February, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(2), 445—449 (1976) 445

Substitution Reactions of Several Lead(II)-Polyamine-*N*-polyacetate Complexes with Indium(III) in Aqueous Solutions

Toru Nozaki and Nagao Suemitsu

Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama-shi 790

(Received January 13, 1975)

The kinetics of the substitution reactions of the lead(II) complexes of EDTA, EDTA·OH, CyDTA, and DTPA with the indium(III) ion have been studied in the pH range from 1.8 to 4.8 at 20 °C and at an ionic strength of 0.1 in the presence of an excess of lead(II) ions. The reaction for the CyDTA system seems to proceed through only the dissociative process, while those for the EDTA, EDTA·OH, and DTPA systems proceed through both the steps forming a binuclear intermediate and the dissociative steps, in which the reactions forming indium complexes proceed mainly through the paths involving $InOH^{2+}$.

Many of the substitution reactions of divalent metal complexes of ethylenediamine-*N,N,N′,N′*-tetraacetate (EDTA) and 1,2-cyclohexanediaminetetraacetate (CyDTA) with other divalent metal ions have been reported. However, only a few substitution reactions of divalent metal complexes with trivalent metal ions have been studied. Recently, the reaction paths of this type of substitution reaction have been shown by Takahashi and his co-workers.[1]

In the same way as in the previous work,[2] the kinetics of the substitution reactions of the lead(II) complexes of EDTA, *N*-(hydroxyethyl)ethylenediamine-*N,N′,N′*-triacetate (EDTA·OH), CyDTA, and diethylenetriamine-*N,N,N′,N″,N″*-pentaacetate (DTPA) with the indium(III) ion, which has the same electronic configuration as the gallium(III) ion, have been studied in the pH range from 1.8 to 4.2 at 20 °C and at an ionic strength of 0.1 in order to investigate the effects of the ligand and of the species of the indium(III) ion on the rate and the reaction process, and in order to compare the rates with those for gallium(III). In the present paper the rate equations will be presented on the basis of the kinetic results, and the mechanisms of the reactions will be discussed by relating the terms in the observed rate constants of the reactions to the rate constants of the reaction paths of a known type.[1]

Experimental

Stock solutions of indium(III) and lead(II) were prepared by dissolving a weighed amount of metallic indium (99.99%) in perchloric acid, and by converting lead(II) nitrate into the perchlorate with perchloric acid, respectively. The solutions were diluted to a constant volume with redistilled water and were standardized by chelatometric titration with EDTA. Standard solutions of polyamine-*N*-polyacetate were prepared by dissolving a weighed amount of EDTA, EDTA·OH, CyDTA, or DTPA (Dotite reagent), which had been dried at 80 °C for 3 hr without further purification, in redistilled water containing equimolar quantities of sodium hydroxide.

The pH values of the solutions of the lead(II) complexes and indium(III) were adjusted to given values with sodium hydroxide and perchloric acid, using a pH meter equipped with a calomel electrode in which sodium chloride was substituted for potassium chloride to avoid potassium-perchlorate interference. After mixing, the pH of the resulting solutions was constant during the reactions. The ionic strength of each of the solutions was adjusted to 0.1 with sodium perchlorate. The initial concentrations of PbX_t, where X_t denotes all the species of the polyamine-*N*-polyacetate anions, In(III), and Pb^{2+} were 5.0×10^{-6}, 5.0×10^{-6}, and $(1.0-8.0)\times10^{-3}$ M respectively. The substitution reactions were run in the pH range from 1.8 to 4.2 at 20 °C and at an ionic strength of 0.1 in the presence of an excess of lead(II) ions and in the absence of a buffer solution.

The reactions were followed by measuring the changes in the percent transmittances of the mixed solutions of the lead(II)-EDTA, -EDTA·OH, -CyDTA, and -DTPA complexes at maximum absorption wavelengths[3] of 240, 240, 225, and 250 nm respectively. The reacted amount of PbX_t with In(III), x, in the molar concentration for the initial reaction time, t (min), can be expressed as follows:

$$x = \frac{a\cdot\varepsilon_{PbX_t}+b\cdot\varepsilon_{In}+c\cdot\varepsilon_{Pb}-D}{(\varepsilon_{PbX_t}-\varepsilon_{Pb})-(\varepsilon_{InX_t}-\varepsilon_{In})}$$

where a, b, c are the initial concentrations of the lead complexes PbX_t, the In(III) ions, and Pb^{2+} respectively, and where ε_{PbX_t}, ε_{Pb}, ε_{InX_t}, and ε_{In} are the molar extinction coefficients for PbX_t, Pb^{2+}, all the species of the indium(III) complexes, InX_t, and the In(III) ions, again respectively, at the maximum absorption wavelengths of the lead complexes, and where D refers to the measured absorbance of the mixed solution.

Results and Discussion

Reaction Orders. The reaction orders with respect to the lead complexes and the indium(III) ions were examined by changing the concentration of the complexes from 2.0×10^{-6} to 9.0×10^{-6} M and that of the indium ions from 2.0×10^{-6} to 1.1×10^{-5} M in the presence of excessive lead ions at a constant pH. The reactions were found to be first-order in both $[PbX_t]$ and [In(III)].

Effects of an Excess of Lead(II) Ions. Using the Bydalek and Margerum method,[4] the effects of excessive lead ions on the rates were investigated. The rates for all the systems decreased with an increase in the concentration of added lead ions, as is shown in Fig. 1.

pH Dependences. The effects of the pH on the initial rates are shown in Fig. 2. The rates were too fast and too slow to be measured below and above the pH ranges from 2.6 to 4.1, from 3.2 to 4.3, from 2.6 to 3.6, and from 1.8 to 2.3 for the EDTA, EDTA·OH, CyDTA, and DTPA systems respectively. The slopes suggest that the rate equations involve the terms of $1/[H^+]$ and $[H^+]$ for the EDTA and EDTA·OH systems, $[H^+]$ for the CyDTA system, and $1/[H^+]$ for the DTPA system.

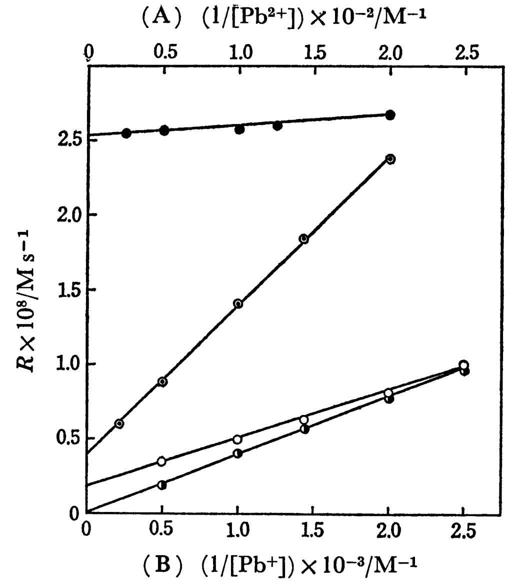

Fig. 1. Effect of the concentration of Pb^{2+} on the rate.

●: DTPA, pH 2.08, scale A; ⊙: EDTA·OH, pH 2.92, scale B; ○: EDTA, pH 2.64, scale B; ◑: CyDTA, pH 2.62, scale B; $[PbX_t]=[In(III)]=5.0\times10^{-6}$ M.

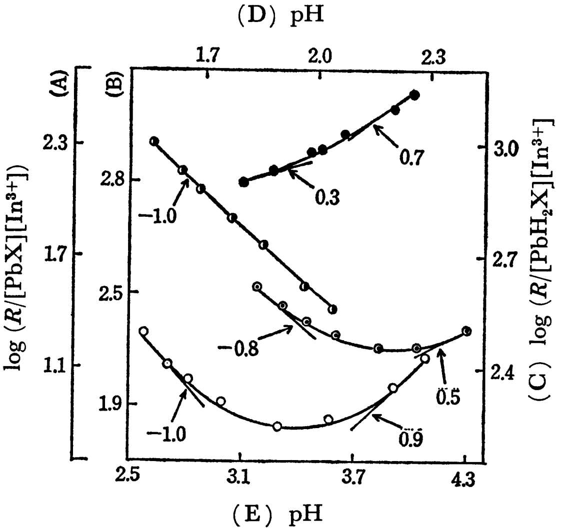

Fig. 2. pH Dependence on the rate R.

		$[Pb^{2+}]$(M)	
●:	DTPA	8.0×10^{-3}	C, D
◑:	CyDTA	1.0×10^{-3}	A, E
⊙:	EDTA·OH	1.0×10^{-3}	B, E
○:	EDTA	2.0×10^{-3}	B, E

$[PbX_t]=[In(III)]=5.0\times10^{-6}$ M.

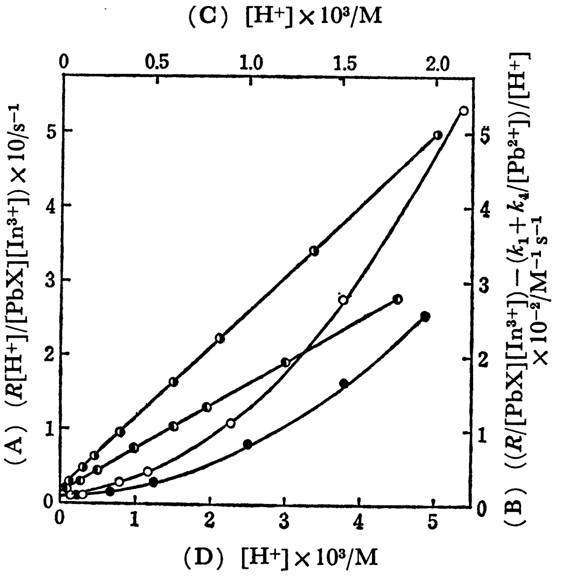

Fig. 3. The rate const for the reaction of the EDTA system.

	$[Pb^{2+}]$ (M)	
○:	1.0×10^{-3}	A, C
●:	2.0×10^{-3}	A, C
◑:	1.0×10^{-3}	B, D
◐:	2.0×10^{-3}	B, D

$[PbX_t]=[In(III))=5.0\times10^{-6}$ M.

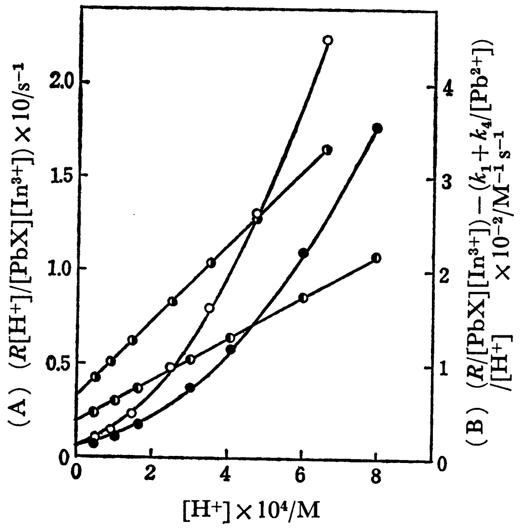

Fig. 4. The rate constants for the reaction of the EDTA·OH.

	$[Pb^{2+}]$ (M)	
○:	1.0×10^{-3}	A
●:	2.0×10^{-3}	A
◑:	1.0×10^{-3}	B
◐:	2.0×10^{-3}	B

$[PbXt]=[In(III)]=5.0\times10^{-6}$ M.

Initial Rate Equations. In order to obtain the rate equations, the initial rates were measured by changing the pH in the presence of a large excess of lead(II) ions of 1.0×10^{-3} M and 2.0×10^{-3} M for the EDTA and EDTA·OH systems, 1.0×10^{-3} M for the CyDTA system, and 8.0×10^{-3} M and 4.0×10^{-2} M for the DTPA system. The concentrations of In^{3+}, PbX, and PbH_2X were calculated from the total concentrations of In(III) and PbX_t by use of the following equations: $[In^{3+}]=[In(III)]/(1+K_h/[H^+])$, $[PbX]=[PbX_t]/(1+K_H[Pb^{2+}])$, and $[PbH_2X]=[PbX_t]/(1+1/K_{2H}[H^+])$ respectively, and the values of $K_h=10^{-3.70}$M,[5] $K_H=66.1$,* 0, and 77.1 M^{-1} for EDTA, EDTA·OH, and CyDTA,[3] again respectively, and $K_{2H}=3.87\times10^4$ M^{-1} for DTPA.[3] The results are shown in Figs. 3, 4, and 5, and in Table 1. From the results and a consideration of the reaction orders and the effects of an excess of lead(II) ions and the pH dependence mentioned above, the initial rate equations can be

---

* Unpublised data.

TABLE 1. RATE CONSTANTS

	EDTA	EDTA·OH	CyDTA	DTPA
k_1 (s^{-1})	1.0×10^{-2}	6.0×10^{-3}		
k_2 ($M^{-1}s^{-1}$)	1.2×10	1.0×10		
k_3 ($M^{-2}s^{-1}$)	1.0×10^{4}	4.3×10^{4}		k_3' 4.9 (s^{-1})
k_4 ($M\,s^{-1}$)	$\leq10^{-7}$	$\leq10^{-7}$	$\leq10^{-7}$	
k_5 (s^{-1})	8.0×10^{-3}	5.6×10^{-2}	5.0×10^{-3}	
k_6 ($M^{-1}s^{-1}$)	9.6×10	3.6×10^{2}	8.2×10	k_6' 1.5×10^{-3} ($M\,s^{-1}$)
k_7 ($M^{-1}s^{-1}$)				4.3×10^{2}
k_8 (s^{-1})				3.5×10^{-1}

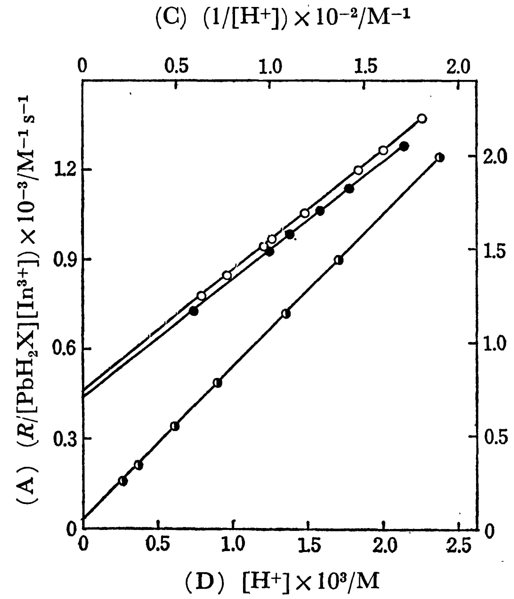

Fig. 5. The rate constants for the reactions of the DTPA and CyDTA systems.

		$[Pb^{2+}]$ (M)	
○:	DTPA	8.0×10^{-3}	A, C
●:	DTPA	4.0×10^{-2}	A, C
◑:	CyDTA	1.0×10^{-3}	B, D

$[PbX_t]=[In(III)]=5.0\times10^{-6}$ M.

expressed as follows:
For the EDTA and EDTA·OH systems:

$$R=\{(k_1+k_4/[Pb^{2+}])/[H^+]+(k_2+k_5/[Pb^{2+}])+(k_3+k_6/[Pb^{2+}])[H^+]\}[PbX][In^{3+}] \qquad (1)$$

for the CyDTA system:

$$R=\{k_5+k_6[H^+]\}[PbX][In^{3+}]/[Pb^{2+}] \qquad (2)$$

for the DTPA system:

$$R=\{(k'_3+k'_6/[Pb^{2+}])/[H^+]+(k_7+k_8/[Pb^{2+}])\}[PbH_2X][In^{3+}] \qquad (3).$$

As has been concluded by previous workers,[1] such reactions proceed through simultaneous reaction paths of the electrophilic substitution reaction and the dissociation reaction of the metal complexes. From a consideration of the species of the indium(III) ions[5] and the lead and indium complexes in an equilibrium state, the following reaction paths from Eqs. (1a) to (6c) for the EDTA, EDTA·OH, and CyDTA systems, and from (2a) to (3b), (5a) to (6c), and (7a) to (8c) for the DTPA system may be considered:

$$PbX^{(n-2)-}+In^{3+}\xrightarrow{k_{1a^+}}InX^{(n-3)-}+Pb^{2+} \qquad (1a)$$

$$PbX^{(n-2)-}+InOH^{2+}\xrightarrow{k_{1b^+}}In(OH)X^{(n-2)-}+Pb^{2+} \qquad (1b)$$

$$PbHX^{(n-3)-}+In^{3+}\xrightarrow{k_{2a^+}}InHX^{(n-4)-}+Pb^{2+} \qquad (2a)$$

$$PbHX^{(n-3)-}+InOH^{2+}\xrightarrow{k_{2b^+}}InX^{(n-3)-}+Pb^{2+}+H_2O \qquad (2b)$$

$$PbH_2X^{(n-4)-}+In^{3+}\xrightarrow{k_{3a^+}}InH_2X^{(n-5)-}+Pb^{2+} \qquad (3a)$$

$$PbH_2X^{(n-4)-}+InOH^{2+}\xrightarrow{k_{3b^+}}InHX^{(n-4)-}+Pb^{2+}+H_2O \qquad (3b)$$

$$PbX^{(n-2)-}\underset{k_{4a^-}}{\overset{k_{4a^+}}{\rightleftharpoons}}Pb^{2+}+X^{n-} \qquad (4a)$$

$$X^{n-}+In^{3+}\xrightarrow{k_{4b^+}}InX^{(n-3)-} \qquad (4b)$$

$$X^{n-}+InOH^{2+}\xrightarrow{k_{4c^+}}In(OH)X^{(n-2)-} \qquad (4c)$$

$$PbHX^{(n-3)-}\underset{k_{5a^-}}{\overset{k_{5a^+}}{\rightleftharpoons}}Pb^{2+}+HX^{(n-1)-} \qquad (5a)$$

$$HX^{(n-1)-}+In^{3+}\xrightarrow{k_{5b^+}}InHX^{(n-4)-} \qquad (5b)$$

$$HX^{(n-1)-}+InOH^{2+}\xrightarrow{k_{5c^+}}InX^{(n-3)-}+H_2O \qquad (5c)$$

$$PbH_2X^{(n-4)-}\underset{k_{6a^-}}{\overset{k_{6a^+}}{\rightleftharpoons}}Pb^{2+}+H_2X^{(n-2)-} \qquad (6a)$$

$$H_2X^{(n-2)-}+In^{3+}\xrightarrow{k_{6b^+}}InH_2X^{(n-5)-} \qquad (6b)$$

$$H_2X^{(n-2)-}+InOH^{2+}\xrightarrow{k_{6c^+}}InHX^{(n-4)-}+H_2O \qquad (6c)$$

$$PbH_2X+In^{3+}\xrightarrow{k_{7a^+}}InH_3X^{+}+Pb^{2+} \qquad (7a)$$

$$PbH_3X+InOH^{2+}\xrightarrow{k_{7b^+}}InH_2X+Pb^{2+}+H_2O \qquad (7b)$$

$$PbH_3X\underset{k_{8a^-}}{\overset{k_{8a^+}}{\rightleftharpoons}}Pb^{2+}+H_3X^{2-} \qquad (8a)$$

$$H_3X^{2-}+In^{3+}\xrightarrow{k_{8b^+}}InH_3X^{+} \qquad (8b)$$

$$H_3X^{2-}+InOH^{2+}\xrightarrow{k_{8c^+}}InH_2X+H_2O \qquad (8c)$$

where X^{n-} denotes the polyamine-*N*-polyacetate anion.

According to Margerum's method,[6] the application of a steady-state approximation to $[X^{n-}]$ gives:

$$[X^{n-}]=\frac{k_{4a^+}[PbX]}{k_{4a^-}[Pb^{2+}]+k_{4b^+}[In^{3+}]+k_{4c^+}[InOH^{2+}]}.$$

From a consideration of the rate constants[6-10] for the exchange of water molecules from the first coordination spheres of metal ions and the experimental conditions, the relation of $k_{4\mathrm{a}^-}[\mathrm{Pb}^{2+}] \gg k_{4\mathrm{b}^+}[\mathrm{In}^{3+}]+k_{4\mathrm{c}^+}[\mathrm{InOH}^{2+}]$ holds. Therefore, the above equation can be transformed to:

$$[\mathrm{X}^{n-}] = (k_{4\mathrm{a}^+}/k_{4\mathrm{a}^-})[\mathrm{PbX}]/[\mathrm{Pb}^{2+}].$$

Since the overall rate, R, is considered to be the sum of the rates of the individual reactions, the initial rate equations are derived as follows:

$$\begin{aligned}
R = {} & k_{1\mathrm{a}^+}[\mathrm{PbX}][\mathrm{In}^{3+}] + k_{1\mathrm{b}^+}[\mathrm{PbX}][\mathrm{InOH}^{2+}] \\
& + k_{2\mathrm{a}^+}[\mathrm{PbHX}][\mathrm{In}^{3+}] + k_{2\mathrm{b}^+}[\mathrm{PbHX}][\mathrm{InOH}^{2}] \\
& + k_{3\mathrm{a}^+}[\mathrm{PbH_2X}][\mathrm{In}^{3+}] + k_{3\mathrm{b}^+}[\mathrm{PbH_2X}][\mathrm{InOH}^{2+}] \\
& + k_{4\mathrm{b}^+}\cdot k_{4\mathrm{a}^+}[\mathrm{PbX}][\mathrm{In}^{3+}]/k_{4\mathrm{a}^-}[\mathrm{Pb}^{2+}] \\
& + k_{4\mathrm{c}^+}\cdot k_{4\mathrm{a}^+}[\mathrm{PbX}][\mathrm{InOH}^{2+}]/k_{4\mathrm{a}^-}[\mathrm{Pb}^{2+}] \\
& + k_{5\mathrm{b}^+}\cdot k_{5\mathrm{a}^+}[\mathrm{PbHX}][\mathrm{In}^{3+}]/k_{5\mathrm{a}^-}[\mathrm{Pb}^{2+}] \\
& + k_{5\mathrm{c}^+}\cdot k_{5\mathrm{a}^+}[\mathrm{PbHX}][\mathrm{InOH}^{2+}]/k_{5\mathrm{a}^-}[\mathrm{Pb}^{2+}] \\
& + k_{6\mathrm{c}^+}\cdot k_{6\mathrm{a}^+}[\mathrm{PbH_2X}][\mathrm{In}^{3+}]/k_{6\mathrm{a}^-}[\mathrm{Pb}^{2+}] \\
& + k_{6\mathrm{c}^+}\cdot k_{6\mathrm{a}^+}[\mathrm{PbH_2X}][\mathrm{InOH}^{2+}]/k_{6\mathrm{a}^-}[\mathrm{Pb}^{2+}] \\
= {} & \{(k_1+k_4/[\mathrm{Pb}^{2+}]/[\mathrm{H}^+] + (k_2+k_5/[\mathrm{Pb}^{2+}]) \\
& + (k_3+k_6/[\mathrm{Pb}^{2+}])[\mathrm{H}^+] \\
& + (k_3{}^*+k_6{}^*/[\mathrm{Pb}^{2+}])[\mathrm{H}^+]^2\}[\mathrm{PbX}][\mathrm{In}^{3+}]
\end{aligned}$$

where

$$\begin{aligned}
& k_1 = k_{1\mathrm{b}^+}\cdot K_\mathrm{h},\ k_2 = k_{1\mathrm{a}^+} + k_{2\mathrm{b}^+}\cdot K_\mathrm{H}\cdot K_\mathrm{h} \\
& k_3 = k_{2\mathrm{a}^+}\cdot K_\mathrm{H} + k_{3\mathrm{b}^+}\cdot K_\mathrm{2H}\cdot K_\mathrm{h},\ k_4 = k_{4\mathrm{c}^+}\cdot k_{4\mathrm{a}^+}\cdot K_\mathrm{h}/k_{4\mathrm{a}^-} \\
& k_5 = k_{4\mathrm{b}^+}\cdot k_{4\mathrm{a}^+}/k_{4\mathrm{a}^-} + k_{5\mathrm{c}^+}\cdot k_{5\mathrm{a}^+}\cdot K_\mathrm{H}\cdot K_\mathrm{h}/k_{5\mathrm{a}^-} \\
& k_6 = k_{5\mathrm{b}^+}\cdot k_{5\mathrm{a}^+}\cdot K_\mathrm{H}/k_{5\mathrm{a}^-} + k_{6\mathrm{c}^+}\cdot k_{6\mathrm{a}^+}\cdot K_\mathrm{H}\cdot K_\mathrm{2H}\cdot K_\mathrm{h}/k_{6\mathrm{a}^-} \\
& k_3{}^* = k_{3\mathrm{a}^+}\cdot K_\mathrm{2H}\cdot K_\mathrm{H},\ k_6{}^* = k_{6\mathrm{b}^+}\cdot k_{6\mathrm{a}^+}\cdot K_\mathrm{H}\cdot K_\mathrm{2H}/k_{6\mathrm{a}^-} \\
& K_\mathrm{h} = [\mathrm{InOH}^{2+}][\mathrm{H}^+]/[\mathrm{In}^{3+}],\ K_\mathrm{H} = [\mathrm{PbHX}]/[\mathrm{PbX}][\mathrm{H}^+] \\
& K_\mathrm{2H} = [\mathrm{PbH_2X}]/[\mathrm{PbHX}][\mathrm{H}^+].
\end{aligned}$$

Neglecting the term of $[\mathrm{H}^+]^2$, since it is not included in the above equations, Rate Equation (1) can be derived for the EDTA and EDTA·OH systems. For the CyDTA system, furthermore, considering that the plot of the rate, R, *vs.* $1/[\mathrm{Pb}^{2+}]$ gives a straight line which passes through the point of origin of the coordinates, as may be seen in Fig. 1, and considering that the term of $1/[\mathrm{H}^+]$ is not included, as has been mentioned above, Rate Equation (2) is obtained. In the same way, the rate equation for the DTPA system can be deduced as Equation (3), where $K_\mathrm{3H}=[\mathrm{PbH_3X}]/[\mathrm{PbH_2X}][\mathrm{H}^+]$

$$\begin{aligned}
& k_3{}' = k_{2\mathrm{a}^+}/K_\mathrm{2H} + k_{3\mathrm{b}^+}\cdot K_\mathrm{h}, \\
& k_6{}' = k_{5\mathrm{b}^+}\cdot k_{5\mathrm{a}^+}/k_{5\mathrm{a}^-}\cdot K_\mathrm{2H} + k_{6\mathrm{c}^+}\cdot K_{6\mathrm{a}^+}\cdot K_\mathrm{h}/k_{6\mathrm{a}^-} \\
& k_7 = k_{3\mathrm{a}^+} + k_{7\mathrm{b}^+}\cdot K_\mathrm{3H}\cdot K_\mathrm{h}, \\
& k_8 = k_{6\mathrm{b}^+}\cdot k_{6\mathrm{a}^+}/k_{6\mathrm{a}^-} + k_{8\mathrm{c}^+}\cdot k_{8\mathrm{a}^+}\cdot K_\mathrm{3H}\cdot K_\mathrm{h}/k_{8\mathrm{a}^-}.
\end{aligned}$$

Reaction Mechanisms. The contribution of each reaction path to the overall rate of the reaction was estimated, the results are shown in Fig. 6, where the numbers of the curves, I, II, III, V, VI, VII, and VIII, denote Reaction Paths (1b), (1a)+(2b), (2a)+(3b), (4b)+(5c), (5b)+(6c), (3a)+(7b), and (6b)+(8c) respectively. For the EDTA, EDTA·OH, and DTPA systems the reactions proceed through the paths forming binuclear intermediate complexes, $\mathrm{PbX_tIn}$, and the dissociative paths. For all the systems, the contribution of the dissociative path of PbX without acid is not found, while those of the other paths change with the pH variation. Since the dissociation of the protonated lead complexes is rapid, the contributions of Paths (5b) and (6c) are predominant in the lower pH range for the EDTA and EDTA·OH systems, but the contribution decreases, and that of Path (1b) increases, with an increase in the pH, as the fractions of PbHX and $\mathrm{PbH_2X}$ decrease and those of PbX and InOH^{2+} increase. For the CyDTA system only the contribution of the dissociative path is found, because the formation of a binuclear intermediate becomes difficult as a result of the steric hindrance of the cyclohexane ring, as Margerum and his co-workers have suggested in their study.[6] For the DTPA system the contributions of Paths (2a) and (3b) become predominant with an increase in the pH, since it is easier for the DTPA complex containing free coordinating groups to form a binuclear intermediate than for the complexes of the other ligands. From a consideration of the effect of the concentration of the lead ions, it is found that, in the dissociative paths, the rapid dissociative equilibria precede the formation of the indium complexes, as may be seen in the substitution reaction[11] of the lead(II)-EDTA complex with copper(II), for the systems other than the CyDTA system the contribution of the path forming a binuclear intermediate increases with an increase in the concentration of the lead(II) ions.

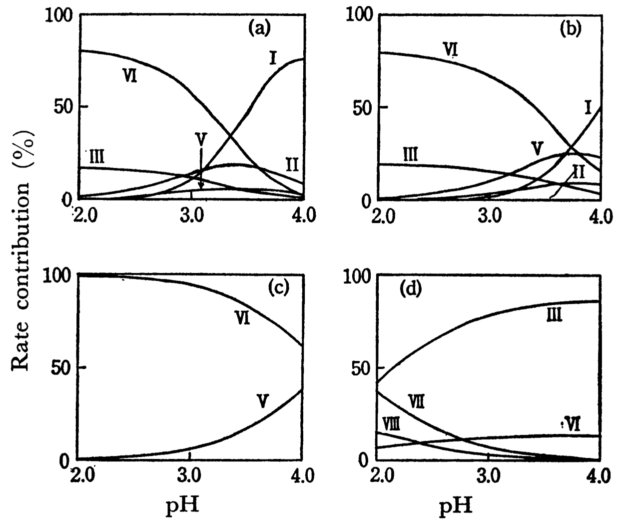

Fig. 6. The rate contribution of each path to the reaction rate.
(a): EDTA, (b): EDTA·OH, (c): CyDTA, (d): DTPA, $[\mathrm{Pb}^{2+}]=2.0\times10^{-3}$ M
Number of curves, I, II, III, VI, VII, and VIII denotes reaction path (1b), (1a)+(2b), (2a)+(3b), (4b)+(5c), (5b)+(6c), (3a)+(7b), and (6b)+(8c), respectively.

In order to determine the contribution of each path involving InOH^{2+} to the rate of the formation of the indium complex through the dissociative step, the rate constants for the formation of InX, InHX, and $\mathrm{InH_2X}$, k_5 and k_6 in Eqs. (1) and (2) for the EDTA, EDTA·OH, and CyDTA complexes, k'_6 and k_8 in Eq. (3) for the DTPA complexes, are rewritten as follows:

$$k_5 = k_{4\mathrm{b}^+}/K_\mathrm{PbX} + k_{5\mathrm{c}^+}\cdot K_\mathrm{h}/K_\mathrm{PbX}\cdot K_{\mathrm{a}n} \tag{4$'$}$$

$$k_6 = k_{5\mathrm{b}^+}/K_\mathrm{PbX}\cdot K_{\mathrm{a}n}+k_{6\mathrm{c}^+}\cdot K_\mathrm{h}/K_\mathrm{PbX}\cdot K_{\mathrm{a}n}\cdot K_{\mathrm{a}(n-1)} \tag{5$'$}$$

for the EDTA, EDTA·OH and CyDTA systems and:

$$k_6' = k_{5b^+}/K_{PbHX}\cdot K_{2H} + k_{6c^+}\cdot K_h/K_{PbH_2X} \qquad (6')$$

$$k_8 = k_{6b^+}/K_{PbH_2X} + k_{8c^+}\cdot K_h/K_{PbH_2X}\cdot K_{a3} \qquad (7')$$

for the DTPA system, where K_{an}, K_{PbX}, K_{PbHX}, and K_{PbH_2X} represent the acid dissociation constants of the ligands and the stability constants of the lead complexes respectively. By a comparison of the values of the first terms and those of the second terms in Eqs. (4′), (5′), (6′), and (7′), using the values of K_h[5], K_{an},[12–15] K_{PbX},[12)16] K_{PbHX},[17] and K_{PbH_2X}[17] obtained by the authors, and the products of the rate constants for the substitution of water molecules from the first coordination spheres of the In^{3+} and $InOH^{2+}$ ions and of the association constants[18] of the ion-pairs according to Eigen,[19] the first terms were found to be negligibly small. Therefore, the above equations are expressed as:

$$k_5 = k_{5c^+}\cdot K_h/K_{PbX}\cdot K_{an} \qquad (4)$$

$$k_6 = k_{6c^+}\cdot K_h/K_{PbX}\cdot K_{an}\cdot K_{a(n-1)} \qquad (5)$$

for the EDTA, EDTA·OH, and CyDTA systems, and as:

$$k_6 = k_{6c^+}\cdot K_h/K_{PbH_2X} \qquad (6)$$

$$k_8 = k_{8c^+}\cdot K_h/K_{PbH_2X}\cdot K_{a3} \qquad (7)$$

for the DTPA system.

As an example, the rate constants for the formation of the InHX of EDTA and CyDTA, and the InH_2X of DTPA and the InHX of EDTA·OH from $InOH^{2+}$ were calculated by means of Eqs. (5) and (7) to be 2.0×10^7, 2.9×10^7, 3.0×10^7, and 4.9×10^6 M^{-1} s^{-1} respectively. The rate constants for EDTA, CyDTA, DTPA, and EDTA·OH were in good agreement with the values of 2.5×10^7 and 5.0×10^6 M^{-1} s^{-1} of the complexes of $InOH^{2+}$ with SO_4^{2-} and of $InOH^{2+}$ with the semixylenol orange anion H_3SXO^-, which have the same charges as H_2X^{2-}, H_3X^{2-}, and H_2X^- respectively. This shows that the rate equations from (1) to (3) and the rate constants and the reaction mechanisms are suitable.

In addition, the reaction rate of indium(III) is 160 times faster than that of gallium(III) for the CyDTA system at pH 2.0. This may be attributed to the difference in the rate constants with regard to the substitution of the water molecules of the $InOH^{2+}$ and $GaOH^{2+}$ ions resulting from the difference in the effective nuclear charge.

The authors wish to thank Professor D.W. Margerum of Purdue University, U.S.A., for his useful discussions.

References

1) T. Takahashi, T. Koiso, and N. Tanaka, *Nippon Kagaku Zasshi*, **1973**, 64.

2) T. Nozaki and K. Kasuga, *ibid.*, **1973**, 2117.

3) T. Nozaki, K. Koshiba, and Y. Ono, *ibid.*, **90**, 1147 (1969).

4) T. J. Bydalek and D. W. Margerum, *J. Amer. Chem. Soc.*, **83**, 4326 (1961).

5) E. M. Hattox and T. DeVries, *ibid.*, **58**, 2128 (1936).

6) D. W. Margerum, P. J. Menardi, and D. L. Janes, *Inorg. Chem.*, **6**, 283 (1967).

7) M. Eigen and E. M. Eyring, *ibid.*, **2**, 636 (1963).

8) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).

9) J. Miceli and J. Stuehr, *J. Amer. Chem. Soc.*, **90**, 6967 (1968).

10) Y. Kawai, T. Takahashi, K. Hayashi, T. Imamura, H. Nakayama, and M. Fujimoto, This Bulletin, **45**, 1417 (1972).

11) N. Tanaka, K. Kato, and R. Tamamushi, *ibid.*, **31**, 238 (1958).

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

13) S. Chaderek and A. E. Martell, *J. Amer. Chem. Soc.*, **77**, 1477 (1955).

14) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **32**, 1682 (1949).

15) E. J. Durham and D. P. Ryskiewick, *J. Amer. Chem. Soc.*, **80**, 4813 (1958).

16) J. H. Holloway and C. N. Reilly, *Anal. Chem.*, **32**, 249 (1960).

17) log $K_{PbHX}=12.5$, log $K_{PbH_2X}=8.5$.

18) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions", J. Willey & Sons, Inc., N. Y. (1958), p. 34.

19) M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 107 (1962).