BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 120—124 (1971)

Kinetics and Mechanism of Aquation and Anation of Some Amino Acid Pentamminecobalt(III) Complexes in Acid Aqueous Solutions

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(Received August 15, 1970)

Kinetics of aquation has been studied with pentamminecobalt(III) complexes containing aliphatic amino acids (γ-aminobutyric acid, ε-aminocaproic acid, α-amino-isobutyric acid, ornithine, and proline), aromatic acids (benzoate, anthranilic, and *p*-aminobenzoic acid), and α-substituted acetates (monochloroacetate and glycolate). Anation rate constants were obtained for glycine, β-alanine, and ε-aminocaproic acid, and equilibrium constants between $[CoH_2O(NH_3)_5]^{3+}$ and $[Co(NH_3)_5amH]^{3+}$ (amH=amino acid), K_{eq} were calculated. The free energy plot $\log k_{aq}$ *vs.* $\log K_{eq}$ gave a straight line with a gradient 0.6. This value has been discussed in terms of two possible mechanisms. The dependence of acid catalysed aquation rate constant, $k_H{}^+$ on pK_a of carboxylate group of the amino acid is written as $\log k_H{}^+ = pK_a + \text{const.}$, while that for α-substituted acetates $\log k_H{}^+ = 0.5\, pK_a + \text{const.}$ Such a difference in the slope is interpreted as due to the electrostatic influence of $-NH_3{}^+$ group of coordinated amino acid.

In our previous paper we reported on the kinetics of aquation of pentammine-amino acid cobalt(III) complexes, in which glycine, β-alanine, sarcosine, and betaine are combined with the cobalt(III) ion as unidentate through carboxylate oxygen.[2] The aquation had different characteristics from those of other carboxylate complexes.[3] We have now extended the study to some other pentammine cobalt(III) complexes containing various kinds of amino acid and α-substituted acetates, and the effect of positive charge of the ammonium group of coordinated amino acid upon aquation rate as well as the free energy relationship[4] has been discussed.

Aquation of amino acid pentamminecobalt(III) cations in an acid solution proceeds as follows:

$$[Co(NH_3)_5amH]^{3+} + H_2O \xrightarrow{k} [CoH_2O(NH_3)_5]^{3+} + amH \qquad (1)$$

where amH denotes the amino acid. The pseudo first order rate constant k was obtained according to the method given in Experimental. When the values k are plotted against the concentration of perchloric acid, straight lines are obtained as exemplified in Fig. 1, the kinetics being expressed by

$$k = k_{H_2O} + k_{H^+}[H^+] \qquad (2)$$

The intercept and the gradient correspond to k_{H_2O} and k_{H^+} respectively. The values are listed in Table 1.

Relationship between pK_a and k_{H^+}. The acid catalysed aquation of carboxylato and amino acid complexes is regarded to take place through the following two steps:

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[2] K. Ogino, T. Murakami, and K. Saito, This Bulletin, **41**, 1615 (1968).

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

[4] C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965).

Table 1. Rate constant of acid-catalysed and uncatalysed path of the aquation of amino acid and α-substituted acetato pentamminecobalt(III) complexes (55°C)

Amino acid (other acid anion)	λ mμ	μ	k_{H_2O} 10^{-6}sec^{-1}	k_{H^+} 10^{-6}M^{-1}sec^{-1}	pK_a (25°C)
γ-Aminobutyric acid	285	0.1	0.2	32	4.03
		1.0	3.0	76	
ε-Aminocaproic acid	290	0.1	0.2	66	4.43
		1.0	4.0	140	
Proline	275	1.0	0.28	1.5	1.95
α-Amino-iso-butyric acid	280	1.0	0.18	1.3	2.36
Ornithine	275	0.1	0.5	≤ 1	1.94
		1.0	0.16	1.1	
Anthranilic acid	502	1.0	0.05	3.0	2.05
p-Aminobenzoic acid	502	1.0	1.4	15	2.38
Benzoate	315	1.0	1.0	28	4.20
Monochloroacetate	284	0.1	0.37	19	2.86
(65°C)			1.8	32	
(75°C)			6.2	130	
Glycolate	299	0.1	0.58	45	3.83
(65°C)			1.6	150	
(75°C)			8.0	440	

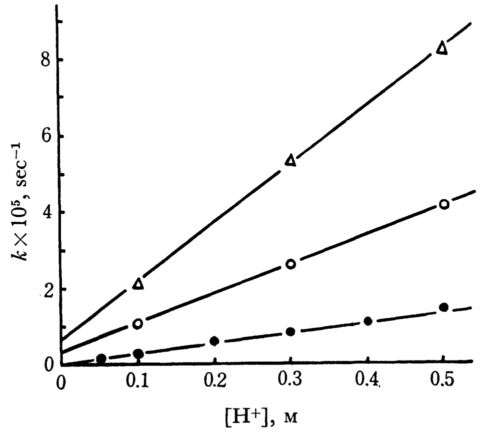
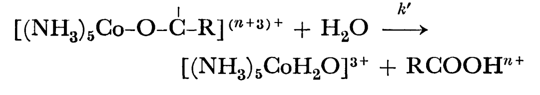
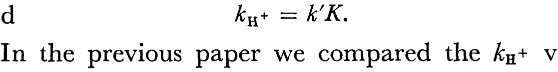


Fig. 1. Relationship between k_{obs} of aquation reactions and the hydrogen ion concentration. (55°C, $\mu=1.0$)
—●— [Co $(NH_3)_5$ β-alaH]$^{3+}$ [2] —○— [Co $(NH_3)_5$ γ-ambutH]$^{3+}$ —△— [Co$(NH_3)_5$ ε-amcapH]$^{3+}$



$$[(NH_3)_5Co\text{-}O\text{-}\overset{\overset{\large O}{\|}}{C}\text{-}R]^{(n+2)+} + H^+ \overset{K}{\rightleftarrows} [(NH_3)_5Co\text{-}O\text{-}\overset{\overset{\large OH}{|}}{C}\text{-}R]^{(3+n)+} \qquad (3)$$



$$[(NH_3)_5Co\text{-}O\text{-}\overset{\overset{\large OH}{|}}{C}\text{-}R]^{(n+3)+} + H_2O \xrightarrow{k'} [(NH_3)_5CoH_2O]^{3+} + RCOOH^{n+} \qquad (4)$$

and $$k_{H^+} = k'K. \qquad (5)$$

In the previous paper we compared the k_{H^+} values of pentamminecobalt(III) complexes of glycine, sarcosine, and betaine and ascribed the small k_{H^+} value to the difficulty with which the protonated species are formed according to Eq. (3). Such a difficulty was considered to come from electrostatic effect due to ammonium group $-NH_xR_{3-x}{}^+$ rather than the hydrogen bonding between ammonium and carboxylate groups coördinated to cobalt(III).[2]

In Fig. 2, the log k_{H^+} values are plotted against

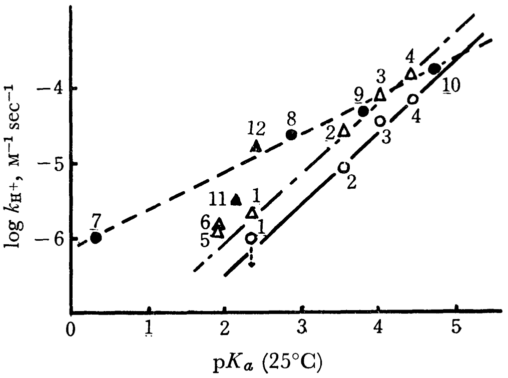


Fig. 2. Relationship between k_{H^+} of aquation reactions and pK_a of the ligands.
—○— (μ=0.1) and —△— (μ=1.0) [Co$(NH_3)_5$amH]$^{3+}$ 1. glycine,* 2. β-alanine,* 3. γ-aminobutyric acid, 4. ε-aminocaproic acid, 5. ornithine, 6. proline.
---●--- (μ=0.1)[Co$(NH_3)_5$(RCOO)]$^{2+}$ 7. trifluoroacetate,** 8. monochloroacetate, 9. glycolate, 10. acetate.**
—▲— (μ=1.0) [Co$(NH_3)_5$ aromatic amH]$^{3+}$ 11. anthranilic acid, 12. p-aminobenzoic acid.
* from Ref. 2. ** Ref. 3, values extrapolated to 55°C on the basis of $\Delta H^{\neq}$ values.

pK_a values of the acids. The diagram consists of two straight lines at a given ionic strength. Complexes of amino acids give one line with a gradient almost unity, and those of other α-substituted acetate anions, one with a gradient *ca.* 0.5. Aromatic amino acid complexes and benzoato complex fall on neither line. Complexes of glycolate and chloroacetate give plots on the line (broken line) together with acetato- and trifluoroacetato-complexes. The influence of substituting hydroxyl group and halogen atom seems to be appropriately reflected in pK_a values, and the kind of substituting group or atom give no particular influence upon k_{H^+} values.

Whenever the pK_a values are the same, the amino acid complexes give smaller k_{H^+} values than the substituted acetato complexes. The solid line in Fig. 2

indicates that the deviation from the broken line decreases with increase in carbon chain length between the $-NH_3^+$ and $-COO^-$ group of the amino acid, and is very small when the ammonium group is on the ε-carbon atom. It is noticeable that the complex of ornithine, which has two $-NH_3^+$ groups on α- and δ-carbon atom gives the plot on the same line as those of other amino acid complexes. The smaller k_{H^+} values of amino acid complexes must be due to the smaller tendency of forming protonated intermediate given by Eq. (3). Such a trend is brought about by the presence of $-NH_3^+$ group near the coordinated carboxylate. As the carbon chain length between $-NH_3^+$ and $-COO^-$ increases, the probability of such an approach would decrease because the freedom of rotation around the C–C axes increases. Our previous consideration that the electrostatic effect of $-NH_3^+$ group is reflected in the equilibrium constant K of Eq. (5), which is responsible in determining the k_{H^+} values, seems thus adequately reinforced.

There is a significant difference between k_{H^+} values of anthranilic and *p*-aminobenzoic acid complexes. The former gives a plot near the straight line for ω-amino acid complexes. Its $-NH_3^+$ group seems to be capable of giving a similar effect to that in ω-amino acids, because it is situated near the coordinated carboxylate. On the other hand, such an influence seems very unlikely for *p*-aminobenzoic acid complex.

The k_{H_2O} *Values.* Monacelli, Basolo, and Pearson reported that an antiparallel relationship is seen between the k_{H_2O} of carboxylatopentamminecobalt(III) complexes and the pK_a of the carboxylic acids.[3] Their results are well understood whenever the aquation takes place *via* S_N1(lim) mechanism, *i. e.* the ease with which the carboxylato-cobalt bond breaks depends fully on the bond strength predicted by the pK_a of the given acid. As shown in Fig. 3B, the k_{H_2O} values of ω-amino acid pentamminecobalt(III) ions do not seem to show significant difference from one another at an ionic strength 0.1. Neither do the α-substituted acetato complexes. At an ionic strength 1.0 (Fig. 3A), the k_{H_2O} seems to increase with rise of pK_a. Since the k_{H_2O} values are obtained by extrapolation, they can involve bigger experimental errors and may not be suitable for detailed discussion. However, the anthranilic acid- and the *p*-aminobenzoic acid complex give remarkably different values from each other, and a steric factor could be involved.

Relationship with the Equilibrium Quotient. The anation reaction of aquopentamminecobalt(III) complexes with amino acids (amH) is written as

$$[CoH_2O(NH_3)_5]^{3+} + amH \rightleftarrows [Co(NH_3)_5amH]^{3+} + H_2O \qquad (6)$$

and the rate constant k_{obs} is expressed by the following equation (see Experimental).

$$k_{obs} = k_{aq} + k_{an}[amH] \qquad (7)$$

The k_{an} is obtained from the gradient of linear plot of k_{obs} *vs.* [amH], which stands for the concentration of amino acid zwitter ion (see Fig. 4). The equilibrium quotient K_{eq} is expressed by

$$K_{eq} = k_{aq}/k_{an} \qquad (8)$$

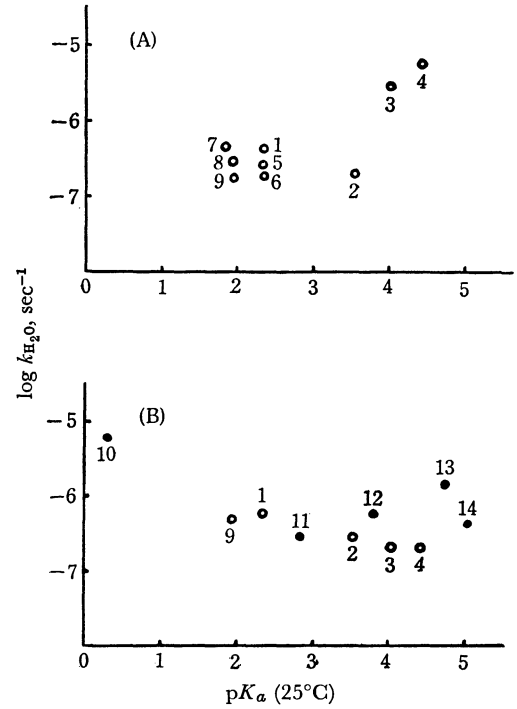


Fig. 3. Relationship between k_{H_2O} of aquation reactions and pK_a of the ligands. (55°C, (A), μ=1.0; (B), μ=0.1) ○ $[Co(NH_3)_5\ amH]^{3+}$: 1. glycine,* 2. β-alanine,* 3. γ-aminobutyric acid, 4. ε-aminocaproic acid, 5. sarcosine,* 6. α-amino-iso-butyric acid, 7. betaine,* 8. proline, 9. ornithine. ● $[Co(NH_3)_5(RCOO)]^{2+}$: 10. trifluoroacetate,** 11. monochloroacetate, 12. glycolate, 13. acetate,** 14. trimethylacetate.** * from Ref. 2. ** Ref. 3, values extrapolated to 55°C.

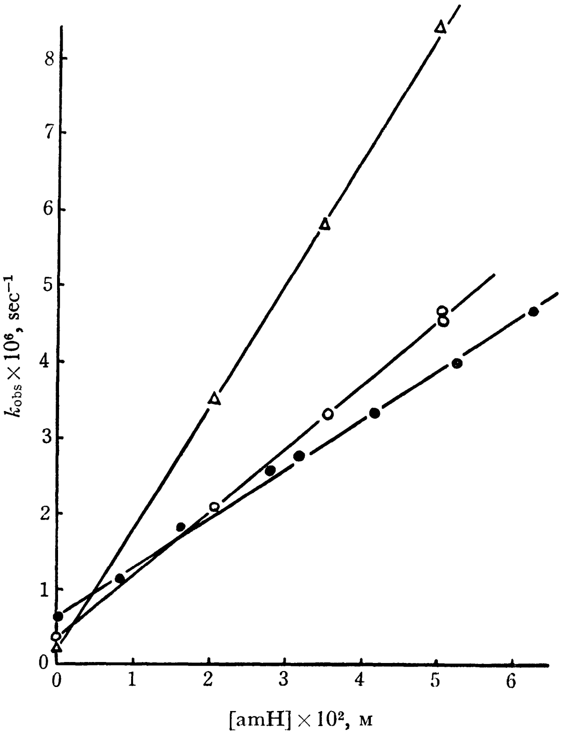


Fig. 4. Relationship between the k_{obs} of anation reactions and the concentration of amino acid zwitter ion. (55°C, μ=0.1) —●— $[Co(NH_3)_5\ glyH]^{3+}$ —○— $[Co(NH_3)_5\ \beta\text{-alaH}]^{3+}$ —△— $[Co(NH_3)_5\ \varepsilon\text{-aminocapH}]^{3+}$

In Table 2 are given k_{an} and K_{eq} values of some ω-amino acid pentamminecobalt(III) complexes.

Langford[4] and Haim[5] examined the linear free energy relationship[6] between the equilibrium quotient and the rate constant for aquation reactions of various acidopentamminecobalt(III) complexes and obtained a gradient unity on their log-log plot,

$$\Delta \ln k_{aq} = \alpha \Delta \ln K_{eq} \qquad (9)$$

Langford claimed that this value suggests a similarity between the transition state and the product, and that the role of the acido anion ligand in the transition state is very similar to that in the product, *i. e.* the solvated anion.

TABLE 2. RATE CONSTANTS OF ANATION AND EQUILIBRIUM QUOTIENTS OF AQUATION-ANATION REACTIONS OF SOME $[Co(NH_3)_5amH]^{3+}$ COMPLEX IONS

Ligand	k_{an} $10^{-5}M^{-1}sec^{-1}$	k_{aq} $10^{-6}sec^{-1}$	K_{eq} $10^{-3}M$
Glycine	7±0.5[a]	0.57[b]	8.1[c]
(65°C)	25±1	1.8[b]	7.2
(75°C)	92±3	7.6[b]	8.3
β-Alanine	8.5	0.3[b]	3.5
ε-Aminocaproic acid	16	0.2	1.3

(55°C unless otherwise stated, $\mu=0.1$)

a) The $\Delta H^{\ddagger}$ is 29 kcal/mol. b) from Ref. 2. c) $\Delta H^{\circ} \fallingdotseq 0$

A similar plot of our results for ω-amino acid pentamminecobalt(III) complexes is shown in Fig. 5. Although the number of plots is only three, an apparent α value 0.6 is obtained. The difference between this value and that for acidopentamminecobalt(III) complexes[4,5] seems significant, although the experimental conditions are not the same (data compiled by Haim[5] are at 25°C, ionic strength variable; ours at 55°C, ionic strength 0.1). It appears as if the transition state in the aquation of $[Co(NH_3)_5amH]^{3+}$ is between the initial and the final state of the reaction. We are thus inclined to consider that some mechanism such as solvent-assisted dissociation mechanism[7] is involved in the k_{H_2O} path. This mechanism was also suggested by Lincoln and Stranks[8] for the aquation of $[Co(NH_3)_5H_3PO_4]^{3+}$ in perchloric acid of medium strength. They found a good correlation between the aquation rate and the activity of water.

Haim[5] discussed the relation between k_{aq} and K_{eq} and gave the equation

$$\log k_{aq} = \log k_x Q_0 - \log K_{eq} \qquad (10)$$

where Q_0 is the ion pair or outer sphere complex formation constant between $[CoH_2O(NH_3)_5]^{3+}$ and the incoming ligand, and k_x the inner sphere-outer sphere interchange velocity of the ion pair. He claimed that Q_0 is principally dependent on the charge of the complex and the incoming ligand, and applied this correlation to acidopentamminecobalt(III) complexes containing uni- and bivalent anions.

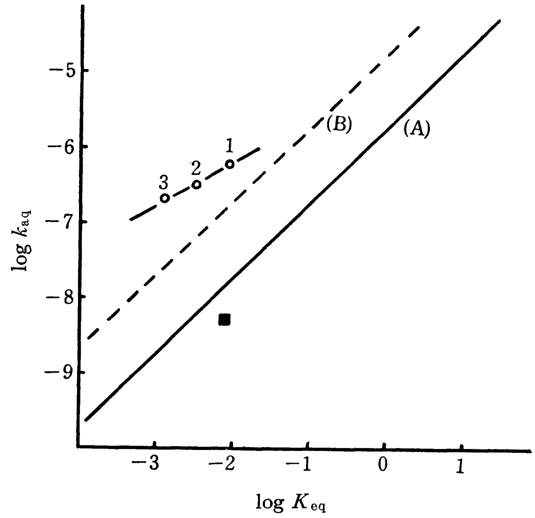


Fig. 5. Linear free energy relationship between the equilibrium quotient K_{eq} and the rate constant for aquation, k_{aq}.
—○— $[Co(NH_3)_5\ amH]^{3+}$ (55°C, $\mu=0.1$): 1. glycine, 2. β-alanine, 3. ε-aminocaproic acid.
■ for $[Co(NH_3)_5\ glyH]^{3+}$ extrapolated to 25°C on the basis of $\Delta H^{\ddagger}$ and ΔH° value in Table 2.
—— (A) $[Co(NH_3)_5\ X]^{2+}$ (X, univalent anions, 25°C[5])
------ (B) $[Co(NH_3)_5\ Y]^{+}$ (Y, bivalent anions, 25°C[5])

In the case of our amino acid complexes, Q_0 is the outer sphere complex formation constant between $[CoH_2O(NH_3)_5]^{3+}$ and the amino acid zwitter ion. Although the net charge of an amino acid is zero, the zwitter ion has a separated minus charge on the carboxylate part, and can undergo ion-pair formation with multivalent complex cation.[9] However, the Q_0 values for varying amino acids could be different, because the electrostatic effect of $-NH_3^+$ can differ according to the carbon chain length between $-NH_3^+$ and $-COO^-$ group. If Q_0 increased with increase in this carbon chain length, the gradient of our diagram could deviate from unity, even if the inner sphere-outer sphere interchange velocity of the ion pair k_x were the same as those of uni- and bivalent incoming ligand. Hence the smaller α value (0.6) of our diagram does not necessarily indicate the participation of solvent assisted dissociation. These two possible interpretations cannot be distinguished at the present stage.

The $\Delta H^{\ddagger}$ value for anation reaction to give $[Co(NH_3)_5glyH]^{3+}$ was obtained to be 29 kcal/mol (Table 2). It is near that for the water exchange of $[CoH_2O(NH_3)_5]^{3+}$ ions,[10] which should involve cobalt-oxygen bond rupture. We can relevantly presume that our reactions also involve cobalt-oxygen bond rupture and formation. The same presumption was made in our previous paper[2] on the basis of comparison among $\Delta H^{\ddagger}$ values of $[Co(NH_3)_5glyH]^{3+}$,[2] $[Co(NH_3)_5(CH_3$-

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[5] A. Haim, *Inorg. Chem.*, **9**, 426 (1970).

[6] J. E. Leffler and E. Grunwald, "Rates and Equilibrium of Organic Reactions," J. Wiley of Sons, New York (1963), p. 156.

[7] R. G. Pearson and R. D. Lanier, *J. Amer. Chem. Soc.*, **85**, 765 (1964).

[8] S. F. Lincoln and D. R. Stranks, *Austr. J. Chem.*, **21**, 67 (1968).

[9] When the plot of $[Co(NH_3)_5glyH]^{3+}$ (glyH=glycine zwitter ion) in Fig. 5 is shifted from 55°C to 25°C on the basis of $\Delta H^{\ddagger 2)}$ and ΔH° value (Table 2), the plot given by full square is obtained. Since the net charge of glycine zwitter ion is zero, the Q_0 value should be smaller than those for univalent anionic ligands.

[10] H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, **80**, 2642 (1958).

COO)]$^{2+}$,[11] and [Co(NH$_3$)$_5$(HCO$_3$)]$^{2+}$.[12,13] If a tracer study with ^{18}O were substantiated with our complexes, unambiguous conclusion could be obtained. Unfortunately, the oxygen exchange rate of free amino acid in water and the water exchange rate of [CoH$_2$O(NH$_3$)$_5$]$^{3+}$ are much greater than the aquation rate of [Co(NH$_3$)$_5$amH]$^{3+}$ ions in neutral and acid solutions and such a tracer study would not be very useful.

Experimental

Materials. Cobalt(III) pentammine complexes containing aliphatic amino acids were synthesized as perchlorate from [CoH$_2$O(NH$_3$)$_5$](ClO$_4$)$_3$ and the amino acids by the method of Fujita *et al.*[14] and identified by the analysis of carbon, hydrogen, and nitrogen, and visible and ultraviolet absorption spectra. Complexes containing aminobenzoic acids[15,16] and α-substituted carboxylates[2,17] were prepared by the methods given in literature. All other chemicals were of guaranteed grade and used without further purification.

Kinetic Runs. Aquation rate was measured spectrophotometrically at the given wavelengths (Table 1) as described previously.[2] Aromatic amino acids have marked absorptions in the ultraviolet region in the free state, and the reaction was followed at the *d–d* transition region.

The rate of anation given by Eq. (6) is expressed by the ordinary second order rate formula

$$\mathrm{d}x/\mathrm{d}t = k_{an}(a-x)(b-x) - k_{aq}x \qquad (11)$$

where x is the concentration of [Co(NH$_3$)$_5$amH]$^{3+}$ ion at time t, and a and b are the initial concentrations of [CoH$_2$O(NH$_3$)$_5$]$^{3+}$ and the amino acid in zwitter ion form, respectively. The last is known from the formal concentration and the acid dissociation constant under the given condition. Whenever b overwhelms a, Eq. (11) is integrated to give

$$\ln\,[(x_\infty - x)/x_\infty] = -(k_{aq} + bk_{an})t \qquad (12)$$

where the suffix ∞ denotes the equilibrated state. When the anation is measured by a spectrophotometric method, Eq. (12) is replaced by

$$\ln\,[(A_\infty - A_t)/(A_\infty - A_0)] = -(k_{aq} + bk_{an})t \qquad (13)$$

where A_0, A_t, and A_∞ are the extinctions of the reaction mixture at the initial state, time t and the final state, respectively. By plotting $\log(A_\infty - A_t)$ *vs.* t, the apparent rate constant k_{obs} given by Eq. (7) is obtained. The A_∞ value was not experimentally determined because the reaction was very slow. A tentative A_∞ was calculated on the basis of an assumed K_{eq},

$$K_{eq} = k_{aq}/k_{an} = (a - x_\infty)(b - x_\infty)/x_\infty \qquad (14)$$

and k_{obs} and k_{an} were obtained by means of Eqs. (13) and (7). The K_{eq} and A_∞ values were recalculated from this k_{an}. Such a stepwise approximation was repeated until a set of self-consistent k_{an} and K_{eq} was obtained.

Anation reactions were studied in weakly acid solutions (pH∼pK_a), where k_{H^+} path of aquation is negligible compared to $k_{\mathrm{H_2O}}$ path and k_{aq} can be approximated to be equal to $k_{\mathrm{H_2O}}$. The rate was followed at the same wavelength at which the aquation was studied.

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[11] F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 1241 (1962).

[12] T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, **90**, 6360 (1968).

[13] D. V. Francis and R. B. Jordan, *ibid.*, **89**, 5591 (1967).

[14] J. Fujita, T. Yasui, and Y. Shimura, This Bulletin, **38**, 654 (1965).

[15] E. S, Gould, *J. Amer. Chem. Soc.*, **87**, 4730 (1965).

[16] E. S. Gould and H. Taube, *ibid.*, **86**, 1318 (1964).

[17] R. D. Butler and H. Taube, *ibid.*, **87**, 5597 (1965).