Kinetics & Mechanism of Substitution of Aquo Ligands from cis-Diaquo-bis(ethylenediamine)cobalt(III) Ion by Glycine in Water-Ethanol Mixture

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The title reaction has been studied spectrophotometrically. The following rate law has been established in the pH

$$\frac{d[Co(en)_2(gly)^{2+}]}{dt} = \frac{k_a \cdot K_E[Co(en)_2(H_2O)_2^{3+}]_{total}[glyH]}{1 + K_E[glyH]}$$

range 2.6 to 4.3 (where K_E is ion pair equilibrium constant between two reacting species and k_a, the rate constant for conversion of outer-sphere complex into inner-sphere complex). The reaction rate is found to be pH dependent in the pH range 2.6 to 4.3. The nature of influence of solvent on K_E and k_a has been deduced by studying the reaction in four different EtOH-water mixtures. K_E values increase with increase in the percentage of organic component, whereas ka values decrease. Activation parameters have been calculated and compared with the isotopic water exchange process. A mechanism involving outer-sphere associative equilibrium between two reacting species followed by dissociative interchange of outer-sphere complex to product has been suggested.

The available reports[1 -5] on aquo-ligand replacement reaction of various anionic ligands with stable aquo-cations, in general, show that the anation of aquo-amine complex proceeds by a outer-sphere association between the complex and the incoming ligand, prior to the slow rate-determining ligand water dissociation whereupon the nearby ligand slips into position vacated by leaving water molecule. This outer-sphere association and the interchange rate constant are influenced by solvents[6 -8]. The interchange process is shown to occur either by a dissociative or an associative path. This controversy regarding mechanism led us to study the kinetics of aquo-ligand substitution in cis-[Co(en)$_2$(H$_2$O)$_2$]$^{3+}$ by a series of amino acids like glycine (gly), alanine (ala), β-alanine (β-ala), proline (pro) etc., in which ligand reactivity is varied by changing the electron density at the donor site. In this paper anation of cis-[Co(en)$_2$(H$_2$O)$_2$]$^{3+}$ by glycine is reported.

Materials and Methods

cis-[Co(en)$_2$(H$_2$O)$_2$](NO$_3$)$_3$ (Complex-I) was prepared by the method of Sergeson[9] and characterised by elemental analyses. Complex-I exhibited absorption maxima at 360 (logε = 1.81) and 495 nm (logε = 1.89) in consonance with the data reported in literature[10]. Due to hygroscopic nature of the product of the reaction between cis-[Co(en)$_2$(H$_2$O)$_2$]$^{3+}$ and glycine, it was difficult to separate it in crystalline form. So Complex-I and glycine were mixed in different molar ratios, viz.

1:1, 1:5 and 1:10 at pH 4.05 in three different reaction vessels and thermostated at 50°C for 24 hr. In each reaction mixture [Complex-I] was kept fixed at 0.005 mol dm^{-3}. Each reaction mixture exhibited maximum absorption at 495 nm with more or less equal absorbances but higher than that of substrate complex at 0.005 mol dm^{-3} concentration. The composition of the product in the reaction mixture was found to be 1:1 as revealed by Job's method of continuous variation. Further the composition of the product in solution as [Co(en)$_2$gly]$^{2+}$ was found to be the same as that of the product obtained by Tsucida and coworkers[11]. In all the experiments AR quality chemicals, doubly distilled ethanol and water were used.

Kinetic run

All the experiments except the dielectric variation were performed in 30% (v/v) EtOH-water mixture. All spectral measurements were made on a Hilger-UVISPEK spectrophotometer at 495 nm, where a substantial difference existed between the absorption of substrate complex and product. Equal volumes of solutions of Complex-I and glycine of desired concentrations were mixed and equilibrated at the desired temperature. The composition of reaction mixture was such that the pseudo-first order rate law was applicable and pseudo-first order rate constants (k_{obs}) were obtained by plotting log($A_\infty - A_0/A_\infty - A_t$) against time, where A_0, A_t and A_∞ are the absorbances initially, after time t and after the completion of reaction respectively. The rate constant values are reproducible within ±3%.
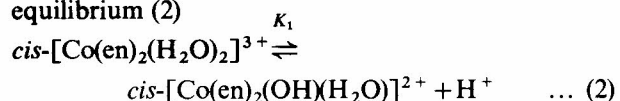
Results and Discussion

Effect of varying [Complex-I] on rate constant

In the first set of experiments [Complex-I] was varied (from 0.0025 to 0.0075 mol dm⁻³) at constant [glycine] (0.075 mol dm⁻³) pH (4.05) and ionic strength. The rate of reaction was first order in [Complex-I] at 55°C, leading to the rate expression (1)

$$\frac{d[\text{Complex-II}]}{dt} = k_{obs}[\text{Complex-I}] \qquad \ldots (1)$$

Effect of varying pH on rate constant

At fixed [Complex-I] (0.005 mol dm⁻³), [glyH] (0.075 mol dm⁻³) and ionic strength ($\mu = 0.03$ mol dm⁻³), the pseudo-first order rate constant at 55°C increased with increase in pH (pH of the solution was adjusted by adding HNO_3 or NaOH). The values of $k_{obs} \times (10^4)$ are 0.58, 1.05, 1.44, 1.57 and 2.59 at pH 2.6, 2.8, 3.1, 3.6 and 4.2, respectively. Within the pH range 2.6 to 4.2 the glycine exists as the zwitterion ($\overset{+}{N}H_3 - CH_2 - COO^-$) in solution[12] and the values of pK_1 and pK_2 at 50° are 2.32 and 9.18 respectively. So change in pH did not alter the ligand reactivity considerably. But considering the acid dissociation equilibrium (2)
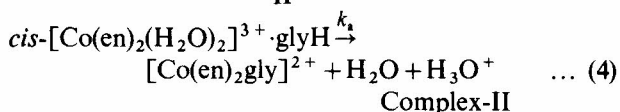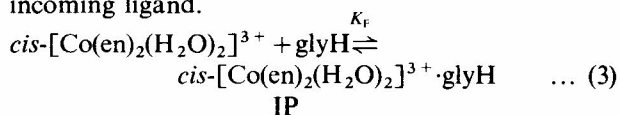
$$\text{cis-[Co(en)}_2(\text{H}_2\text{O})_2]^{3+} \overset{K_1}{\rightleftharpoons}$$
$$\text{cis-[Co(en)}_2(\text{OH})(\text{H}_2\text{O})]^{2+} + \text{H}^+ \qquad \ldots (2)$$

the pK_1 value is observed[13] to be 5.8 at 25°C. As pH of the medium is increased the percentage of hydroxo-aquo complex increases. Water exchange rate with hydroxo-aquo ion is about 60 times more rapid than that with diaquo species owing to well known labilising effect of hydroxide ion adjacent to water ligand by virtue of its lone-pair capable of exerting strong electromeric effect. Hydroxide ion is also a π-donor which facilitates the formation of hydroxo intermediate species and increases the rate.

Effect of varying [glyH] on rate constant

The [glyH] was varied in the range 0.025 to 0.125 mol dm⁻³ at fixed [Complex-I] (0.005 mol dm⁻³), pH 4.05, ionic strength (μ) = 0.03 mol dm⁻³ and temp. = 40°C. The results given in Table 1 show that the rate increased with increase in [glyH] and attained a limiting rate at higher [glyH] due to completion of ion-pair formation[14].

The reactions (3) and (4) can be suggested to explain the variation of rate due to change in concentration of incoming ligand.

$$\text{cis-[Co(en)}_2(\text{H}_2\text{O})_2]^{3+} + \text{glyH} \overset{K_F}{\rightleftharpoons}$$
$$\text{cis-[Co(en)}_2(\text{H}_2\text{O})_2]^{3+} \cdot \text{glyH} \qquad \ldots (3)$$
$$\text{IP}$$

$$\text{cis-[Co(en)}_2(\text{H}_2\text{O})_2]^{3+} \cdot \text{glyH} \overset{k_a}{\rightarrow}$$
$$[\text{Co(en)}_2\text{gly}]^{2+} + \text{H}_2\text{O} + \text{H}_3\text{O}^+ \qquad \ldots (4)$$
$$\text{Complex-II}$$

On the basis of reactions (3) and (4) and considering ion-pair equilibrium and rate-determining step, rate law (5) is, thus, established.

$$\frac{d[\text{Co(en)}_2(\text{gly})^{2+}]}{dt} =$$

$$= \frac{k_a \cdot K_E[\text{cis-Co(en)}_2(\text{H}_2\text{O})_2^{3+}]_{total}[\text{glyH}]}{1 + K_E[\text{glyH}]}$$

$$= k_{obs}[\text{Co(en)}_2(\text{H}_2\text{O})_2^{3+}]_{total} \qquad \ldots (5)$$

where K_E = ion-pair equilibrium constant, k_a = anation rate constant and $[\text{cis-Co(en)}_2(\text{H}_2\text{O})_2^{3+}]_{total}$ represents the total unreacted complex concentration in solution.
Now,

$$k_{obs} = \frac{k_a \cdot K_E[\text{glyH}]}{1 + K_E[\text{glyH}]} \qquad \ldots (6)$$

or

$$\frac{1}{k_{obs}} = \frac{1}{k_a} + \frac{1}{k_a \cdot K_E[\text{glyH}]} \qquad \ldots (7)$$

According to Eq. (7), the plot of $1/k_{obs}$ versus $1/[\text{glyH}]$ at a constant pH should be linear with an intercept = $1/k_a$ and slope = $1/k_a \cdot K_E$. This is found to be so (see Fig. 1) and the values of $k_a \times (10^4)$ thus obtained are 1.3, 6.25, 8.33, 14.28 and 25.00 s⁻¹ at 40°, 49°, 52°, 55° and 60°C respectively. K_E values are found to be 4.0 to 7.5 dm³ mol⁻¹ in the temperature range studied. In proposing the mechanism as represented by Eqs (3) and (4), it was assumed that only cis-diaquo complex is involved in the reaction, because under the experimental condition the cis/trans ratio is around 58 (see ref. 13).

Effect of varying ionic strength

The ionic strength of the reaction mixture was adjusted by adding $NaNO_3$. At fixed [Complex-I] (0.005 mol dm⁻³), [glyH] (0.075 mol dm⁻³), pH = 4.05 and temp. = 55°C, the values of k_{obs} increased slowly with increase in ionic strength of the medium. For example at $\mu = 0.10, 0.13, 0.15$ and 0.20 mol dm⁻³, k_{obs} ($\times 10^4$) are 2.50, 2.55, 2.60 and 2.71 s⁻¹ respectively. Considering the net charge of zwitterion form ($\overset{+}{N}H_3 - CH_2 - COO^-$) as zero, the result goes against the

Table 1 – Variation of Rate Constant (k_{obs}) with [glyH] at Different Temperatures

[pH = 4.05; $\mu = 0.03$ mol dm⁻³; and [Complex] = 0.005 mol dm⁻³]

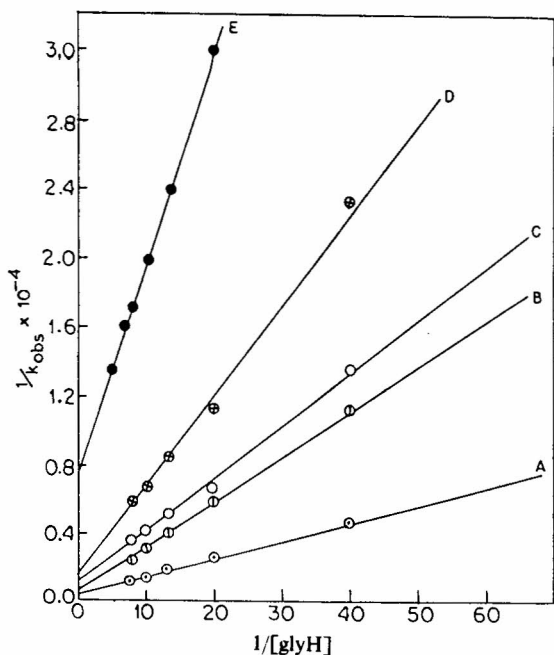| [glyH] mol dm⁻³	$10^4 k_{obs}$ (s⁻¹)				
	40°	49°	52°	55°	60°C
0.025	—	0.42	0.729	0.88	2.11
0.050	0.31	0.88	1.49	1.65	3.84
0.075	0.43	1.19	1.96	2.41	5.18
0.100	0.50	1.49	2.42	3.18	7.10
0.125	0.54	1.69	2.69	3.95	8.75

Fig. 1 — Plot of $1/k_{obs}$ versus $1/[glyH]$ at different temperatures. (A) 60°C, (B) 55°C, (C) 52°C, (D) 49°C, (E) 40°C.

accepted theory[15] for ionic reactions in solution. This anomaly can be explained by the fact that the non-substituting nitrate ion facilitates the metal-water bond cleavage through a specific attack on the coordinated aquo-molecule which is not associated with dipolar glycine. Hence labilisation of this aquo-molecule catalyses the entry of ligand glycine. This typical type of ionic strength effect was observed by Harris and coworkers[3].

Effect of varying dielectric constant on rate constant

The influence of solvent dielectric constant on rate was studied in four different EtOH-water mixtures at 40°C. In each set, ligand concentration was varied from 0.05 to 0.2 mol dm^{-3} at fixed [Complex-I] (0.005 mol dm^{-3}), pH 4.05 and ionic strength ($\mu = 0.03$ mol dm^{-3}). It appears from Table 2 that pseudo-first order rate constant (k_{obs}) increases with decrease in dielectric constant of the medium.

As the reaction occurs through ion-pair equilibrium followed by interchange process, the evaluation of K_E and k_a at different dielectric constants is necessary. The values of k_a and K_E in different EtOH-water mixtures are given in Table 3.

The nature of dependence of K_E on solvent composition agrees with ion-pair formation, since K_E values increase with increase in organic component(EtOH) in the solvent, i.e. with decrease in dielectric constant of the medium. In contrast, k_a values decrease with decrease in dielectric constant of the medium. The influence of dielectric constant on

rate constant can be described by the equation of Laidler and Eyring

$$\frac{d\ln k}{d(1/D)} = \frac{e^2 Z^2}{2kT}(1/r_1 - 1/r^*) \qquad \dots (8)$$

(considering the net charge of isoionic glycine as zero). Here r_1 is the effective radius of ion-pair and r^* is that of activated species. Generally $r_1 < r^*$ for associative activation (where charge of activated species is the same as that of reacting species). But in the present case $r_1 > r^*$, because in activated state one coordinated water molecule comes out from inner-sphere to provide for the incoming ligand and consequently the size of activated species is lowered. In fact plot of $\log k_a$ versus $1/D$ is linear with a negative slope (Fig. 2) which confirms the dissociative interchange process. It may be assumed, however, that influence of dielectric constant on k_a is not very great, since the effective radius (r_1) of ion-pair is much greater than that of a water molecule, so that it will not differ greatly from r^*. As the increasing influence of k_E on k_{obs} is much greater than decreasing influence of k_a on k_{obs}, the overall rate of reaction increases with decrease in dielectric constant of the medium.

Effect of varying temperature on rate constant

The reaction was studied at five different temperatures for different ligand concentrations in 30% (v/v) aq. ethanol and activation parameters were calculated using Eyring equation (Fig. 3), checked by least square method and compared with the data for isotopic water exchange process (see Table 4). The small difference in $\Delta H\ddagger$ and $\Delta S\ddagger$ values is due to the difference in dielectric constant of the medium. In the

Table 2 — Values of k_{obs} in Different EtOH-Water Mixtures

[Glycine] (mol dm^{-3})	$10^{-4} k_{obs}$ (s^{-1})			
	12%(v/v)	24%(v/v)	30%(v/v)	36%(v/v)
0.050	0.25	0.27	0.31	0.35
0.075	0.31	0.39	0.43	0.50
0.100	0.36	0.42	0.50	0.53
0.125	0.49	0.51	0.54	0.57
0.150	0.57	0.60	0.63	0.65
0.200	0.64	0.72	0.74	0.77

Table 3 — Values of k_a and k_E in Different EtOH-Water Mixtures

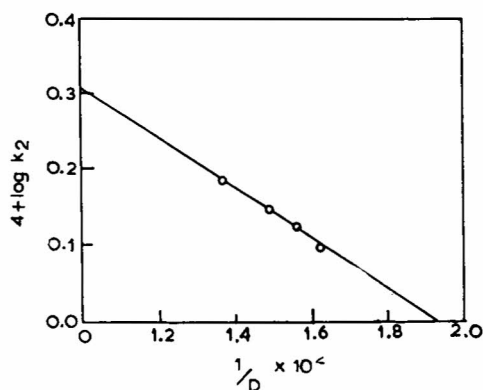| EtOH (%, v/v)	$10^4 k_a$(s^{-1})	K_E
12	1.53	3.77
24	1.40	5.10
30	1.33	7.50
36	1.25	9.00

Fig. 2 — Plot of log k_a versus $1/D$ at 40°C, [Complex-I] = 0.005 mol dm^{-3} and pH = 4.05.

Table 4 — Activation Parameters for Substitution and Water Exchange Process

System	$\Delta H\ddagger$ (kJmol^{-1})	$\Delta S\ddagger$ (JK^{-1} mol^{-1})	Ref.
cis-[Co(en)$_2$(H$_2$O)$_2$]$^{3+}$ —OH$_2$ (exchange)	120.58	+62.81	16
cis-[Co(en)$_2$(H$_2$O)$_2$]$^{3+}$ — g-glycine (substitution)	128.54	+88.34	This work

case of glycine substitution the medium is 30% (v/v) aq. ethanol whereas isotopic water exchange has been studied in aqueous medium. In 30% (v/v) aq. ethanol the dissociation of H$_2$O from the aquo complex is somewhat slower than that in pure water. Thus it can be concluded that the substitution of aquo-ligand from cis-[Co(en)$_2$(H$_2$O)$_2$]$^{3+}$ by glycine proceeds through dissociative interchange (I_d) mechanism.
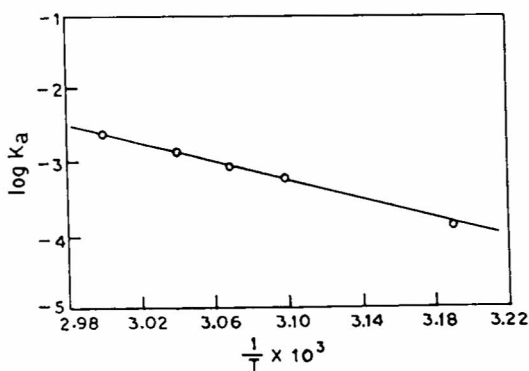

Fig. 3 — Eyring plot of log k_a versus 1/T.

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