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The Aluminium(III) Ion-assisted Aquation of the Pentaammine-fluorochromium(III) Ion

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The aquation of the pentaamminefluorochromium(III) complex was found to be assisted by the aluminium ion. The observed pseudo-first-order rate constant, k_{obsd}, can be written approximately as: $k_{\text{obsd}}=k_{\text{Al}}[\text{Al}^{3+}]$ ($k_{\text{Al}}=7.5\times10^{-4}$ dm^3 mol^{-1} s^{-1} at 35 °C, pH 3.0, $I=2.0$ mol dm^{-3}). The rate constant decreased with an increase in the hydrogen-ion concentration, and this hydrogen-ion dependence was explained by assuming that the attack of aluminium ions on $\text{CrF(NH}_3)_5{}^{2+}$ was blocked by the protonation of the fluoro ligand. The analysis of the experimental results gave 3.0 ± 0.1 for the logarithm of the protonation constant. The effects of $\text{ClO}_4{}^-$ and $\text{Co(CN)}_6{}^{3-}$ on the reaction rate were explained by considering the formation of ion-pairs between the anions and the reacting cations.

Among the reactions of transition-metal complexes, metal ion-induced aquation, or metal ion-assisted aquation, is particularly interesting as a model ionic reaction. In order to understand this kind of reaction in more detail, it is significant to extend the study to the reactions of types that have not yet been studied. The greater part of the studies of the metal ion-assisted aquation have been concerned with the reactions of chloro, bromo, and iodo complexes with soft acids, such as Ag^+, Hg^{2+}, and Tl^{3+}. There have been no detailed studies of the aquation of fluoro complexes induced by hard metal ions.[1,2]

The present paper is concerned with a rarely studied type of reaction, *i.e.*, the dissociation of hard basic anions induced by hard metal ions. The investigation of such a type of reaction is expected to disclose some characteristic behavior which has not appeared in the aquations assisted by soft metal ions. Another purpose of this study is to see how the reaction is influenced by the hexacyanocobaltate(III) ion. This ion tends to form a precipitate with soft metal ions; therefore, its effect on the metal ion-assisted aquations cannot be investigated when the metal ion is soft, as is usually the case; however, it can be examined in the present study where a hard metal ion is used to induce the aquation.

Experimental

Materials. Pentaamminefluorochromium(III) perchlorate was prepared from pentaammineaquachromium(III) ammonium nitrate by the method of Zinato *et al.*[3] The purity of the crystals was confirmed spectrophotometrically and by means of SP-sephadex ion-exchange chromatography; the complex was sorbed on the top of the column and was eluted with a 0.1 mol dm^{-3} sodium sulfate solution. The appearance of a well-formed single band indicated the absence of impurities.

Aluminium perchlorate was prepared by dissolving $\text{AlCl}_3\cdot6\text{H}_2\text{O}$ in an aqueous solution containing perchloric acid in excess. The salt was then precipitated in a rotating evaporator and recrystallized twice from water. The crystals were dissolved in an aqueous solution of perchloric acid for the preparation of a stock solution. The aluminium-ion concentration was determined to be Al_2O_3 by precipitating aluminium hydroxide and igniting it at about 1100 °C.

Sodium hexacyanocobaltate(III) dihydrate was prepared by the conventional method,[4] in which potassium cyanide was replaced by sodium cyanide. Anhydrous sodium perchlorate was prepared from a saturated sodium hydroxide solution and perchloric acid. Heavy-metal impurities in the sodium perchlorate solution were precipitated at pH 9. After the evaporation of the solution, crystals of sodium perchlorate were obtained by cooling (above 60 °C).

The other reagents used were of a guaranteed reagent grade from Wako Pure Chemicals Industries, Ltd.

Kinetic Procedure. The kinetic measurements were made with a Hitachi 200-10 spectrophotometer. The concentration of $[\text{CrF(NH}_3)_5](\text{ClO}_4)_2$ was controlled at 5.0×10^{-3} mol dm^{-3} in all the experiments unless otherwise stated. The change in the absorbance was followed at 510 nm. As the rates were of first-order in the presence of excess aluminium ions (more than five times the amount of the chromium(III) complexes), they were determined by plotting $\ln(D_t-D_\infty)$ against the time, where D_t and D_∞ are the absorbances at the time t and at an infinite time respectively. The pseudo-first-order rate constant, k_{obsd}, was thus obtained as the slope of this plot.

pH *Measurements.* The pH value of the sample solution containing a 0.1 mol dm^{-3} portion of $\text{Al(ClO}_4)_3$ was controlled by the addition of Na_2CO_3 crystals. The solution was used one day after the preparation.[5] The $(\text{pH})_{\text{obsd}}$ values of the sample solutions were determined by means of a Beckman Century SS-1 pH meter, using a Beckman 39301 glass electrode and a 39402 calomel reference electrode. As the internal solution of the reference electrode, a saturated NaCl solution was used to avoid the precipitation of KClO_4. The pH meter was calibrated in terms of the H^+ concentration; *i.e.*, the pH was defined as $-\log[\text{H}^+]$ instead of $(\text{pH})_{\text{obsd}}$.[6] As the pH dependency of the reaction rate was studied in a 0.1 mol dm^{-3} $\text{Al(ClO}_4)_3$ solution, the calibration of $-\log[\text{H}^+]$

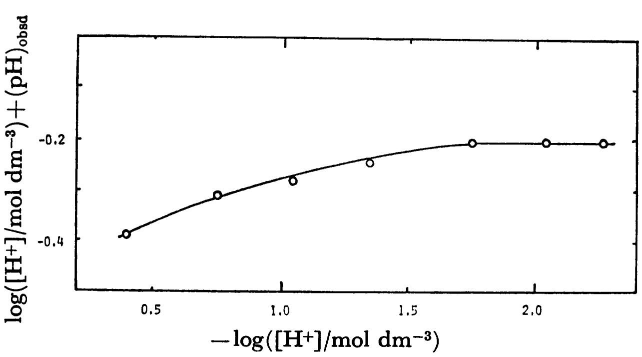

Fig. 1. Deviations of $(\text{pH})_{\text{obsd}}$ from $-\log[\text{H}^+]$ in a 0.10 mol dm^{-3} $\text{Al(ClO}_4)_3$ aqueous solution.

vs. $(pH)_{obsd}$ was carried out for this solution in the pH range where the hydrolysis of aluminium ions could be neglected $(-\log[H^+] < 3.2)$. The results are shown in Fig. 1. The liquid-junction error is independent of the pH above $-\log[H^+] = 1.7$; below that it increases with a decrease in the pH. Therefore, this equation:

$$(pH)_{obsd} + \log[H^+] = -0.21$$

is used above pH 1.7.

Results and Discussion

Spontaneous Aquation. Spontaneous and proton-catalyzed aquations of the pentaamminefluorochromium(III) ion were studied polarographically by Jones and Phillips.⁷⁾

$$CrF(NH_3)_5^{2+} + H_2O \xrightarrow{k_0} Cr(OH_2)(NH_3)_5^{3+} + F^-$$

$$CrF(NH_3)_5^{2+} + H_3O^+ \xrightarrow{k_H} Cr(OH_2)(NH_3)_5^{3+} + HF$$

These reactions were found to be very slow, and the rate constants obtained were $k_0 = 1.4 \times 10^{-5}\ s^{-1}$ (pH range, 1—10.5) and $k_H = 3.5 \times 10^{-5}\ mol^{-1}\ s^{-1}\ dm^3$ (pH <1) at 65 °C. (The ionic strength was maintained at 1.0 by the addition of sodium perchlorate.) In fact, the mechanism of aquation is complex.⁷,⁸⁾ Fluoro, aqua, and ammine mixed-ligand complexes were formed as the by-products, indicating that the aquation was accompanied by the dissociation of the ammine ligands. To confirm the stoichiometry, we carried out spontaneous aquation at 35 °C in the dark. The $CrF(NH_3)_5^{2+}$ and H^+ concentrations were both controlled to 10^{-2} mol dm^{-3}. The reaction was followed for 10 d with a fluoride-ion electrode and by means of the SP-sephadex chromatographic technique. The former detects the fluoride ion released from the complex, and the latter, the complexes produced by the reaction with the aid of spectrophotometric measurements. Although the analysis hardly led to a quantitative conclusion, the following facts were proved: 1) In the early stage of the reaction, *cis*-$[CrF(OH_2)(NH_3)_4]^{2+}$ ($\lambda_{max} = 512$ and 375 nm⁹⁾) is formed. 2) No $[Cr(OH_2)(NH_3)_5]^{3+}$ can be detected throughout the measurement. 3) The release of fluoride ion is much slower than that of ammonia, and less than 5% of the fluoride ions in the complex are released in about 10 d. These results are similar to those obtained by Linhard and Weigel⁸⁾ and to those described by Wong and Kirk for the photoaquation of this complex,¹⁰⁾ but they are different from those reported by Jones and Phillips.⁷⁾

No further investigation of the spontaneous aquation has been made, as it is not our present purpose.

Aluminium(III)-assisted Aquation. The hard aquation, $CrF(NH_3)_5^{2+} \rightarrow Cr(OH_2)(NH_3)_5^{3+}$, easily proceeds in the presence of aluminium ions. The spectrum of the complex changes with isosbestic points at 382, 415, and 480 nm, which shows the absence of by-products. In 0.1 mol dm^{-3} of $Al(ClO_4)_3$, the reaction proceeds to completion after about 1 d (pH 3.3, 35 °C). The pseudo-first-order rate constants, k_{obsd}, obtained depend on the concentration of the aluminium ion. The results summarized in Table 1 show that k_{obsd} can be expressed approximately as $k_{Al}[Al^{3+}]$ if pH is kept constant. An additional term, k_0, for the spontaneous aquation can be neglected under our present experimental conditions.

Table 1. Dependence of the rate constant on the concentration of the aluminium ion (35 °C)

$[Al^{3+}]/mol\ dm^{-3}$	k_{obsd}/s^{-1}
$((pH)_{obsd} = 2.0, I = 3.0\ mol\ dm^{-3})$	
0.50	1.5×10^{-4}
0.20	6.4×10^{-5}
0.10	3.5×10^{-5}
$((pH)_{obsd} = 2.8, I = 2.0\ mol\ dm^{-3})$	
0.30	2.1×10^{-4}
0.20	1.4×10^{-4}
0.12	9.5×10^{-5}
0.10	8.2×10^{-5}

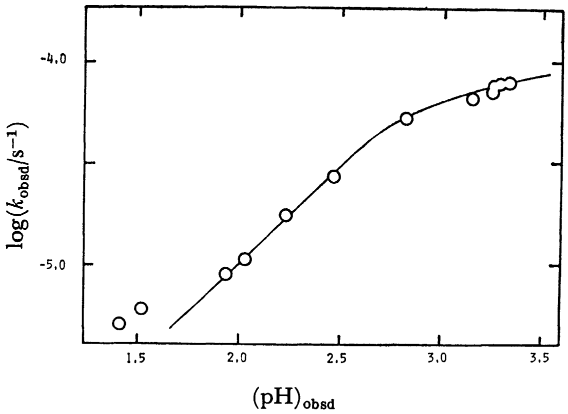

Fig. 2. pH dependence of the pseudo-first-order rate constant (0.10 mol dm^{-3} $Al(ClO_4)_3$ at 35 °C).

Figure 2 shows the pH dependency of the reaction rate in the presence of 0.1 mol dm^{-3} of $Al(ClO_4)_3$. The observed rate constant increases with an increase in the pH value and becomes approximately constant at a $(pH)_{obsd}$ value of about 3.2. This pH dependency of the reaction rate has not been observed for the metal ion-assisted aquations hitherto studied. As the reaction proceeds between $CrF(NH_3)_5^{2+}$ and Al^{3+}, the pH dependency is attributed to the pH-dependent properties of the reactants. One of these properties is the hydrolysis of Al^{3+}, which is known to begin around pH$(-\log[H^+])$ 3. Gradual hydrolysis proceeds up to a pH of about 3.5, where an abrupt change takes place.¹¹⁻¹³⁾ Only $AlOH^{2+}$ is formed in the experimental pH range, and so polynuclear cationic species need not be considered. Figure 2 shows only a slight change in the rate in the pH range where a marked hydrolysis of Al^{3+} occurs. Therefore, the hydrolysis product, $AlOH^{2+}$, appears to have no appreciable effect on the reaction.

Another possibility is that the pH dependence of the rate is due to the protonation of the fluoro ligand of $CrF(NH_3)_5^{2+}$. Such protonation will block the attack of aluminium ions upon the fluoro ligand. Including the protonated complex, the reaction scheme can be formulated as follows:

$$\begin{tikzcd} \mathrm{CrF(NH_3)_5^{2+}} + \mathrm{Al^{3+}} \arrow[r, "k_1"] \arrow[d, shift left] & \mathrm{Cr(OH_2)(NH_3)_5^{3+}} + \mathrm{AlF^{2+}} \\ \mathrm{CrFH(NH_3)_5^{3+}} + \mathrm{Al^{3+}} \arrow[r, "k_2"] \arrow[u, shift left, "K_H"] & \mathrm{Cr(OH_2)(NH_3)_5^{3+}} + \mathrm{AlF^{2+}} + \mathrm{H^+}. \end{tikzcd}$$

In this scheme, k_2 can be assumed to be negligibly small in comparison with k_1. Then, the pseudo-first-order rate constant, k_{obsd}, can be rewritten as:

$$k_{\mathrm{obsd}} = (1 + K_{\mathrm{H}}[\mathrm{H^+}])^{-1}k_1[\mathrm{Al^{3+}}],$$

where K_{H} is the concentration equilibrium constant for the protonation of pentaamminefluorochromium(III) ions. Beginning with this equation, we can carry out a curve fitting such as is shown in Fig. 2 and obtain $\log(k_1[\mathrm{Al^{3+}}]) = -4.00\pm0.05$ and $\log K_{\mathrm{H}} = 3.0\pm0.1$. The failure of fitting in the lowest pH region may be attributed to such side reactions as the dissociation of the ammine ligands, which may not be ignored at such low k_{obsd} values. The value of $\log K_{\mathrm{H}}$ seems to be too large considering the equilibrium constant for $\mathrm{H^+ + F^- = HF}$ ($\log K = 3.2\pm0.2$ at 35 °C.[14]), because the logarithms of the protonation constants of oxoanions are lowered by 2—3 units by their coordination to the pentaamminecobalt(III) cations.[15] This suggests that the Cr–F bond is considerably ionic and that the F ligand is more easily protonated than expected.

Table 2. First-order rate constants at varying temperatures
($(\mathrm{pH})_{\mathrm{obsd}}=3.2$, $[\mathrm{Al(ClO_4)_3}]=0.10$ mol dm^{-3})

	$k_{\mathrm{obsd}}/\mathrm{s}^{-1}$
25 °C	3.2×10^{-5}
30 °C	6.5×10^{-5}
35 °C	8.3×10^{-5}
40 °C	1.6×10^{-4}
45 °C	2.7×10^{-4}

From the rate constants measured at various temperatures (Table 2), the activation enthalpy, $\Delta H^{\ne}$, and the activation entropy, $\Delta S^{\ne}$, can be estimated: $\Delta H^{\ne} = 83\pm5$ kJ mol^{-1} and $\Delta S^{\ne} = -62\pm17$ J K^{-1} mol^{-1}. The activation entropy for a $\mathrm{Cr^{2+}}$-assisted reduction of this complex (-126 J K^{-1} mol^{-1})[16] is about 60 J K^{-1} mol^{-1} smaller than that for this reaction; this relationship holds also between the $\mathrm{CrCl(NH_3)_5^{2+}}$–$\mathrm{Hg^{2+}}$ system and the $\mathrm{CrCl(NH_3)_5^{2+}}$–$\mathrm{Cr^{2+}}$ system.[17,18] The minus sign of the activation entropies reflects the formation of halide-bridged binuclear complexes in the transition states. If the electron transfer proceeds adiabatically in the reduction process, the change in the entropy will be nearly zero in this step and the activation entropy can mostly be ascribed to the formation of the bridged complex. In view of this, the difference in the activation entropy between the reduction and the aquation can be said to be due mainly to the difference in the structure of the activated complex.[19] A more stringent geometrical condition may have to be satisfied in the reduction.

Effects of Anions. Table 3 summarizes the effects of the anions. As five-coordinated intermediates are formed in the metal ion-assisted aquation,[20] such anions as $\mathrm{SO_4^{2-}}$ and $\mathrm{H_2P_2O_7^{2-}}$ may react with the intermediate to form inner-sphere complexes. The instability of the oxoanionopentaamminechromium(III) complexes makes the reactions complicated, however.[21]

Table 3. Effect of anions on the reaction

Anions	
$\mathrm{ClO_4^-}$	Small accelerating effect.
$\mathrm{SO_4^{2-}}$(pH 3)	Formation of sulfato complex, followed by the dissociation of ammine ligands.
$\mathrm{H_2P_2O_7^{2-}}$(pH 2)	Formation of some polynuclear complex.[a]
$\mathrm{Co(CN)_6^{3-}}$	Large accelerating effect.

a) After the absorbance change had almost terminated (for 0.1 mol dm^{-3} $\mathrm{Na_2H_2P_2O_7}$ at 35 °C, one day after the reaction had started), the reaction solution was poured onto a column of SP-sephadex. Then, most of the complex was adsorbed at the top of the column. Elution with one molar sodium sulfate solution did not develop the band. The complex formed is likely to be a highly-charged cation.

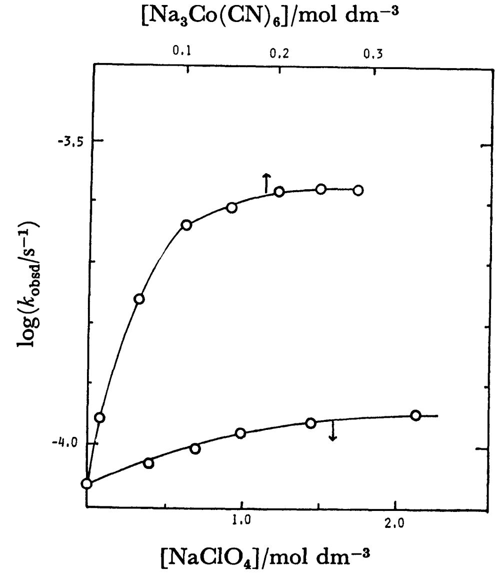

Fig. 3. Effects of anions on the reaction rate ($[\mathrm{Al^{3+}}]=0.10$ mol dm^{-3}, $(\mathrm{pH})_{\mathrm{obsd}}=3.1\pm0.1$).

The role of anions such as $\mathrm{ClO_4^-}$ and $\mathrm{Co(CN)_6^{3-}}$, which are reluctant to coordinate, is to assist the reactant cations in their approaching each other and to increase the chances of the reaction between them. Figure 3 shows the effects of perchlorate and hexacyanocobaltate(III) ions in accelerating the aluminium ion-assisted aquation. The reactions were carried out in the presence of the respective anions at $(\mathrm{pH})_{\mathrm{obsd}}=3.1\pm0.1$, where the reacting species can be considered to be $\mathrm{CrF(NH_3)_5^{2+}}$ and $\mathrm{Al^{3+}}$. A rough analysis was carried out for the relative magnitudes of the effects of $\mathrm{Co(CN)_6^{3-}}$ and $\mathrm{ClO_4^-}$ with the following assumptions. Firstly, the effects of anions on the reaction rate are assumed to be mainly determined by the charge and the radius of the anion. Secondly, the effect of added neutral salts is considered to be the formation of ion-pairs between the reacting cations and the mediating anions. The formation of the ion-pairs with $\mathrm{Na^+}$ is neglected, however. The third is that the activity coefficients of ion-pairs change according to the Davies equation:

$$\log y_{\mathrm{i}} = -0.521\, z_{\mathrm{i}}^{*2}\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3\,I\right), \tag{1}$$

where z_{i}^{*} is the effective charge number of the ion-pairs, and I, the ionic strength. On the basis of the above assumptions, we can express the rate constant of the reaction between A and B ions at saturation as follows:

$$k_{\mathrm{AB}} = k_{\mathrm{AB}}^{0}\,\frac{K_{\mathrm{AB}}}{K_{\mathrm{AB}}^{0}} = k_{\circ}^{0}\,\frac{K_{\mathrm{AB}}}{K_{\mathrm{AB}}^{0}}\exp\left(-\frac{z_{\mathrm{A}}^{*}z_{\mathrm{B}}^{*}\,e^{2}}{kT\varepsilon a}\right), \tag{2}$$

where the superscript 0 indicates the value at an infinite dilution and where the symbols have the following meanings:

K_{AB}: Equilibrium constant between the activated complex and the reactants.
$k_{\circ}^{0}$: Hypothetical rate constant for uncharged ions.
$z_{\mathrm{A}}^{*}e$, $z_{\mathrm{B}}^{*}e$: Effective charges of A and B ions respectively, decreased by the approach of ions of the opposite sign.
k : Boltzmann constant.
T : Absolute temperature.
ε : Dielectric constant of the solvent.
a : Closest distance of the approach of the A and B ions.

For the present system containing sodium perchlorate, the rate constant at the saturation is:

$$k_{12} = k_{\circ}^{0}\,\frac{K_{12}}{K_{12}^{0}}\exp\left(-\frac{2e^{2}}{kT\varepsilon a}\right) = k_{\circ}^{0}\,\frac{y_{1}y_{2}}{y_{12}}\exp\left(-\frac{2e^{2}}{kT\varepsilon a}\right), \tag{3}$$

where the subscript 12 indicates $z_{\mathrm{A}}^{*}=1$ and $z_{\mathrm{B}}^{*}=2$. Using Eq. 1, Eq. 3 is transformed to:

$$\log k_{12} = \log k_{\circ}^{0} - 0.521\,(1+4-9)\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3\,I\right) - 0.86,$$

where T=308 K and a=0.7 nm are used.

The ionic strength at the saturation (Fig. 3) is 1.1± 0.2,[22] which is substituted to give this result:

$$\log k_{12}\ (I = 1.1 \pm 0.2) = \log k_{\circ}^{0} - (0.47 \pm 0.08).$$

On the other hand, ion-pair formation between the reactants and $[\mathrm{Co(CN)_6}]^{3-}$ makes $z_{\mathrm{A}}^{*}=-1$ and $z_{\mathrm{B}}^{*}=0$; therefore, the pseudo-first-order rate constant, k_{10}, at saturation with $[\mathrm{Co(CN)_6}]^{3-}$ will not depend appreciably on the ionic strength. Thus, one obtains this approximate equality:

$$\log k_{10} \approx \log k_{10}^{0} \approx \log k_{\circ}^{0}.$$

From the above argument, the saturation rate constant for the $\mathrm{Al^{3+}}$-assisted aquation of $[\mathrm{CrF(NH_3)_5}]^{2+}$ can be expected to be greater in the sodium hexacyanocobaltate(III) solution than in the sodium perchlorate solution:

$$\log k_{10} = \log k_{12}\ (I = 1.1 \pm 0.2) + (0.47 \pm 0.08).$$

This calculated difference in the saturation rate constant is in good agreement with the experimental results (Fig. 3):

$$\log k_{10}\ (\text{exp.}) = \log k_{12}\ (\text{exp.}) + (0.39 \pm 0.02).$$

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