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The Kinetics of Substitution Reactions Involving Metal Complexes. IX. Reactions between Copper(II) and Propylenediaminetetraacetatoplumbate(II) and between Lead(II) and Propylenediaminetetraacetatozincate(II)

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Kinetic studies of the reactions between copper(II) and propylenediaminetetraacetatoplumbate(II) and between lead(II) and propylenediaminetetraacetatozincate(II) have been carried out. It was revealed from these studies that the reactions proceed through four simultaneous reaction paths, of which two involve electrophilic substitution reactions and the others, the complex-forming reactions between entering metal ions and ligands dissociated from complexes. The rate constants were compared with those of the corresponding reactions involving metal-ethylenediaminetetraacetate and the effects of ligands on the reaction rates were discussed.

In a previous paper,[1] the equilibrium study of propylenediaminetetraacetato complexes was reported. It was found in a preliminary investigation that the substitution reactions involving metal propylenediaminetetraacetate (PDTA) were more sluggish than those of the corresponding reactions involving metal ethylenediaminetetraacetate (EDTA).

In this study, the kinetics of the reactions between copper(II) and lead(II)-PDTA and between lead(II) and zinc(II)-PDTA has been investigated in detail and the results have been compared with those obtained from kinetic studies of the reactions involving metal-EDTA complexes.[2-5]

Experimental

Standard solutions of copper(II), lead(II) and zinc(II) nitrate and disodium dihydrogen propylenediaminetetraacetate (Na_2H_2pdta) were obtained by the procedures reported previously.[1] All the other chemicals used were of analytical reagent grade.

The reactions between copper(II) and lead(II)-PDTA and between lead(II) and zinc(II)-PDTA were followed by measuring the change of the polarographic diffusion current of copper(II) and lead(II) ions, respectively, with time in acetate buffer solutions. The apparatus used was the same as described in a previous paper.[6] Temperature was maintained at 25.0±0.1°C and ionic strength was adjusted to be 0.2 with potassium nitrate.

Results

The overall substitution reaction is represented by the equation,

$$\left\{\begin{array}{l} M^{2+} \\ \downarrow\uparrow \\ MOAc^{+} \\ \downarrow\uparrow \\ M(OAc)_2 \end{array}\right\} + M'pdta^{2-} \rightleftarrows$$

$$Mpdta^{2-} + \left\{\begin{array}{l} M'^{2+} \\ \downarrow\uparrow \\ M'OAc^{+} \\ \downarrow\uparrow \\ M'(OAc)_2 \end{array}\right\} \qquad (1)^{*1}$$

In this study, as was in the previous work,[2,3] both $[M'^{2+}]_{app}$ and $[M'pdta^{2-}]$ were in large excess over $[M^{2+}]_{app}$, where

$$[M^{2+}]_{app} = [M^{2+}] + [MOAc^{+}] + [M(OAc)_2]$$

and

$$[M'^{2+}]_{app} = [M'^{2+}] + [M'OAc^{+}] + [M'(OAc)_2]$$

Thus, the substitution reaction (1) was treated as a pseudo-first-order reaction,

$$\left\{\begin{array}{l} M^{2+} \\ \downarrow\uparrow \\ MOAc^{+} \\ \downarrow\uparrow \\ M(OAc)_2 \end{array}\right\} \underset{k^-}{\overset{k^+}{\rightleftarrows}} Mdpta^{2-} \qquad (2)$$

The rate constant k^+ in Eq. (2) can be obtained in the same way as reported previously.[2,3]

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[1] N. Tanaka and H. Ogino, This Bulletin, **38**, 439 (1965).

[2] N. Tanaka and K. Kato, *ibid.*, **32**, 1376 (1959); **33**, 1236 (1960).

[3] N. Tanaka and H. Ogino, *ibid.*, **36**, 175 (1963).

[4] T. J. Bydalek and D. W. Margerum, *J. Am. Chem. Soc.*, **83**, 4326 (1961); *Inorg. Chem.*, **2**, 678 (1963); D. W. Margerum and T. J. Bydalek, *ibid.*, **1**, 852 (1962).

[5] J. L. Sudmeier and C. N. Reilley, *Inorg. Chem.*, **5**, 1047 (1966).

[6] H. Ogino, This Bulletin, **38**, 771 (1965).

[*1] It is known that copper(II) and lead(II) form monoacetato and diacetato complexes in a solution containing acetate up to 0.2 M in concentration at ionic strength 0.2[7], whereas zinc(II), only monoacetato complex. Hence, no appreciable amount of $Zn(OAc)_2$ is present under the experimental condition.

The values of k^+ obtained were not affected by the change of the initial concentrations of entering metal ions, $[M^{2+}]_{0,\mathrm{app}}$, and were proportional to the concentrations of M′(II)-PDTA. These are the same with the results obtained for the corresponding reactions involving EDTA complexes.[2,3] The apparent second-order rate constants of the forward reaction 1, $k^+/[\mathrm{M'pdta}^{2-}]_0$, were determined at various pH's. The plots of $k^+/[\mathrm{M'pdta}^{2-}]_0$ versus $[H^+]$ are shown in Figs. 1 and 2.

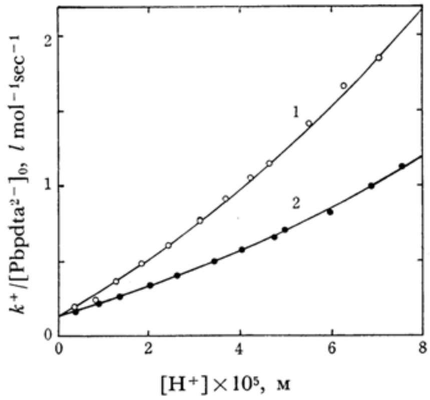

Fig. 1. $k^+/[\mathrm{Pbpdta}^{2-}]_0$ as a function of the hydrogen ion concentration in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 25°C.
Initial concentrations are : $[Pb^{2+}]_{0,\mathrm{app}} = 5.13$ mM (1) and 10.2 mM (2). Concentration of free acetate is 0.091 M.

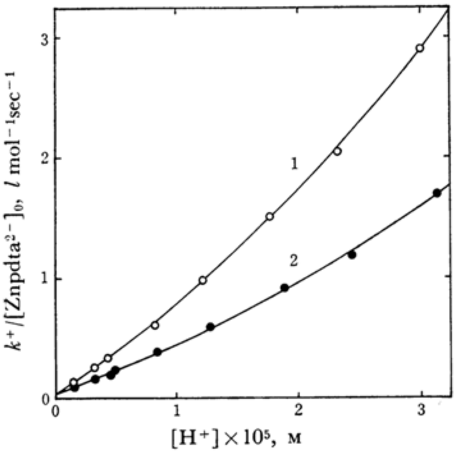

Fig. 2. $k^+/[\mathrm{Znpdta}^{2-}]_0$ as a function of the hydrogen ion concentration in acetate buffer-potassium nitrate solutions of ionic strength 0.2 at 25°C.
Initial concentrations are : $[Zn^{2+}]_{0,\mathrm{app}} = 5.33$ mM (1) and 10.5 mM (2). Concentration of free acetate is 0.098 M.

These plots fit the equations in which the rate is dependent on the second power of hydrogen ion concentrations.

From Fig. 1, the following equations were obtained:

For $[Pb^{2+}]_{0,\mathrm{app}} = 5.13$ mM,

$$\frac{k^+}{[\mathrm{Pbpdta}^{2-}]_0} = 0.13_8 + 1.6_2 \times 10^4[H^+] + 1.16 \times 10^8[H^+]^2 \tag{3}$$

For $[Pb^{2+}]_{0,\mathrm{app}} = 10.2$ mM,

$$\frac{k^+}{[\mathrm{Pbpdta}^{2-}]_0} = 0.13_8 + 0.8_5 \times 10^4[H^+] + 0.58 \times 10^8[H^+]^2 \tag{4}$$

From Fig. 2 the following equations were obtained:

For $[Zn^{2+}]_{0,\mathrm{app}} = 5.33$ mM,

$$\frac{k^+}{[\mathrm{Znpdta}^{2-}]_0} = 0.038 + 6.3_1 \times 10^4[H^+] + 1.08 \times 10^9[H^+]^2 \tag{5}$$

For $[Zn^{2+}]_{0,\mathrm{app}} = 10.5$ mM,

$$\frac{k^+}{[\mathrm{Znpdta}^{2-}]_0} = 0.038 + 3.5_2 \times 10^4[H^+] + 5.4_9 \times 10^8[H^+]^2 \tag{6}$$

The values of $k^+/[\mathrm{M'pdta}^{2-}]_0$ which were determined at various values of $[M'^{2+}]_{0,\mathrm{app}}$ are given in Tables 1 and 2.

TABLE 1. EFFECT OF $[Pb^{2+}]_{0,\mathrm{app}}$ ON $k^+/[\mathrm{Pbpdta}^{2-}]_0$ OF THE REACTION BETWEEN COPPER(II) AND LEAD(II)-PDTA COMPLEXES

$[Pb^{2+}]_{0,\mathrm{app}}$ mM	$[H^+]\times10^5$ M	$k^+/[\mathrm{Pbpdta}^{2-}]_0$ l mol^{-1}sec^{-1}	
		Obsd.	Calcd.
5.13	3.14	0.77	0.77
10.2	3.44	0.50	0.51
15.2	3.78	0.40	0.43
20.3	4.05	0.36	0.38

TABLE 2. EFFECT OF $[Zn^{2+}]_{0,\mathrm{app}}$ ON $k^+/[\mathrm{Znpdta}^{2-}]_0$ OF THE REACTION BETWEEN LEAD(II) AND ZINC(II)-PDTA COMPLEXES

$[Zn^{2+}]_{0,\mathrm{app}}$ mM	$[H^+]\times10^5$ M	$k^+/[\mathrm{Znpdta}^{2-}]_0$ l mol^{-1}sec^{-1}	
		Obsd.	Calcd.
5.33	1.22	0.98	0.97
7.39	1.28	0.78	0.77
10.5	1.28	0.60	0.58
15.8	1.32	0.43	0.44
20.8	1.36	0.38	0.37

These results indicate that the overall reaction (1) between copper(II) and lead(II)-PDTA and that between lead(II) and zinc(II)-PDTA proceed through the following reaction paths.

(i)
$$M^{2+} + M'pdta^{2-} \overset{k_1{}^+}{\rightleftarrows} Mpdta^{2-} + M'^{2+} \tag{7}$$

(ii)
$$H^+ + M'pdta^{2-} \rightleftarrows M'Hpdta^- \tag{8a}$$

$$M^{2+} + M'Hpdta^- \overset{k_{II}{}^+}{\rightleftarrows} MHpdta^- + M'^{2+} \tag{8b}$$

(iii)
$$H^+ + M'pdta^{2-} \rightleftarrows M'^{2+} + Hpdta^{3-} \tag{9a}$$

$$M^{2+} + Hpdta^{3-} \overset{k_{III}{}^+}{\rightleftarrows} Mpdta^{2-} + H^+ \tag{9b}$$

(iv)
$$2H^+ + M'pdta^{2-} \rightleftarrows M'^{2+} + H_2pdta^{2-} \tag{10a}$$

$$M^{2+} + H_2pdta^{2-} \overset{k_{IV}{}^+}{\rightleftarrows} Mpdta^{2-} + 2H^+ \tag{10b}$$

On the basis of this reaction mechanism, Eq. (11) was obtained for the reaction between copper(II) and lead(II)-PDTA,

$$\frac{k^+}{[Pbpdta^{2-}]_0} = \left\{k_1{}^+ + \left(k_2{}^+ + \frac{k_3{}^+\alpha_{Pb(OAc)}}{[Pb^{2+}]_{0,app}}\right)[H^+] + \frac{k_4{}^+\alpha_{Pb(OAc)}}{[Pb^{2+}]_{0,app}}[H^+]^2\right\} \times \frac{1}{\alpha_{Cu(OAc)}} \tag{11}$$

and Eq. (12), for that between lead(II) and zinc(II)-PDTA,

$$\frac{k^+}{[Znpdta^{2-}]_0} = \left\{k_1{}^+ + \left(k_2{}^+ + \frac{k_3{}^+\alpha_{Zn(OAc)}}{[Zn^{2+}]_{0,app}}\right)[H^+] + \frac{k_4{}^+\alpha_{Zn(OAc)}}{[Zn^{2+}]_{0,app}}[H^+]^2\right\} \times \frac{1}{\alpha_{Pb(OAc)}} \tag{12}$$

where

$$k_2{}^+ = k_{II}{}^+ k^{H}_{M'Hpdta}, \quad k_3{}^+ = \frac{k_{III}{}^+}{K_{Hpdta}K_{M'pdta}}$$

$$k_4{}^+ = \frac{K_{III}{}^+}{K_{Hpdta}K_{H_2pdta}K_{M'pdta}}$$

$$\alpha_{Cu(OAc)} = 1 + \beta_{CuOAc}[OAc^-] + \beta_{Cu(OAc)_2}[OAc^-]^2$$

$$\alpha_{Pb(OAc)} = 1 + \beta_{PbOAc}[OAc^-] + \beta_{Pb(OAc)_2}[OAc^-]^2 \tag{13}$$

$$\alpha_{Zn(OAc)} = 1 + \beta_{Zn(OAc)}[OAc^-]$$

$K^{H}_{M'Hpdta}$ represents the equilibrium constant of reaction (8a), $K_{M'pdta}$, the formation constant of $M'pdta^{2-}$, and K_{Hpdta} and K_{H_2pdta}, represent the fourth and the third dissociation constant of propylenediaminetetraacetic acid, respectively. $\beta_{Cu(OAc)_n}$, $\beta_{Pb(OAc)_n}$ and β_{ZnOAc} are the overall formation constants of acetatocopper(II), acetatolead(II) and acetatozinc(II) complexes, respectively. The rate constants in Eqs. (11) and (12) were calculated by the use of Eqs. (3) to (6), and are given in Table 3. The formation constants of various acetato complexes which were used in the calculation are reported in the previous paper.[7)]

TABLE 3. RATE CONSTANTS IN Eqs. 11 AND 12 OBTAINED EXPERIMENTALLY AT IONIC STRENGTH 0.2 AND 25°C

	Cu^{2+}-$Pbpdta^{2-}$ system	Pb^{2+}-$Znpdta^{2-}$ system
$k_1{}^+$, $l\ mol^{-1}sec^{-1}$	0.89	0.66
$k_2{}^+$, $l^2\ mol^{-2}sec^{-1}$	8×10^3	1.1×10^5
$k_3{}^+$, $l\ mol^{-1}sec^{-1}$	3.0×10	3.6×10^3
$k_4{}^+$, $l^2\ mol^{-2}sec^{-1}$	2.5×10^5	6.9×10^7

Table 1 and 2 show that the reaction rate decreases with the increase of $[M'^{2+}]_{0,app}$, as is predicted from Eqs. (11) and (12). Using Eqs. (11) and (12) and the rate constants given in Table 3, the values of $k^+/[M'pdta^{2-}]_0$ were calculated, which are given in Table 1 and 2. These are in satisfactory agreement with the experimental values of $k^+/[M'pdta^{2-}]_0$.

The individual rate constants, $k_{III}{}^+$ and $k_{IV}{}^+$, were calculated using the relations given in Eqs. (13), $k_3{}^+$, $k_4{}^+$ and the reported values of log $K_{Pbpdta} = 18.69$,[6)] log $K_{Znpdta} = 17.14$[6)], $pK_{Hpdta} =$ 10.84[8)] and $pK_{H_2pdta} = 6.20$[8)]. The values of $k_{III}{}^+$, $k_{IV}{}^+$ and $k_1{}^+$ are given in Table 4.

It seems worth while to compare the rate constants of the reactions involving PDTA complexes with those of the corresponding reactions involving EDTA complexes. The rate constants of the corresponding EDTA systems are also given in Table 4. The values of k_{M}^{Hedta} in Table 4 are somewhat different from those reported previously,[2,3)] because the value of 10.25 reported by Grimes *et al.*[8)] was used for pK_{Hedta} in this paper instead of 10.04 used in the previous papers.[2,6)]

Discussion

From the comparison of the data in Table 4 and stability constants of PDTA and EDTA complexes, it may be seen that the ratio $k_{M}^{M'edta}$ to $k_{M}^{M'pdta}$ is approximately equal to the ratio of $K_{M'pdta}$ to $K_{M'edta}$, that is,

$$\frac{k_{Cu}^{Pbedta}}{k_{Cu}^{Pbpdta}} = \frac{5.1}{0.89} = 5.7;$$

$$\frac{K_{Pbpdta}}{K_{Pbedta}} = 10^{18.69-17.76} = 8.5 \tag{14}$$

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

8) J. H. Grimes, A. J. Huggard and S. P. Wilford, *J. Inorg. Nucl. Chem.* **25**, (1963).

TABLE 4. INDIVIDUAL RATE CONSTANTS AT IONIC STRENGTH 0.2 AND 25°C

Reaction	Rate constant, $l\ \mathrm{mol^{-1}sec^{-1}}$
$\mathrm{Cu^{2+} + Pbpdta^{2-}} \xrightarrow{k_{\mathrm{Cu}}^{\mathrm{Pbpdta}}} \mathrm{Cupdta^{2-} + Pb^{2+}}$	$k_{\mathrm{Cu}}^{\mathrm{Pbpdta}} = 0.89$*
$\mathrm{Cu^{2+} + Pbedta^{2-}} \xrightarrow{k_{\mathrm{Cu}}^{\mathrm{Pbedta}}} \mathrm{Cuedta^{2-} + Pb^{2+}}$	$k_{\mathrm{Cu}}^{\mathrm{Pbedta}} = 5.1$*
$\mathrm{Cu^{2+} + Hpdta^{3-}} \xrightarrow{k_{\mathrm{Cu}}^{\mathrm{Hpdta}}} \mathrm{Cupdta^{2-} + H^{+}}$	$k_{\mathrm{Cu}}^{\mathrm{Hpdta}} = 2.2\times 10^{9}$**
$\mathrm{Cu^{2+} + Hedta^{3-}} \xrightarrow{k_{\mathrm{Cu}}^{\mathrm{Hedta}}} \mathrm{Cuedta^{2-} + H^{+}}$	$k_{\mathrm{Cu}}^{\mathrm{Hedta}} = 1.9\times 10^{9}$**
$\mathrm{Cu^{2+} + H_2pdta^{2-}} \xrightarrow{k_{\mathrm{Cu}}^{\mathrm{H_2pdta}}} \mathrm{Cupdta^{2-} + 2H^{+}}$	$k_{\mathrm{Cu}}^{\mathrm{H_2pdta}} = 1.1\times 10^{7}$***
$\mathrm{Pb^{2+} + Znpdta^{2-}} \xrightarrow{k_{\mathrm{Pb}}^{\mathrm{Znpdta}}} \mathrm{Pbpdta^{2-} + Zn^{2+}}$	$k_{\mathrm{Pb}}^{\mathrm{Znpdta}} = 0.66$*
$\mathrm{Pb^{2+} + Znedta^{2-}} \xrightarrow{k_{\mathrm{Pb}}^{\mathrm{Znedta}}} \mathrm{Pbedta^{2-} + Zn^{2+}}$	$k_{\mathrm{Pb}}^{\mathrm{Znedta}} = 8.7$*
$\mathrm{Pb^{2+} + Hpdta^{3-}} \xrightarrow{k_{\mathrm{Pb}}^{\mathrm{Hpdta}}} \mathrm{Pbpdta^{2-} + H^{+}}$	$k_{\mathrm{Pb}}^{\mathrm{Hpdta}} = 7\times 10^{9}$**
$\mathrm{Pb^{2+} + Hedta^{3-}} \xrightarrow{k_{\mathrm{Pb}}^{\mathrm{Hedta}}} \mathrm{Pbedta^{2-} + H^{+}}$	$k_{\mathrm{Pb}}^{\mathrm{Hedta}} = 7\times 10^{9}$**
$\mathrm{Pb^{2+} + H_2pdta^{2-}} \xrightarrow{k_{\mathrm{Pb}}^{\mathrm{H_2pdta}}} \mathrm{Pbpdta^{2-} + 2H^{+}}$	$k_{\mathrm{Pb}}^{\mathrm{H_2pdta}} = 1.4\times 10^{8}$***

* To avoid confusion, symbol $k_1{}^+$ which is given in Eq. (7) and in a previous papers[2,3] is replaced by $k_{\mathrm{M}}^{\mathrm{M'pdta}}$ or $k_{\mathrm{M}}^{\mathrm{M'edta}}$.

** Symbol $k_{\mathrm{III}}{}^+$ is replaced by $k_{\mathrm{M}}^{\mathrm{Hpdta}}$ or $k_{\mathrm{M}}^{\mathrm{Hedta}}$.

*** Symbol $k_{\mathrm{IV}}{}^+$ is replaced by $k_{\mathrm{M}}^{\mathrm{H_2pdta}}$.

and

$$\frac{k_{\mathrm{Pb}}^{\mathrm{Znedta}}}{k_{\mathrm{Pb}}^{\mathrm{Znpdta}}} = \frac{8.7}{0.66} = 13\ ;$$

$$\frac{K_{\mathrm{Znpdta}}}{K_{\mathrm{Znedta}}} = 10^{17.14-15.94} = 16 \tag{15}$$

Therefore, it is suggested that the stability constants of $\mathrm{M'Y^{2-}}$ determine the relative values of the rate constants of reaction,

$$\mathrm{M^{2+} + M'Y^{2-}} \xrightarrow{k_{\mathrm{M}}^{\mathrm{M'Y}}} \mathrm{MY^{2-} + M'^{2+}} \tag{16}$$

with the change of ligands from PDTA to EDTA, where $\mathrm{Y^{4-}}$ denotes a quadrivalent PDTA or EDTA anion.

On the acid-independent electrophilic substitution ($\mathrm{S_E}$) reactions involving Ni(II)-EDTA, Bydalek and Margerum[4] proposed that a dinuclear intermediate with an iminodiacetate segment of EDTA coordinated to the entering metal ion is formed prior to the rate-determing step, and that the rate of the substitution reaction is related to the stability of this intermediate. The direct application of the treatment by Bydalek and Margerum leads to the equation,

$$\frac{K_{\mathrm{M}}^{\mathrm{M'edta}}}{K_{\mathrm{M}}^{\mathrm{M'pdta}}} = \frac{K_{\mathrm{M'segment(EDTA)}}K_{\mathrm{M\ segment(EDTA)}}}{K_{\mathrm{M'segment(PDTA)}}K_{\mathrm{M\ segment(PDTA)}}} \times \frac{K_{\mathrm{M'pdta}}}{K_{\mathrm{M'edta}}} \tag{17}$$

where $K_{\mathrm{M'segment(EDTA)}}$ and $K_{\mathrm{M\ segment(EDTA)}}$ are the stability of M'segment and M segment in dinuclear intermediate, M'…edta…M, $K_{\mathrm{M'segment(PDTA)}}$ and $K_{\mathrm{M\ segment(PDTA)}}$, those of M'segment and M segment in dinuclear intermediate, M'…pdta…M.*2 If the product, $K_{\mathrm{M'segment(PDTA)}}K_{\mathrm{M\ segment(PDTA)}}$, is nearly the same with $K_{\mathrm{M'segment(EDTA)}}\times K_{\mathrm{M\ segment(EDTA)}}$, the results of the calculation given in Eqs. (14) and (15) can be rationalized on the basis of Eq. (17). However, it is expected that the product $K_{\mathrm{M'segment(PDTA)}}K_{\mathrm{M\ segment(PDTA)}}$ is larger than $K_{\mathrm{M'segment(EDTA)}}K_{\mathrm{M\ segment(EDTA)}}$ due to the inductive effect of a methyl group in PDTA. This leads to the following relation:

$$\frac{k_{\mathrm{M}}^{\mathrm{M'edta}}}{k_{\mathrm{M}}^{\mathrm{M'pdta}}} < \frac{K_{\mathrm{M'pdta}}}{K_{\mathrm{M'edta}}} \tag{18}$$

On the other hand, there may be other effects influencing the rate of reactions in question that oppose the effect mentioned above. Recently, Sudmeir and Reilley[5] proposed a general mechanism for the $\mathrm{S_E}$ reactions involving two metal ions

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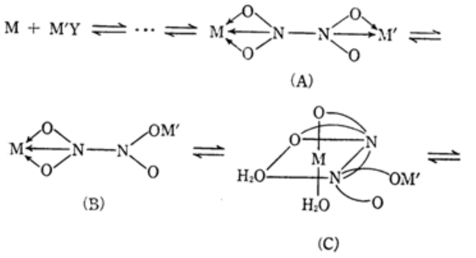
*2 For a detailed description of the derivation of Eq. (17), the papers by Bydalek and Margerum[4] should be consulted.

and one molecule of EDTA (or its analogue), a part of which is given in Eq. (19). For example, if the process from B to C, which is accompanied by the *trans* to *gauche* transformation involving the rotation about ethylenic carbon-carbon bond, is rate-determining, the rate of reaction 16 involving PDTA becomes smaller than that involving EDTA because of a greater rotational barrier in PDTA[5]. In addition, it is required that the final Mpdta^{2-} complexes have the structure in which the orientation of methyl group on the N–C–C–N chelate ring of the coordinated PDTA is equatorial.[9–12] Therefore, the rate of reaction involving PDTA may become smaller than that involving EDTA because of the restriction mentioned above.



$$\cdots \rightleftharpoons MY + M' \qquad (19)$$

Although no attempt was made to identify the most probable intermediate, it seems that the approximate equalities between $k_M^{M'edta}/k_M^{M'pdta}$ and $K_{M'pdta}/K_{M'edta}$ as shown in Eqs. (14) and (15) arise from the compensation of two or three opposing effects mentioned above.

The rate constants of the complex-forming reactions,

$$M^{2+} + HY^{3-} \xrightarrow{k_M^{HY}} MY^{2-} + H^+ \qquad (20)$$

are given in Table 4. It may be seen that there is no essential difference between k_M^{Hpdta} and k_M^{Hedta}. Eigen reported that, in the case of most of the divalent transition metal ions in the first series, the rate-determining step of a complex-forming reaction between metal ion and ligand L corresponds to the following reaction:

$$M(H_2O)_x\cdots L \overset{k_{H_2O}}{\rightleftharpoons} ML\cdot(H_2O)_{x-1}\cdots H_2O \qquad (21)$$

so that the first-order rate constant k_{H_2O} is independent of the nature of the entering ligand.[13,14] Therefore, reaction (20) may be expressed as follows:

$$\begin{aligned} M(H_2O)_x{}^{2+} + HY^{3-} &\overset{K_{ass.}}{\rightleftharpoons} M(H_2O)_x{}^{2+}\cdots HY^{3-} \\ &\overset{k_{H_2O}}{\rightleftharpoons} M(HY)(H_2O)_{x-1}{}^{-}\cdots H_2O \rightleftharpoons \cdots \\ &\rightleftharpoons MY(H_2O)_y{}^{2-} + (x-y)H_2O + H^+ \qquad (22) \end{aligned}$$

where $K_{ass.}$ means the outer-sphere association constant of $M(H_2O)_x{}^{2+}$ with HY^{3-}. From Eqs. (20) and (22), the relation of Eq. (23) can be

$$k_M^{HY} = K_{ass.}k_{H_2O} \qquad (23)$$

derived. It may be considered that $K_{ass.}$ is essentially the same in the reactions involving either PDTA or EDTA because of a similar size and the same charge of ligands. Thus, k_M^{Hpdta} is considered to be approximately equal to k_M^{Hedta}.

In this study, it is shown that the value of k_M^{Hpdta} is larger than that of $k_M^{H_2pdta}$ by 200 times for copper(II) ions and by 50 times for lead(II) ions. It seems that these rate constants reflect the differences of $K_{ass.}$ between 2-3 electrolyte (Cu^{2+} + $Hpdta^{3-}$ and Pb^{2+} + $Hpdta^{3-}$) and 2-2 electrolyte (Cu^{2+} + H_2pdta^{2-} and Pb^{2+} + H_2pdta^{2-}).

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