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Kinetics and Mechanism of Substitution of Aqua-Ligands from *cis*-Diaquobis-[2-(*m*-tolylazo)pyridine]ruthenium(II) Complex by 1,10-Phenanthroline in Aqueous Medium

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The kinetics of substitution of aqua-ligands from above title complex by 1,10-phenanthroline in aqueous medium has bean studied spectrophotometrically at different temperatures (40—55 °C). The following rate law has been established for the reaction systems at pH 5.6.

$$\frac{d[\mathrm{Ru(tap)_2L^{2+}}]}{dt}=\frac{k_1k_2[\mathrm{Ru(tap)_2(H_2O)_2{}^{2+}}][\mathrm{L}]}{k_{-1}+k_2[\mathrm{L}]},$$

where L and tap represent 1,10-phenanthroline and 2-(*m*-tolylazo)pyridine respectively. k_1 is the water dissociation rate constant of $[\mathrm{Ru(tap)_2(H_2O)_2}]^{2+}$ (i.e. complex 1), k_{-1} is the aquation rate constant, and k_2 is the ligand capturing rate constant of the penta coordinated intermediate, $[\mathrm{Ru(tap)_2(H_2O)}]^{2+}$. Ionic strength has a very little effect on the rate constants. The rate increases with the increase in pH in the range of 4.5 to 6.0. Activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) were also calculated. Experimental results are consistent with a dissociative mechanism. The solvent effect study was used to verify the mechanistic conclusion.

Elucidation of the mechanism of aqua-ligand substitutions of Ru(II) complexes has been a subject of recent interest. No single mechanism is adequate to explain the variety of observations in the water displacement reactions of Ru(II) complexes. Thorough survey[1—7] reveals a general pattern of the mechanism in which replacement of water molecule occurred through either purely dissociative or dissociative interchange process. Deviations from the above mechanism are also noticed in which associative mechanism has been suggested.[8] In view of the conflicting mechanisms proposed so far, we have studied the kinetics of substitution of aqua ligands from the complex 1 by 8-hydroxyquinoline[9] which behaved as a good bidentate ligand. The present paper deals with the findings of the reaction between the complex 1 and 1,10-phenanthroline in aqueous medium.

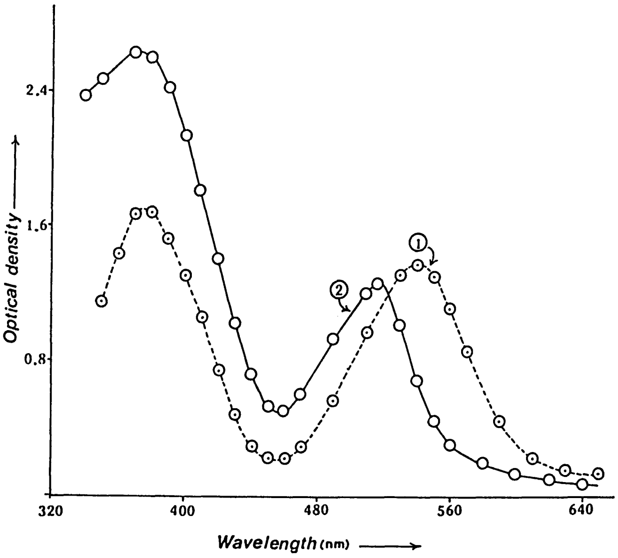

Fig. 1. Spectra of reactant complex *cis*-$[\mathrm{Ru(tap)_2(H_2O)_2}]^{2+}$ (1) and its product $[\mathrm{Ru(tap)_2L}]^{2+}$ (2).

Experimental

Materials. Reactant complex *cis*-$[\mathrm{Ru(tap)_2(H_2O)_2}](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$ having absorption maximum at 536 nm was prepared by the method described in the literature[10,11] and characterized by elemental analysis and spectral data. The pH of the solution was maintained in the acidic region to prevent the oxidation of Ru(II) to Ru(III). The ionic strength of the reaction medium was adjusted with recrystallized $\mathrm{NaClO_4}$. The pH of the medium was adjusted by adding NaOH or $\mathrm{HClO_4}$. The temperature was controlled within ±0.1 °C. The rate constants were reproducible within ±3%.

Kinetic Run. All the kinetic runs were followed by measuring absorbances at 560 nm (using a Hilger UVISPEK Spectrophotometer) where a substantial difference existed in the spectra of the complex 1 and the product (Fig. 1). The spectral change has an isosbestic point at 522 nm. Equal volumes of the complex 1 and L were mixed for kinetical measurements. The composition of the reaction mixture was maintained in such a way that the pseudo-first order rate law becomes applicable. [Complex 1] and [L] were varied in the range 0.5×10^{-4} to 2.0×10^{-4} $\mathrm{mol\,dm^{-3}}$ and 1×10^{-3} to 3×10^{-3} $\mathrm{mol\,dm^{-3}}$ respectively. The pseudo-first order rate constant values (k_{obs}) were obtained by plotting $\ln[(D_0-D_\infty)/(D_t-D_\infty)]$ vs. time (D_∞, D_t, and D_0 are the optical density values at infinite time, at the end of time t, and at the beginning of the reaction respectively). The plot of $\ln[(D_0-D_\infty)/(D_t-D_\infty)]$ vs. time t gave a good straight line passing through the origin (Fig. 2). This linearity is observed from the beginning to the end of the reaction which ruled out the possibility of any kind of consecutive reactions.

Results and Discussion

Stoichiometry. The composition of the product-complex having absorption maximum at 516 nm was determined to be 1:1 metal-ligand ratio by Job's

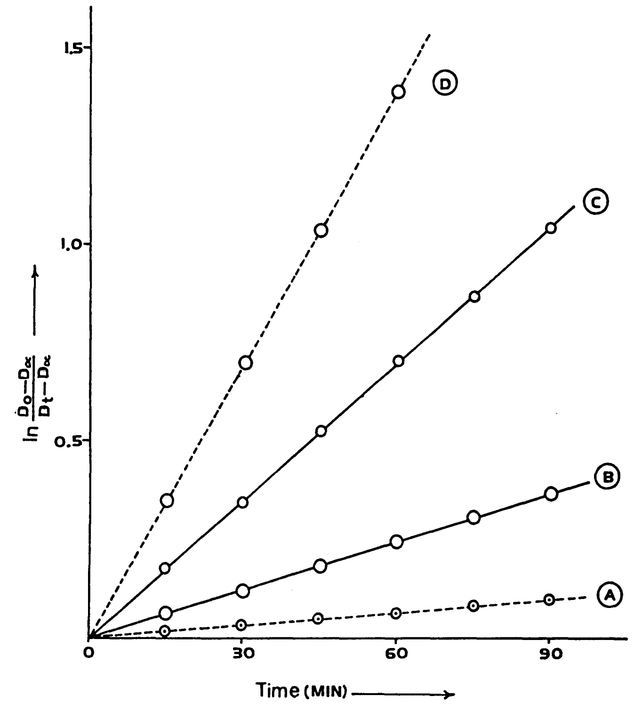

Fig. 2. Plot of $\ln[(D_o-D_\infty)/(D_t-D_\infty)]$ vs. time t at 50 °C in aqueous medium. [complex 1]=0.0001 mol dm^{-3}, [L]=0.002 mol dm^{-3}, ionic strength= 0.0003 mol dm^{-3}, pH=A) 4.5, B) 5.0, C) 5.6, and D) 6.0.

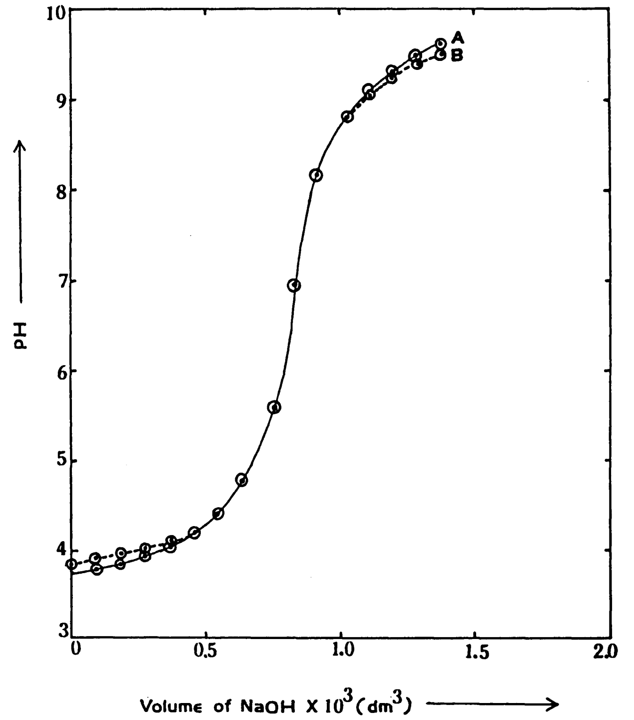

Fig. 3. pH-metric titration curves in aqueous medium. A) Blank titration curve, and B) Titration curve for product-complex.

method of continuous variation. Two possible products were expected in solution: (a) $[Ru(tap)_2L]^{2+}$ and (b) $[Ru(tap)_2(H_2O)(LH)]$.$^{3+}$ To establish the composition of the product between (a) and (b), pH-metric titrations were performed with the reaction product in solution. Sodium hydroxide solution (0.01 mol dm^{-3}) was added to the solution of 0.04 dm^3 of 1×10^{-4} mol dm^{-3} product complex at 298 K using a burrette. The initial concentrations of $HClO_4$ and $NaClO_4$ in the titration mixture were maintained at 2.5×10^{-4} and 0.1 mol dm^{-3} respectively. The pH-metric titration curves showed no proton liberation from the product-complex (Fig. 3), indicating that the product is $[Ru(tap)_2L]^{2+}$ and not the protonated species, $[Ru(tap)_2(H_2O)(LH)]^{3+}$.

Effect of Complex 1 Concentration on Rate. At fixed ligand concentration, [L], (0.002 mol dm^{-3}), the concentration of complex 1, [complex 1], was varied in the range of 0.5×10^{-4} to 2.0×10^{-4} mol dm^{-3} under the conditions of pH and ionic strength at 5.6 and 6×10^{-4} mol dm^{-3} respectively. The $k_{obs}\times10^4\,s^{-1}$ values were found to be 2.85, 2.87, 2.85, and 2.86 at 0.5×10^{-4}, 1×10^{-4}, 1.5×10^{-4}, and 2×10^{-4} mol dm^{-3} complex concentrations respectively. These values of k_{obs} are in good agreement with the first order rate law with respect to the [complex 1].

Effect of Ionic Strength. At fixed [complex 1] (0.0001 mol dm^{-3}), pH 5.6 and [L] (0.001 mol dm^{-3}), the ionic strength was varied by $NaClO_4$. A very little change in the k_{obs} values at 50 °C in aqueous medium was observed with the increase in ionic strength. The $k_{obs}\times10^4\,s^{-1}$ values are 1.57, 1.56, 1.59, and 1.60 at different ionic strengths 0.0003, 0.1, 0.2, and 0.3 mol dm^{-3} respectively. L 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,[12] hence the variation of ionic strength produces no appreciable change in rate. Hence the ionic strength is maintained at low values.

Effect of pH. Large pH-effect on the rate was observed. At a fixed 0.0001 mol dm^{-3} [complex 1], 0.002 mol dm^{-3} [L], and 0.0003 mol dm^{-3} ionic strength the $k_{obs}\times10^4\,s^{-1}$ values at 50 °C in aqueous medium are 0.18, 0.68, 2.87, and 3.83 at pH 4.5, 5.0, 5.6, and 6.0 respectively as shown in Fig. 2. The effect must be attributed to two acid dissociation equilibria of the ligand L and the complex 1. 1,10-Phenanthroline (i.e. L) equilibrates as follows:

$$LH^+ \overset{K_1}{\rightleftharpoons} L + H^+, \qquad (1)$$

where the value of pK_1 is 4.94 at 25 °C.[13] Since the donor ability of nonprotonated 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 1 can be represented as follows:

$$cis\text{-}[Ru(tap)_2(H_2O)_2]^{2+} \overset{K'_1}{\rightleftharpoons} cis\text{-}[Ru(tap)_2(OH)(H_2O)]^+ + H^+, \qquad (2)$$

where the pK'_1 value is 6.55 at 25 °C.[9] The reactivity of hydroxoaqua complex is usually higher than that of diaqua-complex by the well known labilising effect of the coordinated hydroxide ion.[14] 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 $[H^+]$ to a rate equation. At pH 5.6 the complex 1 exists in the diaquo form.

Effect of Ligand Concentration. At fixed [complex 1] (0.0001 mol dm^{-3}), pH 5.6, and ionic strength (0.0003 mol dm^{-3}) the ligand concentrations were varied in the range of 0.001 to 0.003 mol dm^{-3} at four different temperatures in aqueous medium. The results given in Table 1 exhibit that the reaction rate increases with the increase of [L] and reaches a limiting value at higher [L] (Fig. 4). As the incoming ligand (i.e. L) is either neutral or positively charged under the reaction conditions, therefore ionic outer sphere association was not considered in spite of the rate of reaction was found to be dependent on the [L]. The following unimolecular reaction mechanism can be proposed to explain the variation of rate with [L].

Table 1. Values of k_{obs} in Aqueous Medium at Different Temperatures. [complex 1]=0.0001 mol dm^{-3}, pH=5.6, and Ionic Strength=0.0003 mol dm^{-3}

[L]×10^3	k_{obs}×10^4/s^{-1}			
mol dm^{-3}	40 °C	45 °C	50 °C	55 °C
1.0	0.44	0.89	1.57	3.18
1.5	0.63	1.29	2.27	4.89
2.0	0.81	1.63	2.87	5.83
2.5	0.98	1.97	3.41	7.08
3.0	1.15	2.26	4.03	8.08

$$[\mathrm{Ru(tap)_2(H_2O)_2}]^{2+} \underset{k_{-1}(\mathrm{fast})}{\overset{k_1(\mathrm{slow})}{\rightleftharpoons}} [\mathrm{Ru(tap)_2(H_2O)}]^{2+} + \mathrm{H_2O}, \quad (3)$$

$$[\mathrm{Ru(tap)_2(H_2O)}]^{2+} + \mathrm{L} \xrightarrow[\mathrm{fast}]{k_2} [\mathrm{Ru(tap)_2L}]^{2+} + \mathrm{H_2O}. \quad (4)$$

By assuming steady state conditions we can deduce Eq. 5.

$$\frac{\mathrm{d[Ru(tap)_2\ L^{2+}]}}{\mathrm{d}t} = \frac{k_1k_2[\mathrm{Ru(tap)_2(H_2O)_2}^{2+}][\mathrm{L}]}{k_{-1}+k_2[\mathrm{L}]}. \quad (5)$$

At low ligand concentration, $k_{-1} \gg k_2[\mathrm{L}]$, so Eq. 5 reduces to Eq. 6

$$\frac{\mathrm{d[Ru(tap)_2\ L^{2+}]}}{\mathrm{d}t} = \frac{k_1k_2[\mathrm{Ru(tap)_2(H_2O)_2}^{2+}][\mathrm{L}]}{k_{-1}}. \quad (6)$$

This means that a second order rate law is applicable at lower [L]. At high ligand concentration, $k_2[\mathrm{L}] \gg k_{-1}$,

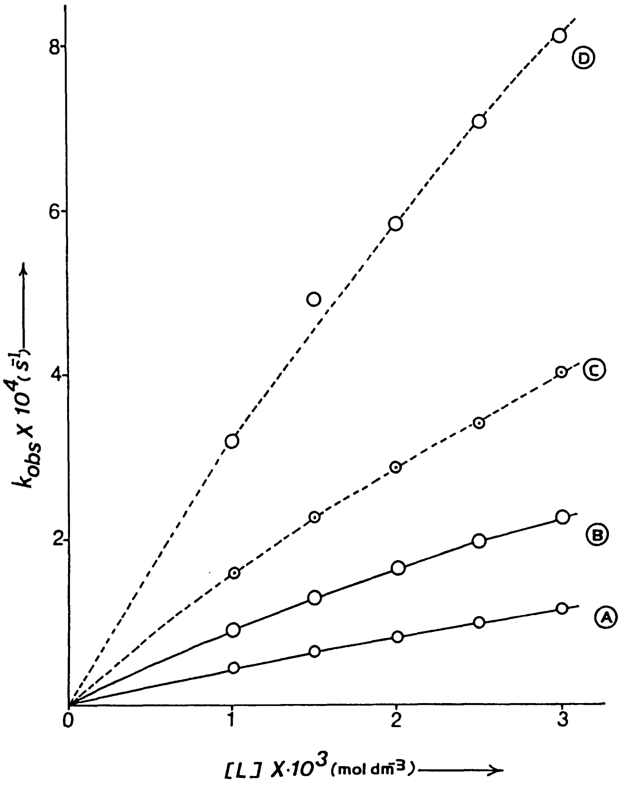

Fig. 4. Effect of ligand concentration (L) on rate constant (k_{obs}) at different temperatures, A) 40 °C, B) 45 °C, C) 50 °C, and D) 55 °C.

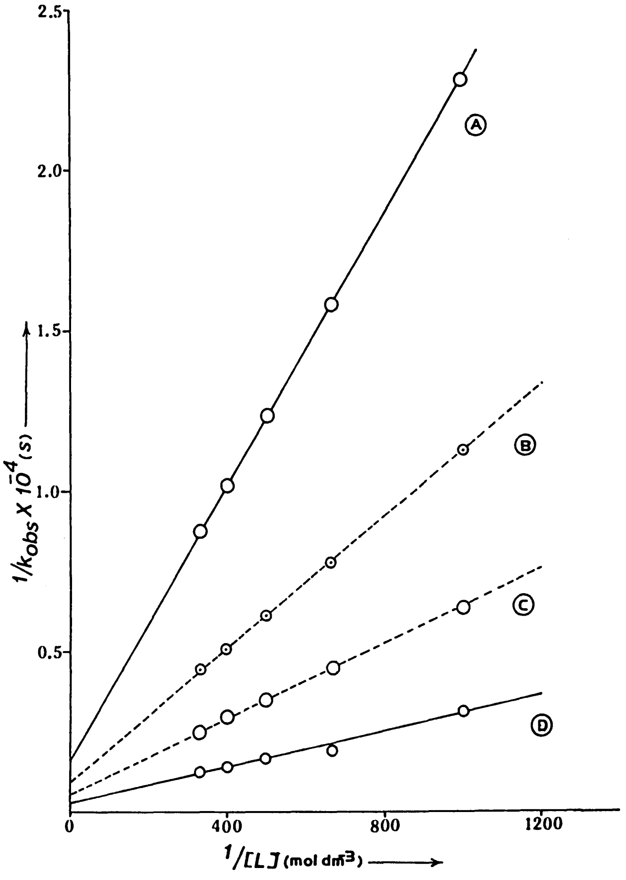

Fig. 5. Plot of 1/k_{obs} vs. 1/[L] at different temperatures A) 40 °C, B) 45 °C, C) 50 °C, and D) 55 °C.

so the rate law reduces to Eq. 7.

$$d[\mathrm{Ru(tap)_2\,L^{2+}}]/dt = k_1[\mathrm{Ru(tap)_2(H_2O)_2}^{2+}]. \qquad (7)$$

This indicates that under these conditions the rate of reaction should be independent of [L]. A limiting rate is reached at high [L] (Fig. 4). From the effect of variation of [complex 1] on the rate it has already been concluded Eq. 8 holds

$$\mathrm{Rate} = k_{\mathrm{obs}}\,[\mathrm{Ru(tap)_2(H_2O)_2}^{2+}]. \qquad (8)$$

From Eq. 5 this gives rise to Eq. 9

$$k_{\mathrm{obs}} = \frac{k_1k_2\,[\mathrm{L}]}{k_{-1}+k_2[\mathrm{L}]} \qquad (9)$$

or

$$1/k_{\mathrm{obs}} = 1/k_1 + k_{-1}/k_1k_2 \cdot 1/[\mathrm{L}]. \qquad (10)$$

Plots of $1/k_{\mathrm{obs}}$ vs. 1/[L] should be linear with an intercept of $1/k_1$. Actually such straight lines were obtained (Fig. 5) at different temperatures. Numerical values of $1/k_1$ and k_{-1}/k_2 were obtained from the intercepts and the ratios of the slope to the intercept. The k_1 and k_{-1}/k_2 values are given in the Table 2. The k_1 value increases and k_{-1}/k_2 value decreases with the increase in temperature. The k_1 value at 45 °C is compared with that of the reaction of the complex 1 with 8-hydroxyquinoline (Table 3). The slight variation in rate constant values in two systems is due to slight difference in pH. The almost similar rate constants indicate that both the reactions proceed with the common dissociative mechanism. From the k_1 values at four different temperatures, the value of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were derived by using the Eyring equation (Fig. 6) and compared with other substitution reaction (Table 3). The almost identical $\Delta H^{\neq}$ value as compared to the reaction of [Ru(tap)$_2$(H$_2$O)$_2$]$^{2+}$ with 8-hydroxyquinoline suggests a dissociative mechanism for the reaction process.

Table 2. k_1 and k_{-1}/k_2 Values at Different Temperatures in Aqueous Medium

	40 °C	45 °C	50 °C	55 °C
$k_1 \times 10^4/\mathrm{s}^{-1}$	6.2	10.7	17.8	32.0
k_{-1}/k_2	0.013	0.011	0.010	0.009

Table 3. Comparison of Activation Parameters and k_1 Values of Analogous Systems

System	$k_1 \times 10^3/\mathrm{s}^{-1}$ at 45 °C	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J K^{-1} mol^{-1}	Ref.
[Ru(tap)$_2$(H$_2$O)$_2$]$^{2+}$ +8-hydroxyquinoline (at pH 5.8)	2.0	82.44	−37.08	9
[Ru(tap)$_2$(H$_2$O)$_2$]$^{2+}$ +1,10-phenanthroline (at pH 5.6)	1.1	88.75	−23.20	This work

Table 4. $k_{\mathrm{obs}} \times 10^4/\mathrm{s}^{-1}$ Values at Different EtOH-H$_2$O Mixtures at 50 °C, pH=5.6, [complex 1]=0.0001 mol dm^{-3}, and Ionic Strength=0.0003 mol dm^{-3}

[L]	EtOH-H$_2$O (v/v %)		
mol dm^{-3}	10	20	30
0.0010	1.19	0.89	0.64
0.0015	1.72	1.30	0.94
0.0020	2.22	1.67	1.21
0.0025	2.76	2.04	1.49
0.0030	3.11	2.47	1.74

Effect of Dielectric Constant. The solvent effect of the aqua-ligand substitution reaction of the complex 1 with 1,10-phenanthroline was studied in three different ethanol-water mixtures (10, 20, and 30% v/v) at 50 °C. The k_{obs} values are given in Table 4. From the plots of $1/k_{\mathrm{obs}}$ vs. 1/[L], k_1 and k_{-1}/k_2 values were calculated. The values of $k_1 \times 10^4\,\mathrm{s}^{-1}$ are 15.4, 13.3, and 11.0 at 10, 20, and 30% (v/v) ethanol-water mixtures respectively. It is observed that the values of k_1 decrease with the increase of organic component of the medium. Actually this is in good agreement with the dissociative mechanism proposed. Laidler-Eyring equation[15] can be used to explain the above facts in the following form.

$$d(\ln k_1)/d(1/D) = e^2Z^2(1/r - 1/r^*)/(2kT), \qquad (11)$$

where Z is the net charge on the complex ion, r and r^* are the effective radii of the reactant and activated species, k = Boltzman constant, T = temperature in absolute degree, and D represents the varying dielectric constant of the medium. According to Eq. 11 if $r^* < r$, plot of $\ln k_1$ vs. $1/D$ will give a straight line having a

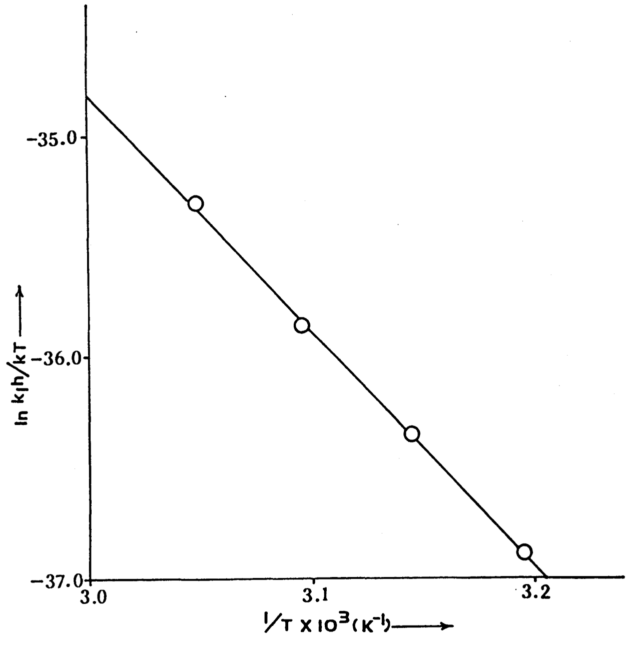

Fig. 6. Eyring plot of $\ln(k_1h/kT)$ vs. $1/T$.

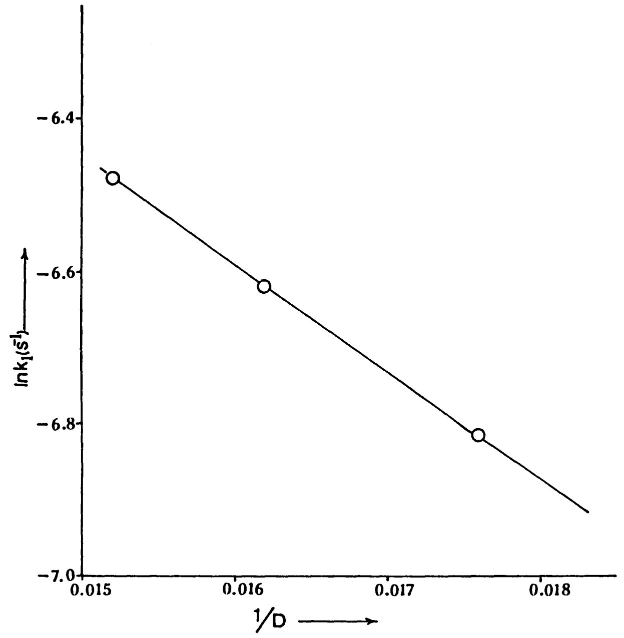

Fig. 7. Plot of $\ln k_1$ vs. $1/D$ at 50 °C.

negative slope. Since one water molecule is lost in the activated state of the dissociative process, the size of the activated complex gets reduced i.e. r^* becomes smaller than r. By plotting $\ln k_1$ vs. $1/D$ we have obtained a good straight line with a negative slope (Fig. 7).

However solvation of 1,10-phenanthroline in ethanol–water mixture is somewhat greater than that in pure water. This is an additional factor which is responsible for decrease in the rate at high concentration of ethanol.

Conclusion

Basing all the above facts we suggest a dissociative mechanism in which *cis*-$[Ru(tap)_2(H_2O)_2]^{2+}$ first dissociates into a penta-coordinated intermediate, $[Ru(tap)_2(H_2O)]^{2+}$ and then the intermediate reacts rapidly with L to form $[Ru(tap)_2 L]^{2+}$.

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