# Kinetics and Mechanism of Anation of *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$ Ion by 8-Quinolinol in Water–Ethanol Mixtures

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**Synopsis.** The anation kinetics of the title complex were investigated spectrophotometrically in 10% (v/v) ethanol–water mixtures and the following rate law has been proposed in the pH range 3.65—6.5.

$$d[Ru(bpy)_2(oxine^-)^+]/dt = \frac{k_1k_2[Ru(bpy)_2(H_2O)_2]^{2+}[oxine]}{k_{-1}+k_2\,[oxine]},$$

where $k_1$ is the water dissociation rate constant of the substrate complex, $k_{-1}$ is the aquation and $k_2$ is the ligand capturing rate constant of the five-coordinate intermediate $[Ru(bpy)_2(H_2O)]^{2+}$. The activation parameters have been calculated and compared with other substitution reactions. Considering all the results, a dissociative mechanism has been suggested.

Through literature survey,[1–11] it is seen that aqua ligand substitutions on Ru center are of great importance. We have reported earlier the substitution reactions of *cis*-diaquabis(2,2′-bipyridine)ruthenium(II) complex ion by a series of ligands e.g. 1,10-phenanthroline, 2,2′-bipyridine, and L-cysteine. It is a very interesting fact that both associative[1] and dissociative[13] mechanisms have been proposed for the same complex ion. Kinetic study of this complex ion with ligands having various types of donor atoms has been a subject of recent interest. Moreover, the above complex ion is aminoacid active. Thus expecting some interesting results, we planned to study the anation kinetics of the title complex by different polydentate ligands in different media. As a part of our studies, we report, herein, the anation studies on *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$ with 8-quinolinol in water–organic medium.

## Experimental

*cis*-$[Ru(bpy)_2CO_3]\cdot 2H_2O$ (A) was prepared by the method described in literature[11] and characterized by elemental analysis and spectral data. Finally, *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$ (complex (I)) was prepared in situ by treating with calculated amount of *p*-toluenesulfonic acid and the spectral data of the solution ($\lambda_{max}$=485 nm) represents complex (I).[1] The product of the reaction between complex (I) and oxine was prepared by mixing them at pH 6.0 on a water bath (temp 50 °C) for 24 h. The red-violet product $[Ru(bpy)_2(oxine^-)]^+$ (II) was then precipitated (as *p*-toluenesulfonate) and characterized by elemental analysis and spectral data.[12] The composition of (II) was also checked by mole ratio method (Fig. 1). The course of the reaction was monitored (440 nm) at pH 6.0. The reaction medium was 10% (v/v) EtOH–$H_2O$ and the rate constants were reproducible within ±3%.

**Kinetic Run.** The substitution reactions were followed spectrophotometrically by using Shimadzu UV-190 spectrophotometer at 440 nm by conventional mixing technique. The pseudo-first-order rate constants ($k_{obs}$) were obtained by plotting $\log(D_\infty - D_0)/(D_\infty - D_t)$ versus time where $D_\infty$, $D_0$, $D_t$ are the O.D. values at infinite time, at the beginning and at the end of time $t$ respectively.

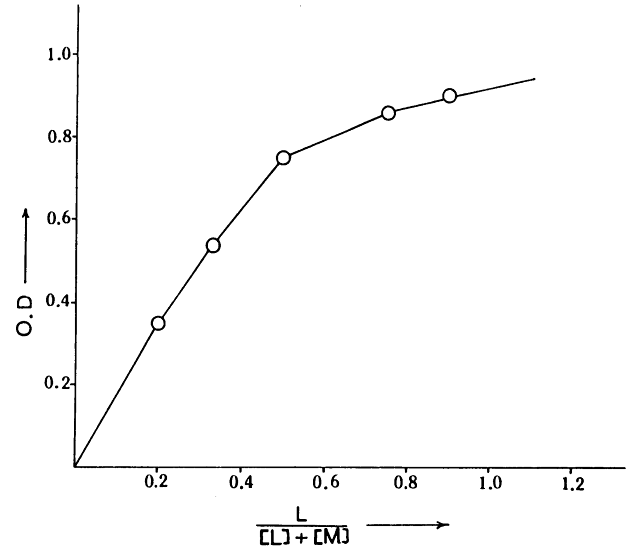
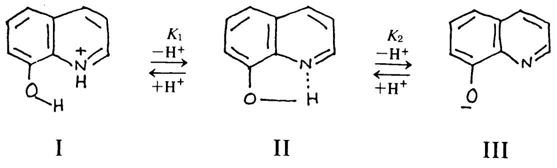


Fig. 1. Mole ratio plot for determining composition of the product at pH=6.0, $[Ru(bpy)_2(H_2O)_2^{2+}]$=[oxine]=$9.5\times10^{-5}$ mol dm$^{-3}$.

## Results and Discussion

**Effect of Varying Complex Concentration on Rate.** Three sets of experiments were carried out at 40 °C maintaining constant ligand concentration of $9.5\times10^{-4}$ M (1 M=1 mol dm$^{-3}$), ionic strength $3.10\times10^{-3}$ mol dm$^{-3}$, pH 6.0 and varying starting complex concentration from $6.3\times10^{-5}$ mol dm$^{-3}$ to $12.7\times10^{-5}$ mol dm$^{-3}$ and the values of the pseudo-first-order rate constants, $k_{obs}/10^5$, were found to be 4.8, 5.12, and 5.10 s$^{-1}$ at [complex (I)] $6.3\times10^{-5}$, $9.5\times10^{-5}$, and $12.7\times10^{-5}$ mol dm$^{-3}$ respectively showing first-order with respect to the complex (I).

**Variation of Rate Constant with pH.** At fixed [complex (I)] ($9.5\times10^{-5}$ mol dm$^{-3}$), [oxine] ($9.5\times10^{-4}$ mol dm$^{-3}$) and ionic strength ($3.1\times10^{-3}$ mol dm$^{-3}$), the $k_{obs}$ values at 40 °C in 10% ethanol–water increased with increase in pH (adjusted by *p*-toluenesulfonic acid and NaOH). The $k_{obs}/10^5$ values are 0.43, 2.88, 3.84, 5.1, and 6.72 at pH 3.65, 5.0, 5.5, 6.0, and 6.5 respectively. Consider the acid dissociation equilibria of the ligand as follows.



I II III

($pK_1$=5.02, $pK_2$=9.81 at 25 °C)
[Ref. 15]

It is obvious that at pH 6.0, form II predominates. On the other hand at the same pH the title complex will exist mainly in diaqua form as its p$K_1$ value[2)] lies between 9 and 10. Hence under the reaction conditions, as the pH is increased the equilibrium will be shifted to right with the increase in donor ability of the ligand, which in turn increases the reaction rate.

**Effect of Varying Oxine Concentration.** The concentration of oxine was varied in the range $9.5\times10^{-4}$ mol dm$^{-3}$ to $28.5\times10^{-4}$ mol dm$^{-3}$ at four different temperatures at a fixed [complex (I)] ($9.5\times10^{-5}$mol dm$^{-3}$), pH (6.0) and ionic strength ($3.1\times10^{-3}$ mol dm$^{-3}$). The results shown in Table 1 indicate that the rate increases with increasing oxine concentration, but gradually reaches a limiting rate. The following scheme can be proposed to explain the nature of variation of the incoming ligand concentration on rate.

$$[\mathrm{Ru(bpy)_2(H_2O)_2}]^{2+} \underset{k_{-1}(\text{fast})}{\overset{k_1(\text{slow})}{\rightleftharpoons}} [\mathrm{Ru(bpy)_2(H_2O)}]^{2+} + \mathrm{H_2O}$$

$$[\mathrm{Ru(bpy)_2(H_2O)}]^{2+} + \text{oxine} \xrightarrow[(\text{fast})]{k_2} [\mathrm{Ru(bpy)_2(oxine^-)}]^{+} + \mathrm{H_3O^+}$$

Assuming steady state conditions and the deaquation equilibrium a familiar rate expression gives the limiting laws [Eqs. 1 and 2].

$$\mathrm{d}[\mathrm{Ru(bpy)_2(oxine^-)^+}]/\mathrm{d}t = \frac{k_1k_2[\mathrm{Ru(bpy)_2(H_2O)_2}^{2+}][\text{oxine}]}{k_{-1}+k_2\,[\text{oxine}]}. \tag{1}$$

Now, at high concentrations of the ligand,

$$\mathrm{d}[\mathrm{Ru(bpy)_2(oxine^-)^+}]/\mathrm{d}t = k_1[\mathrm{Ru(bpy)_2(H_2O)_2}^{2+}], \tag{2}$$

which is independent of the ligand concentration. Now

$$k_{\text{obs}} = \frac{k_1k_2[\text{oxine}]}{k_{-1}+k_2\,[\text{oxine}]},$$

or,

$$1/k_{\text{obs}} = 1/k_1 + k_{-1}/k_1k_2[\text{oxine}]. \tag{3}$$

From the above equation, a plot of $1/k_{\text{obs}}$ versus 1/[oxine] at constant pH is linear with the intercept $1/k_1$ and slope $k_{-1}/k_1k_2$ (Fig. 2). The $k_1$ and $k_{-1}/k_2$ values, at different temperatures are given in Table 2. The $k_1$ and $k_{-1}/k_2$ values for another ligand[13)] are also cited there for comparison. The nearer values of $k_1$ for different ligands indicate a common dissociative pathway as proposed in our reaction scheme.

**Effect of Temperature on Rate.** Activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) obtained from Eyring plot are shown in Table 3. The activation parameters for different reacting systems are also given for comparison.

Table 1. Variation of Rate Constant with [oxine] at Different Temperatures. [complex I]=$9.5\times10^{-5}$ mol dm$^{-3}$, ionic strength ($\mu$)=$3.1\times10^{-3}$ mol dm$^{-3}$, and pH=6.0

| [oxine]/$10^4$ mol dm$^{-3}$ | $k_{\text{obs}}/10^5$ in s$^{-1}$ | | | |
|---|---|---|---|---|
| | 35 °C | 40 °C | 45 °C | 50 °C |
| 9.50 | 2.56 | 5.12 | 6.98 | 11.51 |
| 14.25 | 2.36 | 6.14 | 8.86 | 14.40 |
| 19.00 | 4.22 | 7.68 | 10.97 | 16.45 |
| 23.75 | 4.80 | 8.40 | 12.80 | 19.19 |
| 28.50 | 5.80 | 10.23 | 13.96 | 21.90 |

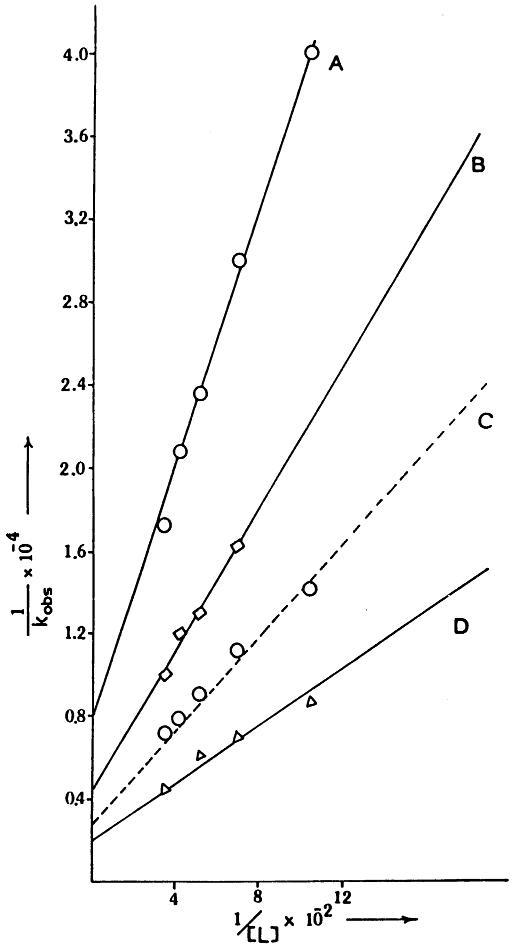


Fig. 2. Plots of $1/k_{\text{obs}}$ versus 1/[L] at different temperatures (A) 35 °C, (B) 40 °C, (C) 45 °C, and (D) 50 °C.

Table 2. Values of $k_1$ and $k_{-1}/k_2$ at Different Temperatures and pH 6.0 and $\mu$=$3.1\times10^{-3}$ mol dm$^{-3}$

| System | $k_1\times10^4$ | | | | $k_{-1}/k_2$ | | | |
|---|---|---|---|---|---|---|---|---|
| | 35 °C | 40 °C | 45 °C | 50 °C | 35 °C | 40 °C | 45 °C | 50 °C |
| $[\mathrm{Ru(bpy)_2(H_2O)_2}]^{2+}$ +oxine | 1.25 | 2.5 | 3.57 | 5.0 | .0042 | .0037 | .0035 | .0033 |
| $[\mathrm{Ru(bpy)_2(H_2O)_2}]^{2+}$ +1,10-phenanthroline (at pH 3.65) | 1.25 | 2.5 | 4.44 | 6.67 | .0156 | .0143 | .0135 | .0125 |

Table 3. Activation Parameters

| System | $\Delta H^{\neq}$<br>kJ mol$^{-1}$ | $\Delta S^{\neq}$<br>J K$^{-1}$ mol$^{-1}$ | Ref. |
|---|---|---|---|
| *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$+oxine | 67.0 | −101.2 | This work |
| *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$+phen | 89.3 | −28.7 | 13 |
| *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$+bpy | 95.7 | −27.8 | 14 |
| *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$+$N_3^-$ | 67.3[a] | −44.4[a] | 1 |
| *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$+$SCN^-$ | 63.5[a] | −71.9[a] | 1 |
| *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$+$NO_2^-$ | 68.2[a] | −47.5[a] | 1 |

a) $\Delta H^{\neq}$ and $\Delta S^{\neq}$ have been calculated from Arrhenius activation parameters.

The heat of activation values are quite comparable to those reported earlier for other anation reactions which also supports the mechanism for unimolecular activation. The measured value of $\Delta S^{\neq}$ is negative. In the reaction studied, electrostriction effect is dominant due to decrease in size of the activated ion. The activated ion is more solvated than the reactant and as a consequence entropy is decreased.

**Mechanism and Conclusion.** The present investigation of aqua ligand substitution suggests the following mechanism. In a slow step, the diaqua complex dissociates into a penta-coordinated intermediate which reacts with oxine and water at a faster rate. Attachment of one of the donors (nitrogen end) of oxine increases the electron density on the metal which also favors the expulsion of the second water molecule and subsequent rapid chelation step.

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