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Kinetics of Aquation of Pentaammineglycinerhodium(III) Ion in Acidic Media

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Synopsis. Acid-catalyzed aquation of pentaammineglycinerhodium(III) ion has been studied kinetically in aqueous perchloric acid media (0.05—0.45 mol dm^{-3}) over a temperature range of 60—80 °C at an ionic strength of 1.0 mol dm^{-3} adjusted with sodium perchlorate. Under these conditions the reaction occurs by two concurrent paths according to the rate law: Rate=k_0[complex]+k_{H^+}[complex][H$^+$], where k_0 and k_{H^+} are the rate constants for the spontaneous and acid-catalyzed pathways, respectively. Analysis of rate data suggests cleavage of metal–oxygen bond in the rate determining step for both the processes.

Kinetics of acid-catalyzed aquation of (carboxylato)- and (aminocarboxylato)pentaamminecobalt(III) complexes have been the subject of several investigations.[1–7] The aquation rates were correlated with the electronic and steric effects of the leaving group. In comparison, limited data[2] is available for the analogous reactions of corresponding rhodium(III) substrate, thus warrants further investigations. An amino acid usually coordinates to a metal ion with its amino and carboxylato group to form a chelate ring. However, in some amino acid cobalt(III) complexes[8,9] glycine has been found to coordinate as an unidentate ligand with its carboxylato end only. Surprisingly, no data is available to date on the nucleophilic substitution reaction of rhodium(III) amino acid complex. This paper reports the results of the kinetics of acid-catalyzed hydrolysis of pentaammineglycinerhodium(III) ion in which amino acid exists in zwitterionic form and coordinated to the metal ion with its carboxylate end. The influence of the protonated amino group on the catalytic rate constant has been discussed. Based on comparison of rate and activation parameters for the present system with other carboxylato complexes, a plausible mechanism is suggested.

Experimental

Materials and Reagents: Pentaammineaquarhodium(III) perchlorate was prepared according to standard procedures.[10] Chemical analysis confirmed the purity, as did a comparison with the published UV-visible spectral data.[11]

Pentaammineglycinerhodium(III) perchlorate was prepared by digesting an aqueous solution (50 cm^3) of pentaammineaquarhodium(III) perchlorate (5 mmol) with five fold excess of glycine at 90 °C for 3 h followed by the slow evaporation of the reaction mixture to one third of its original volume. The solution on cooling separated white crystals of glycine complex, which were collected on a filter and washed with water–ethanol (1:1) mixture. The complex was recrystallized from cold aqueous solution by the addition of 30% perchloric acid, and washed successively with water–ethanol, ethanol, and finally dried in air. Found: C, 4.35; N, 14.90; H, 3.50%. Calcd for [Rh(NH$_3$)$_5$(glyH)](ClO$_4$)$_3$: C, 4.28; N, 14.96; H, 3.56%. Since the complex has been isolated from acidic solution, the amino acid retains an acidic proton and is coordinated as an unidentate neutral ligand as is evident from the elemental analysis. The positions and intensities of the ligand field bands of the complex (λ_{max} 322 nm, ε=144.0 dm^3 mol^{-1} cm^{-1}; λ_{max} 266 nm, ε=111.0 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 pentaamminecarboxylato rhodium(III) ion,[11] in which the ligand undoubtedly coordinates to the metal with its carboxyl group. In accord with the postulate of oxygen-bonded amino acid, IR spectrum of the title complex reveals a strong band at 1630 cm^{-1} assignable to C–O stretching band of the coordinated carboxyl group and the deformation band of –NH$_3^+$ group at 1490 cm^{-1}. ^{1}H NMR spectrum of the complex in DMSO-d_6 exhibits two broad bands at δ=7.5 and 3.75 ppm against TMS as reference with an intensity ratio 1:5 attributable to the –NH$_3^+$ and NH$_3$ protons. Disappearance of these peaks in D$_2$O confirms the assignments.

Measurements. A Varian superscan-3 spectrophotometer was used for absorbance measurements. The pH measurements were made using a PHM-64 research pH meter (Radiometer-Copenhagen). ^{1}H NMR spectra were recorded on a Varian XL 100 spectrometer.

Under experimental acidity range glycine complex has been found to aquate quantitatively leading to aqua product. Final concentration of the free glycine was determined by its reaction with ninhydrin as described in the literature.[6] The course of aquation reaction was monitored by measuring the decrease in absorbance at 325 nm, where the extinction coefficients of the glycine complex and aqua product were 143 and 100 dm^3 mol^{-1} cm^{-1}, respectively. The rate studies were made by a batch sampling technique,[12] with the thermostat controlled to ±0.1 °C. All experiments were carried out in excess of perchloric acid and the pseudo-first-order rate constants, k_{obsd}, were computed from the gradients of the linear plots of ln(A_t−A_∞) versus time by means of a least-squares program. Under identical conditions k_{obsd} evaluated by the spectrophotometric method agreed well with the value obtained by the ninhydrin method. Acid dissociation constant of [Rh(NH$_3$)$_5$(O$_2$CCH$_2$NH$_3$)]$^{3+}$ at 25 °C and ionic strength 1.0 mol dm^{-3} was determined from conventional pH titrations against carbonate free sodium hydroxide solution. The pK_a value has been estimated as 8.80±0.03. It is thus evident that in the range of acid concentration employed for the reaction, the amino acid exists in zwitterionic form.

Results and Discussion

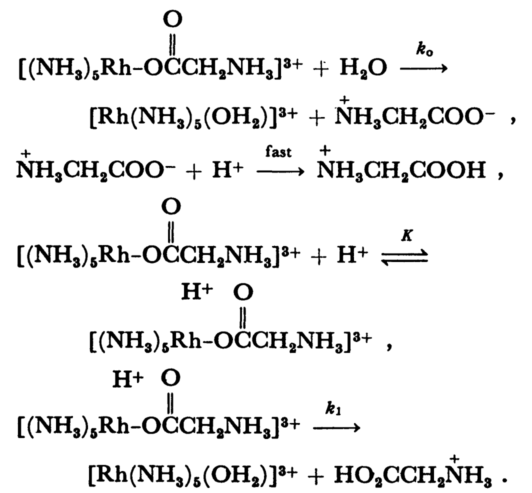
The observed pseudo-first-order rate constants, k_{obsd}, have been determined at 60.0±0.1, 70.0±0.1, and 80.0±0.1 °C, for perchloric acid concentration 0.05—0.45 mol dm^{-3} at ionic strength 1.0 mol dm^{-3} (NaClO$_4$). The variation of k_{obsd} with [HClO$_4$] under otherwise identical conditions is shown in Fig.1 and the results suggest the operation of two concurrent paths:

$$-\mathrm{d}\ln[\text{complex}]/\mathrm{d}t = k_{obsd} = k_o + k_{H^+}[\mathrm{H}^+]\ , \qquad (1)$$

where k_0 and k_{H^+} represent the first order rate constant for acid independent and second order rate constant describing the acid-catalyzed pathways, respectively. Their values at different temperatures, as obtained from the intercepts and slopes of the plots shown in Fig. 1 using a linear regression analysis, are summarized in Table 1 along with the activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values evaluated using transition state equation,

$$k = (RT/Nh)\exp(-\Delta H^{\neq}/RT+\Delta S^{\neq}/R). \qquad (2)$$

Sequences of changes consistent with kinetic results are depicted below:



$$[(NH_3)_5Rh\text{-}O\overset{O}{\overset{\|}{C}}CH_2NH_3]^{3+} + H_2O \xrightarrow{k_0} [Rh(NH_3)_5(OH_2)]^{3+} + \overset{+}{N}H_3CH_2COO^- , \qquad (3)$$

$$\overset{+}{N}H_3CH_2COO^- + H^+ \xrightarrow{\text{fast}} \overset{+}{N}H_3CH_2COOH , \qquad (4)$$

$$[(NH_3)_5Rh\text{-}O\overset{O}{\overset{\|}{C}}CH_2NH_3]^{3+} + H^+ \overset{K}{\rightleftharpoons} [(NH_3)_5Rh\text{-}\overset{H^+}{O}\overset{O}{\overset{\|}{C}}CH_2NH_3]^{3+} , \qquad (5)$$

$$[(NH_3)_5Rh\text{-}\overset{H^+}{O}\overset{O}{\overset{\|}{C}}CH_2NH_3]^{3+} \xrightarrow{k_1} [Rh(NH_3)_5(OH_2)]^{3+} + HO_2CCH_2\overset{+}{N}H_3 . \qquad (6)$$

The Reaction (3) corresponds to uncatalyzed path involving the attack of solvent molecule in the rate-determining step, while the acid-catalyzed path (5 and 6) involves the fast protonation action of substrate in a pre-equilibrium step followed by the rate-determining loss of glycine from conjugate acid. The catalytic rate constant, k_{H^+} is related to K and k_1 by the relation

$$k_{H^+} = Kk_1/(1+K[H^+]) . \qquad (7)$$

The absence of any deviation from linearity for the k_{obsd} vs. $[HClO_4]$ plot even at the highest acid concentration indicates, $K[H^+] \ll 1$ and hence Eq. 7 reduces to $k_{H^+}=Kk_1$. The activation parameters corresponding to k_{H^+} thus involve both rate and equilibrium constants. In conformity with the proposed scheme, the protonated species is found to be more labile than the unprotonated one. This can be ascribed to the fact that the acid catalysis involves protonation of coordinated carboxylate and thereby putting a formal positive charge on ligand oxygen atom. Strong bonding between oxygen atom and H^+ ion in the protonated form of the complex leads to electron withdrawal from Rh–O bond thus facilitating

Table 1. Rate and Activation Parameters for Aquation of Pentaammineglycinerhodium(III) ion. (I=1.0 mol dm^{-3})

Temperature °C	$10^6\,k_0$/s^{-1}	$10^5\,k_{H^+}$/mol^{-1} dm^3 s^{-1}
60.0±0.1	1.5±0.1	5.5±0.1
70.0±0.1	4.5±0.18	18.1±0.2
80.0±0.2	12.4±0.15	55.0±0.2
$\Delta H^{\neq}$/kJ mol^{-1}	102.0±1.7	105.8±0.8
$\Delta S^{\neq}$/JK^{-1} mol^{-1}	−52.3±9.2	−10.9±6.3

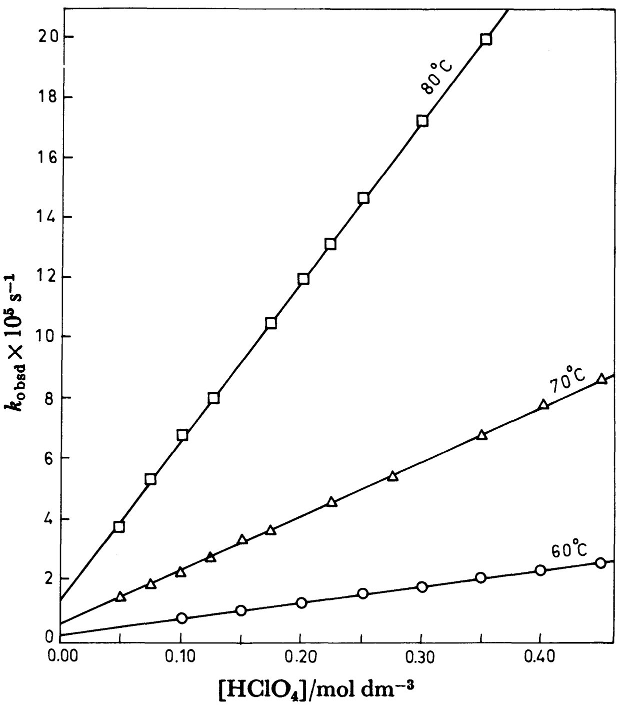


Fig. 1. Effect of acid concentration on k_{obsd} at different temperatures.
$[Rh(NH_3)_5(glyH)]^{3+}$, 0.002 mol dm^{-3}; I, 1.0 mol dm^{-3}.

Table 2. Rate Parameters for Aquation of Pentaamminecarboxylatorhodium(III) Complexes (I=0.1 mol dm^{-3})

	pK_a of the acid	Temp/°C	k_0/s^{-1}	k_{H^+}/mol dm^3 s^{-1}	Ref.
$[Rh(NH_3)_5CF_3COO]^{2+}$	0.3	78.9	1.5×10^{-4}	1.5×10^{-4}	2
$[Rh(NH_3)_5glyH]^{3+}$	2.35	80.0	2.0×10^{-5}	0.8×10^{-4}	Present work
$[Rh(NH_3)_5Hmal]^{2+}$	2.7	80.0	1.8×10^{-5}	3.4×10^{-4}	13
$[Rh(NH_3)_5CH_3COO]^{2+}$	4.75	78.7	4×10^{-6}	26.0×10^{-4}	2
$[Rh(NH_3)_5CH_3CH_2COO]^{2+}$	4.87	80.0	4×10^{-6}	30.0×10^{-4}	13
$[Rh(NH_3)_5(CH_3)_3CCOO]^{2+}$	5.05	78.6	2×10^{-6}	8.9×10^{-4}	2

the rate of release of glycine. The effect of ionic strength (I) on aquation reaction was examined at 80 °C and the values of the rate constants at I=0.1 mol dm^{-3} have been tabulated in Table 2. The uncatalyzed rate constant tend to decrease slightly whereas acid-catalyzed rate constant, $k_{\mathrm{H^+}}$ increases significantly with increase in ionic strength. The equilibrium constant, K, between cations such as that expressed by Eq. 5 generally increases with increasing ionic strength and hence the $k_{\mathrm{H^+}}$ value. The rate parameters for the analogous reaction of other pentaamminecarboxylatorhodium(III) complexes have been summarized in Table 2 for comparison. Basolo et al.[2] while studying aquation of carboxylato complexes observed that k_0 values tend to decrease with increase in pK_a of the acid. This can be explained due to increase in metal-ligand bond strength with increasing basicity of the carboxylate ligand. k_0 value for the title complex nicely fits into the relationship and the reactivity order follows the sequence:

$$\mathrm{CF_3COO^-} > \overset{+}{\mathrm{N}}\mathrm{H_3CH_2COO^-} > \mathrm{CH_2C_2O_4H^-} >$$
$$\mathrm{CH_3COO^-} \simeq \mathrm{CH_3CH_2COO^-} > \mathrm{(CH_3)_3CCOO^-}.$$

$\Delta H^{\ast}$ value for the uncatalyzed path is comparable to that of other carboxylato complexes of rhodium(III). On the basis of comparable $\Delta H^{\ast}$ values it is reasonable to conclude that the uncatalyzed path proceed by mechanism identical to that operative in other carboxylato complexes where cleavage of metal-oxygen bond is suggested to take place in the rate-determining step.[2]

With the exception of glycine and pentaammine(pivalato)rhodium(III) ion, the acid catalyzed rate constant tend to increase with increasing pK_a of the carboxylic acids. The pK_a affects the magnitude of equilibrium constant K, as expressed by Eq. 5 and hence $k_{\mathrm{H^+}}$ value. Low $k_{\mathrm{H^+}}$ value for glycine complex can be ascribed to the retardation of protonation arising from an electrostatic effect of the $-\overset{+}{\mathrm{N}}\mathrm{H_3}$ group present in the neighborhood of carboxyl group, while the impediment of protonation in case of pivalato complex has been explained due to steric factor. The acid hydrolysis of metal carboxylates can proceed either by M–O or C–O bond rupture in the transition state. On the basis of kinetic studies it has been suggested that the cleavage of C–O bond in the transition state leads to a low $\Delta H^{\ast}$ value (67.0—75.0 kJ mol^{-1}) whereas cleavage of M–O falls in the range of 90—110 kJ mol^{-1} for the aquation of Rh(III) complexes.[14] The enthalpy of activation for the title complex ($\Delta H^{\ast}$=105.8±0.8 kJ mol^{-1}) is much higher than that reported for the acid-catalyzed decarboxylation of pentaamminecarbonatorhodium(III) ion ($\Delta H^{\ast}$=71.0±2.1 kJ mol^{-1}),[15] for which C–O bond rupture has been proposed to take place in the transition state. Hence Rh–O bond cleavage in the transition state seems to be more plausible for the present system.

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