

Displacement of aqua ligands from the hydroxopentaaquarhodium(III) ion by 1-hydroxybenzotriazole (HOBt): A kinetic and mechanistic approach

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Abstract. The kinetics of the reaction of HOBt with $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ has been studied spectrophotometrically in aqueous medium as a function of $[\text{Rh}(\text{H}_2\text{O})_5\text{OH}^{2+}]$, $[\text{HOBt}]$, pH and temperature. At pH 4.3, the reaction proceeds via a rapid outer sphere association complex formation step followed by two consecutive steps. The first of these involves ligand-assisted anation, while the second involves chelation as the second aqua ligand is displaced. The association equilibrium constant for the outer sphere complex formation has been evaluated together with the rate constants for the two subsequent steps. The activation parameters for both steps have been evaluated using Eyrings equation. Thermodynamic parameters calculated from the temperature dependence of the outer sphere association equilibrium constants are also consistent with an associative mode of activation. The product of the reaction has been characterized by IR and ESI-mass spectroscopic analysis.

Keywords. Kinetics; hydroxopentaaquarhodium(III); HOBt; mechanism; activation parameters.

1. Introduction

cis-Pt(NH₃)₂Cl₂ (cisplatin) is well-known as an anti-tumour drug.^{1,2} However, there are still difficulties related to its use, because of numerous side effects and its toxicity. Several methods have been developed during the past ten years which have considerably reduced these side effects. Cisplatin is not very soluble in water and tends to hydrolyse at neutral pH. Replacement of chloro ligands by carboxylate groups in carboplatin,³ *cis*-diammine(1,1-cyclobutanedicarboxylate)-platinum(II), reduces the toxicity and increases the solubility in water. Among the platinum family elements, ruthenium has been successfully developed and tumor-inhibiting ruthenium complexes have been investigated in order to gain insight into their biological activities.^{4–10} The tumor inhibiting activities of ruthenium complexes, such as [Ru(NH₃)₃Cl₃], *cis*-[Ru(NH₃)₄Cl₂]Cl or *cis*-[RuCl₂(Me₂SO)₄], have been known for quite some time.¹¹ The complex

cis-[Ru^{II}Cl₂(Me₂SO)₄] presents lower toxicity¹² than cisplatin and also, better antitumor activity *in vivo* (against Ehrlich ascites carcinoma, Lewis lung carcinoma, B16 melanoma, and MCA mammary carcinoma). Extensive studies on N-heterocyclic carbene (NHC) complexes in organometallic chemistry and catalysis has not yet studied. Only a restricted array of biomedical applications has been reported so far for silver, gold, palladium, copper, ruthenium, and rhodium derivatives, mainly for antimicrobial and antitumor purposes.^{13,14} Dimeric μ -acetato complexes of rhodium(II) as well as monomeric square planar rhodium(I) and octahedral rhodium(III) complexes have shown interesting antitumor properties.¹⁵ Some rhodium(III) complexes are reported to have considerably greater cytostatic activity than *cis*-platin,¹⁶ particularly when their action against HCV29T tumor cells is considered. So far, rhodium and iridium complexes, analogs of the corresponding platinum compounds that possess significant antitumor properties, were found to be effective as anti-cancer agents, but some of them exhibited marked toxic effects.^{17,18} For certain ligands, the anation reaction follows **Id** path. A **Ia** path was proposed for the anation

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reaction of $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ by a variety of ligands.^{19–23}

1-Hydroxybenzotriazole (HOBt) is an organic compound used as a racemization suppressor and to improve yield in peptide synthesis.^{24,25} In this paper, we report the interaction of HOBt with hydroxopentaquarhodium(III) ion in aqueous medium and the possible mode of binding is discussed.

2. Experimental

2.1 Materials

$[\text{Rh}(\text{H}_2\text{O})_6](\text{ClO}_4)_3$ was prepared as per the literature method²⁶ and characterized by chemical analysis and spectroscopic data²⁷ ($\lambda_{\text{max}} = 396 \text{ nm}$, $\epsilon = 62 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; $\lambda_{\text{max}} = 311 \text{ nm}$, $\epsilon = 67.4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The reactant complex $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})](\text{ClO}_4)_2$ (complex A) was obtained *in situ* (yield $\sim 90\%$) by adjusting the pH to 4.3. Higher proportions of complex could not be obtained as the solution becomes turbid at higher pH. The reaction product of HOBt and complex A (complex C) was prepared by mixing them in different proportions namely 1:1, 1:2, 1:3, 1:5 and 1:10, and keeping the mixtures at 60°C for 72 h. The absorption spectra of all the mixtures exhibited the same λ_{max} (338 nm) with almost the

same absorbances. The spectra of the product complex C and the reactant complex A are shown in figure 1.

2.2 Product analysis

The composition of the product in the reaction mixture was determined by Job's method of continuous variation (figure 2). The metal: ligand ratio was found to be 1:1. $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ and HOBt were therefore mixed in 1:1 molar ratio at pH 4.3 and a yellow product was obtained on slow evaporation. The IR spectrum of the product as a KBr disc shows strong bands at 3417 , 1638 cm^{-1} and medium bands at 2927 , 2853 , 515 and 428 cm^{-1} . The presence of a strong band at $\sim 3417 \text{ cm}^{-1}$ indicates that the product contains aqua or hydroxyl ligands. The bands at 515 cm^{-1} and 428 cm^{-1} are assignable to the stretching of Rh–N and Rh–O bonds, respectively.²⁸ The strong and broad band at 1638 cm^{-1} indicates that –N=N–group is metalated.

The aqueous solution of $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ and HOBt were mixed in a 2:1 molar ratio and the mixture was thermostated at 60°C for 48 hours and used for ESI-MS measurement. The ESI mass spectra of the resulting solution is shown in figure 3.

It is clear from this spectrum that the ion peak at $m/z = 190.04$ has become the precursor ion species in the mixture solution and this is attributed to

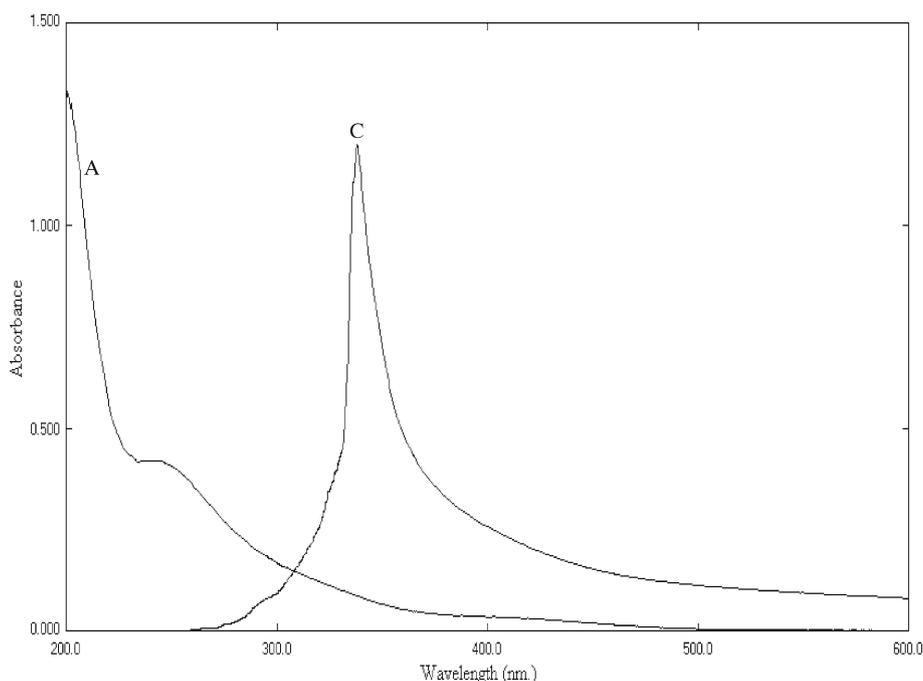


Figure 1. Spectral difference between reactant complex (A) and product complex C: (A) $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+} = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$ (C) $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+} = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{HOBt}] = 7.5 \times 10^{-3} \text{ mol dm}^{-3}$, pH = 4.3, cell used = 1 cm quartz.

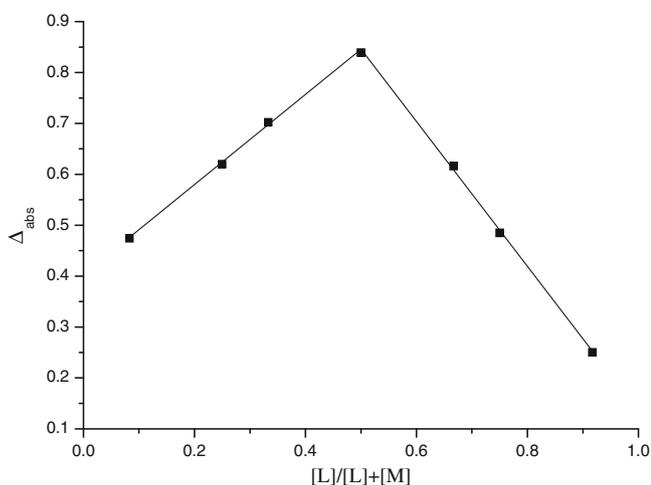


Figure 2. Job's plot for reaction of complex A with HOBT.

$(\text{1Rh}^{3+} + \text{1BtO}^{-} + \text{7H}_2\text{O} + \text{1H}^{+} + \text{1HO}^{-})^{2+}$. The precursor ion is shown in figure 4.

2.3 Measurements

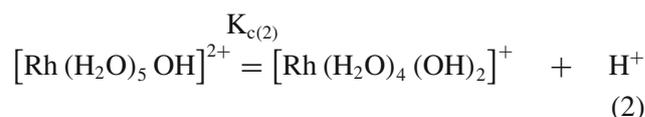
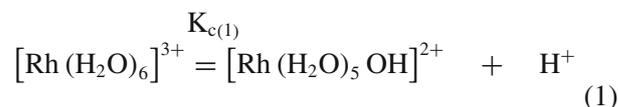
All the spectra and kinetic measurements were recorded with a Shimadzu UV-VIS spectrophotometer (UV-2450 PC), attached to a thermoelectric cell temperature controller (model TCC-240A with an accuracy of $\pm 0.1^\circ\text{C}$). IR Spectra (KBr disc, $4000 - 300\text{ cm}^{-1}$) were measured with a Perkin-Elmer FTIR model RX1 infrared spectrophotometer. ESI-mass spectra recorded using a micromass Q-ToF microTM mass spectrometer in positive ion mode. The pH of the solutions was adjusted with $\text{HClO}_4/\text{NaOH}$ and measured with a Sartorius pH meter (model PB11) to an accuracy of ± 0.01 .

The progress of the reaction was monitored by the absorbance measurements at different intervals of time with a Shimadzu spectrophotometer (UV-2450 PC)

attached to a TCC-Controller (TCC-240A) at 338 nm, where the spectral difference between the reactant and product complexes is maximum. Before each kinetic run the pH of each solution of reactant complex and the HOBT was adjusted to 4.3 and a pseudo-first order condition was maintained throughout. The plot of $\ln(A_\infty - A_t)$ (where A_t and A_∞ are absorbances at time t and after completion of reaction) against time figure 5 were found to be nonlinear; being curved at the initial stage and subsequently linear, indicating that the reaction proceeds via two consecutive steps. From the limiting linear portion of the curve, the values of $k_{2(\text{obs})}$ were obtained. The $k_{1(\text{obs})}$ values were obtained from the slope of $\ln \Delta$ versus time when t is small (figure 6). The reported rate data represented as an average of duplicate runs were reproducible to within $\pm 4\%$.

3. Results and discussion

HOBT has pK_a value of 5.3 at 25°C .²⁹ The ionization of $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ may be given as:



The $\text{pK}_{c(1)}$ and $\text{pK}_{c(2)}$ values of $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ are 3.6 and 4.7, respectively at 25°C .³⁰ Other reports on the $\text{pK}_{c(1)}$ value are 3.2, 3.4 and 3.45 (ref. 30). With increase in pH, the proportion of the more labile hydroxopentaquaquarhodium(III) ion increases. The hydroxide ligand increases the water exchange rate of $[\text{Rh}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ relative to $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$. In the pH range used in these

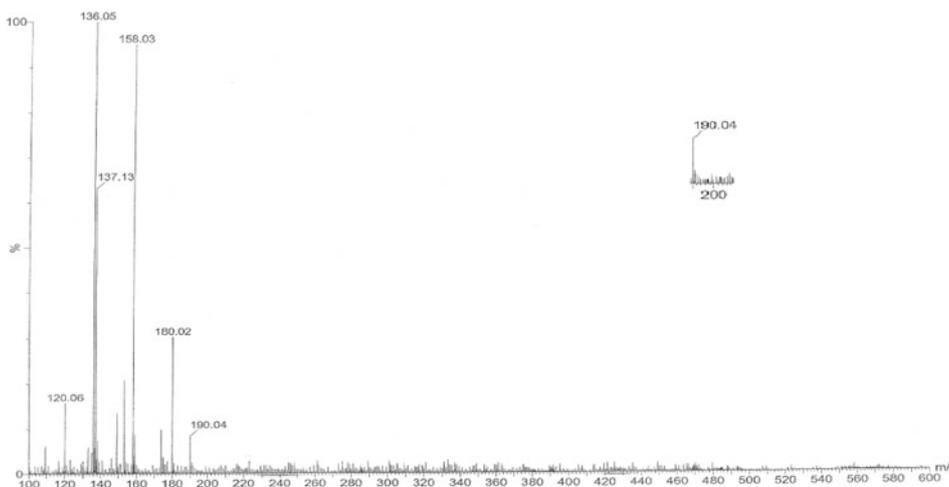
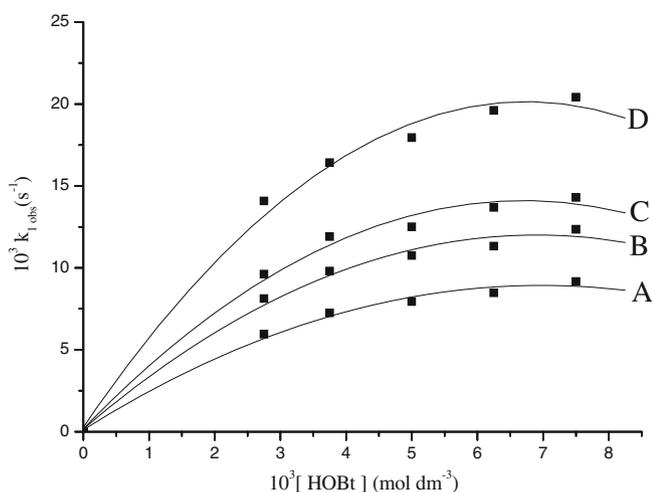
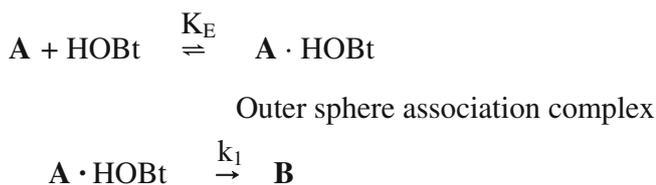


Figure 3. ESI-mass spectra of the product.

Table 1. $10^3 k_{1(\text{obs})}$ and $10^5 k_{2(\text{obs})}$ values for different HOBt concentrations at different temperatures; $[\text{Complex A}] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$, $\text{pH} = 4.3$, ionic strength = $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$.

$10^3 [\text{Ligand}] (\text{mol dm}^{-3})$	$10^3 k_{1(\text{obs})}$ Temperature ($^\circ\text{C}$)				$10^5 k_{2(\text{obs})}$ Temperature ($^\circ\text{C}$)			
	50	55	60	65	50	55	60	65
2.50	6.27	8.13	9.62	14.08	1.28	2.12	3.05	5.23
3.75	7.39	9.80	11.90	16.42	1.28	2.13	3.05	5.23
5.00	8.13	10.75	12.50	17.95	1.29	2.13	3.06	5.24
6.25	8.58	11.33	13.69	19.62	1.29	2.14	3.07	5.25
7.50	9.09	12.35	14.29	20.42	1.30	2.14	3.08	5.25

**Figure 7.** Plot of $k_{1(\text{obs})}$ versus $[\text{HOBt}]$ at different temperature, A = 50°C , B = 55°C , C = 60°C and D = 65°C .**Scheme 2.** Possible reaction sequence for the interaction of HOBt with the title complex.

experimental findings, the scheme 2 may be proposed for the step $\text{A} \rightarrow \text{B}$;

Based on the above scheme, a rate expression can be derived for the $\text{A} \rightarrow \text{B}$ step

$$d[\text{B}]/dt = k_1 K_E [\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+} [\text{HOBt}] \quad (5)$$

$$\text{or, } d[\text{B}]/dt = k_{1(\text{obs})} [\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]_T^{2+}, \quad (6)$$

where T stands for total concentration of Rh(III). We can then write

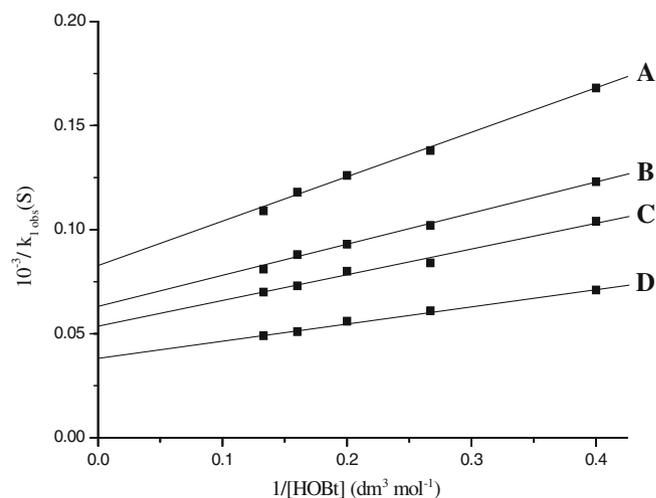
$$k_{1(\text{obs})} = k_1 K_E [\text{HOBt}] / (1 + K_E [\text{HOBt}]), \quad (7)$$

where k_1 is the anation rate constant for the $\text{A} \rightarrow \text{B}$ step, i.e., the anation rate constant for the interchange of outer sphere complex to the inner sphere complex; K_E is the outer sphere association equilibrium constant.

The equation can be represented as

$$1/k_{1(\text{obs})} = 1/k_1 + 1/k_1 K_E [\text{HOBt}]. \quad (8)$$

The plot of $1/k_{1(\text{obs})}$ against $1/[\text{HOBt}]$ should be linear with an intercept of $1/k_1$ and slope $1/k_1 K_E$. This was found to be the case at all temperatures studied. The k_1 and K_E values were calculated from the intercept and slope (figure 8) and are tabulated in table 2.

**Figure 8.** Plot of $1/k_{1(\text{obs})}$ against $1/[\text{HOBt}]$, A = 50°C , B = 55°C , C = 60°C and D = 65°C .**Table 2.** The k_1 , k_2 and K_E values for the substitution reaction.

Temp. ($^\circ\text{C}$)	$10^3 k_1 (\text{s}^{-1})$	$10^5 k_2 (\text{s}^{-1})$	$K_E (\text{dm}^3 \text{ mol}^{-1})$
50	12.18	1.29	383
55	16.08	2.13	409
60	18.77	3.06	428
65	25.99	5.24	467

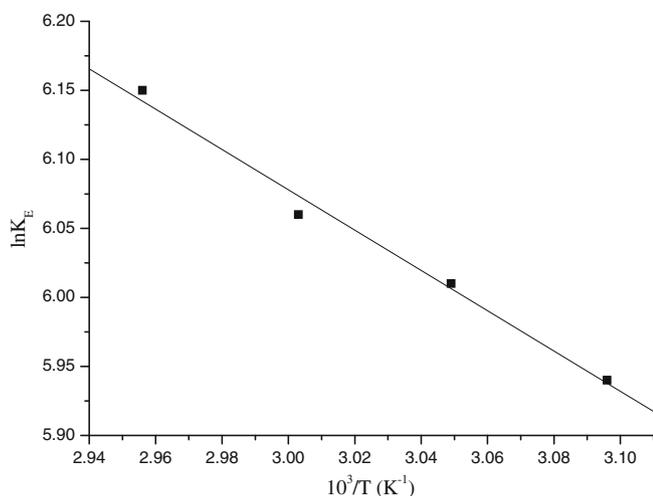


Figure 9. Plot of $\ln K_E$ versus $1/T$.

The second phase of the substitution reaction is the chelation step, to give complex C and is independent of HOBT concentration (figure 9). The $k_{2(\text{obs})}$ values were obtained directly from the limiting slopes of $\ln(A_\infty - A_t)$ versus t plots for different temperatures and are presented in table 2.

Table 3. $10^3 k_{1(\text{obs})}(\text{s}^{-1})$ and $10^5 k_{2(\text{obs})}(\text{s}^{-1})$ values for anation of $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ by HOBT at different pH values in aqueous solution; $[A] = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{HOBT}] = 7.50 \times 10^{-3} \text{ mol dm}^{-3}$, temp. = 60°C , ionic strength = $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$.

pH	$10^3 k_{1(\text{obs})}(\text{s}^{-1})$	$10^5 k_{2(\text{obs})}(\text{s}^{-1})$
3.0	5.32	1.79
3.3	7.15	2.03
3.6	8.73	2.45
4.0	10.46	2.78
4.3	14.29	3.08

3.1 Effect of pH on the reaction rate

The reaction was studied at five different pH values (3.0, 3.3, 3.6, 4.0 and 4.3). The k_{obs} values were found to increase with increase in pH in this range (table 3). The k_{obs} values are given in table 3. The enhancement in rate may be explained based on the acid dissociation equilibria of the reactants. The rate may be based on the equilibria of the reactants. A rate expression for path 1 may be given:

$$k_{(\text{obs})} = \frac{k_1 K_E K_{c(1)} K_a [\text{HOBT}]_t [\text{H}^+]}{[\text{H}^+]^3 + [\text{H}^+]^2 (K_a + K_{c(1)}) + [\text{H}^+] (K_{c(1)} K_a + K_{c(1)} K_{c(2)} + K_{c(1)} K_a K_E [\text{HOBT}]_t) + K_{c(1)} K_{c(2)} K_a} \quad (9)$$

where k_1 and K_E are rate constant and outer-sphere association equilibrium constant and also $K_{c(1)}$, $K_{c(2)}$ and K_a are acid dissociation constants of $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Rh}(\text{H}_2\text{O})_4(\text{OH})]^{2+}$ and for the ligand $-\text{OH}$ respectively.

Further study of the substitution reaction was followed at pH 4.3 to avoid complications caused by adding an additional parameter $[\text{H}^+]$ to the rate equation. At pH 4.3, the complex exists mainly in the hydroxopentaaqua

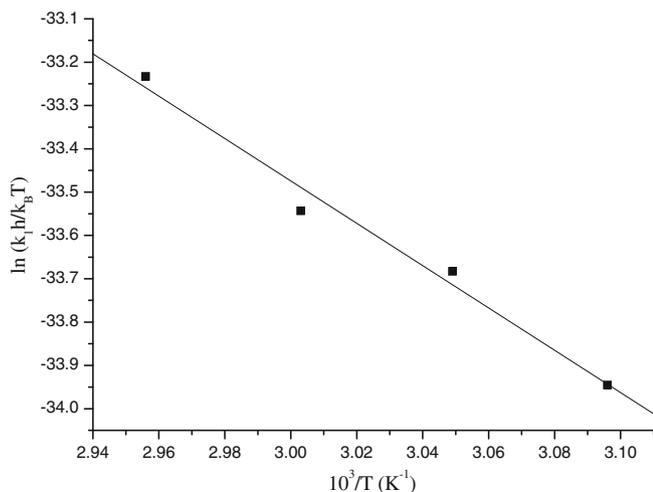


Figure 10. Eyring plot for k_1 .

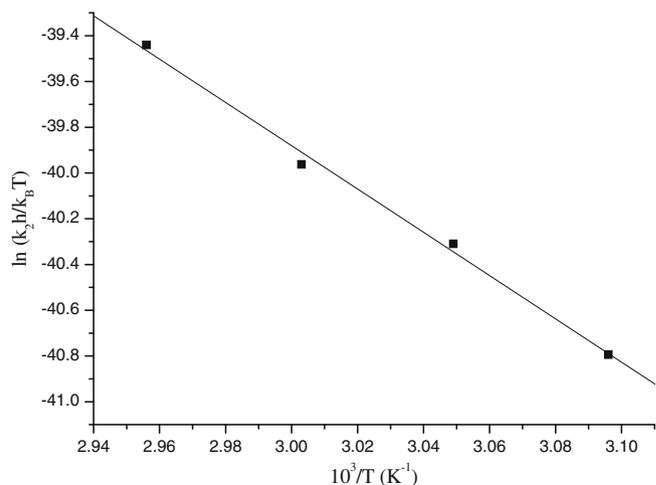


Figure 11. Eyring plot for k_2 .

Table 4. Activation parameter of the anation reaction of $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ with HOBt.

Ligand	ΔH_1^\ddagger (kJ mol ⁻¹)	ΔS_1^\ddagger (JK ⁻¹ mol ⁻¹)	ΔH_2^\ddagger (kJ mol ⁻¹)	ΔS_2^\ddagger (JK ⁻¹ mol ⁻¹)
HOBt	40.7 ± 3.8	-156 ± 12	78.7 ± 3.8	-95 ± 12

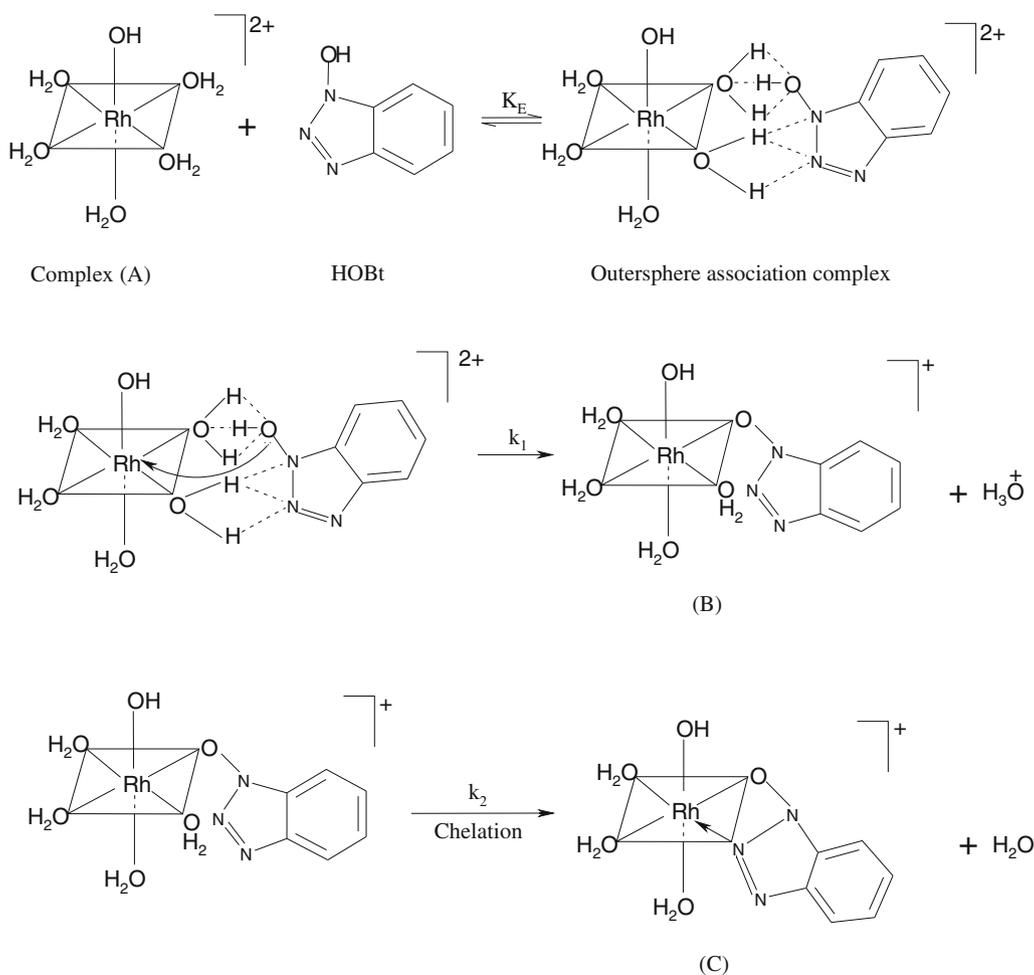
form and the contribution due to the hexaqua species is negligible.

With increase of pH, the complex also changes from aqua to hydroxo aqua form and then the water exchange rate constant of $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ increases relative to $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$.

3.2 Effect of temperature on the reaction rate

The reaction was studied at four different temperatures for different ligand concentrations and the results are listed in tables 1 and 2. From the temperature dependence of the K_E values (figure 9) ΔH° and ΔS° values are calculated to be 12.14 ± 0.9 kJ mol⁻¹ and 87 ± 3 J K⁻¹ mol⁻¹, respectively. Thus from the

thermodynamic consideration the negative ΔG° (-13.8 kJ mol⁻¹) also supports the spontaneous formation of the outer sphere association complex. The activation parameters for both the steps $\mathbf{A} \rightarrow \mathbf{B}$ and $\mathbf{B} \rightarrow \mathbf{C}$ were evaluated from the linear Eyring plots (figures 10 and 11). The activation enthalpies and entropies are $\Delta H_1^\ddagger = 40.7 \pm 3.8$ kJ mol⁻¹, $\Delta S_1^\ddagger = -156 \pm 12$ JK⁻¹ mol⁻¹, $\Delta H_2^\ddagger = 78.7 \pm 3.8$ kJ mol⁻¹, $\Delta S_2^\ddagger = -95 \pm 12$ JK⁻¹ mol⁻¹ (table 4). Further, from the temperature dependence of the K_E values ΔH° and ΔS° values are calculated to be 12.14 ± 0.9 kJ mol⁻¹ and 87 ± 3 J K⁻¹ mol⁻¹, respectively. Thus from the thermodynamic consideration the negative ΔG° (-13.8 kJ mol⁻¹) also supports the spontaneous formation of the outer sphere association complex.

**Figure 12.** Plausible mechanism for the substitution of aqua ligands from $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ by HOBt.

The low ΔH^\ddagger values are in support of the ligand participation in the transition state for both the steps. The high negative ΔS^\ddagger values suggest a more compact transition state, where both the incoming and departing ligands are attached in the transition state, than the starting complexes and this is also in support of the assumption of a ligand participated transition state.

4. Mechanism

The mechanism of substitution of aqua ligands in ion $[\text{Rh}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ can be explained in terms of rapid outer sphere association complex formation, followed by two consecutive steps; the first is dependent of ligand concentration and second is the chelation i.e., ring closure step, which is independent of ligand concentration. At the experimental pH 4.3 complex exists as hydroxo aqua species. At the outset of each step an outersphere association complex is formed, which is stabilized through H-bonding, this is followed by an interchange from outersphere to inner sphere complex. The outersphere association equilibrium constant, a measure of the extent of H-bonding for each step at different temperatures are collected in table 2. From the temperature dependence of the K_E , the thermodynamic parameters calculated (figure 9) are: $\Delta H^\circ = 12.14 \pm 0.9 \text{ kJ mol}^{-1}$, $\Delta S^\circ = 87 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$. The negative ΔG° for the first equilibrium step also supports the spontaneous formation of an outer sphere association complex. The activation parameters ($\Delta H_1^\ddagger = 40.7 \pm 3.8 \text{ kJ mol}^{-1}$, $\Delta S_1^\ddagger = -156 \pm 12 \text{ JK}^{-1} \text{ mol}^{-1}$) for the first step and the second step ($\Delta H_2^\ddagger = 78.7 \pm 3.8 \text{ kJ mol}^{-1}$, $\Delta S_2^\ddagger = -95 \pm 12 \text{ JK}^{-1} \text{ mol}^{-1}$) suggest an associative mode of activation for the substitution process. The enthalpy of activation (ΔH_1^\ddagger and ΔH_2^\ddagger) values and negative (ΔS_1^\ddagger and ΔS_2^\ddagger) values implies a good degree of ligand participation in the transition state. The positive enthalpy change for breaking the M-OH₂ bond is partially compensated by the formation of M-L bond in the transition state. The participation of HOBT in the transition state results in a more compact state due to the low ΔH^\ddagger values and large negative ΔS^\ddagger values are obtained.

5. Conclusion

Based on the above facts, a plausible mechanism for the substitution has been proposed as shown (figure 12). The hydroxide group first attacks the Rh(III) center by the removal of a proton i.e., follows k1 path. Then the four-membered ring is completed by the ring N atom. As Rh(III) is the border-line metal

ion, the possibility of N- coordination in the first step also cannot be ruled out. Then the monobonded species may undergo protolytic equilibrium (due to the pendent -OH functional group of the ligand) followed by chelation via rate determining process; it may involve competitive chelation by both pendent -OH and its dissociated (-O⁻) groups.

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