

Mechanism of Aquation of Malonatopentaamminerhodium (III) Ion in Aqueous Acidic Media

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Acid-catalysed aquation of malonatopentaamminerhodium (III) ion has been studied kinetically in aqueous perchloric acid (0.04-0.4 mol dm⁻³) media over a temperature range of 55-80°C at an ionic strength of 1.0 mol dm⁻³ adjusted with sodium perchlorate. Under these conditions, the observed pseudo-first order rate constants are described by the relationship: $k_{\text{obs}} = k_0 + k_{\text{H}}[\text{H}^+]$, where k_0 and k_{H} stand for the rate constants of spontaneous and acid-catalysed pathways respectively. The rate and activation parameters for the k_0 and k_{H} paths have been determined. The results indicate that the unbound carboxyl group does not exert any specific catalytic effect on the spontaneous and acid-catalysed paths of the aquation reaction. Analysis of the rate data suggests Rh-O bond cleavage in the transition state for both the paths.

Kinetics of acid catalysed aquation of carboxylatopentaammine-cobalt (III) complexes derived from mono and dicarboxylic acids have been the subject of several investigations¹⁻⁷. In contrast, very few investigations of the analogous reactions of isostructural and isoelectronic rhodium(III) substrates have been reported². In order to examine the effects of structural variation in the carboxylate ligand on the aquation rate, several mono and bifunctional carboxylatopentaamminerhodium (III) complexes were synthesised and their hydrolysis in aqueous acidic media have been studied kinetically. This paper describes the synthesis and kinetics of aquation of malonatopentaamminerhodium (III) ion in acidic media. Based on comparison of rate and activation parameters for the complex under investigation with those of other carboxylatopentaamminerhodium (III) ions, a plausible mechanism is suggested.

Materials and Methods

Aquopentaamminerhodium (III) perchlorate, $[\text{Rh}(\text{NH}_3)_5\text{OH}_2](\text{ClO}_4)_3$ (complex-I) was prepared following the method described in literature⁸. The purity of the sample was checked by elemental and spectral analyses⁹.

Malonatopentaamminerhodium (III) perchlorate, $[\text{Rh}(\text{NH}_3)_5\text{Hmal}](\text{ClO}_4)_2$ (complex-II) was prepared for the first time by refluxing an aqueous solution (50 ml) of complex-I (0.05 mol dm⁻³) with ten-fold excess of malonic acid at 90°C for 1 hr followed by slow evaporation of the reaction mixture to about one third of its original volume and cooling in ice. To the ice cold solution aqueous perchloric acid (1:1) was added dropwise with stirring to obtain complex-II as a white crystalline solid. The solid was filtered off, washed successively with cold water, ethanol, ether and dried

in air. (Found: C, 7.25; H, 3.60; N, 14.20. $[\text{Rh}(\text{NH}_3)_5(\text{O}_3\text{CCH}_2\text{CO}_2\text{H})](\text{ClO}_4)_2$ requires C, 7.35; H, 3.67; N, 14.29%).

The positions and intensities of the *d-d* bands of the complex (λ_{max} 322, 265 nm; ϵ , 166, 130 dm³mol⁻¹cm⁻¹) corresponding to $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$ transitions respectively, matched well with those of other carboxylatopentaamminerhodium (III) (N₅O type) complexes⁹. Infrared spectrum of the complex revealed two strong bands at 1630 and 1725 cm⁻¹ attributable to $\nu_{\text{as}}\text{C}=\text{O}$ modes of the coordinated and free carboxyl groups respectively. PMR spectrum of the complex in DMSO-*d*₆ exhibited a broad band at δ 3.8 assignable to amine hydrogens and methylene protons appeared as a singlet at δ 3.2 downfield from TMS internal reference. Presence of one equivalent of titratable proton in the complex confirmed the mode of bonding of malonate in the molecule.

Measurements: PMR spectrum was recorded on a Varian XL 100 (100 MHz) spectrometer. A Varian Superscan-3 UV-visible spectrophotometer was employed for absorbance measurements. Under experimental acidity range complex-II was found to aquate quantitatively leading to aquo product. The course of aquation reaction in dilute perchloric acid (0.04-0.4 mol dm⁻³) and in the temperature of 55-80°C was monitored by measuring the decrease in absorbance with time at 325 nm, where the extinction coefficients of complex-II and aquo product were 164 and 100 dm³mol⁻¹cm⁻¹ respectively. The rate constants (k_{obs}) were obtained from the slopes of the linear plots of $\ln(A_t - A_\infty)$ versus time (*t*) by means of a least-squares program. The absorbance of the experimental solution after digesting for several (six and higher) half-lives agreed well with that of aquo

complex, indicating the absence of any complication due to reverse anation reaction. Reported k_{obs} values represent the average of at least duplicate runs which agree within $\pm 3\%$.

Acid dissociation constant of $(\text{NH}_3)_5\text{RhO}_2\text{CCH}_2\text{CO}_2\text{H}^{2+}$ ion at 25°C and ionic strength 1.0 mol dm^{-3} was determined from conventional pH titration against standard carbonate-free sodium hydroxide solution using a PHM-64 research pH meter (Radiometer, Copenhagen). The pK_a value was estimated as 3.80 ± 0.05 , indicating that the complex-II exists in the acid form in the range of $[\text{H}^+]$ employed in the present work.

Results and Discussions

The spectrophotometrically determined pseudo-first order rate constant (k_{obs}) for the aquation of complex-II have been evaluated under different sets of experimental conditions, viz. at different [acid], temperatures and ionic strengths of the medium. The variation of k_{obs} on [acid] at different temperatures and ionic strengths maintained with sodium perchlorate is illustrated in Fig. 1. Results show that k_{obs} increases linearly with increase in [perchloric acid] and fits best the relationship (1)

$$k_{\text{obs}} = k_0 + k_{\text{H}}[\text{H}^+] \quad \dots (1)$$

where k_0 stands for first-order rate constant for spontaneous and k_{H} , second-order rate constant

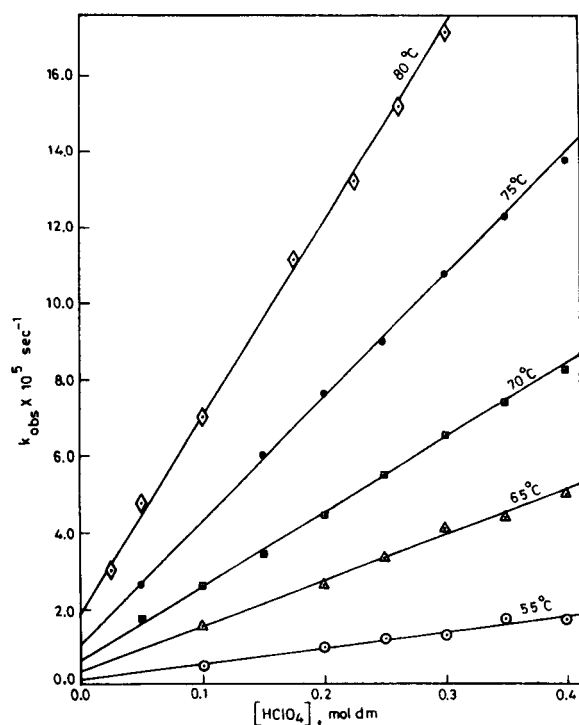
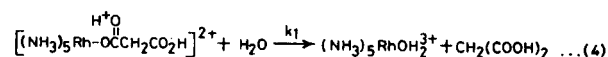
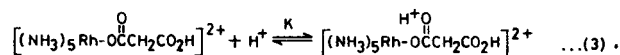
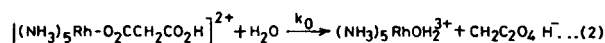


Fig. 1—Effect of varying [acid] on k_{obs} at different temperatures [Complex] = $0.002 \text{ mol dm}^{-3}$; $\mu = 1.0 \text{ mol dm}^{-3}$

Table 1—Rate and Activation Parameters for Spontaneous and Acid-catalysed Aquation of Malonatopentaamminerhodium (III) Ion

Temp. ($^\circ\text{C}$)	μ (mol dm^{-3})	$10^6 k_0$ (s^{-1})	$10^5 k_{\text{H}}$ ($\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$)
55.0 ± 0.1	1.0	1.2 ± 0.2	4.2 ± 0.04
65.0 ± 0.1	1.0	3.6 ± 0.2	12.0 ± 0.03
70.0 ± 0.1	0.1	6.5 ± 0.4	12.8 ± 0.05
	1.0	6.4 ± 0.3	19.5 ± 0.03
75.0 ± 0.2	1.0	10.7 ± 0.3	32.3 ± 0.05
80.0 ± 0.2	0.1	18.3 ± 0.6	34.0 ± 0.2
	1.0	18.6 ± 0.5	51.2 ± 0.2
$\Delta H^\ddagger$ (kJ mol^{-1})		102.4 ± 2.9	94.9 ± 1.2
$\Delta S^\ddagger$ ($\text{JK}^{-1} \text{mol}^{-1}$)		-46.3 ± 6.2	-42.2 ± 3.4

describing the acid-catalysed pathways respectively. Their values at different temperatures, as obtained from the intercepts and slopes of the linear plots of Fig. 1 using a linear regression analysis, are summarised in Table 1 alongwith the activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values evaluated from Eyring equation. Consistent with the experimental observations the aquation may follow the mechanism shown in Scheme 1:



Scheme 1

The reaction (2) corresponds to uncatalysed path involving attack of solvent molecule in the rate-determining step, whereas acid-catalysed paths (3 and 4) are believed to involve fast protonation pre-equilibrium of the substrate followed by the rate-limiting loss of carboxylic acid from the protonated species. The catalytic rate constant, k_{H} is related to K and k_1 by the relation (5)

$$k_{\text{H}} = Kk_1 / 1 + K[\text{H}^+] \quad \dots (5)$$

The absence of any deviation from linearity of the plot of k_{obs} versus $[\text{H}^+]$, even at highest [acid] indicates, $K[\text{H}^+] \ll 1$, and hence Eq. (5) reduces to $k_{\text{H}} = Kk_1$. The magnitude of the acid-catalysed rate constant, k_1 , can be estimated in the following manner. The linearity of k_{obs} versus $[\text{H}^+]$ plot at $[\text{H}^+] \leq 0.4 \text{ mol dm}^{-3}$ suggests the value of protonation constant, $K < 1 \text{ mol dm}^{-3}$. The value of k_1 then turns out to be $\sim 3.4 \times 10^{-4} \text{ s}^{-1}$ at 80°C , which is ~ 20 times higher than that of k_0 . This reflects much higher reactivity of the protonated form, $(\text{NH}_3)_5\text{RhH}_2\text{mal}^{3+}$. This can be explained considering that acid catalysis involves

Table 2—Rate Parameters for Aquation of Carboxylatopentaamminerhodium (III) Complexes
($\mu = 0.1 \text{ mol dm}^{-3}$)

Complex	pK_a of acid	Temp. (°C)	k_o (s^{-1})	k_H^+ ($\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$)	Reference
$[\text{Rh}(\text{NH}_3)_5\text{CF}_3\text{COO}]^{2+}$	0.3	78.9	1.5×10^{-4}	$\sim 1.5 \times 10^{-4}$	2
$[\text{Rh}(\text{NH}_3)_5\text{glyH}]^{3+}$	2.35	80.0	2.0×10^{-5}	0.8×10^{-4}	13
$[\text{Rh}(\text{NH}_3)_5\text{Hmal}]^{2+}$	2.7	80.0	1.8×10^{-5}	3.4×10^{-4}	Present work
$[\text{Rh}(\text{NH}_3)_5\text{CH}_3\text{COO}]^{2+}$	4.75	78.7	$\sim 4 \times 10^{-6}$	26.0×10^{-4}	2
$[\text{Rh}(\text{NH}_3)_5\text{CH}_3\text{CH}_2\text{COO}]^{2+}$	4.87	80.0	4.5×10^{-6}	29.2×10^{-4}	14
$[\text{Rh}(\text{NH}_3)_5(\text{CH}_3)_3\text{CCOO}]^{2+}$	5.05	78.6	2.0×10^{-6}	8.9×10^{-4}	2

addition of proton on coordinated carboxylate thereby putting a formal positive charge on ligand oxygen atom. Strong bonding between oxygen atom and H^+ in the protonated form of the complex leads to electron withdrawal from $\text{Rh}-\text{O}$ bond thus facilitating its fission and providing easy entry for a water molecule from the solvation sheath to form the aquo product. Evidence for the protonation of carbonyl oxygen in cobalt (III) complexes have been reported by several workers^{11,12}.

The influence of ionic strength on aquation reaction has been examined at two different temperatures and corresponding values of the rate constants are listed in Table 1. Analysis of the results indicates that the uncatalysed rate constant, k_o , remains unaffected as expected by the variation of ionic strength whereas acid-catalysed rate constant, k_H , increases significantly with increasing ionic strength. This can be ascribed to an increase in equilibrium constant, K , with increase in ionic strength and hence an increase in the k_H value. In order to estimate the position of bond rupture in the spontaneous and acid-catalysed paths of complex-II, the rate parameters for analogous reaction of other carboxylatopentaamminerhodium (III) complexes have been summarised in Table 2 for comparison. The k_o values for acetato, propionato and trimethylacetato (pivalato) complexes are observed to be comparable but are approximately one or two orders of magnitude lower than those of malonato, glycinate and trifluoroacetato complexes. The values of the uncatalysed rate constant follow the order: $\text{CF}_3\text{COO}^- > \text{N}^+\text{H}_3\text{CH}_2\text{COO}^- > \text{CH}_2\text{C}_2\text{O}_4\text{H}^- > \text{CH}_3\text{COO}^- \approx \text{CH}_3\text{CH}_2\text{COO}^- > (\text{CH}_3)_3\text{CCOO}^-$. This order of reactivities of complexes is in agreement with the fact that k_o decreases with increasing pK of the carboxylic acids. The position of the malonato (complex-II) in the above sequence suggests that the unbound carboxyl group does not exert any intramolecular catalytic effect in the spontaneous process. The activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, corresponding to k_o are comparable to those for the acid-catalysed rate constant, k_H . Similarity in activation parameters seem to suggest that same type

of mechanism is operative in the transition state for spontaneous and acid-catalysed paths. Comparison of k_H values indicates that with the exception of glycine and pivalato complexes, the acid-catalysed rate constant increases with increasing pK of the carboxylic acids. The magnitude of equilibrium constant, K as expressed in Eq. (3) is expected to increase with increasing basicity, i.e. pK of the acid and thus leads to the enhancement of k_H value. Low value for glycine complex can be ascribed to the retardation of protonation arising from an electrostatic effect of the $-\text{NH}_3$ group present in the neighbourhood of carboxyl, while the impediment of protonation in the case of pivalato complex is due to steric effect. The acid hydrolysis of metal carboxylates can proceed either by metal-oxygen or by a carbon-oxygen bond cleavage in the transition state. On the basis of kinetic data it has been unequivocally established¹⁵ that the enthalpy of activation corresponding to cleavage of $\text{C}-\text{O}$ bond lies between 67 and 75 kJ mol^{-1} whereas $\Delta H^\ddagger$ value for the cleavage of $\text{Rh}-\text{O}$ bond falls in the range of 90 to 110 kJ mol^{-1} . The enthalpy of activation computed for the present system ($\Delta H^\ddagger = 94.9 \pm 1.5 \text{ kJ mol}^{-1}$) is observed to be much higher than the value reported for acid-catalysed decarboxylation of $\text{Rh}(\text{NH}_3)_5\text{CO}_3^+$ ion ($\Delta H^\ddagger = 71.0 \pm 2.1 \text{ kJ mol}^{-1}$)¹⁶. The latter process has been proposed to involve $\text{C}-\text{O}$ bond rupture in the rate-determining step. Hence the cleavage of $\text{Rh}-\text{O}$ bond in the transition state seems to be more plausible for the present system.

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