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Kinetic and mechanistic studies on the interaction between azide and *cis*-diaqua-chloro-tris-(dimethyl sulfoxide)-ruthenium(II) complex in aqueous medium

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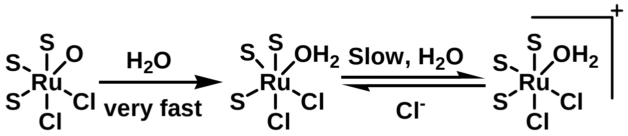
ABSTRACT

The kinetics of interaction between azide and *cis*-$[RuCl(Me_2SO)_3(H_2O)_2]^+$ have been studied spectrophotometrically as a function of$[RuCl(Me_2SO)_3(H_2O)_2^+]$, [azide] and temperature at a particular pH(5.0), where the substrate complex exists predominantly as a diaqua species(in aqueous solution) and azide as the monoanionic species. The reaction has been found to proceed via two distinct consecutive steps i.e., it shows a non-linear dependence on the concentration of azide: both processes are [ligand] dependant. The rate constants for the processes are: $k_1 \sim 10^{-3}\ s^{-1}$ and $k_2 \sim 10^{-5}\ s^{-1}$. The activation parameters were calculated from Eyring plots suggest an associative mechanism for the interaction process. From the temperature dependence of the outersphere association equilibrium constants, the thermodynamic parameters were also calculated, which gives a negative G° value at all temperature studied, supporting the spontaneous formation of an outersphere association complex.

INTRODUCTION

A variety of displacement reactions of ruthenium(II), in which one unidentate ligand is replaced by another, have been reported in the literature. Anation studies on different substrates indicate both dissociative[1,2] as well as associative[3] mode of activation. No single mechanism is adequate to explain the variety of observations in ligand replacement reactions on ruthenium(II). On the other hand there is a steadily increasing interest in transition metal complexes other than the traditional Pt-based compounds for use as chemotherapeutic agents against cancer. *Cis*-platin[4] and carboplatin[5] are two well–known drugs for cancer chemotherapy, but certain tumours are resistant to two drugs. Also platinum complexes induce toxic effects such as nephrotoxicity and neurotoxicity. Complexes of other **(4d)** and **(5d)** metal ions, especially ruthenium, rhodium, iridium and palladium, have been reported to have antibacterial power[6,7]. Complexes of these metal ions with nucleic acid constituents[5,8,9], di[10] and tri[11] peptides and other bioactive ligands[12-15] were studied. Mechanistic study on formation of these complexes by anation reaction may help to understand the mode of *in vivo* activities of these complexes. Especially ruthenium complexes are becoming more and more popular due to their well developed synthetic chemistry and great flexibility to fine-tune properties by modification to the ligand sphere. Ruthenium(II) complexes are less toxic than *cis*-platin[16,17]. A number of ruthenium compounds serve as bacterial mutagens which indicate that at least some ruthenium complexes are capable of damaging genetic materials[18-21]. The studies on the bioactivities of ruthenium(II/III) complexes are still a developing area.



Scheme 1 : Chemical behavior of *cis*-[Ru(Me_2SO)$_4$$Cl_2$] in aqueous medium

It was already established that [Ru(dmso)$_4$Cl$_2$] has anticancer and antitumor activity[22] but no study were done in aqueous medium. This is the first report where the kinetic study on [Ru(dmso)$_4$Cl$_2$] is done in aqueous medium.

Sodium azide is a useful probe reagent, mutagen, and preservative. In hospitals and laboratories, it is abiocide; it is especially important in bulk reagents and stock solutions which may otherwise support bacterial growth where the sodium azide acts as a bacteriostatic by inhibiting cytochrome oxidase in gram-negative bacteria; gram-positive (pneumococci, lactobacilly) are resistant[23], a characteristic similar to antibiotic resistance. It is also used in agriculture for pest control. Azide inhibits cytochrome oxidase by binding irreversibly to the heme cofactor in a process similar to the action of carbon monoxide. Sodium azide particularly affects organs that undergo high rates of respiration, such as the heart and the brain.

With this background we planned to study the interaction of *cis*-[RuCl(Me_2SO)$_3$(H_2O)$_2$]$^+$, the reactive species of [Ru(dmso)$_4$Cl$_2$] in aqueous medium, with different bioactive ligands e.g., azide, glycylglycine, glycyl-l-leucine, glycyl-l-valine etc. and with certain nucleocides and nucleotides. In the present work the kinetic and mechanistic details of the interaction of azide in the aqueous medium at pH 5.0 was examined. The importance of the work lies in the fact that in the aqueous medium the bonding mode of the substrate complex is very interesting and the reactivity of this complex in solution is promising.

EXPERIMENTAL

The reactant *cis*-[Ru(Me_2SO)$_4$$Cl_2$] was prepared and characterized according to the method reported by Evans et al.[24]. The substrate complex [RuCl(Me_2SO)$_3$(H_2O)$_2$]$^+$ **(1)** was prepared *in situ* by dissolving the above reactant complex in the aqueous solution[25].

$$\text{A + ligand} \underset{}{\overset{K_{E1}}{\rightleftharpoons}} \text{A.ligand}$$

Outer sphere association complex

$$\text{A.ligand} \xrightarrow{K_1} \text{B}$$

Scheme 2

Cis-[Ru(Me_2SO)$_4$$Cl_2$] once dissolved in water, immediately releases the O-bonded dimethyl sulfoxide molecule[26]. This step was confirmed by conductivity study[25].

The product **(2)** of the reaction between the substrate complex and azide was prepared by mixing different molar ratios of reactants, viz., 1:1, 1:2 and 1:3 at pH 5.0 and thermostating the mixture at 60°C for 72h. The absorption spectra of the resultant solutions were recorded using an aqueous ligand solution of appropriate molarity in the reference cell, and it was found that the maximum spectral difference between the product complex and the substrate complex, [RuCl(Me_2SO)$_3$(H_2O)$_2$]$^+$ **(1)** was observed at 257 nm (Figure 1). The product composition was checked by Job's method of continuous variation as shown in figure 2 and was found to have a 1:2 metal : ligand ratio in the product. The pH was adjusted by adding a very small amount of dilute p-toluene sulphonic acid and NaOH solution so that the concentration of the reaction mixture remains constant. The low pH was used to avoid the oxidation of Ru(II) to Ru(III)[27].

Measurements of pHs were carried out with the help of a Sartorius digital pH meter (model PB-11) with an accuracy of ± 0.01 units. Doubly distilled water was used to prepare all the solutions. All chemicals used were of AR grade.

The IR spectrum of the product shows strong bands at 3427 cm^{-1}, 2925 cm^{-1}, 2854 cm^{-1}, 2123 cm^{-1}, 2037 cm^{-1}, 1134 cm^{-1}, 638 cm^{-1} and 351 cm^{-1}. Band appears at 2036 cm^{-1} due to antisymmetric stretching of azide. The additional band at 2123 cm^{-1} shows substitution occurs with terminally azide, indicating Ru^{2+}-N=N=N structure. The presence of stretching frequency at ~351 cm^{-1}[28] for Ru-Cl bond indicates that product contains Ru-Cl bond. The IR study reveals that the Ru-Cl bond remains intact in the product.

The aqueous solution of **(complex 1)** and azide were mixed in a 1:2 molar ratio and the mixture was

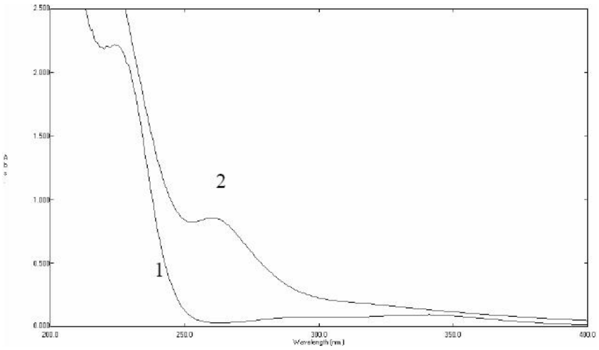


Figure 1 : Spectral difference between substrate complex and product. (1) $[RuCl(Me_2SO)_3(H_2O)_2^+]$ = 1.010^{-4} mol dm^{-3}; (2) $[RuCl(Me_2SO)_3(H_2O)_2^+]$ = 1.0×10^{-4} mol dm^{-3}, [azide] = 2.0×10^{-3} mol dm^{-3}, pH = 5.0

thermostated at 50°C for 48 hours and used for ESI mass spectra (Figure 3) of the resulting solution.

It is clear from this spectrum that the species at m/z 500.7 has become the precursor species in the mixture solution and this is tentatively attributed to $[Ru + 3\ dmso + 2\ N_3^- + Cl^- + 2Na^+]^+$.

Kinetic studies

Kinetic measurements were carried out on a Shimadzu UV1601PC spectrophotometer attached to a thermoelectric cell temperature controller (model Shimadzu, TCA 240, accuracy ± 0.1ºC). The conventional mixing technique was followed and pseudo-first order conditions were employed throughout. The progress of the reaction was followed by measuring the increase in absorbance at 257 nm, where the spectral difference between the substrate and the product complex is maximum. The $k_{1(obs)}$ and $k_{2(obs)}$ values were calculated graphically (Figure 4 and 5) using the method of Wyeh and Hamm[29]. We did not use Origin or Excel softwares because where the first part is curved and second part is linear then Weyh and Hamm method gives good result. The rate data represented as an average of duplicate runs are reproducible within ± 4%.

RESULTS AND DISCUSSION

The pKa value[30] of the azide is 4.59 at 25ºC. Thus at pH=5.0 the ligand exists mainly as N_3^-. The interaction with the HN_3 may be neglected in comparison to interaction with N_3^-

$$HN_3 \xrightleftharpoons{Ka} N_3^- + H^+ \text{ ; pKa = 4.59 at 25ºC} \qquad (1)$$

TABLE 1 : 10^3 $k_{1(obs)}$ values for different ligand concentrations at different temperatures

10^3 [Ligand] (mol dm^{-3})	Temperatures (°C)			
	35	40	45	50
1.0	0.74	1.21	1.62	1.97
2.0	1.70	2.19	3.06	3.75
3.0	2.36	2.95	3.77	4.47
4.0	2.82	3.50	4.23	5.23
5.0	2.98	3.79	4.63	5.37

TABLE 2 : 10^5 $k_{2(obs)}$ values for different ligand concentrations at different temperatures [complex 1] = 1.0×10^{-4} mol dm^{-3}, pH =5.0

10^3 Ligand] (mol dm^{-3})	Temperatures (°C)			
	35	40	45	50
1.00	1.69	2.38	3.57	6.25
2.00	3.33	4.76	7.14	13.87
3.00	4.55	6.56	9.09	15.29
4.00	5.56	7.38	10.00	16.67
5.00	5.88	8.33	11.11	19.19

The $\ln(A\infty - A_t)$ *versus* time, t plot indicates that the reaction is not a single step process, a two step consecutive process may be assumed, both steps are[ligand] dependent.

The rate constant for such process can be evaluated by assuming the following scheme.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

A is the substrate complex, B is the intermediate with ligand azide and C is the final product complex $[Ru(Me_2SO)_3(Cl)(L)_2]$.

Calculation of k_1 value for A→B step

The rate constant $k_{1(obs)}$ for A→B step can be evaluated by the method of Weyh and Hamm using the usual consecutive rate law:

$$(A_\infty - A_t) = a_1 \exp(-k_{1(obs)} t) + a_2 \exp(-k_2 t) \text{ or}$$

$$(A - A_t) - a_2 \exp(-k_2 t) = a_1 \exp(-k_{1(obs)} t)$$

where a_1 and a_2 are rate constants dependent upon the rate constants and extinction coefficient. Values of $[(A_\infty - A_t) - a_2 \exp(-k_2 t)]$ are obtained from X-Y at different time t (Figure 4). So $\ln \Delta$ = constant - $k_{1(obs)}$ t. $k_{1(obs)}$ is derived from the slope of the $\ln \Delta$ *versus* t (where t is small) (Figure 5). A similar procedure is applied for each ligand concentration in the 1.00×10^{-3} mol dm^{-3} to 5.00×10^{-3} mol dm^{-3} range, at constant [**(1)**] (1.0×10^{-4}

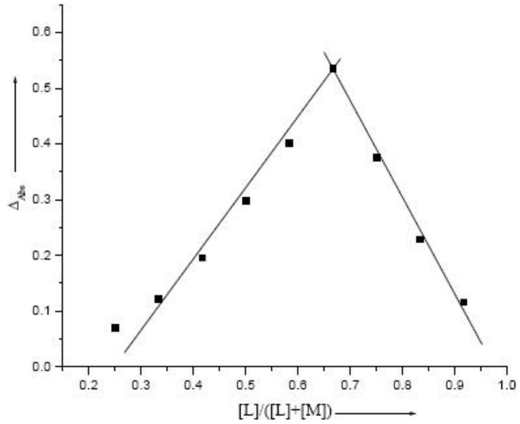


Figure 2 : Job's plot :[$RuCl(Me_2SO)_3(H_2O)_2^+$] = 1.0×10^{-4} mol dm^{-3}, [azide] = 1.0×10^{-4} mol dm^{-3}, pH = 5.0

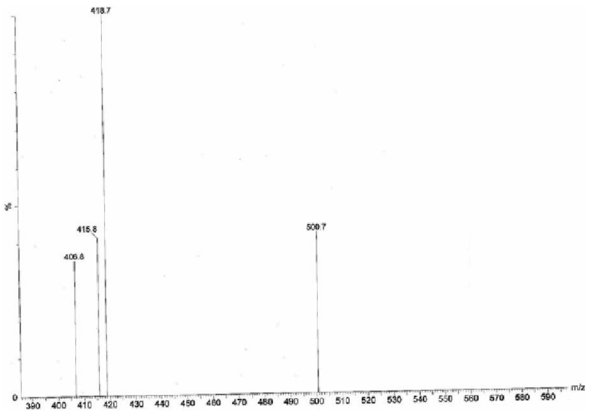


Figure 3 : ESI mass spectrometry of azide substituted complex (complex 2)

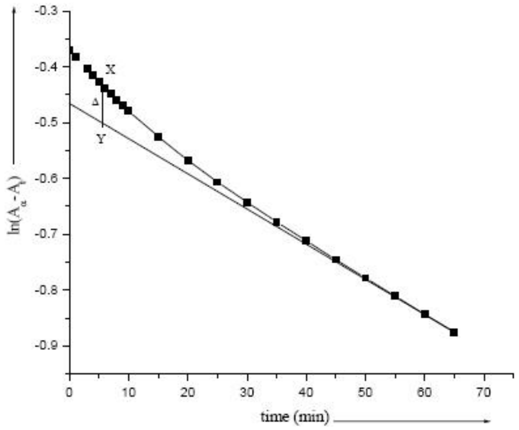


Figure 4 : A typical plot of ln (A∞-A_t) versus time t. [complex]= 1.0×10^{-4} mol dm^{-3}, [azide] = 5.0×10^{-3} mol dm^{-3}; pH = 5.0, Temp.= 40°C

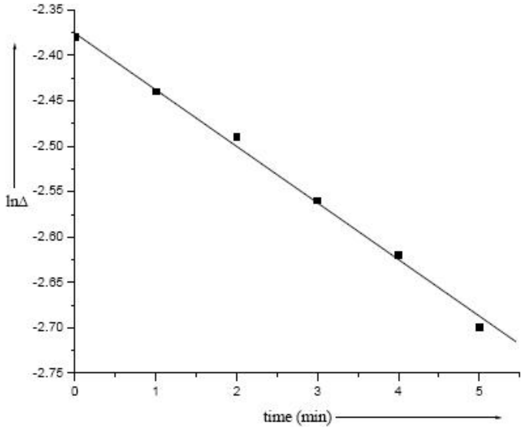


Figure 5 : A typical plot of ln Δ versus time t. [complex]= 1.0×10^{-4} mol dm^{-3}, [azide] = 5.0×10^{-3} mol dm^{-3}; pH = 5.0 ,Temp.= 40°C

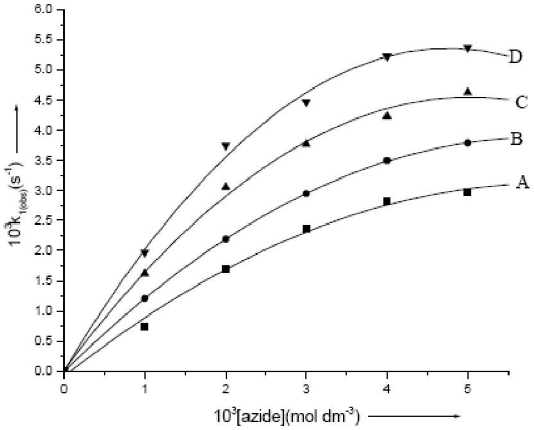


Figure 6 : Plot of $k_{1(obs)}$ *versus*[azide] at different temperatures. A = 35, B = 40, C =45, and D = 50°C

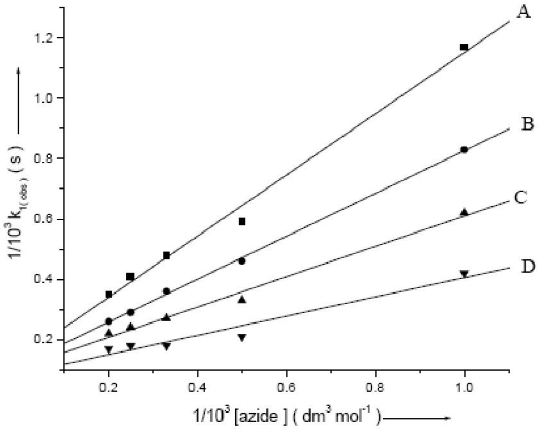


Figure 7 : Plot of 1/ $k_{1(obs)}$ *versus* 1/[azide] at different temperatures, A = 35 , B = 40 , C = 45, and D = 50°C

mol dm^{-3}) at pH = 5.0 and at different temperatures viz. 35, 40, 45 and 5°C respectively. The $k_{1(obs)}$ values are collected in TABLE 1.

The rate increases with increase in [ligand] and reaches a limiting value (Figure 6 & 7), which is probable due to the completion of the outersphere asso-

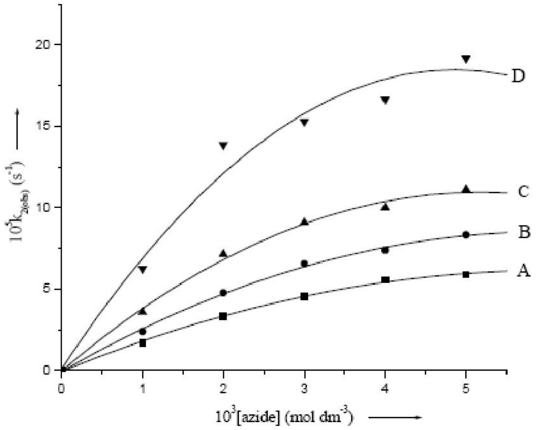


Figure 8 : Plot of $k_{2(obs)}$ *versus*[azide] at different temperatures. A = 35, B = 40, C =45, and D = 50°C

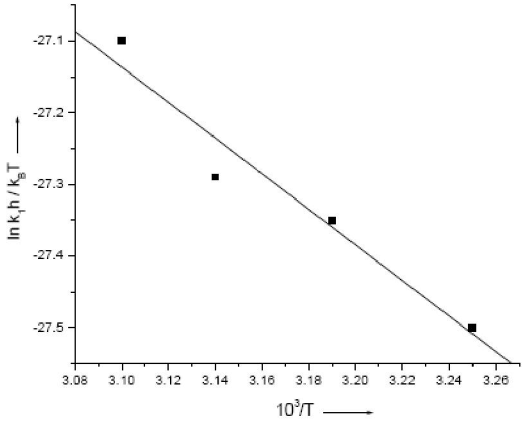


Figure 10 : Eyring plot (ln $k_1 h / k_B T$ *versus* 1/T) for the step A→B

TABLE 3 : $10^3 k_{1(obs)}$ and K_{E1} values at different temperatures

Temperatures (°C)	10^3 k_1 (s^{-1})	K_{E1} (dm^{-3} mol^{-1} s^{-1})
35	7.30	135
40	8.62	163
45	9.35	213
50	11.49	273

ciation complex formation. Since the metal ion reacts with immediate environment, further change in [ligand] beyond the saturation point will not affect the reaction rate and a gradual approach towards limiting rate is observed. At this stage the interchange of the ligands from outer sphere to the inner sphere occurs, i.e., azide attacks the Ru(II) atom of the substrate complex and forming intermediate. The outer sphere association complex is stabilised through H-bonding between the incoming azide ion and the coordinated water molecule[31,32].

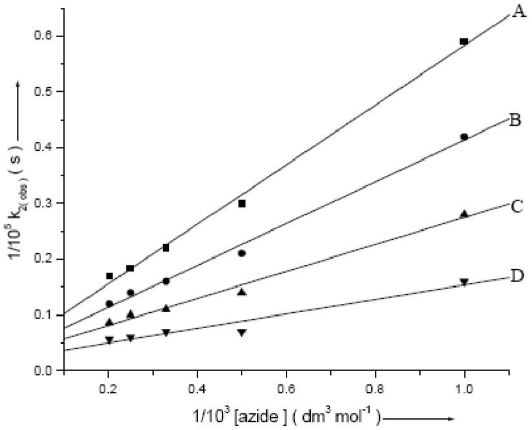


Figure 9 : Plot of 1/ $k_{2(obs)}$ *versus* 1/[azide] at different temperatures, A = 35, B = 40, C = 45, and D = 50°C

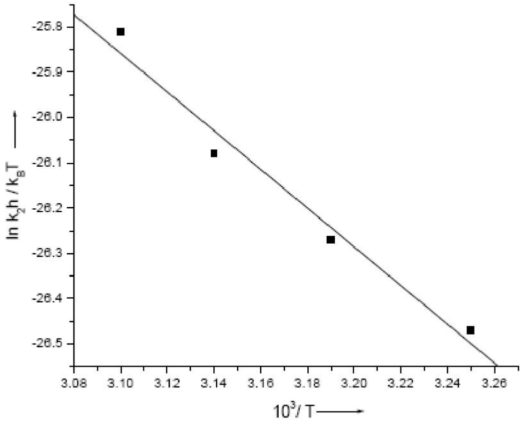


Figure 11 : Eyring plot (ln $k_2 h / k_B T$ *versus* 1/ T) for the step B→C

TABLE 4 : $10^5 k_{2(obs)}$ and K_{E2} values at different temperatures

Temperatures (°C)	10^5 k_2 (s^{-1})	K_{E2} (dm^{-3} mol^{-1} s^{-1})
35	20.47	91
40	25.54	105
45	31.25	145
50	41.67	160

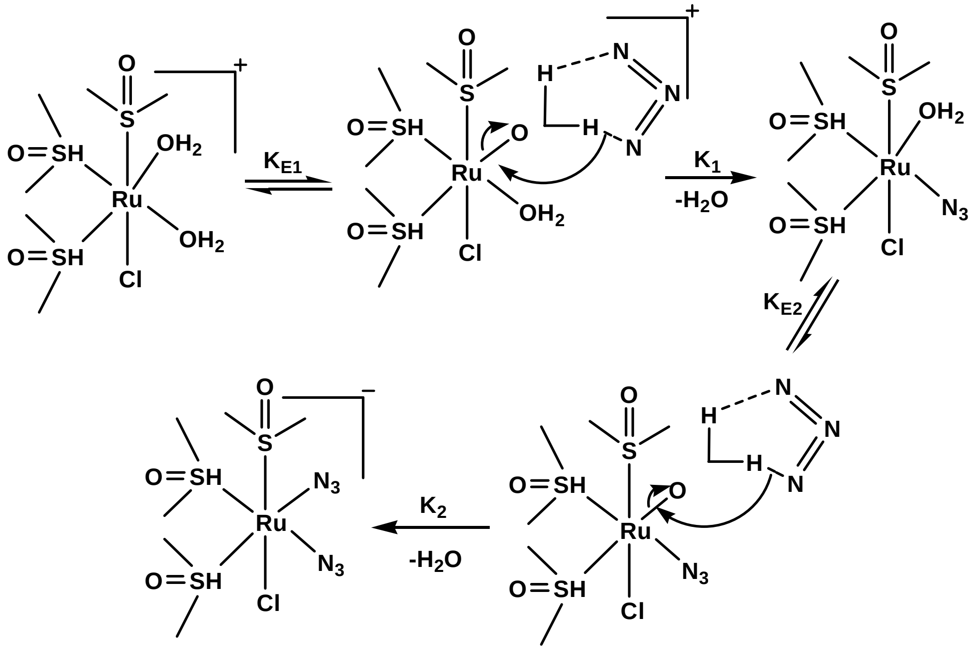
Based on scheme 2 a rate expression can be derived for A→B step

$$\frac{d[B]}{dt} = \frac{k_1 K_{E1}[A][ligand]}{(1 + K_{E1}[ligand])} \quad (1)$$

$$\frac{d[B]}{dt} = k_{1(obs)}[A]_T \quad (2)$$

T stands for total concentration of Ru(II).Thus it can be written,

$$k_{1(obs)} = \frac{k_1 K_{E1}[ligand]}{(1 + K_{E1}[ligand])} \quad (3)$$



Scheme 3

TABLE 5 : The 10^3 $k_{1(obs)}$ and 10^5 $k_{2(obs)}$ values at different pH values; $[RuCl(Me_2SO)_3(H_2O)_2^+] = 1.0\times10^{-4}$ mol dm^{-3}, [azide] = 3.0×10^{-3} mol dm^{-3}, temp. = 50^oC

pH	10^3 $k_{1(obs)}$ (s^{-1})	10^5 $k_{2(obs)}$ (s^{-1})
4.0	3.97	8.67
4.5	4.07	11.46
5.0	4.47	15.29
5.5	4.98	16.89
6.0	5.39	17.21

where k_1 is the anation rate constant for the formation of intermediate **(B)** from the substrate complex, *cis*-$[RuCl(Me_2SO)_3(H_2O)_2]^+$ **(A)**. K_{E1} is the outersphere association equilibrium constant.

The equation can be written as

$$\frac{1}{k_{1(obs)}} = \frac{1}{k_1} + \frac{1}{k_1K_{E1}[ligand]} \qquad (4)$$

The plot of 1/ $k_{1(obs)}$ *versus* 1/[ligand] should be linear (Figure 6) with an intercept of 1/ k_1 and slope 1/ k_1K_{E1}.

The k_1 and K_{E1} values obtained from the intercept and from slope to intercept ratios are given in TABLE 3.

Calculation of k_2 for step B→C step

The rate constants were calculated from latter linear portions of the graphs and are collected in TABLE 3. This is again dependent on [Ligand] and shows a limiting value at higher concentration of the ligand (Figure 8). A new azide ligand attacks the ruthenium(II) center. The intermediate here also possibly stable through hydrogen bonding between coordinated H_2O and the approaching azide. The k_2 and K_{E2} for the B to C step is calculated similar to eq. (4) (Figure 9) and collected in TABLE 4.

TABLE 6 : Activation parameters for [complex 1] by azide in aqueous medium, pH = 5.0

Ligand	$\Delta H_1^{\neq}$ (kJ mol $^{-1}$)	$\Delta S_1^{\neq}$ (J K^{-1} mol^{-1})	$\Delta H_2^{\neq}$ (k J mol^{-1})	$\Delta S_2^{\neq}$ (J K^{-1} mol^{-1})
Azide	20.1 ± 3.49	-162 ± 11	35.5 ± 4.2	-105 ± 13

Based on the experimental findings a two-step associative interchange mechanism is proposed for the substitution process.

Effect of change in pH on the reaction rate

The reaction was studied at five different pH values. The $k_{(obs)}$ values are found to increase with increase in pH in the pH range studied. The $k_{1(obs)}$ values are collected in TABLE 5. The enhancement in rate may be due to the increase in percentage of more reactive ligand N_3^- from HN_3 [which is known from its pK_a values] with the increase of pH.

Effect of temperature on the reaction rate

Four different temperatures with varied ligand concentrations were chosen and the results are listed in TABLE 6. As there is no report in the literature, we could not compare our data with another system. The activation parameters for the step (1) → B and B → (2) are evaluated from the linear Eyring plots (Figure 10 and 11). As this study is first on this system, we could not compare with other reports.

The low $\Delta H\neq$ values are in support of the ligand participation in the transition state for both steps. The positive energy required for the bond breaking process is partly compensated for by the negative energy obtained from bond formation in the transition state and, hence, a low value of $\Delta H\neq$ is observed. The highly negative $\Delta S\neq$ values, on the other hand, suggest a more compact transition state than the starting complexes and this is also in support of the assumption of a ligand participated transition state. $\Delta H_2\neq$ is higher than $\Delta H_1\neq$ which is quite expected for the second step which is slower than the first step.

Mechanism and discussion

In the studied reaction condition i.e., at the pH 5.0, azide exists in the deprotonated form. The interaction of azide with the title ruthenium complex proceeds via two distinct consecutive substitution steps of aqua molecules ($k_1 \sim 10^{-3}\ s^{-1}$ and $k_2 \sim 10^{-5}\ s^{-1}$). Each step proceeds via an associative interchange activation. At the outset of each step outer sphere association complex results, which is stabilized through H-bonding and is followed by an interchange from the outer sphere to the inner sphere complex. The outer sphere association equilibrium constants, a measure of the extent of H-bonding for each step at different temperatures are evaluated. From the temperature dependence of the K_{E1} and K_{E2} the thermodynamic parameters are calculated $\Delta H^\circ_1 = 36.1 \pm 4.0$ kJ mol^{-1}, $\Delta S^\circ_1 = 87 \pm 12$ J K^{-1} mol^{-1} and $\Delta H^\circ_2 = 30.8 \pm 4.5$ kJ mol^{-1}, $\Delta S^\circ_2 = 108 \pm 14$ J K^{-1} mol^{-1}. ΔG° values, calculated for both steps at all temperature studied, have a negative magnitude which is once again in favor of the spontaneous formation of an outer sphere association complex. A plausible mechanism is shown in scheme 3.

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