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Multidentate Ligand Kinetics. IV. Computer Simulation of the Steady State of the Free Ligands in a Coordination Chain Reaction

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The ligand-substitution reactions between two multidentate ligand complexes in the presence of free ligands proceed by means of a coordination chain-reaction mechanism. The reaction was simulated on a computer under various conditions. The character of the steady state of the free ligands in the coordination chain reaction was discussed. The conditions under which the coordination chain reaction proceeds with the steady state of the free ligands were determined. The diagrams of the time development of the free ligands were found to be useful for studies using the coordination chain reaction.

In previous works,[1-3] the ligand-substitution reactions between two multidentate ligand complexes were studied in the presence of free ligands:

$$ML + ZX \longrightarrow MX + ZL, \quad (R1)$$

where ML, ZX, MX, and ZL are multidentate ligand complexes; the charges will be omitted hereafter for the sake of simplicity.

The reactions were shown to proceed by means of a coordination chain-reaction mechanism:

$$ML + X \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MX + L, \quad (R2)$$

$$ZX + L \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} ZL + X, \quad (R3)$$

where X and L denote free ligands.

In the course of our studies, the rate law was derived from a steady-state treatment on the assumption that the concentrations of the free ligands (X and L) remain constant throughout the substitution. This assumption, however, was not examined.

Coordination chain reactions can be applied to the determination of trace metal ions.[4-6] In the analytical applications, the above assumption is taken to hold. However, in general, a coordination chain-reaction system can not necessarily be expected to satisfy the above assumption.

If the time development of the free-ligand concentration in the system can be known, it is useful for the studies using a coordination chain reaction. In this paper, coordination chain reactions were simulated on a computer under various conditions, and the concentration-time profiles for all the components were calculated. The purpose of this paper is to ascertain the conditions under which the reaction proceeds with the steady state of the free ligands.

Computational Method

The six-variable, four-rate constant isothermal model represented by Reactions R2 and R3 can be described by the following differential equations:

$$\frac{d[ML]}{dt} = -k_2[ML][X] + k_{-2}[MX][L], \quad (1)$$

$$\frac{d[ZX]}{dt} = -k_3[ZX][L] + k_{-3}[ZL][X], \quad (2)$$

$$\frac{d[MX]}{dt} = k_2[ML][X] - k_{-2}[MX][L], \quad (3)$$

$$\frac{d[ZL]}{dt} = k_3[ZX][L] - k_{-3}[ZL][X], \quad (4)$$

$$\frac{d[X]}{dt} = -k_2[ML][X] + k_{-2}[MX][L] + k_3[ZX][L] - k_{-3}[ZL][X], \quad (5)$$

$$\frac{d[L]}{dt} = k_2[ML][X] - k_{-2}[MX][L] - k_3[ZX][L] + k_{-3}[ZL][X]. \quad (6)$$

Using the known starting conditions and rate constants, the six above simultaneous differential equations were integrated by the numerical integration method of Runge-Kutta-Gill.[7] The starting conditions in the integration were as follows:

$$[ML]_0 = a\ \mathrm{M}(1\ \mathrm{M} = 1\ \mathrm{mol\ dm^{-3}}), \quad (7)$$

$$[ZX]_0 = b\ \mathrm{M}, \quad (8)$$

$$[MX]_0 = [ZL]_0 = 0\ \mathrm{M}, \quad (9)$$

$$\begin{matrix}[X]_0 = c\ \mathrm{M} \\ [L]_0 = 0\ \mathrm{M}\end{matrix} \quad \text{or} \quad \begin{matrix}[X]_0 = 0\ \mathrm{M} \\ [L]_0 = c\ \mathrm{M}\end{matrix}, \quad (10)$$

where $[\ ]_0$ indicates the initial concentration of the species and where a, b, and c are not zero. In these calculations, it has been premised that $k_3 \geqq k_2$ and $[ZX]_0 \geqq [ML]_0$.[8]

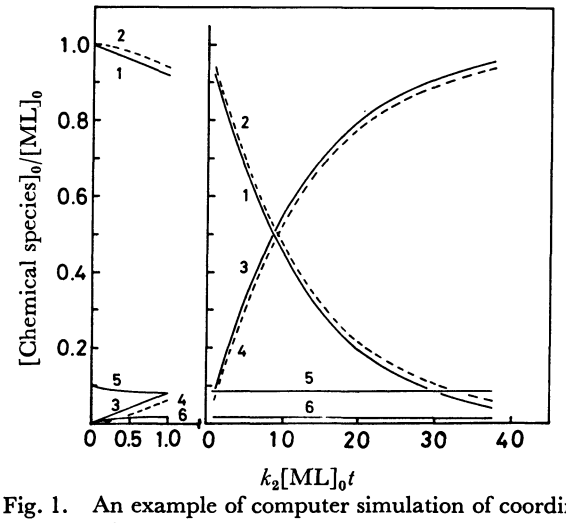

Fig. 1. An example of computer simulation of coordination chain reaction.[11]
Conditions: $[ML]_0=[ZX]_0=1$ M, $[MX]_0=[ZL]_0=0$ M, $[X]_0=0.1$ M, $[L]_0=0$ M; $k_2=1\ M^{-1}\ s^{-1}$, $k_3=4\ M^{-1}\ s^{-1}$, $k_{-2}=k_{-3}=0\ M^{-1}\ s^{-1}$. 1: ML, 2: ZX, 3: MX, 4: ZL, 5: X, 6: L.

The concentration-time profiles for all the components were obtained from the integration. The relative concentrations, expressed in terms of $[ML]_0$ as a unit, were then plotted against $k_2[ML]_0t$ (Fig. 1); this representation is convenient for the general treatment of the concentration-time profiles, since the ordinate and abscissa have no dimensions.[9]

In the studies using the coordination chain reaction, the reaction is usually run in the presence of the free ligand, and the relative concentration of the free ligand presented initially is ordinarily smaller than 0.1. Therefore, in this study, the simulations were carried out under the condition that $\frac{[\text{free ligand}]_0}{[ML]_0} \leqq 0.1$.

Calculations were carried out with an ACOS 900 computer of the Tohoku University Computation Center.

Results and Discussion

In order to clarify the nature of the coordination chain reaction, the reaction system was classified into the several cases shown in Table 1; *e.g.*, in the case of the I_1 system, the rate constants, k_{-2} and k_{-3}, can be regarded as zero, while the initial concentrations of ML and ZX are equal to one another.

The total free ligand concentration ([X]+[L]) is equal to the initial ligand concentration, c, throughout the substitution reaction. Therefore, if the X ligand reaches a steady state, the L ligand also reaches a steady state; the steady state of the free ligands can, then, be studied by examining the concentration-time profile for one of the two free ligands. In this study, the concentration-time profile for the X ligand was noted.

Reaction System I. *System* I_1 ($k_{-2}=k_{-3}=0$, $[ZX]_0=[ML]_0$): Figure 2 shows the time development of the concentration of X with the following specifications: $[X]_0/[ML]_0=0.1$ for Fig. 2.A and $[L]_0/[ML]_0=0.1$ for Fig. 2.B.

It may be seen that the greater the k_3/k_2 ratio, the closer the concentration of X comes to the steady state, and that the steady-state approximation in Fig. 2.A is superior to that in Fig. 2.B.

The concentration of the X ligand in the steady state can be estimated as follows. From $d[X]/dt=0$, the following relationship is obtained:

$$-k_2[ML][X] + k_3[ZX][L] = 0. \quad (11)$$

Since the $[X] \gg [L]$ inequality and the $[ML]_0=[ZX]_0$ equation hold, the following relation can be derived:

$$[ML] \approx [ZX]. \quad (12)$$

On the other hand, the following relationship also holds:

$$[X] + [L] = c. \quad (13)$$

Thus, from Eqs. 11, 12, and 13, the concentration of the X ligand in the steady state is obtained as

$$[X] \approx \frac{k_3/k_2}{1+k_3/k_2}c. \quad (14)$$

The concentration of X as estimated by means of Eq. 14 agrees very well with the concentration of X in the leveling-off range of Fig. 2.

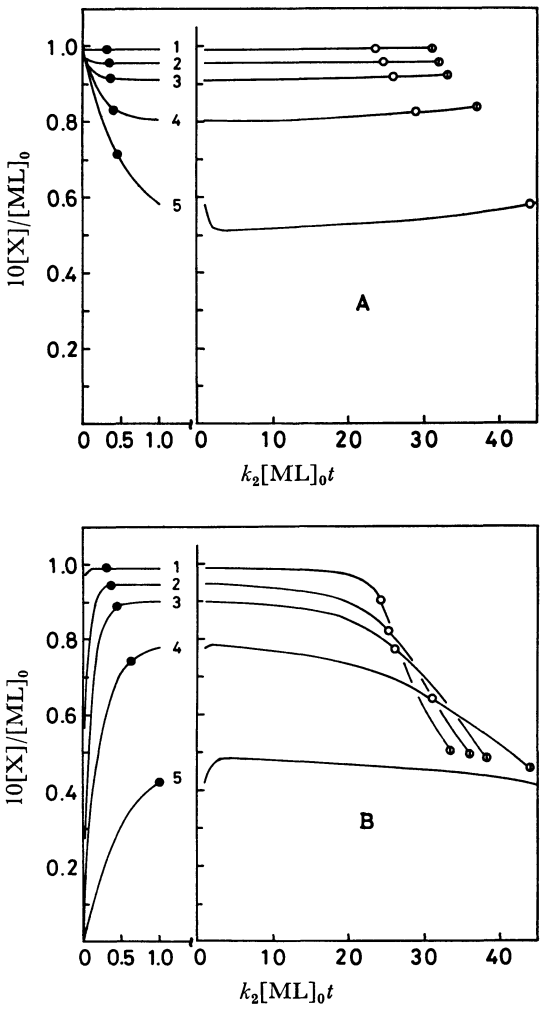

Fig. 2. The time development of the concentration of X for the system I_1 ($k_{-2}=k_{-3}=0$, $[ZX]_0=[ML]_0$). k_3/k_2; (1): 100, (2): 20, (3): 10, (4): 4, (5): 1. A shows the case in which $[X]_0/[ML]_0=0.1$, and B the case in which $[L]_0/[ML]_0=0.1$. Circles indicate the points of 3% (●), 90% (○), and 95% (◌) of the reaction proceeding, here and in the following figures.

Figure 3 shows the effect of variations in the initial concentration of the free ligand on the time development of the concentration of X.

It appears that the smaller the initial concentration of the free ligand, the more precise the steady-state

Table 1. Classification of coordination chain-reaction system

I		II		III	
I_1	I_2	II_1	II_2	III_1	III_2
$k_{-2}=k_{-3}=0$	$k_{-2}=k_{-3}=0$	$k_{-2}=0$	$k_{-2}=0$	$k_{-3}=0$	$k_{-3}=0$
$[ZX]_0=[ML]_0$	$[ZX]_0 \geqq 2[ML]_0$	$[ZX]_0=[ML]_0$	$[ZX]_0 \geqq 2[ML]_0$	$[ZX]_0=[ML]_0$	$[ZX]_0 \geqq 2[ML]_0$

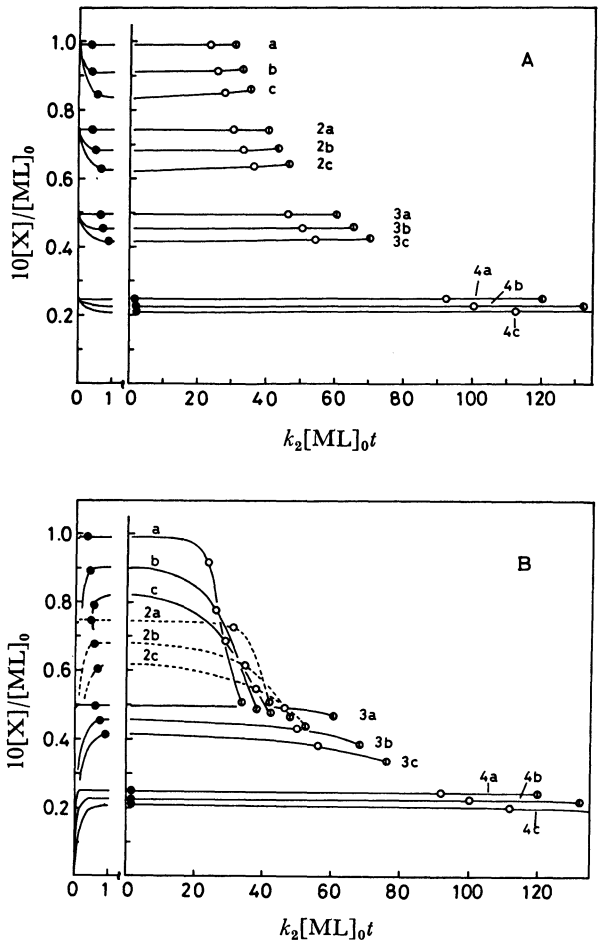

Fig. 3. The effect of the initial concentration of the free ligand on the development of the concentration of X for the system I_1 ($k_{-2}=k_{-3}=0$, $[ZX]_0=[ML]_0$). k_3/k_2, ([ligand]$_0$/[ML]$_0$); a: 100 (0.1), b: 10 (0.1), c: 5 (0.1),2a: 100 (0.075), 2b: 10 (0.075), 2c: 5 (0.075), 3a: 100 (0.050), 3b: 10 (0.050), 3c: 5 (0.050), 4a: 100 (0.025), 4b: 10 (0.025), 4c: 5 (0.025). A shows the case in which the ligand present initially is X, and B the case in which the ligand present initially is L.

approximation of X becomes, and that when the initial concentration of L is large, a good steady-state approximation of X can not be obtained (Fig. 3.B); moreover, the smaller the initial concentration of the free ligand, the longer the reaction time.

System I_2 ($k_{-2}=k_{-3}=0$, $[ZX]_0 \geqq 2[ML]_0$): Figure 4 shows the time dependence of the concentration of X for the I_2 system.

Where the X ligand is present initially (Case A), the concentration of X decreases at first, but very soon the concentration begins to increase. On the other hand, where L is present initially, the concentration of X increases rapidly at first, and later comes close to that in Case A. These modes differ from those of the I_1 system. Figure 5 shows the effect of the initial concentration of the free ligand on the time development of the concentration of X.

In system I, if the calculated curve of X is expressed as $([X]/[ML]_0)/c$ *vs.* $ck_2[ML]_0t$, the curve is little affected by the variations in the initial concentration

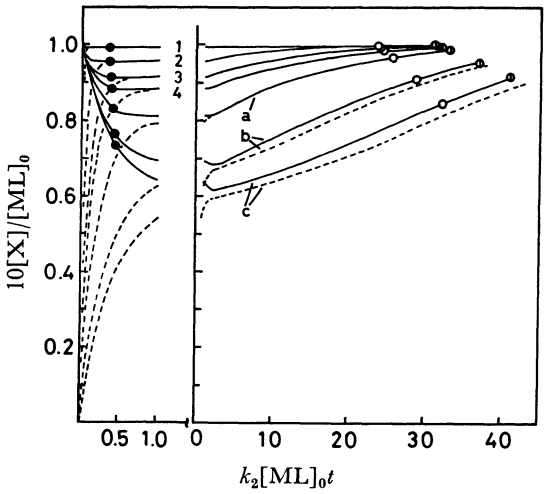

Fig. 4. The time development of the concentration of X for the system I_2 ($k_{-2}=k_{-3}=0$, $[ZX]_0 \geqq 2[ML]_0$).[12] $k_3/k_2 \cdot [ZX]_0/[ML]_0$; (1): 100, (2): 20, (3): 10, (4): 7. $[ZX]_0/[ML]_0$, (k_3/k_2); a: 4 (1.0), b: 2 (1.0), c: 1.5 (1.0). Full lines show the case in which $[X]_0/[ML]_0=0.1$, and dotted lines the case in which $[L]_0/[ML]_0=0.1$.

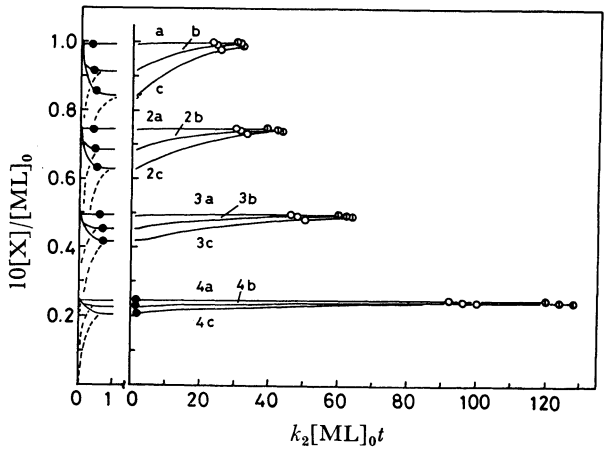

Fig. 5. The effect of the initial concentration of the free ligand on the time development of the concentration of X for the system I_2 ($k_{-2}=k_{-3}=0$, $[ZX]_0 \geqq 2[ML]_0$).[12] $k_3/k_2 \cdot [ZX]_0/[ML]_0$, ([ligand]$_0$/[ML]$_0$); a: 100 (0.1), b: 10 (0.1), c: 5 (0.1), 2a: 100 (0.075), 2b: 10 (0.075), 2c: 5 (0.075), 3a: 100 (0.050), 3b: 10 (0.050), 3c: 5 (0.050), 4a: 100 (0.025), 4b: 10 (0.025), 4c: 5(0.025). Full lines show the case in which the ligand presented initially is X, and dotted lines the case in which the ligand presented initially is L.

of the free ligand, except where $c=[L]_0$ and $[ZX]_0=[ML]_0$.

Therefore, X was henceforth used as the ligand present initially, and the concentration was set at $[X]_0/[ML]_0=0.1$; by these settings, the treatment of the system would be simplified.

Reaction System II. System II_1 ($k_{-2}=0$, $[ZY]_0=[ML]_0$): Figure 6 shows the time development of the concentration of X for the II_1 system. In this system, the time development of X is affected very much by the reverse reaction of R3; only when the k_3/k_{-3} ratio becomes more than 10^4, can the reverse reaction of R3

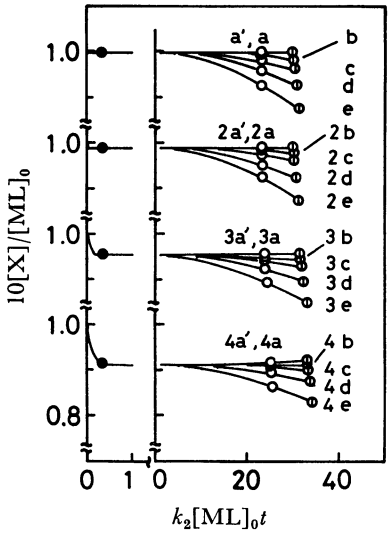

Fig. 6. The time development of the concentration of X for the system II_1 ($k_{-2}=0$, $[ZX]_0=[ML]_0$).
k_{-3}/k_{-2}, (k_3/k_2); a': 0 (1000), a: 0.1 (1000), b: 1 (1000), c: 2 (1000), d: 5 (1000), e: 10 (1000), 2a': 0 (100), 2a: 0.01 (100), 2b: 0.1 (100), 2c: 0.2 (100), 2d: 0.5 (100), 2e: 1.0 (100), 3a': 0 (20), 3a: 0.002 (20), 3b: 0.02 (20), 3c: 0.04 (20), 3d: 0.10 (20), 3e: 0.20 (20), 4a': 0 (10), 4a: 0.001 (10), 4b: 0.01 (10), 4c: 0.02 (10), 4d: 0.05 (10), 4e: 0.10 (10). The initial free ligand concentration ($[X]_0/[ML]_0$) is 0.1.

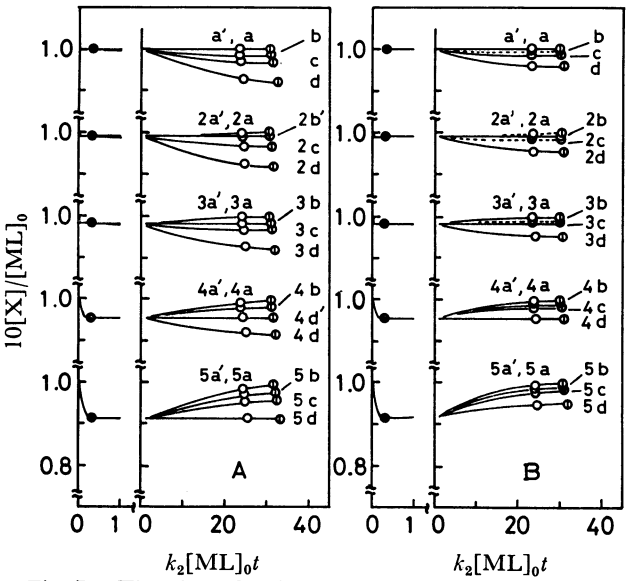

Fig. 7. The time development of the concentration of X for the system II_2 ($k_{-2}=0$, $[ZX]_0 \geqq 2[ML]_0$).[12]
k_{-3}/k_2, ($k_3/k_2 \cdot [ZX]_0/[ML]_0$); a': 0 (1000), a: 1 (1000), b: 10 (1000), c: 20 (1000), d: 50 (1000), 2a': (100), 2a: 0.1 (100), 2b': 0.5 (100), 2b: 1 (100), 2c: 2 (100), 2d: 5 (100), 3a': 0 (50), 3a: 0.05 (50), 3b: 0.5 (50), 3c: 1.0 (50), 3d: 2.5 (50), 4a': 0 (20), 4a: 0.02 (20), 4b: 0.2 (20), 4c: 0.4 (20), 4d': 0.5 (20), 4d: 1.0 (20), 5a': 0 (10), 5a: 0.01 (10), 5b: 0.1 (10), 5c: 0.2 (10), 5d: 0.5 (10). The initial free ligand concentration ($[X]_0/[ML]_0$) is 0.1. A shows the case in which $[ZX]_0/[ML]_0=2$, and B the case in which $[ZX]_0/[ML]_0 \geqq 10$.

be neglected.

System II_2 ($k_{-2}=0$, $[ZY]_0 \geqq 2[ML]_0$): Figure 7 shows the time development of the concentration of X for the II_2 system. In Fig. 7.A ($[ZX]_0=2[ML]_0$), it may be seen that, when the k_{-3}/k_2 ratio is equal to 0.5 (2b', 3b, 4d', 5d), the concentration of X is in a steady state.

The concentration of X in the steady state can be calculated as follows. From $d[X]/dt=0$, the following equation is obtained:

$$-k_2[ML][X] + k_3[ZX][L] - k_{-3}[ZL][X] = 0. \quad (15)$$

Combining Eqs. 13 and 15, the following equation is derived:

$$[X] = \frac{k_3[ZX]}{k_2[ML]+k_{-3}[ZL]+k_3[ZX]}c. \quad (16)$$

If the $k_{-3}/k_2=0.5$ and $[ZX]_0/[ML]_0=2$ equations hold, Eq. 16 can be rewritten as[10]

$$[X] = \frac{2k_3/k_2}{(2[ML]+[ZL])/[ZX]+2k_3/k_2}c \approx \frac{2k_3/k_2}{1+2k_3/k_2}c. \quad (17)$$

On the other hand, in Fig. 7.B ($[ZX]_0/[ML] \geqq 10$) it may be seen that, when the k_{-3}/k_2 ratio is equal to unity (a, 2b, 3c, 4d), the concentration of X is in a steady state.

The concentration of X in the steady state can also be calculated as follows. From Eq. 16, the following equation is obtained:

$$[X] = \frac{(k_3/k_2)([ZX]/[ML]_0)}{([ML]+(k_{-3}/k_2)[ZL])/[ML]_0+(k_3/k_2)([ZX]/[ML]_0)}c. \quad (18)$$

Since the $[X] \gg [L]$ inequality holds, the form of $[ML]_0=[ML]+[MX] \approx [ML]+[ZL]$ is obtained; moreover, the $k_{-3}/k_2=1$ equation holds under these conditions; thus, the following relationship is derived:

$$\frac{[ML]+(k_{-3}/k_2)[ZL]}{[ML]_0} \approx 1. \quad (19)$$

From Eqs. 18 and 19, and $[ZX]/[ML]_0 \approx [ZX]_0/[ML]_0$, the following equation is derived:

$$[X] \approx \frac{(k_3/k_2)([ZX]_0/[ML]_0}{1+(k_3/k_2)([ZX]_0/[ML]_0)}c. \quad (20)$$

The concentrations of X, as estimated by Eqs. 17 and 20, agree very well with those of the steady state of X in Figs. 7.A and 7.B respectively.

Reaction System III ($k_{-3}=0$). Figure 8 shows the time development of the concentration of X for the III_1 system ($k_{-3}=0$, $[ZX]_0=[ML]_0$). As is shown in Fig. 8, the shape of the diagram for the time development of the concentration of X is not appreciably affected by the reverse reaction of R2. However, the reaction rate is greatly affected by it. These tendencies also appear in the III_2 system ($k_{-3}=0$, $[ZX]_0 \geqq 2[ML]_0$), as is shown in Fig. 9.

From Figs. 8 and 9, it can be said that, in the III_1 system, when the k_3/k_{-2} ratio is greater than about 10^3, the III_1 system is approximately equal to the I_1 system, and that, in the III_2 system, when the $(k_3/k_{-2})([ZX]_0/[ML]_0)$ value is greater than about 10^2, the III_2 system is close to the I_2 system.

On the other hand, from Figs. 6 and 7, it can be said that, in the II_1 system, when the k_3/k_{-3} ratio is greater than about 10^4, the II_1 system is close to the I_1 system,

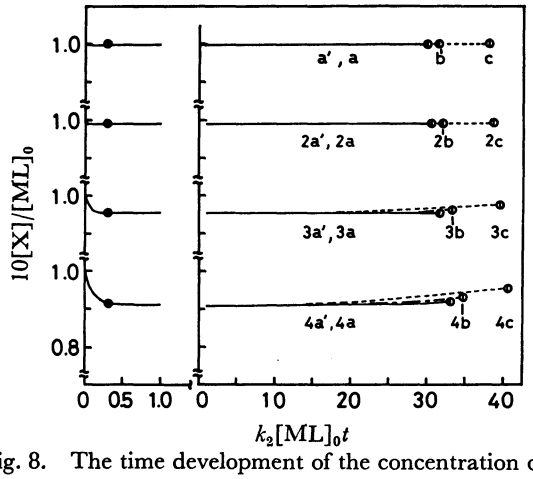

Fig. 8. The time development of the concentration of X for the system III_1 ($k_{-3}=0$, $[ZX]_0=[ML]_0$). k_{-2}/k_2, (k_3/k_2); a': 0 (1000), a: 1 (1000), b: 10: (1000), c: 50 (1000), 2a': 0 (100), 2a: 0.1 (100), 2b: 1 (100), 2c: 5 (100), 3a': 0 (20), 3a: 0.02 (20), 3b: 0.2 (20), 3c: 1.0 (20), 4a': (10), 4a: 0.01 (10), 4b: 0.1 (10), 4c: 0.5 (10). The initial free ligand concentration ($[X]_0/[ML]_0$) is 0.1.

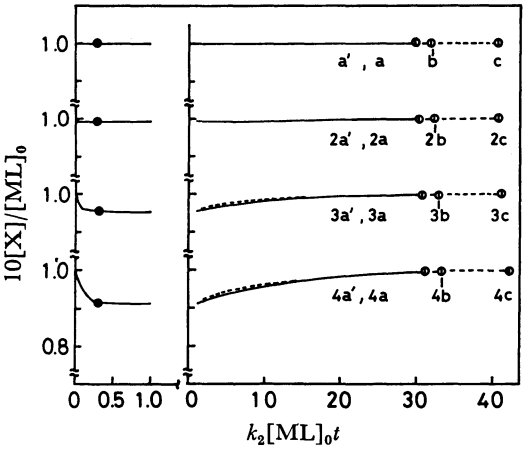

Fig. 9. The time development of the concentration of X for the system III_2 ($k_{-3}=0$, $[ZX]_0 \geqq 2[ML]_0$).[12] k_{-2}/k_2, (k_3/k_2 $[ZX]_0/[ML]_0$); a': 0 (1000), a: 10(1000), b: 100 (1000), c: 500 (1000), 2a': 0 (100), 2a: 1 (100), 2b: 10 (100), 2c: 50 (100), 3a': 0 (20), 3a: 0.2 (20), 3b: 2 (20), 3c: 10 (20), 4a': 0 (10), 4a: 0.1 (10), 4b: 1 (10), 4c: 5 (10). The initial concentrations of X and ZX are as follows: $[X]_0/[ML]_0=0.1$ and $[ZX]_0/[ML]_0 \geqq 10$.

and that, in the II_2 system, when the $(k_3/k_{-3})([ZX]_0/[ML]_0)$ value is greater than about 10^3, the II_2 system is close to the I_2 system.

In the II and III systems, one of the reverse reactions of R2 and R3 was considered to be negligible. From the above considerations, criteria for the omission of the reverse reaction may be presented as follows: $k_3/k_{-2} \approx 10^3$ for the II_1 system, $(k_3/k_{-2})([ZX]_0/[ML]_0) \approx 10^2$ for the II_2 system, $k_3/k_{-3} \approx 10^4$ for the III_1 system, and $(k_3/k_{-3})([ZX]_0/[ML]_0) \approx 10^3$ for the III_2 system; *i.e.*, for example, when $[ML]_0=[ZX]_0$, if the k_3/k_{-2} ratio is greater than 10^3, the system may be taken as the II_1 system, and when $[ZX]_0 \geqq 2[ML]_0$, if the value $(k_3/k_{-2})([ZX]_0/[ML]_0)$ is greater than 10^2, the system may be taken as the II_2 system.

Reaction Rate. When the reaction rate of R1 is defined as the rate of the decrease in ML, the reaction rate of R1 can be written as

$$-\frac{d[ML]}{dt} = k_2[X]_s[ML] - k_{-2}[L][ZX]. \quad (21)$$

Therefore, if k_{-2} is negligibly small and if the concentration of X is constant throughout the reaction, the reaction can be regarded as a pseudo first-order reaction:

$$-\frac{d[ML]}{dt} = k_2[X]_s[ML] = k_o[ML], \quad (22)$$

where $[X]_s$ represents the concentration of X in the steady state.

It should be emphasized that the concentration of X in the steady state is not always equal to that of the ligand present initially. As is shown in Eqs. 14, 17, and 20, the ratio $[X]_s/c$ is little changed by the variations in the initial concentration of the free ligand. Thus, the following equation can be written:

$$\frac{[X]_s}{c} = a \quad (a \leqq 1), \quad (23)$$

where a is constant. Therefore, Eq. 22 can be rewritten as

$$-\frac{d[ML]}{dt} = k_2[X]_s[ML] = ack_2[ML] = k_o[ML]. \quad (24)$$

Consequently,

$$k_o = ack_2. \quad (25)$$

Therefore, if the pseudo first-order rate constant, k_o, is plotted against the free-ligand concentration present initially, the slope of the straight line represents, ak_2; only when $[X]_s=c$, is the value of the slope equal to k_2.

In the previous works,[1-3] it was a little laborious to derive Eq. 24. However, the conditions under which Eq. 24 is derived can be obtained from the diagrams presented above. Thus, the diagrams are useful for studies using a coordination chain reaction. One important fact is that a desired coordination chain reaction can be designed from the individual reactions (R2 and R3) on the basis of the diagrams presented above.

Simulation of the Practical Coordination Chain Reaction. As an example, the ligand-substitution reaction between the ethylenediaminetetraacetatocuprate(II) ion (Cu-(II)-edta) and the triethylenetetraminelead(II) ion (Pb(II)-trien) was undertaken. The reaction was considered to proceed by means of a coordination chain reaction mechanism:

$$\text{Cu(II)-edta} + \text{trlien} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{Cu(II)-trien} + \text{edta}, \quad (R4)$$

$$\text{Pb(II)-trien} + \text{edta} \xrightarrow{k_3} \text{Pb(II)-edta} + \text{trien}. \quad (R5)$$

The known information about these reactions at pH 9.0 is as follows. The conditional equilibrium constant (K) of R4 is 4.2×10, while the conditional rate constant, k_2, is 1.17×10^4 M^{-1} s^{-1} (this was measured at pH 9.0, 25.0 °C and $I=0.2$); hence, if follows that $k_{-2}=k_2/K=$

2.8×10^2 M^{-1} s^{-1}. The conditional equilibrium constant of R5 is so large ($K=4.8\times10^7$) that the reverse reaction of R5 can be neglected in the kinetic study. Furthermore, the reaction of R5 is very fast; this fact was taken into account by setting k_3 large (*e.g.*, $k_3=1\times10^7$ M^{-1} s^{-1}).

In accordance with the above classification, this system can be taken as the III system. Moreover, this system can also be treated as the I system, since the k_3/k_{-2} ratio is larger than 10^3.

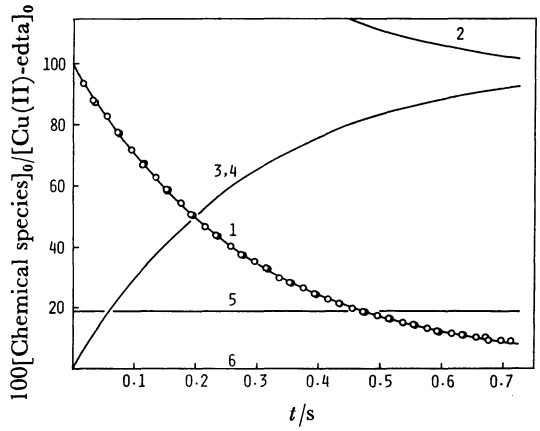

Fig. 10. Computer simulation of the Cu(II)-edta–Pb(II)trien system.[13]
Conditions: $[Cu(II)\text{-edta}]_0=1.86\times10^{-3}$ M, $[Pb(II)\text{-trien}]_0=3.62\times10^{-3}$ M, $[Cu(II)\text{-trien}]_0=[Pb(II)\text{-edta}]_0=0$ M, $[trien]_0=3.5\times10^{-4}$ M, $[edta]_0=0$ M; $I=0.2$ M, pH=9.0, 25.0 °C; $k_2=1.01\times10^4$ M^{-1} s^{-1}, $k_{-2}=k_2/K=2.8\times10^2$ M^{-1} s^{-1}, $k_3=1.0\times10^7$ M^{-1} s^{-1}, $k_{-3}=0$ M^{-1} s^{-1}.
1: Cu(II)-edta, 2: Pb(II)-trien, 3: Cu(II)-trien, 4: Pb(II)-edta, 5: trien, 6: edta. The circles indicate the experimental values.[14]

Figure 10 shows the results of the computer simulation of the Cu(II)-edta–Pb(II)-trien system (under the above conditions).[15] The experimental values (points of circle) agree with the calculated values. The calculated concentration of free trien is constant throughout the reaction and is nearly equal to the concentration of added free trien; these facts can also be predicted from Fig. 4, from which it follows that

$$\frac{k_3}{k_2}\frac{[ZX]_0}{[ML]_0}=\frac{k_3}{k_2}\frac{[Pb(II)\text{-trien}]_0}{[Cu(II)\text{-edta}]_0}=1.9\times10^3.$$

Using the diagrams stated above, the reaction of the practical system may be predicted.

References

1) T. Katsuyama and T. Kumai, *Bull. Chem. Sco. Jpn.*, **48**, 3581 (1975).
2) T. Katsuyama and T. Kumai, *Bull. Chem. Soc. Jpn.*, **51**, 1072 (1078).
3) T. Katsuyama and T. Kumai, *Bull. Chem. Soc. Jpn.*, **55**, 1050 (1982).
4) D. W. Margerum and R. K. Steinhaus, *Anal. Chem.*, **37**, 222 (1965).
5) R. H. Stehl, D. W. Margerum, and J. J. Latterll, *Anal. Chem.*, **39**, 1346 (1967).
6) D. W. Margerum and R. H. Stehl, *Anal. Chem.*, **39**, 1351 (1967).
7) J. Yamauchi, S. Moriguchi, and S. Hitotsumatsu "Denshi Keisanki No Tame No Suchi Keisan-ho," Baifukan, Tokyo (1975), Vol. 1, p. 123.
8) The rate determining step in the reaction model represented by Reactions R2 and R3 is defined as R2.
9) If the values of $[ZX]_0/[ML]_0$, $[\text{free ligand}]_0/[ML]_0$, and k_n/k_2 ($n=-2, \pm3$) in one system are equal to the respective values in the other system, these systems give the same relative concentration-$k_2[ML]_0t$ curve.
10) $(2[ML]+[ZL])/[ZX]=N/D\approx1$ can be derived as follows. N is written as $N=2[ML]+[ZL]=2([ML]+[ZL])-[ZL]$. As the $[X]\gg[L]$ inequality holds, [ZL] is approximately equal to [MX]. Consequently, $N\approx2[ML]_0-[ZL]$. On the other hand, $D=[ZX]=[ZX]_0-[ZL]=2[ML]_0-[ZL]$. Thus, $N/D\approx1$.
11) In the diagram, the following relationships hold: $[X]+[L]=c$ and $[L]=c-[X]=[MX]-[ZL]=[ZX]-[ML]$. In general, the following relationships also hold: $[X]+[L]=c$ and $[L]=c-[X]=|[MX]-[ZL]|=|([ZX]-(n-1)[ML]_0)-[ML]|$, where n ($n\geqq1$) is equal to the $[ZX]_0/[ML]_0$ ratio; these relationships were confirmed to hold from the simulations.
12) If the $[ZX]_0/[ML]_0$ ratio is greater than about r(r: 5 for Figs. 4 and 5, and 10 for Figs. 7 and 9),the reactions which have the same value of the product of k_3/k_2 and $[ZX]_0/[ML]_0$ give almost the same time development of the concentration of X.
13) In the simulation, the time developments of all the species were little affected by the variation in k_3.
14) In the kinetic measurements, a stopped-flow technique was employed with a Hitachi Model RSP-2 Rapid-scan Spectrophotometer. The reactions were followed at 575 nm.
15) In this simulation, the value of $k_2=1.01\times10^4$ M^{-1} s^{-1} was used. This value agrees closely with that obtained from other experiments.