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

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(Received September 28, 1962)

Recent studies on a series of substitution reactions between metal ions and metal-ethylenediaminetetraacetate (EDTA) complexes in acetate buffer solutions[1-5] have revealed that these reactions proceed through both the hydrated metal ions and the metal acetato complexes. The reaction through acetato complexes was suggested in some of the previous papers[1-3], while in the others it was treated somewhat quantitatively by the approximate method[4,5].

In this study, a rigorous treatment of the effect of acetate ions on the substitution reaction has been developed and applied to the reaction between lead(II) ions and zinc-EDTA complexes. The reaction mechanisms which involve reaction paths through hydrated ions and those through acetato complexes have been assumed and the rate constants for the rate-determining steps in those reaction paths have been determined.

Experimental

Reagents.—The preparation of the solutions of lead(II) nitrate and disodium ethylenediaminetetraacetate was described in the previous papers[2,6]. A solution of zinc nitrate was prepared by dissolving an appropriate amount of pure zinc metal in nitric acid, and standardized amperometrically against

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[1] N. Tanaka and K. Kato, This Bulletin, 32, 1376 (1959).

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

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

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

[5] N. Tanaka, H. Osawa and M. Kamada, ibid., 36, 67 (1963).

[6] N. Tanaka, K. Kato and R. Tamamushi, ibid., 31, 283 (1958).

the standardized EDTA solution. All other chemicals used were of analytical reagent grade.

Apparatus and Procedure.—The rate of the reaction between lead(II) ions and zinc-EDTA complexes was followed by measuring the decrease of the polarographic diffusion current of lead(II) ions with time in acetate buffer solutions. For the measurements of the current-time curves, a Yanagimoto PB-4 pen-recording polarograph was used. A dropping mercury electrode used had an m value of 2.12 mg./sec. and a drop time t_d of 3.92 sec., being measured at −0.60 V. vs. SCE in an air-free 0.2 M potassium nitrate solution containing 0.01% gelatin at 25.0°C. The pH of the solution was measured accurately with a Hitachi EHP-1 pH meter, after the measurement of the current-time curves. Ionic strength of the solution was adjusted to be 0.2 with potassium nitrate, and gelatin was added as a maximum suppressor by 0.01% in concentration. All measurements were carried out at 25.0°C.

Results and Discussion

In the solution containing acetate ions up to 0.2M in concentration, lead(II) forms mono- and diacetato complexes, whereas zinc(II) forms only a monoacetato complex⁷⁾. The overall substitution reaction between lead(II) and zinc-EDTA complexes is written as the following:

$$\left\{\begin{array}{l}\mathrm{Pb^{2+}}\\ \downarrow\uparrow\\ \mathrm{PbOAc^{+}}\\ \downarrow\uparrow\\ \mathrm{Pb(OAc)_2}\end{array}\right\} + \mathrm{ZnY^{2-}} \rightleftarrows \mathrm{PbY^{2-}} + \left\{\begin{array}{l}\mathrm{Zn^{2+}}\\ \downarrow\uparrow\\ \mathrm{ZnOAc^{+}}\end{array}\right\} \qquad (1)$$

where Y^{4-} denotes a tetravalent EDTA anion.

When both zinc ions and zinc-EDTA complexes are present in a large excess over lead ions, the substitution reaction 1 can be treated as a pseudo-first-order reaction,

$$\left\{\begin{array}{l}\mathrm{Pb^{2+}}\\ \downarrow\uparrow\\ \mathrm{PbOAc^{+}}\\ \downarrow\uparrow\\ \mathrm{Pb(OAc)_2}\end{array}\right\} \underset{k^-}{\overset{k^+}{\rightleftharpoons}} \mathrm{PbY^{2-}} \qquad (2)$$

The rate equation for the reaction 2 is expressed as¹⁾

$$-\frac{\mathrm{d}[\mathrm{Pb^{2+}}]_{\mathrm{app}}}{\mathrm{d}t} = k^+[\mathrm{Pb^{2+}}]_{\mathrm{app}} - k^-[\mathrm{PbY^{2-}}] \qquad (3)$$

where $[\mathrm{Pb^{2+}}]_{\mathrm{app}}$ is the concentration of lead(II) that can be determined polarogaphically as the simple ion, and given by the equation

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

Integrating Eq. 3,

$$\ln\{[\mathrm{Pb^{2+}}]_{\mathrm{app}} - [\mathrm{Pb^{2+}}]_{\mathrm{e,app}}\} = -(k^+ + k^-)t + \ln\{[\mathrm{Pb^{2+}}]_{\mathrm{0,app}} - [\mathrm{Pb^{2+}}]_{\mathrm{e,app}}\} \qquad (5)$$

is obtained, where subscripts 0 and e represent the initial and the equilibrium conditions, respectively. The left-hand side of Eq. 5 is plotted against time and from the slope the value of $(k^+ + k^-)$ is determined. At the equilibrium of the reaction, the relation

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

may be satisfied, where $K^{\mathrm{Pb}}_{\mathrm{Zn,app}}$ represents the apparent equilibrium constant for reaction 1 expressed as

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

The values of $K^{\mathrm{Pb}}_{\mathrm{Zn,app}}$ were determined polarographically to be 10.3 and 5.0 in acetate buffer solutions which contain 0.05M and 0.1M of acetate ions, respectively.

The apparent rate constants of the forward reaction 1, $k^+/[\mathrm{ZnY^{2-}}]_0$, were obtained at various pH's and at two different concentrations of Zn(II) and acetate ions. The plots of $k^+/[\mathrm{ZnY^{2-}}]_0$ versus $[\mathrm{H^+}]$ gave straight lines as shown in Fig. 1.

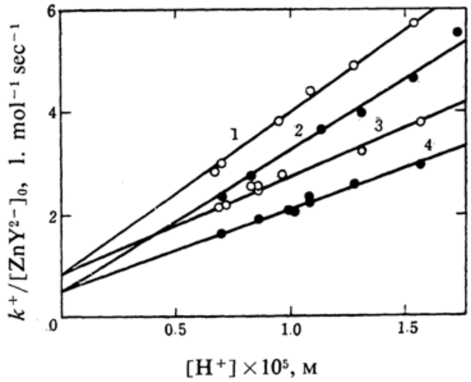

Fig. 1. $k^+/[\mathrm{ZnY^{2-}}]_0$ as a function of the hydrogen ion concentration in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 25°C. Initial concentrations are: $[\mathrm{Pb^{2+}}]_{\mathrm{0,app}} = 2.06 \times 10^{-4}$ M; $[\mathrm{ZnY^{2-}}]_0 = 5.25 \times 10^{-3}$ M; $[\mathrm{Zn^{2+}}]_{\mathrm{0,app}} = 5.05 \times 10^{-3}$ M (curves 1 and 2) and 1.02×10^{-2} M (curves 3 and 4). Concentrations of free acetate are 0.049 M for curves 1 and 3 and 0.098 M for curves 2 and 4.

Bril, Bril and Krumholz⁸⁾ found that the reaction proceeds simultaneously through three different reaction paths. This was confirmed by Tanaka and Kato³⁾, who presumed that the reaction proceeds not only through hydrated metal ions but also through acetato complexes. Considering these facts, the following mechanisms were set down for reaction 1.

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

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

$$\text{(i)}\quad \mathrm{Pb^{2+}+ZnY^{2-}} \overset{k^+_{1h}}{\rightleftharpoons} \mathrm{PbY^{2-}+Zn^{2+}} \tag{6}$$

$$\mathrm{PbOAc^{+}+ZnY^{2-}} \overset{k^+_{\mathrm{I}c}}{\rightleftharpoons} \mathrm{PbY^{2-}+ZnOAc^{+}} \tag{6$'$}$$

$$\text{(ii)}\quad \mathrm{ZnY^{2-}+H^{+}} \rightleftharpoons \mathrm{ZnHY^{-}} \tag{7}$$

$$\mathrm{Pb^{2+}+ZnHY^{-}} \overset{k^+_{\mathrm{II}h}}{\rightleftharpoons} \mathrm{PbHY^{-}+Zn^{2+}} \tag{8}$$

$$\mathrm{PbOAc^{+}+ZnHY^{-}} \overset{k^+_{\mathrm{II}c}}{\rightleftharpoons} \mathrm{PbHY^{-}+ZnOAc^{+}} \tag{8$'$}$$

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

$$\text{(iii)}\quad \mathrm{ZnY^{2-}+H^{+}} \underset{k^-_{a}}{\rightleftharpoons} \mathrm{Zn^{2+}+HY^{3-}} \tag{10}$$

$$\mathrm{Pb^{2+}+HY^{3-}} \overset{k^+_{\mathrm{III}h}}{\rightleftharpoons} \mathrm{PbY^{2-}+H^{+}} \tag{11}$$

$$\mathrm{PbOAc^{+}+HY^{3-}} \overset{k^+_{\mathrm{III}c}}{\rightleftharpoons} \mathrm{PbY^{2-}+H^{+}+OAc^{-}} \tag{11$'$}$$

In reaction paths (iii), the concentration of $\mathrm{HY^{3-}}$ is expected to be extremely small during the reaction, and the steady state approximation may be applied. In addition, the condition,

$$k^-_{a}[\mathrm{Zn^{2+}}] \gg k^+_{\mathrm{III}h}[\mathrm{Pb^{2+}}] + k^+_{\mathrm{III}c}[\mathrm{PbOAc^{+}}]$$

is satisfied, as was justified by Bril et al.[8)]

In the present treatment, it is assumed that the equilibria between hydrated ions and acetato complexes are maintained while the substitution reaction takes place. This assumption seems to be reasonable from the results in Table II given below. From these assumptions one obtains Eq. 12 for the rate equation for reaction 1, where

$$k^+_{1c} = k^+_{\mathrm{I}c} K_{\mathrm{PbOAc}},\ k^+_{2h} = k^+_{\mathrm{II}h} K^{\mathrm{H}}_{\mathrm{ZnHY}},$$

$$k^+_{2c} = k^+_{\mathrm{II}c} K^{\mathrm{H}}_{\mathrm{ZnHY}} K_{\mathrm{PbOAc}},\ k^+_{3h} = \frac{k^+_{\mathrm{III}h}}{K_{\mathrm{ZnY}} K_{\mathrm{HY}}},$$

$$k^+_{3c} = \frac{k^+_{\mathrm{III}c}}{K_{\mathrm{ZnY}} K_{\mathrm{HY}}} K_{\mathrm{PbOAc}} \tag{13}$$

TABLE I. RATE CONSTANTS IN EQ. 14 OBTAINED EXPERIMENTALLY AT IONIC STRENGTH 0.2 AT 25°C

	Rate constant	
k^+_{1h}	5	$\mathrm{l.mol^{-1}sec^{-1}}$
k^+_{1c}	4×10	$\mathrm{l^2mol^{-2}sec^{-1}}$
k^+_{2h}	$\sim2\times10^5$	$\mathrm{l^2mol^{-2}sec^{-1}}$
k^+_{2c}	$\sim7\times10^6$	$\mathrm{l^3mol^{-3}sec^{-1}}$
k^+_{3h}	4×10^3	$\mathrm{l.mol^{-1}sec^{-1}}$
k^+_{3c}	1×10^5	$\mathrm{l^2mol^{-2}sec^{-1}}$

$K_{\mathrm{Pb(OAc)}_n}$ and K_{ZnOAc} represent the overall formation constants of acetato lead(II) and acetatozinc(II) complexes, respectively. $K^{\mathrm{H}}_{\mathrm{ZnHY}}$ represents the equilibrium constant of reaction 7, K_{ZnY}, the formation constant of $\mathrm{ZnY^{2-}}$ and K_{HY}, the fourth dissociation constant of ethylenediaminetetraacetic acid.

From Eqs. 3 and 12, Eq. 14 is obtained, where the initial concentrations, $[\mathrm{Zn^{2+}}]_0$ and $[\mathrm{ZnY^{2-}}]_0$, are substituted for $[\mathrm{Zn^{2+}}]$ and $[\mathrm{ZnY^{2-}}]$, respectively. Since both $\mathrm{Zn^{2+}}$ and $\mathrm{ZnY^{2-}}$ are present in the solution in a large excess over lead ions, the change of their concentrations during the reaction can be neglected.

The rate constants in Eq. 14 were obtained from the analysis of plots in Fig. 1, and are given in Table I. The formation constants of acetatolead(II) and acetatozinc(II) complexes which were used in the calculation are reported in the previous paper[7)]. The concentration of uncomplexed acetate in the solution was calculated by successive approximation.

The rate constants for reactions 6, 6′, 8, 8′, 11 and 11′ were calculated from the relations given in Eqs. 13. The values of $K^{\mathrm{H}}_{\mathrm{ZnHY}}$, K_{ZnY} and K_{HY} which were used in the calculation were reported previously[3)]. The obtained rate constants for reactions 6, 6′, 8, 8′, 11 and 11′ are given in Table II. The values in Table II indicate that the all reactions proceeding

$$-\frac{\mathrm{d}[\mathrm{Pb^{2+}}]_{\mathrm{app}}}{\mathrm{d}t} = \frac{k^+_{1h} + k^+_{1c}[\mathrm{OAc^-}] + (k^+_{2h} + k^+_{2c}[\mathrm{OAc^-}])[\mathrm{H^+}] + (k^+_{3h} + k^+_{3c}[\mathrm{OAc^-}])\dfrac{1+K_{\mathrm{ZnOAc}}[\mathrm{OAc^-}]}{[\mathrm{Zn^{2+}}]_{\mathrm{app}}}[\mathrm{H^+}]}{1+\sum\limits_{n=1}^{2} K_{\mathrm{Pb(OAc)}_n}[\mathrm{OAc^-}]^n} \times [\mathrm{Pb^{2+}}]_{\mathrm{app}}[\mathrm{ZnY^{2-}}] \tag{12}$$

$$\frac{k^+}{[\mathrm{ZnY^{2-}}]_0} = \frac{k^+_{1h} + k^+_{1c}[\mathrm{OAc^-}] + (k^+_{2h} + k^+_{2c}[\mathrm{OAc^-}])[\mathrm{H^+}] + (k^+_{3h} + k^+_{3c}[\mathrm{OAc^-}])\dfrac{1+K_{\mathrm{ZnOAc}}[\mathrm{OAc^-}]}{[\mathrm{Zn^{2+}}]_{\mathrm{o,app}}}[\mathrm{H^+}]}{1+\sum\limits_{n=1}^{2} K_{\mathrm{Pb(OAc)}_n}[\mathrm{OAc^-}]^n} \tag{14}$$

TABLE II. RATE CONSTANTS FOR REACTIONS 6, 6′, 8, 8′, 11 AND 11′ AT IONIC STRENGTH 0.2 AT 25°C

Rate constant, l. mol^{-1} sec^{-1}					
$k_{\mathrm{I}h}^{+}$	$k_{\mathrm{I}c}^{+}$	$k_{\mathrm{II}h}^{+}$	$k_{\mathrm{II}c}^{+}$	$k_{\mathrm{III}h}^{+}$	$k_{\mathrm{III}c}^{+}$
5	0.3	$\sim 3\times 10^{2}$	$\sim 7\times 10$	3×10^{9}	6×10^{8}

through Pb^{2+} are faster than the corresponding reactions through $PbOAc^{+}$. It is considered to be mainly due to the difference in charge of the reacting species.

From Eq. 12, it is predicted that the reaction rate decreases with the increase of acetate ion concentration. With Eq. 14, $k^{+}/[ZnY^{2-}]_0$ was calculated as a function of the concentration of acetate ion, using the rate constants given in Table I and the formation constants of acetato complexes. Two sets of calculations which were made at two different hydrogen ion concentrations are shown in Fig. 2, where the experimental values of $k^{+}/[ZnY^{2-}]_0$ measured at various acetate concentrations are also given. These are in satisfactory agreement with the calculated curves. This fact leads to a definite conclusion that the reaction proceeds not only through hydrated metal ions but also through acetato complexes. It also suggests that the contribution of the reaction through diacetato complexes is of least significance.

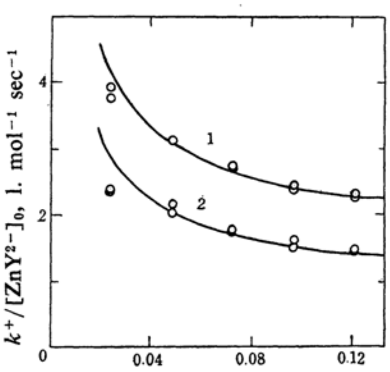

Fig. 2. $k^{+}/[ZnY^{2-}]_0$ as a function of the acetate concentration in acetate buffer-potassium nitrate solutions of $[H^{+}]=1.17\times 10^{-5}$ M (curve 1) and $[H^{+}]=0.63\times 10^{-5}$ M (curve 2). Initial concentrations are: $[Pb^{2+}]_{0,\mathrm{app}}=1.65\times 10^{-4}$ M; $[ZnY^{2-}]_0=5.00\times 10^{-3}$; $[Zn^{2+}]_{0,\mathrm{app}}=1.00\times 10^{-2}$ M.
— indicates the theoretical curve and ○, the experimental value.

Summary

The effect of acetate ions on the substitution reaction between lead(II) and zinc-EDTA complexes has been investigated. The reaction was treated as to proceed through both hydrated metal ions and monoacetato complexes, and the rate equation was derived. The rate constants for six elementary reactions of which three involve the hydrated lead(II) ion and the others involve the monoacetatolead-(II) complex were determined at ionic strength 0.2 at 25.0°C. The values indicate that all the reactions proceeding through hydrated lead ions are faster than the corresponding reactions through monoacetato lead complexes. The results also suggest that the rate of the reaction through diacetatolead(II) complexes is much slower than those of the reactions through hydrated ions and monoacetato complexes.

The authors thank the Ministry of Education for the financial support granted for this research. A part of the experimental work was carried out with the assistance of Dr. Gen Satô.

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