BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (9), 2710—2712 (1979)

Kinetics and Mechanism of Formation of Pentaammine(glycine)rhodium(III) Ion from Pentaammineaquarhodium(III) Ion and Glycine in Weakly Acidic Media

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(Received July 25, 1978)

The rates of formation of pentaammine(glycine)rhodium(III) ion from pentaammineaquarhodium(III) ion and glycine in weakly acidic media have been studied spectrophotometrically at different glycine and acid concentrations in the temperature range of 60—80 °C. The rate has been found to be insensitive towards the change in ionic strength from $\mu=0.5$ to 2.0 M of the medium. The activation parameters, ΔH^* and ΔS^* values are 22.2 ± 1.0 kcal mol^{-1} and -9.2 e.u. respectively. The results are in accord with a mechanism involving a fast 1:1 outer-sphere association between the pentaammineaquarhodium(III) ion and glycine in zwitter ionic form followed by its transformation into the product by a process where the incoming ligand is appreciably bonded to the metal ion in the transition state.

Kinetics and mechanism of the substitution reactions involving replacement of coordinated water in pentaamminеaquacobalt(III), ($3d^6$) ion by various nucleophiles including neutral and anionic in nature have been the subject of several investigations. However, there has been increasing interest in recent years on rhodium(III), ($4d^6$) complexes, which furnish further data for a comparative analysis of the reactivity of related octahedral structures. Though the rates of reactions have been generally found dependent upon the entering ligand concentration, they actually proceed by different mechanisms due to bond formation by the incoming nucleophile which is more significant in the transition state in the case of rhodium(III) than in cobalt(III) as is evident from the water exchange and anation reactions of the complexes of the type $M(NH_3)_5OH_2^{3+}$, where M=Co(III)[1,3a–c] and Rh(III).[2,4,5] In order to test further the generality of nucleophilic attack of the entering group on the substrate Rh(III) complex, it appeared worthwhile to extent the work to uncharged ligands, and with this end in view the kinetics of reactions of pentaammineaquarhodium(III) ion with glycine in weakly acidic media (pH=*ca.* 2—4) forming pentaammine(glycine)rhodium(III) ion $[Rh(NH_3)_5glyH]^{3+}$ has been studied in detail. In order to study the kinetics of such reaction the hitherto unknown $Rh(NH_3)_5glyH^{3+}$ in the form of perchlorate salt has been isolated. The results presented here show indeed a difference in mechanistic behaviour between cobalt(III) and rhodium(III) ions in conformity with the investigations reported earlier.

Experimental

Materials. The pentaammineaquarhodium(III) perchlorate was prepared from pentaamminechlororhodium(III) complex as described in the literature.[6] The purity of the complex was checked by elemental and spectral analyses.[7]

The pentaammine(glycine)rhodium(III) perchlorate was prepared for the first time by refluxing an aqueous solution (50 ml) of pentaammineaquarhodium(III) perchlorate (0.0005 mol) and an excess of glycine(0.005 mol) for few hours at 90 °C. The solution was then concentrated to one third of its original volume and kept in a refrigerator. The resulting crystals were filtered and washed with a water–ethanol(1:1) mixture. The complex was recrystallized from a cold aqueous solution by the addition of 30% perchloric acid. The recrystallized product was washed first with a water–ethanol mixture and finally with absolute ethanol. The purity of the complex was ascertained by the elemental analysis: Calcd for $[Rh(NH_3)_5glyH](ClO_4)_3$: C, 4.28; N, 14.96; H, 3.56%. Found: C, 4.45; N, 14.85; H, 3.58%.

Glycine used were of reagent grade (G. R., E. Merck). All other chemicals used were either of reagent grade purity or prepared in the pure state by suitable methods.

Besides elemental analysis, spectral measurements of glycine complex of rhodium(III) furnish further evidence regarding the mode of bonding of amino acid in the complex. It is well known that an amino acid usually coordinates to a metal ion with its amino and carboxyl groups. In some complexes of cobalt(III),[8,9] however, glycine has been observed to act as an unidentate ligand although no such complexes of rhodium(III) have been isolated before. The analytical results of pentaammine complex clearly indicate the unidentate nature of coordinated glycine molecule. Since the complex was obtained from an acidic solution, the amino acid retains an acidic proton and is coordinated as a neutral ligand in agreement with the elemental analysis. Glycine may be bound with the rhodium(III) ion as an unidentate ligand either with an oxygen atom of the carboxyl group or with the nitrogen atom of the amino group. The results of the absorption measurements for the present complex, however, suggest that the coordination of glycine correspond to the former. The position and intensities of the first and second bands of the glycine complex (λ_{max}; 322 nm, $\varepsilon_M=144.0$, λ_{max}; 266 nm, $\varepsilon_M=111.0$) corresponding to ${}^1A_{1g}\rightarrow{}^1T_{1g}$ and ${}^1A_{1g}\rightarrow{}^1T_{2g}$ transitions, match very well with those of the pentaammine carboxylatorhodium(III) ion[7] in which the ligand undoubtedly coordinates to rhodium(III) ion with its carboxyl group. In accord with the postulate of the oxygen-bonded amino acid, IR spectrum of the complex shows a close similarity to that of the corresponding Co(III) complex, with a strong band at about 1630 cm^{-1} assignable to C–O stretching band of the coordinated carboxyl group and the deformation band of $-NH_3^+$ group at about 1490 cm^{-1}.

Apparatus and Procedure. The kinetic measurements were performed employing a Carl-Zeiss(VSU-2P) spectrophotometer with a quartz cell of suitable light path. The pH measurements were made using a radiometer pH meter with a glass electrode and a reference calomel electrode connected to the experimental solution through 1 M NaCl–1 M $NaClO_4$ salt bridges connected in series. The course

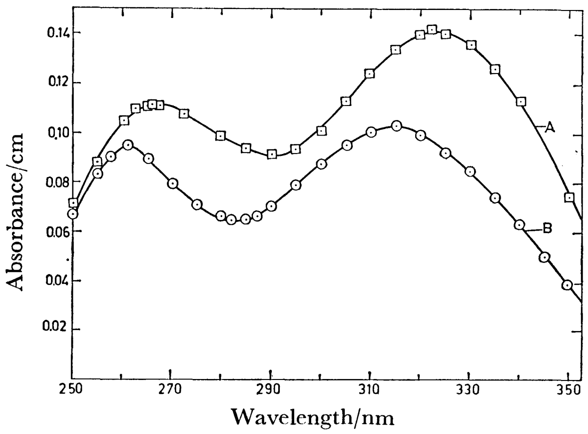

Fig. 1. Absorption spectra.
A: $[Rh(NH_3)_5glyH](ClO_4)_3$, 0.001 M; B: $[Rh(NH_3)_5OH_2](ClO_4)_3$, 0.001 M.

of the anation reactions of pentaammineaquarhodium(III) ion with glycine in weakly acidic media was followed by observing the increase in absorbance at 322 nm where the molar extinction coefficients of the reacting complex and the product differ appreciably (Fig. 1). A sample queching technique was used. Ionic strength of the solutions was kept constant with sodium perchlorate. The absorbances of the solutions at the end of the reactions were found to be in close agreement with those of the solution containing isolated complex, indicating that under the experimental conditions there was no interference due to reverse aquation of the glycine complex. The concentrations of the reactants were such that the pseudo first order rate law was applicable and the pseudo first order anation rate, k_{obsd}, was evaluated graphically for each experiment by plotting log $(A_\infty—A_0)/(A_\infty—A_t)$ *versus* time (t), where A denotes measured absorbance and subscripts denote time as usual. A_∞ is the calculated value for complete transformation of the aqua complex to the pentaammine(glycine)rhodium(III) complex.

Results and Discussion

The pseudo first order rate constant, k_{obsd}, was evaluated under different sets of experimental conditions (*viz.* glycine concentration, acid concentration, temperature and ionic strength). It has been observed that at constant pH, (*i.e.*, keeping T_G/T_A constant, where T_G and T_A are the concentrations of total glycine and perchloric acid respectively in the experimental solution) the rate shows first order dependence on total glycine concentration (Fig. 2), and at a fixed glycine concentration the rate decreases with increase in acid concentration (Fig. 3). The experimental conditions were so chosen that the reacting complex present in the aqua form and the results are consistent with the sequence of changes as delineated below:

$$GH + H^+ \rightleftharpoons GH_2^+ \tag{1}$$

$$R^{3+}\text{-}OH_2 + GH \rightleftharpoons R^{3+}\text{-}OH_2\cdots GH \text{ (outer sphere association)} \tag{2}$$

$$\Big\downarrow k' \text{ slow}$$

$$R^{3+}\text{-}GH + H_2O \tag{3}$$

where $R^{3+}=Rh(NH_3)_5^{3+}$.

According to the above scheme,

$$k_{obsd} = K_{o.s.}\cdot k'[GH] \tag{4}$$

where $K_{o.s.}$ is the outer sphere association constant.

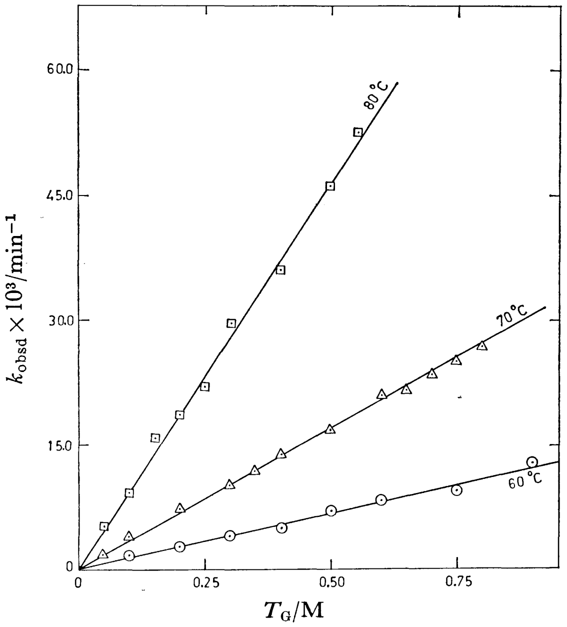

Fig. 2. Dependence of k_{obsd} on total glycine concentration (T_G). $[Rh(NH_3)_5OH_2^{3+}]$, 0.001 M; $T_G/T_A=20.0$; $T_A=[HClO_4]$; $\mu(HClO_4+NaClO_4)$, 1.0.

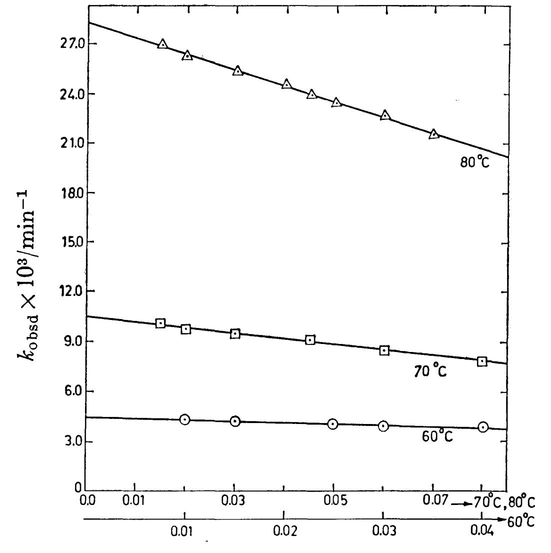

Fig. 3. Dependence of k_{obsd} on total perchloric acid concentration (T_A) at constant glycine concentration. $[Rh(NH_3)_5OH_2^{3+}]$, 0.001 M; $T_G=0.3$ M; $\mu(HClO_4+NaClO_4)$, 1.0.

From the protonation equilibrium of glycine (Eq. 1), the value of GH in terms of T_G and T_A can be expressed in the following manner:

$$T_G = [GH] + [GH_2^+],$$

$$T_A = [GH_2^+] + [H^+],$$

$$K_H = T_A - [H^+]/(T_G - T_A + [H^+])[H^+]. \tag{5}$$

On simplifying Eq. 5 and neglecting insignificant $[H^+]^2$ term we have $[H^+]=T_A/K_H T_G-K_H T_A+1$.

Substituting the value of $[H^+]$

$$[GH] = T_G(1+T_G K_H - T_A K_H)/(1+T_G K_H). \tag{6}$$

Hence Eq. 4 can be written as

Table 1. Values of the rate constants and activation parameters ($\mu = 1.0$)

Temp °C	$k/10^2\ M^{-1}\ min^{-1}$			Average
	I[a]	II[b]	III[c]	
60	1.35	1.47	1.38	1.40
70	3.42	3.50	3.38	3.43
80	9.36	9.40	9.45	9.40

ΔH^*, 22.2±1.0 kcal mol^{-1}. ΔS^*, −9.2 e.u.

a) From k_{obsd} *vs.* T_G plot at fixed value of T_G/T_A. b) From intercept of k_{obsd} *vs.* T_A plot at fixed value of T_G. c) From slope of k_{obsd} *vs.* T_A plot at fixed value of T_G.

Table 2. Activation parameters for the reactions of $M(NH_3)_5OH_2^{3+}$ ions ($M = Co$ or Rh)

System	ΔH^* kcal mol^{-1}	ΔS^* e.u.	Ref.
$Co(NH_3)_5OH_2^{3+}/O^{18}H_2$	26.6±0.3	6.7	1
$Co(NH_3)_5OH_2^{3+}$/glyH	27.6	5.2	11
	29.0	—	12
$Rh(NH_3)_5OH_2^{3+}/O^{18}H_2$	23.9±0.3	−3.0	2
$Rh(NH_3)_5OH_2^{3+}$/glyH	22.2±1.0	−9.2	Present work

$$k_{obsd} = kT_G - kT_AT_GK_H/(1+T_GK_H) \quad (7)$$

where $k = k' \cdot K_{o.s.}$ and K_H = equilibrium constant for the protonation of glycine (Eq. 1). Under the experimental conditions the value[10] of K_H is *ca.* 200 and hence $T_GK_H \gg 1$. Consequently Eq. 7 may be written as

$$k_{obsd} \approx k(T_G - T_A) \quad (8)$$

$$\approx k(1 - T_A/T_G)T_G. \quad (9)$$

The observed dependence of rate on T_A and T_G mentioned above are in conformity with the Eqs. 8 and 9 respectively. The value of k for any particular temperature could be evaluated independently from (i) the slope of k_{obsd} *vs.* T_G plot (Fig. 2) and also from (ii) the slope and intersept of k_{obsd} *vs.* T_A plot (Fig. 3). The values thus obtained are in good agreement with each other and are listed in Table 1. In case of anation of amino acid complex, $K_{o.s.}$ represents the outer sphere complex formation constant between $[Rh(NH_3)_5OH_2]^{3+}$ and the amino acid zwitter ion. Although the net charge of amino acid is zero, the zwitter ion has a separated negative charge on the carboxylate part and can undergo ion pair formation with multivalent cation. Since the net charge of glycine zwitter ion is zero, the $K_{o.s.}$ value should be smaller than those for anionic ligands. The influence of ionic strength on the anation reaction has been studied and the value of rate constant at fixed T_G/T_A has been found to be almost independent of the variation of ionic strength from $\mu = 0.5$ to 2.0 M of the medium. This lack of dependence of rate on ionic strength clearly excludes the participation of either G^- or GH_2^+ ion as a reactive species in the anation process. Hence, the overall reaction is best accounted for as an ion pair equilibrium followed by the slow interchange of the bound water and the entering ligand in the ion pair. The ΔH^* and ΔS^* values for the reactions were evaluated in the usual way by making use of Eyring equation from the k values at different temperatures (Table 1). The activation parameters for the water exchange and formation of glycine complex of similar octahedral cobalt(III) and rhodium(III) complexes are collected in Table 2 for the sake of comparison. A perusal of the results reveals that ΔH^* values for the water exchange[2] and for the present system of rhodium(III) complex are fairly close and much smaller than those of the corresponding cobalt(III) systems.[1,11,12] On the basis of the values of the activation parameters, the water exchange of $[Co(NH_3)_5OH_2]^{3+}$ and replacement of aqua ligand by glycine have been proposed to take place by dissociative mechanism. However, if the same type of mechanism is operative for the present system, owing to the greater loss of crystal field energy one would expect a higher enthalpy of activation for the rhodium(III) complex compared to analogous and isoelectronic (d^6) cobalt(III) substrates. Thus the experimental results cannot be explained by above mechanism, but suggest significant bond formation by the reagent in the transition state in the transformation of the outer sphere associated species. Moreover, a decrease of ΔS^* towards a negative value, going from cobalt(III) to rhodium(III) system is also in keeping with a mechanism involving a more pronounced participation of the incoming ligand in the transition state for the latter. Hence, on the basis of ΔH^* and ΔS^* values it may be concluded that the transformation of outer sphere complex into the product occurs by a sort of associative process in which the bond making and bond breaking in the transition state proceed synchronously.

The authors thank Professor K. Saito of Tohoku University, Japan, for the sample of $RhCl_3 \cdot 3H_2O$ used in the preparation of the title compounds. Helpful discussions with Professor D. Banerjea are gratefully acknowledged.

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