November, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (11), 2935—2939 (1977) 2935

Ion-Pair Effect on the Rate of the Base Hydrolysis of the Pentaamminechlorocobalt(III) Complex

Masayasu Iida* and Hideo Yamatera

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

(Received May 16, 1977)

The rate of the base hydrolysis of pentaamminechlorocobalt(III) ions was measured in the presence of multivalent anions at a constant ionic strength. The results were analyzed in view of the S_N1 C.B. mechanism considering the formation of ion-pairs. The ion-pairing has the effect of suppressing the acid dissociation of the complex or the formation of its conjugate base, which acts as the intermediate of the reaction. This effect out-weighs the adverse effect of the probable acceleration of the rate-determining step of the base hydrolysis. The association constants obtained for $[CoCl(NH_3)_5]^{2+}\cdot SO_4^{2-}$ and $[CoCl(NH_3)_5]^{2+}\cdot P_3O_9^{3-}$ were 40±5, and 82±5, respectively ($I=0.1$, 25 °C).

The effect of multivalent anions on the rates of the acid and base hydrolyses of pentaamminechlorocobalt(III) ions has been studied by Monk *et al.*, who found that ion-pairing accelerated the acid hydrolysis[1] and retarded the base hydrolysis.[2,3] If the latter is assumed to be a simple bimolecular reaction, the retardation can be explained on electrostatic grounds by the reduced positive charge of the ion-pair. However, among several possible mechanisms[4] thus far proposed for this base hydrolysis, the most widely accepted is the S_N1 C.B. mechanism, with which Monk *et al.*[3] failed to explain the retardation effect.

In this paper, the effect of multivalent anions on the rate of the base hydrolysis of pentaamminechlorocobalt(III) cations at a constant ionic strength is analyzed in view of the S_N1 C.B. mechanism and is explained by considering the formation of the ion-pairs of the ammine and the amido complexes with the multivalent anions.

Experimental

Materials. *Pentaamminechlorocobalt(III) Perchlorate*: The chloride of the complex, prepared by the method of Hynes *et al.*,[5] was dissolved in hot water and was then converted to the perchlorate by treating it with concentrated perchloric acid and by then cooling the solution in ice. The complex was identified spectrophotometrically.

Sodium Perchlorate: Sodium perchlorate was prepared from a saturated sodium hydroxide solution and perchloric acid. Heavy metal impurities in the sodium perchlorate were precipitated as hydroxides at pH 9, and the removal of heavy metals was confirmed by means of PAN(= 1-(2-pyridylazo)-2-naphthol).

Sodium Acetate: Anhydrous sodium acetate, a guaranteed reagent of Wako Pure Chemical Co, was used after dried at 110 °C.

Sodium Sulfate: Anhydrous sodium sulfate, a guaranteed reagent of Wako Pure Chemical Co, was recrystallized from water at 80 °C and dried at 100 °C.

Sodium Trimetaphosphate:[6] Disodium hydrogenphosphate was heated at about 800 °C for 200 h, after which the product was cooled very slowly. Then the sodium trimetaphosphate thus produced was extracted with a small amount of water and recrystallized by the addition of alcohol and cooling in a refrigerator. The purity of the twice-recrystallized salt was confirmed by paper chromatography.

Kinetic Runs. The rate was measured spectrophotometrically by following the change in the absorbance of solutions containing the complex (2.0×10^{-4} M (= mol dm^{-3})), an ammonia (2×10^{-3} M)-ammonium perchlorate (2×10^{-4} M) buffer, added salts (in appropriate concentrations), and sodium perchlorate, the last being added so as to adjust the ionic strength to 0.1. The reaction mixture, contained in a 1-cm quartz cell, was placed in the cell compartment of a Carl-Zeiss spectrophotometer, PMQ II, maintained at 25± 0.05 °C by circulating water from a thermostat.

pH Measurement. After the reaction had reached completion, the pH value of the sample solution was measured with a Beckman Research pH meter standardized with a buffer solution of Na_2CO_3–$NaHCO_3$ (pH 10.02 at 25 °C). As the internal solution of the reference electrode, a saturated NaCl solution was used so as to avoid the precipitation of $KClO_4$. The change in the liquid junction potential due to the displacement of the added salts was assumed to be negligible.

Results and Discussion

The experimental conditions and the rate constant observed for each run are shown in Fig. 1 and Tables 1—5. The rates were determined by plotting $\ln(D_\infty - D_t)$ against the time t, where D_∞ and D_t are the absorbances at an infinite time and at the time t respectively. The pseudo-first-order rate constant, k_{obsd} was thus

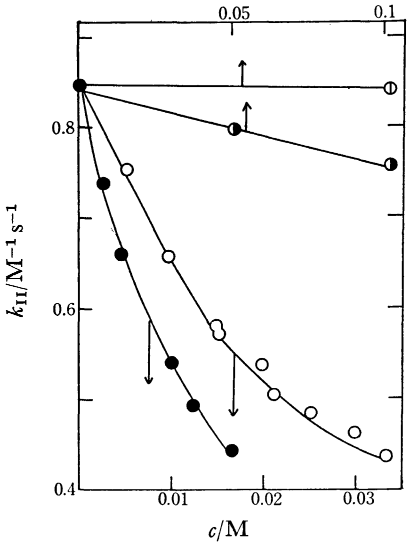

Fig. 1. Effects of added salts on the rate of base hydrolysis of $[CoCl(NH_3)_5]^{2+}$. $I=0.1$. KCl: ⦶, CH_3CO_2Na: ◑, Na_2SO_4: ○, $Na_3P_3O_9$: ●.

---

*Present address: Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630.

TABLE 1. EFFECT OF ACETATE IONS ON THE RATE OF THE BASE HYDROLYSIS OF $[CoCl(NH_3)_5]^{2+}$

Run	$\frac{[NaClO_4]}{M}$	$\frac{[CH_3CO_2Na]}{M}$	pH	$\frac{10^4 k_{obsd}}{s^{-1}}$	$\frac{k_{II}}{M^{-1}s^{-1}}$
1	0.10	0	10.25	1.46	0.839
2	0.05	0.05	10.26	1.42	0.780
3	0	0.10	10.27	1.40	0.752

TABLE 2. EFFECT OF SULFATE IONS ON THE RATE OF THE BASE HYDROLYSIS OF $[CoCl(NH_3)_5]^{2+}$ (Ionic strength=0.1)

Run	$\frac{[NaClO_4]}{M}$	$\frac{[Na_2SO_4]}{M}$	pH	$\frac{10^4 k_{obsd}}{s^{-1}}$	$\frac{k_{II}}{M^{-1}s^{-1}}$
1	1.000	0	10.28	1.658	0.870
			10.28	1.604	0.842
			10.22[a]	1.397	0.842
2	0.085	0.005	10.29	1.462	0.750
3	0.070	0.010	10.29	1.262	0.650
4	0.055	0.015	10.30	1.155	0.585
5	0.050	0.016	10.29[a]	1.117	0.573
6	0.040	0.020	10.32	1.132	0.542
7	0.025	0.025	10.33	1.044	0.488
8	0.010	0.030	10.31[a]	0.948	0.464
9	0	0.033	10.34	0.963	0.440
			10.23[a]	0.734	0.432

a) The buffer solutions used in these runs were not identical with those used in the other runs.

TABLE 3. CONCENTRATIONS OF EACH ION IN THE $NaClO_4$-Na_2SO_4 SYSTEMS

Run	$\frac{[ClO_4^-]}{M}$	$\frac{[SO_4^{2-}]}{M}$	$\frac{[Na^+ \cdot SO_4^{2-}]}{M}$	$\frac{[Na^+]}{M}$	I
1	0.1	0	0	0.1	0.1
2	0.085	0.00424	0.000765	0.0942	0.0985
3	0.070	0.00852	0.00148	0.0885	0.0970
4	0.055	0.0129	0.00209	0.0820	0.0958
5	0.050	0.0144	0.00230	0.0810	0.0955
6	0.040	0.0173	0.00265	0.0774	0.0947
7	0.025	0.0219	0.00309	0.0719	0.0938
8	0.010	0.0265	0.00347	0.0665	0.0931
9	0	0.0297	0.00362	0.0631	0.0928

TABLE 4. EFFECT OF TRIMETAPHOSPHATE IONS ON THE RATE OF THE BASE HYDROLYSIS OF $[CoCl(NH_3)_5]^{2+}$ (Ionic strength=0.1)

Run	$\frac{[NaClO_4]}{M}$	$\frac{[Na_3P_3O_9]}{M}$	pH	$\frac{10^4 k_{obsd}}{s^{-1}}$	$\frac{k_{II}}{M^{-1}s^{-1}}$
1	0.085	0.0035	10.19	1.14	0.737
2	0.070	0.0050	10.19	1.02	0.657
			10.19	1.04	0.672
3	0.040	0.0100	10.20	0.859	0.542
			10.20	0.864	0.545
4	0.025	0.0125	10.24	0.868	0.500
			10.24	0.894	0.515
5	0	0.0167	10.26	0.806	0.443

TABLE 5. CONCENTRATIONS OF EACH ION IN THE $NaClO_4$-$Na_3P_3O_9$ SYSTEMS

Run	$\frac{[ClO_4^-]}{M}$	$\frac{[P_3O_9^{3-}]}{M}$	$\frac{[Na^+ \cdot P_3O_9^{3-}]}{M}$	$\frac{[Na^+]}{M}$	I
1	0.1	0	0	0.1	0.1
2	0.085	0.00164	0.00086	0.0916	0.0974
3	0.070	0.00339	0.00161	0.0834	0.0951
4	0.040	0.00723	0.00277	0.0672	0.0917
5	0.025	0.00934	0.00316	0.0592	0.0905
6	0	0.0132	0.00349	0.0465	0.0897

obtained as the slope of this plot. Therefore, the rate of the reaction measured in the buffer solution is:

$$\text{Rate} = k_{obsd}[CoCl(NH_3)_5^{2+}]_0, \tag{1}$$

where $[CoCl(NH_3)_5^{2+}]_0$ is the total concentration of the complex.

On the other hand, according to the S_N1 C.B. mechanism, the following reaction scheme has been proposed:

$$[CoCl(NH_3)_5]^{2+} + OH^- \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} [CoCl(NH_2)(NH_3)_4]^+ + H_2O, \tag{2}$$

$$[CoCl(NH_2)(NH_3)_4]^+ \xrightarrow[\text{slow}]{k} [Co(NH_2)(NH_3)_4]^{2+} + Cl^-, \tag{3}$$

$$[Co(NH_2)(NH_3)_4]^{2+} + H_2O \xrightarrow[\text{fast}]{} [Co(OH)(NH_3)_5]^{2+}, \tag{4}$$

where K is the equilibrium constant and k is the rate constant of the rate-determining step (3). Unless otherwise stated, the equilibrium constants appearing in this paper are the concentration equilibrium constants under the present experimental conditions (I=0.1, 25 °C).[7] In such a case, the rate equation for the hydrolysis would be:

$$\begin{aligned}\text{Rate} &= k[CoCl(NH_2)(NH_3)_4^+] \\ &= kK[CoCl(NH_3)_5^{2+}][OH^-] \\ &= k\frac{K_a}{K_w}[CoCl(NH_3)_5^{2+}][OH^-],\end{aligned} \tag{5}$$

where K_a represents the acid dissociation constant of the ammine complex, and K_w, the ionic product of water.

Considering $[CoCl(NH_3)_5^{2+}] \gg [CoCl(NH_2)(NH_3)_4^+]$ under the present experimental conditions, a comparison of Eqs. 1 and 5 would give:

$$k_{obsd} = k\frac{K_a}{K_w}[OH^-]. \tag{6}$$

The concentration of hydroxide ions can be related to the measured pH by:

$$\log[OH^-] = pH - 14 - \log y_{OH}.$$

Under the condition of a constant ionic strength, y_{OH} is almost kept constant, and the observed differences in the pH among the different solutions can be attributed to the effects of the added salts on the $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ equilibrium. To allow for the pH change, the second-order rate constant, k_{II}, defined by Eq. 7 will be used in the following discussion.

$$k_{II} = k_{obsd}/y_{OH}[OH^-]. \tag{7}$$

Figure 1 shows that k_{II} changed with the change in the amount of salt added at the constant ionic strength of 0.1. Thus, the simple reaction scheme (Eqs. 2, 3, and 4) is not adequate in the presence of multivalent anions. However, the scheme given below is considered to relate the observed change in the reaction rate to the ion-pairing between the complex cations and the added anions:

$$\begin{tikzcd}
{[CoCl(NH_3)_5]^{2+}} \arrow[rr, harpoon, shift left, "K_{22}"] \arrow[d, harpoon, shift right] & & {[CoCl(NH_3)_5]^{2+}\cdot X^{n-}} \arrow[ll, harpoon, shift left] \arrow[d, harpoon, shift right] \\
{[CoCl(NH_2)(NH_3)_4]^{+}} \arrow[rr, harpoon, shift left, "K_{12}"] \arrow[u, harpoon, shift right, "K_a"'] \arrow[dr, "k^{\circ}"] & & {[CoCl(NH_2)(NH_3)_4]^{+}\cdot X^{n-}} \arrow[ll, harpoon, shift left] \arrow[u, harpoon, shift right, "K_a^{IP}"'] \arrow[dl, "k^{IP}"] \\
& {[Co(NH_2)(NH_3)_4]^{2+}} \arrow[d, "fast"] & \\
& {[Co(OH)(NH_3)_5]^{2+}} &
\end{tikzcd} \tag{8}$$

where X^{n-} represents the added multivalent anions, K_{22} and K_{12} are the ion association constants; K_a and K_a^{IP}, the acid dissociation constants, and k° and k^{IP}, the rate constants of the rate-determining steps. In this reaction scheme, the rate expression is:

$$\begin{aligned}
\text{Rate} &= k^{\circ}[CoCl(NH_2)(NH_3)_4{}^{+}] \\
&\quad + k^{IP}[CoCl(NH_2)(NH_3)_4{}^{+}\cdot X^{n-}] \\
&= \frac{k^{\circ}K_a}{K_w}[CoCl(NH_3)_5{}^{2+}][OH^-] \\
&\quad + \frac{k^{IP}K_a{}^{IP}}{K_w}[CoCl(NH_3)_5{}^{2+}\cdot X^{n-}][OH^-]
\end{aligned} \tag{9}$$

For a weakly basic solution where $[CoCl(NH_3)_5{}^{2+}] \gg [CoCl(NH_2)(NH_3)_4{}^{+}]$, Eq. 9 becomes:

$$\text{Rate} = \frac{(k^{\circ}K_a + k^{IP}K_a{}^{IP}K_{22}[X^{n-}])[OH^-]}{K_w(1+K_{22}[X^{n-}])}[CoCl(NH_3)_5{}^{2+}]_0$$

Relating this equation to Eq. 1, one obtains:

$$k_{obsd} = \frac{(k^{\circ}K_a + k^{IP}K_a{}^{IP}K_{22}[X^{n-}])[OH^-]}{K_w(1+K_{22}[X^{n-}])}$$

Then Eq. 7 leads to:

$$k_{II} = \frac{k^{\circ}K_a + k^{IP}K_a{}^{IP}K_{22}[X^{n-}]}{K_w y_{OH}(1+K_{22}[X^{n-}])} \tag{10}$$

Substituting $k_{II}{}^{\circ}$ for $(k^{\circ}K_a)/(K_w y_{OH})$ in Eq. 10 and using the relation:

$$K_a{}^{IP}/K_a = K_{12}/K_{22} \tag{11}$$

one obtains:

$$k_{II} = k_{II}{}^{\circ}\frac{1+(k^{IP}/k^{\circ})K_{12}[X^{n-}]}{1+K_{22}[X^{n-}]} \tag{12}$$

This equation will be used below for the explanation of the change in k_{II} shown in Fig. 1.

Monk *et al.*[2] observed little change in the rate when sodium perchlorate was replaced by potassium chloride. On the other hand, our experiments have shown that acetate ions have the effect of decreasing the reaction rate (Table 1). Thus, the substitution of acetate for perchlorate resulted in a slight decrease in k_{obsd} in spite of the increased pH of the solution; therefore, the second-order rate constant, k_{II}, showed an unmistakable decrease. Since electrostatic theories[8] of ion association predict only a slight difference between perchlorate and acetate ions in the tendency to form ion-pairs, the observed reaction rates seem to suggest some interaction such as hydrogen-bonding operating between the acetate and the complex ion.

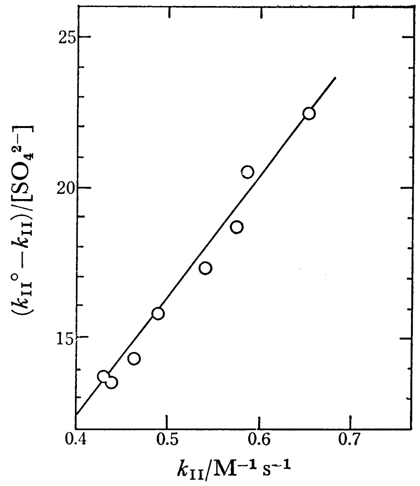

Fig. 2. Determination of the formation constant of the $[CoCl(NH_3)_5]^{2+}\cdot SO_4{}^{2-}$, ion-pair. (slope$=K_{22}$)

The substitution of sodium sulfate for sodium perchlorate caused a remarkable decrease in k_{obsd} (Table 2). For a quantitative treatment of the effect of the ion-pair formation between the bivalent complex cations and sulfate ions, the net concentration of free sulfate ions must be known. The decrease in the concentration of free sulfate ions due to the formation of hydrogensulfate ions and of the ion-pairs with the complex cations was estimated to be negligible at very low concentrations of hydrogen ions ($\approx 10^{-10}$ M) and the complex cations (2×10^{-4} M). On the other hand, the formation of the $Na^+\cdot SO_4{}^{-2}$ ion-pairs cannot be neglected.[9] The third column of Table 3 gives the concentrations of free sulfate ions, which were calculated by using the value of 2.0 (at $I=0.1$) for the formation constant of the $Na^+\cdot SO_4{}^{2-}$ ion-pairs. The last column of the table shows how the ionic strength decreases as a result of the ion-pair formation. According to the Brønsted-Bjerrum equation,[10] this decrease in the ionic strength will cause a decrease in the reaction rate of only 3% at most, a magnitude of the same order as the experimental error. This Brønsted-Bjerrum neutral-salt effect was, therefore, disregarded. For the analysis of the experimental results, Eq. 12 was transformed to:

$$(k_{II}{}^{\circ}-k_{II})/[X^{n-}] = K_{22}k_{II} - (k^{IP}/k^{\circ})K_{12}k_{II}{}^{\circ}. \tag{13}$$

By taking X^{n-} as free sulfate ions, $(k_{II}{}^{\circ}-k_{II})/[X^{n-}]$ was plotted against k_{II}. As Fig. 2 shows, a linear relationship was observed, and the slope gives the K_{22} value of 40±5. Then, in order to avoid mathematical difficulty at $[X^{n-}]=0$, Eq. 13 was transformed to:

$$k_{II}(1+K_{22}[X^{n-}]) = k_{II}{}^{\circ} + (k^{IP}/k^{\circ})K_{12}[X^{n-}]k_{II}{}^{\circ}.$$

With the K_{22} value determined above, the left-hand side of this equation was plotted against $[X^{n-}]$ ($=[SO_4{}^{2-}]$). This plot gave the values of $k_{II}{}^{\circ}$ and $(k^{IP}/k^{\circ})K_{12}k_{II}{}^{\circ}$, from which $(k^{IP}/k^{\circ})K_{12}$ was found to be 6±1.

TABLE 6. ASSOCIATION CONSTANTS OF $[CoCl(NH_3)_5]^{2+}\cdot X^{n-}$ ($X^{n-}=SO_4^{2-}$, $NaP_3O_9^{2-}$, and $P_3O_9^{3-}$)

	(i) $\log K_{22}(I=0)$	
$[CoCl(NH_3)_5]^{2+}\cdot SO_4^{2-}$	2.40±0.05	This work
	2.48	Ref. 11 (solubilities)
	2.49	Ref. 1 (kinetic data)
$[CoCl(NH_3)_5]^{2+}\cdot (NaP_3O_9)^{2-}$	2.4 ±0.1	This work
Theoretical ($a=6$ Å)[a]	1.98	Ref. 8 (Yokoyama-Yamatera Eq.)
	1.80	Ref. 8 (Fuoss Eq.)
($a=7$ Å)	1.87	Ref. 8 (Yokoyama-Yamatera Eq.)
	1.71	Ref. 8 (Fuoss Eq.)
	(ii) $\log K_{23}$ ($I=0$)	
$[CoCl(NH_3)_5]^{2+}\cdot P_3O_9^{3-}$	3.20±0.03	This work
$Mg^{2+}\cdot P_3O_9^{3-}$	3.31	Ref. 13
$Ca^{2+}\cdot P_3O_9^{3-}$	3.45	Ref. 13
$Sr^{2+}\cdot P_3O_9^{3-}$	3.35	Ref. 13
Theoretical ($a=7$ Å)	2.70	Ref. 8 (Yokoyama-Yamatera Eq.)
	2.60	Ref. 8 (Fuoss Eq.)

a) The notation a represents the closest distance of the approach of ions.

In Table 6, the K_{22} value here obtained is compared with other experimental and theoretical values. Our K_{22} value is in good agreement with those obtained by Monk *et al.* in a solubility study[11] and in a kinetic study of acid hydrolysis,[1] but it is about three times greater than the theoretical values. This difference can be attributed to the fact that the complex ion is not spherical but has an electric dipole moment in addition to the electric charge.

The value of K_{12} for the 1—2 ion-pair can be estimated with the Yokoyama-Yamatera equation[12] to be 4.7 ($I=0$), which is in reasonable agreement with the experimental K_{12} values for alkali metal sulfates, 5—10 ($I=0$).[13] Then, with K_{12} ($I=0.1$)$=2$, one obtains $k^{IP}/k^{\circ}=3\pm0.5$. This value can be compared with the corresponding value of 2.35 experimentally obtained by Monk *et al.* for the acid hydrolysis,[1] if allowance is made for the probable overestimate in the present k^{IP}/k° value. This overestimate is due to the neglect of the polarity of the complex ion, leading to an underestimated K_{12} value.

In a system with added sodium trimetaphosphate, the reaction scheme is more complicated. The decrease in free trimetaphosphate ions by the formation of hydrogentrimetaphosphate ions ($pK_{a1}=2.05$)[14] as well as by the ion-pair formation with the complex cations can be ignored, as in the case of sulfate. The formation of ion-pairs between sodium and trimetaphosphate ions, $Na^+ + P_3O_9^{3-} \rightleftharpoons Na^+\cdot P_3O_9^{3-}$, was studied by Gardner *et al.*,[15] who found the ion-association constant to be 25.1 at an infinite dilution. Then, the ion-association constant at $I=0.1$ would be 5.7. This value was used in the calculation of the net concentrations of the ions derived from the added sodium trimetaphosphate (Table 5). Although the decrease in the ionic strength is larger in this case than in the case of the sulfate ions, its effect on the reaction rate was estimated to be still of a magnitude within the limits of experimental error. Ignoring the formation of the ion-pairs with univalent anions, as in the case of the sulfate ions, the reaction scheme is:

$$\begin{tikzcd}
{[CoCl(NH_3)_5]^{2+}\cdot(NaP_3O_9)^{2-}} \arrow[r, phantom, "\overset{K_{22}}{\rightleftharpoons}"] \arrow[d, phantom, "\Updownarrow K_a^{(2)}"] & {[CoCl(NH_3)_5]^{2+}} \arrow[r, phantom, "\overset{K_{23}}{\rightleftharpoons}"] \arrow[d, phantom, "\Updownarrow K_a"] & {[CoCl(NH_3)_5]^{2+}\cdot P_3O_9^{3-}} \arrow[d, phantom, "\Updownarrow K_a^{(1)}"] \\
{[CoCl(NH_2)(NH_3)_4]^{+}\cdot(NaP_3O_9)^{2-}} \arrow[r, phantom, "\overset{K_{12}}{\rightleftharpoons}"] \arrow[dr, "k^{IP(2)}"'] & {[CoCl(NH_2)(NH_3)_4]^{+}} \arrow[r, phantom, "\overset{K_{13}}{\rightleftharpoons}"] \arrow[d, "k^{\circ}"] & {[CoCl(NH_2)(NH_3)_4]^{+}\cdot P_3O_9^{3-}} \arrow[dl, "k^{IP(1)}"] \\
 & {[Co(NH_2)(NH_3)_4]^{2+}} \arrow[d, "\text{fast}"] & \\
 & {[Co(OH)(NH_3)_5]^{2+}} &
\end{tikzcd} \tag{14}$$

where the definitions of the parameters are similar to those in the case of Eq. 8. In this scheme, the rate expression is:

$$k_{II} = k_{II}^{\circ}\frac{1+(k^{IP(1)}/k^{\circ})K_{13}[P_3O_9^{3-}]+(k^{IP(2)}/k^{\circ})K_{12}[Na^+\cdot P_3O_9^{3-}]}{1+K_{23}[P_3O_9^{3-}]+K_{22}[Na^+\cdot P_3O_9^{3-}]}. \tag{15}$$

As a first approximation, ignoring the formation of the $Na^+\cdot P_3O_9^{3-}$ ion-pairs, one can simplify Eq. 15 to obtain:

$$k_{II} = k_{II}^{\circ}\frac{1+(k^{IP(1)}/k^{\circ})K_{13}[P_3O_9^{3-}]_0}{1+K_{23}[P_3O_9^{3-}]_0}, \tag{16}$$

where $[P_3O_9^{3-}]_0$ is the total concentration of sodium trimetaphosphate. With Eq. 16, the experimental results were analyzed in a manner similar to that used in the case of sulfate; the values $K_{23}=75\pm5$ and $(k^{IP(1)}/k^{\circ})K_{13}=9\pm2$ were thus obtained. Since Eq. 15 involves too many parameters, all the parameters except for K_{23} and K_{22} were estimated by theory or by analogy. The K_{13} and K_{12} values were calculated by means of the Yokoyama-Yamatera theory of ion-association,[8] which gave $K_{13}=5.1$ and $K_{12}=1.5$ under the present experimental condition (or 22.3 and 4.0 respectively at $I=0$), assuming the closest distance of approach of ions to be 7 Å ($=0.7$ nm). The values for $k^{IP(1)}/k^{\circ}$ and $k^{IP(2)}/k^{\circ}$ were estimated at 2.5[16] and 2.0[1] respectively from the values for analogous acid hydrolyses. Using these parameter values and starting with the $K_{23}=75$ obtained with Eq. 16, successive approximations with Eq. 15 resulted in the final values, $K_{23}=82\pm5$ and $K_{22}=40\pm10$. Since no experimental results on the same system are found in the literature, the constants are compared with those for the systems of similar charge types, such as bivalent metal ions–trimetaphosphate ions and pentaamminechlorocobalt(III) ions–sulfate ions. The comparison in Table 6 shows that the values obtained are of reasonable magnitude.

It has been shown above that the experimental results can be explained on the basis of the scheme shown in Eqs. 8 and 14 giving ion-association constants of an acceptable magnitude. The discussion also shows that the retardation of the base hydrolysis of pentaamminechlorocobalt(III) ions by multivalent anions can be attributed mainly to the multivalent anions preferring the ammine complex rather than the amido complex (the reaction intermediate) in the ion association or, in other words (using Eq. 11), to the suppression of the acid dissociation of the ammine complex by the ion-pairing. The probable acceleration effect at the rate-determining step, represented by the k^{IP}/k° term is relatively small, so that the net effect of ion-pairing is the retardation of the rate of hydrolysis.

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education.

References

1) S. H. Laurie and C. B. Monk, *J. Chem. Soc.*, **1965**, 724.

2) M. R. Wendt and C. B. Monk, *J. Chem. Soc., A*, **1969**, 1624.

3) M. B. M. Campbell, M. R. Wendt, and C. B. Monk, *J. Chem. Soc., Dalton Trans.*, **1972**, 1714.

4) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2 nd ed, John Wiley & Sons, New York (1967), p. 183.

5) W. A. Hynes, L. K. Yanowski, and M. Shiller, *J. Am. Chem. Soc.*, **60**, 3053 (1938).

6) S. Ohashi, private communication; *cf.* R. N. Bell, *Inorg. Syn.*, **3**, 103 (1950).

7) The thermodynamical equilibrium constant or the equilibrium constant at $I=0$ can be calculated by the use of the Davies equation for activity coefficients:

$$\log y_i = -0.5115 z_i^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I \right)$$

where y_i is the activity coefficient of the i ion, z_i is the charge number of the i ion, and I is the ionic strength.

8) H. Yokoyama and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **48**, 1770 (1975); N. Bjerrum, *Kgl. Danske Videnskab. Selskab.*, **7**, No. 9 (1926); R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958); W. Ebeling, *Z. Phys. Chem. (Leipzig)*, **238**, 400 (1968).

9) I. L. Jenkins and C. B. Monk, *J. Am. Chem. Soc.*, **72**, 2695 (1950).

10) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, New York (1961), p. 150.

11) D. W. Archer, D. A. East, and C. B. Monk, *J. Chem. Soc.*, **1965**, 720.

12) Although the Yokoyama-Yamatera equation[8] was derived for symmetrical electrolytes, its application to unsymmetrical electrolytes is permitted as an approximation.

13) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London (1964), pp. 194, 235.

14) C. W. Davies and C. B. Monk, *J. Chem. Soc.*, **1949**, 413.

15) G. L. Gardner and G. H. Nancollas, *Anal. Chem.*, **41**, 202 (1969).

16) This estimation resulted from the experiments measuring the effect of trimetaphosphate anions on the rate of acid hydrolysis of the complex (unpublished results).