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Kinetics of the Aquation of Pentammine Amino Acid Cobalt(III) Complexes

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The rate of aquation of pentamminecobalt(III) complexes of the general formula $[Co(NH_3)_5amH]^{3+}$ (amH stands for an amino acid molecule with proton on the nitrogen atom), containing unidentate glycine, β-alanine, sarcosine and betaine, has been measured at 55°C, and ionic strength 0.1 and 1.0 in the acid concentration range up to 0.5 M. The kinetic term is expressed by

$$\text{Rate} = [\text{complex}](k_{H_2O}+k_{H^+}[H^+])$$

The k_{H_2O} and k_{H^+} values for glycine, β-alanine, sarcosine and betaine complex are respectively as follows (at $\mu=1.0$): k_{H_2O}, 0.40×10^{-6}, $\lesssim0.2\times10^{-6}$, 0.25×10^{-6}, and 0.44×10^{-6} sec^{-1}; k_{H^+}, 2.0×10^{-6}, 26×10^{-6}, 1.8×10^{-5}, and 1.0×10^{-6} M^{-1} sec^{-1}. The k_{H^+} values increase with increase in pK_a values of the amino acids, but are smaller than those for the aquation of carboxylatopentamminecobalt(III) complexes. This difference seems to be due to the electrostatic shielding of the carboxylate group by the protonated amino group.

An amino acid usually coordinates to a metal with its amino and carboxylate group to form a chelate ring. Recently, complexes were also prepared in which the amino acid coordinates as a unidentate ligand only with its carboxylate end, to form pentamminecobalt(III) complex.[1,2] Such a complex is similar to a carboxylatopentamminecobalt(III) complex, in the context that the ligands coordinate to the cobalt(III) ion with the carboxylate end. The reaction kinetics of acid hydrolysis of carboxylatopentamminecobalt(III) complexes was studied by Monacelli, Basolo and Pearson and the mechanism disucssed with special reference to the acid catalysis.[3] It seems interesting to carry out similar kinetic studies with pentammine amino acid cobalt(III) complexes, in which the protonated amino group can be linked with the carboxylate *via* hydrogen bonding. We have measured the rate of acid hydrolysis of the following complexes in aqueous solution,

$$[Co(NH_3)_5amH]^{3+} + H_2O \rightarrow [Co(NH_3)_5H_2O]^{3+} + amH \quad (1)$$

where "am" expresses amino acid anion, and compared the results with those of carboxylatopentammine complexes.

Experimental

Materials. Three complexes of the general formula $[Co(NH_3)_5amH](ClO_4)_3$ were prepared with glycine, β-alanine and betaine as described in the literature[1] and identified by elemental analyses of carbon, hydrogen and nitrogen, and absorption spectra. The sarcosine complex, a new compound, was also prepared by a similar method.

Found: C, 6.97; H, 4.72; N, 15.42; H_2O, 3.46%. Calcd for $[Co(NH_3)_5OOCCH_2NH_2(CH_3)](ClO_4)_3\cdot H_2O$: C, 6.56; H, 4.40; N, 15.32; H_2O, 3.28%.

The ionic strength was adjusted with sodium perchlorate, which was prepared from sodium carbonate and perchloric acid of guaranteed grade. Other reagents were all of guaranteed grade and used without further purification.

Experimental Procedure. A weighed amount of the complex ($\simeq10^{-4}$ mol) was added into an aqueous solution (100 ml) of a given ionic strength (0.1 or 1.0) and acid concentration (0.01—0.5 M) at a given temperature. The complex dissolved rapidly. Aliquots were withdrawn at appropriate intervals, cooled and the absorbances measured, or the amount of liberated amino acid determined with ninhydrin.

Spectrophotometric Method. The progress of reaction was best chased by measuring the change in extinction at 275 mμ, regardless of the kind of coordinated amino acid. The values of ε_{275} for glycine, sarcosine, betaine, β-alanine and aquo complex are 190, 206, 255, 400 and 3.1, respectively. The withdrawn aliquot was placed in a 10 mm quartz cell and the extinction measured at room temperature with a HITACHI EPU-IIA spectrophotometer. The reaction rate was slow enough, so that neither the time taken for the measurement nor the temperature change during the measurement does not affect the result. The pseudo first order rate constant k_{obs} was obtained by plotting

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$\log(\varepsilon-\varepsilon_a)$ *vs.* t, where ε is the apparent molar extinction coefficient of reaction mixture at time t and ε_a that of the aquopentammine complex.

Ninhydrin Method. This method was used only for the glycine complex. Free glycine should be separated from the aquopentammine and the glcyinepentammine complex. A 5 m*l* portion of the reaction mixture was passed through a column (10 mm in diameter, 10 cm in length) of the cation exchanger Amberlite CG-50 (Type 1, H-form) and the column washed with a citrate buffer of pH 5 (total effluent 50 m*l*). The complexes were completely captured by the resin, whereas the free amino acid was quantitatively recovered in the effluent and determined spectrophotometrically at 565 mμ by the Yemm-Cocking's method with ninhydrin.[4] The rate constant k_{obs} is given by plotting $\log(a-x)$ *vs.* t, where a is the initial concentration of the complex and x the concentration of isolated glycine.

Results

The plots of $\log(\varepsilon-\varepsilon_a)$ *vs.* t and $\log(a-x)$ *vs.* t were all linear under the experimental conditions and the rate constant was independent of the initial concentration of the complex as exemplified in Table 1. Figure 1 shows the relationship between the rate constant k_{obs} and the hydrogen ion concentration for the glycine, the sarcosine, the betaine and the β-alanine complex in aqueous solutions of ionic strength 1.0, and Fig. 2 those for the glycine and the β-alanine complex in solutions of ionic strength 0.1. The results are those obtained by the spectrophotometric method unless otherwise stated. All of these plots are regarded to be linear. Therefore, the observed pseudo first order rate constant k_{obs} can be expressed by Eq. (2), as a linear function of the hydrogen ion concentration.

$$k_{obs} = k_{H_2O} + k_{H^+}[H^+] \quad (2)$$

The uncatalysed rate constant k_{H_2O} and the acid catalysed rate constant k_{H^+} are calculated from the diagrams and shown in Table 2, together with the pK_a values of the amino acids.

It has been known that some pentamminecobalt(III) complexes tend to liberate ammonia as shown in Eqs. (3) and (4). (X, univalent anion)

$$[CoX(NH_3)_5]^{2+} + H_2O \rightarrow [CoX(NH_3)_4(H_2O)]^{2+} + NH_3 \quad (3)$$

$$[Co(NH_3)_5H_2O]^{3+} + H_2O \rightarrow [Co(NH_3)_4(H_2O)_2]^{3+} + NH_3 \quad (4)$$

The products can further undergo hydrolysis to liberate more ammonia.[5,6] Whenever a spectrophotometric method is used for a slow reaction, contribution of such side reactions should be taken into consideration.

Ammonium ions pass through the exchanger

TABLE 1. THE RATE CONSTANT AT VARYING INITIAL CONCENTRATIONS OF THE GLYCINE COMPLEX
(55°C, μ=0.1, by the ninhydrin method)

a mM	$k_{obs}\times10^6$ sec^{-1}
1.0	0.74
2.0	0.73
3.0	0.73

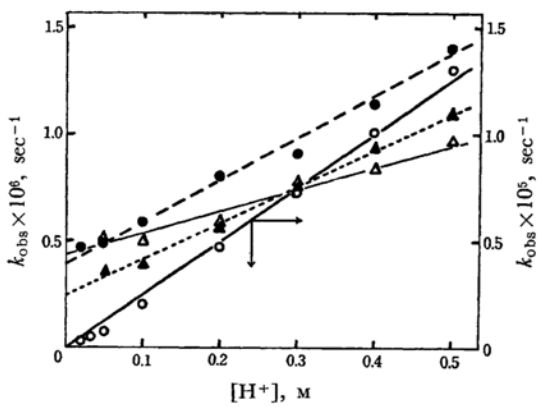

Fig. 1. Relationship between the observed rate constant k_{obs} and the hydrogen ion concentration, at 55°C and μ=1.0.
--●-- $[Co(NH_3)_5OOCCH_2NH_3]^{3+}$ (glycine)
—○— $[Co(NH_3)_5OOCCH_2CH_2NH_3]^{3+}$ (β-alanine)[a]
---▲--- $[Co(NH_3)_5OOCCH_2NH_2(CH_3)]^{3+}$ (sarcosine)
—△— $[Co(NH_3)_5OOCCH_2N(CH_3)_3]^{3+}$ (betaine)
a) The scale of the ordinate for this complex is 10-fold of that for other complexes.

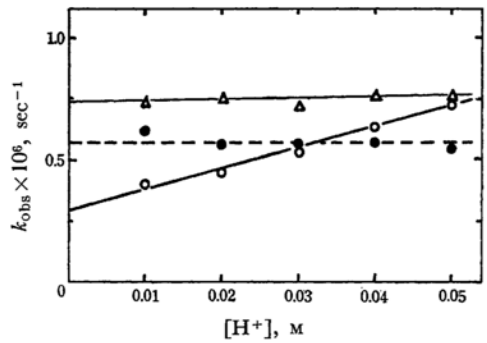

Fig. 2. Relationship between the observed rate constant k_{obs} and the hydrogen ion concentration, at 55°C and μ=0.1.
—△— $[Co(NH_3)_5OOCCH_2NH_3]^{3+}$ (glycine)[a]
--●-- $[Co(NH_3)_5OOCCH_2NH_3]^{3+}$ (glycine)
—○— $[Co(NH_3)_5OOCCH_2CH_2NH_3]^{3+}$ (β-alanine)
a) By the ninhydrin method.

4) E. W. Yemm and E. C. Cocking, *Analyst*, **80**, 209 (1955).

5) F. Basolo, J. G. Bergmann and R. G. Pearson, *J. Phys. Chem.*, **56**, 22 (1952).

6) A. B. Lamb and J. W. Marden, *J. Am. Chem. Soc.*, **33**, 1873 (1911).

TABLE 2. RATE CONSTANTS OF AQUATION OF $[Co(NH_3)_5amH]^{3+}$ AND $[Co(NH_3)_5L]^{2+}$, AT 55°C AND $\mu=0.1$ AND 1.0

Ligand	pK_a [a]	μ	$k_{H_2O}\times10^6$ sec^{-1}	$k_{H^+}\times10^6$ $M^{-1}\,sec^{-1}$
Glycine ($H_3{}^+NCH_2COO^-$)	2.35	0.1	0.73[b]	$\lesssim1$[b]
		0.1	0.57	$\lesssim1$
		0.1	1.8[e]	$\lesssim1$[e]
		0.1	7.6[f]	$\lesssim1$[f]
β-Alanine ($H_3{}^+NCH_2CH_2COO^-$)	3·55	0.1	0.30	8.6
Acetate (CH_3COO^-)[c]	4.76	0.1	1.4	170
Trifluoroacetate (CF_3COO^-)[c]	0.3	0.1	~6[d]	~1[d]
Glycine ($H_3{}^+NCH_2COO^-$)	2.35	1.0	0.40	2.0
		1.0	1.1[e]	7.4[e]
		1.0	1.9[f]	27[f]
Sarcosine ($(CH_3)^+NH_2CH_2COO^-$)	2.35	1.0	0.25	1.8
Betaine ($(CH_3)_3{}^+NCH_2COO^-$)	1.84	1.0	0.44	1.0
β-Alanine ($H_3{}^+NCH_2CH_2COO^-$)	3.55	1.0	$\lesssim$0.2	26

a) Values for the acids at 25°C and $\mu=0$.
b) By the ninhydrin method.
c) Results from Ref. 3.
d) Extrapolated values from the data at 60, 70 and 79°C (Ref. 3).
e) Values at 65°C.
f) Values at 75°C.

column under the given condition and react with ninhydrin to give a similar coloration to that with glycine. Hence the ninhydrin method can easily overestimate the amount of glycine to give apparently greater rate constants. The presence of ammonium ions was confirmed with Nessler's reagent in the reaction mixtures kept at 55°C for more than 50 hr. The rate constant obtained by the ninhydrin method (k_{H_2O}, 0.73×10^{-6} sec^{-1} at 55°C, $\mu=0.1$) is slightly larger than that by the spectrophotometric method (k_{H_2O}, 0.57×10^{-6} sec^{-1}). However the difference is small especially when the rate is calculated from the kinetic data obtained at earlier stages of reaction, as in most cases by the spectrophotometric method. Hence it is quite certain that this method really gives the rate of reaction (1).

TABLE 3. THE ACTIVATION PARAMETERS FOR THE UNCATALYSED AQUATION OF PENTAMMINECOBALT(III) COMPLEXES, AT $\mu=0.1$

Ligand	$\Delta H^{\neq}$ kcal mol^{-1}	$\Delta S^{\neq}$ cal $mol^{-1}\,deg^{-1}$	Ref.
Glycine	29	+1	This work
Acetate	25	−8	3
Trifluoroacetate	26	−2	3

TABLE 4. THE ACTIVATION PARAMETERS FOR AQUATION OF THE GLYCINE COMPLEX, AT $\mu=1.0$

	$\Delta H^{\neq}$ kcal mol^{-1}	$\Delta S^{\neq}$ cal $mol^{-1}\,deg^{-1}$
k_{H_2O}	22	−20
k_{H^+}	29	+ 3

Activation parameters for the glycine complex were obtained by the measurements at 55, 65, and 75°C and ionic strength 0.1 and 1.0. The results are listed in Tables 3 and 4 together with those of related compounds.

Discussion

Equation (2) suggests that two reaction paths are involved in these aquations as exemplified in Eqs. (5) to (7).

$$[(NH_3)_5Co\text{-}O\overset{O}{\overset{\|}{C}}CH_2NH_3]^{3+} + H_2O \xrightarrow{k_{H_2O}} [(NH_3)_5CoH_2O]^{3+} + {}^-OOCCH_2NH_3{}^+ \quad (5)$$

$$[(NH_3)_5Co\text{-}O\overset{O}{\overset{\|}{C}}CH_2NH_3]^{3+} + H^+ \overset{K}{\rightleftharpoons} [(NH_3)_5Co\text{-}O\overset{H^+O}{\overset{\|}{C}}CH_2NH_3]^{3+} \quad (6)$$

$$[(NH_3)_5Co\text{-}O\overset{H^+O}{\overset{\|}{C}}CH_2NH_3]^{3+} + H_2O \xrightarrow{k'} [(NH_3)_5CoH_2O]^{3+} + {}^-OOCCH_2NH_3{}^+ + H^+ \quad (7)$$

The reaction (5) is the path independent of the hydrogen ion concentration and its rate constant is k_{H_2O}. The reactions (6) and (7) correspond to the path catalysed by acids and its rate constant k_{H^+} is expressed by Eq. (8).

$$k_{H^+} = k'K \quad (8)$$

The uncatalysed rate constants (k_{H_2O}) tend to decrease slightly with the increase in ionic strength (Table 2), whereas the acid catalysed rate constants (k_{H^+}) are significantly greater in solutions of $\mu=1.0$ than in $\mu=0.1$. The equilibrium constant K between cations such as that expressed by Eq. (6), generally increases with increase in ionic strength. Therefore, the increase in k_{H^+} values with the increase in ionic strength could be ascribed to the increase in K.

Basolo *et al.* reported that the aquations of carboxylatopentamminecobalt(III) complexes, Eq. (9), proceed by similar mechanisms to Eqs. (5) to (7).[3]

$$[Co(NH_3)_5OOCR]^{2+} + H_2O \rightarrow [Co(NH_3)_5H_2O]^{3+} + {}^-OOCR \qquad (9)$$

The rate constants, k_{H_2O} and k_{H^+}, for the acetato and the trifluoroacetato complex are also shown in Table 2 for comparison. The values for the trifluoroacetato complex were obtained by extrapolating their results to 55°C. The aquation of the amino acid complexes is considerably slower than that of the carboxylato complexes. The k_{H_2O} values in solutions of ionic strength 0.1 decrease in the order, trifluoroacetato, acetato, glycine and β-alanine complex. Basolo *et al.* stated that the k_{H_2O} values of carboxylato complexes tend to decrease with increase in pK_a values of the acids. However, the results in Table 2 do not indicate that such a relation fits the amino acid complexes. On the other hand, the k_{H^+} values for the carboxylato and the amino acid complexes increase with increase in pK_a values within each of these two groups of acid. The pK_a values affect the equilibrium constant K of Eq. (6), and hence the k_{H^+} values.

The k_{H^+} values of the amino acid complexes are much smaller than expected from the relationship between pK_a values and k_{H^+} values for carboxylato complexes. Concerning the glycine and the sarcosine complex, the hydrogen bonding between carboxylate and ammonium group could impede the protonation given by Eq. (6) to decrease the k_{H^+} values. The k_{H^+} value of the betaine complex, which cannot form such a hydrogen bond, is, however, still smaller than those of the two amino acid complexes. Therefore the retardation of protonation should rather be ascribed to an electrostatic effect due to the ammonium group present in the neighborhood of the carboxylate group. Thus the carboxylate end is "shielded" from the approach of a hydrogen ion by both the central cation and the ammonium group, to give a smaller K value.

A similar electrostatic effect is also seen in the hydrolysis of organic esters. Walker and Owens measured the rate of acid-catalysed hydrolysis of chloride of cyclohexyl betainate and found that the rate is *ca.* 1/80 of that of cyclohexyl acetate.[7] The retardation is understood as due to the influence of an electron-attracting group (*e.g.*, $-N^+(CH_3)_3$), rather than to that of steric hindrance or salt effect.[8]

The β-alanine complex has a considerably greater k_{H^+} value than α-amino acid complexes. Its ammonium group would shield the coordinated carboxylate group to a less extent than an α-amino acid does. Such a small influence of $-NH_3^+$ group upon the carboxylate seems to be also reflected in the large pK_a value of β-alanine.

The entropy of activation of the glycine complex is more positive than that of the acetato complex (Table 3). Such a difference might suggest that the local orientation of solvent water around the leaving group at the activated state would be less for the glycine complex, in which the negative charge of the carboxylate group is partly compensated by the influence of the ammonium group.

Bunton and Llewellyn disclosed that the aquation of acetatopentamminecobalt(III) complex takes place through the break of Co–O bond on the basis of a tracer study with oxygen-18.[9] On the other hand, the similar aquation of carbonatopentamminecobalt(III) complex proceeds *via* the cleavage of C–O bond,[10] and has an enthalpy of activation 17.1 kcal mol^{-1}.[11] The enthalpy of activation of the glycine complex is nearer to that of the acetato complex than to that of the carbonato complex, so that the break of Co–O bond appears to be more plausible on the aquation of the glycine complex.

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