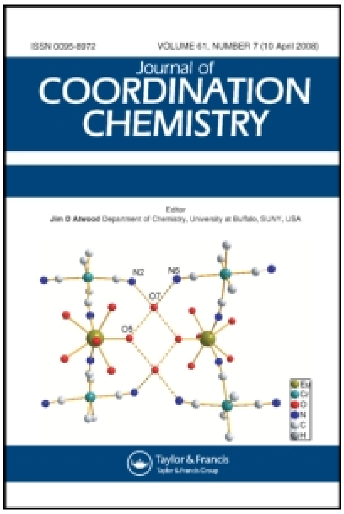

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KINETICS AND MECHANISM OF FORMATION OF PROPIONATOPENTAAMMINE RHODIUM(III) ION FROM AQUOPENTAAMMINERHODIUM(III) AND PROPIONATE IN WEAKLY ACIDIC MEDIA

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The kinetics of the anation reaction of aquopentaamminerhodium(III) ion by propionate to form the hitherto unknown propionatopentaammine rhodium(III) have been studied spectrophotometrically in the temperature range 60.0–80.0 ±0.1°C and acidity range $2.5 \leqslant \mathrm{pH} \leqslant 4.7$ for total propionate concentration up to 0.4 M and at ionic strength 1.0 M adjusted with $NaClO_4$. Experimental acidity range includes acidic and its conjugate basic form of the anating ligand. Analysis of the rate data indicates that the anation by propionic acid (HPr) follow a second order kinetics (k_0) whereas kinetic results of anation by propionate ion (Pr^-) provides evidence for the formation of outersphere association between $Rh(NH_3)_5OH_2^{+3}$ with propionate ion (Q_1) followed by the rate determining (k_1) outersphere–innersphere interconversion reaction. The theoretical rate law in accordance with the proposed mechanism fits the equation,

$$k_{\mathrm{obs}} = \frac{k_0[\mathrm{HPr}] + k_1 Q_1[\mathrm{Pr}^-]}{1 + Q_1[\mathrm{Pr}^-]}$$

Typical experimental results at 60.0 ± 0.1°C are $k_0 = 1.75 \pm 0.25 \times 10^{-5}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, $Q_1 = 1.43\ \mathrm{M}^{-1}$, and $k_1 = 3.67 \pm 0.2 \times 10^{-4}\ \mathrm{s}^{-1}$. The activation parameters for k_0 and k_1 paths are $\Delta H^\ddagger = 21.3 \pm 1.0, 22.2 \pm 0.4$ kcalmole^{-1} and $\Delta S^\ddagger = -17.0 \pm 1.1$ and -8.2 ± 1.0 cal. deg^{-1} respectively. Comparison of the activation parameters for the present system with the results obtained with respect to other anation reactions of Co(III) and Rh(III) complexes strongly suggest for an associative activation in the case of rhodium(III) systems.

INTRODUCTION

During the past few years kinetics of anation reactions of aquopentaamminecobalt(III) has been studied for a variety of entering ligands.[1-9] In contrast, limited data exists for the anation kinetics of aquopentaammine-rhodium(III) and gaining importance only in recent years,[10-12] as these provide information for a comparative analysis of reactivity of related octahedral and isoelectronic systems. Though the anation reactions of analogous complexes of Co(III) and Rh(III) often exhibit similar rate law, they actually proceed by different mechanistic pathways due to bond formation by entering ligand being more significant in the transition state in the case of Rh(III) than in the Co(III). The general applicability of the nucleophilic attack of the entering nucleophile on the Rh(III) substrate can be tested by extending the study to the anation reaction of $Rh(NH_3)_5OH_2^{+3}$ by carboxylate ligands which, so far, have been only sparingly studied.[13-16] Hence it appeared worth while to attempt a systematic study of the formation of carboxylato-pentaamminerhodium(III) complexes. In the present work, the results of the anation of $Rh(NH_3)_5OH_2^{+3}$ by propionate have been studied over a wide pH range to distinguish between the anation kinetics of the protonated and deprotonated forms of the anating species. In order to study the kinetics of such reactions, the hitherto unknown $[Rh(NH_3)_5CH_3CH_2COO](ClO_4)_2$ has been isolated. The results presented here show indeed a difference in mechanistic behaviour between Co(III) and Rh(III) ions in conformity with the investigations reported earlier. As an extension the kinetics of acid catalysed aquation and formation of propionato and malonatopentaamminerhodium(III)

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have been investigated and results of which will be reported subsequently.

EXPERIMENTAL

The aquopentaamminerhodium(III)perchlorate was prepared from chloropentaamminerhodium(III) chloride following the method described in the literature.[17] The purity of the complex was checked by elemental and spectral analysis.[18]

The propionatopentaamminerhodium(III) perchlorate was prepared for the first time by digesting hydroxopentaamminerhodium(III)hydroxide with excess of propionic acid at 90°C for 1 hour followed by slow evaporation of the reaction mixture nearly to dryness. The residual mass was dissolved in minimum amount of water and filtered. The filtrate was treated with cold $HClO_4$ to obtain the desired product in the perchlorate form. The white crystals thus obtained were washed with alcohol, ether and finally dried in air. The purity of the complex was checked by elemental analysis:

Calcd for $[Rh(NH_3)_5CH_3CH_2COO](ClO_4)_2$;
C, 7.78; N, 15.2; H, 4.35%
Found C, 7.78; N, 15.0; H, 4.30%

The position and intensities of the first and second ligand field bands of the propionato complex (λ_{max}; 322nm, $\varepsilon_M = 156$, λ_{max}; 265nm $\varepsilon_M = 125$) correspond to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions respectively (Figure 1). Chemicals of analytical and reagent grade were used throughout the experiment. Distilled water redistilled with alkaline $KMnO_4$ in an all glass still was used for making experimental solutions.

APPARATUS AND PROCEDURE

The kinetic measurements were performed employing Toshniwal UV–Visible and Varian Superscan 3 UV–

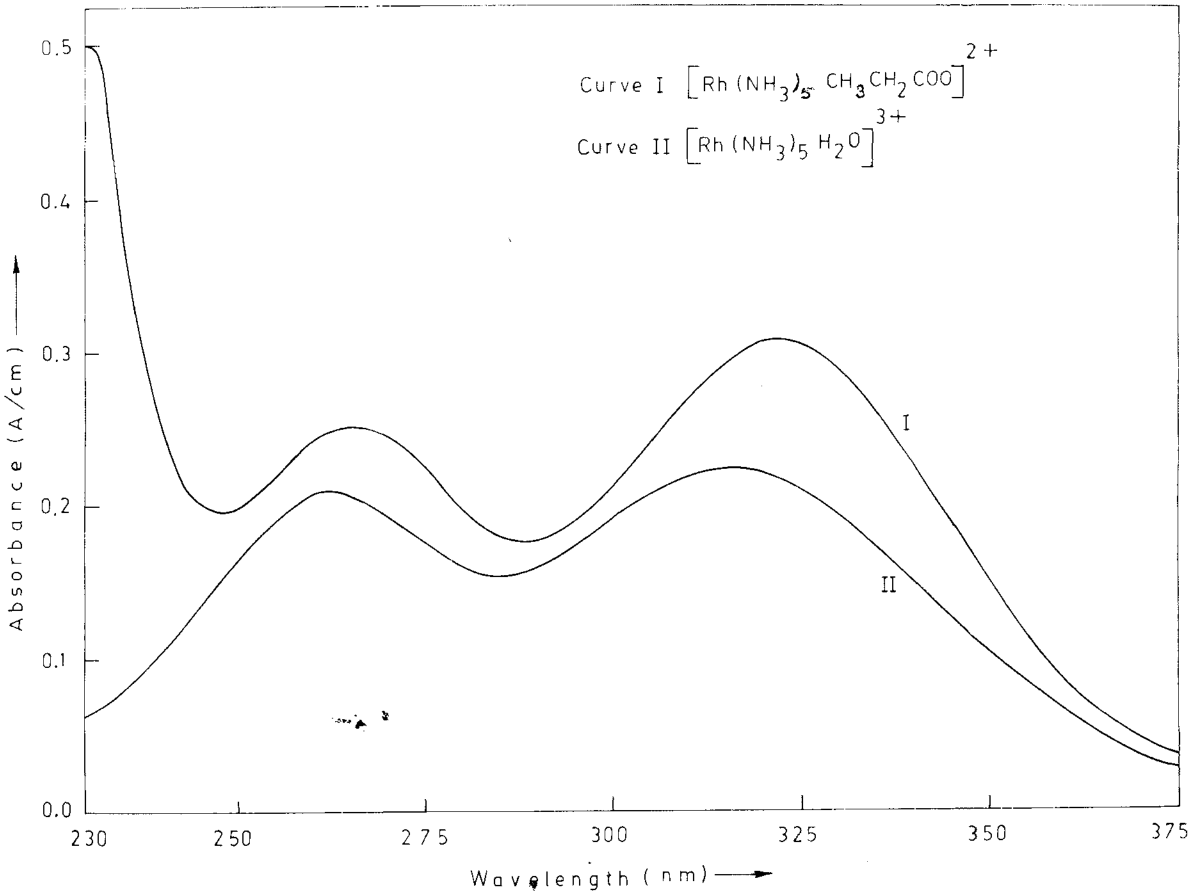

FIGURE 1 Absorption spectra I: $[Rh(NH_3)_5CH_3CH_2COO](ClO_4)_2 = 0.002$ M; II: $[Rh(NH_3)_5OH_2](ClO_4)_3 = 0.002$ M.

Visible spectrophotometers with a quartz cell of suitable light path. The pH measurements were made using ECIL digital pH meter. The pH values of the experimental buffer reaction mixtures were found to be within 0.02 units even before and after the reaction. All pH measurements were carried out at 25.0 ± 0.05°C. The glass electrode was standardized with potassium hydrogenphthalate buffer of known pK_a at 25.0°C. Experimental temperature for kinetic runs was maintained within ±0.1°C using high boiling paraffin oil bath with help of Jumo contact thermometer coupled with Jumo electronic relay. The course of the anation reaction of aquopentaamminerhodium(III) with propionate ion in the acidity range $2.5 \leq pH \leq 4.7$ was followed by measuring the increase in absorbance at 322nm (Figure 1). To follow the reaction a solution containing requisite quantities of propionic acid adjusted to a particular pH and sodium perchlorate (for adjustment of ionic strength to 1.0 M) was thermostated at the experimental temperature. After attaining thermal equilibrium, the requisite quantity of the complex, $[Rh(NH_3)_5OH_2](ClO_4)_3$ was added and the solution was thoroughly mixed and diluted to a definite volume with water thermostated at the experimental temperature. An aliquot of the solution was immediately removed using a pipette jacketed with ice to quench the reaction and its absorbance was measured at suitable wavelength. This procedure was repeated at subsequent time intervals. The absorbance of the solutions at the end of the reactions were found to be in close agreement with those of the solutions containing isolated complex showing the absence of any complication due to reverse aquation of the propionato complex. The experimental conditions were such that the pseudo first order rate law was applicable and the pseudo first order rate constant, k_{obs}, for each experiment was evaluated graphically by plotting $\log(A_\infty - A_0)/(A_\infty - A_t)$ versus time (t), using for A_∞, the calculated value of the absorbance corresponding to complete transformation into the product.

RESULTS AND DISCUSSION

The pseudo first order rate constant was evaluated under different sets of experimental conditions (viz., propionate concentration, pH and temperature). In evaluating the rate constants under all experimental conditions, the reaction was followed up to well over 50 to 90% of the total change in absorbance expected for the complete transformation of the aquo complex into the propionato complex. The experimental acidity range viz., $2.5 \leq pH \leq 4.7$ includes acidic (propionic acid) and its conjugate basic (propionate) form of the eliminate the participation of $Rh(NH_3)_5OH^{+2}$ species. The observed initial rate constant, k_{obs} for the anation by propionic acid/propionate were determined at 60.0 ± 0.1°, 70.0 ± 0.1° and 80.0 ± 0.1°C for total propionate and pH range are summarized in Table I. Typical plots of k_{obs} versus total propionate at 60.0 ± 0.1°C are illustrated in Figure 2. The slopes of the linear plots of k_{obs} versus total propionate increases with increase in pH. The deviation from linearity was observed at pH ≥ 4.0 indicative of the participation of an ion-pair formed between $Rh(NH_3)_5OH_2^{+3}$ and $CH_3CH_2COO^-$, since the latter species was present in appreciable quantities (Figure 2). Similar tends in k_{obs}

TABLE I
Observed rate constants (k_{obs}) as a function of total propionate and pH at different temperatures

Total Propionate M		0.05	0.08	0.10	0.12	0.15	0.16	0.20	0.24	0.25	0.27	0.30	0.35	0.40
Temp(°C)	pH	$10^5k_{obs}(sec^{-1})$												
60.0 ± 0.1	2.5			0.2		0.299		0.36		0.466		0.544	0.6	0.7
	3.6			0.414				0.71				1.06		1.44
	3.9	0.39		0.70		1.00		1.39		1.7		2.08		
	4.3	0.64	1.0	1.26	1.39		1.92	2.38	2.80		2.99	3.24		
	4.7	1.08	1.70		2.6		3.34	4.16	4.64		5.00	5.2		
70.0 ± 0.1	2.5			0.407		0.575		0.791		0.998		1.23		
	3.6			1.8		2.46		3.6		4.2		4.99		
	4.3	2.0	3.2	4.0	4.80		6.0	7.7	8.88		90.4	10.3		
	4.7	3.3	5.4		7.67		10.0	12.0	14.5		15.35			
80.0 ± 0.1	2.5			1.013		1.45		2.18		2.54		2.99		
	3.6			5.2		7.55		9.81		12.6		14.5		
	4.3	6.2	9.58	11.74	13.63		18.42	23.6	26.58		29.66	31.85		
	4.7	10.4	16.03		22.8		29.9	37.0	42.0					

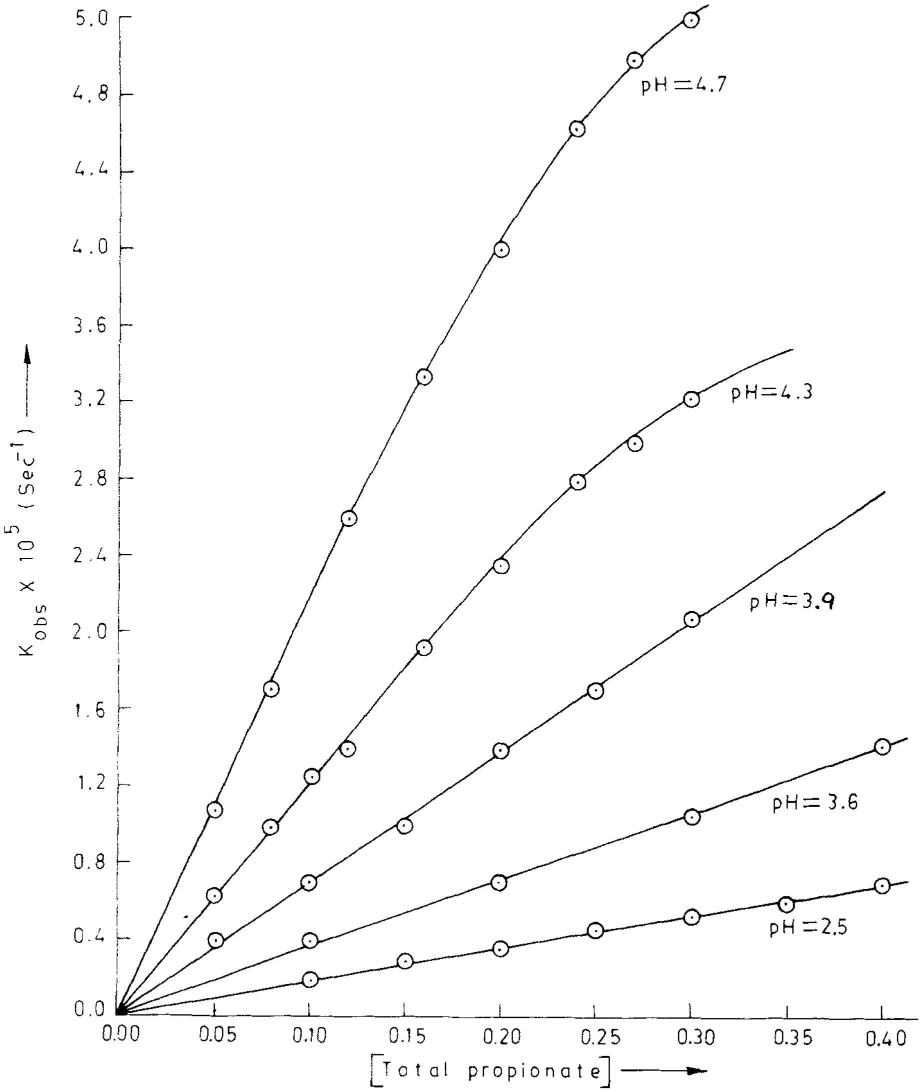

FIGURE 2 k_{obs} versus Total propionate for various pH values at 60.0 ± 0.1°C (μ = 1.0 M).

were observed at other temperatures (viz. 70.0 ± 0.1° and 80.0 ± 0.1°C). The experimental results are consistent with the following mechanism as depicted below:

$$[\mathrm{Rh(NH_3)_5H_2O}]^{+3} + \mathrm{CH_3CH_2COOH} \xrightarrow{k_0} [\mathrm{Rh(NH_3)_5CH_3CH_2COO}]^{+2} + \mathrm{H_3O^+} \quad (1)$$

$$[\mathrm{Rh(NH_3)_5H_2O}]^{+3} + \mathrm{CH_3CH_2COO^-} \underset{\text{fast}}{\overset{Q_1}{\rightleftharpoons}} [\mathrm{Rh(NH_3)_5H_2O^{+3}CH_3CH_2COO^-}]$$

$$\Big\downarrow \text{slow}\ k_1$$

$$[\mathrm{Rh(NH_3)_5CH_3CH_2COO}]^{+2} + \mathrm{H_2O} \quad (2)$$

The theoretical rate law for the suggested mechanism leads to

$$k_{obs} = -\frac{d\ln[\mathrm{Rh(NH_3)_5OH_2}]^{+3}}{dt} \qquad (3)$$

$$k_{obs} = \frac{k_0[\mathrm{CH_3CH_2COOH}] + k_1Q_1[\mathrm{CH_3CH_2COO^-}]}{1 + Q_1[\mathrm{CH_3CH_2COO^-}]} \qquad (4)$$

At low pH, where mainly CH_3CH_2COOH is present, analysis of the experimental results indicate that the anation rate is second order with respect to propionic acid. Under these conditions, the Eq. (4) can be simplified to

$$k_{obs} = k_0[CH_3CH_2COOH] + k_1Q_1[CH_3CH_2COO^-]$$

The observed rate data under these conditions followed second order kinetics such that

$$k_{obs} = k_{an}[\text{total propionate}] \qquad (5)$$

where k_{an} is the second order rate constant. The Eq. (5) on rearrangement leads to

$$k_{an} = k_0 + (k_1Q_1 - k_0)\frac{[CH_3CH_2COO^-]}{[\text{total propionate}]} \qquad (6)$$

The values of k_0 at each experimental temperature were obtained from the intercept of k_{an} versus $[CH_3CH_2COO^-]/[\text{total propionate}]$ plot. The Eq. (4) on rearrangement can be written as

$$\frac{k_{obs} - k_0[CH_3CH_2COOH]}{[CH_3CH_2COO^-]} = k_1Q_1 - Q_1k_{obs} \qquad (7)$$

The corresponding values of k_1 and Q_1 at each experimental temperature were obtained from the plot of

$$\frac{k_{obs} - k_0[CH_3CH_2COOH]}{[CH_3CH_2COO^-]} \text{ versus } k_{obs}$$

under the acidity range of pH ≈ pK of the anating ligand where the contribution of the basic form to the rate of reaction is significant (Figure 3).

ΔH^0 and ΔS^0 for the ionpairing equilibrium is calculated from a linear plot of ln Q vs. $1/T$ and are listed in Table II. The magnitude of entropy change ($\Delta S^0 = 14.1 \pm 2.0$ e.u.) suggests a loss of two water molecules from the second coordination sphere, probably one from the solvation of propionate and the other as a second sphere of solvent site replaced by propionate. Also the value of ionpairing equilibrium, Q_1, is somewhat smaller than 3 to 12 M^{-1} range found for $Co(NH_3)_5H_2O^{+3}$ as would be anticipated for the larger Rh(III) case.[19]

The $\Delta H^‡$ and $\Delta S^‡$ values corresponding to k_0 and k_1 path were evaluated with the help of Eyring equation using the respective anation rate constants at different temperatures were presented in Table II. As in the case of Co(III) system, the anation rate by propionate ion (k_1Q_1) is found to be much higher than that by propionic acid (k_0). This is generally explained in terms of higher reactivity of the deprotonated (basic) form of the carboxylic acid. For the sake of comparison, the activation parameters for the water exchange and formation of propionate complex of similar octahedral cobalt(III) and rhodium(III) complexes by propionate ion are given in Table III. A comparison of the results reveals that $\Delta H^‡$ values for water exchange and for the present system of rhodium(III) complex are fairly close and much smaller than those of the corresponding cobalt(III) systems. Based on the values of the activation parameters, the replacement of aquo ligand

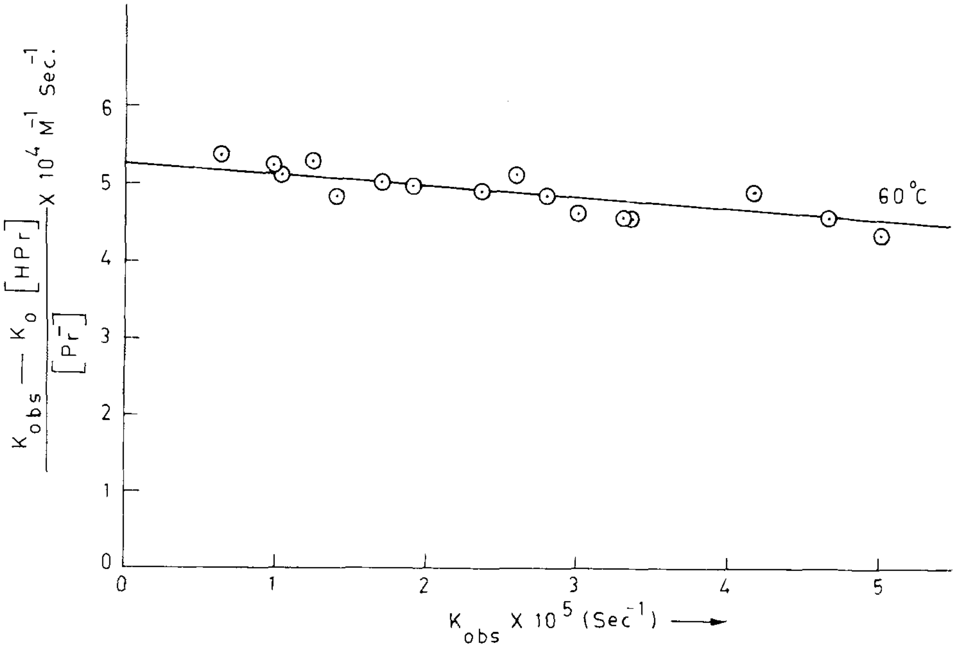

FIGURE 3 $(k_{obs} - k_0[HPr])/[Pr^{-1}]$ versus k_{obs} for the anation reaction of $[Rh(NH_3)_5OH_2]^{+3}$ by propionic acid at 60.0 ± 0.1°C.

TABLE II
Rate and activation parameters for the anation of $[Rh(NH_3)_5H_2O]^{+3}$ with propionic acid/propionate ion at different temperatures (μ = 1.0 M)

Temp. (°C)	$k_0 \times 10^5$ M^{-1} sec^{-1}	$k_1 \times 10^4$ sec^{-1}	Q_1 M^{-1}	$k_1Q_1 \times 10^4$ M^{-1} sec^{-1}
60.0 ± 0.1	1.75 ± 0.25	3.67 ± 0.2	1.43	5.25
70.0 ± 0.1	3.96 ± 0.30	10.24 ± 0.5	1.66	17.0
80.0 ± 0.1	10.22 ± 0.35	25.0 ± 1.0	2.10	52.5
$\Delta H^\ddagger$ kcal/mole	21.3 ± 1.0	22.2 ± 0.4	ΔH^0, −4.47 ± 0.68 kcal/mole	
$\Delta S^\ddagger$ cal/deg.mol	−17.0 ± 1.1	−8.2 ± 1.0	ΔS^0, 14.1 ± 2.0 e.u.	

TABLE III
Activation parameters for the reactions of $M(NH_3)_5OH_2^{+3}$ ions (M = Co or Rh)

	$\Delta H^\ddagger$	$\Delta S^\ddagger$	
System	kcal/mole	cal/deg mol	Ref.
$Co(NH_3)_5OH_2^{+3}/O^{18}H_2$	26.6 ± 0.3	6.7	20
$Co(NH_3)_5OH_2^{+3}/CH_3CH_2COO^-$	25.4 ± 3.2	−1.5 ± 11.5	21
$Rh(NH_3)_5OH_2^{+3}/O^{18}H_2$	23.9 ± 0.3	−3.0	22
$Rh(NH_3)_5OH_2^{+3}/CH_3CH_2COO^-$	22.4 ± 0.4	−8.2 ± 1.0	Present work

in $[Co(NH_3)_5OH_2]^{+3}$ by propionate ion has been proposed to take place by interchange dissociative (I_d) mechanism.[21] If the same type of mechanism is thought to be operative for the interchange process (k_1) in the present system, owing to the greater loss of the crystal field energy one would expect a higher enthalpy of activation for the Rh(III) complex compared to isostructural and isoelectronic (d^6) Co(III) substrates. The reverse trend in the magnitude of $\Delta H^\ddagger$ cannot be explained by above mechanism, but suggests significant bond formation by the incoming nucleophile in the transition state in the transformation of ion pair into the product complex. Moreover, a decrease of $\Delta S^\ddagger$ towards a negative value, going from Co(III) to Rh(III) system is also in conformity with mechanism involving a more pronounced participation of the incoming nucleophile in the transition state for the latter. Hence it may be concluded on the basis of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values that the reaction mechanism for the Rh(III) anation is more associative (I_a) in character than the I_d mechanism suggested for the Co(III) system.

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