Kinetic and mechanistic studies on substitution reaction of aqua-ligands from cis-diaqua-bis[2-(m-tolylazo)-pyridine]ruthenium(II) ion with 2,2'-bipyridine in aqueous medium

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The kinetics of substitution of aqua-ligands from cis-diaqua-bis[2-(m-tolylazo)pyridine]ruthenium(II) ion by 2,2'-bipyridine in aqueous medium has been studied spectrophotometrically at different temperatures (40-55°C). A rate law has been established. The reaction rates are found to be pH dependent in the pH range of 4.5 to 6.0. Ionic strength has a very little effect on the rate constants. Activation parameters (∆H° and ∆S°) have been evaluated and compared with the reactions by 8-hydroxyquinoline and 1,10-phenanthroline. All the experimental results are consistent with a dissociative mechanism. The effect of variation of dielectric constant of the medium has been used to verify the mechanistic conclusion.

In recent years much attention has been devoted to the aqua-ligands substitution reactions of ruthenium(II) complexes as they do not follow a single mechanism. Thorough literature survey reveals a general pattern of the mechanism in which replacement of water molecules occurred through either purely dissociative or dissociative interchange pathway. Deviations from the above mechanism are also noticed in which associative mechanism has been suggested. In view of the conflicting mechanisms proposed so far, we have studied the kinetics of substitution of aqua-ligands from cis-diaqua-bis[2-(m-tolylazo)pyridine]ruthenium(II) ion by 8-hydroxyquinoline, 1,10-phenanthroline and 2,2'-bipyridine to see whether any mechanistic generalisation can be made.

The present paper is related to the findings of the reaction:

\[ c i s \left[ Ru(tap)_{2}(H_2O)\right]^+ + \text{bipy} \rightarrow [Ru(tap)_{2}(bipy)]^{2+} + 2H_2O \]

where tap and bipy represent 2-(m-tolylazo)pyridine and 2,2'-bipyridine respectively.

Materials and Methods
Reactant complex cis-[Ru(tap)_{2}(H_2O)]-(ClO_4)_2.H_2O (complex-I) was prepared by following literature method and characterised by elemental analysis, and spectral data obtained were compared with the data reported in the literature. Absorption spectra of 1 x 10^{-4} mol dm^{-3} solutions at pH 5.6, recorded on a Hilger UVISPEK spectrophotometer, exhibited λ_max at 536 nm. The ionic strength of the reaction medium was adjusted by adding recrystallised NaClO_4. The pH of the medium was adjusted by adding NaOH or HClO_4. The product (complex-II) resulting from the reaction between complex-I and 2,2'-bipyridine (L) was prepared by mixing the reactants in different molar ratios of 1:1, 1:2 and 1:3 ([complex-I],[L],[complex-I] being 1 x 10^{-4} mol dm^{-3}) and thermostating at 50°C for 48 hr at pH 5.6. The absorption spectra of the resultant solutions were taken and found that all the three compositions exhibited identical natures having λ_max at 518 nm. The 1:1 metal-ligand composition of complex-II in solution was verified by Jobs method of continuous variation.

In all the experiments AR grade chemicals were used and doubly distilled water was used for preparing solution. The course of the reaction was followed by measuring the absorbances at 560 nm (using a Hilger UVISPEK spectrophotometer) where a substantial difference existed in the spectra of complex-I and complex-II. The reaction rate was monitored from the decrease of intensity at 560 nm. Equal volumes of complex-I and L of desired concentrations were mixed in such a way that the pseudo-first order rate law becomes applicable. The pseudo-first order rate constant values (k_obs) were obtained by plotting ln[(D_0 - D_a)/(D_t - D_a)] versus time where D_0, D_a and D_t are the optical density values at the beginning of the reaction, at infinite time and at the end of time t respectively. The pseudo-first order plots were linear passing through the
The rate of reaction between an ion and a neutral species is much higher than that of the protonated species, the reaction rate increases with the increase in pH. The acid dissociation equilibrium of complex-I is represented by Eq. (3):

$$[\text{Ru(tap)}_2(\text{H}_2\text{O})_2]^{2+} \rightleftharpoons [\text{Ru(tap)}_2(\text{OH})(\text{H}_2\text{O})]^{+} + \text{H}^+$$

where the $pK_i$ value is observed to be 6.55 at 25°C. The reactivity of hydroxoaquacomplex is usually higher than that of diaqua complex by the well known labilising effect of the coordinated hydroxide ion\(^{-}\). Hence the reaction rate increases again with the increase in pH. Notwithstanding in the present kinetic runs, the substitution reactions were followed at a constant pH of 5.6 to avoid complications caused by adding an additional parameter of $[\text{H}^+]$ to the rate equation. At pH 5.6 complex-I exists mainly in the diaqua form.

(iii) Effect of pH on rate constant

Under the conditions of $pH = 5.6$, [complex-I] = $1 \times 10^{-4}$ mol dm\(^{-3}\), and $[\text{L}] = 2 \times 10^{-3}$ mol dm\(^{-3}\), the rate constant was varied using NaClO\(_4\). A very little change in the $k_{\text{obs}}$ values at 50°C in aqueous medium was observed with increase in ionic strength. The $k_{\text{obs}} \times 10^5$ (s\(^{-1}\)) values are 20.30, 20.14, 20.65, 20.05 and 20.29 at different ionic strengths 0.01, 0.05, 0.1, 0.2 and 0.3 respectively. The incoming ligand is not protonated at pH = 5.6. The rate of reaction between an ion and a neutral molecule in solution should have been independent of ionic strength of the medium\(^{-}\), hence the variation of ionic strength produces no appreciable change in rate constant values.

(iv) Effect of varying [ligand] on rate constant

The concentration of 2,2'-bipyridine was varied in the range of $1 \times 10^{-3}$ to $3 \times 10^{-3}$ mol dm\(^{-3}\) under the conditions of [complex-I] = $1 \times 10^{-4}$ mol dm\(^{-3}\), $pH = 5.6$ and ionic strength = 0.01 mol dm\(^{-3}\). The results presented in Table 1 show that the rate increases with increase in $[\text{L}]$, and tend to approach a limiting value at higher [ligand] at each temperature. Though the rate of reaction is dependent on $[\text{L}]$, outer sphere association is not considered since the incoming ligand species are either neutral or positively charged under the reaction conditions. The unimolecular reaction mechanism shown in Scheme 1 can be proposed to explain the variation of rate with $[\text{L}]$.

$$[\text{Ru(tap)}_2(\text{H}_2\text{O})_2]^{2+} \rightleftharpoons [\text{Ru(tap)}_2(\text{OH})(\text{H}_2\text{O})]^{+} + \text{H}_2\text{O}$$

Table 1: Variation of rate constants with $[\text{L}]$ at different temperatures

<table>
<thead>
<tr>
<th>$[\text{L}] \times 10^{-3}$ (mol dm(^{-3}))</th>
<th>$k_{\text{obs}} \times 10^3$ (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>2.9</td>
</tr>
<tr>
<td>1.5</td>
<td>4.2</td>
</tr>
<tr>
<td>2.0</td>
<td>5.6</td>
</tr>
<tr>
<td>2.5</td>
<td>6.7</td>
</tr>
<tr>
<td>3.0</td>
<td>7.7</td>
</tr>
</tbody>
</table>

The rate of reaction is first order in complex-I. The acid dissociation equilibrium of 2,2'-bipyridine (i.e. L) is represented by Eq. (2):

$$K_i = \frac{[\text{L}][\text{H}^+]}{[\text{L}^+]}$$

where $K_i$ = 6.55 at 25°C. The donor ability of the nonprotonated origin. This linearity is observed from the beginning to the end of the reaction which ruled out the possibility of any kind of consecutive reactions. The rate constants were reproducible within ±3%.

Results and Discussion

(i) Effect of varying [complex-I] on rate constant

The [complex-I] was varied in the range of $0.5 \times 10^{-4}$ to $1.5 \times 10^{-4}$ mol dm\(^{-3}\) under the conditions of $pH = 5.6$, $[\text{L}] = 2 \times 10^{-3}$ mol dm\(^{-3}\) and ionic strength = 0.01 mol dm\(^{-3}\). The $k_{\text{obs}} \times 10^5$ (s\(^{-1}\)) values were found to be 20.14, 20.06, 20.30 and 20.11 at [complex-I] of $0.5 \times 10^{-4}$, $0.75 \times 10^{-4}$, $1.0 \times 10^{-4}$ and $1.5 \times 10^{-4}$ mol dm\(^{-3}\) respectively at 50°C in aqueous medium. The rate of reaction is first order with respect to the [complex-I]. The rate law is represented by Eq. (1).

$$\frac{d[\text{complex-II}]}{dt} = k_{\text{obs}} [\text{complex-I}]$$

(ii) Effect of ionic strength on rate constant

Under the conditions of $pH = 5.6$, [complex-I] = $1 \times 10^{-4}$ mol dm\(^{-3}\), and $[\text{L}] = 2 \times 10^{-3}$ mol dm\(^{-3}\), the ionic strength was varied by NaClO\(_4\). A very little change in the $k_{\text{obs}}$ values at 50°C in aqueous medium was observed with increase in ionic strength. The $k_{\text{obs}} \times 10^5$ (s\(^{-1}\)) values are 20.30, 20.14, 20.65, 20.05 and 20.29 at different ionic strengths 0.01, 0.05, 0.1, 0.2 and 0.3 respectively. The incoming ligand is not protonated at pH = 5.6. The rate of reaction between an ion and a neutral molecule in solution should have been independent of ionic strength of the medium\(^{-}\), hence the variation of ionic strength produces no appreciable change in rate constant values.

(iii) Effect of pH on rate constant

Under the conditions of [complex-I] = $1 \times 10^{-4}$ mol dm\(^{-3}\), $[\text{L}] = 2 \times 10^{-3}$ mol dm\(^{-3}\), ionic strength = 0.01 mol dm\(^{-3}\) and temperature = 50°C the pH of the aqueous medium was varied in the range of 4.5 to 6.0. The $k_{\text{obs}} \times 10^5$ (s\(^{-1}\)) values were 1.49, 5.65, 13.37, 20.30 and 26.34 at pH values 4.5, 5.0, 5.3, 5.6 and 6.0 respectively. The increasing rate of reaction with the increase in pH must be attributed to two acid dissociation equilibria of the ligand L and the complex-I. The acid dissociation equilibrium of 2,2'-bipyridine (i.e. L) is represented by Eq. (2):

$$K_i = \frac{[\text{L}][\text{H}^+]}{[\text{L}^+]}$$

where the value of $pK_i$ is observed\(^{14}\) to be 4.44 at 25°C. Since the donor ability of the nonprotonated...
The rate of formation of the final product can be obtained by applying steady state principle (Eq. 4).

\[
d\frac{[\text{Ru(tap)}_2]\text{L}^{2+}}{dt} = \frac{k_1k_2[Ru(tap)_2(H_2O)]^{2+}[\text{L}]}{k_1 + k_2[\text{L}]} \quad \ldots (4)
\]

Two limiting cases of this rate expression can be achieved: (a) If [L] is low and \( k_1 \gg k_2[\text{L}] \), then Eq. (4) reduces to Eq. (5)

\[
d\frac{[\text{Ru(tap)}_2]\text{L}^{2+}}{dt} = k_1[Ru(tap)_2(H_2O)]^{2+} \quad \ldots (5)
\]

i.e. a second order rate dependent on [ligand] would be obtained. (b) If [L] is high and \( k_2[\text{L}] \gg k_1 \), then Eq. (4) is reduced to Eq. (6)

\[
d\frac{[\text{Ru(tap)}_2]\text{L}^{2+}}{dt} = k_1 \frac{[\text{Ru(tap)}_2(H_2O)]^{2+}}{[\text{L}]} \quad \ldots (6)
\]

i.e. a first order reaction rate independent of [ligand] would be observed. Thus the reaction rate may or may not depend on the concentration of the entering ligand under different reaction conditions. Generally a gradual change from second order to first order kinetics is expected with the increase in [ligand]. A limiting rate is reached at high concentration of ligand. From the effect of variation in [complex-I] on the rate it has already been concluded that Eq. (1) holds. Eq. (7) has been obtained from Eq. (1).

\[
\text{Rate} = k_{\text{obs}}[\text{Ru(tap)}_2(H_2O)]^{2+} \quad \ldots (7)
\]

Equation (8) is obtained from Eqs (4) and (7)

\[
k_{\text{obs}} = k_1k_2[\text{L}]/(k_1 + k_2[\text{L}]) \quad \ldots (8)
\]

or, \( 1/k_{\text{obs}} = 1/k_1 + 1/k_2 + 1/[\text{L}] \quad \ldots (9) \)

It is evident from Eq. (9) that a plot of \( 1/k_{\text{obs}} \) versus \( 1/[\text{L}] \) should be linear with an intercept of \( 1/k_1 \). Actually such linear plots were obtained (Fig. 1). From such linear plots at different temperatures \( k_1 \) values and \( k_{-1}/k_2 \) values were obtained from the intercepts \( 1/k_1 \) and the ratios of the slope to the intercept respectively. The \( k_1 \) and \( k_{-1}/k_2 \) values, reproducible within \( \pm 4\% \), are given in Table 2. The \( k_1 \) value increases and \( k_{-1}/k_2 \) value decreases with increase in temperature. These rate data were compared with that of aqua ligand substitution of \( \text{cis}-[\text{Ru(tap)}_2(H_2O)]^{2+} \) by 1,10-phenanthroline \(^{10}\) (Table 2). The \( k_{-1}/k_2 \) values reveal that 1,10-phenanthroline (i.e. phen) is a better nucleophile for \( [\text{Ru(tap)}_2(H_2O)]^{2+} \) than 2,2'-bipyridine. The \( k_1 \) values at a given tem-

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**Table 2** — Values of \( k_1 \) and \( k_{-1}/k_2 \) at different temperatures [complex-I] = \( 1 \times 10^{-4} \) mol dm\(^{-3} \), ionic strength = 0.01 mol dm\(^{-3} \), pH = 5.6

<table>
<thead>
<tr>
<th>System</th>
<th>( k_1 \times 10^4 ) (s(^{-1} ))</th>
<th>( k_{-1}/k_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40°</td>
<td>45°</td>
</tr>
<tr>
<td>Complex-I + 2,2'-bipyridine</td>
<td>6.5</td>
<td>11.4</td>
</tr>
<tr>
<td>Complex-II + 1,10-phenanthroline</td>
<td>6.2</td>
<td>10.7</td>
</tr>
</tbody>
</table>

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**Fig. 1** — Plot of \( 1/k_{\text{obs}} \) versus \( 1/[\text{L}] \) at different temperatures (A) 40°, (B) 45°, (C) 50°, and (D) 55°C.
temperature are almost identical for both the ligands indicating that both the reactions proceed with a common dissociative pathway as proposed in the reaction Scheme 1.

**(v) Effect of varying dielectric constant of the medium on the rate constant**

The solvent effect of the aqua substitution reaction between complex-I and 2,2'-bipyridine has been studied in three ethanol-water mixtures (10, 20 and 30% v/v) at 50°C. In this experiment [ligand] was varied from $1 \times 10^{-3}$ to $3 \times 10^{-3}$ mol dm$^{-3}$ under the conditions of [complex-I] = $1 \times 10^{-4}$ mol dm$^{-3}$, pH = 5.6, and ionic strength = 0.01 mol dm$^{-3}$. It has been observed that the pseudo-first order rate constants ($k_{\text{obs}}$) decrease with decrease in dielectric constant of the medium. The $k_{\text{obs}}$ values are given in Table 3. From the plots of $1/k_{\text{obs}}$ versus $1/[L]$, $k_1$ and $k_1/k_2$ values were calculated. The $k_1 \times 10^4$ (s$^{-1}$) values are 16.67, 14.29 and 11.63 at 10%, 20% and 30% (v/v) ethanol-water mixtures respectively. It is observed that the $k_1$ values decrease with the increase in organic component of the medium. This result is also consistent with the dissociative mechanism proposed. Laidler-Eyring equation can be used to explain the above facts (Eq. 10).

$$d(\ln k_1)/d(1/D) = e^2Z^2(1/r - 1/r^*)/(2kT)$$

**(vi) Effect of temperature on rate constant**

The substitution reaction of aqua ligands from complex-I by 2,2'-bipyridine has been studied at four different temperatures for different [ligand] in aqueous medium. Activation parameters ($\Delta H^*$ and $\Delta S^*$) of this system were evaluated from the Eyring plot of $\ln (k_1/h/kT)$ versus $1/T$. The activation parameters thus obtained have been compared with that for the substitution of aqua-ligands of the complex-I by 8-hydroxyquinoline$^9$ (i.e. oxine) and 1,10-phenanthroline$^{10}$. The almost identical $\Delta H^*$ value for these systems (Table 4) suggests a dissociative mechanism for the reaction process.

Considering all the above results we suggest a dissociative mechanism for the reaction process. On the slow step complex-I first dissociates into a pentacoordinated intermediate, $[\text{Ru}(\text{tap})_2(\text{H}_2\text{O})]^2^+ $ with the loss of one water molecule. Then this intermediate reacts rapidly with 2,2'-bipyridine to form $[\text{Ru}(\text{tap})_2(\text{bipy})]$. Attachment of one donor nitrogen atoms of 2,2'-bipyridine to the intermediate increases the electron density on ruthenium(II) and as a result the second water molecule is labilised, leading to rapid chelation.

**Acknowledgement**

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<table>
<thead>
<tr>
<th>Table 4 — Activation parameters</th>
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<tbody>
<tr>
<td>System</td>
</tr>
<tr>
<td>cis-[Ru(tap)$_2$(H$_2$O)$_2$]$^2^+$ + bipy</td>
</tr>
<tr>
<td>cis-[Ru(tap)$_2$(H$_2$O)$_2$]$^2^+$ + oxine</td>
</tr>
<tr>
<td>cis-[Ru(tap)$_2$(H$_2$O)$_2$]$^2^+$ + phen</td>
</tr>
</tbody>
</table>
References