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The Anation Kinetics of *cis*$[Co(en)_2(H_2O)_2](NO_3)_3$ by Anthranilic Acid in Aqueous Medium

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The detailed anation kinetics of *cis*$[Co(en)_2(H_2O)_2]$ $(NO_3)_3$ by anthranilic acid has been studied as a function of substrate complex concentration, temperature, ionic strength, pH and medium dielectric constant. It is observed that increasing ionic strength does not have any effect on the rate constant and the anation rate decreases with the increase of pH. Plots of $1/K_{obs}$ *vs.* $1/[Anth]^-$ was linear with positive intercept at different temperatures indicating $[Co(en)_2(Anth)]^{2+}$ formation. Activation parameters have been evaluated from Eyring plot and a dissociative interchanging mechanism has been suggested, which is supported by the decrease of reaction rate with increase in dielectric constant. The K_{obs} values of $[Co(en)_2Anth]^{2+}$ are in good agreement with the first order rate law with respect to *cis*$[Co(en)_2(H_2O)_2](NO_3)_3$.

Key Words: Kinetics, Mechanism, Anation, Anthranilic acid, Eyring plot, Ionic strength.

INTRODUCTION

Kinetic and mechanistic studies on the substitution reactions in metal complexes still remain a lively issue, due to their importance in the preparative, catalytical, biochemical and analytical procedures of coordination chemistry. Among the different types of nucleophilic substitution reactions, one of the most important types of substitution reaction is anation.The anation kinetic reaction involves the replacement of coordinated water molecule and is the reverse of an acid hydrolysis reaction. The study of the anation kinetics mostly involves the complexes of Cr(II)[1,2], Fe(III)[3], Ru(II/III)[4,5] and Co(II/III)[6]. Anation reaction of the Co(II/III) complexes does not follow any single mechanism and are much faster, hence requires sophisticated techniques. The reaction of $[Co(NH_3)5(H_2O)]^{3+}$ with various ligands are fairly insensitive to nature of the ligands and suggested a dissociative mechanism[7]. The anation kinetics of pentammine cobalt(III) complexes with halides[8-10], glycine[11], deprotonated forms of phthalic acid[12],

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carboxylic acids such as oxalic acid[13], formic acid[14], acetic acid[15], propionic acids[16], have been studied extensively. Recently, kinetics and mechanism of anation reactions of various metal complexes with different ligands[17-19] have been reported.

Even though much of work has been done on anation kinetics of cobalt complexes, anation reaction of cobalt amines with anionic, bidentate ligands are scarce. A survey of the literature reveals that the anation mechanism reaction of pentammine complexes with bidentate donor ligands is not covered. It should be of interest to select a bidentate donor ligand like anthranilic acid an incoming ligand with $-NH_2$ and $-COO^-$ donor groups where $-NH_2$ a neutral group and $-COO^-$ an anionic group with σ electronic pair which anation reactions are not investigated so far.

It has also been observed that no single mechanism is adequate to explain the variety of observations in the water displacement reactions of cobalt(III) complexes. Either a purely dissociative (or) a dissociative interchange mechanism has been postulated for such reactions[20-23]. Thus in view of the diverging mechanisms proposed so far by so many authors for different cobalt (III) complexes, we have decided to study the anation reactions of *cis*$[Co(en)_2(H_2O)_2](NO_3)_3$ with anthranilic acid as a function of substrate complex concentration, ionic strength, pH, temperature and medium dielectric constant.

EXPERIMENTAL

All the chemicals used in the experiment were of AR grade. The water used for the preparation solution was double distilled. The *cis*-diaquo-*bis*(ethylenediamine)cobalt(III)nitrate (complex-1) was prepared and characterized as reported in literarure[24,25]. The product $[Co(en_2)anth]^{2+}$ (complex-2) was prepared by mixing the complex-1 and anthranilic acid in 1:10 ratio in reaction vessel and thermostated at 45ºC for *ca.* 36 h.The pH of the solution was fixed at 5.2 at constant ionic strengh of 0.1 M KNO_3.

Kinetic measurements

The kinetic measurements were made on Hitachi UV-Visible spectrometer at 410 nm. The anthranilic acid, *cis*-diaquo-*bis*(ehylenediamine) cobalt(III) nitrate and electrolyte in water were thermostated at the required temperature and at desired pH for 0.5 h. Nitrogen was bubbled through the solution before and after mixing. After the solution attained equilibrium, the reaction was initiated by adding the cobalt(III) complex solution to the ligand solution present in the reaction vessel and the absorbance at zero time (A_o) was noted. The progress of the reaction was monitored by estimating the amount of product at regular intervals and noting the absorbance of product (A_t) at required wavelength.

The absorbance was measured at a fixed wavelength, where a substantial difference exists in the absorption of *cis*-diaquo-*bis*(ethylenediamine) cobalt(III) nitrate complex and its reaction product. The concentration of ligand was 10-50 times more than substrate complex [anth >> Co(III)]. So that the pseudo-first order condition is applicable and the pseudo-first rate constant values (K_{obs}) were obtained by plotting log $[(A_\alpha\text{-}A_o)/(A\alpha\text{-}A_t)]$ against time (where A_o, A_t and A_α indicate the absorbance of complex at initial stage, at any instant of time and at infinite time, respectively) which were linear passing through origin.

RESULTS AND DISCUSSION

The complex-1 exhibited λ_{max} at 495 nm (log E = 1.89) and 360 nm (log E = 1.82). The spectrum (λ_{max} 322 nm) of the product complex shows good complexation between the complex-1 and the incoming ligand. It is to be noted that λ_{max} of the complex-1 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.

Effect of $[Co(en)_2(H_2O)_2]^{3+}$ (complex-1) variation on reaction rate: In these set of experiments performed at 26ºC in aqueous medium maintaining constant $[Anth]^-$ (0.1 mol dm^{-3}) pH (7.00) ionic strength (0.02 mol dm^{-3}) and varying (complex-1) from 5×10^{-3} to 12×10^{-3} mol dm^{-3}. The 10^4 K_{obs} (s^{-1}) values were found to be 7.10, 7.42, 7.34 and 7.38 at the (complex-1) 5×10^{-3}, 8×10^{-3}, 10×10^{-3} and 12×10^{-3} mol dm^{-3}, respectively. These K_{obs} values are in good agreement with the first order rate law with respect to the (complex-1).

$$\frac{d[Co(en)_2(Anth)]^{2+}}{dt} = K_{obs}[Co(en)_2(H_2O)OH]^{2+}$$

Effect of ionic strength variation on reaction rate: At fixed (complex-1) (5×10^{-3} mol dm^{-3}), pH (7.00), temperature (26ºC) and $(anth)^-$ (0.1 mol dm^{-3}) the ionic strength of the medium was varied by adding KNO_3. Very little change in the K_{obs} values were observed with the increase in ionic strength. The 10^4 K_{obs} (s^{-1}) values were 7.21, 7.28, 7.22 and 7.28 in aqueous medium at different ionic strength m = 0.02, 0.05, 0.08 and 0.12 mol dm^{-3}, respectively. The observed rate constants are independent of ionic strength since there is no change in the net charge of the complexes.

Effect of $(Anth)^-$ variation on reaction rate: At constant [complex-1) (5×10^{-3} mol dm^{-3}), pH (7.00) and ionic strength (0.02 mol dm^{-3}) the $(Anth)^-$ was varied in the range 0.05 to 0.3 mol dm^{-3} at 4 different temperatures (26-40ºC) in aqueous medium. The results presented in Table-1 show that the reaction rate increases with the increase in concentration of $[anth]^-$ and tends to approach a limiting value at higher $[Anth]^-$ at each temperature.

TABLE -1
VARIATION OF RATE CONSTANT WITH (LIGAND)
AT DIFFERENT TEMPERATURES

[Complex-1] = 5×10^{-3} mol dm^{-3}; Ionic strength (μ) = 0.02 mol dm^{-3}, pH = 7.0

$[Anth]^-$ (mol dm^{-3})	$K_{obs} \times 10^4$ (s^{-1})			
	26°C	30°C	35°C	40°C
0.05	4.61	9.45	–	29.30
0.10	7.21	13.90	24.10	42.90
0.15	9.60	16.89	30.20	48.40
0.20	10.20	18.95	33.51	53.30
0.25	10.91	19.01	34.70	55.10
0.30	–	–	36.70	–

The incoming ligand is negatively charged under the reaction conditions, this suggests ion-pair formation between the substrate complex ion and the negative end of anthranilic acid. When the anthranilic acid is brought into reaction with the doubly charged complex ion, it occupies a site close to the complex ion and forms an ion-pair species rapidly. The bound ligand molecule those occupies the site vacated by the departing water is a slower step and hence the rate determining step. Increasing ligand concentration increases the ion-pair concentration in solution.

$$cis[Co(en)_2(H_2O)(OH)]^{2+} + [anth]^- \underset{fast}{\overset{K_E}{\rightleftharpoons}} cis[Co(en)_2(H_2O)(OH)]^{2+}\cdot[anth]^- \qquad (1)$$

$$cis[Co(en)_2(H_2O)(OH)]^{2+}\cdot[anth]^- \underset{slow}{\overset{K_a}{\rightleftharpoons}} cis[Co(en)_2(H_2O)(OH)]^{2+} + H_2O + OH^- \qquad (2)$$

where K_E ion-pair equilibrium constant, K_a anation rate constant. For the above mechanism, the rate at constant pH and ionic strength comes out to be

$$-\frac{[Co(en)_2(anth)]^{2+}}{dt} = \frac{K_aK_E[Co(en)_2(H_2O)(OH)]^{2+}\ [anth]^-}{1+K_E[anth]^-} \qquad (3)$$

This indicates the increasing rate with the increase of ligand concentration.

$$k_{obs} = \frac{K_aK_E[Anth]^-}{\{1+K_E[Anth]^-\}} \qquad (4)$$

$$\frac{1}{k_{obs}} = \frac{1}{K_a} + \frac{1}{K_aK_E[Anth]^-} \qquad (5)$$

According to eqn. 5 the plot of $1/K_{obs}$ *vs.* $1/[Anth]^-$ [at a constant pH and ionic strength] should be linear with an intercept of $1/K_a$ and slope $1/K_aK_E$. Actually such straight lines were obtained at four different temperatures (Fig. 1). The K_a values at different temperatures are given in Table-2. The K_E values evaluated graphically are temperature independent.

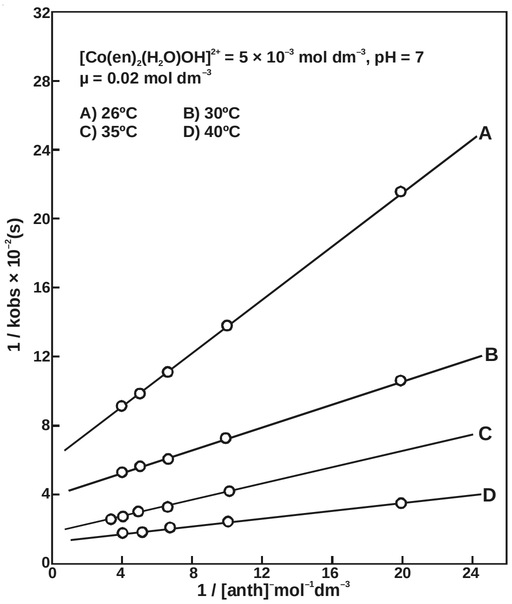


Fig. 1. Plot of $1/k_{obs}$ *vs.* $1/[Anth]^-$ at different temperature in aqueous medium

TABLE-2

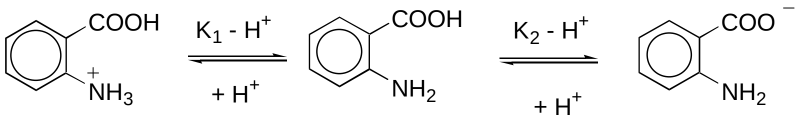
K_a AND K_E VALUES AT DIFFERENT TEMPERATURES

pH = 7.0; Ionic strength = 0.02 mol dm^{-3}

Temp. (ºC)	$(1/Anth)^-$ (mol^{-1} dm^{-3})	$1/K_{obs} \times 10^3$ (s^{-1})	$K_a \times 10^2$ (s^{-1})	K_E
26	20.00	2.170	0.176	7.12
	10.00	1.380		
	6.67	1.050		
	5.00	0.980		
	4.00	0.917		
30	20.00	1.06	0.262	10.45
	10.00	0.72		
	6.67	0.59		
	5.00	0.55		
	4.00	0.52		
35	20.00	0.41	0.492	11.86
	10.00	0.33		
	6.67	0.30		
	5.00	0.29		
	4.00	0.27		
40	20.00	0.34	0.682	16.86
	10.00	0.23		
	6.67	0.21		
	5.00	0.19		
	4.00	0.18		

Effect of pH variation on reaction rate:

At a fixed concentration (complex-1, 5 × 10^{-3} mol dm^{-3}); ($[anth]^-$,0.1 mol dm^{-3}) and ionic strength (0.02 mol dm^{-3}) the pseudo-first order rate constant 10^4 K_{obs} (s^{-1}) values at 26ºC in aqueous medium were found to be 7.21, 5.95, 3.81 and 2.83 at pH 7.00, 7.50, 8.00 and 8.50, respectively. The results presented in Table-3 shows that the reaction rate decreases with increase in pH. The effect must be attributed to acid-dissociation equilibrium of the incoming ligand and the substrate complex. The acid dissociation equilibrium of anthranilic acid can be represented by eqn. 6 where the pK_1 and pK_2 values are 2.17 and 4.85, respectively[26] at 26ºC.



(6)

TABLE-3
VARIATION OF PSEUDO FIRST ORDER RATE CONSTANT (K_{obs}) WITH pH AT DIFFERENT $[anth]^-$ CONCENTRATION IN AQUEOUS MEDIUM
Temp. = 26°C (Complex-1) = 5 × 10^{-3} mol dm^{-3}; μ = 0.02 mol dm^{-3}

$[Anth]^-$ (mol dm^{-3})	$K_{obs} \times 10^4$ (s^{-1}) at pH			
	7.00	7.50	8.00	8.50
0.10	7.21	5.95	3.81	2.83
0.15	9.60	7.81	5.31	4.35
0.20	10.20	9.00	6.76	5.77
0.25	10.91	10.26	8.51	7.26

It is obvious that within the pH range of 7.00 to 8.50 the anthranilic acid ligand exists as an anionic species in solution. Therefore the reactivity of the anthranilic acid ligand was not altered in the 7.00 to 8.5 pH range. Thus, in order to explain the effect of pH on the reaction rate 26ºC, the following acid dissociation equilibrium may be considered.

$$cis[Co(en)_2(H_2O)_2]^{3+} \xrightleftharpoons{K'_1} cis[Co(en)_2(H_2O)(OH)]^{2+} + H^+ \quad (7)$$

$$cis[Co(en)_2(H_2O)(OH)]^{2+} \xrightleftharpoons{K'_2} cis[Co(en)_2(OH)_2]^{+} + H^+ \quad (8)$$

here the pK'_1 and pK'_2 values were 5.8 and 8.1 at 26ºC, respectively[27]. As the pH of the medium is increased, the percentage of labile dihydroxo complex increases. The hydroxo-aquo species is a very reactive species compared to dihydroxo complex. The formation of hydroxo aquo species would increase the rate of water dissociation due to high labilization influence of hydroxide ligand[25] by virtue of its lone pair of electrons and due to capable of exerting strong electronic effect. The hydroxide ion is not only a strong σ bonding ligand but also a strong π donor as well which facilitates the formation of *cis*$[Co(en)_2(OH)]^{2+}$ intermediate. However at higher pH it is converted into dihydroxo complex which reacts very slowly due to formation of two strong (Co–OH) bonds in *cis*$[Co(en)_2(OH)_2]^+$ and thus decreases the rate. Hence the reaction rate decreases with increase of pH.

Effect of Temperature variation on reaction rate: The anation reaction of complex-1 by anthranilic acid was studied at four different temperatures (26-40ºC) for different $[anth]^-$ concentration in aqueous medium. The activation parameters $\Delta H^{\#}$ (72 kJ/mol) and $\Delta S^{\#}$ (30 J/mol/deg) were calculated using Eyring equations.

Effect of medium dielectric constant variation on reaction rate: The solvent effect on the reaction has been studied in three ethanol-water mixtures (10, 20 and 30%, v/v) at 26ºC. In this experiment the $[anth]^-$ concentration was varied in the range of 0.05 to 0.25 mol dm^{-3} at a constant pH (7.00), ionic strength (0.02 mol dm^{-3}) and [complex-1] (5×10^{-3} mol dm^{-3}). At any temperature, increase of the organic component (*i.e.* decrease of the dielectric constant) decreases the value of anation rate constant (K_{obs}).

From the $1/K_{obs}$ *vs.* $1/[Anth]^-$, the K_a and K_E values were determined for different compositions. It is observed that the K_a values decreases with the increase in organic component of the medium. The effect of dielectric constant on the reaction rate can be represented by Laidler-Eyring equation[28], this equation can be represented in a simplified form:

$$\frac{d(\ln K_a)}{d\left(\frac{1}{D}\right)} = \frac{e^2 Z^2 \left(\frac{1}{r_1} - \frac{1}{r_2}\right)}{2KT} \tag{9}$$

where Z is the charge on the ion-pair, r_1 and r_2 the effective radius of the ion-pair in the ground state and in activated state, respectively. K = Boltzman constant, T = temperature degrees absolute and D = the changing dielectric constant. For a dissociative interchange (Id) process, one water molecule is lost in the activated state and consequently the size of the activated species is lowered therefore $r_2 < r_1$, hence according to eqn. 9, the plot of ln K_a *vs.* 1/D should be linear with a negative slope. In practice, we have obtained a good straight line with a negative slope (Fig. 2). For a dissociative interchange mechanism, a water molecule is dissociated from the metal ion and as a result the metal ion attracts the negatively charged oxygen atom of the carboxyl ate group of anthranilic acid.

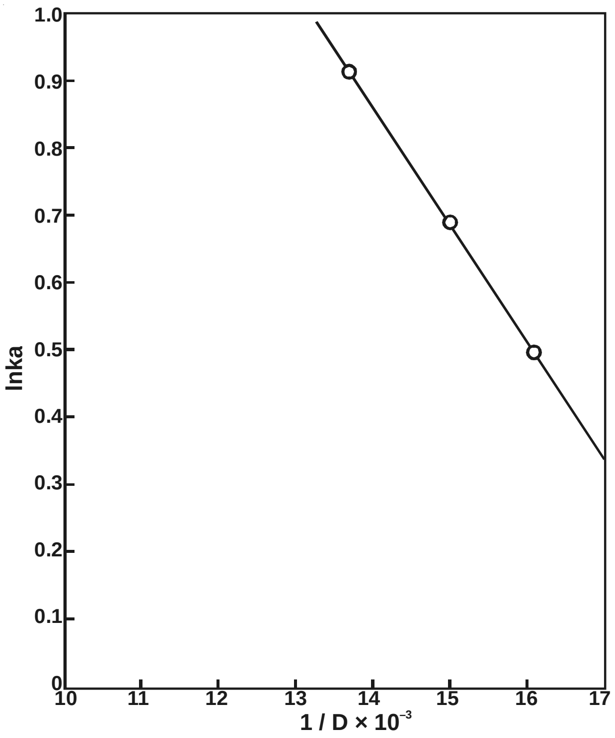
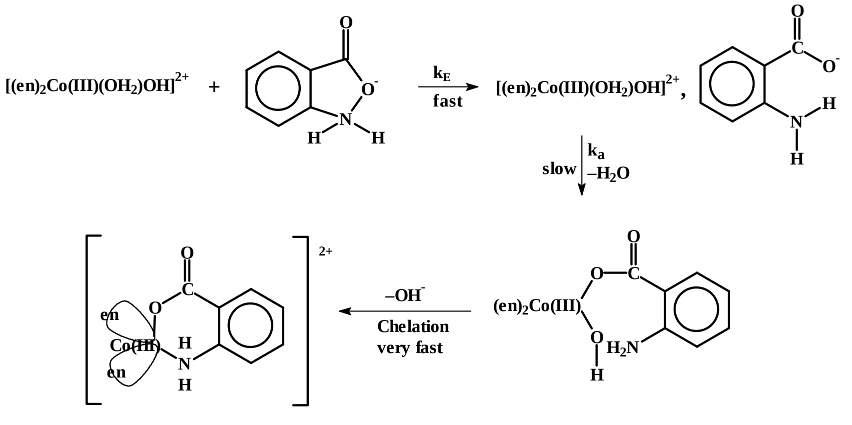


Fig. 2. Plot of ln k'_a *vs.* 1/D at 26ºC



Scheme-I

Mechanism and conclusion

The anation rate of *cis*$[Co(en)_2(H_2O)_2]^{3+}$ by anthranilic acid increases with the increase of ligand concentration and approaches a limiting value at higher ligand concentration, which supports the unimolecular mechanism. Both the pseudo-first order rate constant (k_{obs}) and the anation rate constant (k_a) decreases with the decrease in the dielectric constant of the medium, which leads strong support in favor of the dissociative interchange mechanism (Id). In our proposed mechanism *cis*$[Co(en)_2(H_2O)_2](NO_3)_3$ first forms an ion-pair with the incoming anthranilic acid ligand in a very rapid step, then slow replacement of water molecule occurs through a dissociative pathway (**Scheme-I**) in which attachment of donor oxygen atom of anthranilic acid takes the position vacated by leaving water molecule, which increases the electron density on cobalt(III) centre as a result the second water molecule is labilized, leading to rapid chelation. Based on the above discussion, the dissociative mechanism is possible given in **Scheme-I**.

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