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Kinetics and Mechanism of Anation of Pentaammineaquarhodium(III) Ion by Malonate in Weakly Acidic Media[1)]

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Anation of pentaammineaquarhodium(III) ion by malonic acid, hydrogenmalonate, and malonate ions to form the hitherto unknown pentaamminemalonatorhodium(III) complex has been studied as a function of [H$^+$] for the acidity range $1.4 \leq \mathrm{pH} \leq 5.0$, [total malonate], 0.3 mol dm^{-3} in the temperature range of 60 to 80 °C and at ionic strength 1.0 mol dm^{-3} adjusted with sodium perchlorate. Ion pairing is not significant between the complex and malonic acid but kinetically identifiable with hydrogenmalonate and malonate ions. Ion pair association constants for the hydrogenmalonate (Q_1) and malonate ion (Q_2) at 60 °C are 1.8 and 7.5 mol^{-1} dm^3 respectively. The values of the rate constants at 60 °C for anation by malonic acid, hydrogenmalonate, and malonate ions are $k_0=3.04\pm0.2\times10^{-5}$ mol^{-1} dm^3 s^{-1}, $k_1=1.73\pm0.2\times10^{-4}$ s^{-1}, and $k_2=3.46\pm0.4\times10^{-4}$ s^{-1}. The activation parameters, ΔH^* and ΔS^* corresponding to anation rate constants, k_0, k_1, and k_2 are reported and the results discussed with reference to analogous reactions of Rh(III) and Co(III).

The kinetics and mechanism of replacement of the aqua ligand in pentaammineaquacobalt(III) ion by various anionic ligands have been the subject of several investigations. In contrast, limited data exist for the analogous reactions of corresponding rhodium(III) substrate and receiving attention in recent years, as these provide important mechanistic information for a comparative analysis of the 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 mechanism due to bond formation by the entering group being more significant in the case of rhodium than in cobalt as evident from water exchange and anation reactions of the complexes of the type $[\mathrm{M(NH_3)_5(OH_2)}]^{3+}$, where M=Co(III)[2—10)] and Rh(III).[11—17)] The general applicability of the pronounced nucleophilic participation of the anating ligand in the transition state can be tested by extending the study to the anation reaction of $[\mathrm{Rh(NH_3)_5(OH_2)}]^{3+}$ by carboxylate ligands which, so far, have been only sparingly studied.[18—20)] In the present work, anation of pentaammineaquarhodium(III) ion by malonate has been presented. The reaction has been studied in aqueous malonate buffer of varying pH in order to assess the anation rate profile of malonic acid, hydrogenmalonate, and malonate ions. The results presented here show indeed a difference in mechanistic behavior between Co(III) and Rh(III).

Experimental

Materials and Reagents. Pentaammineaquarhodium(III) perchlorate was prepared according to standard procedures[21)] and purified by recrystallization. Chemical analysis confirmed the purity, as did a comparison with published UV-visible spectral data.[22)]

Pentaamminemalonatorhodium(III) perchlorate was prepared for the first time by digesting an aqueous solution of pentaammineaquarhodium(III) perchlorate with slight excess of malonic acid at 80 °C for 3 h followed by slow evaporation of the reaction mixture to one third of its original volume. Aqueous perchloric acid (30%) was added to the ice-cold reaction mixture to obtain the desired product as perchlorate salt. The white crystals that separated were filtered, washed successively with cold dilute perchloric acid, ethanol, and ether. The product was finally dried in air. The purity of the complex was ascertained by elemental analysis. Found: C, 7.30; H, 3.62; N, 14.20%. Calcd for $[\mathrm{Rh(O_2CCH_2CO_2H)(NH_3)_5](ClO_4)_2}$: C, 7.35; H, 3.67; N, 14.29%.

The positions and intensities of the d–d bands of the complex ($\lambda_{\max}$ 322 nm, ε 165 dm^3 mol^{-1} cm^{-1}, $\lambda_{\max}$ 265 nm, ε 130 dm^3 mol^{-1} cm^{-1}) corresponding to $^1A_{1g}\rightarrow{}^1T_{1g}$ and $^1A_{1g}\rightarrow{}^1T_{2g}$ transitions respectively match well with those of the pentaamminecarboxylatorhodium(III) (N$_5$O type) complexes. Infrared spectrum of Nujol mull of hydrogenmalonato complex reveals two strong bands at 1630 and 1725 cm^{-1} assignable to carbonyl asymmetric stretching frequencies of coordinated and free carboxyl groups in the complex. Presence of one equivalent of titrable proton unambigously confirms the mode of bonding of coordinated malonate ligand in the molecule. Other chemicals used were of reagent grade quality or prepared in the pure state by suitable methods.

Rate Measurements. The kinetic measurements were performed employing a Varian Superscan-3UV-visible spectrophotometer. The acidities of the experimental solutions were attained by the addition of sodium hydroxide and perchloric acid as the case may be and measured by means of a PHM 64 (Radiometer Copenhagen) research pH meter. The course of the anation reaction of pentaammineaquarhodium(III) ion with malonate over the acidity range $1.4\leq\mathrm{pH}\leq5.0$, for total malonate concentration up to 0.3 mol dm^{-3} in the temperature range of 60 to 80 °C was followed by measuring the increase in absorbance at 322 nm, where extinction coefficients of $[\mathrm{Rh(O_2CCH_2CO_2H)(NH_3)_5}]^{2+}$ and $[\mathrm{Rh(NH_3)_5(OH_2)}]^{3+}$ ions were 165 and 102 dm^3 mol^{-1} cm^{-1} respectively. The rate studies were made at ionic strength 1.0 mol dm^{-3} (NaClO$_4$) by a batch sampling technique,[20)] with the thermostat controlled to ±0.1 °C. The composition of the experimental solutions was such that the pseudo-first-order rate law was applicable and the pseudo-first-order rate constants, k_{obsd}, were computed from the gradients of the linear plots of $\log(A_\infty - A_t)$ vs. t by means of a least-squares program. Reported k_{obsd} values represent the average of at least duplicate runs which agreed within ±3%.

Table 1. Observed Rate Constants (k_{obsd}) as a Function of $[Malonate]_T$ and pH at Various Temperatures

Temp/°C	pH	Total malonate/mol dm^{-3}																
		0.02	0.03	0.04	0.05	0.06	0.08	0.10	0.12	0.125	0.15	0.16	0.175	0.18	0.20	0.225	0.25	0.30
		$k_{obsd}/10^{-5}\,s^{-1}$																
60.0	1.4						0.3	0.4	0.5		0.6			0.7	0.8		0.9	1.1
	1.7							0.5			0.7				1.0		1.2	1.4
	2.0							0.7			1.0				1.3			2.0
	2.5				0.5			1.1			1.6				2.2			
	2.9			0.7	0.8		1.3	1.6	1.9		2.4			2.6	2.9		3.1	
	3.4				1.1			2.2			3.3				3.8		4.3	
	3.8				1.4		2.1	2.6	3.0		3.6			4.1	4.4			
	4.5				3.1		4.7	5.3	6.4		7.1				7.9			
	4.8				4.1		6.2		8.8		10.2			11.3	11.8			
	5.0				5.1		6.8	8.3	9.5		11.5			12.9	13.2			
70.0	1.4						0.7		1.0		1.2			1.4	1.5		2.1	2.5
	1.7				0.7						2.5				3.0		4.3	4.9
	2.0							1.9			2.7				3.7			5.7
	2.5				1.9			3.5			5.7				7.3			8.8
	2.9				3.1			5.7			8.7		9.5		10.3	10.9	11.5	
	3.4				4.0			7.9			11.5				14.0		16.0	18.0
	3.8				5.0			9.5			14.5		15.4		17.0	18.0	19.1	
	4.5			7.5	8.8		14.4		20.5		23.5							
	4.8		8.1		12.0		18.4	21.5	24.6		28.1			30.0				
	5.0			12.1	14.5		22.0	26.1	28.8		32.0			34.0				
80.0	1.4				1.2			1.9							4.0		4.8	6.4
	1.7				2.0			4.0			5.8				7.2			11.8
	2.0							6.4			8.9						14.1	16.9
	2.5	2.4			5.4			11.3			16.0				20.8			
	2.9				8.6		13.2	17.5	20.5		24.6		28.7			33.3	36.3	
	3.4			9.6			19.0		27.7			32.5			37.8			
	3.8				14.9		24.5	29.6		36.1	45.0		51.9		55.6	57.6		
	4.8	14.8	22.0	28.1	34.2	38.7	48.2	56.2										
	5.0	16.9		31.8		46.1	58.0	67.5	75.2									

Results and Discussion

Pentaammineaquarhodium(III) ion reacts with malonic acid, hydrogenmalonate ion, and malonate ion to form either $[Rh(O_2CCH_2CO_2H)(NH_3)_5]^{2+}$ or $[Rh(O_2CCH_2CO_2)(NH_3)_5]^{+}$ complex depending on the pH of the solution. The interpretation of the rate data, however, was not complicated by the presence of $[Rh(O_2CCH_2CO_2)(NH_3)_5]^{+}$ species at high pH, as it showed absorbance identical to that of protonated one at the experimental wavelength. In order to assess the anation rate profiles of malonic acid, hydrogenmalonate, and malonate ions, the reaction has been studied over a wide enough pH range to encompass all possible acidic and basic forms of anating species. The participation of $[Rh(NH_3)_5(OH)]^{2+}$ species is essentially eliminated by fixing the upper pH limit at 5.0 (pK_a of $[Rh(NH_3)_5(OH_2)]^{3+}$ at μ, 1.0 mol dm^{-3}=6.94[23]). Acid dissociation constant of $[Rh(O_2CCH_2CO_2H)(NH_3)_5]^{2+}$ at 25 °C and ionic strength 1.0 mol dm^{-3} was determined from conventional pH titrations employing a PHM 64 research pH meter. The pK_a value was estimated as 3.8±0.05, which is significantly lower than that of $CH_2C_2O_4H^-$ ion. This is ascribed to an increase in acidity of the ligand when coordinated to a metal ion. Values of the pseudo-first-order rate constant (k_{obsd}) under different sets of experimental conditions are summarized in Table 1. Representative plots of k_{obsd} versus malonate concentration for varying pH at 60 °C are illustrated in Fig. 1. The plots are noted to be linear at low pH, while curvature becomes apparent at pH$\geq$2.5. Deviation from linearity at pH 2.5 and above suggests that the reactant association is not significant between aqua complex and malonic acid but kinetically identifiable with hydrogen malonate and malonate ions respectively, as the concentration of the latter species increases with increase in pH of the solution. Similar trends in k_{obsd} have also been noted at other experimental temperatures. The linearity of the plot at low pH suggests simple second-order kinetics for anation by malonic acid, as also reported for cobalt(III) analog.[10] The anation by basic forms of the anating ligand is thus proposed to involve the formation of ion pairs in a preequilibrium step followed by the rate determining interchange of coordinated aqua ligand by carboxylate ion. Consistent with the experimental results the anation scheme may be depicted as follows:

$$[Rh(NH_3)_5(OH_2)]^{3+} + CH_2C_2O_4H_2 \xrightarrow{k_0} [Rh(O_2CCH_2CO_2H)(NH_3)_5]^{2+} + H_3O^+$$

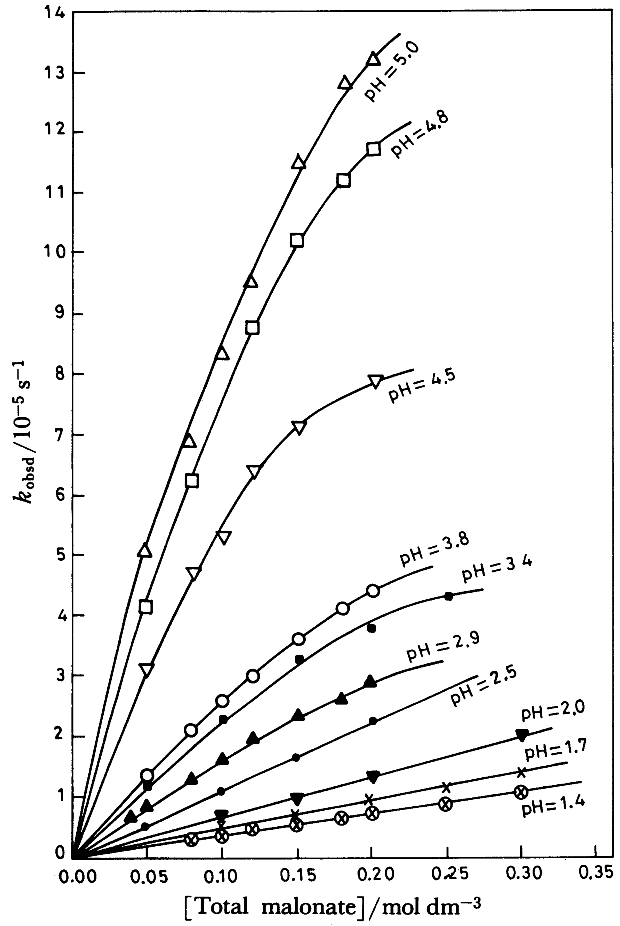

Fig. 1. k_{obsd} vs. [Total malonate] for various pH at 60.0±0.1 °C.
[Complex]; 0.002 mol dm^{-3}, μ; 1.0 mol dm^{-3}.

$$[Rh(NH_3)_5(OH_2)]^{3+} + CH_2C_2O_4H^- \overset{Q_1}{\rightleftharpoons} [Rh(NH_3)_5OH_2^{3+}\cdot CH_2C_2O_4H^-]$$

$$[Rh(NH_3)_5OH_2^{3+}\cdot CH_2C_2O_4H^-] \xrightarrow{k_1} [Rh(O_2CCH_2CO_2H)(NH_3)_5]^{2+} + H_2O$$

$$[Rh(NH_3)_5(OH_2)]^{3+} + CH_2C_2O_4^{2-} \overset{Q_2}{\rightleftharpoons} [Rh(NH_3)_5OH_2^{3+}\cdot CH_2C_2O_4^{2-}]$$

$$[Rh(NH_3)_5OH_2^{3+}\cdot CH_2C_2O_4^{2-}] \xrightarrow{k_2} [Rh(O_2CCH_2CO_2)(NH_3)_5]^{+} + H_2O,$$

where k_0 signifies second order rate constant for anation of $[Rh(NH_3)_5(OH_2)]^{3+}$ by malonic acid, k_1, Q_1, and k_2, Q_2 are the rate and association constants of the hydrogenmalonate and malonate ion pair respectively. The theoretical rate law in accordance with the suggested scheme fits the equation

$$k_{obsd} = -\,d\ln[Rh(III)]_T/dt = \frac{k_0[CH_2C_2O_4H_2]+k_1Q_1[CH_2C_2O_4H^-]+k_2Q_2[CH_2C_2O_4^{2-}]}{1+Q_1[CH_2C_2O_4H^-]+Q_2[CH_2C_2O_4^{2-}]}. \tag{1}$$

At pH<3.5, the contribution of terms involving $CH_2C_2O_4^{2-}$ is too small to have any meaningful significance, and hence Eq. 1 reduces to

$$k_{obsd} = \frac{k_0[CH_2C_2O_4H_2]+k_1Q_1[CH_2C_2O_4H^-]}{1+Q_1[CH_2C_2O_4H^-]}. \tag{2}$$

At low pH, where mainly $CH_2C_2O_4H_2$ is present, the anation reaction follows simple second-order kinetics. Under these conditions, Eq. 2 can be simplified to

$$k_{obsd} = k_0[CH_2C_2O_4H_2]+k_1Q_1[CH_2C_2O_4H^-], \tag{3}$$

as $1+Q_1[CH_2C_2O_4H^-]\simeq 1$. The observed rate data under these conditions followed second-order kinetics such that

$$k_{obsd} = k_{an}[\text{total malonate}], \tag{4}$$

where k_{an} is the second-order rate constant. The Eqs. 3 and 4 on rearrangement leads to

$$k_{an} = k_0 + (k_1Q_1-k_0)\frac{[CH_2C_2O_4H^-]}{[\text{total malonate}]}. \tag{5}$$

The values of k_0 at each experimental temperature were obtained from the intercept of k_{an} versus $[CH_2C_2O_4H^-]$/[total malonate] plot. The Eq. 3 on rearrangement can be written as

$$\frac{k_{obsd}-k_0[CH_2C_2O_4H_2]}{[CH_2C_2O_4H^-]} = k_1Q_1-Q_1k_{obsd}. \tag{6}$$

The interchange rate constant (k_1) and association constant (Q_1) at each experimental temperature were evaluated from the slope and intercept of $\{k_{obsd}-k_0[CH_2C_2O_4H_2]\}/[CH_2C_2O_4H^-]$ versus k_{obsd} (Fig. 2) plot under the acidity range of pH$\simeq$pK_1 of malonic acid where the contribution of $CH_2C_2O_4H^-$ to the rate of reaction becomes significant. At pH≥4.0, the contribution of $k_0[CH_2C_2O_4H_2]$ to k_{obsd} is negligibly small and Eq. 1 reduces to

$$k_{obsd} = \frac{k_1Q_1[CH_2C_2O_4H^-]+k_2Q_2[CH_2C_2O_4^{2-}]}{1+Q_1[CH_2C_2O_4H^-]+Q_2[CH_2C_2O_4^{2-}]}. \tag{7}$$

The values of k_2 and Q_2 at each experimental temperature were estimated from the slope and intercept of the straight line plot of $\{k_{obsd}+(k_{obsd}-k_1)Q_1[CH_2C_2O_4H^-]\}/[CH_2C_2O_4^{2-}]$ versus k_{obsd} (Fig. 3). Activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ corresponding to anation rate constants were calculated using Eyring equation. Values of the anation rate constants and corresponding activation parameters together with their standard deviations as deduced by least-squares analysis are presented in Table 2. A comparison of the anating reactivity of malonic acid and its conjugate bases derived from second-order rate constants, k_0, k_1Q_1, and k_2Q_2 follow the sequence: $CH_2C_2O_4H_2 < CH_2C_2O_4H^- < CH_2C_2O_4^{2-}$. This can be explained satisfactorily considering higher reactivity of the deprotonated

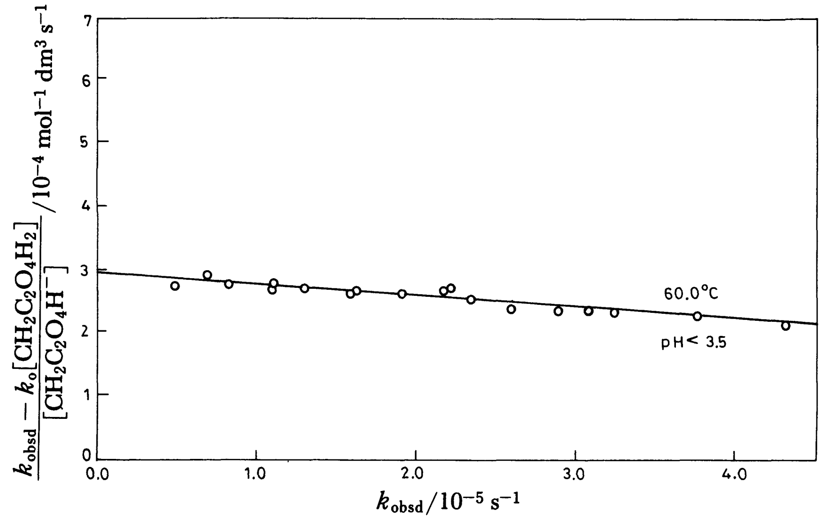

Fig. 2. $\frac{k_{\text{obsd}} - k_o[\text{CH}_2\text{C}_2\text{O}_4\text{H}_2]}{[\text{CH}_2\text{C}_2\text{O}_4\text{H}^-]}$ vs. k_{obsd} at 60.0±0.1℃.

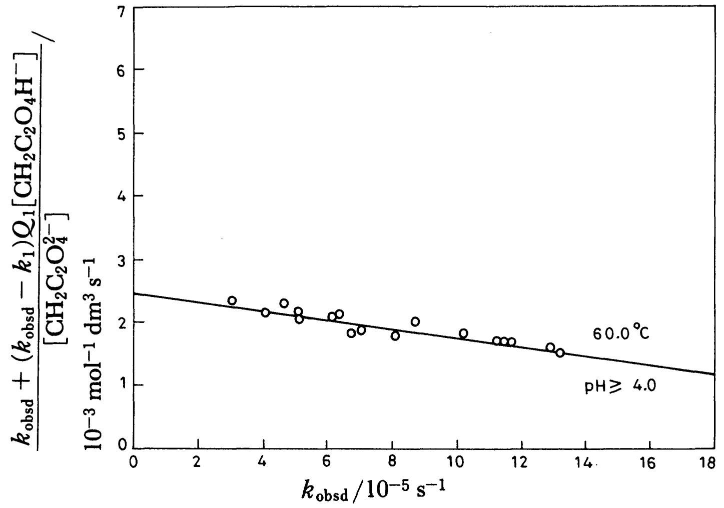

Fig. 3. $\frac{k_{\text{obsd}} + (k_{\text{obsd}} - k_1)Q_1[\text{CH}_2\text{C}_2\text{O}_4\text{H}^-]}{[\text{CH}_2\text{C}_2\text{O}_4^{2-}]}$ vs. k_{obsd} at 60.0±0.1℃.

Table 2. Rate and Activation Parameters for the Anation of $[\text{Rh(NH}_3)_5(\text{OH}_2)]^{3+}$ by Malonic Acid/Malonate Ions ($\mu = 1.0\ \text{mol dm}^{-3}$)

Rate parameter	Temperature/°C			Activation parameters	
	60.0±0.1	70.0±0.1	80.0±0.1	$\Delta H^{\neq}/\text{kJ mol}^{-1}$	$\Delta S^{\neq}/\text{J K}^{-1}\text{mol}^{-1}$
$k_0/10^{-5}\ \text{mol}^{-1}\text{dm}^3\text{s}^{-1}$	3.04±0.2	7.22±0.2	15.44±0.3	79.0±2.9	−97.0±12.0
$Q_1/\text{mol}^{-1}\text{dm}^3$	1.7±0.1	1.8±0.3	1.9±0.2		
$k_1/10^{-4}\text{s}^{-1}$	1.73±0.2	5.96±0.5	16.93±0.7	104.0±5.6	−4.0±1.7
$Q_2/\text{mol}^{-1}\text{dm}^3$	7.1±0.3	7.8±0.3	7.6±0.4		
$k_2/10^{-4}\text{s}^{-1}$	3.46±0.4	9.1±0.7	24.24±1.0	96.5±6.0	−20.9±9.2

forms of the acid. Anation of pentaammineaquarhodium(III) ion by oxalic,[18] malonic, and propionic acid[20] studied so far offers a meaningful relation between k_o and pK values of the carboxylic acids. The value of k_o is found to decrease with an increase in pK value, i.e. with increasing basicity and O–H bond strength, of the acid, making the reaction more difficult to occur. This effect is accompanied by the increase in activation parameter as is expected for a less reactive species. The k_o value for the present system is comparable with the analogous reaction for cobalt(III) analog. In both cases no evidence for an ion pair is kinetically observed and the anation proceeded via a second-order kinetics, suggesting a similarity in mechanism for both the systems. The observed rate constant for anation of $[Co(NH_3)_5(OH_2)]^{3+}$ ion by malonic acid at pH=1.5 is reported to decrease by a factor of 1.4 when D_2O instead of H_2O is used as solvent.[10] Based on the results of isotope effect and the relation between k_0 and pK values of the carboxylic acid, the O–H bond fission on the –COOH group of the carboxylic acid has been suggested of significant importance in the rate-determining step of the anation mechanism.[10] Low $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values corresponding to k_0 for the complex under present investigation also corroborate the possibility of associative activation in the transition state. The value of essentially temperature-independent ion pair association constant (Q) is observed to be greater for malonate than for hydrogen malonate ion as expected on the basis of higher charge on the former, but are considerably higher than that for strong acid anions of the same charge viz., Cl^-, Br^-, SO_4^{2-}.[13] This may be attributed to the less extensive solvation of the carboxylates in comparison to that of strong acid anions.

According to Swaddle,[24] the magnitude of enthalpy of activation for anation rate constant offers better criteria to distinguish between the associative and dissociative character of interchange reactions. Similarity in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values corresponding to interchange rate constants, k_1 and k_2 for the present system seem to suggest near identity of the respective transition states. Moreover, both sets of activation parameters are observed to be fairly close to that of water exchange[11] of $[Rh(NH_3)_5(OH_2)]^{3+}$ ion as well as the substitution reaction involving replacement of coordinated aquo ligand by Cl^-, Br^-, I^-,[12,13] N_3^-, CH_3COO^-,[14] and $CH_3CH_2COO^-$[20] ions. The anation and water exchange reactions of $[Rh(NH_3)_5(OH_2)]^{3+}$ ion have been suggested to proceed by an interchange associative (I_a) mechanism. The negative volume of activations for the aquo exchange in $[Rh(NH_3)_5(OH_2)]^{3+}$ ($\Delta V^{\neq}$, -4.1 ± 0.4 cm^3 mol^{-1})[16] and solvent exchange in $[Rh(NH_3)_5(dmf)]^{3+}$ ($\Delta V^{\neq}$, -1.4 cm^3 mol^{-1}),[17] lend additional support to the associative character for rhodium(III) substrate. The $\Delta H^{\neq}$ values for the anation of $[Rh(NH_3)_5(OH_2)]^{3+}$ by hydrogenmalonate and malonate ions are observed to be 12—21 kJ mol^{-1} lower than for analogous reactions of cobalt(III) substrate. On the basis of the activation parameters, the anation of $[Co(NH_3)_5(OH_2)]^{3+}$ with hydrogenmalonate and malonate ions have proposed to take place by interchange dissociative (I_d) mechanism.[10] If the same type of mechanism is thought to be operative for the interchange reactions for the present system, owing to the greater loss of ligand field energy one would expect a higher enthalpy of activation for the Rh(III) complex compared to isostructural and isoelectronic (d^6) Co(III) substrate. The reverse trend in magnitude of $\Delta H^{\neq}$ cannot be explained by above mechanism but suggests significant bond formation by the entering group in the transition state in course of transformation of ion pair into the product complex. Moreover, a decrease in $\Delta S^{\neq}$ towards a more negative value, going from Co(III) to Rh(III) substrate, is also in conformity with a mechanism involving a more pronounced participation of the incoming nucleophile in the transition state for the latter.

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