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The Kinetics of Substitution Reactions Involving Metal Complexes. X. Reactions of Zinc(II) with Ethylenediaminetetraacetatocobaltate(II) and Trimethylenediaminetetraacetatocobaltate(II)

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Kinetics of the substitution reactions of zinc(II) with ethylenediaminetetraacetatocobaltate(II) and with trimethylenediaminetetraacetatocobaltate(II) have been studied. These reactions proceed predominantly through three simultaneous reaction paths, of which two involve electrophilic substitution reactions and the rest does the dissociation reaction of the complex. The rates of the reactions involving trimethylenediaminetetraacetatocobaltate(II) are larger than those involving ethylenediaminetetraacetatocobaltate(II) for all of the three simultaneous reaction paths. These results are discussed on the basis of the nature of the ligands and the stability of reaction intermediates.

In a previous paper,1) kinetic studies of the reactions involving metal propylenediaminetetraacetate (PDTA) were carried out, and the results were compared with those of the corresponding reactions involving metal ethylenediaminetetraacetate (EDTA). It was revealed from the studies that the acid-independent electrophilic substitution reactions involving metal-PDTA complexes are slower than those involving metal-EDTA complexes and that there was no essential difference in the rates of complex-forming reactions with PDTA and with EDTA.

Since it seems important and necessary to extend the study to the investigation on the effect of various ligands on the reaction rate and mechanism, kinetic studies of the reactions of zinc(II) with cobalt(II) complexes containing EDTA or trimethylenediaminetetraacetate (TRDTA) are dealt with in this paper.

Derivation of the Rate Equation

In the previous paper,2) it was reported that cobalt(II)-EDTA and cobalt(II)-TRDTA give a polarographic one-electron oxidation wave in acetate buffer - potassium nitrate media. In this study, the reaction was initiated by adding a known amount of cobalt(II)-EDTA or cobalt(II)-TRDTA solution into an acetate buffer - potassium nitrate solution containing zinc(II) ions in a large excess, and the rate of the reaction was followed by measuring the change with time of the anodic current of cobalt(II)-EDTA or cobalt(II)-TRDTA.

In the previous papers, kinetic studies involving cobalt(II)-EDTA3,4) and zinc(II)-EDTA5-7) were reported. From the mechanisms and the magnitude of individual rate constants of those reactions, the reactions of zinc(II) with cobalt(II)-EDTA or with cobalt(II)-TRDTA are considered to proceed through the following reaction paths:

$$\text{(i)}\quad \mathrm{Zn^{2+} + CoY^{2-}} \underset{k_{\mathrm{Co}}^{\mathrm{ZnY}}}{\overset{k_{\mathrm{Zn}}^{\mathrm{CoY}}}{\rightleftharpoons}} \mathrm{ZnY^{2-} + Co^{2+}} \qquad (1)$$

$$\text{(ii)}\quad \mathrm{H^{+} + CoY^{2-}} \rightleftharpoons \mathrm{CoHY^{-}} \qquad (2a)$$

$$\mathrm{Zn^{2+} + CoHY^{-}} \underset{k_{\mathrm{Co}}^{\mathrm{ZnHY}}}{\overset{k_{\mathrm{Zn}}^{\mathrm{CoHY}}}{\rightleftharpoons}} \mathrm{ZnHY^{-} + Co^{2+}} \qquad (2b)$$

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

$$\mathrm{Zn^{2+} + Y^{4-}} \rightleftharpoons \mathrm{ZnY^{2-}} \qquad (3b)$$

$$\text{(iv)}\quad \mathrm{H^{+} + CoY^{2-}} \underset{k_{\mathrm{Co}}^{\mathrm{HY}}}{\overset{k_{\mathrm{H}}^{\mathrm{CoY}}}{\rightleftharpoons}} \mathrm{Co^{2+} + HY^{3-}} \qquad (4a)$$

$$\mathrm{Zn^{2+} + HY^{3-}} \rightleftharpoons \mathrm{ZnY^{2-} + H^{+}} \qquad (4b)$$

where $\mathrm{Y^{4-}}$ denotes a quadrivalent EDTA or TRDTA anion.

On the basis of this reaction mechanism, the expression for the rate of the disappearance of $[\mathrm{CoY^{2-}}]_{\mathrm{app}}$ can be derived as

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1) H. Ogino and N. Tanaka, This Bulletin, **40**, 852 (1967).

2) N. Tanaka and H. Ogino, *ibid.*, **38**, 1054 (1965).

3) N. Tanaka, H. Osawa and M. Kamada, *ibid.*, **36**, 67 (1963).

4) N. Tanaka, H. Osawa and M. Kamada, *ibid.*, **36**, 530 (1963).

5) K. Kato, *ibid.*, **33**, 600 (1960).

6) N. Tanaka and K. Kato, *ibid.*, **33**, 1236 (1960).

7) N. Tanaka and H. Ogino, *ibid.*, **36**, 175 (1963).

$$-\frac{\mathrm{d}[\mathrm{CoY}^{2-}]_{\mathrm{app}}}{\mathrm{d}t}=$$
$$\frac{[\mathrm{CoY}^{2-}]_{\mathrm{app}}}{\alpha_{\mathrm{CoY(H)}}}\{k^{\mathrm{CoY}}+k_{\mathrm{Zn}}^{\mathrm{CoY}}[\mathrm{Zn}^{2+}]$$
$$+(k_{\mathrm{H}}^{\mathrm{CoY}}+k_{\mathrm{Zn}}^{\mathrm{CoHY}}K_{\mathrm{CoHY}}^{\mathrm{H}}[\mathrm{Zn}^{2+}])[\mathrm{H}^+]\}$$
$$-\frac{[\mathrm{ZnY}^{2-}]_{\mathrm{app}}[\mathrm{Co}^{2+}]}{\alpha_{\mathrm{ZnY(H)}}}$$
$$\times\left\{k_{\mathrm{Co}}^{\mathrm{ZnY}}+k_{\mathrm{Co}}^{\mathrm{ZnHY}}K_{\mathrm{ZnHY}}^{\mathrm{H}}[\mathrm{H}^+]\right.$$
$$\left.+\left(\frac{k_{\mathrm{Co}}^{\mathrm{Y}}}{K_{\mathrm{ZnY}}}+\frac{k_{\mathrm{Co}}^{\mathrm{HY}}}{K_{\mathrm{ZnY}}K_{\mathrm{HY}}}[\mathrm{H}^+]\right)\frac{1}{[\mathrm{Zn}^{2+}]}\right\} \quad (5)$$

where

$$[\mathrm{CoY}^{2-}]_{\mathrm{app}}=[\mathrm{CoY}^{2-}]+[\mathrm{CoHY}^-]$$
$$[\mathrm{ZnY}^{2-}]_{\mathrm{app}}=[\mathrm{ZnY}^{2-}]+[\mathrm{ZnHY}^-]$$
$$\alpha_{\mathrm{CoY(H)}}=1+K_{\mathrm{CoHY}}^{\mathrm{H}}[\mathrm{H}^+]$$
$$\alpha_{\mathrm{ZnY(H)}}=1+K_{\mathrm{ZnHY}}^{\mathrm{H}}[\mathrm{H}^+]$$
$$K_{\mathrm{CoHY}}^{\mathrm{H}}=\frac{[\mathrm{CoHY}^-]}{[\mathrm{H}^+][\mathrm{CoY}^{2-}]}$$
$$K_{\mathrm{ZnHY}}^{\mathrm{H}}=\frac{[\mathrm{ZnHY}^-]}{[\mathrm{H}^+][\mathrm{ZnY}^{2-}]} \quad (6)$$

K_{ZnY} represents the formation constant of ZnY^{2-} and K_{HY}, the fourth dissociation constant of EDTA or TRDTA.

Since the concentration of zinc(II) ions is much larger than $[\mathrm{CoY}^{2-}]_{\mathrm{app}}$, the change of $[\mathrm{Zn}^{2+}]$ can be neglected during the reaction. Considering this and integrating Eq. (5), we obtain

$$\log\frac{[\mathrm{CoY}^{2-}]^2{}_{0,\mathrm{app}}-[\mathrm{CoY}^{2-}]_{\mathrm{e,app}}[\mathrm{CoY}^{2-}]_{\mathrm{app}}}{[\mathrm{CoY}^{2-}]_{0,\mathrm{app}}([\mathrm{CoY}^{2-}]_{\mathrm{app}}-[\mathrm{CoY}^{2-}]_{\mathrm{e,app}})}=$$
$$2.303\frac{[\mathrm{CoY}^{2-}]_{0,\mathrm{app}}+[\mathrm{CoY}^{2-}]_{\mathrm{e,app}}}{[\mathrm{CoY}^{2-}]_{0,\mathrm{app}}-[\mathrm{CoY}^{2-}]_{\mathrm{e,app}}}k^+t \quad (7)$$

where

$$k^+=\frac{1}{\alpha_{\mathrm{CoY(H)}}}\{k^{\mathrm{CoY}}+k_{\mathrm{Zn}}^{\mathrm{CoY}}[\mathrm{Zn}^{2+}]_0$$
$$+(k_{\mathrm{H}}^{\mathrm{CoY}}+k_{\mathrm{Zn}}^{\mathrm{CoHY}}K_{\mathrm{CoHY}}^{\mathrm{H}}[\mathrm{Zn}^{2+}]_0)[\mathrm{H}^+]\} \quad (8)$$

Subscripts e and 0 mean equilibrium and zero time, respectively.

Assuming that the substitution reaction proceeds through only hydrated zinc(II) ions which are in equilibrium with acetatozinc(II) complexes, Eq. (8) is replaced by the following equation:

$$k^+\alpha_{\mathrm{CoY(H)}}=k^{\mathrm{CoY}}+k_{\mathrm{Zn}}^{\mathrm{CoY}}\frac{[\mathrm{Zn}^{2+}]_{0,\mathrm{app}}}{\alpha_{\mathrm{Zn(OAc)}}}$$
$$+\left\{k_{\mathrm{H}}^{\mathrm{CoY}}+k_{\mathrm{Zn}}^{\mathrm{CoHY}}K_{\mathrm{CoHY}}^{\mathrm{H}}\frac{[\mathrm{Zn}^{2+}]_{0,\mathrm{app}}}{\alpha_{\mathrm{Zn(OAc)}}}\right\}[\mathrm{H}^+] \quad (9)$$

where

$$[\mathrm{Zn}^{2+}]_{0,\mathrm{app}}=[\mathrm{Zn}^{2+}]_0+[\mathrm{ZnOAc}^+]_0$$
$$\alpha_{\mathrm{Zn(OAc)}}=1+\beta_{\mathrm{ZnOAc}}[\mathrm{OAc}^-]$$

β_{ZnOAc} represents the formation constant of acetatozinc(II) complex.

Considering that the anodic current, $\bar{i}$, given by cobalt(II)-EDTA or cobalt(II)-TRDTA complex is proportional to $[\mathrm{CoY}^{2-}]_{\mathrm{app}}$, Eq. (7) is rewritten as follows:

$$\log\frac{\bar{i}_0{}^2-\bar{i}_{\mathrm{e}}\bar{i}}{\bar{i}_0(\bar{i}-\bar{i}_{\mathrm{e}})}=2.303\frac{\bar{i}_0+\bar{i}_{\mathrm{e}}}{\bar{i}_0-\bar{i}_{\mathrm{e}}}k^+t \quad (10)$$

where subscripts 0 and e have the same meanings as in Eq. (7). Equation (10) shows that the plots of its left-hand side against t should give a straight line and that the value of k^+ can be calculated from the slope.

Experimental

Standard solutions of zinc(II) and cobalt(II) nitrates, disodium dihydrogen ethylenediaminetetraacetate ($\mathrm{Na_2H_2edta}$) and disodium dihydrogen trimethylenediaminetetraacetate ($\mathrm{Na_2H_2trdta}$) were obtained by the procedures reported previously.[8,9] All other chemicals used were of analytical reagent grade. The apparatus used was the same as described in the previous paper.[9]

Temperature was maintained at 25.0±0.1°C and ionic strength was adjusted to be 0.2 with potassium nitrate.

Results

Figure 1 shows examples of a current-time curve and a plot of the left-hand side in Eq. (10) against time, which were both obtained for the reaction of zinc(II) with cobalt(II)-EDTA complex. The plot gives a straight line as is expected from Eq. (10).

The values of k^+ were not affected by the change in the initial concentration of cobalt(II)-EDTA as expected from Eq. (9).

The values of k^+ were determined at various pH's and $[\mathrm{Zn}^{2+}]_{0,\mathrm{app}}$. The plots of $k^+\alpha_{\mathrm{Coedta(H)}}$ versus $[\mathrm{H}^+]$ are shown in Fig. 2, where the value of $K_{\mathrm{CoHedta}}^{\mathrm{H}}$ reported by Schwarzenbach *et al.*[10] was used in the calculation. These plots indicate that the rate is dependent on a first power of the hydrogen ion concentration. It was also confirmed from the analysis of Fig. 2 that the rate is proportional to the value of $[\mathrm{Zn}^{2+}]_{0,\mathrm{app}}$ provided the hydrogen ion concentration is kept constant. These results are consistent with Eq. (9). Similar results were obtained in the reaction of zinc(II) with cobalt(II)-TRDTA complex.

In the determination of the individual rate constants given in Eq. (9), a graphical method was employed. For example, the extrapolation of the plots in Fig. 2 to zero hydrogen ion concentration

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[8] N. Tanaka and H. Ogino, This Bulletin, **38**, 439 (1965).
[9] H. Ogino, *ibid.*, **38**, 771 (1965).
[10] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta,* **37**, 937 (1954).

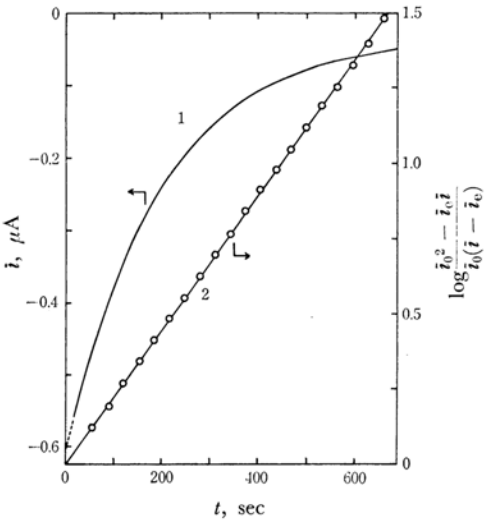

Fig. 1. A current-time curve (curve 1) and the left-hand side of Eq. (10) as a function of time (curve 2) obtained for the reaction of zinc(II) with cobalt(II)-EDTA complex at ionic strength 0.2 and 25°C. Measurement was made at +0.20V *vs.* SCE.
Initial concentrations are: $[\mathrm{Coedta}^{2-}]_{0,\mathrm{app}}=2.06\times10^{-4}$ M, $[\mathrm{Zn}^{2+}]_{0,\mathrm{app}}=20.6$ mM, $[\mathrm{H}^+]=3.29\times10^{-5}$ M, $[\mathrm{OAc}^-]=0.093_8$ M.

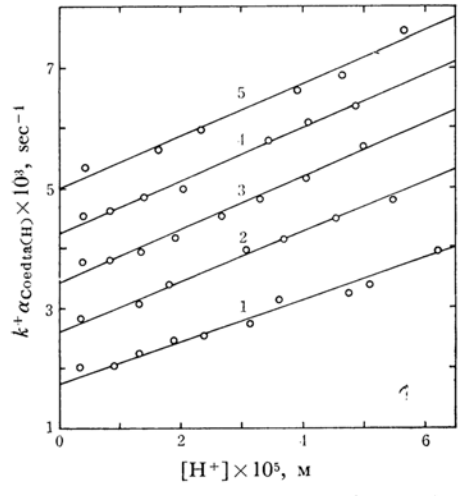

Fig. 2. $k^+\alpha_{\mathrm{Coedta(H)}}$ as a function of the hydrogen ion concentration at ionic strength 0.2 and 25°C. Concentrations are: $[\mathrm{Zn}^{2+}]_{0,\mathrm{app}}=10.3$ mM (1), 15.5 mM (2), 20.6 mM (3), 25.8 mM (4) and 30.6 mM (5); $[\mathrm{OAc}^-]=0.096_8$ M (1), 0.095_3 M (2), 0.093_8 M (3), 0.092_3 M (4) and 0.090_9 M (5).

gives

$$\lim_{[\mathrm{H}^+]\to0} k^+\alpha_{\mathrm{Coedta(H)}} = k^{\mathrm{Coedta}} + k_{\mathrm{Zn}}^{\mathrm{Coedta}}\frac{[\mathrm{Zn}^{2+}]_{0,\mathrm{app}}}{\alpha_{\mathrm{Zn(OAc)}}} \tag{11}$$

or

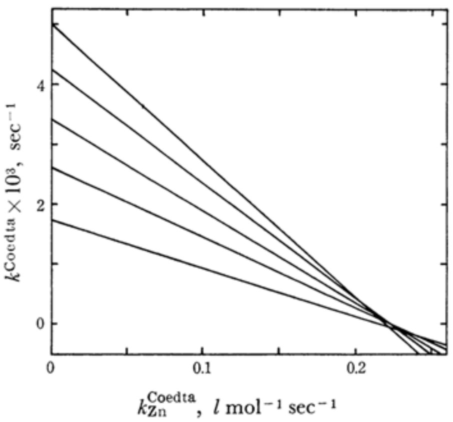

Fig. 3. Graphical evaluation of k^{Coedta} and $k_{\mathrm{Zn}}^{\mathrm{Coedta}}$.

$$k^{\mathrm{Coedta}} = A - B\,k_{\mathrm{Zn}}^{\mathrm{Coedta}} \tag{12}$$

where

$$A = \lim_{[\mathrm{H}^+]\to0} k^+\alpha_{\mathrm{Coedta(H)}},\quad B = \frac{[\mathrm{Zn}^{2+}]_{0,\mathrm{app}}}{\alpha_{\mathrm{Zn(OAc)}}}$$

Values of k^{Coedta} were plotted as a function of $k_{\mathrm{Zn}}^{\mathrm{Coedta}}$, as shown in Fig. 3. The formation constant of acetatozinc(II) complex reported in the previous paper[11] was used in the calculation. From the slope of the plots shown in Fig. 2, the values of $k_{\mathrm{Zn}}^{\mathrm{Coedta}}$ and $k_{\mathrm{H}}^{\mathrm{Coedta}}$ were obtained by a similar treatment. The individual rate constants of the reaction of zinc(II) with cobalt(II)-TRDTA complex were also evaluated by the graphical method mentioned above. The value of $K_{\mathrm{CoHtrdta}}^{\mathrm{H}}$ reported by Anderegg[12] was used in the calculation. The values thus obtained are given in Table 1.

Discussion

It is shown in Table 1 that all rate constants of the reactions involving cobalt(II)-TRDTA complexes are larger than those of the corresponding reactions involving cobalt(II)-EDTA complexes.

The kinetic studies of the substitution reactions involving nickel(II)-EDTA and its homologs were made by Bydalek *et al.*[13-15] They proposed that comparisons of the rate constants obtained in their studies can be made in terms of calculated intermediate stability constant ratios for the reaction in-

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[11] N. Tanaka and K. Kato, This Bulletin, **33**, 417 (1960).
[12] G. Anderegg, *Helv. Chim. Acta,* **47**, 1801 (1964).
[13] T. J. Bydalek and D. W. Margerum, *Inorg. Chem.,* **2**, 678 (1963).
[14] T. J. Bydalek and M. L. Blomster, *ibid.,* **3**, 667 (1964).
[15] T. J. Bydalek and A. H. Constant, *ibid.,* **4**, 833 (1965).

TABLE 1. RATE CONSTANTS AT IONIC STRENGTH 0.2 AND 25°C

Reaction	Rate constant
$Zn^{2+} + Coedta^{2-} \xrightarrow{k_{Zn}^{Coedta}} Znedta^{2-} + Co^{2+}$	$k_{Zn}^{Coedta} = 0.23\ l\ mol^{-1}\ sec^{-1}$
$Zn^{2+} + CoHedta^{-} \xrightarrow{k_{Zn}^{CoHedta}} ZnHedta^{-} + Co^{2+}$	$k_{Zn}^{CoHedta} = \sim 5 \times 10^{-1}\ l\ mol^{-1}\ sec^{-1}$
$Coedta^{2-} \xrightarrow{k^{Coedta}} Co^{2+} + edta^{4-}$	$k^{Coedta} < 5 \times 10^{-4}\ sec^{-1}$
$H^{+} + Coedta^{2-} \xrightarrow{k_{H}^{Coedta}} Co^{2+} + Hedta^{3-}$	$k_{H}^{Coedta} = 3 \times 10\ l\ mol^{-1}\ sec^{-1}$
$Zn^{2+} + Cotrdta^{2-} \xrightarrow{k_{Zn}^{Cotrdta}} Zntrdta^{2-} + Co^{2+}$	$k_{Zn}^{Cotrdta} = 2._5\ l\ mol^{-1}\ sec^{-1}$
$Zn^{2+} + CoHtrdta^{-} \xrightarrow{k_{Zn}^{CoHtrdta}} ZnHtrdta^{-} + Co^{2+}$	$k_{Zn}^{CoHtrdta} = \sim 1 \times 10^{2}\ l\ mol^{-1}\ sec^{-1}$
$Cotrdta^{2-} \xrightarrow{k^{Cotrdta}} Co^{2+} + trdta^{4-}$	$k^{Cotrdta} < 5 \times 10^{-3}\ sec^{-1}$
$H^{+} + Cotrdta^{2-} \xrightarrow{k_{H}^{Cotrdta}} Co^{2+} + Htrdta^{3-}$	$k_{H}^{Cotrdta} = 5 \times 10^{2}\ l\ mol^{-1}\ sec^{-1}$

termediates of the nickel(II)-EDTA and its homologs.

In Table 2 are given the comparisons of rate constants obtained in the present study and calculated ratios of the intermediate stability constant selected so as to match best with the ratios of the rate constants. The intermediate stability constants, K_R, were calculated with Eq. (13) as defined by Bydalek *et al.*[13]

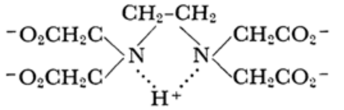
TABLE 2. COMPARISONS OF RATE CONSTANTS

Obsd.	Calcd.*
$\dfrac{k^{Coedta}}{k_{H}^{Coedta}} < 2 \times 10^{-5}$	$\dfrac{1}{K_{Himda}K_{el}} = 7.1 \times 10^{-11}$
$\dfrac{k^{Cotrdta}}{k_{H}^{Cotrdta}} < 1 \times 10^{-5}$	
$\dfrac{k_{H}^{Coedta}}{k_{Zn}^{Coedta}}\ 1.3 \times 10^{2}$	$\dfrac{K_{Himda}K_{el}}{K_{Znimda}} = 3.1 \times 10^{2}$
$\dfrac{k_{H}^{Cotrdta}}{k_{Zn}^{Cotrdta}}\ 2 \times 10^{2}$	
$\dfrac{k_{Zn}^{Cotrdta}}{k_{Zn}^{Coedta}}\ 1._1 \times 10$	$\dfrac{K_{Coedta}}{K_{Cotrdta}} = 1.7 \times 10$
$\dfrac{k_{H}^{Cotrdta}}{k_{H}^{Coedta}}\ 1._7 \times 10$	

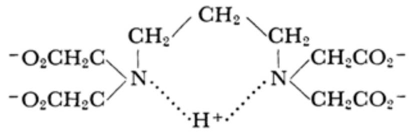
* In this calculation the following stability constants are used: The values of 9.65[16] and 7.66[16] are used for $\log K_{Himda}$ and $\log K_{Znimda}$, respectively, assuming *N*-methyliminodiacetate as a model, and the values of 14.48[9] and 15.71[9], for $\log K_{Cotrdta}$ and $\log K_{Coedta}$ respectively.

$$K_R = \frac{K_{entering\ ion\ segment}\ K_{Co\ segment}}{K_{Co\ complex}} \qquad (13)$$

In some cases, corrections for an electrostatic attraction were necessary and were made using the value of $\log K_{el} = 0.5$.[13] In the calculations in Table 2, it was assumed that the value of $K_{M\ segment}$ of the intermediate involving EDTA was essentially the same as that involving TRDTA. The third dissociation constant of TRDTA is higher than that of EDTA. This is mainly due to particular hydrogen bridged structures[17]:



$Hedta^{3-}$



$Htrdta^{3-}$

Therefore, the increase of intermediate stability constant due to larger basicity of TRDTA than EDTA seems to be not so significant.[*1]

The results of calculations given in Table 2 suggest that zinc(II) ion forms iminodiacetate segment in the dinuclear intermediate Zn···Y···Co, which is formed prior to the rate determining step in

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16) L. G. Sillén and A. E. Martell, "Stability Constants," Chemical Society, London (1964).

17) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **31**, 1029 (1948).

[*1] For other assumptions required in the calculations of intermediate stability constants, the papers by Bydalek *et al.*[13-15] should be consulted.

Reaction (1). Therefore, a cobalt(II) ion in this reaction intermediate coordinates to the iminodiacetate segment, whatever the kind of coordination is.

The value of $k_{\mathrm{H}}^{\mathrm{Cotrdta}}$ is 17 times larger than that of $k_{\mathrm{H}}^{\mathrm{Coedta}}$. From the values of $k_{\mathrm{H}}^{\mathrm{CoY}}$ and those of equilibrium constants of various reactions, the rate constants of the reverse reaction, $k_{\mathrm{Co}}^{\mathrm{HY}}$, which corresponds to the rate of the complex-forming reaction, can be determined with the equation,

$$k_{\mathrm{Co}}^{\mathrm{HY}} = k_{\mathrm{H}}^{\mathrm{CoY}} K_{\mathrm{CoY}} K_{\mathrm{HY}} \tag{14}$$

From $k_{\mathrm{H}}^{\mathrm{Coedta}}$, $k_{\mathrm{Co}}^{\mathrm{Hedta}}$ was calculated as,

$$\begin{aligned} k_{\mathrm{Co}}^{\mathrm{Hedta}} &= (3 \times 10) \times (10^{15.71}) \times (10^{-10.26}) \\ &= 8 \times 10^{6}\, l\, \mathrm{mol}^{-1}\, \mathrm{sec}^{-1} \end{aligned} \tag{15}$$

and from $k_{\mathrm{H}}^{\mathrm{Cotrdta}}$, $k_{\mathrm{Co}}^{\mathrm{Htrdta}}$ was calculated as,

$$\begin{aligned} k_{\mathrm{Co}}^{\mathrm{Htrdta}} &= (5 \times 10^{2}) \times (10^{14.48}) \times (10^{-10.27}) \\ &= 8 \times 10^{6}\, l\, \mathrm{mol}^{-1}\, \mathrm{sec}^{-1} \end{aligned} \tag{16}$$

The values of $k_{\mathrm{Co}}^{\mathrm{Hedta}}$ and $k_{\mathrm{Co}}^{\mathrm{Htrdta}}$ are essentially the same. This supports the previous conclusion[1] that the second-order rate constants of the complex-forming reactions of a metal ion with related (the same charge and similar size) ligands are approximately equal.

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