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The Effect of Phthalate Ion and Acetate Ion on the Rate of the Reaction between Nickel(II) and Cobalt(II)-Nitrilotriacetate Complexes

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A kinetic study of the substitution reactions of nickel(II) ions and cobalt(II)-nitrilotriacetate complexes in phthalate and in acetate buffer has been carried out using a procedure previously reported. The reaction was made to proceed through both hydrated nickel(II) ions and monophthalatonickel(II) complexes or monoacetatonickel(II) complexes. The rate constants for eight elementary reaction paths, four of which involve the hydrated nickel(II) ions, while the others involve the monophthalatonickel(II) complexes (the monoacetatonickel(II) complexes in the case of the measurements in acetate media), were determined at an ionic strength of 0.2 at 25°C. The values obtained indicate that all the reactions proceeding through the monophthalatonickel(II) complexes are slower than the corresponding reactions proceeding through hydrated nickel(II) ions; however, all the reactions proceeding through monoacetatonickel(II) complexes are faster than the corresponding reactions proceeding through hydrated nickel(II) ions. Thus, the kinetic reactivity is in the order of: $\mathrm{NiOAc^+} > \mathrm{Ni^{2+}} > \mathrm{NiPh}$, where $\mathrm{Ph^{2-}}$ indicates a bivalent phthalate anion.

A previous study[1] showed that monoacetatocobalt(II) ions react with ethylenediaminetetraacetate (EDTA) anions and Mn(II)-EDTA complexes faster than with hydrated cobalt(II) ion. This trend has been considered to be due to the characteristics of $\mathrm{CoOAc^+}$, the value of the stability constant of which is rather small, and not to those of EDTA and cobalt(II); confirmation was sought in the present study. Since it seems to be important and necessary to extend the study to the investigation of the effect of various anions on the rates of the reactions, and to compare the corresponding reactions, the effect of the phthalate ion and of the acetate ion on the rate of the reaction between nickel(II) and cobalt(II)-nitrilotriacetate (NTA) complexes was examined in the present study.

Experimental

For potassium biphthalate, guaranteed reagents were used without further purification. All the other chemicals and solutions were prepared and standardized in ways described in a previous paper.[2] The method and the procedure employed in the present study were, in principle, the same as those described in previous papers.[1,2]

Results

Under the conditions of the present experiments, the formation of complexes with a metal-to-ligand ratio of 1 : 2 was considered to be negligible. Therefore, the overall substitution reactions between nickel(II) and cobalt(II)-NTA complexes are expressed by:

$$\left\{\begin{matrix}\mathrm{Ni^{2+}}\\ \uparrow\downarrow\\ \mathrm{NiZ^{(2-z)+}}\end{matrix}\right\} + \mathrm{CoX^-} \overset{V^{+}_{0,\mathrm{app}}}{\rightleftharpoons} \mathrm{NiX^-} + \left\{\begin{matrix}\mathrm{Co^{2+}}\\ \uparrow\downarrow\\ \mathrm{CoZ^{(2-z)+}}\end{matrix}\right\} \qquad (1)$$

where $\mathrm{Z^{z-}}$ indicates a bivalent phthalate anion ($\mathrm{Ph^{2-}}$) or an acetate ion ($\mathrm{OAc^-}$) and $\mathrm{X^{3-}}$, a tervalent NTA anion.

The apparent concentrations of nickel(II) ions, $[\mathrm{Ni^{2+}}]_{\mathrm{app}}$ that can be determined polarographically are given by:

$$[\mathrm{Ni^{2+}}]_{\mathrm{app}} = [\mathrm{Ni^{2+}}] + [\mathrm{NiZ^{(2-z)+}}] \qquad (2)$$

In a previous paper,[2] kinetic studies of the reactions between nickel(II) ions and Co(II)-, and Cu(II)-NTA complexes in acetate media were reported. On the basis of the same treatment as in previous studies,[1,2] the reactions of Eq. (1) may be considered to proceed through the following reaction paths:

$$\text{(i)}\quad \mathrm{Ni^{2+}} + \mathrm{CoX^-} \overset{k^{+}_{1h}}{\rightleftharpoons} \mathrm{NiX^-} + \mathrm{Co^{2+}} \qquad (3)$$

$$\mathrm{NiZ^{(2-z)+}} + \mathrm{CoX^-} \overset{k^{+}_{1z}}{\rightleftharpoons} \mathrm{NiX^-} + \mathrm{CoZ^{(2-z)+}} \qquad (3')$$

$$\text{(ii)}\quad \mathrm{CoX^-} + \mathrm{H^+} \rightleftharpoons \mathrm{CoHX} \qquad (4)$$

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[1] M. Kimura, This Bulletin, **42**, 404 (1969).

[2] N. Tanaka and M. Kimura, *ibid.*, **40**, 2100 (1967).

$$\mathrm{Ni^{2+} + CoHX} \underset{}{\overset{k^+_{\mathrm{II}h}}{\rightleftharpoons}} \mathrm{NiHX + Co^{2+}} \qquad (5)$$

$$\mathrm{NiZ^{(2-z)+} + CoHX} \overset{k^+_{\mathrm{II}z}}{\rightleftharpoons} \mathrm{NiHX + CoZ^{(2-z)+}} \qquad (5')$$

$$\mathrm{NiHX} \rightleftharpoons \mathrm{NiX^- + H^+} \qquad (6)$$

$$\text{(iii)}\quad \mathrm{CoX^-} \rightleftharpoons \mathrm{X^{3-}} + \left\{\begin{matrix} \mathrm{Co^{2+}} \\ \uparrow\downarrow \\ \mathrm{CoZ^{(2-z)+}} \end{matrix}\right\} \qquad (7)$$

$$\mathrm{Ni^{2+} + X^{3-}} \overset{k^+_{\mathrm{III}h}}{\rightleftharpoons} \mathrm{NiX^-} \qquad (8)$$

$$\mathrm{NiZ^{(2-z)+} + X^{3-}} \overset{k^+_{\mathrm{III}z}}{\rightleftharpoons} \mathrm{NiX^- + Z^{z-}} \qquad (8')$$

$$\text{(iv)}\quad \mathrm{CoX^- + H^+} \rightleftharpoons \mathrm{HX^{2-}} + \left\{\begin{matrix} \mathrm{Co^{2+}} \\ \uparrow\downarrow \\ \mathrm{CoZ^{(2-z)+}} \end{matrix}\right\} \qquad (9)$$

$$\mathrm{Ni^{2+} + HX^{2-}} \overset{k^+_{\mathrm{IV}h}}{\rightleftharpoons} \mathrm{NiHX} \qquad (10)$$

$$\mathrm{NiZ^{(2-z)+} + HX^{2-}} \overset{k^+_{\mathrm{IV}z}}{\rightleftharpoons} \mathrm{NiHX + Z^{z-}} \qquad (10')$$

On the basis of this reaction mechanisms, Eq. (11) is obtained from reaction (1):

$$\begin{aligned} V^+_{0,\mathrm{app}} = \frac{[\mathrm{CoX^-}]_0[\mathrm{Ni^{2+}}]_{0,\mathrm{app}}}{1+\beta_{\mathrm{NiZ}}[\mathrm{Z}^{-z}]} \Big\{ & k^+_{1h} + k^+_{1z}[\mathrm{Z}^{z-}] + k^+_{2h}[\mathrm{H^+}] \\ & + k^+_{2z}[\mathrm{Z}^{z-}][\mathrm{H^+}] + (k^+_{3h} + k^+_{3z}[\mathrm{Z}^{z-}] + k^+_{4h}[\mathrm{H^+}] \\ & + k^+_{4z}[\mathrm{Z}^{z-}][\mathrm{H^+}]) \frac{1+\beta_{\mathrm{CoZ}}[\mathrm{Z}^{z-}]}{[\mathrm{Co^{2+}}]_{0,\mathrm{app}}} \Big\} \end{aligned} \qquad (11)$$

$$\begin{aligned} \text{where: } & k^+_{1z} = k^+_{1z}\beta_{\mathrm{NiZ}},\ k^+_{2h} = k^+_{\mathrm{II}h}K^{\mathrm{H}}_{\mathrm{CoHZ}},\ k^+_{2z} = k^+_{\mathrm{II}z}\beta_{\mathrm{NiZ}}K^{\mathrm{H}}_{\mathrm{CoHZ}} \\ & k^+_{3h} = k^+_{\mathrm{III}h}/K_{\mathrm{CoX}},\ k^+_{3z} = k^+_{\mathrm{III}z}\beta_{\mathrm{NiZ}}/K_{\mathrm{CoX}}, \\ & k^+_{4h} = k^+_{\mathrm{IV}h}/(K_{\mathrm{CoX}}K_{\mathrm{HX}}),\ k^+_{4z} = k^+_{\mathrm{IV}z}\beta_{\mathrm{NiZ}}/(K_{\mathrm{CoX}}K_{\mathrm{HX}}) \end{aligned} \qquad (11')$$

TABLE 1. $V^+_{0,\mathrm{app}}$ FOR THE SUBSTITUTION REACTIONS BETWEEN Ni(II) AND Co(II)-NTA COMPLEXES IN PHTHALATE BUFFER-POTASSIUM NITRATE SOLUTION AT IONIC STRENGTH 0.2 AT 25°C
$[\mathrm{Ni^{2+}}]_{0,\mathrm{app}} = 0.202$ mM and 0.404 mM for *

$[\mathrm{Ph^{2-}}]$ M	pH	$[\mathrm{CoX^-}]_0$ mM	$[\mathrm{Co^{2+}}]_{0,\mathrm{app}}$ mM	$V^+_{0,\mathrm{app}} \times 10^7$ M sec^{-1}
0.02	4.98	1.17	0.41	2.87
0.02	4.98	1.17	0.79	1.78
0.02	4.98	1.17	1.18	1.24
0.02	4.98	1.17	1.56	1.00
0.02	5.06	1.17	0.41	2.57
0.02	5.06	1.17	0.79	1.47
0.02	5.06	1.17	1.18	1.15
0.02	5.06	1.17	1.56	0.84
0.02	5.25	1.36	0.57	3.35*
0.02	5.25	1.36	0.95	2.24*
0.02	5.25	1.36	1.34	1.68*
0.02	5.25	1.36	1.72	1.28*
0.02	5.50	1.36	0.57	3.23*
0.02	5.50	1.36	0.95	2.02*
0.02	5.50	1.36	1.34	1.70*
0.02	5.50	1.36	1.72	1.30*
0.02	5.90	1.36	0.57	2.37*
0.02	5.90	1.36	0.95	1.52*
0.02	5.90	1.36	1.34	1.08*
0.02	5.90	1.36	1.72	0.94*
0.04	5.06	1.17	0.41	3.60
0.04	5.06	1.17	0.79	2.00
0.04	5.06	1.17	1.18	1.87
0.04	5.06	1.17	1.56	1.38
0.04	5.17	1.17	0.41	3.43
0.04	5.17	1.17	0.79	1.97
0.04	5.17	1.17	1.18	1.36
0.04	5.17	1.17	1.56	1.38
0.04	5.40	1.36	0.57	4.00*
0.04	5.40	1.36	0.95	2.70*
0.04	5.40	1.36	1.34	2.20*
0.04	5.40	1.36	1.72	1.59*
0.04	5.56	1.36	0.57	3.79*
0.04	5.56	1.36	0.95	2.63*
0.04	5.56	1.36	1.34	1.85*
0.04	5.56	1.36	1.72	1.48*
0.04	5.98	1.36	0.57	2.74*
0.04	5.98	1.36	0.95	1.82*
0.04	5.98	1.36	1.34	1.42*
0.04	5.98	1.36	1.72	1.08*
0.06	5.17	0.68	0.49	2.55
0.06	5.17	0.68	0.86	1.58
0.06	5.17	0.68	1.25	1.25
0.06	5.17	0.68	1.63	0.97
0.06	5.18	0.68	0.49	2.21
0.06	5.18	0.68	0.86	1.33
0.06	5.18	0.68	1.25	1.11
0.06	5.18	0.68	1.63	0.67
0.06	5.18	0.68	0.49	2.39
0.06	5.18	0.68	0.86	1.51
0.06	5.18	0.68	1.25	1.29
0.06	5.18	0.68	1.63	0.90
0.06	5.35	1.17	0.41	3.29
0.06	5.35	1.17	0.79	2.14
0.06	5.35	1.17	1.18	1.71
0.06	5.35	1.17	1.56	1.24
0.06	5.36	0.68	0.49	1.91
0.06	5.36	0.68	0.86	1.27
0.06	5.36	0.68	1.25	0.97
0.06	5.36	0.68	1.63	0.67
0.06	5.46	1.36	0.57	5.17
0.06	5.46	1.36	0.95	3.21
0.06	5.46	1.36	1.34	2.61
0.06	5.46	1.36	1.72	2.00
0.06	5.65	1.36	0.57	4.80
0.06	5.65	1.36	0.95	2.92
0.06	5.65	1.36	1.34	2.37
0.66	5.65	1.36	1.72	1.66
0.06	6.05	1.36	0.57	3.10
0.06	6.05	1.36	0.95	1.84
0.06	6.05	1.36	1.34	1.60
0.06	6.05	1.36	1.72	1.20

TABLE 2. $V^{+}_{0,\mathrm{app}}$ FOR THE SUBSTITUTION REACTIONS BETWEEN Ni(II) AND Co(II)-NTA COMPLEXES IN ACETATE BUFFER-POTASSIUM NITRATE SOLUTIONS AT IONIC STRENGTH 0.2 AT 25°C
$[\mathrm{Ni}^{2+}]_{0,\mathrm{app}} = 0.202$ mM, $[\mathrm{CoX}^-]_0 = 0.68$ mM and 1.36 mM for *

$[\mathrm{OAc}^-]$ M	pH	$[\mathrm{Co}^{2+}]_{0,\mathrm{app}}$ mM	$V^{+}_{0,\mathrm{app}} \times 10^7$ Msec^{-1}
0.02	4.94	0.49	1.78
0.02	5.10	0.49	1.50
0.02	5.27	0.49	1.18
0.02	5.74	0.57	1.35*
0.02	5.74	0.72	0.84*
0.02	5.74	1.34	0.79*
0.02	5.74	1.72	0.63*
0.02	4.94	0.86	1.09
0.02	4.94	1.25	0.84
0.02	4.94	1.63	0.76
0.02	5.10	0.86	1.00
0.02	5.10	1.25	0.88
0.02	5.10	1.63	0.72
0.02	5.27	0.86	0.79
0.02	5.27	1.25	0.62
0.02	5.27	1.63	0.50
0.04	4.97	0.49	2.35
0.04	4.97	0.86	1.60
0.04	4.97	1.25	1.31
0.04	4.97	1.63	1.03
0.04	5.12	0.49	1.94
0.04	5.12	0.86	1.22
0.04	5.12	1.25	1.03
0.04	5.12	1.63	0.81
0.04	5.29	0.49	1.62
0.04	5.29	0.86	1.05
0.04	5.29	1.25	0.97
0.04	5.29	1.63	0.70
0.04	5.50	0.57	1.93*
0.04	5.50	0.73	1.29*
0.04	5.50	1.34	0.99*
0.04	5.50	1.73	0.70*
0.04	5.83	0.57	1.44*
0.04	5.83	0.73	1.01*
0.04	5.83	1.34	0.77*
0.04	5.83	1.73	0.77*
0.10	4.99	0.86	2.43
0.10	4.99	1.25	2.17
0.10	4.99	1.63	1.56
0.10	5.14	0.49	3.14
0.10	5.14	0.86	2.03
0.10	5.14	1.25	1.70
0.10	5.14	1.63	1.25
0.10	5.30	0.49	2.62
0.10	5.30	0.86	1.57
0.10	5.30	1.25	1.18
0.10	5.30	1.63	1.02
0.10	5.56	0.57	3.04*
0.10	5.56	0.73	1.77*
0.10	5.56	1.34	1.65*
0.10	5.56	1.73	1.15*
0.10	5.91	0.57	2.01*
0.10	5.91	0.73	1.45*
0.10	5.91	1.34	1.08*
0.10	5.91	1.73	1.00*
0.20	5.17	0.86	2.92
0.20	5.17	1.25	2.11
0.20	5.17	1.63	1.68
0.20	5.36	0.49	3.66
0.20	5.36	0.86	2.31
0.20	5.36	1.25	1.70
0.20	5.36	1.63	1.42
0.20	5.58	0.49	2.83
0.20	5.58	0.86	1.63
0.20	5.58	1.25	1.17
0.20	5.58	1.63	0.91
0.20	5.95	0.57	2.80*
0.20	5.95	0.73	1.86*
0.20	5.95	1.34	1.33*
0.20	5.95	1.72	1.12*

The apparent initial rates were measured under varied conditions. The results are given in Tables 1 and 2.

Equation (11) indicates that, if the values of $V^{+}_{0,\mathrm{app}}/([\mathrm{CoX}^-]_0[\mathrm{Ni}^{2+}]_{0,\mathrm{app}})$ are plotted against $1/[\mathrm{Co}^{2+}]_{0,\mathrm{app}}$ under conditions at which all quantities but $[\mathrm{Co}^{2+}]_{0,\mathrm{app}}$ are kept constant, a straight line should be obtained with a slope given by:

$$\frac{1+\beta_{\mathrm{Co}z}[\mathrm{Z}^{z-}]}{1+\beta_{\mathrm{Ni}z}[\mathrm{Z}^{z-}]}\left\{k^{+}_{3h}+k^{+}_{3z}[\mathrm{Z}^{z-}]+(k^{+}_{4h}+k^{+}_{4z}[\mathrm{Z}^{z-}])[\mathrm{H}^+]\right\} \tag{12}$$

The slopes obtained from the plots of $V^{+}_{0,\mathrm{app}}/([\mathrm{CoX}^-]_0[\mathrm{Ni}_0{}^{2+}]_{0,\mathrm{app}})$ *versus* $1/[\mathrm{Co}^{2+}]_{0,\mathrm{app}}$ were plotted against the hydrated ion concentration according to Eq. (12). These plots gave straight lines, as is shown in Fig. 1.

The rate constants in Eq. (11) were obtained by analyzing the plots of Fig. 1 and the data given in Table 1 and Table 2; they are given in Table 3.

The rate constants for reactions (3), (3′), (8), (8′), (10), and (10′) calculated from the relations given in Eq. (11′), are given in Table 4. The formation constants, K_{CoX}, β_{CoOAc}, β_{NiOAc}, β_{CoPh}, and β_{NiPh}, and the dissociation constant, K_{HX}, which were used in these calculations are given in Table 5.

The values of β_{NiOAc}[3] and β_{CoOAc}[4] were

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[3] Y. Saito, Ph. D. thesis, Tohoku University (1967).

[4] H. Ogino, *ibid.*, (1965).

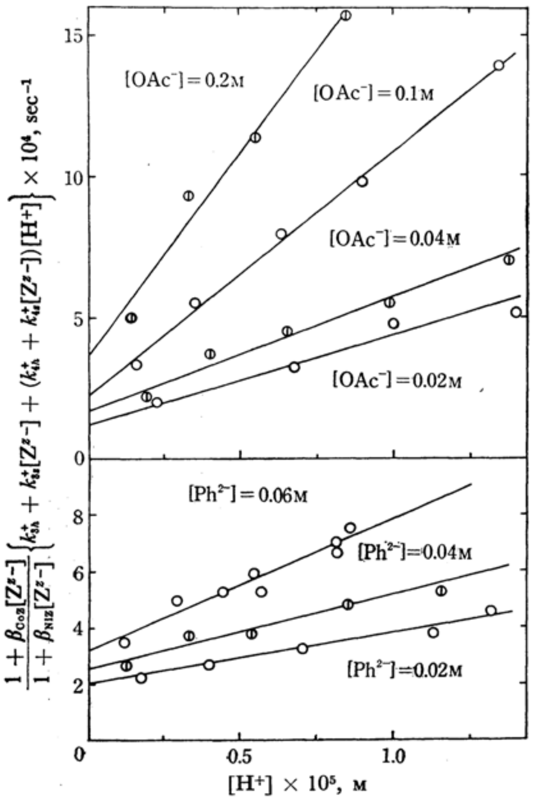

Fig. 1. Eq. (12) as a function of the hydrogen ion concentration.
The conditions are the same as in Tables 1 and 2.

determined by the polarographic method at an ionic strength of 0.2 at 25°C. The value of β_{NiPh} determined at an ionic strength of 0.1 at 25°C by Yasuda *et al.*[5] was used after correction for the ionic strength. The value of β_{CoPh} determined at an ionic strength of 0.4 at 18—25°C by Bobtelsky and Bar-Godda[6] was used without any correction. The thermodynamic constant of K_{HX} determined by Hughes and Martell[7] at 0, 10, 20, and 30°C was used after correction for the temperature and the ionic strength. The value of K_{CoX} determined at an ionic strength of 0.1 at 20°C by Schwarzenbach and Gut[8] was used after correction for the ionic strength.

Discussion

The values in Table 4 indicate that the kinetic reactivity of nickel is in the order of: $\mathrm{NiOAc^+} > \mathrm{Ni^{2+}} > \mathrm{NiPh}$. This may be compared with the results obtained in the case of the substitution reactions involving cobalt(II) ions,[1] copper(II) ions,[9] and lead (II) ions.[10] The ratios of the rate constant for the two reactions:

$$\mathrm{M^{2+}} + \mathrm{L^{3-}} \xrightarrow{k^{\mathrm{L}}_{\mathrm{M}}} \mathrm{ML^-}$$

$$\mathrm{MZ^{(2-z)+}} + \mathrm{L^{3-}} \xrightarrow{k^{\mathrm{L}}_{\mathrm{MZ}}} \mathrm{ML^-} + \mathrm{Z^{z-}}$$

can now be discussed. Previous studies dy the present author showed that the comparison of

TABLE 3. RATE CONSTATS IN EQ. (11) OBTAINED FOR THE SUBSTITUTION REACTIONS AT IONIC STRENGTH 0.2 AT 25°C

Reaction system	Rate constant*							
	k^+_{1h}	k^+_{1z}	k^+_{2h}	k^+_{2z}	k^+_{3h}	k^+_{3z}	k^+_{4h}	k^+_{4z}
NiPh-CoX⁻	$\sim 3\times10^{-2}$	~ 3	$\sim 2\times10^{4}$	$\sim 2\times10^{6}$	1.5×10^{-4}	3.3×10^{-3}	~ 7	$\sim 7\times10^{2}$
NiOAc⁺-CoX⁻	$\sim 6\times10^{-2}$	$\sim 2\times10^{-1}$	$\sim 3\times10^{4}$	$\sim 1\times10^{5}$	1.1×10^{-4}	2.3×10^{-3}	2×10	9×10^{2}

* Units of rate constants: $\mathrm{sec^{-1}}$ for k^+_{3h}; $l\ \mathrm{mol^{-1}sec^{-1}}$ for k^+_{1h}, k^+_{3z} and k^+_{4h}; $l^2\mathrm{mol^{-2}sec^{-1}}$ for k^+_{1z}, k^+_{2h} and k^+_{4h}; $l^3\mathrm{mol^{-3}sec^{-1}}$ for k^+_{2z}.

TABLE 4. RATE CONSTANTS FOR FORWARD REACTIONS OF REACTIONS (3), (3′), (8), (8′), (10) AND (10′) OBTAINED AT IONIC STRENGTH 0.2 AT 25°C

Reaction system	Rate constant, $l\ \mathrm{mol^{-1}sec^{-1}}$					
	$k^+_{\mathrm{I}h}$	$k^+_{\mathrm{I}z}$	$k^+_{\mathrm{III}h}$	$k^+_{\mathrm{III}z}$	$k^+_{\mathrm{IV}h}$	$k^+_{\mathrm{IV}z}$
NiPh-CoX⁻	$\sim 3\times10^{-2}$	$\sim 3\times10^{-2}$	$3._{2}\times10^{6}$	$1._{0}\times10^{6}$	~ 40	~ 40
NiOAc⁺-CoX⁻	$\sim 6\times10^{-2}$	$\sim 6\times10^{-2}$	$2._{4}\times10^{6}$	$1._{3}\times10^{7}$	80	1×10^{2}

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5) M. Yasuda, K. Suzuki and K. Yamasaki, *J. Phys. Chem.*, **60**, 1649 (1956).

6) M. Bobtelsky and I. Bar-Godda, *Bull. Soc. Chim. France,* **1953**, 276.

7) V. L. Hughes and A. E. Martell, *J. Am. Chem. Soc.*, **78**, 1319 (1956).

8) G. Schwarzenbach and R. Gut, *Helv. Chim. Acta*, **34**, 1589 (1956).

9) N. Tanaka and M. Kimura, This Bulletin, **41**, 2375 (1968).

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

TABLE 5. FORMATION CONSTANTS AT IONIC STRENGTH 0.2 AT 25°C

$\log K_{CoX}$[8]	10.34	β_{NiOAc}[3]	3.7
pK_{HX}[7]	9.62	β_{CoOAc}[4]	1.2
		β_{NiPh}[5]	91
		β_{CoPh}[6]	65

the rate constant is $k^{HY}_{Co} < k^{HY}_{CoOAc}$,[1] but that, on the contrary, $k^{X}_{Cu} > k^{X}_{CuOAc}$.[9] Recently, however, Tanaka and Ogino[10] reported on the kinetics of the substitution reaction between lead(II) and zinc(II)-EDTA complexes. Their results showed that the comparison of the rate constant is $k^{HY}_{Pb} > k^{HY}_{PbOAc}$.

Since it seems important and interesting to investigate the relations between the stability constant of $MZ^{(2-z)+}$ and the ratios of the rate constants, k^{L}_{M}/k^{L}_{MZ}, the plots of k^{L}_{M}/k^{L}_{MZ} against β_{MZ} are given in Fig. 2 together with the results obtained by other researchers.

Figure 2 indicates that the kinetic reactivity of the weak complexe, *i. e.*, $MZ^{(2-z)+}$, may be mainly due to the stability of the weak complex. Inner-sphere complexes, such as $MZ(H_2O)_{n-z}$, which may correspond with $CuOAc^+$, NiPh, and $PbOAc^+$ in Fig 2, seem to have less kinetic reactivity than the corresponding hydrated metal ions. However, outer-spher complexes, that is outer-spher ion-association complexes, such as $M(H_2O)_n{}^{2+}\text{–}Z^{z-}$, or outer-sphere hydrogen-bonding complexes, such as $M(H_2O)_n^{2+}O\langle{}^{H}_{H}\rangle Z^{z-}$, seem to have larger kinetic reactivities than the corresponding hydrated metal ions. Monoacetatonickel(II) and monoacetatocobalt(II) complexes may be considered to be outer-sphere complexes on the basis of their stability constants.

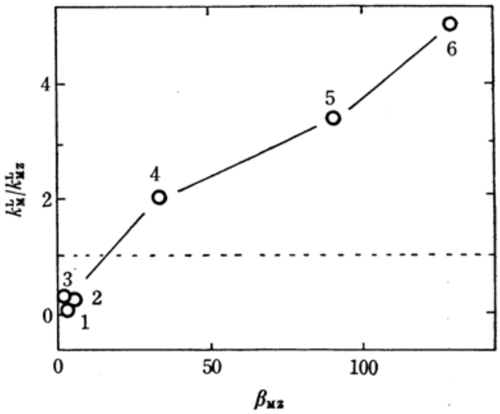

Fig. 2. The relation between k^{L}_{M}/k^{L}_{MZ} and β_{MZ}.
1: Ref. (2)
2: The present study
3: Ref. (1)
4: Ref. (9)
5: The present study
6: Ref. (10)

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