The Kinetics of Substitution Reactions Involving Metal Complexes. VI. Reaction between Lead(II) and Ethylenediaminetetraacetatocobaltate(II) Complexes in Aqueous Solutions

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A series of substitution reactions involving metal-ethylenediaminetetraacetate (EDTA) complexes has been studied[1-7]. The reactions were found to proceed through three simultaneous reaction paths in the case of the substitution reactions of lead(II) and copper(II)-EDTA[3,4], lead(II) and zinc(II)-EDTA[2,6] and copper(II) and zinc(II)-EDTA[5], but through four simultaneous reaction paths in the case of the substitution reaction of copper(II) and cadmium(II)-EDTA[1,7].

In the present paper, the kinetic study of the substitution reaction between lead(II) ions and cobalt(II)-EDTA complexes is presented. From the rate constants of substitution of coordinated water[8,9], it was expected that the rate of dissociation of cobalt(II)-EDTA complexes is considerably slower than those of copper(II)-, zinc(II)- and cadmium(II)-EDTA complexes. This expectation was confirmed in the present study by the fact that the dissociation of cobalt(II)-EDTA complexes acts as a rate-determining reaction.

Derivation of the Rate Equation

Let us consider the acetate buffer solution which contains lead(II) ions and cobalt(II)-EDTA complexes. In the solution containing acetate ions less than 0.2 M in concentration, lead(II) forms mono- and diacetato complexes[10] and cobalt(II), monoacetato complex[11]. As for the EDTA complexes, the equilibria

$$\mathrm{CoY^{2-} + H^+ \rightleftharpoons CoHY^-},$$
$$\mathrm{PbY^{2-} + H^+ \rightleftharpoons PbHY^-}$$

must be taken into consideration when pH of the solution is less than 5, where Y^{4-} means a tetravalent EDTA anion. Consequently, the overall substitution reaction is represented by the equations

$$\mathrm{Pb^{2+} + 2OAc^- \rightleftharpoons PbOAc^+ + OAc^- \rightleftharpoons Pb(OAc)_2} \quad (1)$$

$$\mathrm{Pb^{2+}} + \left\{\begin{matrix}\mathrm{CoY^{2-}} \\ \downarrow\uparrow \\ \mathrm{CoHY^-}\end{matrix}\right\} \rightleftharpoons \left\{\begin{matrix}\mathrm{PbY^{2-}} \\ \downarrow\uparrow \\ \mathrm{PbHY^-}\end{matrix}\right\} + \mathrm{Co^{2+}} \quad (2)$$

$$\mathrm{Co^{2+} + OAc^- \rightleftharpoons CoOAc^+} \quad (3)$$

As described in the previous papers[6,10], the concentration of simple lead ions that can be determined polarographically is an apparent concentration $[\mathrm{Pb^{2+}}]_{\mathrm{app}}$ which, under the present experimental conditions, is given by

$$[\mathrm{Pb^{2+}}]_{\mathrm{app}} = [\mathrm{Pb^{2+}}] + [\mathrm{PbOAc^+}] + [\mathrm{Pb(OAc)_2}] \quad (4)$$

In the preliminary experiments in which the apparent initial rate of the reaction, $-\Delta[\mathrm{Pb^{2+}}]_{0,\mathrm{app}}/\Delta t$, was determined, the following facts were recognized, where the subscript 0 means the initial state.

(1) At the given pH and the given concentrations of $[\mathrm{Pb^{2+}}]_{0,\mathrm{app}}$, $[\mathrm{Co^{2+}}]_{0,\mathrm{app}}$ and $[\mathrm{OAc^-}]$, the apparent initial rate was proportional to the initial concentration of cobalt(II)-EDTA complex, $[\text{Co-EDTA}]_0$, given by

$$[\text{Co-EDTA}]_0 = [\mathrm{CoY^{2-}}]_0 + [\mathrm{CoHY^-}]_0$$

(2) At the given pH and the given concentrations of $[\text{Co-EDTA}]_0$, $[\mathrm{Co^{2+}}]_{0,\mathrm{app}}$ and $[\mathrm{OAc^-}]$, the apparent initial rate varied with the change of $[\mathrm{Pb^{2+}}]_{0,\mathrm{app}}$ according to the relation

$$-\frac{\Delta[\mathrm{Pb^{2+}}]_{0,\mathrm{app}}}{\Delta t}\Big/[\text{Co-EDTA}]_0 = k'[\mathrm{Pb^{2+}}]_{0,\mathrm{app}} + k'' \quad (5)$$

(3) The relation given by Eq. 5 held at any pH where the experiments were carried

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out. In addition, the values of k' and k'' in Eq. 5 which were obtained at various pH's satisfied the relations

$$k' = k_{\xi}'[\mathrm{H}^+] + k_{\eta}' \tag{6}$$

and

$$k'' = k_{\xi}''[\mathrm{H}^+] + k_{\eta}'' \tag{7}$$

These facts, which were analogous to those found in the preliminary study of the substitution reaction between lead(II) and nickel(II)-EDTA complexes12), suggested that the overall reaction would proceed, under the experimental conditions, through four simultaneous reaction paths,

$$\text{(i)}\quad \mathrm{Pb^{2+} + CoY^{2-}} \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} \mathrm{PbY^{2-} + Co^{2+}} \tag{8}$$

$$\text{(ii)}\quad \mathrm{Pb^{2+} + CoHY^{-}} \underset{k_2^-}{\overset{k_2^+}{\rightleftharpoons}} \mathrm{PbHY^{-} + Co^{2+}} \tag{9a}$$

$$\mathrm{PbHY^{-} \rightleftharpoons PbY^{2-} + H^+} \tag{9b}$$

$$\text{(iii)}\quad \mathrm{CoY^{2-}} \underset{k_{3a}^-}{\overset{k_{3a}^+}{\rightleftharpoons}} \mathrm{Co^{2+} + Y^{4-}} \quad \text{(rate-determining)} \tag{10a}$$

$$\mathrm{Pb^{2+} + Y^{4-}} \underset{k_{3b}^-}{\overset{k_{3b}^+}{\rightleftharpoons}} \mathrm{PbY^{2-}}\left(\underset{-\mathrm{H^+}}{\overset{+\mathrm{H^+}}{\rightleftharpoons}} \mathrm{PbHY^-}\right) \tag{10b}$$

$$\text{(iv)}\quad \mathrm{CoHY^{-}} \underset{k_{4a}^-}{\overset{k_{4a}^+}{\rightleftharpoons}} \mathrm{Co^{2+} + HY^{3-}} \quad \text{(rate-determining)} \tag{11a}$$

$$\mathrm{Pb^{2+} + HY^{3-}} \underset{k_{4b}^-}{\overset{k_{4b}^+}{\rightleftharpoons}} \mathrm{PbHY^{-}}\left(\underset{+\mathrm{H^+}}{\overset{-\mathrm{H^+}}{\rightleftharpoons}} \mathrm{PbY^{2-}}\right) \tag{11b}$$

It is assumed that in these reactions only the hydrated lead(II) ion $\mathrm{Pb^{2+}}$ is a reactive species. The apparent initial rate for the forward reaction is, then, derived as,

$$-\frac{\Delta[\mathrm{Pb^{2+}}]_{0,\mathrm{app}}}{\Delta t} = (k_1^+[\mathrm{CoY^{2-}}]_0 + k_2^+[\mathrm{CoHY^-}]_0)[\mathrm{Pb^{2+}}]_0 + k_{3a}^+[\mathrm{CoY^{2-}}]_0 + k_{4a}^+[\mathrm{CoHY^-}]_0 \tag{12}$$

Introducing the formation constants of acetatolead(II) complexes $K_{\mathrm{Pb(OAc)}_n}$ and the equilibrium constant $K^{\mathrm{H}}_{\mathrm{CoHY}}$ $(=[\mathrm{CoHY^-}]/([\mathrm{CoY^{2-}}][\mathrm{H^+}]))$, Eq. 13 is obtained for the apparent initial rate of the reaction.

$$-\frac{\Delta[\mathrm{Pb^{2+}}]_{0,\mathrm{app}}}{\Delta t} = \left[\{k_1^+ + k_2^+ K^{\mathrm{H}}_{\mathrm{CoHY}}[\mathrm{H^+}]\} \times \frac{[\mathrm{Pb^{2+}}]_{0,\mathrm{app}}}{1 + \sum_{n=1}^{2} K_{\mathrm{Pb(OAc)}_n}[\mathrm{OAc^-}]^n} + k_{3a}^+ + k_{4a}^+ K^{\mathrm{H}}_{\mathrm{CoHY}}[\mathrm{H^+}]\right] \frac{[\text{Co-EDTA}]_0}{1 + K^{\mathrm{H}}_{\mathrm{CoHY}}[\mathrm{H^+}]} \tag{13}$$

For the sake of convenience, Eq. 13 is rewritten as

$$-\frac{\Delta[\mathrm{Pb^{2+}}]_{0,\mathrm{app}}}{\Delta t}\,\frac{1}{[\text{Co-EDTA}]_0} = \frac{1}{\alpha\beta}\{k_1^+ + k_2^+ K^{\mathrm{H}}_{\mathrm{CoHY}}[\mathrm{H^+}]\}[\mathrm{Pb^{2+}}]_{0,\mathrm{app}} + \frac{1}{\alpha}\{k_{3a}^+ + k_{4a}^+ K^{\mathrm{H}}_{\mathrm{CoHY}}[\mathrm{H^+}]\} \tag{14}$$

$$\alpha = 1 + K_{\mathrm{Co\quad Y}}[\mathrm{H^+}]$$

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

Experimental

Reagents.—The solution of disodium ethylenediaminetetraacetate (EDTA) was standardized against the standard copper(II) solution by amperometric titration using a dropping mercury electrode as an indicator electrode13). The standard solution of lead(II) nitrate was prepared from the guaranteed grade reagent, and the concentration of lead(II) was determined amperometrically with the standardized EDTA solution13). The standard solution of cobalt(II) nitrate was obtained by dissolving cobalt metal in reagent grade nitric acid and standardized against the standardized EDTA solution amperometrically and also volumetrically with murexide14). Although the polarographic analysis showed that the cobalt metal contained 0.2% of nickel as impurity, the metal was used without further purification. It was taken into consideration that the substitution reaction between lead(II) and nickel(II)-EDTA complexes proceeds at much slower rate than the reaction between lead(II) and cobalt(II)-EDTA complexes12), and consequently a small amount of nickel contained in the cobalt metal would not interfere to an appreciable extent in the present experiments. All other chemicals used were of guaranteed reagent grade.

Apparatus and Procedure. — The initial rate of reaction was determined by measuring the change of the polarographic diffusion current of lead ions at −0.60 V. vs. SCE as a function of time in acetate buffer solutions. The current-time curves were recorded with a Shimadzu RP-2 pen-recording polarograph using a dropping mercury electrode. The dropping mercury electrode used had an *m* value of 2.93 mg./sec. and a drop time of 3.16 sec./drop, being measured in an air-free 0.2 M potassium

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

13) N. Tanaka, M. Kodama, M. Sasaki and M. Sugino, *Japan Analyst* (*Bunseki Kagaku*), 6, 86 (1957).

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nitrate solution with open circuit at 55 cm. of mercury column at 25°C.

Measurements were made at 5 and 15°C in acetate buffer solutions of pH from 4.75 to 5.66. The ionic strength was adjusted to be 0.2 with potassium nitrate. Gelatin was added as a maximum suppressor by 0.01% in concentration. The pH of the solution was measured with a Hitachi Model EHP-1 pH-meter, within the accuracy of 0.02 pH unit, immediately after the measurement of the current-time curves.

Results

Since α and β in Eq. 14 are constant at the given pH and the given concentration of acetate, a plot of the left-hand side of Eq. 14 versus $[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}$ should give a straight line with a slope of

$$\frac{1}{\alpha\beta}\{k_1{}^{+}+k_2{}^{+}K_{\mathrm{CoHY}}^{\mathrm{H}}[\mathrm{H}^{+}]\} \tag{15}$$

and the intercept at $[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}=0$ given by

$$\frac{1}{\alpha}\{k_{3a}{}^{+}+k_{4a}{}^{+}K_{\mathrm{CoHY}}^{\mathrm{H}}[\mathrm{H}^{+}]\} \tag{16}$$

The apparent initial rates were determined at various lead(II) concentrations with the reaction mixtures of the given pH which contained acetate buffer of the given acetate concentration and cobalt(II) ions and cobalt(II)-EDTA complexes in large excess over lead(II) ions. These measurements were carried out at various pH's ranging from 4.75 to 5.66. The plots of the left-hand side of Eq. 14 versus $[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}$ obtained at 15°C are shown in Fig. 1. The intercepts at $[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}=0$ and the slopes of these plots were determined by the method of least square. In these measurements at 15°C, the pH of the solutions was varied from 5.04 to 5.66 and consequently the value of α in Eq. 14 changes from 1.00_9 to 1.00_3. In the present calculation α was assumed to be unity, taking into consideration the accuracy of the measurement of the apparent initial rate and the deviations of the plots in Fig. 1. Then, the intercepts at $[\mathrm{Pb}^{2+}]_{0,\mathrm{aPp}}=0$ in Fig. 1 correspond simply to $\{k_{3a}{}^{+}+k_{4a}{}^{+}K_{\mathrm{CoHY}}^{\mathrm{H}}[\mathrm{H}^{+}]\}$ and the slopes to

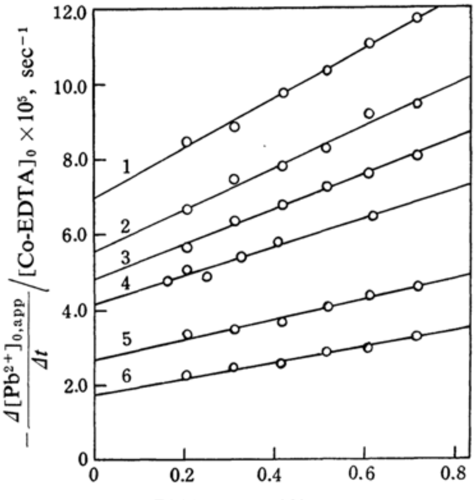

Fig. 1. $(-\Delta[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}/\Delta t)/[\mathrm{Co\text{-}EDTA}]_0$ as a function of the initial concentration of lead(II) ion in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 15°C. Initial concentrations are: $[\mathrm{Co}^{2+}]_{0,\mathrm{app}}=5.14\times10^{-3}$; $[\mathrm{Co\text{-}EDTA}]_0=4.91\times10^{-3}$ M. pH: (1), 5.04; (2), 5.11; (3), 5.21; (4), 5.30; (5), 5.47; (6), 5.66. Concentration of free acetate is 0.090 M.

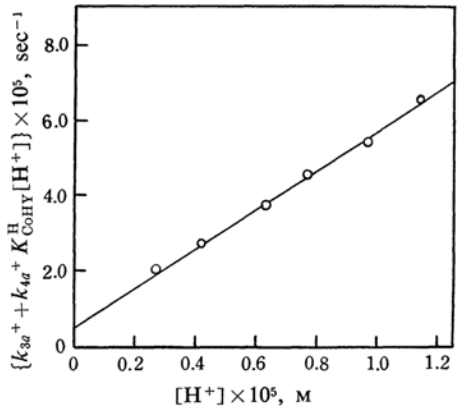

Fig. 2. The observed values for $\{k_{3a}{}^{+}+k_{4a}{}^{+}\cdot K_{\mathrm{CoHY}}^{\mathrm{H}}[\mathrm{H}^{+}]\}$ at various hydrogen ion concentrations in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 15°C. Initial concentrations are: $[\mathrm{Co}^{2+}]_{0,\mathrm{app}}=5.14\times10^{-3}$ M; $[\mathrm{Co\text{-}EDTA}]_0=4.91\times10^{-3}$ M. Concentration of free acetate is 0.090 M.

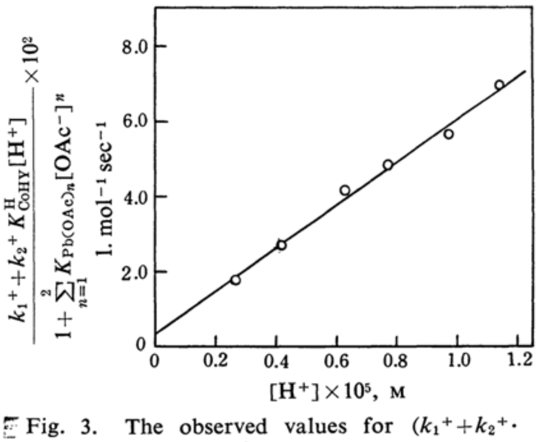

Fig. 3. The observed values for $(k_1{}^{+}+k_2{}^{+}\cdot K_{\mathrm{CoHY}}^{\mathrm{H}}[\mathrm{H}^{+}])/(1+\sum_{n=1}^{2}K_{\mathrm{Pb(OAc)}_n}[\mathrm{OAc}^{-}]^n)$ at various hydrogen ion concentrations. The conditions are the same as Fig. 2.

TABLE I. RATE CONSTANTS FOR REACTIONS (8), (9a), (10a) AND (11a) OBTAINED EXPERIMENTALLY AT IONIC STRENGTH 0.2 AT VARIOUS TEMPERATURES

Temp. °C	k_1^+ l. mol^{-1} sec^{-1}	k_2^+ l. mol^{-1} sec^{-1}	k_{3a}^+ sec^{-1}	k_{4a}^+ sec^{-1}
5	—*	48	—*	4.4×10^{-3}
15	(0.1)**	122	(4×10^{-6})**	7.3×10^{-3}

* The rate constant can not be determined from the plots corresponding to those in Figs. 2 and 3.
** The value is less accurate.

$\{k_1^+ + k_2^+ K^{\mathrm{H}}_{\mathrm{CoHY}}[\mathrm{H}^+]\}/\beta$. The values of $\{k_{3a}^+ + k_{4a}^+ K^{\mathrm{H}}_{\mathrm{CoHY}}[\mathrm{H}^+]\}$ and $\{k_1^+ + k_2^+ K^{\mathrm{H}}_{\mathrm{CoHY}}[\mathrm{H}^+]\}/\beta$ obtained are plotted against the hydrogen ion concentration in Figs. 2 and 3. From these plots, the values of k_1^+, k_2^+, k_{3a}^+ and k_{4a}^+ were determined, when $K^{\mathrm{H}}_{\mathrm{CoHY}}$ at 15°C was estimated from the value given by Schwarzenbach, Gut and Anderegg[15] and β was calculated with the aid of the formation constant $K_{\mathrm{Pb(OAc)}_n}$ reported previously[10]. Similar results were also obtained in the experiments carried out at 5°C. The rate constants k_1^+, k_2^+, k_{3a}^+ and k_{4a}^+ at 5 and 15°C are given in Table I.

Discussion

The assumption that reactions 10a and 11a are rate-determining in reaction paths iii and iv, respectively, should be discussed, though it is confirmed by the experimental results. Let us consider reaction path iii, for example. The initial rate of the reaction (v_3), which is measured by the decrease of $[\mathrm{Pb}^{2+}]_{\mathrm{app}}$, is given as

$$v_3 = k_{3b}^+ [\mathrm{Pb}^{2+}]_0 [\mathrm{Y}^{4-}]_0 \qquad (17)$$

Applying the steady state treatment, $[\mathrm{Y}^{4-}]_0$ is represented as

$$[\mathrm{Y}^{4-}]_0 = \frac{k_{3a}^+ [\mathrm{CoY}^{2-}]_0}{k_{3a}^- [\mathrm{Co}^{2+}]_0 + k_{3b}^+ [\mathrm{Pb}^{2+}]_0} \qquad (18)$$

Introducing Eq. 18 into Eq. 17, v_3 is written as

$$v_3 = \frac{k_{3a}^+ k_{3b}^+ [\mathrm{Pb}^{2+}]_0 [\mathrm{CoY}^{2-}]_0}{k_{3a}^- [\mathrm{Co}^{2+}]_0 + k_{3b}^+ [\mathrm{Pb}^{2+}]_0} \qquad (19)$$

In Eq. 19, if the condition,

$$k_{3a}^- [\mathrm{Co}^{2+}]_0 \ll k_{3b}^+ [\mathrm{Pb}^{2+}]_0$$

is satisfied, Eq. 19 is simplified to

$$v_3 = k_{3a}^+ [\mathrm{CoY}^{2-}]_0 \qquad (20)$$

Eq. 20 indicates that the rate of the reaction is independent of the concentration of lead(II) ions present in the solution. A similar treatment is applied to reaction path iv, when the same relation that the reaction rate is independent of the concentration of lead(II) ions is obtained. These results agree with the experimental observations. At this point, the substitution reaction between lead(II) and cobalt(II)-EDTA is entirely different from those reported previously[1-7].

In this study, k_1^+ and k_{3a}^+ at 5°C could not be determined, and those at 15°C were less accurate than other rate constants. This was presumably due to the fact that the reactions through paths i and iii make only a small contribution to the whole reaction. The contribution of the each reaction path was calculated under the appropriate conditions, and is given in Table II, which indicates that the reaction through paths i and iii is less than 10% of the whole reaction.

Equation 13 predicts that the reaction rate decreases with increasing concentration of acetate ion. This has been found and confirmed experimentally with several substitution reactions studied previously. Using Eq. 14, the values of $(-\Delta[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}/\Delta t)/[\mathrm{Co\text{-}EDTA}]_0$ were calculated at various concentrations of acetate ion with the rate constants given in

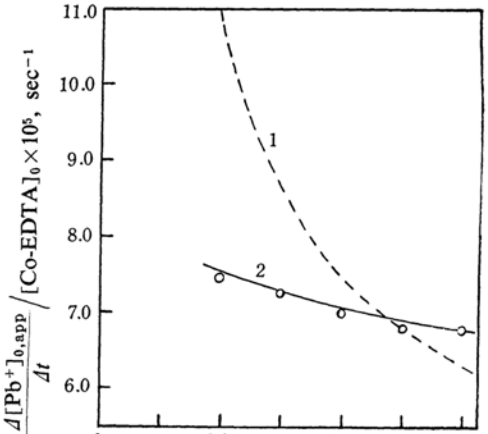

Fig. 4. $(-\Delta[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}/\Delta t)/[\mathrm{Co\text{-}EDTA}]_0$ as a function of the acetate ion concentration in acetate buffer-potassium nitrate solutions of pH 5.22 and ionic strength 0.2 at 15°C. Initial concentrations are: $[\mathrm{Pb}^{2+}]_{0,\mathrm{app}} = 5.00\times10^{-4}$ M; $[\mathrm{Co}^{2+}]_{0,\mathrm{app}} = 5.14\times10^{-3}$ M; $[\mathrm{Co\text{-}EDTA}]_0 = 4.91\times10^{-3}$ M. Curve 1 represents the theoretical values calculated with Eq. 14, while curve 2, that calculated with Eq. 22. ○ indicates the experimental value.

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

TABLE II. CONTRIBUTION OF EACH REACTION PATH TO OVERALL SUBSTITUTION REACTION AT pH 5.21, 15°C AND 0.2 IONIC STRENGTH*

Reaction path	Expression for reaction rate**	Reaction rate sec^{-1}	Contribution to total reaction rate %
(i)	$k_1{}^+[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}/\alpha\beta$	$2.6_5\times10^{-6}$	2.9
(ii)	$k_2{}^+K^{\mathrm{H}}_{\mathrm{CoHY}}[\mathrm{H}^+][\mathrm{Pb}^{2+}]_{0,\mathrm{app}}/\alpha\beta$	$2.0_6\times10^{-5}$	29.1
(iii)	$k_{3a}{}^+/\alpha$	4.0×10^{-6}	5.5
(iv)	$k_{4a}{}^+K^{\mathrm{H}}_{\mathrm{CoHY}}[\mathrm{H}^+]/\alpha$	4.5×10^{-5}	62.6

* $[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}=5.18\times10^{-4}$ M, $[\mathrm{Co}^{2+}]_{0,\mathrm{app}}=5.14_4\times10^{-3}$ M, $[\text{Co-EDTA}]_0=4.90_5\times10^{-3}$ M, $[\mathrm{OAc}^-]=0.090$ M

** $\alpha=1+K^{\mathrm{H}}_{\mathrm{CoHY}}[\mathrm{H}^+]$; $\beta=1+\sum_{n=1}^{2}K_{\mathrm{Pb(OAc)}_n}[\mathrm{OAc}^-]^n$

Table I. These values are plotted against acetate ion concentration in Fig. 4 (curve 1), where the experimental values for $(-\Delta\cdot[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}/\Delta t)/[\text{Co-EDTA}]_0$ obtained at various concentrations of acetate ion are also given. Figure 4 indicates that the values of $(-\Delta[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}/\Delta t)/[\text{Co-EDTA}]_0$ calculated with Eq. 14 fairly deviate from the experimental ones, as has been noticed in the studies on other substitution reactions[4-7]. The discrepancy apparently arises from the assumption that the reaction proceeds through only hydrated ions.

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

$$\text{(i)}\quad \mathrm{Pb}^{2+}+\mathrm{CoY}^{2-}\overset{k_{1h}{}^+}{\rightleftharpoons}\mathrm{PbY}^{2-}+\mathrm{Co}^{2+}\tag{8'}$$

$$\mathrm{PbOAc}^{+}+\mathrm{CoY}^{2-}\overset{k_{1c}{}^+}{\rightleftharpoons}\mathrm{PbY}^{2-}+\mathrm{CoOAc}^{+}\tag{8''}$$

$$\text{(ii)}\quad \mathrm{Pb}^{2+}+\mathrm{CoHY}^{-}\overset{k_{2h}{}^+}{\rightleftharpoons}\mathrm{PbHY}^{-}+\mathrm{Co}^{2+}\tag{9a'}$$

$$\mathrm{PbOAc}^{+}+\mathrm{CoHY}^{-}\overset{k_{2c}{}^+}{\rightleftharpoons}\mathrm{PbHY}^{-}+\mathrm{CoOAc}^{+}\tag{9a''}$$

where $k_{ih}{}^+$ and $k_{ic}{}^+$ mean the rate constants of the reactions which proceed through the hydrated ion and monoacetato complex, respectively. Reaction paths iii and iv are not concerned with this treatment because the rate-determining steps of these paths are the dissociation of cobalt(II)-EDTA complexes and involve no acetato complex.

Since it seemed extremely difficult, however, to determine all of these rate constants, $k_{ih}{}^+$ and $k_{ic}{}^+$, separately because of insufficient accuracy in the measurement, a procedure similar to that reported previously[7] was taken up as the first approximation.

In reaction paths i and ii, the ratios of $k_{ic}{}^+$ and $k_{ih}{}^+$ are assumed to be the same and denoted with x.

$$\frac{k_{ic}{}^+}{k_{ih}{}^+}=x\tag{21}$$

Introducing the relation of Eq. 21 into Eq. 13 and rearranging, one obtains Eq. 22.

$$\left\{-\frac{\Delta[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}}{\Delta t}\frac{\alpha}{[\text{Co-EDTA}]_0}-k_{3a}{}^+-k_{4a}{}^+K^{\mathrm{H}}_{\mathrm{CoHY}}[\mathrm{H}^+]\right\}\frac{\beta}{[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}}$$
$$=\{k_{1h}{}^++k_{2h}{}^+K^{\mathrm{H}}_{\mathrm{CoHY}}[\mathrm{H}^+]\}\times\{1+xK_{\mathrm{PbOAc}}[\mathrm{OAc}^-]\}\tag{22}$$

Equation 22 indicates that the plot of the left-hand side of the equation against the acetate ion concentration should give a straight line with a slope of $xK_{\mathrm{PbOAc}}\{k_{1h}{}^++k_{2h}{}^+K^{\mathrm{H}}_{\mathrm{CoHY}}[\mathrm{H}^+]\}$ and an intercept of $\{[k_{1h}{}^++k_{2h}{}^+K^{\mathrm{H}}_{\mathrm{CoHY}}[\mathrm{H}^+]\}$ at zero acetate concentration.

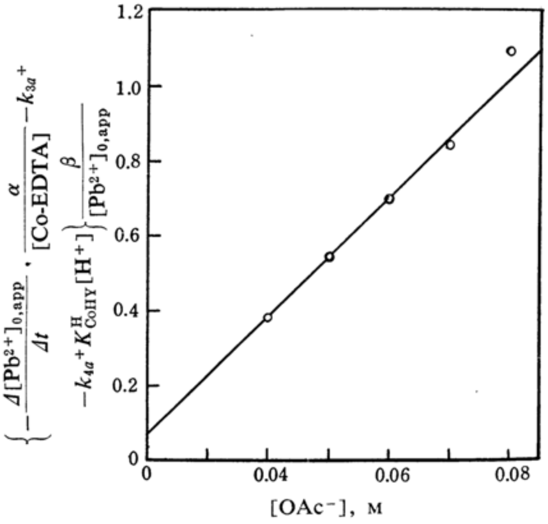

Fig. 5. Left-hand side of Eq. 22 as a function of the acetate ion concentration. The conditions are the same as Fig. 4.

The experimental values obtained at varied acetate concentrations were utilized in a plot given in Fig. 5. A straight line in Fig. 5 shows the validity of the treatment. The values of k_{ih}^+ and k_{ic}^+ were calculated with the value of x which was determined from this plot. Using k_{ih}^+, k_{ic}^+, k_{3a}^+ and k_{4a}^+, $(-\Delta[\mathrm{Pb}^{2+}]_{0,\mathrm{app}}/\Delta t)/[\text{Co-EDTA}]_0$ was calculated at various concentrations of acetate ion and is given in Fig. 4 (curve 2). It is seen that curve 2 is in satisfactory agreement with the experimental observations. 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 lead(II) and ethylenediaminetetraacetatocobaltate(II) complexes in aqueous solutions has been carried out by a similar method as reported previously[3-7]. The reaction was found to proceed through four simultaneous reaction paths and to be characterized by involving the dissociation of ethylenediaminetetraacetatocobaltate(II) complexes as a rate-determining process. The rate constants of the rate-determining steps of four reaction paths were determined at ionic strength 0.2 at 5 and 15°C. It was confirmed also that this substitution reaction proceeds through both hydrated and monoacetato lead(II) ions.

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