

Kinetics and mechanism of the reaction of hydroxopenta-aquarhodium(III) ion with nicotinic acid in aqueous media

S. Mohanty^a, S. Anand^a, G. S. Brahma^b, D. Baral^b and P. Mohanty^{b*}

^aRegional Research Laboratory, Bhubaneswar-751 013, India

^bDepartment of Chemistry, Utkal University, Bhubaneswar-751 004, India

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The kinetics of the reaction of nicotinic acid (H_2L^+) with hydroxopenta-aquarhodium(III) has been studied over the range $2.58 \leq 10^3[\text{H}_2\text{L}^+] \leq 12.9$, $3.50 \leq \text{pH} \leq 4.30$, $45^\circ \leq t \leq 65^\circ$ at $I = 0.1 \text{ mol dm}^{-3}$ (NaClO_4). The reaction takes place via an outer sphere association between RhOH^{2+} and HL (conjugate base of H_2L^+) followed by transformation of the outer into an inner sphere complex (chelate is formed) by slow interchange. The anation rate constant (k_{an}) of RhOH^{2+} at 25° and $I = 0.1 \text{ mol dm}^{-3}$ (NaClO_4) is estimated to be $3.78 \times 10^{-5} \text{ s}^{-1}$. ΔH^\ddagger and ΔS^\ddagger for k_{an} path are found to be $33.3 \pm 4 \text{ kJ mol}^{-1}$ and $-218 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. Anation reaction of RhOH^{2+} follows an I_a path.

The metal rhodium is a typical one among platinum group of metals due to its proficiency in catalytic applications and variability of mechanism that it exhibits while undergoing ligand substitution reactions. For the substitution reactions at Rh^{III} center the mechanistic path cover from interchange dissociative I_d to interchange associative I_a depending on the ligand type¹.

The present study portrays the kinetic behavior of nicotinic acid as an anating ligand towards hydroxopenta-aquarhodium(III) cation. Attempts have been made to isolate the substituted product and characterize it.

Results and discussion

Effect of $[\text{Rh}^{3+}]$ on reaction rate :

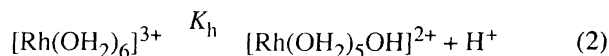
In the first set of kinetic experiments, $[\text{Rh}^{3+}]$ was varied at fixed [nicotinic acid] of $7.74 \times 10^{-3} \text{ mol dm}^{-3}$. The ionic strength, pH and temperature were kept constant. The pseudo-first order plots were linear ($r = 0.99$) in each case, giving $10^5 k_{\text{obs}} = (11.5 \pm 0.2) \text{ s}^{-1}$ and showing that the reaction is first order in $[\text{Rh}^{3+}]_{\text{T}}$, ($\text{T} = \text{total}$). The independence of k_{obs} at 55° under the condition $[\text{H}_2\text{L}^+]_{\text{T}} = 7.74 \times 10^{-3}$, $I = 0.1 \text{ mol dm}^{-3}$ and $\text{pH} \approx 4.3$ over a $[\text{Rh}^{3+}]_{\text{T}}$ range from 2.58×10^{-4} to 5.16×10^{-4} is in agreement with first order dependence on $[\text{Rh}^{3+}]_{\text{T}}$. The rate law therefore, is given by eq. (1).

$$\text{Rate} = -d[\text{Rh}^{3+}]/dt = k_{\text{obs}}[\text{Rh}^{3+}]_{\text{T}} \quad (1)$$

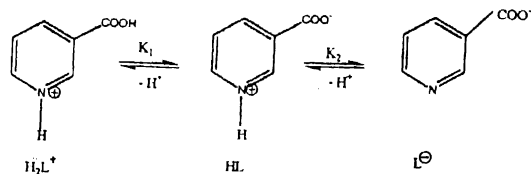
Effect of pH on reaction rate :

Under the conditions $t = 55^\circ$, $[\text{Rh}^{3+}] = 2.58 \times 10^{-4}$, $[\text{H}_2\text{L}^+]_{\text{T}} = 7.74 \times 10^{-3}$ and $I = 0.1 \text{ mol dm}^{-3}$ (NaClO_4). When pH was varied from 3.5 to 4.30, $10^5 k_{\text{obs}}$ values were found to increase from 8.00 to 11.63 s^{-1} .

At $\text{pH} = 3.50, 4.09, 4.22$ and 4.30 the values of $10^5 k_{\text{obs}}$ are 8.00, 9.32, 9.90 and 10.63 s^{-1} . The increase in k_{obs} due to increase in pH may be due to increase in the concentration of RhOH^{2+} . Dissociation of $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ takes place as given in eq. (2).



The $\text{p}K_h$ value of $[\text{Rh}(\text{OH}_2)_6]^{3+}$ is 3.3 at $25^\circ(2)$. Thus with the increase in pH the percentage of more labile hydroxopenta-aquarhodium(III) species in solution is increased. The presence of OH^- ligand in the hydroxo-aqua species in several cases increased lability (due to π bonding) and therefore increased rates are found with $\text{Co}^{3+(3a)}$, $\text{Al}^{3+(3b)}$, $\text{Ga}^{3+(3c)}$, $\text{Mn}^{3+(3d)}$, $\text{Fe}^{3+(3e)}$, $\text{Cr}^{3+(3p)}$ or $\text{Rh}^{3+(3g)}$. The hydroxide ligand increases the water exchange rate constant of $[\text{Rh}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ relative to $[\text{Rh}(\text{OH}_2)_6]^{3+}$. Nicotinic acid also participates in the acid base reaction equilibria. By increasing the pH of the medium the concentration of the conjugate base from H_2L^+ increases. $\text{p}K_1$ and $\text{p}K_2$ of nicotinic acid⁴ are 2.09 and 4.70 at 20° and 0.5 ionic strength respectively.



At lower $\text{pH} = 3.68$, the HL form will predominate as the pH is increased from 3.68 to 4.3, the concentration of L^- will also increase. If L^- would have participated in the

reaction, the reaction should have showed second order inverse dependence in $[H^+]$. Hence the active species involved in the anation reaction is probably HL.

Thus the effect of pH can be explained by eq. (3).

$$k_{obs} = k_1 + k_2 K_h [H^+]^{-1} \quad (3)$$

Here k_1 and k_2 are the observed rate constants when $[Rh(OH_2)_6]^{3+}$ and $[Rh(OH_2)_5OH]^{2+}$ are the reacting species respectively. The plot of k_{obs} (55°) vs $[H^+]^{-1}$ was linear with intercept = 7.55×10^{-5} and slope = 1.425×10^{-9} . The correlation coefficient was found to be 0.999.

Effect of $[H_2L^+]$ on reaction rate :

The effect of varying $[H_2L^+]_T$ on the reaction rate was studied at fixed $[H^+]$ and between 45 to 65°. At fixed $[Rh^{III}]_T = 2.58 \times 10^{-4}$, $I = 0.1$, the concentration of $10^{-3} [H_2L^+]_T$ was varied from 2.58 to 12.92 mol dm⁻³. The results are given in Table 1. It is observed that as $[H_2L^+]_T$

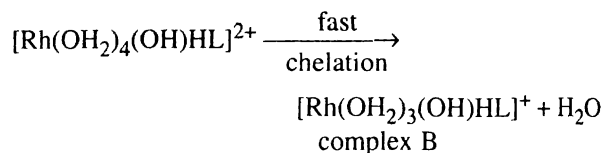
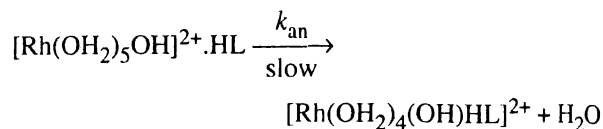
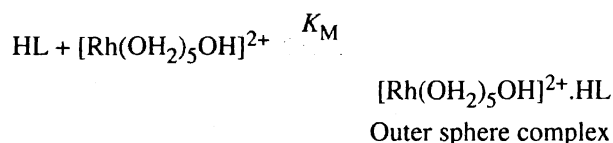
Table 1. Values of $10^5 k_{obs}$ (s⁻¹) at different $[HL^+]$ and at different temperatures

$[Rh^{3+}]_T = 2.58 \times 10^{-4}$, $I = 0.1$ mol dm⁻³ (NaClO₄), pH = 4.3

$10^3 [HL]$ (mol dm ⁻³)	Temp (°C)		
	45	55	65
2.58	4.45 (4.44)	8.15 (8.05)	11.93 (11.99)
5.16	6.00 (5.92)	10.43 (10.43)	15.25 (15.21)
7.74	6.62 (6.67)	11.63 (11.57)	16.63 (16.71)
10.32	7.20 (7.12)	12.50 (12.23)	17.60 (17.57)
12.92	7.40 (7.42)	12.78 (12.68)	18.00 (18.14)
$10^4 k_{an}/s^{-1}$	0.89	1.48	2.08
K_M	386.54	463.19	528.27

Data in the parenthesis are for k_{cald} .

increases k_{obs} increases in a nonlinear fashion, indicating outer-sphere complexation between the reactant species. The reaction sequence given below (Scheme 1) is consistent with the experimental data.



(Outer sphere complex = O.S)

The rate law for the anation reaction can be derived in the following manner.

$$\text{Rate} = k_{an} [O.S]_e = k_{an} K_M [RhOH^{2+}]_e [HL]_e \quad (4)$$

$$\begin{aligned} [RhOH^{2+}]_T &= [RhOH^{2+}]_e + [O.S]_e \\ &= [RhOH^{2+}]_e + K_M [RhOH^{2+}]_e [HL]_e \\ &= [RhOH^{2+}]_e \{1 + K_M [HL]_e\} \\ [RhOH^{2+}]_e &= [RhOH^{2+}]_T / \{1 + K_M [HL]_e\} \end{aligned} \quad (5)$$

Substituting the value of $[RhOH^{2+}]_e$ in eq. (4)

$$\text{Rate} = k_{an} K_M [RhOH^{2+}]_T [HL]_e / \{1 + K_M [HL]_e\} \quad (6)$$

$$\text{Rate} = k_{obs} [RhOH^{2+}]_T \quad (7)$$

The eq. (6) can be written as

$$\begin{aligned} k_{obs} &= k_{an} K_M [HL]_e / \{1 + K_M [HL]_e\} \\ \text{or, } k_{obs}^{-1} &= k_{an}^{-1} + (k_{an} \times K_M)^{-1} [HL]^{-1} \end{aligned} \quad (8)$$

The plot of k_{obs}^{-1} versus $[HL]^{-1}$ should be linear with an intercept = k_{an}^{-1} and slope = $(k_{an} \times K_M)^{-1}$. This plot was linear at all the experimental temperatures studied. k_{an} was determined from the reciprocal of the intercept and K_M was calculated from intercept/slope ratio. The values of k_{an} , K_M are given in Table 1.

Effect of temperature on the rate :

The reactions were studied at three different temperatures with different ligand concentrations. Activation parameters were calculated using Eyring equation and compared with literature data of the analogous systems (Table 2). The low ΔH^\ddagger value compared with the aqua exchange process⁵ together with highly negative ΔS^\ddagger value, suggest an associative mechanism k_{an} (25°) = 3.78×10^{-5} s⁻¹ which is found to be greater than $10^9 k_{ex}$ (25°) = 2.0 also supports the above proposition⁶. The values of ΔH^\ddagger and ΔS^\ddagger are 33.3 ± 4 kJ mol⁻¹ and -218 ± 12 JK⁻¹ mol⁻¹ respectively. ΔH^0 and ΔS^0 values were calculated from the $\ln K_M$ versus T^{-1} plot⁷. ΔH^0 was calculated from the slope and ΔS^0 was calculated from the intercept with $r = 0.995$. ΔH^0 and ΔS^0 values were found to be 37.99 kJ mol⁻¹ and -42.1 JK⁻¹ mol⁻¹

Table 2. Activation parameters for analogous systems

System	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	Ref.
Rh(OH ₂) ₅ OH ²⁺	103.0	–	5
Pyridine-2-aldoxime	87.5	–52.3	12
DL-Methionine	75.0	–81.3	3a
L-Cysteine	72.6 ± 0.6	–91 ± 2	13
Adenosine	93.0 ± 5.5	–49 ± 16	14
Cytidine	62.7 ± 4.2	–129 ± 12	4
L-Aspartic acid	62.0 ± 1.2	–120.8 ± 3.4	1
Uridine	46.5 ± 1.4	–181 ± 4	15
Picolinic acid	35.46 ± 0.95	–214.7 ± 2.84	1
Nicotinic acid	33.3 ± 4	–218 ± 12	This work

respectively. ΔG^0 value of the anation reaction was found to be -13.99 kJ mol⁻¹. Negative value of ΔG^0 supports the spontaneous formation of an outer sphere association complex.

Characterisation of the product complex :

A mixture of Rh(H₂O)₆(ClO₄)₃ and nicotinic acid in a molar proportion 1 : 1 at pH ≈ 4.3 was heated over a water bath for 10 h. Then the solution was left overnight at room temperature. The resulting solid was washed with ethanol and diethyl ether. The UV-Vis spectra of the product in aqueous medium closely resembles with the spectrum of reaction mixture at infinite time.

IR spectra were taken in a JASCO FT-IR-5300 spectrophotometer. In the substituted product, most of the peaks of nicotinic acid retain its identity. The infrared frequencies associated with the carboxylato proton of the substituted product appearing at 1521 cm⁻¹(s) and 1385 cm⁻¹(w) with 101 cm⁻¹ and 13 cm⁻¹ downshift from 1622 cm⁻¹ and 1398 cm⁻¹ respectively indicate the coordination of carboxylato group to Rh³⁺ ion, through O-atom. The infrared frequencies associated with C=N portion of the substituted product appearing at 1635 cm⁻¹ with a 67 cm⁻¹ downshift from 1701 cm⁻¹ (C=N stretching frequency of pure nicotinic acid) indicate coordination of pyridine nitrogen to Rh³⁺(8). 1541 cm⁻¹ and 1458 cm⁻¹ peaks of the product indicate the coordination of the ligand through conjugation 3674 cm⁻¹ and 3649 cm⁻¹ ν_{str} (O–H) of the aqua Rh³⁺ complex has been retained is an indication of presence of coordinated water. ν_{def} (O–H) at 1699 cm⁻¹ is also an indication of the presence of coordinated water in the product complex⁹. From the individual assignment of different bands it can be presumed that the substituted species is a mono-chelate.

Experimental

The complex [Rh(OH₂)₆](ClO₄)₃ was prepared according to the published method¹⁰. The complex was characterized spectrally ($\lambda_{\text{max}} = 396$ nm, $\epsilon = 62$, $\lambda_{\text{max}} = 311$ nm, $\epsilon = 67.4$ mol⁻¹ dm³cm⁻¹) and by elemental analysis¹¹.

The experimental condition was maintained to obtain the substrate complex [Rh(H₂O)₅OH]²⁺ by adjusting the pH of the solution to ≈ 4.3 where most of the hexaaquarhodium(III) gets converted into hydroxopenta-aqua species. Above pH 4.5, precipitation of Rh³⁺ occurred.

The ligand nicotinic acid may act as a bidentate (O, N) donor. The product of the reaction between Rh³⁺ complex and nicotinic acid was prepared by mixing them in different mole ratios viz. 1 : 2, 1 : 4, 1 : 8 and 1 : 10 and thermostating at 60° for 12 h. The absorption spectra exhibited the same λ_{max} (398 nm) with almost same absorbances. Upon addition of same acidic aquarhodium(III) solution to a solution of nicotinic acid, an increase in absorbance in the visible range occurred. The absorption spectra of nicotinic acid, Rh³⁺ and mixture (Rh³⁺ + nicotinic acid) at the same pH indicate the formation of an nicotinic acid-rhodium(III) complex (Fig. 1). The absorbance increase of the mixture at different time intervals is also shown in the Fig. The ligand

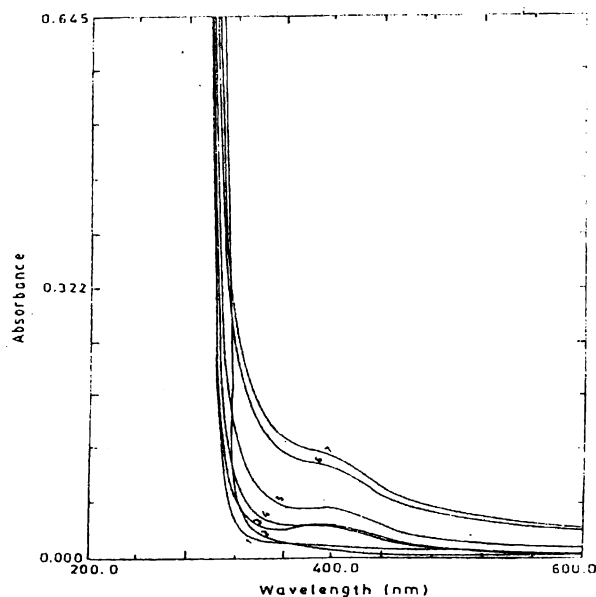


Fig. 1. Repetitive spectral scan of the Rh^{III} and nicotinic acid mixture. (1) [Rh^{III}] = 2.58×10^{-4} , $I = 0.1$ mol dm⁻³ (NaClO₄), pH = 4.3 at 65°. (2) [Nicotinic acid]_T = 12.92×10^{-3} , $I = 0.1$ mol dm⁻³ (NaClO₄), pH = 4.3 at 65°. (3) [Rh^{III}] = 2.58×10^{-4} mol dm⁻³ [Nicotinic acid]_T = 12.92×10^{-3} , $I = 0.1$ mol dm⁻³ (NaClO₄), pH = 4.3 at 65° and at 0 min, (4) at 15 min, (5) at 45 min, (6) at 90 min, (7) at 130 min.

binds to Rh^{3+} only through the carboxylate oxygen and through ring nitrogen. The composition of the complex formed, as determined by Job's method was found to be 1 : 1 (metal : ligand). The pH of the solution was adjusted with NaOH/HClO₄ and the measurements were carried out on Elico digital pH meter with an accuracy of ± 0.01 . Doubly distilled water was used to prepare all the kinetic solutions. The other chemicals used were of A.R. grade. The absorbance measurements for kinetic studies were done using a Shimadzu UV-2101PC scanning spectrophotometer. Reaction progress was monitored at 315 nm, pseudo-first order conditions were maintained throughout the runs by using a large (\geq ten fold) excess of picolinic acid. The rate constant k_{obs} were obtained from the slopes of $\ln(A_{\infty} - A_t)$ versus t plots eq. (9).

$$\ln(A_{\infty} - A_t) = k_{obs} t + C \quad (9)$$

Here A_t and A_{∞} are the absorbances of the reaction mixture at the time t and at equilibrium respectively. The reported rate data represented as an average of duplicate runs were reproducible to within $\pm 3\%$. The correlation coefficient of plots used to determine k_{obs} were found to be 0.99 in most of the cases. There is a good agreement between the k_{obs} and k_{cald} values.

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