The Kinetics of Substitution Reactions Involving Metal Complexes. II. Effect of Acetate Ions on the Reaction between Copper(II) and Lead-Ethylenediaminetetraacetate Complexes

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In the previous paper[1], 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 time in acetate buffer solutions. The reaction was found to proceed, under the experimental conditions, simultaneously through three different reaction paths, and the rate constants of the elementary reactions of those reaction paths were determined.

Although the reaction rate was measured in acetate buffer solutions, the effect of acetate ion concentration was not taken into consideration, all measurements being

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

carried out at 0.1 M of acetate in concentration. Ackermann and Schwarzenbach[2] found that the overall reaction rate of the substitution reaction of copper(II) ions and cadmium-EDTA complexes increased with the decreasing concentration of acetate ions, but they gave no quantitative explanation of this phenomenon. The increase of the reaction rate with the decrease of the acetate ion concentration was also found by the present authors in the case of the substitution reaction of copper(II) ions and lead-EDTA complexes.

In this paper, the effect of acetate ions on the rate of the substitution reaction of copper(II) ions and lead-EDTA complexes is investigated. The experimental results reported in the previous paper[1] are treated on the basis of the formation of acetato complexes of metal ions in acetate media and on the assumption that the substitution reaction proceeds through the hydrated metal ions which are in equilibrium with the acetato complexes. The rate constants of the elementary reactions reported previously are recalculated with the equations newly derived.

Derivation of the Rate Equation

Let us consider the acetate buffer solution which contains copper(II) ions and lead-EDTA complexes. In the solution containing acetate ions less than 0.2 M in concentration, copper(II) and lead(II) form mono- and diacetato complexes[3]. Therefore, the overall substitution reaction is represented by the equations

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

$$\mathrm{Cu^{2+} + PbY^{2-} \rightleftarrows CuY^{2-} + Pb^{2+}} \qquad (2)$$

$$\mathrm{Pb^{2+} + 2\ OAc^- \rightleftarrows PbOAc^+ + OAc^- \rightleftarrows Pb(OAc)_2} \qquad (3)$$

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

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

In the polarographic measurement in acetate media, it is impossible to determine separately either the concentration of hydrated copper(II) ions or that of acetato-copper(II) complexes. On the contrary, the diffusion current of copper(II) obtained in acetate media corresponds to the sum of the diffusion current of the hydrated copper(II) ions and that of the acetato-copper(II) complexes. In other words, the concentration that can be determined polarographically is $[\mathrm{Cu^{2+}}]_{\mathrm{app}}$ given by the equation[4]

$$[\mathrm{Cu^{2+}}]_{\mathrm{app}} = [\mathrm{Cu^{2+}}] + [\mathrm{CuOAc^+}] + [\mathrm{Cu(OAc)_2}] \qquad (5)$$

The rate equation for reaction 4, therefore, is expressed as

$$-\frac{\mathrm{d}[\mathrm{Cu^{2+}}]_{\mathrm{app}}}{\mathrm{d}t} = k^+[\mathrm{Cu^{2+}}]_{\mathrm{app}} - k^-[\mathrm{CuY^{2-}}] \qquad (6)$$

Integrating Eq. 6,

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

is obtained. At the equilibrium of the reaction, the relation

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

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

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

Subscripts e and 0 mean equilibrium and zero time, respectively. The value of $\mathrm{K^{Cu}_{Pb,app}}$ must be determined polarographically as the same concentration of acetate as the reaction rate is observed.

In the previous study[1], it was found that the substitution reaction between copper(II) and lead-EDTA complexes proceeds through the simultaneous reaction paths

$$\text{(i)}\quad \mathrm{Cu^{2+} + PbY^{2-}} \underset{k_1^-}{\overset{k_1^+}{\rightleftarrows}} \mathrm{CuY^{2-} + Pb^{2+}} \qquad (7)$$

$$\text{(ii)}\quad \mathrm{PbY^{2-} + H^+ \rightleftarrows PbHY^-} \qquad (8a)$$

$$\mathrm{Cu^{2+} + PbHY^-} \underset{k_{\mathrm{II}}^-}{\overset{k_{\mathrm{II}}^+}{\rightleftarrows}} \mathrm{CuHY^- + Pb^{2+}} \qquad (8b)$$

$$\mathrm{CuHY^- \rightleftarrows CuY^{2-} + H^+} \qquad (8c)$$

$$\text{(iii)}\quad \mathrm{PbY^{2-} + H^+ \rightleftarrows Pb^{2+} + HY^{3-}} \qquad (9a)$$

$$\mathrm{Cu^{2+} + HY^{3-}} \underset{k_{\mathrm{III}}^-}{\overset{k_{\mathrm{III}}^+}{\rightleftarrows}} \mathrm{CuY^{2-} + H^+} \qquad (9b)$$

and the rate equation

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

[3] N. Tanaka and K. Kato, unpublished work.

[4] Cf., N. Tanaka and K. Kato, This Bulletin, **32**, 516 (1959).

$$-\frac{\mathrm{d}[\mathrm{Cu}^{2+}]}{\mathrm{d}t}=\left\{k_1{}^+ + k_2{}^+[\mathrm{H}^+] + k_3{}^+\frac{[\mathrm{H}^+]}{[\mathrm{Pb}^{2+}]}\right\} \times [\mathrm{Cu}^{2+}][\mathrm{PbY}^{2-}] - \left\{k_1{}^- + k_2{}^-[\mathrm{H}^+] + k_3{}^-\frac{[\mathrm{H}^+]}{[\mathrm{Pb}^{2+}]}\right\}[\mathrm{Pb}^{2+}][\mathrm{CuY}^{2-}] \tag{10}$$

was derived, where

$$\left.\begin{aligned} k_2{}^+ &= k_{\mathrm{II}}^+ K_{\mathrm{PbHY}}^{\mathrm{H}}, & k_2{}^- &= k_{\mathrm{II}}^- K_{\mathrm{CuHY}}^{\mathrm{H}} \\ k_3{}^+ &= k_{\mathrm{III}}^+/(K_{\mathrm{PbY}}K_{\mathrm{HY}}), & k_3{}^- &= k_{\mathrm{III}}^- \end{aligned}\right\} \tag{11}$$

As has been mentioned above, the concentration which was actually measured polarographically was not the concentration of hydrated copper(II) ions in Eq. 10, 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 ions which are in equilibrium with the acetato complexes, the apparent rate of the reaction $(=-\mathrm{d}[\mathrm{Cu}^{2+}]_{\mathrm{app}}/\mathrm{d}t)$ which is determined polarographically is expressed as

$$-\frac{\mathrm{d}[\mathrm{Cu}^{2+}]_{\mathrm{app}}}{\mathrm{d}t}=\left\{k_1{}^+ + k_2{}^+[\mathrm{H}^+] + k_3{}^+\frac{[\mathrm{H}^+]}{[\mathrm{Pb}^{2+}]}\right\} \times [\mathrm{Cu}^{2+}][\mathrm{PbY}^{2-}] - \left\{k_1{}^- + k_2{}^-[\mathrm{H}^+] + k_3{}^-\frac{[\mathrm{H}^+]}{[\mathrm{Pb}^{2+}]}\right\}[\mathrm{Pb}^{2+}][\mathrm{CuY}^{2-}] \tag{12}$$

From Eq. 5, the concentration of the hydrated copper(II) ions is given as

$$[\mathrm{Cu}^{2+}]=\frac{[\mathrm{Cu}^{2+}]_{\mathrm{app}}}{1+\sum_{n=1}^{2}K_{\mathrm{Cu(OAc)}_n}[\mathrm{OAc}^-]^n} \tag{13}$$

where $K_{\mathrm{Cu(OAc)}_n}$ represents the overall formation constant of acetatocopper(II) complexes expressed with

$$K_{\mathrm{Cu(OAc)}_n}=\frac{[\mathrm{Cu(OAc)}_n{}^{(2-n)+}]}{[\mathrm{Cu}^{2+}][\mathrm{OAc}^-]^n}$$

Similarly the concentration of the hydrated lead(II) ions is given as

$$[\mathrm{Pb}^{2+}]=\frac{[\mathrm{Pb}^{2+}]_{\mathrm{app}}}{1+\sum_{n=1}^{2}K_{\mathrm{Pb(OAc)}_n}[\mathrm{OAc}^-]^n}$$

where $K_{\mathrm{Pb(OAc)}_n}$ means the overall formation constant of acetatolead(II) complexes.

Introducing Eqs. 13 and 14 into Eq. 12, Eq. 15 is obtained. Eq. 15 is now considered to be a general formula which expresses the rate of the substitution reaction between copper(II) and lead-EDTA complexes in acetate media.

Determination of the Rate Constants

From Eqs. 6 and 15, the relations given by Eqs. 16 and 17 are obtained, where the initial concentrations, $[\mathrm{Pb}^{2+}]_0$ and $[\mathrm{PbY}^{2-}]_0$, are substituted for $[\mathrm{Pb}^{2+}]$ and $[\mathrm{PbY}^{2-}]$, respectively. Since both $[\mathrm{Pb}^{2+}]$ and $[\mathrm{PbY}^{2-}]$ are present in the reaction mixture in a large excess over the concentration of copper(II), the changes of their concentrations during the reaction can be neglected.

$$-\frac{\mathrm{d}[\mathrm{Cu}^{2+}]_{\mathrm{app}}}{\mathrm{d}t}=\left\{\frac{k_1{}^+ + k_2{}^+[\mathrm{H}^+] + k_3{}^+[\mathrm{H}^+]\dfrac{1+\sum_{n=1}^{2}K_{\mathrm{Pb(OAc)}_n}[\mathrm{OAc}^-]^n}{[\mathrm{Pb}^{2+}]_{\mathrm{app}}}}{1+\sum_{n=1}^{2}K_{\mathrm{Cu(OAc)}_n}[\mathrm{OAc}^-]^n}\right\}[\mathrm{Cu}^{2+}]_{\mathrm{app}}[\mathrm{PbY}^{2-}] - \left\{\frac{k_1{}^- + k_2{}^-[\mathrm{H}^+] + k_3{}^-[\mathrm{H}^+]\dfrac{1+\sum_{n=1}^{2}K_{\mathrm{Pb(OAc)}_n}[\mathrm{OAc}^-]^n}{[\mathrm{Pb}^{2+}]_{\mathrm{app}}}}{1+\sum_{n=1}^{2}K_{\mathrm{Pb(OAc)}_n}[\mathrm{OAc}^-]^n}\right\}[\mathrm{Pb}^{2+}]_{\mathrm{app}}[\mathrm{CuY}^{2-}] \tag{15}$$

$$\frac{k^+}{[\mathrm{PbY}^{2-}]_0}\equiv\frac{k_1{}^+ + k_2{}^+[\mathrm{H}^+] + k_3{}^+[\mathrm{H}^+]\dfrac{1+\sum_{n=1}^{2}K_{\mathrm{Pb(OAc)}_n}[\mathrm{OAc}^-]^n}{[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}}}{1+\sum_{n=1}^{2}K_{\mathrm{Cu(OAc)}_n}[\mathrm{OAc}^-]^n} \tag{16}$$

$$\frac{k^-}{[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}}\equiv\frac{k_1{}^- + k_2{}^-[\mathrm{H}^+] + k_3{}^-[\mathrm{H}^+]\dfrac{1+\sum_{n=1}^{2}K_{\mathrm{Pb(OAc)}_n}[\mathrm{OAc}^-]^n}{[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}}}{1+\sum_{n=1}^{2}K_{\mathrm{Pb(OAc)}_n}[\mathrm{OAc}^-]^n} \tag{17}$$

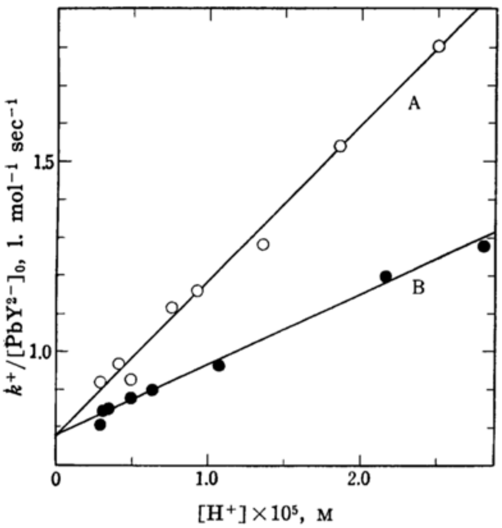

Fig. 1. $k^+/[PbY^{2-}]_0$ as a function of the hydrogen ion concentration in acetate buffer—potassium nitrate solutions of ionic strength 0.2 at 25°C. Initial concentrations are: $[Cu^{2+}]_{0,app}=1.86\times10^{-4}$ M; $[PbY^{2-}]_0=4.05\times10^{-3}$ M; $[Pb^{2+}]_{0,app}=3.95\times10^{-3}$ M (curve A) and 9.97×10^{-3} M (curve B). Concentratrations of free acetate are: 0.095 M (A) and 0.088 M (B).

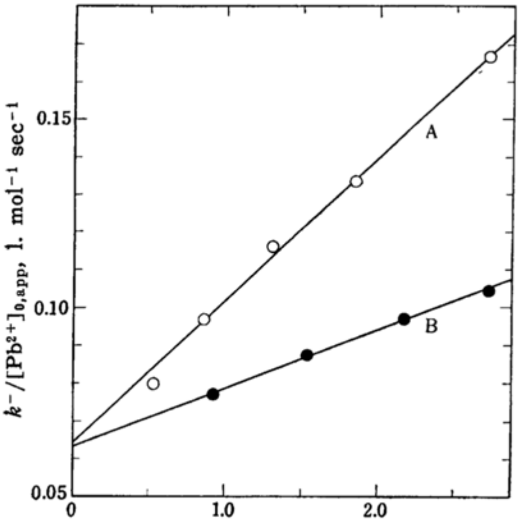

Fig. 2. $k^-/[Pb^{2+}]_{0,app}$ as a function of the hydrogen ion concentration in acetate buffer—potassium nitrate solutions of ionic strength 0.2 at 25°C. Initial concentrations are: $[CuY^{2-}]_0=4.65\times10^{-4}$ M; $[PbY^{2-}]_0=4.05\times10^{-3}$ M; $[Pb^{2+}]_{0,app}=3.95\times10^{-3}$ M (curve A) and 9.97×10^{-3} M (curve B). Concentrations of free acetate are: 0.095 M (A) and 0.088 M (B).

The experimental results which were reported in the previous paper[1] were utilized for the calculation of the rate constants in Eq. 15. The relations of $k^+/[PbY^{2-}]_0$ vs. $[H^+]$ and $k^-/[Pb^{2+}]_{0,app}$ vs. $[H^+]$ are plotted in Figs. 1 and 2. The values of the rate constants calculated are given in Table I. The formation constants of acetatocopper(II) and acetatolead(II) complexes which were used in the calculation are those which were determined polarographically at ionic strength 0.2 at 15, 25 and 35°C[3]. They are given in Table II. The concentration of uncomplexed acetate in the solution was calculated by successive approximation.

The rate constants of both elementary reactions 8b and 9b can be calculated from the relations given in Eqs. 11, using the values of K^{H}_{PbHY}, K_{PbY} and K_{HY} which are given in Table III. The values of K_{PbY} at 15, 25 and 35°C were obtained by dividing the values of K_{CuY} by those of K^{Cu}_{Pb}. The

TABLE I. RATE CONSTANTS IN EQ. 15 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^+	k_1^-	k_2^-	k_3^-
15	1.7	6×10^3	18			
25	5.1	3×10^4	58	1.0	3×10^3	14
35	17	$1._5\times10^5$	160			

TABLE II. FORMATION CONSTANTS OF ACETATO COMPLEXES OF COPPER(II) AND LEAD(II) AT IONIC STRENGTH 0.2 AT VARIOUS TEMPERATURES

Temp., °C	K_{CuOAc}	$K_{Cu(OAc)_2}$	K_{PbOAc}	$K_{Pb(OAc)_2}$
15	41	190	130	750
25	52	93	130	390
35	69	82	120	380

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

Temp., °C	$\log K_{PbY}$	pK_{HY}	$\log K^{H}_{PbHY}$
15	18.17	10.20	—
20	—	—	2.7
25	17.76	10.04	—
35	17.36	9.91	—

TABLE IV. 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_1^+	k^+_{II}	k^+_{III}
15	1.7	10	1.7×10^9
25	5.1	60	3.0×10^9
35	17	300	4.5×10^9

TABLE V. RATE CONSTANTS, HEAT OF ACTIVATION AND ENTROPY OF ACTIVATION FOR REACTIONS 7, 8b AND 9b

Reaction	Rate constant, expressed in l. mol^{-1} sec^{-1}	$\Delta H^{\neq}$, kcal. mol^{-1}	$\Delta S^{\neq}$, e. u.
$Cu^{2+} + PbY^{2-} \rightarrow CuY^{2-} + Pb^{2+}$	$k_1^+ = 2.7 \times 10^{15} \exp(-20{,}000/\boldsymbol{R}T)$	19	10
$Cu^{2+} + PbHY^{-} \rightarrow CuHY^{-} + Pb^{2+}$	$k_{\mathrm{II}}^+ = 2.5 \times 10^{22} \exp(-28{,}000/\boldsymbol{R}T)$	27	42
$Cu^{2+} + HY^{3-} \rightarrow CuY^{2-} + H^{+}$	$k_{\mathrm{III}}^+ = 3.2 \times 10^{15} \exp(-\ 8{,}200/\boldsymbol{R}T)$	7.6	10

formation constants of CuY^{2-}, K_{CuY}, at 15, 25 and 35°C at ionic strength 0.2 were calculated, from the value obtained by Schwarzenbach et al.[5] at 20°C at ionic strength 0.1, with the aid of the Debye-Hückel equation and the heat of formation of CuY^{2-}, -8.2 kcal./mol., reported by Charles[6]. The equilibrium constants of reaction 2 at zero acetate concentration, K_{Pb}^{Cu}, used in this calculation are those determined by the present authors[3]. The rate constants of three elementary reactions 7, 8b and 9b thus calculated are summarized in Table IV.

Discussion

Linear relations were found between the logarithm of rate constant and the reciprocal of absolute temperature for three elementary reactions 7, 8b and 9b.

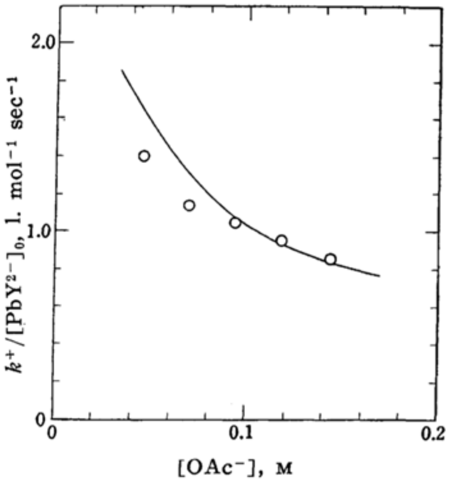

Fig. 3. $k^+/[PbY^{2-}]_0$ as a function of the acetate concentration in acetate buffer—potassium nitrate solutions of pH 5.14 and ionic strength 0.2 at 25°C. Initial concentrations are: $[Cu^{2+}]_{0,app} = 1.96 \times 10^{-4}$ M; $[PbY^{2-}]_0 = 4.90 \times 10^{-3}$ M; $[Pb^{2+}]_{0,app} = 4.90 \times 10^{-3}$ M. — indicates the theoretical curve and ○, the experimental value.

This made it possible to express the rate constants in the form of the Arrhenius equation and to calculate the heat of activation and the entropy of activation. The results are given in Table V.

From Eq. 15, it is predicted that the reaction rate decreases with the increase of acetate concentration. Using Eq. 16, the values of $k^+/[PbY^{2-}]_0$ were calculated at various acetate concentrations with the rate constants given in Table I and the formation constants of the acetato complexes. They are plotted against acetate concentration as shown in Fig. 3. The reaction rates were experimentally measured at various acetate concentrations, keeping the other conditions constant, with the same procedure as given in the previous paper[1]. Those values are also shown in Fig. 3, which are in fair agreement with the calculated ones. The deviation of the expermental values from the calculated ones is apparent at lower acetate concentration. This has not been clearly understood, but is considered to be due to a contribution of the reactions in which acetatocopper(II) complexes participate.

Summary

The effect of acetate ions on the rate of the substitution reaction of copper(II) and lead-EDTA complexes is explained quantitatively on the basis of the formation of acetato complexes of copper(II) and lead(II) in acetate media and on the assumption that the substitution reaction proceeds only through the hydrated metal ions. The rate constants, the heats of activation and the entropies of activation for three elementary reactions are recalculated with the experimental results obtained previously.

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[6] R. G. Charles, *J. Am. Chem. Soc.*, **76**, 5854 (1954).