A Kinetic Study of the Ligand Substitution Reaction of Tetramethylenediaminetetraacetatocobaltate(II) with Trimethylenediaminetetraacetate

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The kinetics of the ligand substitution reaction of tetramethylenediaminetetraacetatocobaltate(II)(cobalt(II)–TDTA) with trimethylenediaminetetraacetate (TRDTA) was investigated by two different polarographic methods. The kinetic data at pH 4.9 to 5.6 were obtained by means of a conventional method in which the reaction was initiated by the mixing of two reactant solutions and was followed polarographically. However, this method could not be applied to solutions with pH values lower than 4.9, for the rate of the reaction is immeasurably fast in such a low pH region. The kinetic data at pH values down to 3.7 were obtained by analyses of the polarographic current which was observed in solutions containing TRDTA and the substitution-inert cobalt(III)–TDTA complex. From these data, it was found that the reaction proceeds through four simultaneous reaction paths, two paths of which are the nucleophilic substitution reactions, while the others are the dissociation reactions of cobalt(II)–TDTA complex ions.

In this paper, the kinetics of the ligand substitution reaction of tetramethylenediaminetetraacetatocobaltate(II) (cobalt(II)–TDTA)[1] with trimethylenediaminetetraacetate (TRDTA) will be studied by the polarographic method. The kinetics of this reaction cannot be investigated by the methods which are usually applied to many other systems. For example, the nuclear magnetic resonance method cannot be applied to this system, for cobalt(II) ions are paramagnetic. As the spectral data of cobalt(II)–TDTA and cobalt(II)–TRDTA are essentially identical, the spectrophotometric method cannot be applied to this reaction either. It will be shown in this paper that polarography provides very useful methods for the kinetic study of this reaction. The results obtained in this work will be compared with the related ones reported previously.[2,3]

Experimental

Reagents. The trimethylenediaminetetraacetic acid (H_4trdta)[4], tetramethylenediaminetetraacetic acid (H_4tdta),[5] and potassium tetramethylenediaminetetraacetatocobaltate(III) (K[Cotdta]·$3H_2O$)[5] were prepared and recrystallized by methods described previously. The preparation and standardization of a solution of cobalt(II) nitrate,[6] disodium dihydrogen trimethylenediaminetetraacetate(Na_2H_2trdta)[7] and disodium dihydrogen tetramethylenediaminetetraacetate (Na_2H_2tdta)[3] were done in ways reported in the literature. All the other chemicals were of an analytical-reagent grade and were used without further purification.

Kinetic Measurement and Apparatus. It has been reported that cobalt(II)–TRDTA shows a polarographic one-electron oxidation wave, with a half-wave potential of +0.05 V *vs.* SCE, in an acetate buffer–potassium nitrate solution.[8] TRDTA, TDTA, and cobalt(II)–TDTA do not show any polarographic waves under these experimental conditions. The kinetic measurements were made by two different methods, both utilizing the anodic wave of cobalt(II)–TRDTA; these methods were designated as Methods A and B.

In Method A, which is a conventional one, the reaction was initiated by the addition of a known amount of cobalt(II)–TDTA solution to an acetate buffer-potassium nitrate solution containing TRDTA in a large excess; the rate of the reaction was measured by following the increase in the anodic current due to the formation of cobalt(II)-TRDTA at +0.15 V *vs.* SCE. The overall reaction of TRDTA with cobalt(II)–TDTA is expressed by Eq. (1):

$$\left\{\begin{array}{c}\mathrm{CoY^{2-}}\\ \downarrow\uparrow\\ \mathrm{CoHY^{-}}\end{array}\right\} + \left\{\begin{array}{c}\mathrm{Z^{4-}}\\ \downarrow\uparrow\\ \mathrm{HZ^{3-}}\\ \downarrow\uparrow\\ \vdots\\ \downarrow\uparrow\\ \mathrm{H_4Z}\end{array}\right\} \underset{k^-}{\overset{k^+}{\rightleftharpoons}} \left\{\begin{array}{c}\mathrm{CoZ^{2-}}\\ \downarrow\uparrow\\ \mathrm{CoHZ^{-}}\end{array}\right\} + \left\{\begin{array}{c}\mathrm{Y^{4-}}\\ \downarrow\uparrow\\ \mathrm{HY^{3-}}\\ \downarrow\uparrow\\ \vdots\\ \downarrow\uparrow\\ \mathrm{H_4Y}\end{array}\right\} \qquad (1)$$

where Y^{4-} and Z^{4-} mean quadridentate TDTA and TRDTA anions respectively; $CoHY^-$ and $CoHZ^-$, hydrogen complexes of cobalt(II)-TDTA and -TRDTA respectively, and k^+ and k^-, the rate constants for the forward and the backward reactions. Under these experimental conditions, the backward reaction can be neglected; therefore, the reaction studied can be treated as a pseudo first-order reaction:

$$\text{Rate} = k^+_{\text{obs}}[\text{CoY}]_{\text{app}} \qquad (2)$$

where:

$$[\text{CoY}]_{\text{app}} = [\text{CoY}^{2-}] + [\text{CoHY}^-]$$

and where k^+_{obs} means a pseudo-first-order rate constant. Solving the rate law in essentially the same way as has been reported previously,[2] the equation:

$$\log \frac{\bar{i}_{\text{e}}}{\bar{i}_{\text{e}} - \bar{i}} = \frac{1}{2.303} k^+_{\text{obs}}\, t \qquad (3)$$

was obtained, where $\bar{i}$ and $\bar{i}_{\text{e}}$ denote the current at time

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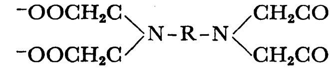
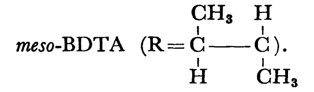
[1] The general formula of the ligands in this paper is:



$$\begin{array}{l}^-\mathrm{OOCH_2C}\\ ^-\mathrm{OOCH_2C}\end{array}\!\!>\mathrm{N{-}R{-}N}<\!\!\begin{array}{l}\mathrm{CH_2COO^-}\\ \mathrm{CH_2COO^-}\end{array}.$$

The abbreviated names of the ligands are:
TDTA ($R=CH_2CH_2CH_2CH_2$), TRDTA ($R=CH_2CH_2CH_2$), EDTA ($R=CH_2CH_2$), PDTA ($R=CH_2\underset{|}{C}H$ with CH_3 on C), and



meso-BDTA $\left(R=\overset{\mathrm{CH_3}}{\underset{\mathrm{H}}{\mathrm{C}}}\!-\!\!-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\right)$.

[2] H. Ogino and N. Tanaka, This Bulletin, **40**, 857 (1967). In that paper, 2.303 in Eqs. (7) and (10) should read 1/2.303. The values of k^+ were calculated with the correct equations.

[3] H. Ogino, T. Baba and N. Tanaka, *ibid.*, **42**, 1578 (1969).

[4] N. Tanaka and H. Ogino, *ibid.*, **37**, 877 (1964).

[5] H. Ogino, S. Kobayashi and N. Tanaka, *ibid.*, **43**, 97 (1970).

[6] N. Tanaka and H. Ogino, *ibid.*, **38**, 439 (1965).

[7] H. Ogino, *ibid.*, **38**, 771 (1965).

[8] N. Tanaka and H. Ogino, *ibid.*, **38**, 1054 (1965).

t and at an infinite time respectively. The values of k^{+}_{obs} were calculated from Eq. (3). The measurements were made in solutions at an ionic strength of 0.2 (KNO_3) and in the pH range from 4.9 to 5.6. All the polarograms were recorded by means of a Yanagimoto PB-4 pen-recording polarograph, using a dropping mercury electrode (DME) which had an m value of 1.16 mg sec^{-1} and a drop time t_d of 6.55 sec in a deaerated 0.1 M acetate buffer–0.1 M potassium nitrate solution containing 0.005% gelatin at 25 °C, -0.50 V *vs.* SCE, and a mercury height of 60 cm.

Method B consists of analyses of the polarographic kinetic current which was observed in solutions containing TRDTA and the substitution-inert cobalt(III)-TDTA complex. The current-time curves during the life of a mercury drop were recorded by means of a Rikendenshi SP-J1 recorder with a DC-201 preamplifier. The DME used had an m value of 1.87 mg sec^{-1} and a t_d value of 4.84 sec in a deaerated 0.1 M potassium nitrate solution containing 0.005% gelatin at 25 °C, -1.0 V *vs.* SCE, and a mercury height of 50 cm. The ionic strength employed was 0.5 (KNO_3), and the pH range was from 3.7 to 4.6.

All the measurements were carried out at 25 °C. Gelatin was added as a maximum suppressor in a concentration of 0.005%. The pH of the solutions was measured with a Hitachi-Horiba F-5 pH meter.

Results

Results Obtained by Method A. The values of k^{+}_{obs} were found to be a linear function of the initial concentration of TRDTA, $[Z]_0$, and of the hydrogen ion concentration, as is shown in Fig. 1, provided that all other experimental conditions were kept constant. Under these experimental conditions, the predominant species of TRDTA was H_2Z^{2-}.[9] On the basis of the above results, the reaction of cobalt(II)–TDTA with TRDTA was considered to proceed through the following four simultaneous reaction paths:

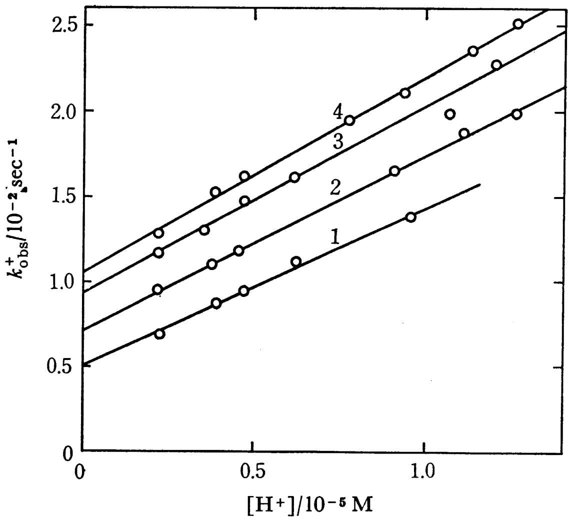


Fig. 1. The value of k^{+}_{obs} as a function of the hydrogen ion concentration at ionic strength 0.2 (KNO_3) and 25 °C containing 0.2 mM cobalt(II)-TDTA, 0.1 M acetate buffer and 0.005% gelatin. Initial concentrations of TRDTA, $[Z]_0$, are: 4 mM (1), 6 mM (2), 8 mM (3), and 10 mM (4).

$$CoY^{2-} + H_2Z^{2-} \overset{k^{\mathrm{CoY}}_{\mathrm{H_2Z}}}{\rightleftharpoons} CoZ^{2-} + H_2Y^{2-} \tag{4}$$

$$CoHY^{-} + H_2Z^{2-} \overset{k^{\mathrm{CoHY}}_{\mathrm{H_2Z}}}{\rightleftharpoons} CoHZ^{-} + H_2Y^{2-} \tag{5}$$

$$CoY^{2-} \overset{k^{\mathrm{CoY}}}{\rightleftharpoons} Co^{2+} + Y^{4-} \tag{6}$$

$$CoY^{2-} + H^+ \overset{k^{\mathrm{CoY}}_{\mathrm{H}}}{\rightleftharpoons} Co^{2+} + HY^{3-} \tag{7}$$

On the basis of the reaction mechanism, the following equation was derived:

$$\begin{aligned} k^{+}_{\mathrm{obs}} &= k^{\mathrm{CoY}}_{\mathrm{H_2Z}}[H_2Z^{2-}] + k^{\mathrm{CoHY}}_{\mathrm{H_2Z}}K^{\mathrm{H}}_{\mathrm{CoHY}}[H^+][H_2Z^{2-}] + k^{\mathrm{CoY}} \\ &\quad + k^{\mathrm{CoY}}_{\mathrm{H}}[H^+] = k^{\mathrm{CoY}}_{\mathrm{H_2Z}}\frac{[H^+]^2}{\alpha_{\mathrm{Z(H)}}K_3K_4}[Z]_f \\ &\quad + k^{\mathrm{CoHY}}_{\mathrm{H_2Z}}K^{\mathrm{H}}_{\mathrm{CoHY}}\frac{[H^+]^3}{\alpha_{\mathrm{Z(H)}}K_3K_4}[Z]_f + k^{\mathrm{CoY}} + k^{\mathrm{CoY}}_{\mathrm{H}}[H^+] \end{aligned} \tag{8}$$

where:

$$\alpha_{\mathrm{Z(H)}} = 1 + \frac{[H^+]}{K_4} + \frac{[H^+]^2}{K_3K_4} + \frac{[H^+]^3}{K_2K_3K_4} + \frac{[H^+]^4}{K_1K_2K_3K_4}$$

$$K^{\mathrm{H}}_{\mathrm{CoHY}} = \frac{[CoHY^-]}{[CoY^{2-}][H^+]}$$

K_1, K_2, K_3, and K_4 are the acid dissociation constants of H_4Z,[9] and $[Z]_f$ means the total concentration of the uncomplexed ligand, Z. In the pH range of the present experiment, the value of $\alpha_{\mathrm{Z(H)}}$ was practically identical with $[H^+]^2/K_3K_4$.[10] Since TRDTA was present in a large excess, $[Z]_f$ was almost the same as its initial concentration, $[Z]_0$, during the reaction process; therefore, Eq. (8) can be rewritten as:

$$k^{+}_{\mathrm{obs}} = (k^{\mathrm{CoY}} + k^{\mathrm{CoY}}_{\mathrm{H_2Z}}[Z]_0) + (k^{\mathrm{CoY}}_{\mathrm{H}} + k^{\mathrm{CoHY}}_{\mathrm{H_2Z}}K^{\mathrm{H}}_{\mathrm{CoHY}}[Z]_0)[H^+] \tag{9}$$

Equation (9) clearly indicates that the plots of the values of the intercepts and slopes of the straight lines shown in Fig. 1 against $[Z]_0$ should yield linear relations. They are reproduced in Fig. 2. Each rate constant given in Eq. (9) was determined from the values of the intercepts and the slopes of the straight lines shown in Fig. 2; all are given in Table 2.

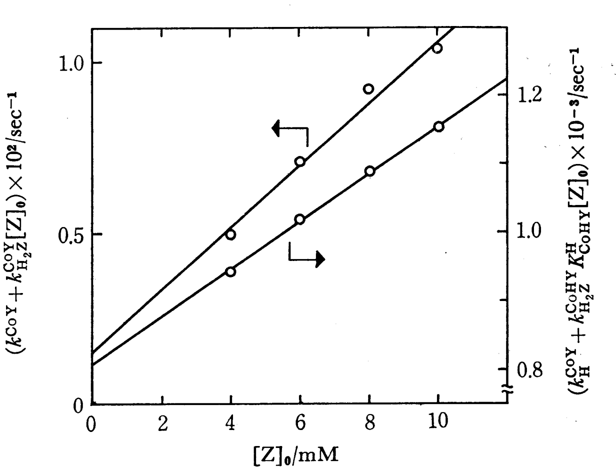


Fig. 2. The plots of $(k^{\mathrm{CoY}}_{\mathrm{H}}+k^{\mathrm{CoHY}}_{\mathrm{H_2Z}}K^{\mathrm{H}}_{\mathrm{CoHY}}[Z]_0)$ and $(k^{\mathrm{CoY}}+k^{\mathrm{CoY}}_{\mathrm{H_2Z}}[Z]_0)$ against $[Z]_0$ at ionic strength 0.2 and 25 °C containing 0.2 mM cobalt(II)-TDTA, 0.1 M acetate buffer and 0.005% gelatin.

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[9] G. Anderegg, *Helv. Chim. Acta*, **47**, 1801 (1964).

[10] The error of this assumption is less than 0.5%.

Results Obtained by Method B. The cobalt(III)-TDTA ion gives a limiting diffusion current corresponding to a one-electron reduction which starts at a more positive potential than the dissolution of mercury. The addition of TRDTA causes a decrease in the limiting current at the potential range more positive than about −0.1 V *vs.* SCE, as is shown in Fig. 3.

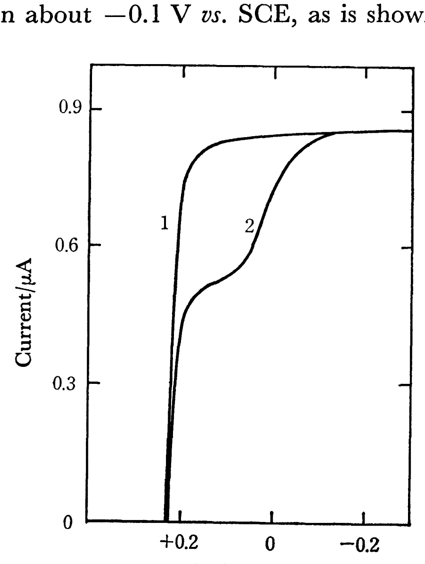

Fig. 3. Polarograms of 0.4 mM cobalt(III)-TDTA in the presence of 40 mM TDTA (curve 1) and 40 mM TDTA +4 mM TRDTA (curve 2) in solutions of ionic strength 0.5 (KNO_3) and pH 3.74 containing 80 mM acetate buffer and 0.005% gelatin.

TABLE 1. DEPENDENCE OF THE VALUE i_k (AT $t=t_d$) ON THE MERCURY HEIGHT

Mercury height/cm	40.7	51.0	60.8
$i_k/\mu A$ (at $t=t_d$)	0.25_5	0.26_1	0.26_0

Measurements were made under the following conditions: 0.4 mM cobalt(III)-TDTA, 8 mM TRDTA, 32 mM TDTA, 80 mM acetate buffer and 0.005% gelatin at ionic strength 0.5 (KNO_3), pH 3.79 and 25 °C. The applied potential was +0.13 V *vs.* SCE.

The value of the instantaneous current at $t=t_d$ corresponding to the decrease in the limiting current, which was denoted as i_k, was found to be independent of the mercury height of DME. This is shown in Table 1, which reveals that i_k is a kinetic current. These phenomena can be interpreted by means of the following equations:

$$\text{Co(III)-TDTA} + \text{e} \longrightarrow \text{Co(II)-TDTA} \qquad (10a)$$

$$\text{Co(II)-TDTA} + \text{TRDTA} \rightleftharpoons \text{Co(II)-TRDTA} + \text{TDTA} \qquad (10b)$$

$$\text{Co(II)-TRDTA} \longrightarrow \text{Co(III)-TRDTA} + \text{e} \qquad (10c)$$

The electrode process expressed by Eqs. (10a) to (10c) is the so-called ECE mechanism (electrochemical-chemical-electrochemical mechanism), which has previously been treated theoretically.[11] If the concentrations of TDTA and TRDTA are in excess over that of cobalt(II)-TDTA, the substitution reaction (10b) can be expressed as a pseudo first-order reaction:

$$\text{Co(II)-TDTA} \underset{l_b}{\overset{l_f}{\rightleftharpoons}} \text{Co(II)-TRDTA} \qquad (11)$$

where l_f and l_b mean the rate constants for the forward and the backward reactions respectively. The apparent equilibrium constant of Reaction (11), K, is given as:

$$K = \frac{l_f}{l_b} = \frac{[\text{Co(II)-TRDTA}]}{[\text{Co(II)-TDTA}]} = \frac{K_{\text{CoZ}}[\text{Z}^{4-}]}{K_{\text{CoY}}[\text{Y}^{4-}]} = \frac{\alpha_{\text{Y(H)}}K_{\text{CoZ}}[\text{Z}]_f}{\alpha_{\text{Z(H)}}K_{\text{CoY}}[\text{Y}]_f} \qquad (12)$$

where K_{CoY} and K_{CoZ} denote the stability constants for the cobalt(II)-TDTA and cobalt(II)-TRDTA complexes respectively. The value of $(\alpha_{\text{Y(H)}}\ K_{\text{CoZ}})/(\alpha_{\text{Z(H)}}\ K_{\text{CoY}})$ was polarographically determined in this work to be $11._8$. The value of K given in Eq. (12) was kept larger than unity by adjusting the concentrations of TDTA and TRDTA. For this condition, the following equation has been derived[11]:

For $K>1$:

$$\left|\frac{i_k}{i_d}\right| = \frac{K}{K-1}\left\{1-\exp(-lt)-2\theta\exp(-K^2\theta^2)\int_\theta^{K\theta}\exp(\lambda^2)\mathrm{d}\lambda\right\} \qquad (13)$$

where:

$$l = l_f + l_b$$

$$\theta = \sqrt{\frac{lt}{K^2-1}}$$

and where the symbol i_d indicates the diffusion current observed in the absence of Reaction (10b). In this method, the word "current," denoted by i_k or i_d, means an instantaneous current observed four seconds after the beginning of the mercury-drop growth. The rate constants, l_f and l_b, can be determined from Eq. (13) by using the value of $|i_k/i_d|$, which is obtained experimentally.

The pH dependence of the l_f values at various initial concentrations of TRDTA, $[\text{Z}]_0$, was also examined, as is shown in Fig. 4; the figure reveals that l_f is a first-

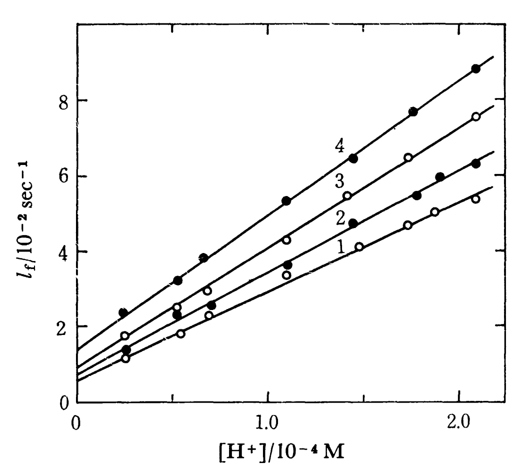

Fig. 4. The value of l_f as a function of the hydrogen ion concentration at ionic strength 0.5 (KNO_3) and 25 °C containing 0.4 mM cobalt(III)-TDTA, 24 mM TDTA, 80 mM acetate buffer and 0.005% gelatin.
Initial concentrations of TRDTA are: 4 mM (1), 6 mM (2), 8 mM (3), and 10 mM (4).

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[11] K. Ogino (née Ebata) and N. Tanaka, This Bulletin, **39**, 2672 (1966).

TABLE 2. RATE CONSTANTS OBTAINED BY METHODS A AND B AT 25 °C

Reaction	Rate constant	
	Method A (μ=0.2)	Method B (μ=0.5)
$CoY^{2-} + H_2Z^{2-} \xrightarrow{k^{CoY}_{H_2Z}} CoZ^{2-} + H_2Y^{2-}$	$8.9\times10^{-1}\,M^{-1}\,sec^{-1}$	$4\times10^{-1}\,M^{-1}\,sec^{-1}$
$CoHY^{-} + H_2Z^{2-} \xrightarrow{k^{CoHY}_{H_2Z}} CoHZ^{-} + H_2Y^{2-}$	$3.5\times10^{4}/K^{H}_{CoHY}\,M^{-1}\,sec^{-1}$	$2.3\times10^{4}/K^{H}_{CoHY}\,M^{-1}\,sec^{-1}$
$CoY^{2-} \xrightarrow{k^{CoY}} Co^{2+} + Y^{4-}$	$1.5\times10^{-3}\,sec^{-1}$	$6\times10^{-3}\,sec^{-1}$
$CoY^{2-} + H^{+} \xrightarrow{k^{CoY}_{H}} Co^{2+} + HY^{3-}$	$8.1\times10^{2}\,M^{-1}\,sec^{-1}$	$1._3\times10^{2}\,M^{-1}\,sec^{-1}$

order function with respect to both the hydrogen ion concentration and $[Z]_0$. These experimental results are understandable by assuming the same four reaction paths as Eqs. (4) to (7) for Reaction (10b), resulting in the same equation as in the case of Eq. (9)[12]:

$$l_f = (k^{CoY}+k^{CoY}_{H_2Z}[Z]_0) + (k^{CoY}_{H}+k^{CoHY}_{H_2Z}K^{H}_{CoHY}[Z]_0)[H^+] \quad (14)$$

Each rate constant was obtained in the same way as in Method A, on the basis of Fig. 4 and Eq. (14). The results are summarized in Table 2.

Discussion

It was revealed that the reaction of cobalt(II)-TDTA with TRDTA proceeds through four simultaneous reaction paths in the pH range from 3.7 to 5.6; these reaction paths consist of two nucleophilic ligand substitution reactions and two dissociation reactions of cobalt(II)-TDTA. The values of rate constants obtained by the two different methods are, as a whole, in good agreement with each other.

It should be noted that, in a lower pH range, reactions other than (4) to (7), such as:

$$CoY^{2-} + H_3Z^{-} \overset{k^{CoY}_{H_3Z}}{\rightleftharpoons} CoZ^{2-} + H_3Y^{-} \quad (15)$$

$$CoHY^{-} + H_3Z^{-} \overset{k^{CoHY}_{H_3Z}}{\rightleftarrows} CoHZ^{-} + H_3Y^{-} \quad (16)$$

may proceed. However, since the concentration of H_3Z^- is less than 6% of $[Z]_f$ even at pH 3.7, and since the values of $k^{CoY}_{H_3Z}$ and $k^{CoHY}_{H_3Z}$ seem to be smaller than those of $k^{CoY}_{H_2Z}$ and $k^{CoHY}_{H_2Z}$ respectively,[13] it seems reasonable to neglect the contributions of Reactions (15) and (16) to the total reaction.

The dissociation rate constants of cobalt(II)-TDTA and some related complexes are summarized in Table 3. These data show that the cobalt(II)-TDTA complex dissociates easier than the other complexes shown in Table 3. This may be due to the instability of the seven-membered diamine chelate ring which is present in the cobalt(II)-TDTA complex.

TABLE 3. DISSOCIATION RATE CONSTANTS

Ligand (L)	μ	k^{CoL}/sec^{-1}	k^{CoL}_{H}/(M^{-1} sec^{-1})	Ref.
EDTA	0.2	$<5\times10^{-4}$	3×10	2[a]
TRDTA	0.2	$<5\times10^{-3}$	5×10^{2}	2[a]
TDTA	0.2	1.5×10^{-3}	8.1×10^{2}	This work[a]
	0.5	6×10^{-3}	$1._3\times10^{2}$	This work[b]
meso-BDTA	0.2	—	5.1	3[a]
PDTA	0.2	—	4.3	3[a]

a) Method A, b) Method B.

TABLE 4. COMPARISON BETWEEN THE OBSERVED AND THE CALCULATED VALUES OF ($k^{Cotdta}_{H}/k^{CoL}_{H}$)

Observed	Calculated
$\dfrac{k^{Cotdta}_{H}}{k^{Cbtrdta}_{H}} = \begin{Bmatrix} 1._6 \text{ (Method A)} \\ 0.2_6 \text{ (Method B)} \end{Bmatrix}$	$\dfrac{K_{Cotrdta}}{K_{Cotdta}} = 0.69_5$[a]
$\dfrac{k^{Cotdta}_{H}}{k^{Coedta}_{H}} = \begin{Bmatrix} 2._7\times10 \text{ (Method A)} \\ 4._3 \text{ (Method B)} \end{Bmatrix}$	$\dfrac{K_{Coedta}}{K_{Cotdta}} = 4._5$[b] or $1._2\times10$[c]

a) This value was determined in this work polarographically.
b) Obtained in this work. c) From Ref. 9.

Table 4 compares the ratios of the observed rate constants, k^{CoY}_{H}/k^{CoL}_{H}, and the estimated ones which were calculated on the basis of the method proposed by Bydalek and Margerum.[15] Since TDTA is very similar to EDTA and TRDTA, the k^{CoY}_{H}/k^{CoL}_{H} ratio can be expected to be approximately the same as the reverse ratio of the stability constant, K_{CoL}/K_{CoY}, as has been shown in previous paper.[2,3] The observed ratios are practically identical with the calculated ones.

In Method A, it is necessary to stir and homogenize the solution for at least 5 to 10 seconds when the reaction is initiated. Therefore, it is desirable to measure the reaction which has a longer half-life than 40—50 seconds when DME is used. In this work, the rate of the reaction increases with the decrease in the pH of the solution. The kinetic measurements were not done in the pH range lower than 4.9 by Method A, for the rate of the reaction is immeasurably fast in this pH range. On the other hand, Method B, based on the

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[12] In this study, it is assumed that $\alpha_{Z(H)}$ is equal to $[H^+]^2/K_3K_4$. The contribution of terms other than $[H^+]^2/K_3K_4$ to $\alpha_{Z(H)}$ is 6% at pH 3.7, and decreases with an increase in the pH to reach 0.7% at pH 4.6.

[13] In many kinds of multidentate-ligand substitution reactions, such as $ML+L' \rightleftarrows ML'+L$, which have thus far been investigated, the rate constants decrease in this order: $k^{ML}_{L'} > k^{ML}_{HL'} > k^{ML}_{H_2L'}$. This indicates that a reaction rate decreases with an increase in the extent of the protonation of an attacking ligand.[14] Therefore, it is reasonable to assume that the value of $k^{CoY}_{H_3Z}$ in the Co(II)-TDTA-TRDTA system is much less than that of $k^{CoY}_{H_2Z}$.

[14] For instance, M. Kodama, C. Sasaki, and M. Murata, This Bulletin, **41**, 1333 (1968); M. Kodama, *ibid.*, **42**, 2532 (1969).

[15] T. J. Bydalek and D. W. Margerum, *Inorg. Chem.*, **2**, 678 (1963).

ECE mechanism, is quite useful for such a fast reaction as long as the following conditions are fulfilled; that is, the rates of the electrode reactions (10a) and (10c) are much faster than the chemical reaction (10b). This indicates that the measurement can be performed even in a pH range lower than 4.9 by utilizing this method.

There seems to be no example of the application of the electrode process, followed by chemical and electrochemical reactions (ECE mechanism), to the multidentate-ligand substitution reaction. In this study, the kinetic treatment over a wider pH range could be carried out by utilizing Method B together with Method A, and it was confirmed that Method B is applicable to the kinetic study of the multidentate-ligand substitution reactions.

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