The Kinetics of Substitution Reactions Involving Metal Complexes. V. Reaction between Copper(II) and Ethylenediaminetetraacetatocadmate(II) Complexes in Aqueous Solutions

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(Received April 13, 1962)

The substitution reaction of copper(II) ion and ethylenediaminetetraacetatocadmate(II) complex (Cd(II)-EDTA) was first studied by Ackermann and Schwarzenbach[1]. From the polarographic measurement of the reaction rate at 0°C and ionic strength 1.0 at 5×10^{-6} to 1.4×10^{-4} M of hydrogen ion, they concluded that the reaction proceeds simultaneously through four different reaction paths. Although their measurements were carried out in acetate buffer solutions and the decrease of the reaction rate was observed with increasing concentrations of acetate ion, Ackermann and Schwarzenbach did not take consideration of this fact in the treatment of the reaction kinetics.

This observation and a series of kinetic studies on the substitution reactions involving metal complexes[2-5] carried out in this laboratory suggested us to reinvestigate the substitution reaction of copper(II) ion and Cd(II)-EDTA and to compare the mechanisms and the rate constants of those substitution reactions obtained under the same experimental conditions.

In this study, therefore, the reaction rates were measured by the polarographic method at 5 and 15°C at lower concentrations of hydrogen ion than those reported by Ackermann and Schwarzenbach. The effect of acetate ion on the reaction rate was taken into consideration. A new reaction path was found in which the rate was inversely proportional to the hydrogen ion concentration of the solution. The contribution of this reaction path was more important at lower hydrogen ion concentrations.

Experimental

Reagents.—Preparations and standardizations of the solutions of copper(II) nitrate, cadmium(II) nitrate, disodium ethylenediaminetetraacetate (EDTA) and sodium acetate-acetic acid buffers were described in the previous paper[6]. The cadmium nitrate solution was found to contain 0.08% of lead(II) ion as impurity, being determined by the a. c. polarographic method. The preliminary experiments indicated that this concentration of lead(II) ion gave no appreciable effect on the reaction rate under investigation and therefore no further purification was carried out. Other reagents used for supporting electrolytes were of guaranteed reagent grade and used without further purification.

Apparatus and Procedure.—The rate of the reaction between copper(II) ion and Cd(II)-EDTA complex was followed by measuring the change of polarographic limiting current of copper(II) ion at -0.12 V. vs. SCE with time. A Shimadzu RP-2 pen-recording polarograph was employed for the measurement of current-time curves. The dropping mercury electrode used had an m value of 2.57 mg./sec. and a drop time t_d of 3.52 sec. in an air-free acetate buffer of pH 4.7 containing 0.1 M acetate, 0.1 M potassium nitrate and 0.01% gelatin at 25°C with open circuit. A saturated calomel electrode (SCE) was used as reference electrode which was connected to the electrolytic solution with the aid of a Hume and Harris type agar bridge[7]. Dissolved oxygen in the solution was removed by bubbling nitrogen gas through the solution. Gelatin was added as maximum suppressor by 0.01% in concentration. The pH of solution was measured by means of Hitachi EHP-1 pH meter, within the accuracy of 0.02 pH unit, immediately after the measurement of current-time curve.

The reactions were initiated by injecting the known amount of the deaerated copper(II) nitrate solution at the rate of 1 ml. per second with a calibrated syringe into acetate buffer solution which contained cadmium(II) ion and Cd(II)-EDTA complex in excess. The ionic strength of the solution was adjusted to be 0.2 with potassium nitrate. The solution was thoroughly stirred by bubbling nitrogen gas for ten seconds. With this technique, a reproducible current-time curve was obtained from 20 sec. after the initiation of reaction.

Results and Discussion

Copper(II) forms mono- and diacetato complexes, whereas cadmium(II) does only monoacetato complex in the solution which contains less than 0.2 M of acetate ions. The overall substitution reaction between copper(II) ion

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[1] H. Ackermann and G. Schwarzenbach, *Helv. Chim. Acta*, 35, 485 (1952).
[2] N. Tanaka, K. Kato and R. Tamamushi. This Bulletin, 31, 283 (1958).
[3] N. Tanaka and K. Kato, ibid., 32, 1376 (1959).
[4] K. Kato, ibid., 33, 600 (1960).
[5] N. Tanaka and K. Kato, ibid., 33, 1236 (1960).
[6] N. Tanaka, M. Kamada, H. Osawa and G. Satô, ibid., 33, 1412 (1960).
[7] D. N. Hume and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, 15, 465 (1943).

and Cd(II)-EDTA complex in acetate buffer solution is represented with the following equations.

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

$$Cu^{2+} + CdY^{2-} \rightleftarrows CuY^{2-} + Cd^{2+} \quad (2)$$

$$Cd^{2+} + OAc^- \rightleftarrows CdOAc^+ \quad (3)$$

In Eq. 2, Y^{4-} denotes tetravalent EDTA anion. In the case when both Cd^{2+} and CdY^{2-} are present in a large excess over the copper(II) ion, Eq. 2 can be simplified to

$$Cu^{2+} \underset{k^-}{\overset{k^+}{\rightleftarrows}} CuY^{2-} \quad (4)$$

The rate equation for Eq. 4 is written as

$$-\frac{d[Cu^{2+}]_{app}}{dt} = k^+[Cu^{2+}]_{app} - k^-[CuY^{2-}] \quad (5)$$

where $[Cu^{2+}]_{app}$ is the apparent concentration of copper(II) ion that can be determined polarographically, or the sum of hydrated copper(II) ion and mono- and diacetato copper(II) complexes.

Integrating Eq. 5

$$\ln\{[Cu^{2+}]_{app} - [Cu^{2+}]_{e,app}\} = -(k^+ + k^-)t + \ln\{[Cu^{2+}]_{0,app} - [Cu^{2+}]_{e,app}\} \quad (6)$$

is obtained, where suffixes 0 and e denote the initial and the equilibrium state respectively. At the equilibrium the following relation may be satisfied.

$$k^+/k^- = \frac{[CuY^{2-}]_e}{[Cu^{2+}]_{e,app}} \fallingdotseq K^{Cu}_{Cd,app}\frac{[CdY^{2-}]_0}{[Cd^{2+}]_{0,app}} \quad (7)$$

$K^{Cu}_{Cd,app}$ means the apparent equilibrium constant of Eq. 2 at a certain acetate concentration, and is given as

$$K^{Cu}_{Cd,app} = \frac{[CuY^{2-}]_e[Cd^{2+}]_{e,app}}{[Cu^{2+}]_{e,app}[CdY^{2-}]_e} \quad (8)$$

The values of $K^{Cu}_{Cd,app}$ were determined polarographically to be 102 at 15°C and 113 at 5°C in the presence of 0.091 M of acetate. These values were introduced in Eq. 7, and k^+ was determined from Eqs. 6 and 7.

The apparent overall rate constants of forward reaction of Eq. 4 ($k^+/[CdY^{2-}]_0$) were measured at varied initial concentrations of copper(II) ion and those of Cd(II)-EDTA complex under other conditions kept constant, and found to be independent of the variables as shown in Table I. This observation led to the conclusion that the overall substitution reaction proceeds according to the pseudo first order rate law.

TABLE I. $k^+/[CdY^{2-}]_0$ VALUES AT VARIOUS INITIAL CONCENTRATIONS OF COPPER(II) ION OR Cd(II)-EDTA COMPLEX
(15°C, $\mu=0.2$, $[OAc^-]=0.091$ M, pH=5.50, $[Cd^{2+}]_{0,app}=1.028\times10^{-2}$ M)

$[Cu^{2+}]_{0,app}$ M×10^4	$[CdY^{2-}]_0$ M×10^3	$k^+/[CdY^{2-}]_0$ l.mol^{-1} sec^{-1}
0.99	5.00	0.72_4
1.98	5.00	0.73_2
2.97	5.00	0.73_2
1.98	9.98	0.72_0

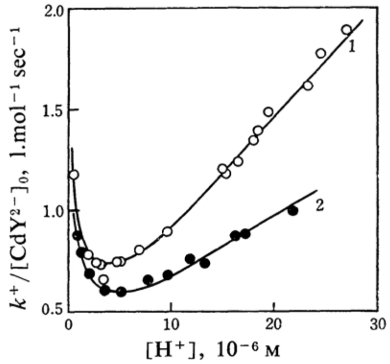

Fig. 1. $k^+/[CdY^{2-}]_0$ as a function of the hydrogen ion concentration in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 15°C. Initial concentrations are: $[Cu^{2+}]_{0,app}=1.98\times10^{-4}$ M; $[CdY^{2-}]_0=5.00\times10^{-3}$ M; $[Cd^{2+}]_{0,app}=1.028\times10^{-2}$ M (curve 1) and 2.056×10^{-2} M (curve 2). Concentration of free acetate is 0.091 M.

Two sets of $k^+/[CdY^{2-}]_0$, in each of which the values of $k^+/[CdY^{2-}]_0$ were measured at various hydrogen ion concentrations under other conditions kept constant, were obtained at two different concentrations of cadimium(II) ion. The values obtained are plotted against the hydrogen ion concentration as shown in Fig. 1, where it should be noticed that, in the region of low hydrogen ion concentration, $k^+/[CdY^{2-}]_0$ increases with decreasing concentration of hydrogen ion.

These experimental results suggest that the substitution reaction between copper(II) ion and Cd(II)-EDTA complex proceeds simultaneously through the following four reaction paths:

i) $$Cu^{2+} + CdY^{2-} \overset{k_I^+}{\rightleftarrows} CuY^{2-} + Cd^{2+} \quad (9)$$

ii) $$CdY^{2-} + H^+ \rightleftarrows CdHY^- \quad (10a)$$

$$Cu^{2+} + CdHY^- \overset{k_{II}^+}{\rightleftarrows} CuHY^- + Cd^{2+} \quad (10b)$$

$$CuHY^- \rightleftarrows CuY^{2-} + H^+ \quad (10c)$$

iii) $$CdY^{2-} + H^+ \rightleftarrows Cd^{2+} + HY^{3-} \quad (11a)$$

$$Cu^{2+} + HY^{3-} \overset{k_{III}^+}{\rightleftarrows} CuY^{2-} + H^+ \quad (11b)$$

iv) $$CdY^{2-} + H_2O \rightleftarrows CdOHY^{3-} + H^+ \qquad (12a)$$

$$Cu^{2+} + CdOHY^{3-} \underset{}{\overset{k_{IV}^+}{\rightleftarrows}} CuOHY^{3-} + Cd^{2+} \qquad (12b)$$

$$CuOHY^{3-} + H^+ \rightleftarrows CuY^{2-} + H_2O \qquad (12c)$$

If the substitution reaction is assumed to proceed only through the hydrated ions which are in equilibrium with the acetato complexes, the apparent rate of the forward reaction ($v^+ = k^+[Cu^{2+}]_{app}$) is represented by Eq. 13.

$$v^+ = k^+[Cu^{2+}]_{app} = \left\{ \frac{k_1^+ + k_2^+[H^+] + k_3^+[H^+]\frac{1 + K_{CdOAc}[OAc^-]}{[Cd^{2+}]_{app}} + k_4^+\frac{1}{[H^+]}}{1 + \sum_{n=1}^{2} K_{Cu(OAc)_n}[OAc^-]^n} \right\} \times [Cu^{2+}]_{app}[CdY^{2-}] \qquad (13)$$

$$\left. \begin{array}{ll} k_2^+ = k_{II}^+ K_{CdHY}^{H} & k_3^+ = k_{III}^+ / K_{CdY}K_{HY} \\ k_4^+ = k_{IV}^+ K_{CdOHY} & \end{array} \right\} \qquad (14)$$

In Eqs. 13 and 14, K_{CdHY}^{H} means the equilibrium constant of reaction 10a, K_{CdY}, the formation constant of CdY^{2-}, K_{HY}, the fourth dissociation constant of ethylenediaminetetraacetic acid, K_{CdOHY}, the equilibrium constant for reaction 12a, and K_{CdOAc} and $K_{Cu(OAc)_n}$ represent the overall formation constants of acetatocadmium(II) and acetatocopper(II) complexes, respectively. Some of these constants were determined in our laboratory[6,8] and others were cited from literatures, if necessary, after correction for the ionic strength and/or temperature with the same procedures as described previously[2-4]. These constants are given in Table II.

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

Temp., °C	5	15	20
$\log K_{CdY}$	16.53	16.34	—
pK_{HY}	10.34	10.16	—
$\log K_{CdHY}^{H}$	—	—	2.8
K_{CuOAc}	—	41	—
$K_{Cu(OAc)_2}$	—	190	—
K_{CdOAc}	—	27	—

From Eq. 13 is obtained,

$$K^+/[CdY^{2-}]_0 = A[H^+] + B + C\frac{1}{[H^+]} \qquad (15)$$

$$\left. \begin{array}{l} A = \dfrac{k_2^+ + k_3^+ \dfrac{1 + K_{CdOAc}[OAc^-]}{[Cd^{2+}]_{0,app}}}{1 + \sum_{n=1}^{2} K_{Cu(OAc)_n}[OAc^-]^n} \\ B = k_1^+/(1 + \sum_{n=1}^{2} K_{Cu(OAc)_n}[OAc^-]^n) \\ C = k_4^+/(1 + \sum_{n=1}^{2} K_{Cu(OAc)_n}[OAc^-]^n) \end{array} \right\} \qquad (16)$$

where the initial concentrations, $[Cd^{2+}]_0$ and $[CdY^{2-}]_0$, are substituted for $[Cd^{2+}]$ and $[CdY^{2-}]$, respectively.

Rearranging Eq. 15,

$$k^+[H^+]/[CdY^{2-}]_0 = A[H^+]^2 + B[H^+] + C \qquad (17)$$

$$\left(\frac{k^+[H^+]}{[CdY^{2-}]_0} - C\right) \Big/ [H^+] = A[H^+] + B \qquad (18)$$

are obtained. Since both Cd^{2+} and CdY^{2-} are present in the reaction mixture in a large excess over the concentration of copper(II) ion, the change of their concentrations during the reaction can be neglected.

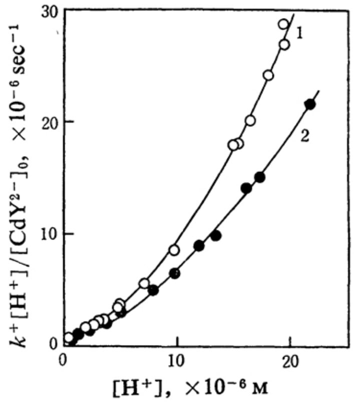

Fig. 2. $k^+[H^+]/[CdY^{2-}]_0$ as a function of the hydrogen ion concentration in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 15°C. Initial concentrations are: $[Cu^{2+}]_{0,app} = 1.98 \times 10^{-4}$ M; $[CdY^{2-}]_0 = 5.00 \times 10^{-3}$ M; $[Cd^{2+}]_{0,app} = 1.028 \times 10^{-2}$ M (curve 1) and 2.056×10^{-2} M (curve 2). Concentration of free acetate is 0.091 M.

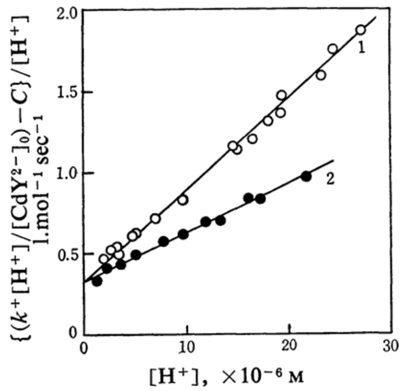

Fig. 3. $\{(k^+[H^+]/[CdY^{2-}]_0) - C\}/[H^+]$ as a function of the hydrogen ion concentration in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 15°C. Initial concentrations are: $[Cu^{2+}]_{0,app} = 1.98 \times 10^{-4}$ M; $[CdY^{2-}]_0 = 5.00 \times 10^{-3}$ M; $[Cd^{2+}]_{0,app} = 1.028 \times 10^{-2}$ M (curve 1) and 2.056×10^{-2} M (curve 2). Concentration of free acetate is 0.091 M.

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

TABLE III. RATE CONSTANTS IN EQ. 13 OBTAINED EXPERIMENTALLY, AND THOSE FOR REACTIONS 10b, 11b AND 12b AT IONIC STRENGTH 0.2 AT VARIOUS TEMPERATURES

Temp. °C	Rate constant					
	k_1^+ l.mol^{-1} sec^{-1}	k_2^+ l^2 mol^{-2} sec^{-1}	k_{II}^+ l.mol^{-1} sec^{-1}	k_3^+ l.mol^{-1} sec^{-1}	k_{III}^+ l.mol^{-1} sec^{-1}	k_4^+ sec^{-1}
5	0.95	$1.7_0\times10^4$	$26._9$	$3.7_6\times10^2$	$5.7_0\times10^8$	$9.4_5\times10^{-7}$
15	2.2	$2.9_0\times10^4$	$45._9$	$9.0_7\times10^2$	$1.3_2\times10^9$	$3.7_8\times10^{-6}$

In Figs. 2 an 3, $k^+[H^+]/[CdY^{2-}]_0$ and $\{(k^+[H^+]/[CdY^{2-}]_0)-C\}/[H^+]$ are plotted against $[H^+]$, respectively, using the values of k^+ obtained at various hydrogen ion concentrations. The values for A, B and C were determined from these plots; A from the slope of the plot in Fig. 3, B from the intercept of the plot in Fig. 3 and C from the intercept of the plot in Fig. 2. With these values and equilibrium constants given in Table II, the rate constants were calculated using Eqs. 14 and 16, and they are summarized in Table III.

The rate constant k_{III}^+ had been determined in the kinetic studies of the substitution reaction between copper(II) ion and lead(II)-EDTA complex2,3), and that between copper(II) ion and zinc(II)-EDTA complex4). It is in reasonable agreement with the value of k_{III}^+ obtained in this study, as shown in Table IV.

TABLE IV. THE RATE CONSTANTS OF ELEMENTARY REACTIONS OF THE SUBSTITUTION REACTION, $M^{m+}+M'Y^{(m'-4)+} \rightleftarrows MY^{(m-4)+}+M'^{m'+}$, AT 15°C $\mu=0.2$ AND $[OAc^-]=0.09$ M

M	M′	k_1^+ l.mol^{-1} sec^{-1}	k_{II}^+ l.mol^{-1} sec^{-1}	k_{III}^+ l.mol^{-1} sec^{-1}
Cu^{2+}	Pb^{2+}	1.7	10	1.7×10^9
Cu^{2+}	Zn^{2+}	19	60	2.0×10^9
Cu^{2+}	Cd^{2+}	2.2	45.9	$1.3_2\times10^9$
Pb^{2+}	Zn^{2+}	4.6	800	1.0×10^{10}

Ackermann and Schwarzenbach1) investigated the kinetics of the substitution reaction between copper(II) ion and Cd(II)-EDTA complex at 0°C in the solutions of ionic strength 1.0 containing 0.09 M of acetate ion and $5\times10^{-6}\sim1.4\times10^{-4}$ M of hydrogen ion, when they concluded that the reaction proceeds simultaneously through four different paths as follows:

$$Cu^{2+} + \left\{\begin{array}{c} CdY^{2-} \\ \downarrow\uparrow \\ CdHY^{-} \\ \downarrow\uparrow \\ Cd^{2+} + HY^{3-} \\ \downarrow\uparrow \\ Cd^{2+} + H_2Y^{2-} \end{array}\right\} \rightarrow Cd^{2+} + CuY^{2-} + \left\{\begin{array}{c} H^+ \\ H^+ \\ 2H^+ \end{array}\right\}$$

Their experimental conditions, however, were apparently unfavorable to find out the reaction path given by Eqs. 12a, 12b and 12c.

Equation 13 predicts that the reaction rate decreases with the increasing concentration of acetate ion. This was previously recognized experimentally by Ackerman and Schwarzenbach, who stated that the decrease in reaction rate was due to the formation of acetato copper(II) complex. Using Eqs. 15 and 16, the values of $k^+/[CdY^{2-}]_0$ were calculated at various concentrations of acetate ion with the rate constants given in Table III. These values are plotted against acetate ion concentration in Fig. 4, where the experimental values for $k^+/[CdY^{2-}]_0$ obtained at various concentrations of acetate ion are also given. Figure 4 indicates that the calculated values of $k^+/[CdY^{2-}]_0$ considerably deviate from the experimental ones. This tendency has been noticed in the studies on other substitution reactions3-5). The discrepancy seemed to come from the assumption that the reaction proceeds through only hydrated ions.

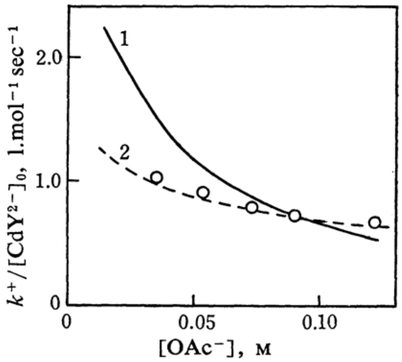

Fig. 4. $k^+/[CdY^{2-}]_0$ as a function of the acetate ion concentration in acetate buffer-potassium nitrate solutions of pH 5.50 and ionic strength 0.2 at 15°C. Initial concentrations are: $[Cu^{2+}]_{0,app}=1.98\times10^{-4}$ M; $[CdY^{2-}]_0=5.00\times10^{-3}$ M; $[Cd^{2+}]_{0,app}=1.028\times10^{-2}$ M. ○ indicates the experimental value. Curve 1 is calculated with Eq. 13 and curve 2, with Eq. 19.

Then, the reaction was assumed as to proceed through both hydrated ion and monoacetato complex. The rate-determining steps in the simultaneous substitution reaction are as follows.

$$\text{i)}\quad Cu^{2+} + CdY^{2-} \overset{k_{1h}^+}{\rightleftarrows} CuY^{2-} + Cd^{2+} \qquad (9')$$

$$CuOAc^+ + CdY^{2-} \overset{k_{1c}^+}{\rightleftarrows} CuY^{2-} + CdOAc^+ \qquad (9'')$$

ii) $$\mathrm{Cu^{2+} + CdHY^{-} \overset{k_{\mathrm{IIh}}^{+}}{\rightleftarrows} CuHY^{-} + Cd^{2+}} \quad (10b')$$

$$\mathrm{CuOAc^{+} + CdHY^{-} \overset{k_{\mathrm{IIc}}^{+}}{\rightleftarrows} CuHY^{-} + CdOAc^{+}} \quad (10b'')$$

iii) $$\mathrm{Cu^{2+} + HY^{3-} \overset{k_{\mathrm{IIIh}}^{+}}{\rightleftarrows} CuY^{2-} + H^{+}} \quad (11b')$$

$$\mathrm{CuOAc^{+} + HY^{3-} \overset{k_{\mathrm{IIIc}}^{+}}{\rightleftarrows} CuY^{2-} + H^{+} + OAc^{-}}$$

iv) $$\mathrm{Cu^{2+} + CdOHY^{3-} \overset{k_{\mathrm{IVh}}^{+}}{\rightleftarrows} CuOHY^{3-} + Cd^{2+}} \quad (12b')$$

$$\mathrm{CuOAc^{+} + CdOHY^{3-} \overset{k_{\mathrm{IVc}}^{+}}{\rightleftarrows} CuOHY^{3-} + CdOAc^{+}} \quad (12b'')$$

where $k_{i\mathrm{h}}^{+}$ and $k_{i\mathrm{c}}^{+}$ mean the rate constants of the reactions which proceed through the hydrated ion and monoacetato complex, respectively. Since it seemed extremely difficult, however, to determine all of these rate constants separately because of insufficient accuracy in the measurement, the following procedure was taken up as the first approximation. In all reactions from (9') to (12b'') the ratios of $k_{i\mathrm{c}}^{+}$ to $k_{i\mathrm{h}}^{+}$ (i. e. $k_{i\mathrm{c}}^{+}/k_{i\mathrm{h}}^{+}$) are assumed to be the same and denoted with x. The rate equation is written as Eq. 19.

$$v^{+}=\frac{k_{1\mathrm{h}}^{+}+k_{2\mathrm{h}}^{+}[\mathrm{H}^{+}]+k_{3\mathrm{h}}^{+}\dfrac{1+K_{\mathrm{CdOAc}}[\mathrm{OAc}^{-}]}{[\mathrm{Cd}^{2+}]_{\mathrm{app}}}+k_{4\mathrm{h}}^{+}\dfrac{1}{[\mathrm{H}^{+}]}}{1+\sum_{n=1}^{2}K_{\mathrm{Cu(OAc)}_n}[\mathrm{OAc}^{-}]^{n}}\times(1+xK_{\mathrm{CuOAc}}[\mathrm{OAc}^{-}])[\mathrm{Cu}^{2+}]_{\mathrm{app}}[\mathrm{CdY}^{2-}] \quad (19)$$

Comparing Eq. 19 with Eq. 13,

$$k_{i}^{+}=k_{i\mathrm{h}}^{+}(1+xK_{\mathrm{CuOAc}}[\mathrm{OAc}^{-}]) \quad (20)$$

is derived. With the values of k_i^{+} obtained experimentally at various concentrations of acetate ion $k_{i\mathrm{h}}^{+}$ and x were determined by the graphical method. For the latter, 0.26 at 5°C and 0.37 at 15°C were obtained. The apparent rate constants $k^{+}/[\mathrm{CdY}^{2-}]_0$ at various concentrations of acetate ion were evaluated with the values of $k_{i\mathrm{h}}^{+}$ and x using Eq. 20. The results are in satisfactory agreement with the experimental values as shown in Fig. 4 (curve 2). Although this treatment is not strictly rigorous, it proves that the substitution reaction proceeds through both hydrated ions and monoacetato complexes.

Summary

The kinetic study of the substitution reaction of copper(II) and ethylenediaminetetraacetatocadmate(II) complexes in acetate buffer solutions has been carried out by the same method as reported previously[2-5]. The reaction was found, under the experimental conditions, to proceed simultaneously through four different reaction paths, and the rate constants for the elementary reactions of those reaction paths were determined at ionic strength 0.2 at 5 and 15°C. It was confirmed also that this substitution reaction proceed through both hydrated ion and monoacetato complex.

The authors thank the Ministry of Education for the financial support granted for this research.

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