Kinetics and mechanism of substitution in cis-diaqua-bis[2-(m-tolylazo)pyridine]ruthenium(II) ion by salicylaldoxime

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The kinetics and mechanism of the title reaction have been investigated spectrophotometrically as a function of [reactant complex], pH (4-6), [incoming ligand], temperature (35-50°C) and medium dielectric constant. The kinetic and activation parameters measured for this reaction fall within the characteristic range of those respective parameters for the substitution of the title complex by many other ligands previously reported and are insensitive to the nature of incoming ligands. A dissociative mechanism is proposed. The effect of medium dielectric constant variation on the reaction rate is also a logical consequence of such mechanism.

Kinetic and mechanistic studies on the substitution reactions in metal complexes still remain a lively issue due to their importance in the preparative, biochemical and analytical procedures of coordination chemistry. In the last few decades, ligand substitution reactions in octahedral complexes of trivalent cobalt\(^1\) and chromium\(^2\) have been investigated extensively. But similar experiments on Ru(II) complexes have received very little attention. Either a purely dissociative or a dissociative interchange mechanism has been postulated for the water replacement reactions of Ru(II) complexes\(^3-9\). Deviations of the above mechanisms are also noticed in which associative mechanism has been proposed\(^10-12\). These mechanistic controversies led us to study the kinetics of substitutions of cis-[Ru(tap)\(_2\)(H\(_2\)O)\(_2\)]\(^2+\) (where tap represents 2-(m-tolylazo)-pyridine) by 8-hydroxyquinoline\(^13\), 1,10-phenanthroline\(^14\), 2,2'-bipyridine\(^15\) and pyridine-2-aldoxime\(^16\) in which a dissociative mechanism has been proposed. All the ligands investigated\(^13-16\) behave as neutral ligands under the present reaction conditions. In this paper we report the results of the kinetic studies on the title reaction in which salicylaldoxime behaves as a negatively charged ligand under the conditions of investigation. It is anticipated that if a dissociative mechanism still applies to this reaction, then the kinetic and activation parameters of this system would be almost identical with the respective values of those parameters for the substitution of cis-[Ru(tap)\(_2\)(H\(_2\)O)\(_2\)]\(^2+\) by many other ligands previously reported\(^14-16\).

Experimental

The reactant cis-[Ru(tap)\(_2\)(H\(_2\)O)\(_2\)]\(^2+\)ClO\(_4\)\(_2\)H\(_2\)O (complex-I) having maximum absorption at 536 nm (\(e = 12150\)) was prepared and characterised according to the published procedures\(^17,18\). The composition of the product complex (complex-II) was determined by recording the spectra of three different solutions thermally equilibrated at 50°C for 48 hrs in which the concentrations of complex-I and salicylaldoxime were maintained at 1:1, 1:2 and 1:3 ratios. All the three compositions exhibited identical spectra having maximum absorption at 549 nm (\(e = 8940\)). The 1:1 stoichiometry of the product of reaction between complex-I and salicylaldoxime was also checked by Job's method of continuous variation. Spectral changes with time associated with the product complex illustrated in Fig. 1 showed clean isosbestic points throughout the period in which the data were collected. Dou-

![Fig. 1 — Absorption spectra for solutions (50°C) at pH = 5.6, \(\mu = 0.01\) mol dm\(^{-3}\) (NaClO\(_4\)) of [Ru(tap)\(_2\)(H\(_2\)O)\(_2\)]\(^2+\) (1.5 \times 10\(^{-4}\) mol dm\(^{-3}\)) and salicylaldoxime (1.5 \times 10\(^{-3}\) mol dm\(^{-3}\))](image)
bly distilled water was used throughout the experiments. Sodium perchlorate was recrystallized from water. All other chemicals used in the experiments were of reagent grade.

The rate of substitution reaction was studied spectrophotometrically with the help of a Shimadzu UV-190 spectrophotometer by using a conventional mixing technique. The absorbance changes were monitored at 455 nm, where a substantial difference existed in the spectra of complex-I and complex II as a function of time. Kinetic runs were carried out under pseudo-first order conditions keeping at least ten fold excess of [substituting ligand] over [Ru(II) species] and the corresponding pseudo-first order plots were linear up to 2-3 half-lives of the reaction. The reported \( k_{\text{obs}} \) values represent an average of four to six replicate runs. The pH of the solution was adjusted by adding NaOH or HClO\(_4\) and measured by using a systronic digital pH-meter. All solutions were maintained at an ionic strength (\( \mu \)) of 0.01 mol dm\(^{-3} \) with added NaClO\(_4\). All the rate constants were reproducible within \( \pm 3\% \) error limit.

**Results and discussion**

The reaction was found to be first order in [complex-I]. The substitution reaction has been investigated in the pH range 4-6 and in aqueous medium at fixed [salicylaldoxime] \((2.25 \times 10^{-4} \text{ mol dm}^{-3})\), ionic strength \(0.01 \text{ mol dm}^{-3}\), temperature \(50{}^\circ\text{C}\) and [complex-I] \((1.5 \times 10^{-4} \text{ mol dm}^{-3})\). The \( k_{\text{obs}} \) values so obtained are compared with those for the substitution of complex-I by pyridine-2-aldoxime under similar conditions employed for the study (Table I). The slight differences of \( k_{\text{obs}} \) values at each pH for the two systems lends strong support in favour of dissociative mechanism. Hence, the acid dissociation equilibria (1) and (2) of salicylaldoxime plays a minor role in explaining the pH dependence of \( k_{\text{obs}} \) values.

\[
\begin{align*}
\text{SalH}_2 & \rightleftharpoons \text{SalH}^- + \text{H}^+ & \kappa_1 \\
\text{SalH}^- & \rightleftharpoons \text{Sal}^{2-} + \text{H}^+ & \kappa_2 \\
\end{align*}
\]

The \( pK_1 \) and \( pK_2 \) values are reported\(^9\) to be <3 and 10.2 respectively. The pH dependence of \( k_{\text{obs}} \) values may be attributed to the acid dissociation equilibrium (3) of complex-I.

\[
[Ru(tap)_2(H_2O)]^{2+} \rightleftharpoons [Ru(tap)_2(H_2O)(OH)]^+ + \text{H}^+ \quad \ldots (3)
\]

The \( pK_1 \) value is determined pH metrically and found to be 6.6 at 25°C. At higher pH the percentage of hydroxoaqua form increases. Hydroxoaqua species being a labile complex due to well known labilising effect of the coordinated hydroxide ion \(^20\), increases the reaction rate.

At fixed [complex-I] \((1 \times 10^{-4} \text{ mol dm}^{-3})\), ionic strength \(0.01 \text{ mol dm}^{-3}\) and pH \((5.6)\) the concentration of the incoming ligand was varied in the range of \(1.5 \times 10^{-2} \text{ to } 1 \times 10^{-2} \text{ mol dm}^{-3}\) for four different temperatures \(35-50{}^\circ\text{C}\) in aqueous medium. The results illustrated in Fig. 2 indicate that \( k_{\text{obs}} \) values increase with increase in [ligand] and tend to approach a limiting value at higher concentration. To explain the variation of rate with salicylaldoxime concentration we propose a unimolecular reaction mechanism (Scheme 1).

![Figure 2](image-url)

**Table I**—pH-Dependence of \( k_{\text{obs}} \) values at 50°C in aqueous medium. [complex-I] = \(1.5 \times 10^{-4} \text{ mol dm}^{-3}\), [ligand] = \(2.25 \times 10^{-4} \text{ mol dm}^{-3}\), \( \mu \) = 0.01 mol dm\(^{-3}\) (NaClO\(_4\)).

<table>
<thead>
<tr>
<th>pH</th>
<th>( k_{\text{obs}} \times 10^4 \text{ (s}^{-1}))</th>
<th>Salicylaldoxime</th>
<th>Pyridine-2-aldoxime*</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>0.24</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>0.68</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>1.32</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td>5.6</td>
<td>2.31</td>
<td>1.97</td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>3.16</td>
<td>2.76</td>
<td></td>
</tr>
</tbody>
</table>

*Values taken from ref. (16)
NOTES 1083

\[
\text{[Ru(taph)(H}_2\text{O})_2\text{]}^{2+} + \text{H}_2\text{O} \xrightarrow{k_1 \text{ (slow)}} \text{[Ru(taph)(H}_2\text{O})_2\text{]}^{2+} + \text{H}_2\text{O} \\
\text{[Ru(taph)(H}_2\text{O})_2\text{]}^{2+} + \text{SalH}^- \xrightarrow{k_2 \text{ (fast)}} \text{[Ru(taph)(SalH)]}^{+} + \text{H}_2\text{O}
\]

(Scheme 1)

Rate Eq. (4) can be deduced from Scheme 1 by applying the steady-state approximation

\[
\frac{d\text{[Ru(taph)(SalH)]}^{+}}{dt} = \frac{k_1 k_2 \text{[Ru(taph)(H}_2\text{O})_2\text{]}^{2+} \text{[SalH}^-]}{k_{-1} + k_2 \text{[SalH}^-]}
\]

... (4)

If [SalH\(^-\)] is low and \(k_{-1} > > k_2 \text{[SalH}^-]\), then Eq. (4) reduces to Eq. (5)

\[
\frac{d\text{[Ru(taph)(SalH)]}^{+}}{dt} = \frac{k_1 k_2 \text{[Ru(taph)(H}_2\text{O})_2\text{]}^{2+} \text{[SalH}^-]}{k_{-1}}
\]

... (5)

This means that a second order rate law is applicable at lower [ligand]. Conversely, if [SalH\(^-\)] is high and \(k_2 \text{[SalH}^-] > > k_{-1}\), then Eq. (4) reduces to Eq. (6)

\[
\frac{d\text{[Ru(taph)(SalH)]}^{+}}{dt} = \frac{k_1 \text{[Ru(taph)(H}_2\text{O})_2\text{]}^{2+}}{k_{-1}/k_2}
\]

... (6)

This indicates that a first order rate law is applicable at higher [ligand]. Thus the reaction rate may or may not depend on the entering [ligand] under different conditions. Generally a gradual change from second order to first order kinetics is expected with the increase in [ligand]. It was found to be so (Fig. 2). Now Eq. (7) is obtained from the effect of varying [complex-I] on rate and Eq. (4).

\[
k_{\text{obs}} = k_1 k_2 \text{[SalH}^-]/(k_{-1} + k_2 \text{[SalH}^-])
\]

... (7)

or,

\[
1/k_{\text{obs}} = 1/k_1 + (k_{-1}/k_2)\text{1/[SalH}^-])
\]

... (8)

According to Eq. (8) the plots of \(1/k_{\text{obs}}\) versus \(1/[\text{SalH}^-]\) should be linear with an intercept of \(1/k_1\) and a slope of \(k_{-1}/(k_1 k_2)\). Actually such straight lines are observed at different temperatures (Fig. 3). The \(k_1\) and \(k_{-1}/k_2\) values are evaluated from the intercepts and the ratios of slope to intercept of such plots respectively. The \(k_1\) and \(k_{-1}/k_2\) values for this system have been compared with those for substitution of cis-[Ru(taph)(H\(_2\)O)]\(_2\)\(^2+\) by 1,10-phenanthroline\(^4\), 2,2'-bipyridine\(^5\) and pyridine-2-aldoxime\(^6\) in Table 2. It is observed that the \(k_1\) values at 35-50°C range are almost identical for substitution of cis-[Ru(taph)(H\(_2\)O)]\(_2\)\(^2+\) by a wide variety of ligands indicating that all these reactions proceed with a common dissociative pathway.

The temperature effect has been investigated at four different temperatures and rate and activation parameters are summarised in Table 2. The almost constant enthalpy for the whole series of ligands is interpreted by assuming that \(\Delta H_t\) is not sensitive to the nature of incoming ligands. This observation is consistent with the view that the activation process is a bond-breaking one and so a dissociative mechanism applies for these type of reactions. In the D-mechanism the \(\Delta S_t\) should be controlled by two factors: (a) The activated complex being higher in energy will have a looser structure than the reactants and hence there will be a greater randomness of motion in the activated state. The formation of the latter will thus be accompanied by an increase in entropy. In the present case, formation of two species [Ru(taph)(H\(_2\)O)]\(_2\)\(^2+\) and H\(_2\)O from [Ru(taph)(H\(_2\)O)]\(_2\)\(^2+\) will cause an increase in entropy. (b) In D-mechanism the size of the activated complex (pentacoordinate) is smaller than that of reactant (octahedral). As such activated...
complex will attract more molecules of the polar solvent (here H₂O) than reactant ion (electrostriction effect). Hence the randomness in the system is decreased in the transition state and a negative value of entropy of activation is expected to be observed.

The measured ΔS¹ is, therefore, really the resultant of these two opposing factors and a small negative value is observed. Taube and coworkers also obtained similar negative values of ΔS¹ for substitution reactions of [Ru(NH₃)₅(H₂O)]³⁺ complex with a wide variety of ligands and these reactions were classified as involving a dissociative mechanism. Equally convincing is Taube's correlation which illustrates that dissociative pathways occurring by trigonalbipyramidal intermediates give positive ΔS¹ values, while negative ΔS¹ values are observed with square-pyramidal intermediates.

Medium polar effects on the substitution of octahedral metal complexes have successfully been used to verify mechanism. Effect of solvent composition on the water replacement reactions of cis-[Ru(tap)₂(H₂O)]²⁺ by salicylaldoxime was studied in three different ethanol-water mixtures (10, 20 and 30% v/v) at 45°C. In this set of experiment the ligand concentration was varied in the range of 1.5 × 10⁻³ to 4.5 × 10⁻³ mol dm⁻³ at a constant pH (5.6), ionic strength (0.01 mol dm⁻³) and [complex-I] (1 × 10⁻⁴ mol dm⁻³). From the plots of ln k₁ versus 1/D at 45°C for complex-I + salicylaldoxime system (where r and r* are the effective radii of the reactant and activated species, respectively, Z = net charge on the complex ion, k = Boltzman constant, T = temperature in absolute degree and D = medium dielectric constant). For a dissociative activation process, one water molecule is lost in the activated state and consequently the size of the activated species is lowered i.e. r* < r. Hence, according to Eq. (9), the plot of ln k₁ versus 1/D should be linear with a negative slope. In practice, we obtained such straight lines (Fig. 4).

All the observation discussed above are consistent with the view that activation for substitution reaction of cis-[Ru(tap)₂(H₂O)]²⁺ ion by salicylaldoxime is largely a bond breaking process and that a dissociative mechanism operates. On the slow step cis-[Ru(tap)₂(H₂O)]²⁺ first dissociates into a pentacoordinated intermediate, [Ru(tap)₂(H₂O)]²⁺ with the loss of one water molecule. Then this intermediate reacts rapidly with salicylaldoxime to form [Ru(tap)₂(SalH)]⁺. The decrease in k₁ values with decrease in medium dielectric constant is also a logical consequence.

### Table 2—Rate and activation parameters for substitution of cis-[Ru(tap)₂(H₂O)]²⁺ by various ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>10⁴ k₁ (s⁻¹)</th>
<th>10³ k₋₁/k₂</th>
<th>ΔH° (kJ mol⁻¹)</th>
<th>ΔS¹ (JK⁻¹mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,10-Phenanthroline</td>
<td>—</td>
<td>—</td>
<td>17.8</td>
<td>—</td>
</tr>
<tr>
<td>2,2'-Bipyridine</td>
<td>—</td>
<td>—</td>
<td>19.2</td>
<td>—</td>
</tr>
<tr>
<td>Pyridine-2-aldoxime</td>
<td>3.0</td>
<td>24</td>
<td>89.9 ± 0.5</td>
<td>—19.1 ± 0.3</td>
</tr>
<tr>
<td>Salicylaldoxime</td>
<td>2.6</td>
<td>20</td>
<td>89.7</td>
<td>—21.3</td>
</tr>
</tbody>
</table>

\[ d(ln k₁)/d(1/D) = e²Z²(1/r - 1/r*)/(2kT) \]  \( \text{Eq. 9) } \]
for the proposed mechanism depicted in Scheme 1.

Acknowledgement

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References