The Kinetics of Substitution Reactions Involving Metal Complexes. VIII. Reaction between Copper(II) and Ethylenediaminetetraacetato-cobaltate(II) Complexes in Aqueous Solutions

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In the previous paper[1] the kinetics of the substitution reaction of lead(II) ions and ethylenediaminetetraacetatocobaltate(II) complexes (cabalt(II)-EDTA) was dealt with. The reaction was found to proceed through four simultaneous reaction paths including the reaction paths in which the dissociation of cobalt(II)-EDTA complexes is rate-determining. This kind of rate-determining step was not observed in other substitution reactions[2-8] except the

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[1] N. Tanaka, H. Osawa, and M. Kamada, This Bulletin, **36**, 67 (1963).

[2] H. Ackermann and G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 485 (1952).

[3] K. Bril, S. Bril and P. Krumholz, *J. Phys. Chem.*, **59**, 596 (1955); **60**, 251 (1956).

[4] N. Tanaka, K. Kato and R. Tamamushi, This Bulletin, **31**, 283 (1958).

[5] N. Tanaka and K. Kato, ibid., **32**, 1376 (1959).

[6] K. Kato, ibid., **33**, 600 (1960).

[7] N. Tanaka and K. Kato, ibid., **33**, 1236 (1960).

[8] N. Tanaka and M. Kamada, ibid., **35**, 1596 (1962).

substitution reaction involving nickel(II)-EDTA complexes⁹⁾.

In this paper, the kinetic study of the reaction between copper(II) ions and cobalt(II)-EDTA complexes

$$\mathrm{Cu^{2+} + CoY^{2-} \rightleftarrows CuY^{2-} + Co^{2+}} \qquad (1)$$

is presented.

Derivation of the Rate Equation

In the preliminary experiments that were carried out in the presence of large excess of cobalt(II) ions and cobalt(II)-EDTA complexes over copper(II) ions, the following facts were found out.

(1) In the solutions of the given pH and the given concentrations of $[\mathrm{Co^{2+}}]_{0,\mathrm{app}}$, $[\mathrm{Cu^{2+}}]_{0,\mathrm{app}}$ and $[\mathrm{OAc^-}]$, the apparent reaction rate of the forward reaction is proportional to the initial concentration of Co(II)-EDTA ($[\mathrm{CoY^{2-}}]_0$), and $k^+/[\mathrm{CoY^{2-}}]_0$ is independent of $[\mathrm{CoY^{2-}}]_0$, where k^+ means the apparent rate constant of the forward reaction, the subscript 0 means zero time, and $[\mathrm{Cu^{2+}}]_{\mathrm{app}}$ and $[\mathrm{Co^{2+}}]_{\mathrm{app}}$ represent the apparent concentrations that can be determined polarographically¹⁰⁾. In the solutions that contain less than 0.2 M of acetate ions, $[\mathrm{Cu^{2+}}]_{\mathrm{app}}$ and $[\mathrm{Co^{2+}}]_{\mathrm{app}}$ are given by

$$\begin{aligned}[\mathrm{Cu^{2+}}]_{\mathrm{app}} &= [\mathrm{Cu^{2+}}] + [\mathrm{CuOAc^+}] \\ &\quad + [\mathrm{Cu(OAc)_2}] \\ [\mathrm{Co^{2+}}]_{\mathrm{app}} &= [\mathrm{Co^{2+}}] + [\mathrm{CoOAc^+}] \qquad (2)\end{aligned}$$

(2) In the solutions of the given pH and the given concentrations of $[\mathrm{Co^{2+}}]_{0,\mathrm{app}}$, $[\mathrm{CoY^{2-}}]_0$ and $[\mathrm{OAc^-}]$, the apparent reaction rate is proportional to $[\mathrm{Cu^{2+}}]_{0,\mathrm{app}}$, and $k^+/[\mathrm{CoY^{2-}}]_0$ is independent of $[\mathrm{Cu^{2+}}]_{0,\mathrm{app}}$.

(3) In the solutions of the given concentrations of $[\mathrm{Co^{2+}}]_{0,\mathrm{app}}$, $[\mathrm{CoY^{2-}}]_0$, $[\mathrm{Cu^{2+}}]_{0,\mathrm{app}}$ and $[\mathrm{OAc^-}]$, $k^+/[\mathrm{CoY^{2-}}]_0$ is a linear function of the hydrogen ion concentration, and given by the equation

$$k^+/[\mathrm{CoY^{2-}}]_0 = k_\xi + k_\eta [\mathrm{H^+}] \qquad (3)$$

where k_η is dependent on the value of $[\mathrm{Co^{2+}}]_{0,\mathrm{app}}$.

(4) In the solutions of the given pH and the given concentrations of $[\mathrm{CoY^{2-}}]_0$, $[\mathrm{Cu^{2+}}]_{0,\mathrm{app}}$ and $[\mathrm{OAc^-}]$, $k^+/[\mathrm{CoY^{2-}}]_0$ is a linear function of the reciprocal of $[\mathrm{Co^{2+}}]_{0,\mathrm{app}}$ and given by the equation,

$$k^+/[\mathrm{CoY^{2-}}]_0 = k_\varepsilon + k_\gamma/[\mathrm{Co^{2+}}]_{0,\mathrm{app}} \qquad (4)$$

These observed facts clearly indicate that the mechanism of the reaction between copper(II) ions and cobalt(II)-EDTA complexes would be the same as the reaction between copper(II) ions and lead(II)-EDTA complexes⁵⁾ but not the reaction between lead(II) ions and cobalt(II)-EDTA complexes¹⁾.

After the analogy of the reaction between copper(II) ions and lead(II)-EDTA complexes, the present reaction is considered to proceed through three simultaneous reaction paths.

$$\text{(i)} \quad \mathrm{Cu^{2+} + CoY^{2-}} \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} \mathrm{CuY^{2-} + Co^{2+}} \qquad (5)$$

$$\text{(ii)} \quad \mathrm{CoY^{2-} + H^+ \rightleftharpoons CoHY^-} \qquad (6a)$$

$$\mathrm{Cu^{2+} + CoHY^-} \underset{k_{\mathrm{II}}^-}{\overset{k_{\mathrm{II}}^+}{\rightleftharpoons}} \mathrm{CuHY^- + Co^{2+}} \qquad (6b)$$

$$\mathrm{CuHY^- \rightleftharpoons CuY^{2-} + H^+} \qquad (6c)$$

$$\text{(iii)} \quad \mathrm{CoY^{2-} + H^+} \underset{k_a^-}{\overset{k_a^+}{\rightleftharpoons}} \mathrm{Co^{2+} + HY^{3-}} \qquad (7a)$$

$$\mathrm{Cu^{2+} + HY^{3-}} \underset{k_{\mathrm{III}}^-}{\overset{k_{\mathrm{III}}^+}{\rightleftharpoons}} \mathrm{CuY^{2-} + H^+} \qquad (7b)$$

Assuming that the reaction proceeds through the hydrated ions, the apparent rate of the forward reaction v^+ is expressed as Eq. 8.

$$\begin{aligned} v^+ &= k^+ [\mathrm{Cu^{2+}}]_{\mathrm{app}} \\ &= \left\{ \frac{k_1^+ + k_2^+[\mathrm{H^+}] + k_3^+[\mathrm{H^+}]\dfrac{1 + K_{\mathrm{CoOAc}}[\mathrm{OAc^-}]}{[\mathrm{Co^{2+}}]_{\mathrm{app}}}}{1 + \sum\limits_{n=1}^{2} K_{\mathrm{Cu(OAc)}_n} [\mathrm{OAc^-}]^n} \right\} \\ &\quad \times [\mathrm{Cu^{2+}}]_{\mathrm{app}} [\mathrm{CoY^{2-}}] \qquad (8)\end{aligned}$$

where

$$k_2^+ = k_{\mathrm{II}}^+ K^{\mathrm{H}}_{\mathrm{CoHY}}, \quad k_3^+ = k_{\mathrm{III}}^+/(K_{\mathrm{CoY}} K_{\mathrm{HY}}) \qquad (9)$$

$K_{\mathrm{Cu(OAc)}_n}$, K_{CoOAc} and K_{CoY} represent the formation constants of acetatocopper(II), acetatocobalt(II) and cobalt(II)-EDTA complexes, respectively, K_{HY}, the fourth dissociation constant of ethylenediaminetetraacetic acid, and $K^{\mathrm{H}}_{\mathrm{CoHY}}$, the equilibrium constant of Eq. 6a.

Experimental

The preparation of the solutions of copper(II) nitrate, cobalt(II) nitrate, disodium ethylenediaminetetraacetate and sodium acetate-acetic acid buffers was described in the previous paper¹⁰⁾. Sodium carbonate, acetic acid and other reagents used for the supporting electrolyte were of guaranteed reagent grade and used without further purification.

The rate of the reaction between copper(II) ions and cobalt(II)-EDTA complexes was followed by measuring the change of the polarographic diffusion current of copper(II) ions with time in acetate buffer solutions at 5 and 15°C. The apparatus used was the same as described in the previous

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9) N. Tanaka, Y. Sakuma and G. Satô, presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto (1959), Lecture No. 1032.

10) N. Tanaka, M. Kamada, H. Osawa and G. Satô, This Bulletin, 33, 1412 (1960).

paper[1]. The experimental procedure was also given previously[4,6,8].

Results

Since the kinetic measurements are carried out in the solutions that contain cobalt(II) ions and cobalt(II)-EDTA complexes in excess over copper(II) ions, the substitution reaction can be treated as a pseudo first-order reaction, and the apparent reaction rate is expressed as

$$-\frac{\mathrm{d}[\mathrm{Cu}^{2+}]_{\mathrm{app}}}{\mathrm{d}t}=k^{+}[\mathrm{Cu}^{2+}]_{\mathrm{app}}-k^{-}[\mathrm{CuY}^{2-}] \tag{10}$$

where k^+ and k^- are the apparent rate constants for the forward and the reverse reaction, respectively.

Comparing Eq. 8 with Eq. 10, Eq. 11 is obtained

$$\frac{k^{+}}{[\mathrm{CoY}^{2-}]_0}=\left\{\frac{k_1^{+}+k_2^{+}[\mathrm{H}^{+}]+k_3^{+}[\mathrm{H}^{+}]\dfrac{1+K_{\mathrm{CoOAc}}[\mathrm{OAc}^{-}]}{[\mathrm{Co}^{2+}]_{0,\mathrm{app}}}}{1+\sum\limits_{n=1}^{2}K_{\mathrm{Cu(OAc)}_n}[\mathrm{OAc}^{-}]^{n}}\right\} \tag{11}$$

where the initial concentrations, $[\mathrm{Co}^{2+}]_{0,\mathrm{app}}$ and $[\mathrm{CoY}^{2-}]_0$, are substituted for $[\mathrm{Co}^{2+}]_{\mathrm{app}}$ and $[\mathrm{CoY}^{2-}]$, respectively.

The values of $k^+/[\mathrm{CoY}^{2-}]_0$ were obtained at various pH's at two different concentrations of cobalt(II) ions but at the same concentrations of other species, and plotted against the hydrogen ion concentration. The plots for 15°C are given in Fig. 1, which indicate linear relations existing between $k^+/[\mathrm{CoY}^{2-}]_0$ and $[\mathrm{H}^+]$. Similar relations were observed also at 5°C.

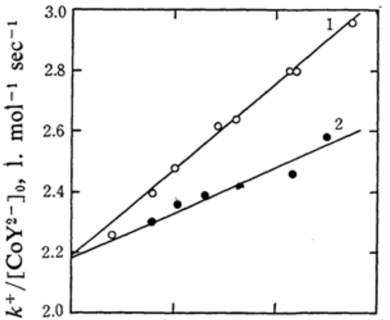

Fig. 1. $k^+/[\mathrm{CoY}^{2-}]_0$ as a function of the hydrogen ion concentration in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 15°C. Initial concentrations are: $[\mathrm{Cu}^{2+}]_{0,\mathrm{app}}=2.0\times10^{-4}$ M; $[\mathrm{CoY}^{2-}]_0=5.00\times10^{-3}$ M; $[\mathrm{Co}^{2+}]_{0,\mathrm{app}}=5.00\times10^{-3}$ M (curve 1) and 15.00×10^{-3} M (curve 2). Concentration of free acetate is 0.10 M.

The rate constants in Eq. 8 were calculated from the plots in Fig. 1, when $K_{\mathrm{Cu(OAc)}_n}$ and K_{CoOAc} that were reported in the previous papers[10,11] were employed. With these constants, the rate constants for both elementary reactions 6b and 7b were calculated using Eqs. 9 and the values of $K^{\mathrm{H}}_{\mathrm{CoHY}}$, K_{CoY} and K_{HY} which were evaluated with the same procedure as described previously[4,6]. The results were given in Table I.

TABLE I. RATE CONSTANTS FOR REACTIONS 5, 6b AND 7b AT IONIC STRENGTH 0.2

Temp. °C	Rate constant, l. mol^{-1} sec^{-1}		
	k_1^+	k_{II}^+	k_{III}^+
5	7.0	(1.2×10^2)[a]	(3.1×10^8)[a]
15	15.3	(1.5×10^2)[a]	(6.2×10^8)[a]

a) Values in parentheses are less accurate.

Discussion

The rate constant k_{III}^+ for the reaction

$$\mathrm{Cu}^{2+}+\mathrm{HY}^{3-}\xrightarrow{k_{\mathrm{III}}^{+}}\mathrm{CuY}^{2-}+\mathrm{H}^{+}$$

has been determined in the studies of other substitution reactions. These are given in Table II with the value obtained in this study, where it is seen that the value obtained with the substitution reaction between copper(II) ions and cobalt(II)-EDTA complexes is considerably smaller than those obtained with other substitution reactions.

In reaction path iii, the concentration of HY^{3-} is given by

$$[\mathrm{HY}^{3-}]=\frac{k_a^{+}[\mathrm{CoY}^{2-}]+k_{\mathrm{III}}^{-}[\mathrm{CuY}^{2-}]}{k_a^{-}[\mathrm{Co}^{2+}]+K_{\mathrm{III}}^{+}[\mathrm{Cu}^{2+}]}[\mathrm{H}^{+}] \tag{12}$$

The rate of reaction path iii, therefore, is expressed as Eq. 13, where v_3^+ and v_3^- are the rates of the forward and the reverse reaction of path iii, respectively. When the condition

$$k_{\mathrm{III}}^{+}[\mathrm{Cu}^{2+}]\ll k_a^{-}[\mathrm{Co}^{2+}] \tag{14}$$

is assumed, Eq. 13 can be reduced to a simpler

$$v_3=v_3^{+}-v_3^{-}=\frac{k_a^{+}k_{\mathrm{III}}^{+}[\mathrm{CoY}^{2-}][\mathrm{Cu}^{2+}]-k_a^{-}k_{\mathrm{III}}^{-}[\mathrm{CuY}^{2-}][\mathrm{Co}^{2+}]}{k_a^{-}[\mathrm{Co}^{2+}]+k_{\mathrm{III}}^{+}[\mathrm{Cu}^{2+}]}[\mathrm{H}^{+}] \tag{13}$$

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[11] N. Tanaka and K. Kato, This Bulletin, 33, 417 (1960).

TABLE II. RATE CONSTANT k_{III}^+ FOR THE REACTION $Cu^{2+}+HY^{3-} \rightarrow CuY^{2-}+H^+$ OBTAINED WITH VARIOUS SUBSTITUTION REACTIONS

Substitution reaction	k_{III}^+, l. mol^{-1} sec^{-1}		Ref.
	5°C	15°C	
$Cu^{2+}+PbY^{2-} \rightleftarrows CuY^{2-}+Pb^{2+}$	—	1.7×10^9	(5)
$Cu^{2+}+ZnY^{2-} \rightleftarrows CuY^{2-}+Zn^{2+}$	—	2.0×10^9	(6)
$Cu^{2+}+CdY^{2-} \rightleftarrows CuY^{2-}+Cd^{2+}$	5.7×10^8	1.3×10^9	(8)
$Cu^{2+}+CoY^{2-} \rightleftarrows CuY^{2-}+Co^{2+}$	3.1×10^8	6.2×10^8	This study

TABLE III. CONTRIBUTION OF EACH REACTION PATH TO THE OVERALL REACTION $[Cu^{2+}]_{0,\mathrm{app}}=2.0\times10^{-4}$ M, $[CoY^{2-}]_0=5.00\times10^{-3}$ M

$[Co^{2+}]_{0,\mathrm{app}}\times10^3$ M	Reaction path	A[a]		B[b]	
		Rate$\times10^6$, mol. l^{-1} sec^{-1}	%	Rate$\times10^6$, mol. l^{-1} sec^{-1}	%
5.00	i	2.1_9	90	2.1_9	78
	ii	0.0_7	3	0.1_8	6
	iii	0.1_6	7	0.4_3	16
	Total	2.4_2		2.8_0	
15.00	i	2.1_9	95	2.1_9	88
	ii	0.0_7	3	0.1_8	7
	iii	0.0_4	2	0.1_3	5
	Total	2.3_0		2.5_0	

[a] $[H^+]=3.95\times10^{-6}$ M

[b] $[H^+]=1.06\times10^{-5}$ M

form and the apparent rate of the forward reaction v_3^+ is given by

$$\begin{aligned} v_3^+ &= k_3^+ \frac{[H^+]}{[Co^{2+}]}\ [Cu^{2+}]\ [CoY^{2-}] \\ &= k_3^+ \frac{1+K_{\mathrm{CoOAc}}[OAc^-]}{1+\sum_{n=1}^{2}K_{\mathrm{Cu(OAc)}_n}[OAc^-]^n}\ \frac{[H^+]}{[Co^{2+}]_{\mathrm{app}}} \\ &\quad \times [Cu^{2+}]_{\mathrm{app}}[CoY^{2-}] \end{aligned} \tag{15}$$

In the substitution reaction between copper(II) ions and cobalt(II)-EDTA complexes, the condition given in Eq. 14 was found not to be satisfied. The ratio of $k_a^-[Co^{2+}]$ to $k_{\mathrm{III}}^+[Cu^{2+}]$ $(=(k_a^-[Co^{2+}])/(k_{\mathrm{III}}^+[Cu^{2+}]))$ that was calculated with k_{III}^+ and k_a^- obtained in this and the previous[1] studies respectively ranged from 0.7 to 4 under the experimental condition. When Ep. 14 is not fulfilled, $k^+/[CoY^{2-}]_0$ can not be a linear function of $1/[Co^{2+}]_{0,\mathrm{app}}$.

The experimental results, however, showed that $k^+/[CoY^{2-}]_0$ was proportional to the reciprocal of $[Co^{2+}]_{0,\mathrm{app}}$ and independent of $[Cu^{2+}]_{0,\mathrm{app}}$. This discrepancy may arise from a small contribution of reaction path iii to the overall reaction. Percentage of the contribution of each reaction path to the overall reaction is given in Table III, which clearly shows that the reaction proceeding through reaction path iii gives only minor contribution to the whole reaction. This fact supports the linearity between $k^+/[CoY^{2-}]_0$ vs. $1/[Co^{2+}]_{0,\mathrm{app}}$ obtained in the experiments. Consequently, it seems reasonable to consider that the rate constant of reaction path i, k_1^+, obtained in this study is acceptable.

It is interesting to compare the substitution reaction between copper(II) ions and cobalt(II)-EDTA complexes with that between lead(II) ions and cobalt(II)-EDTA complexes. In the former the contribution of the reaction path i to the whole reaction is approximately 90%, whereas in the latter it is only several per cents. In reaction path iii, the dissociation of cobalt(II)-EDTA complexes is rate-determining in the reaction between lead (II) ions and cobalt(II)-EDTA complexes but not in the reaction between copper(II) ions and cobalt(II)-EDTA complexes. This suggests that the dissociation of cobalt(II)-EDTA complex is not so slow.

Summary

The kinetic study of the substitution reaction of copper(II) ions and cobalt(II)-EDTA complexes in acetate buffer solutions has been carried out with the same procedure as that reported previously. The reaction was found to proceed, under the experimental conditions, through three simultaneous reaction paths similar to those found in the substitution

reaction of copper(II) ions and lead(II)-EDTA complexes. The rate constants for three elementary reactions of those reaction paths were determined at ionic strength 0.2 at 5 and 15°C. A reaction path in which the dissociation of cobalt(II)-EDTA complex is rate-determining was not observed in this substitution reaction.

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