Difference in the Kinetic Behavior on the AC-Catalyzed Decomposition (AC=Activated Carbon) of $[Co(C_2O_4)_3]^{3-}$ and $[Co(NH_3)_5(H_2O)]^{3+}$, and on the AC-Catalyzed Ligand-Substitution Reactions between Each Complex and EDTA in an Aqueous Solution

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The decomposition reaction of tris(oxalato)cobaltate(III) ion, $[Co(ox)_3]^{3-}$, occurred to produce cobalt(II) ion and carbon dioxide by adding activated carbon (AC) in an aqueous solution, taking a rate law of the first order with respect to the concentrations of not only $[Co(ox)_3]^{3-}$, but also AC. The rate of decomposition was independent of the pH values over a wide range of 2—8. On the contrary, the pentaammineaquacobalt(III) ion, $[Co(NH_3)_5(H_2O)]^{3+}$, did not decompose at all under the same conditions. When the same reaction mixtures as mentioned above contained ethylenediaminetetraacetate (EDTA), which denotes all forms of H_4edta, H_3edta^-, H_2edta^{2-} etc., both of the complexes, $[Co(ox)_3]^{3-}$ and $[Co(NH_3)_5(H_2O)]^{3+}$, converted quantitatively to $[Co(edta)]^-$, taking a first-order rate law with respect to the concentration of either $[Co(ox)_3]^{3-}$ or $[Co(NH_3)_5(H_2O)]^{3+}$. The rate was proportional to the added AC amounts, and was extremely inhibited by adding 8-quinolinol (oxine), methanol, or ethanol. The pH dependence on the reaction rates was extremely different in $[Co(ox)_3]^{3-}$ and $[Co(NH_3)_5(H_2O)]^{3+}$; the rate in the former case was independent of the pH in the 2—5, and decreased at less than 2 and at larger than 5; that in the latter case was maximum at around pH 6, and decreased accordingly to pH's less or larger than ca. 6, and became almost zero at pH 2. Such differences in the kinetic behavior are discussed.

In our previous paper[1)] the kinetics and mechanisms of AC catalysis for the ligand-substitution reaction between the inert complex $[Co(NH_3)_5Cl]^{2+}$ and EDTA in an aqueous solution were reported, where not only the pH effect, but also the inhibiting effect, on the rate were not studied. Thus, the present work was performed in order to compare and confirm the mechanisms of AC catalysis, changing the types of the analogous cobalt(III) complexes. Since 8-quinolinol (or oxine) is a strong adsorbent onto AC, the inhibiting effect of oxine on the AC catalyzed-reaction rate in the present study confirms that the surface of AC particles acts as an active site. We studied the effect of methanol and ethanol with the purpose of examining the existence or non-existence of a cation-radical intermediate, such as $AC^{+}\cdot[Co(ox)_3]^{4-}$ or $AC^{+}\cdot[Co(NH_3)_5(H_2O)]^{2+}$, in the light of the opposite sign in the cobalt complexes.

Experimental

Reagents. After activated carbon (AC) (Wako Pure Chemical Co., Ltd.) was stirred to wash with 1 mol dm^{-3} hydrochloric acid for 3—4 h, it was washed thoroughly with distilled water, kept over night in distilled water and then filtered. The AC obtained was dried at 100—120 °C. The AC powders were over 100 mesh (i.e., over 90% passed through 100 mesh filter). $K_3[Co(ox)_3]\cdot 3H_2O$ and $[Co(NH_3)_5(H_2O)]Cl_3$ were synthesized following a method described in the literature[2—4)] and recrystallized twice. Disodium dihydrogen ethylenediaminetetraacetate ($Na_2[(H_2edta)]$) and other chemicals used were of guaranteed-reagent grade. Deionized water was further distilled in a glass still.

Procedure. The reaction was initiated by adding the AC into 100 cm^3 solutions containing the cobalt(III) complexes without or with EDTA in a given pH. The pH values were changed by using H_2SO_4, $NaHSO_4$, CH_3COOH, CH_3COONa, H_3PO_4, NaH_2PO_4, Na_2HPO_4, or Na_3PO_4. Preliminary experiments showed that the reaction scarcely occurred without stirring the reaction solution, and was dependent on the stirring velocity. Further, it was confirmed that the reaction rate became constant under rigorous stirring. Thus, the reaction mixture was always stirred regorously with a magnetic stirrer in order to make a homogeneous suspension of the AC powder for the given times. After filtration, the concentrations of the cobalt(III) complexes remaining and the product of $[Co(edta)]^-$ were determined spectrophotometrically. The maximum molar absorption coefficients of $[Co(ox)_3]^{3-}$ are 166 and 219 dm^3 mol^{-1} cm^{-1} at 600 and 421 nm, respectively, and those of $[Co(NH_3)_5(H_2O)]^{3+}$, 47.9 and 47.8 dm^3 mol^{-1} cm^{-1} at 490 and 345 nm, respectively. The maximum molar absorption coefficient of $[Co(edta)]^-$ is 324 dm^3 mol^{-1} cm^{-1} at 536 nm. The concentrations of $[Co(ox)_3]^{3-}$ and $[Co(edta)]^-$ in the reacting solution in the presence of EDTA were determined using the following equations:

$$[Co^{III}]_{t=t} + [[Co(edta)]^-]_{t=t} = [Co^{III}]_{t=0} \quad (1)$$

$$A_{536} = \varepsilon_1[Co^{III}]_{t=t} + \varepsilon_2[[Co(edta)]^-]_{t=t}. \quad (2)$$

Here, $Co^{III} = [Co(ox)_3]^{3-}$ or $[Co(NH_3)_5(H_2O)]^{3+}$, and A_{536} indicates the absorbance of the reaction mixture at 536 nm; the values of ε_1 and ε_2 are 47 (or 31) and 324 dm^3 mol^{-1} cm^{-1} as the absorption coefficients at 536 mn for the $[Co(ox)_3]^{3-}$ (or $[Co(NH_3)_5(H_2O)]^{3+}$) and $[Co(edta)]^-$ species, respectively.

There were clearly the isosbestic points in the spectral change in the case of the reaction between $[Co(ox)_3]^{3-}$ and EDTA (see Fig. 1).

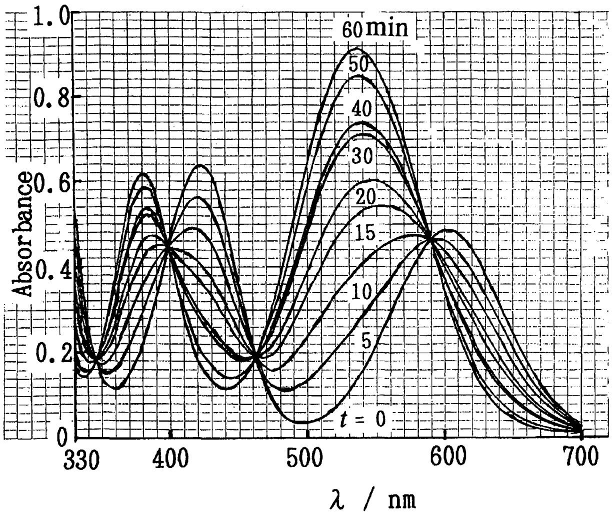

Fig. 1. An example of the photoabsorption spectra change by the ligand-substitution reaction between $[Co(ox)_3]^{3-}$ and EDTA with the progress of the reaction times. Initial conditions are 3×10^{-3} mol dm^{-3} $K_3[Co(ox)_3]$, 5×10^{-3} mol dm^{-3} $Na_2[H_2edta]$, 0.05 mol dm^{-3} CH_3COOH–CH_3COONa (pH 4.7), AC=10 mg/100 cm^3, and 20—23 °C.

The concentrations of the oxalate ion dissociated by the decomposition of $[Co(ox)_3]^{3-}$ in the absence of EDTA were determined by titration with a permanganate ($KMnO_4$) solution after removing AC from the reaction mixture of $[Co(ox)_3]^{3-}$, which had decomposed thoroughly.

Results and Discussion

Rate Law. All of the kinetic experiments showed that concentrations of the cobalt(III) complexes decreased following the rate law of Eq. 3 up to completion of the reaction, and that the rate constants in the first-order plots increased proportionally to the amounts of added AC. Thus, the rate law was the same as in the case of $[Co(NH_3)_5Cl]^{2+}$ in a previous study,[1]

$$-d[Co^{III}]/dt = k_{obsd}[Co^{III}]. \tag{3}$$

The rate law was satisfied in both cases of the decomposition rate of $[Co(ox)_3]^{3-}$ in the absence of EDTA, and the ligand-substitution reaction rate of $[Co(ox)_3]^{3-}$ or $[Co(NH_3)_5(H_2O)]^{3+}$ in the presence of EDTA. Further, linear plots of ln $[Co^{III}]$ vs. t continued up to the completion of the reaction in a given pH, even when containing oxine or alcohols. This indicated no remarkable change in the catalytic activities of AC during the reaction times. The deviation in the obtained rate constants (k_{obsd}) at several runs was less than ca. 20% under the given conditions (refer to Fig. 4). As a preliminary experiment, after all of the tris(oxalato)cobaltate(III) ion in the absence of EDTA had decomposed in a solution saturated with air, oxygen, or nitrogen gas, and then after removing the AC, the concentrations of the oxalate ion were determined by the titration method with the standard potassium permanganate ($KMnO_4$) solution. All of the results obtained under several different conditions showed the ratio $[[Co(ox)_3]^{3-}]_{decomposed} : [ox]_{left}$ to be 2 : 5. Thus, the following stoichiometric equation can be written: $2[Co(ox)_3]^{3-} \rightarrow 2Co^{2+} + 5ox^{2-} + 2CO_2$. This is the same as in cases of the decomposition of $[Co(ox)_3]^{3-}$ in a strongly acid solution without AC[5] and in those of the photo-sensitized decomposition of $[Co(ox)_3]^{3-}$ using $[Ru(bpy)_3]^{2+}$ as a sensitizer.[6]

Effect of 8-Quinolinol (Oxine). Preliminary experiments showed that the reaction rates in all cases were proportional to the AC amounts. This fact indicates that the catalyzed reaction rate is dependent on the surface area and the powder size of AC; as written in the reagent section, the AC powders used were over 100 mesh. Thus, we examined the effect of an adsorbing agent oxine on the AC-catalytic reaction rate. As a preliminary experiment, adsorption isotherm plots for the oxine adsorption onto AC were made; it was confirmed that over 90% oxine of 10^{-4}—10^{-3} mol dm^{-3} could adsorb on the AC-surface under the conditions given in Fig. 2. The AC-catalyzed reaction kinetics containing oxine were carried out as follows: A solution containing the given amounts of AC with oxine was stirred for 30 min, which was preliminarily determined as the adsorption-equilibrium time, and was then mixed with Co^{III} solution in the absence or presence of EDTA. The observed rate constants in Eq. 3 were plotted against the concentrations of oxine (Fig. 2). The rate constants in all cases decreased greatly with increasing the oxine concentrations. This was due to a decrease in the active area on AC due to oxine adsorption.

Effect of Methanol and Ethanol. The rates of all cases in Eq. 3 decreased extremely upon the presence of either

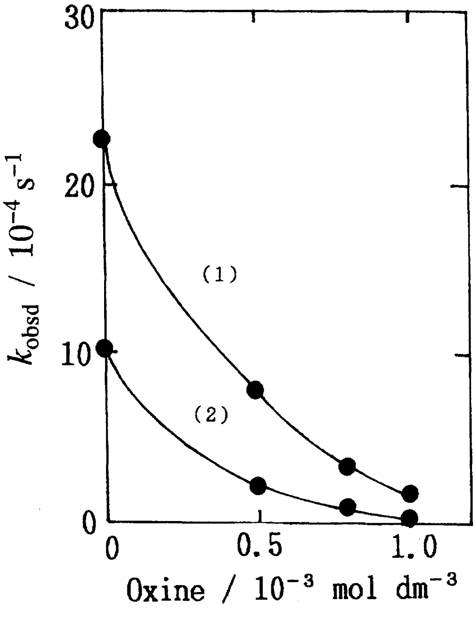

Fig. 2. Effect of oxine. Curves (1) and (2) indicate the cases of $[Co(ox)_3]^{3-}$ and $[Co(NH_3)_5(H_2O)]^{3+}$, respectively. Conditions are $[Co^{III}]_{t=0}$ = 2.0×10^{-3} mol dm^{-3}, $[EDTA]_{t=0}$ =0 for (1); 3.0×10^{-3} mol dm^{-3} for (2), 0.05 mol dm^{-3} CH_3COOH–CH_3COONa (pH 4.7), AC=50 mg/100 cm^3, and 24—27 °C.

methanol or ethanol (see Fig. 3), being similar to the case concerning the oxine effect of Fig. 2. This indicates that the inhibiting effect of alcohols is not caused by a permittivity decrease according to the addition of alcohols, but by the adsorption of alcohols onto the AC surface, being the same as in the case of oxine, and that such an inhibition is not related to the charge sign of the cobalt(III) complexes.

pH Effect on the Rate. As can be seen from Fig. 4, the case of $[Co(ox)_3]^{3-}$ was very different from that of $[Co(NH_3)_5(H_2O)]^{3+}$. The great decreases in k_{obsd} at a pH range less than 2 in the case of $[Co(ox)_3]^{3-}$ and at pH's less than 6 in the case of $[Co(NH_3)_5(H_2O)]^{3+}$ in the presence of EDTA are thought to be due to an increase in the protonation species of $[H_n edta]^{(4-n)-}$. However, the pH values in the initiation of such a decrease are extremely different in both complexes. In the case of $[Co(ox)_3]^{3-}$, the rate remained almost constant in the pH range 2.0—4.5, and might have been controlled by the lability or instability of the cobalt(III) species on the surface of AC. Namely, despite an increase in the protonated species of EDTA with decreasing pH's toward pH 2, the rate was constant within the pH range, having the same behavior as that in the absence of EDTA (compare the plots ● and ○ in (A) of Fig. 4). However, in the case of $[Co(NH_3)_5(H_2O)]^{3+}$, the rate is thought to be controlled by the reaction rate between $\{AC^+\cdot[Co(NH_3)_5(H_2O)]^{2+}\}$ and $[H_n edta]^{(4-n)-}$ to form $\{AC^+\cdot[Co(edta)]^{2-}\}$, which is rapidly converted to AC and $[Co(edta)]^-$. This is the same as in the reaction mechanism on $[Co(NH_3)_5Cl]^{2+}$ in the previous study.[1)]

The reaction rates in both complexes (see plots ● in Fig. 4) decreased at pH's larger than 5—6. At this pH range the predominant species of EDTA were H_2edta^{2-} and $Hedta^{3-}$. The fewer proton species in EDTA results in a larger capability in coordination to cobalt(III) or (II) ions. Nevertheless, the rates decreased with increasing pH. Thus, this is probably due to the inertness increase of the cobalt species in the proposed intermediates, $\{AC\cdot[Co(ox)_3]^{3-}\}$ and $\{AC^+\cdot[Co(NH_3)_5(H_2O)]^{2+}\}$, for the ligand-substitution reactions with EDTA. As another explanation in the case of the ammine complex, the rate decrease may be due to the hydrated species, $[Co(NH_3)_5(OH)]^{2+}$, which is formed at a larger pH. In fact, the ammine complex was precipitated at larger pH's than 7. On the other hand, the oxalato complex was not precipitated, even at pH 10, at all. This indicates that

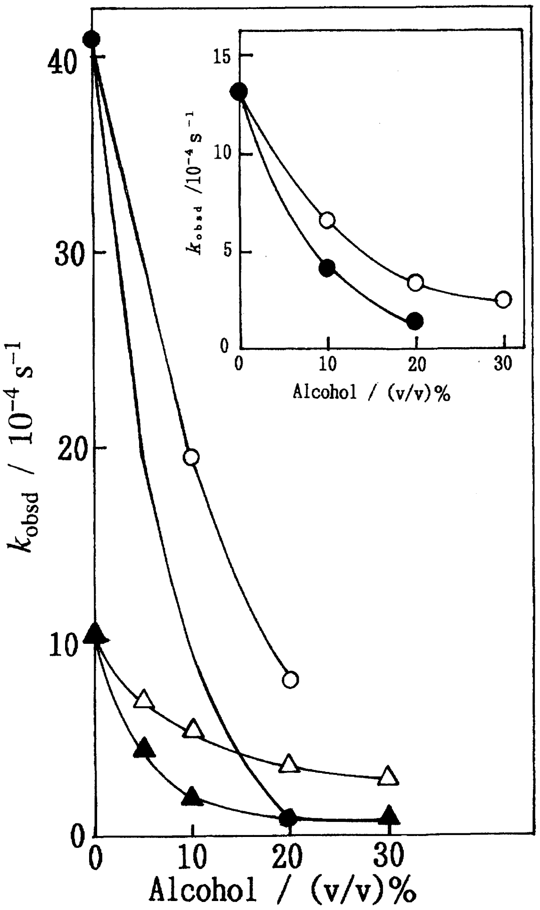

Fig. 3. Effect of alcohols. Plots ○ and △ indicate the effects of methanol, ● and ▲, those of ethanol, where plots ○ and ● indicate the cases of $[Co(ox)_3]^{3-}$, and △ and ▲, those of $[Co(NH_3)_5(H_2O)]^{3+}$. Conditions are $[Co^{III}]_{t=0} = [EDTA]_{t=0} = 2.0\times10^{-3}$ mol dm^{-3}, 0.05 mol dm^{-3} CH_3COOH–CH_3COONa (pH 4.7—5.1), AC=50 mg/100 cm^3, and 24—28 °C, where cases in the inset are without EDTA and 20—23 °C.

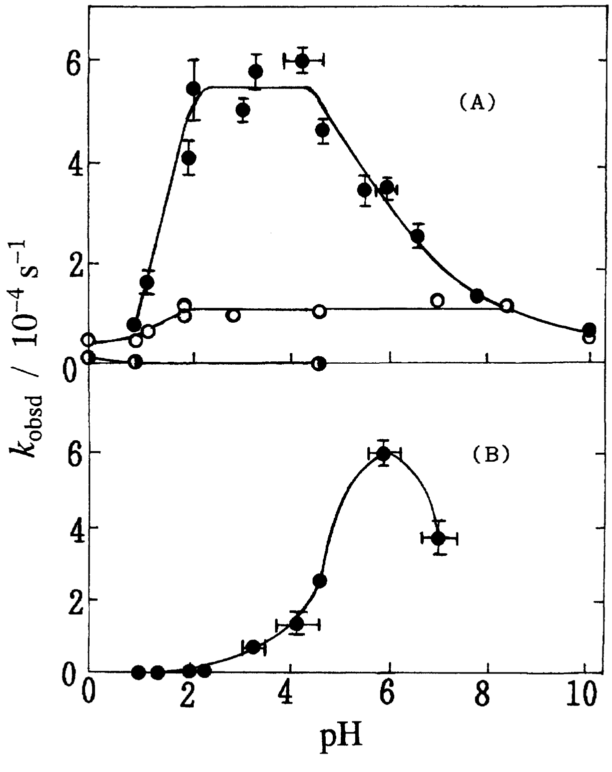

Fig. 4. Effect of pH. (A) and (B) indicate the cases of $[Co(ox)_3]^{3-}$ and $[Co(NH_3)_5(H_2O)]^{3+}$, respectively. Conditions are $[Co^{III}]_{t=0} = 2.0\times10^{-3}$ mol dm^{-3}, $[EDTA]_{t=0} = 3.0\times10^{-3}$ mol dm^{-3}, AC =10 mg/100 cm^3 for (A) and 50 mg/100 cm^3 for (B), and 16—21 °C, where plots ○ and ◑ in (A) indicate the case without EDTA and that without both EDTA and AC, respectively.

the oxalato complex is extremely stable against hydrolysis (or the ligand-substitution by OH^-) in an alkaline solution, and that the substitution inertness of the complex increased with increasing pH's in solution.

Further, it was noted that the AC-catalyzed ligand-substitution rate in the oxalato complex became almost the same as the AC-catalyzed decomposition rate at pH's less than 1 or larger than 8, and that the decomposition rate of $[Co(ox)_3]^{3-}$ was much accelerated by AC, even in a solution of pH zero. These facts are also related to the reaction mechanisms of the oxalato complex. Namely, an unstable species of $\{AC \cdot [Co(ox)_3]^{3-}\}$, in which the cobalt(III) ion is capable of oxidizing the oxalate ligand, is formed quickly and followed to decompose or be substituted by EDTA.

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