The Kinetics of Substitution Reactions Involving Metal Complexes. III. Reaction between Copper(II) and Zinc-Ethylenediaminetetraacetate Complexes in Aqueous Solutions*

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In the previous papers[1,2], the substitution reaction of copper(II) ions and lead-ethylenediaminetetraacetate (EDTA) complexes was reported. The rate of the reaction was followed by measuring the change of the polarographic diffusion current of copper(II) ions with the time. The reaction was found to proceed simultaneously through three different reaction paths.

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

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

under the experimental conditions, and the rate constants of the elementary reactions of those reaction paths were determined. The effect of acetate ions on the rate of the substitution reaction was explained quantitatively on the basis of the formation of acetato complexes of copper(II) and lead(II) and on the assumption that the substitution reaction proceeds only through the hydrated metal ions.

Since it seemed worth while to extend the study to the substitution reactions involving EDTA-complexes of other metal ions, the substitution reaction of copper(II) ions and zinc-EDTA complexes

$$\mathrm{Cu}^{2+} + \mathrm{ZnY}^{2-} \rightleftarrows \mathrm{CuY}^{2-} + \mathrm{Zn}^{2+}$$

was dealt with. The results are presented in this paper.

Experimental

The preparation of solutions of copper(II) nitrate and disodium ethylenediaminetetraacetate was described in the previous paper1). A solution of zinc nitrate was prepared by dissolving a known amount of pure zinc metal in reagent-grade nitric acid.

The rate of the reaction between copper(II) ions and zinc-EDTA complexes was followed by measuring the change with the time in the polarographic diffusion current of copper(II) ions in acetate buffer solutions. Current-time curves were obtained with a Shimadzu RP-2 pen-recording polarograph. The dropping mercury electrode described in the previous paper1) was used. This had an *m* value of 1.27 mg./sec. and a drop time of 3.69 sec. in an air-free solution of 0.1 M potassium chloride at 25°C with open-circuit.

Measurements were made at 15 and 0°C in acetate buffers of pH 4.4 to 5.0 which contained 0.1 M of sodium acetate unless otherwise stated. The ionic strength was adjusted to be 0.2 with potassium nitrate. Gelatin was added as a maximum suppressor by 0.01% in concentration.

Results and Discussion

In the solution containing acetate ions less than 0.2 M in concentration, copper(II) forms mono- and diacetato complexes, whereas zinc(II) forms only a monoacetato complex3). Therefore, the overall substitution reaction of copper(II) ions and zinc-EDTA complexes in acetate buffer solution is represented by the equations

$$\mathrm{Cu}^{2+} + 2\,\mathrm{OAc}^- \rightleftarrows \mathrm{CuOAc}^+ + \mathrm{OAc}^- \rightleftarrows \mathrm{Cu(OAc)}_2 \tag{1}$$

$$\mathrm{Cu}^{2+} + \mathrm{ZnY}^{2-} \rightleftarrows \mathrm{CuY}^{2-} + \mathrm{Zn}^{2+} \tag{2}$$

$$\mathrm{Zn}^{2+} + \mathrm{OAc}^- \rightleftarrows \mathrm{ZnOAc}^+ \tag{3}$$

where Y^{4-} means a completely dissociated EDTA anion. Under the condition that both zinc ions and zinc-EDTA complexes are present in a large excess over copper(II) ions, the substitution reaction 2 can be simplified to

$$\mathrm{Cu}^{2+} \underset{k^-}{\overset{k^+}{\rightleftarrows}} \mathrm{CuY}^{2-} \tag{4}$$

The rate equation for reaction 4 is expressed as2)

$$-\frac{\mathrm{d}[\mathrm{Cu}^{2+}]_{\mathrm{app}}}{\mathrm{d}t} = k^+[\mathrm{Cu}^{2+}]_{\mathrm{app}} - k^-[\mathrm{CuY}^{2-}] \tag{5}$$

where $[\mathrm{Cu}^{2+}]_{\mathrm{app}}$ is the concentration of copper(II) that can be determined polarographically, and given by the equation

$$[\mathrm{Cu}^{2+}]_{\mathrm{app}} = [\mathrm{Cu}^{2+}] + [\mathrm{CuOAc}^+] + [\mathrm{Cu(OAc)}_2] \tag{6}$$

Integrating Eq. 5,

$$\ln\{[\mathrm{Cu}^{2+}]_{\mathrm{app}} - [\mathrm{Cu}^{2+}]_{\mathrm{e,app}}\} = -(k^+ + k^-)t + \ln\{[\mathrm{Cu}^{2+}]_{0,\mathrm{app}} - [\mathrm{Cu}^{2+}]_{\mathrm{e,app}}\}$$

is obtained, where subscripts 0 and e denote the initial and the equilibrium conditions, respectively. At the equilibrium of the reaction, the relation

$$\frac{k^+}{k^-} = \frac{[\mathrm{CuY}^{2-}]_{\mathrm{e}}}{[\mathrm{Cu}^{2+}]_{\mathrm{e,app}}} \fallingdotseq K^{\mathrm{Cu}}_{\mathrm{Zn,app}} \frac{[\mathrm{ZnY}^{2-}]_0}{[\mathrm{Zn}^{2+}]_{0,\mathrm{app}}}$$

may be satisfied, where $K^{\mathrm{Cu}}_{\mathrm{Zn,app}}$ represents the apparent equilibrium constant expressed as

$$K^{\mathrm{Cu}}_{\mathrm{Zn,app}} = \frac{[\mathrm{Zn}^{2+}]_{\mathrm{e,app}}[\mathrm{CuY}^{2-}]_{\mathrm{e}}}{[\mathrm{Cu}^{2+}]_{\mathrm{e,app}}[\mathrm{ZnY}^{2-}]_{\mathrm{e}}}$$

The values of $K^{\mathrm{Cu}}_{\mathrm{Zn,app}}$ were determined polarographically to be 76 at 15°C and 92 at 0°C in acetate buffer solutions which contained 0.1 M of sodium acetate.

The apparent rate constant, $k^+/[\mathrm{ZnY}^{2-}]_0$, was obtained at varied pH's at two different concentrations of zinc ions but at constant concentration of other species present. In Fig. 1 the values obtained at 15°C are plotted against the hydrogen ion concentration. This clearly indicates that a linear relation exists between $k^+/[\mathrm{ZnY}^{2-}]_0$ and $[\mathrm{H}^+]$. A similar relation was also found at 0°C.

On the basis of the dependencies of the observed apparent rate constants on the concentration of uncomplexed zinc ions, which are identical to those of the substitution reaction of copper(II) ions and lead-EDTA complexes1,2), the following mechanisms were set down for reaction 2:

$$\text{(i)}\quad \mathrm{Cu}^{2+} + \mathrm{ZnY}^{2-} \overset{k_1^+}{\rightleftarrows} \mathrm{CuY}^{2-} + \mathrm{Zn}^{2+} \tag{7}$$

$$\text{(ii)}\quad \mathrm{ZnY}^{2-} + \mathrm{H}^+ \rightleftarrows \mathrm{ZnHY}^- \tag{8a}$$

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3) N. Tanaka and K. Kato, ibid., 33, 417 (1960).

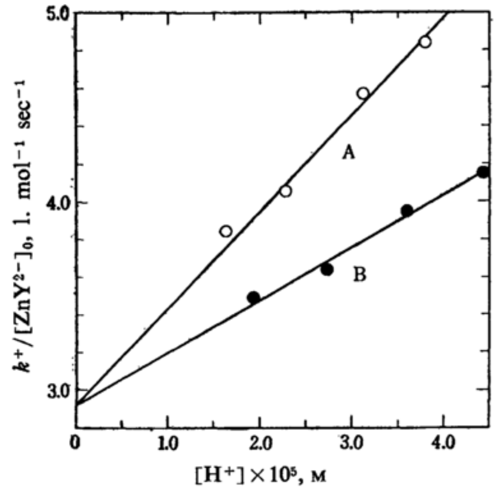

Fig. 1. $k^+/[ZnY^{2-}]_0$ as a function of the hydrogen ion concentration in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 15°C. Initial concentrations are: $[Cu^{2+}]_{0,\mathrm{app}}=1.20\times10^{-4}$ M; $[ZnY^{2-}]_0=4.03\times10^{-3}$ M; $[Zn^{2+}]_{0,\mathrm{app}}=1.12\times10^{-2}$ M (curve A) and 2.64×10^{-2} M (curve B). Concentrations of free acetate are: 0.096 M (A) and 0.091 M (B).

$$Cu^{2+} + ZnHY^- \overset{k_{II}^+}{\rightleftarrows} CuHY^- + Zn^{2+} \tag{8b}$$

$$CuHY^- \rightleftarrows CuY^{2-} + H^+ \tag{8c}$$

$$\text{(iii)}\quad ZnY^{2-} + H^+ \rightleftarrows Zn^{2+} + HY^{3-} \tag{9a}$$

$$Cu^{2+} + HY^{3-} \overset{k_{III}^+}{\rightleftarrows} CuY^{2-} + H^+ \tag{9b}$$

As has been mentioned previously[2)], the concentration which was actually measured polarographically was not the concentration of hydrated copper(II) ions but the sum of the concentrations of hydrated ions and acetato complexes. If it is assumed that the substitution reaction proceeds through only the hydrated metal ions which are in equilibrium with the acetato complexes, the apparent rate of the forward reaction ($v^+=k^+[Cu^{2+}]_{\mathrm{app}}$) determined polarographically is expressed as

$$v^+=\left\{\frac{k_1^+ + k_2^+[H^+] + k_3^+[H^+]\dfrac{1+K_{ZnAOc}[OAc^-]}{[Zn^{2+}]_{\mathrm{app}}}}{1+\sum_{n=1}^{2}K_{Cu(OAc)_n}[OAc^-]^n}\right\}\times[Cu^{2+}]_{\mathrm{app}}[ZnY^{2-}] \tag{10}$$

where

$$k_2^+=k_{II}^+K_{ZnHY}^{H},\quad k_3^+=k_{III}^+/(K_{ZnY}K_{HY}) \tag{11}$$

K_{ZnHY}^{H} represents the equilibrium constant of reaction 8a, K_{ZnY}, the formation constant of ZnY^{2-} and K_{HY}, the fourth dissociation constant of ethylenediaminetetraacetic acid. $K_{Cu(OAc)_n}$ and K_{ZnOAc} represent the overall formation constants of acetatocopper(II) and acetatozinc(II) complexes, respectively.

From Eqs. 5 and 10, the relation

$$\frac{k^+}{[ZnY^{2-}]_0}=\frac{k_1^+ + k_2^+[H^+] + k_3^+[H^+]\dfrac{1+K_{ZnOAc}[OAc^-]}{[Zn^{2+}]_{0,\mathrm{app}}}}{1+\sum_{n=1}^{2}K_{Cu(OAc)_n}[OAc^-]^n} \tag{12}$$

is obtained, where the initial concentrations, $[Zn^{2+}]_0$ and $[ZnY^{2-}]_0$, are substituted for $[Zn^{2+}]$ and $[ZnY^{2-}]$, respectively. Since both Zn^{2+} and ZnY^{2-} are present in the reaction mixture in a large excess over the concentration of copper(II), the changes of their concentrations can be neglected.

The rate constants in Eq. 10 were calculated from the plots of $k^+/[ZnY^{2-}]_0$ against hydrogen ion concentration, which are tabulated in Table I. The values of K_{CuOAc}, $K_{Cu(OAc)_2}$ and K_{ZnOAc} used in this calculation were 41, 190 and 5.7, respectively. These were all determined polarographically at ionic strength 0.2 at 15°C[3)]. The concentration of uncomplexed acetate in the solution was calculated by successive approximation.

TABLE I. RATE CONSTANTS IN EQ. 10 OBTAINED EXPERIMENTALLY AT IONIC STRENGTH 0.2 AT VARIOUS TEMPERATURES

Temp., °C	Rate constant, l. mol^{-1} sec^{-1}		
	k_1^+	k_2^+	k_3^+
0	5.2	3×10^4	7.1×10^2
15	19	5×10^4	2.1×10^3

The rate constants of both elementary reactions 8b and 9b were calculated from the relations given in Eq. 11, using the values of K_{ZnHY}^{H}, K_{ZnY} and K_{HY} in Table II. The value of K_{ZnHY}^{H} which was determined by Schwarzenbach et al.[4)] at 20°C at ionic strength 0.1 was used after correction for ionic strength with the Debye-Hückel equation. The values of K_{ZnY} at 15 and 0°C were obtained by dividing the value of K_{CuY} by those of K_{Zn}^{Cu}. As for K_{CuY}, the values obtained by Schwarzenbach et al.[4)]

[4)] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, 37, 937 (1954).

were used after correction for temperature and ionic strength[2]. The equilibrium constants of reaction 2 at zero acetate concentration, $K^{\mathrm{Cu}}_{\mathrm{Zn}}$, used in this calculation were 320 at 15°C[3] and 310 at 0°C, the latter of which was estimated by extrapolation. The rate constants of three elementary reactions 7, 8b and 9b thus calculated are summarized in Table III.

TABLE II. EQUILIBRIUM CONSTANTS AT IONIC STRENGTH 0.2 AT VARIOUS TEMPERATURES

Temp., °C	$\log K_{\mathrm{ZnY}}$	$\mathrm{p}K_{\mathrm{HY}}$	$\log K^{\mathrm{H}}_{\mathrm{ZnHY}}$
0	16.51	10.41	—
15	16.17	10.20	—
20	—	—	2.9

TABLE III. RATE CONSTANTS FOR REACTIONS 7, 8b AND 9b AT IONIC STRENGTH 0.2 AT VARIOUS TEMPERATURES

Temp., °C	Rate constant, l. mol^{-1} sec^{-1}		
	k_{I}^+	k_{II}^+	k_{III}^+
0	5.2	40	8.9×10^8
15	19	60	2.0×10^9

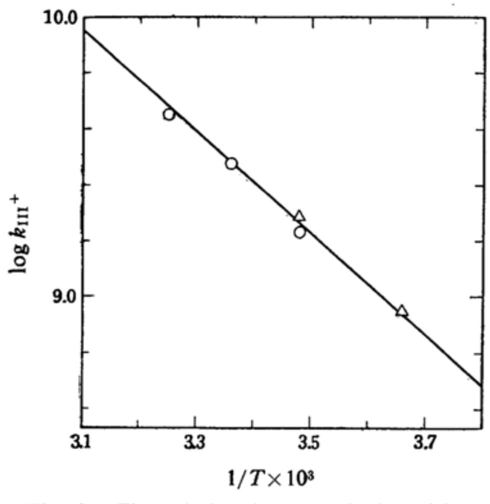

Fig. 2. The relation between the logarithm of rate constant and the reciprocal of absolute temperature for the reaction $Cu^{2+} + HY^{3-} \xrightarrow{k_{\mathrm{III}}^+} CuY^{2-} + H^+$. ○ indicates the value obtained in the reaction of copper(II) ions and lead-EDTA complexes and △, in the reaction of copper(II) ions and zinc-EDTA complexes.

From these results, the rate constants expressed in the form of the Arrhenius equation were derived and the heats of activation and the entropies of activation were calculated for three elementary reactions 7, 8b and 9b. The results are given in Table IV.

The rate constants of reaction 9b were obtained at 15 and 0°C in this study as given in Table III. The logarithmic values of k_{III}^+ are plotted against the reciprocal of absolute temperature as shown in Fig. 2. The rate constants of the same reaction were previously obtained at 15, 25 and 35° in the study of the substitution reaction of copper(II) ions and lead-EDTA complexes[2]. They are also shown in Fig. 2, which are in good agreement with the present ones. This fact supports the validity of the method for the determination of the rate constants proposed in this series of papers.

From Eq. 10, it is predicted that the reaction rate decreases with the increase of acetate concentration. Using Eq. 12, the values of $k^+/[ZnY^{2-}]_0$ were calculated at various acetate concentrations with the rate constants given in Table I and

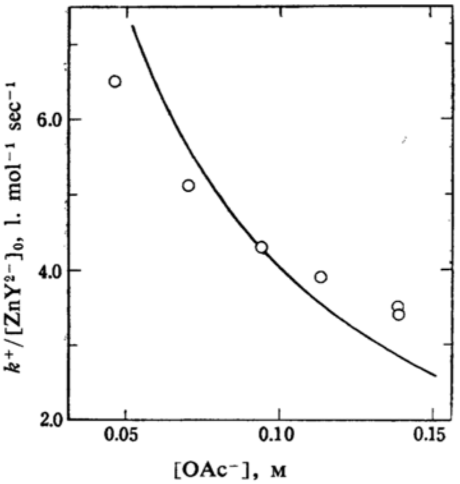

Fig. 3. $k^+/[ZnY^{2-}]_0$ as a function of the acetate concentration in acetate buffer-potassium nitrate solutions of pH 4.70 and ionic strength 0.2 at 15°C. Initial concentrations are:

$[Cu^{2+}]_{0,\mathrm{app}}=1.20\times10^{-4}$ M;
$[ZnY^{2-}]_0=4.03\times10^{-3}$ M;
$[Zn^{2+}]_{0,\mathrm{app}}=1.12\times10^{-2}$ M

—— indicates the theoretical curve and ○, the experimental value.

TABLE IV. RATE CONSTANTS, HEATS OF ACTIVATION AND ENTROPIES OF ACTIVATION FOR REACTIONS 7, 8b AND 9b

Reaction	Rate constant, expressed in l. mol^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal. mol^{-1}	$\Delta S^{\ddagger}$, e. u.
$Cu^{2+} + ZnY^{2-} \rightarrow CuY^{2-} + Zn^{2+}$	$k_{\mathrm{I}}^+ = 1.5\times10^{11}\exp(-13{,}000/\boldsymbol{R}T)$	12	-9.3
$Cu^{2+} + ZnHY^- \rightarrow CuHY^- + Zn^{2+}$	$k_{\mathrm{II}}^+ = 6.3\times10^5\exp(-5{,}300/\boldsymbol{R}T)$	4.7	-34
$Cu^{2+} + HY^{3-} \rightarrow CuY^{2-} + H^+$	$k_{\mathrm{III}}^+ = 3.4\times10^{15}\exp(-8{,}200/\boldsymbol{R}T)$	7.6	11

the formation constants of the acetato complexes. In Fig. 3, they are plotted against acetate concentration and compared with the values which were experimentally measured at various acetate concentrations, the other conditions being kept constant. The deviation of the experimental values from the calculated ones is considered as probably due to a contribution of the reactions in which acetatocopper(II) complexes participate.

Summary

The kinetic study of the substitution reaction of copper(II) and zinc-EDTA complexes in acetate buffer solutions was carried out with the same procedure as reported previously[1,2]. The reaction was found to proceed simultaneously through three different reaction paths under the experimental conditions. The rate constants for three elementary reactions of those reaction paths were determined at 15 and 0°C, and the heats of activation and the entropies of activation for the reactions were calculated.

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