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Kinetics of Multidentate Ligand Substitution Reactions. XVI. Substitution Reactions of 1,2-Cyclohexanediamine-*N*,*N*,*N'*,*N'*-tetraacetic Acid (CyDTA) with the Zinc(II)–Ethylenediaminemonoacetate (EDMA) and –Ethylenediamine-*N*,*N'*-diacetate (EDDA) Complexes and That of Ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic Acid (EDTA) with the Nickel(II)–EDDA Complex

Mutsuo KODAMA

Department of Chemistry, College of General Education, Hirosaki University, Bunkyo, Hirosaki, Aomori 036

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The kinetics of the substitution reactions of CyDTA with zinc(II)–EDMA and –EDDA complexes and that of EDTA with the nickel(II)–EDDA complex were studied systematically by using the polarographic technique. All the substitution reactions were found to be first-order with respect to the CyDTA or EDTA anion and also first-order with respect to the 1 : 1-ratio EDMA or EDDA complex. From a comparison of the observed rate constants with those estimated on the basis of the proposed reaction intermediates, the detailed reaction mechanisms were discussed. The rates of the reactions of zinc(II)–EDMA complex and nickel(II)–EDDA complex could be understood in terms of the ethylenediamine reaction mechanism, but that of the reaction of the zinc(II)–EDDA complex with the CyDTA anion could not. This discrepancy may be ascribed by the steric hindrance of the CyDTA anion to the formation of an ethylenediamine reaction intermediate in the reaction of the zinc(II)–EDDA complex.

In a previous paper,[1] the present author studied the steric effect of the cyclohexane ring on the rate of the substitution reactions of metal(II)–aminopolycarboxylate complexes. In this paper, the present author will deal with the kinetics of the substitution reactions of CyDTA with the zinc(II)–EDMA and –EDDA complexes as an extention of an earlier investigation of the steric effects of the CyDTA anion on the reaction of the metal(II)–aminopolycarboxylate complex. In order to describe more precisely the nature of the steric effect of the CyDTA anion, the substitution reaction of EDTA with the nickel(II)–EDDA complex will also be studied.

Experimental

Reagents. The preparation and standardization of zinc(II) and nickel(II) solutions were described in previous papers.[2,3] Reagent-grade EDDA, CyDTA, and glycine were recrystallized from their aqueous solutions by adding pure hydrochloric acid and ethanol. The preparation and recrystallization of EDMA were also described previously.[4] The other chemicals used in this study were of an analytical reagent-grade and were used without further purification.

Apparatus and Experimental Procedures. The apparatus and the experimental procedures were the same as those described previously.[1] In this study, all the measurements were conducted in solutions with an ionic strength of 0.30 ($NaClO_4$) at 25 °C. No buffer reagent was used, because the sample solutions always contained a large excess of uncomplexed EDMA, EDDA, or Gly, and had enough buffer capacity in the pH ranges studied ($9.50<\mathrm{pH}<10.50$ in the EDMA system and $9.00<\mathrm{pH}<10.20$ in the EDDA system). In the case of the zinc(II) system, the kinetic measurements were carried out in sample solutions containing large excesses of uncomplexed CyDTA and EDMA or EDDA over the complexed EDMA or EDDA. In the reaction of the nickel(II) complex, the kinetic measurements were carried out in solutions containing large excesses of complexed and uncomplexed EDDA over EDTA. Therefore, all the reactions could be treated as pseudo-first-order reactions. The rate of the substitution reaction of the zinc(II) complex was determined by measuring the change in the reduction wave-height of the zinc(II)–EDMA or –EDDA complex. On the other hand, the rate of the reaction involving the nickel(II)–EDDA complex was determined by observing the change in the dissolution wave due to the uncomplexed EDTA.

Results and Discussion

The reaction of CyDTA with the zinc(II)–EDMA complex showed the same kinetic behavior as that with the zinc(II)–*N*-(2-hydroxyethyl)iminodiacetate (HIDA) complex,[1] suggesting the following reaction mechanism (I):

$$\mathrm{MX}_2^{(2-2m)+} \rightleftharpoons \mathrm{MY}^{(2-m)+} + \mathrm{X}^{m-} \quad (1_a) \text{ in a rapid equil.}$$

$$\text{(I)} \quad \mathrm{MX}^{(2-m)+} + \begin{cases} \mathrm{HY}^{3-} \overset{k_\mathrm{H}}{\rightleftharpoons} \mathrm{MY}^{2-} + \mathrm{HX}^{(1-m)} & (1_b) \\ \mathrm{Y}^{-4} \overset{k_0}{\rightleftharpoons} \mathrm{MY}^{2-} + \mathrm{X}^{m-} & (2_c) \end{cases} \quad \text{rds}$$

Therefore, the k_0 and k_H values were determined from the intercept and slope of the linear relation between $k_\mathrm{ap}^{+}\cdot(1+K_2\cdot[\mathrm{X}]_\mathrm{f}/(\alpha_\mathrm{H})_\mathrm{x})\cdot(\alpha_\mathrm{H})_\mathrm{Y}/[\mathrm{Y}]_\mathrm{f}$ and $[\mathrm{H}^+]$ (Table 1). Here, all the symbols used have their usual meanings.[1] The substitution reactions of the nickel(II)–EDDA complex with EDTA was studied in sample solutions containing excess glycinate. In this reaction, the k_ap^{+} value determined from the slope of the linear relation between $\log(i_0/i_t)$ and t was independent of the concentration of the uncomplexed EDDA and of the initial concentration of EDTA. However, it decreased appreciably with an increase in the Glut concentration $[\mathrm{G}]_\mathrm{f}$, and the plot of the $[\mathrm{Ni(II)}]/k_\mathrm{ap}^{+}\cdot(\alpha_\mathrm{H})_\mathrm{Y}$ against the concentration of the Glut anion, $[\mathrm{G}]_\mathrm{f}/(\alpha_\mathrm{H})_\mathrm{G}$, gave a straight line with an intercept of a finite value (Fig. 1). This indicates the formation of a 1 : 1 : 1-ratio mixed ligand complex, MXG^-, corresponding to the following reaction mechanism (II):

$$\mathrm{MXG}^- \rightleftharpoons \mathrm{MX}^0 + \mathrm{G}^- \quad (2_a) \text{ in a rapid equil.}$$

$$\text{(II)} \quad \mathrm{MX}^0 + \begin{cases} \mathrm{HY}^{3-} \overset{k_\mathrm{H}}{\rightleftharpoons} \mathrm{MY}^{2-} + \mathrm{HX}^- & (2_b) \\ \mathrm{Y}^{4-} \overset{k_0}{\rightleftharpoons} \mathrm{MY}^{2-}. + \mathrm{X}^{2-} & (2_c) \end{cases} \quad \text{rds}$$

TABLE 1. RATE CONSTANTS ($\mu=0.30$, 25°C)

A) Ni(II) system

log K_{MX}	System	Observed rate constant		Rate constant ratio		
				Obsd		Calcd (En mechanism)
		k_0	k_H	k_0	k_H	
13.20	EDDA	7.0	3.72	1.0	1.0	1.0
10.44	EDMA[7]	1.5×10^3	3.90×10^2	$10^{2.30}$	$10^{2.02}$	$10^{2.26}$

B) Zn(II) system

log K_{MX}	System	Observed rate constant		k_0 ratio		
				Obsd	Calcd	
		k_0	k_H		En mecha.	Gly mecha.
8.02	HIDA	2.7×10^4	2.60×10^2	1.0	—	1.0
8.22	EDMA	5.6×10^2	3.20×10^1	$10^{-1.68}$	$10^{-1.74}$	—
10.79	EDDA	1.9×10^1	$6.0_0\times10^{-1}$	$10^{-3.15}$	$10^{-4.00}$	$10^{-2.77}$

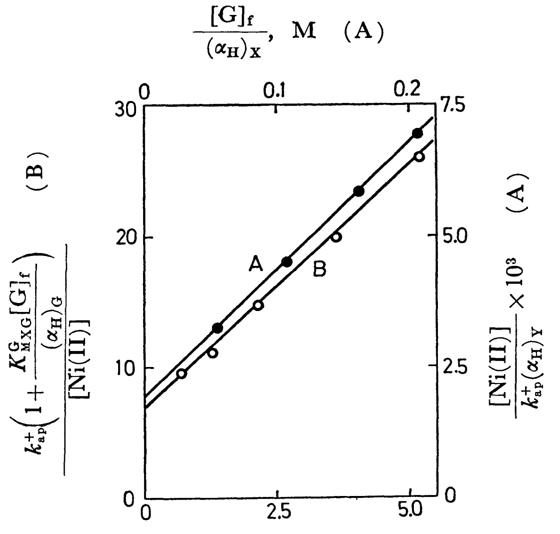

Fig. 1. The relation between $[Ni(II)]/k^+_{ap}\cdot(\alpha_H)_Y$ and $[G]_f/(\alpha_H)_G$ and that between $k^+_{ap}\cdot(\alpha_H)_Y\cdot(1+K^G_{MXG}\cdot[G]_f/(\alpha_H)_G)/[Ni(II)]$ and $[H^+]$.

$\mu=0.30$, 25 °C
$[EDDA]_f=28.3$ mM, $[EDTA]_i=0.566$ mM

A) The relation between $[Ni(II)]/k^+_{ap}\cdot(\alpha_H)_Y$ and $[G]_f/(\alpha_H)_G$
pH=9.70, $[Ni(II)]=5.66$ mM
$[G]_f$ ranged from 80 to 290 mM

B) The relation between $k^+_{ap}\cdot(\alpha_H)_Y(1+K^G_{MXG}\cdot[G]_f/(\alpha_H)_G)/[Ni(II)]$ and $[H^+]$
$[Ni(II)]=7.55$ mM, $[G]_f=28.3$ mM
pH ranged from 9.20 to 10.20

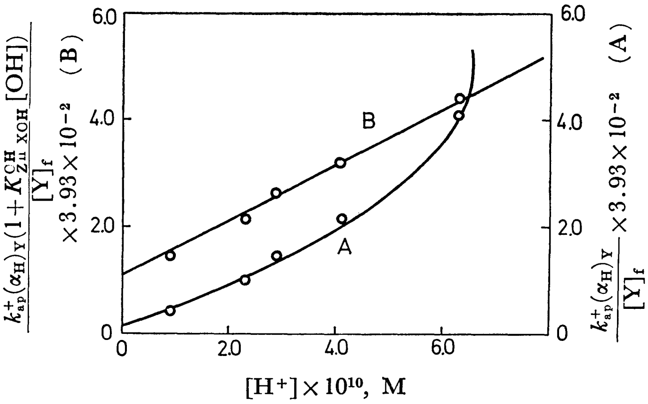

Fig. 2. The plot of $k^+_{ap}\cdot(\alpha_H)_Y/[Y]_f$ or $k^+_{ap}(\alpha_H)_Y(1+K^{OH}_{ZnX(OH)}[OH^-])/[Y]_f$ against $[H^+]$.

$[Zn(II)]=1.0$ mM, $[EDDA]_f=20.0$ mM
$[CyDTA]_i=10$ mM
$\mu=0.30$, 25 °C

A) The plot of $k^+_{ap}\cdot(\alpha_H)_Y/[Y]_f$ against $[H^+]$

B) The plot of $k^+_{ap}\cdot(\alpha_H)_Y(1+K^{OH}_{ZnX(OH)}[OH^-])/[Y]_f$ against $[H^+]$

Since the 1 : 1 : 1-ratio mixed ligand complex of the nickel(II)-ion involving the EDDA and Glut anions can be synthesized easily by mixing $NiCl_2$, EDDA, and Glut solutions and by evaporating the resulting mixture to dryness,[5] the above conclusion seems reasonable. From the ratio between the slope and the intercept of the above linear relation, the equilibrium constant, $K^G_{MXG}=[MXG^-]/[MX^0]\cdot[G^-]$, was determined to be 13.1. For the above reaction mechanism, the apparent rate constant, k^+_{ap}, is given by $[Y]_f(k_0+k_H\cdot[H^+]/K_4)/(\alpha_H)_Y\cdot(1+K^G_{MXG}\cdot[G]_f/(\alpha_H)_G)$. Therefore, the k_0 and k_H values were determined from the intercept and slope of the linear relation between $k^+_{ap}\cdot(\alpha_H)_Y\cdot(1+K^G_{MGX}\cdot[G]_f/(\alpha_H)_G)/[Y]_f$ and $[H^+]$ (Fig. 1). They are also listed in Table 1.

The substitution reaction of the zinc(II)–EDDA complex with CyDTA was studied in solutions not containing glycinate. As in the case of the nickel(II)–EDDA system, the k^+_{ap} value was independent of the cocentration of the uncomplexed EDDA and of the initial concentration of the zinc(II)–EDDA complex. However, the plot of k^+_{ap} multiplied by $(\alpha_H)_Y/[Y]_f$ against the hydrogen ion concentration, $[H^+]$, gave no linear relation (Fig. 2). This may suggest the formation of a mixed-ligand complex involving the hydroxide anion. Since the zinc(II)–EDDA complex forms a mixed-ligand complex, $ZnX(NCS)^-$, with NCS^-,[6] it is natural to assume the formation of the 1 : 1 : 1-ratio mixed ligand complex, $ZnX(OH)^-$. If the slow reaction pathways, (2_b) and (2_c), are preceded by the rapid dissociation of $ZnX(OH)^-$ into ZnX^0, corresponding to the k_{ap}^+ value of $[Y]_f(k_0+k_H[H^+]/K_4)/(\alpha_H)_Y(1+K_{ZnX(CH)}^{OH}[OH^-])$, the equilibrium constant, $K_{ZnX(CH)}^{CH}(=[ZnX(OH)^-]/[ZnX^0]\cdot[OH^-])$, should be given by Eq. (1):

$$k_{ZnX(OH)}^{OH}=\frac{1}{K_w}\frac{(P_1\cdot[H^+]_1-P_2\cdot[H^+]_2)([H^+]_1-[H^+]_2\cdot)-(P_1\cdot[H^+]_1-P_3\cdot[H^+]_3)\cdot([H^+]_1-[H^+]_3)}{(P_1-P_2)([H^+]_1-[H^+]_3)-(P_1-P_3)([H^+]_1-[H^+]_2)} \tag{1}$$

and the plot of $k_{ap}^+\cdot(1+K_{ZnX(OH)}^{OH}\cdot[OH^-])\cdot(\alpha_H)_Y/[Y]_f$ against $[H^+]$ should give a straight line with an intercept of a finite value. By using the $K_{ZnX(CH)}^{OH}$ value of 2×10^4 estimated with the aid of Eq. (1), the $k_{ap}^+\cdot(\alpha_H)_Y\cdot K_{ZnX(OH)}^{OH}\cdot[OH^-])/[Y]_f$ value was plotted against $[H^+]$. As is illustrated by the straight line (B) in Fig. 2, the above plot invariably gave a linear relation with an intercept of a finite value. From the intercept and the slope of the above linear relation, the k_0 and k_H values for the substitution reaction of the zinc(II)–EDDA complex with CyDTA were determined (Table 1). Previously,[1] the present author systematically studied the substitution reaction of the zinc(II)–HIDA complex with CyDTA at 0 °C and drew the conclusion that the reaction proceeds through the glycinate-reaction mechanism. In this paper, this reaction was studied at 25 °C, and the k_0 and k_H values were determined to be 2.7×10^4 and $2.6_0\times10^2$ respectively.

Previously,[7] the present author mentioned that the substitution reaction of the nickel(II)–EDMA complex with EDTA proceeds through the ethylene diamine(En)-reaction intermediate, where the leaving EDMA and entering EDTA anions are bonded to the nickel(II) ion through ethylenediamine- and glycinate-chelate rings respectively. Therefore, it is reasonable to assume the En mechanism for the substitution reaction of the nickel(II)–EDMA complex with EDTA. The relative rate constant for the reaction of the nickel(II)–EDDA complex with EDTA was calculated on the basis of the En-reaction intermediate by means of this relation; $k=k_{rds}\cdot K_L\cdot K_A\cdot K_{st}\cdot K_{elec}/K_{MX}$,[1] and was compared with the observed one (Table 1). Here, all the symbols in the above relation have their usual meanings.[1] The good agreement between the calculated and observed relative rate constants supports the above En-mechanism explanation. Since the steric hindrance to the CyDTA anion in its reaction with the zinc(II)–HIDA complex is considered to be quite the same as those of the reactions with the zinc(II)–EDMA and –EDDA complexes, one can also calculate the relative rate constants with reference to the zinc(II)–HIDA system on the basis of the proposed reaction intermediate. Since, in the substitution reaction, the zinc(II)-aminopolycarboxylate complex shows kinetic behavior very similar to that of the corresponding nickel(II) complex,[8] one can assume the En-reaction mechanism for the reactions of CyDTA with the zinc(II)–EDMA and –EDDA complexes. As is shown in Table 1, the k_0 ratio between the HIDA and EDMA systems calculated by assuming the En-reaction mechanism for the EDMA system agreed well with the observed one. However, the rate of the substitution reaction of the zinc(II)–EDDA complex with CyDTA cannot be understood by assuming the En mechanism. This discrepancy may be ascribed to the steric effect of the CyDTA anion on the reaction mechanism. The k_{rds} values for the Gly and En mechanisms were approximated by the dissociation rate constants of the 1 : 1-ratio zinc(II)–Gly and –En complexes respectively. The dissociation rate constant of the zinc(II)–Gly complex was estimated to be 1.5×10^3 from the formation rate constant, k_f, with the aid of the $K_{MX}=k_f/k_d$ relation. The k_f value was calculated by using the $k_{Zn}^{-H_2O}$ value of 3.2×10^7 and the K_{os} value of 5 on the basis of the usual water-exchange mechanism.[9] The dissociation rate constant of the 1 : 1-ratio zinc(II)–En complex was evaluated as 3.0×10^2 from the dissociation constant of the 1 : 1-ratio zinc(II)–ammine complex[10] by correcting it for the rotational barrier around the C–N bond.[11] In order to explain more thoroughly the fact that the CyDTA reaction with the zinc(II)–EDMA complex proceeds through the En mechanism, whereas that with the zinc(II)–EDDA complex does not, the steric effect of the CyDTA on the formation of the reaction intermediate in the reactions of the EDMA and EDDA complexes was investigated by using the molecular model. A close molecular model examination revealed that the ethylenediamine reaction intermediate can be formed without any difficulty in the EDDA∼EDTA and EDMA∼CyDTA systems. However, it is almost impossible to build the En intermediate in the EDDA∼CyDTA system because of the steric interaction of the CyDTA with the free carboxylate group of the EDDA anion. For this reason, the substitution reaction of CyDTA with the zinc(II)–EDDA complex could not proceed through the En reaction intermediate. As has been mentioned above, it is impossible to form the En-reaction intermediate from the EDDA and CyDTA anions. However, the glycinate reaction intermediate could be formed, although with some difficulty. The relative rate constant calculated on the basis of the Gly mechanism is also listed in Table 1 and compared with the observed one. The agreement between the two values can be regarded as satisfactory. This agreement and the conclusion obtained in the molecular-model examination suggest that the glycinate reaction mechanism can be assumed for the reaction of the zinc(II)–EDDA complex with with CyDTA.

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