3} mol dm^{-3}

[OPDA] mol dm^{-3}	Percentage of EtOH (v/v) in medium K_{obs} X 10^4 (s^{-1})		
	20	30	40
0.05	4.808	3.104	2.687
0.10	8.928	5.432	4.309
0.15	11.249	7.048	5.254
0.20	14.513	8.312	6.248
0.25	17.018	9.425	6.849

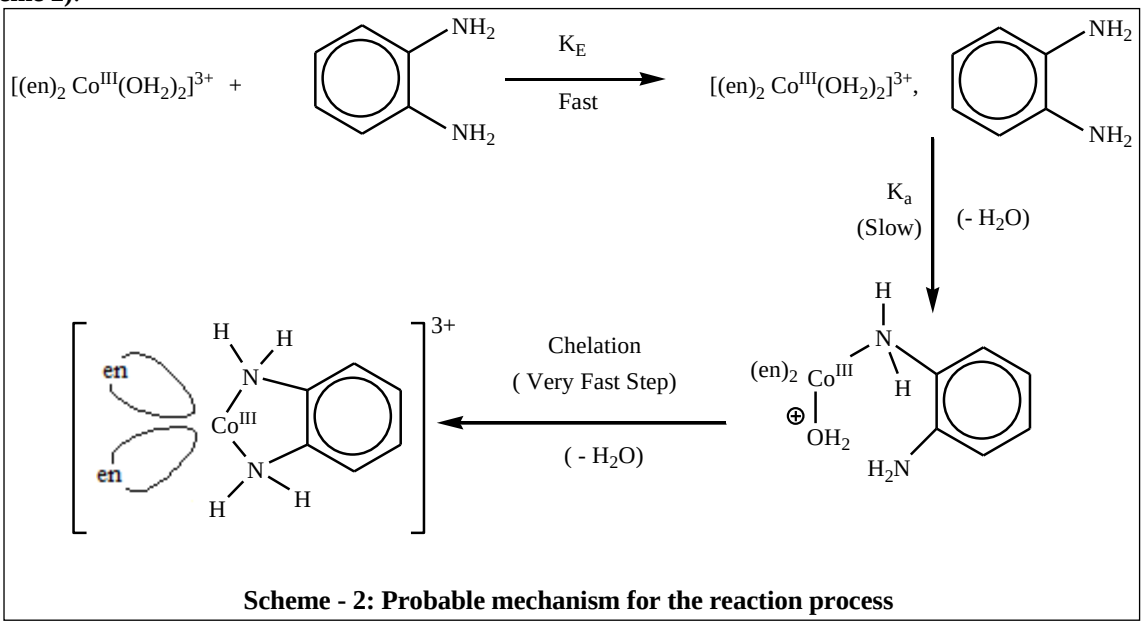
TABLE – 4: K_a AND K_E VALUES FOR DIFFERENT EtOH – H_2O MIXTURES AT 45°C
μ = 0.2 mol dm^{-3}

% of EtOH – H_2O medium	10^3 K_a (s^{-1})	K_E
20	4.545	0.0487
30	1.785	0.0125
40	1.111	0.0088

MECHANISM AND CONCLUSION

The anation rate of $cis[Co(en)_2(H_2O)_2]^{3+}$ by OPDA increases with the increase of ligand concentration and approaches a limiting value at higher [OPDA] in 20% (v/v) EtOH-H_2O medium, which supports the uni molecular

mechanism. Both the pseudo-first order rate constant (K_{obs}) and the anation rate constant (K_a) decreases with the decrease of dielectric constant of the medium which supports the dissociative interchange mechanism (Id). In our proposed mechanism, cis$[Co(en)_2(H_2O)_2]^{3+}$ first forms an ion-pair with the incoming o-phenylenediamine ligand in a very rapid step. Slow replacement of water molecule occurs through a dissociative pathway in which attachment of donor nitrogen atom of OPDA takes the position vacated by the leaving water molecule which increases the electron density on cobalt(III) centre and as a result, the second water molecule is labilised leading to rapid chelation **(Scheme 2)**.



Scheme - 2: Probable mechanism for the reaction process

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