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DOUBLE LIGAND-EXCHANGE REACTIONS BETWEEN THE PENTAAMMINEFLUOROCOBALT(III) ION AND THE DICARBOXYLATO COMPLEXES OF ALUMINIUM(III)

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Double ligand-exchange reactions such as $CoF(NH_3)_5{}^{2+} + AlA_n{}^{3-2n} \longrightarrow CoA(NH_3)_5{}^{+} + AlFA_{n-1}{}^{4-2n}$ (A^{2-}= oxalate ion or malonate ion) were found to proceed in about 90% yield under the conditions, $[A^{2-}]_{total} > [Al^{3+}]_{total} >> [CoF(NH_3)_5{}^{2+}]$.

In a previous study we found that the aquation, $CoF(NH_3)_5{}^{2+} \longrightarrow Co(OH_2)(NH_3)_5{}^{3+}$, was effectively assisted by aluminium ions and that the reaction rate is first-order with respect to the concentration of each reactant.[1)] Posey and Taube,[2)] Reynolds *et al.*,[3)] and Jackson *et al.*[4)] have studied the competition reactions accompanying the assisted aquations of the pentaamminecobalt(III) complexes in the presence of various anions. Their results have shown that the yields of the anionopentaammine-cobalt(III) complexes were less than 50% under the experimental conditions.

The present study was undertaken to gain more detailed information on the kinetics and the mechanism of the aluminium ion-assisted aquation of $[CoF(NH_3)_5]^{2+}$. In order to reveal the specific effects of anions, the aquations were allowed to proceed in the presence of the oxalate and the malonate ion which have strong affinity to the aluminium ion.

The $[CoF(NH_3)_5](ClO_4)_2$ crystals and the $Al(ClO_4)_3$ stock solutions were prepared and analyzed as previously reported.[1)] Anhydrous sodium oxalate was a guaranteed reagent from Wako Pure Chemicals Industries, Ltd. and was dried at 300 °C for one hour before use. Anhydrous sodium malonate, an extra pure reagent from Nakarai Chemicals Industries, was recrystallized from water-methanol solution, dried in vacuo at 60 °C, and used. A 5.0×10^{-3} mol dm^{-3} solution of $[CoF(NH_3)_5](ClO_4)_2$ was allowed to react with a 5.1×10^{-2} mol dm^{-3} $Al(ClO_4)_3$ in the presence of dicarboxylate anions at 25.0±0.1 °C. The reactions were monitored spectrophotometrically at 500 nm. The pseudo-first-order rate constants, k_{obsd}, were obtained from $\ln(D_\infty - D_t)$ vs. t plots, where D_t and D_∞ are the absorbances at time t and at an infinite time respectively. After the absorbance change had almost terminated, the reaction solution was added to a column of SP-Sephadex and was eluted with a 0.15 mol dm^{-3} sodium sulfate solution. Two bands were observed; the first was assigned to $CoA(NH_3)_5^+$ 5,6) and the second to $Co(OH_2)(NH_3)_5^{3+}$ from their spectra. Their yields were estimated from spectrophotometric measurements of each portion of the eluate. In order to confirm the stoichiometry of the reaction, the final reaction solutions were examined by ^{19}F NMR. The procedure was the same as that previously described.1) The pH values of the final reaction solutions were measured with a conventional pH meter. The pH was adjusted to the range where the reaction rates are little affected by pH; such a pH range was 1.8-3.5 when $[A^{2-}]_{total}/[Al^{3+}]_{total}<2.5$, and at higher anion concentrations, the ranges were 2.5-3.2 for ox^{2-} and 3.5-4.5 for mal^{2-}.

Figure 1 shows the yields of $CoA(NH_3)_5^+$ for various concentrations of the anions. The yields obtained here are much larger than those reported for related reactions by previous workers.2-4) These high yields can be ascribed to the specific effects of the dicarboxylate ions upon the $CoF(NH_3)_5^{2+} + Al^{3+}$ reaction.

The ^{19}F NMR measurements were made for three samples varying in the concentration of the added sodium oxalate with unchanged conditions of $[CoF(NH_3)_5^{2+}]_{initial}$= 0.050 mol dm^{-3} and $[Al^{3+}]_{total}$= 0.20 mol dm^{-3}. The solutions with $[ox^{2-}]_{total}$= 0.20, 0.41, and 0.61 mol dm^{-3} showed the chemical shifts(δ) of the main peak, -35.2, -38.4, and -38.8 with reference to F^-, respectively. The signal of $CoF(NH_3)_5^{2+}$ could not be detected. A solution of [NaF] = 0.050 mol dm^{-3}, $[Al^{3+}]_{total}$= 0.20 mol dm^{-3}, and $[ox^{2-}]_{total}$= 0.41 mol dm^{-3} was also measured as a reference and gave a peak at -38.5 from F^-. As the chemical shift of AlF^{2+} peak is -36.1 from F^-,1) the above results suggest the formation of the fluoride—aluminium bonding. (The small differences among the F chemical shifts may

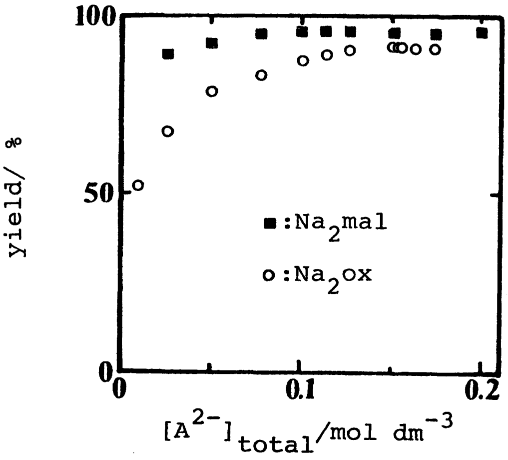

Fig. 1. The yield of $CoA(NH_3)_5^+$ depending on the concentration of the anions.

be due to the effect of oxalate ligands bonded to the same aluminium ion.) Comparison of the peak areas between the samples and the reference reveals that most of the fluoride ions in the initial $CoF(NH_3)_5^{2+}$ had moved to the aluminium ions in every case. The ^{19}F NMR and chromatographic studies lead to a conclusion that the reaction, $CoF(NH_3)_5^{2+} + AlA_n^{3-2n} \longrightarrow CoA(NH_3)_5^{+} + AlFA_{n-1}^{4-2n}$, proceeded in about 90% yield when $[A^{2-}]_{total} > [Al^{3+}]_{total} \gg [CoF(NH_3)_5^{2+}]_{initial}$. The reaction of this type seems to be classified as a double ligand-exchange reaction, which is a very rare type among the reactions of the octahedral inert complexes.[7)]

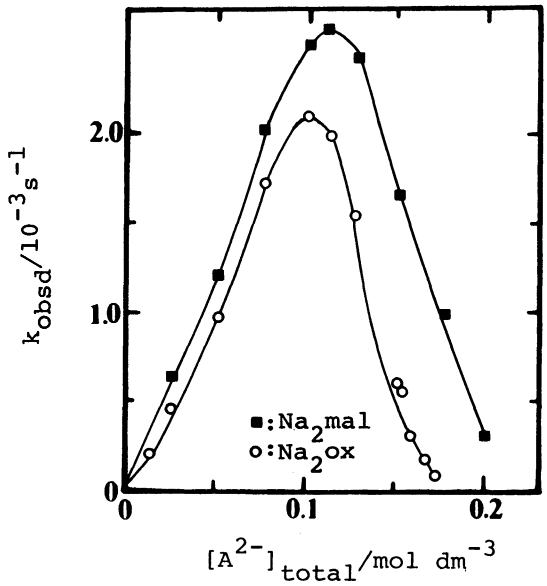

Fig. 2. Dependence of the rate constant on the concentration of the anions.

Figure 2 shows the change of the rate constants with varying concentrations of the anions. The results reveal that the anions have two effects on the reaction rates; an accelerating effect at lower concentrations and a masking effect at higher concentrations. In the lower concentration range, the strong electrostatic attraction of the dicarboxylate ions for cations assists the reactant cations in approaching each other and in getting greater chances of their reacting. The effect is appreciably larger than the effect of $Co(CN)_6^{3-}$ on $CrF(NH_3)_5^{2+} + Al^{3+}$ reaction.[8)] As soon as the aluminium ion extracted the fluoride ion from $CoF(NH_3)_5^{2+}$, the dicarboxylate ion would rapidly enter into the coordination sphere of the cobalt(III). At the higher concentrations, on the contrary, the anions crowding around the aluminium ion block the latter from attacking the fluoride ion of $CoF(NH_3)_5^{2+}$. The reaction rate showed a maximum approximately at the position of $[A^{2-}]_{total}/[Al^{3+}]_{total} = 2$, decreasing on both side with a less steep slope on the left side. The characteristics of the curves can be understood by considering the successive formation constants for the Al^{3+}—dicarboxylate complexes: $\log K_1 = 6.06$, $\log K_2 = 5.03$, and $\log K_3 = 4.03$ for Al^{3+}—ox^{2-} system (I= 1.0 mol dm^{-3}),[9)] and $\log K_1 = 5.24$, $\log K_2 = 4.16$, and $\log K_3 = 4.06$ for Al^{3+}—mal^{2-} system (I= 0.2 mol dm^{-3}).[10)] These values give us the following information: 1) the highest AlA_2^{-} percentages should be found around $[A^{2-}]_{total}/[Al^{3+}]_{total} = 2.0$; 2) more than 90% of the aluminium ions should be present in the form of AlA_3^{3-} at $[A^{2-}]_{total}/[Al^{3+}]_{total} = 3.0$; 3) in the range of $[A^{2-}]_{total}/[Al^{3+}]_{total} < 1$, Al(III) should exist dominantly in the form of AlA^+. Thus the experimental results suggest that the reactivity decreases in the order, $AlA_2^- > AlA^+ > AlA_3^{3-}$. The slight shift of the maximum of the curve toward right as observed for the malonate system is attributable to the lower formation constants of the Al^{3+}—mal^{2-} complexes. Both the larger effect of the malonate ion on the reaction rate and the higher yield of $CoA(NH_3)_5^+$ for A = malonate may be due to the flexibility of the chelate rings formed by malonate ligands, which will facilitate the contact of the central aluminium ion of the malonato complex with the fluoride ligand of the cobalt(III) complex and the coordination of the malonate ion with the cobalt(III).

The kinetic results will be discussed in detail in a later paper.

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