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Electrode Processes Followed by Chemical Reactions Involving Electroactive Species. II. A Study on the Substitution Reaction Involving Chromium(II)

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The one-electron reduction wave of hexamminechromium(III) ions at the dropping mercury electrode splits into two steps by the presence of manganese(II) and ethylenediaminetetraacetatomanganate(II) (MnY^{2-}; Y^{4-} represents a quadrivalent ethylenediaminetetraacetate anion) ions. The limiting current of the first step was considered to depend on the rate of the formation of CrY^{2-} by the substitution reaction of MnY^{2-} and chromium(II) ions which were produced at the electrode by the reduction of the chromium(III) complex ions. From the change in the limiting current of the first step by the change of the concentrations of Mn^{2+}, MnY^{2-} and H^+, the rate constants of the complex-forming reaction

$$Cr^{2+} + HY^{3-} \underset{k_{1b}}{\overset{k_{1f}}{\rightleftharpoons}} CrY^{2-} + H^+$$

were obtained to be $k_{1f}=8\times10^7$ l.mol^{-1}sec^{-1}, $k_{1b}=4\times10^4$ l.mol^{-1}sec^{-1} (ionic strength 1.0, 25°C).

In the previous papers[1,2] the mechanisms of the electrode reaction of hexamminechromium(III) in the presence of ethylenediaminetetraacetate (EDTA) was reported. The one-electron reduction wave of hexamminechromium(III) is affected by the presence of ethylenediaminetetraacetatomanganate(II) ions. The mechanism of this phenomenon is considered to be one similar to that observed in the presence of EDTA; chromium(II) ions produced at the electrode by the reduction of the chromium(III) complex react with manganese(II)-EDTA to form chromium(II)-EDTA complexes, which are oxidized at the electrode as long as the potential is sufficiently positive, resulting in a decrease of the net cathodic current. The reactions can be expressed as*

$$Cr(NH_3)_6^{3+} + e \rightarrow Cr^{2+} + 6NH_3 \quad (1a)$$

$$Cr^{2+} + MnY^{2-} \rightleftharpoons CrY^{2-} + Mn^{2+} \quad (1b)$$

$$CrY^{2-} \rightleftharpoons CrY^{-} + e \quad (1c)$$

where Y^{4-} represents a quadrivalent EDTA anion.

The determination of rate constants by means of the analysis of the limiting kinetic current due to the following chemical reaction seems to be convenient for reactions involving unstable substances, though it has been applied to the actual reaction only in a few cases involving organic substances.[3-5] Equations giving the relation between the current at a constant potential and the rate constants of the following chemical reaction were given by Alberts and Shain.[4] In this paper, these equations are applied to the determination of the rate constants of Reaction 1b, a substitution reaction of chromium(II) and manganese(II)-EDTA complex ions.

Experimental

Hexamminechromium(III) chloride was prepared according to the method of Mori.[6] The solution of manganese(II) chloride was standardized amperometrically against the solution of disodium ethylenediaminetetraacetate, which in turn was standardized against a standard copper(II) nitrate solution.

Solutions containing manganese(II) and manganese(II)-EDTA complex ions were obtained by adding appropriate amounts of the manganese(II) chloride and the ethylenediaminetetraacetate solutions before each measurement. The pH of the solution was adjusted with acetate buffer solution and the ionic strength was adjusted to be 1.0 with sodium chloride. Gelatin was added as a maximum suppressor by 0.005 %.

1) N. Tanaka and K. Ebata, *J. Electroanal. Chem.*, **8**, 120 (1964).

2) K. Ebata, *Sci. Repts. Tohoku Univ. Ser. I*, **47**, 191 (1964).

* It was shown previously[1] that the aquation of hexamminechromium(II) ions is more rapid than the direct substitution with EDTA. Since the reaction of chromium(II) with manganese(II)-EDTA is much slower than that with EDTA, it may be considered that the reaction of chromium(II) with manganese(II)-EDTA takes place via an aquo complex.

3) I. Tachi and M. Senda, "Advances in Polarography," Vol. 2, Ed. by I. S. Longmuir, Pergamon Press, London (1960), p. 454.

4) G. S. Alberts and I. Shain, *Anal. Chem.*, **35**, 1859 (1963).

5) R. S. Nicholson, J. M. Wilson and M. L. Olmstead, ibid., **38**, 542 (1966).

6) M. Mori, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zassi)*, **74**, 253 (1953).

The current-time curves during the life of a mercury drop were recorded using a Rikadenki ERJ1 recorder with an RLDC-201 preamplifier. In the following sections of this paper, the word "current", denoted by i, means the instantaneous current observed 4 seconds after the beginning of the mercury drop growth, unless otherwise stated. The dropping mercury electrode used had an m value of 1.42 mg./sec. and a drop time, t_d, 5.54 sec. in a deaerated 0.1 M sodium perchlorate solution at −0.5 V. vs. SCE and 60 cm. mercury height. A saturated calomel electrode (SCE) with a large surface area served as an anode. All measurements were carried out at 25°C.

Results

When manganese(II) and manganese(II)-EDTA complex ions are present in the solution in a large excess over chromium(III) complex ions, Eqs. 1a to 1c can be symbolyzed as

$$A_1 + n_1e \rightarrow A_2 \tag{2a}$$

$$A_2 \underset{l_b}{\overset{l_f}{\rightleftharpoons}} A_3 \tag{2b}$$

$$A_3 + n_2e \rightleftharpoons A_4 \tag{2c}$$

where A_1, A_2, A_3 and A_4 correspond to $Cr(NH_3)_6^{3+}$, Cr^{2+}, CrY^{2-} and CrY^- in Eqs. 1a to 1c respectively, and l_f and l_b are the forward and the backward first-order rate constant of Reaction 2b. Symbols n_1 and n_2 represent numbers of electrons involved in electrochemical reactions; positive and negative values of n's correspond to the reduction and the oxidation process respectively. In the system given by Eqs. 2a to 2c, the case $n_1n_2<0$ is physically impossible if A_1 is a substitution-labile complex. For Reactions 1a to 1c, where A_1 is a substitution-inert complex ion, the value of n_1 is 1 and that of n_2 is −1.

Substances A_1, A_2 and A_3 in Eqs. 2a to 2c obey the following equations when the mass transfer process is controlled by the linear diffusion.

$$\frac{\partial[A_1]}{\partial t} = D_1\frac{\partial^2[A_1]}{\partial x^2} \tag{3a}$$

$$\frac{\partial[A_2]}{\partial t} = D_2\frac{\partial^2[A_2]}{\partial x^2} - l_f[A_2] + l_b[A_3] \tag{3b}$$

$$\frac{\partial[A_3]}{\partial t} = D_3\frac{\partial^2[A_3]}{\partial x^2} + l_f[A_2] - l_b[A_3] \tag{3c}$$

where $[A_j]$ and D_j are the concentration and the diffusion coefficient of species A_j, respectively. The initial and the boundary conditions are

$$t = 0,\ x>0\text{: } [A_1]=[A_1]_0,\ [A_2] = [A_3] = 0 \tag{4}$$

$$t>0,\ x = 0\text{: } [A_1] = [A_3] = 0 \tag{5a}$$

$$D_2\frac{\partial[A_2]}{\partial x} = -D_1\frac{\partial[A_1]}{\partial x} \tag{5b}$$

$$t>0,\ x\rightarrow\infty\text{: } [A_1]=[A_1]_0,\ [A_2] = [A_3] = 0 \tag{6}$$

where $[A_1]_0$ is the concentration of A_1 in the bulk of the solution. The boundary condition 5a expresses that, in the potential region in question, the rates of electrochemical reactions 2a and 2c are much greater than the rate of diffusion.

The solution to the equations was given by Alberts and Shain[4] under the assumption that $D_2=D_3$. The kinetic part of the current, i_k, is given by one of Eqs. 8, 12 and 13, according to the magnitude of the equilibrium constant of Reaction 2b*:

$$K = \frac{l_f}{l_b} = \frac{[A_3]_e}{[A_2]_e} \tag{7}$$

where $[A_j]_e$ is the concentration of A_j at equilibrium.

(a) For $K > 1$:

$$i_k = i_d\frac{n_2}{n_1}\frac{K}{K-1}\left\{1 - \exp(-lt) - 2\theta\exp(-K^2\theta^2)\int_\theta^{K\theta}\exp(\lambda^2)d\lambda\right\} \tag{8}$$

where

$$l = l_f + l_b \tag{9}$$

$$\theta = \sqrt{\frac{lt}{K^2-1}} \tag{10}$$

and i_d is the diffusion current observed in the absence of Reaction 2b:

$$i_d = n_1Fq[A_1]_0\sqrt{\frac{D_1}{\pi t}} \tag{11}$$

where q is the area of the electrode surface.

(b) For $K = 1$:

$$i_k = i_d\frac{n_2}{n_1}\left[1 - \frac{1}{lt}\left\{1 - \exp(-lt)\right\}\right] \tag{12}$$

(c) For $K < 1$:

$$i_k = i_d\frac{n_2}{n_1}\frac{K}{1-K}\left[\theta\sqrt{\pi}\exp(K^2\theta'^2)\times\left\{\mathrm{erf}(\theta') - \mathrm{erf}(K\theta')\right\} - \left\{1 - \exp(-lt)\right\}\right] \tag{13}$$

where

$$\theta' = \sqrt{\frac{lt}{1-K^2}} \tag{14}$$

$$\mathrm{erf}(\lambda) = \frac{2}{\sqrt{\pi}}\int_0^\lambda \exp(-y^2)dy \tag{15}$$

When $K^2\ll1$ is satisfied, θ' can be simplified as

$$\theta' = \sqrt{lt} \tag{16}$$

Thus, when the value of K is known, rate constants l_f and l_b can be computed from the value of i_k/i_d which is obtained experimentally.

The addition of manganese(II) chloride to the solution of hexamminechromium(III) caused a

* More simplified solutions of Eqs. 3a to 3c, obtained at several limited conditions, are given in Ref. 2.

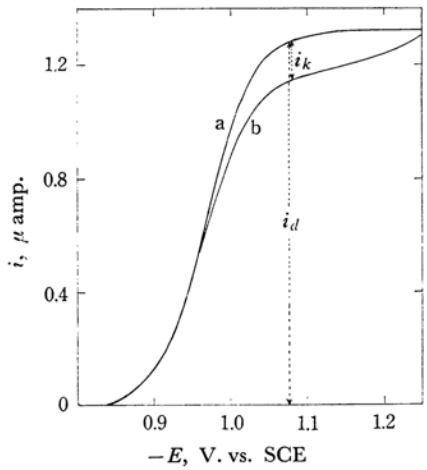

Fig. 1. Current-potential curves of 0.4 mM $Cr(NH_3)_6^{3+}$ in the presence of 0.089 M Mn^{2+} (curve a) and 0.074 M Mn^{2+} + 0.0039$_8$ M MnY^{2-} (curve b) in solutions of ionic strength 1.0 (NaCl) and pH 4.94 containing 0.1 M acetate buffer and 0.005% gelation.

small positive shift (2—3 mV. by 0.1 M $MnCl_2$) in the half-wave potential of hexamminechromium-(III) without changing the shape of the wave. When both manganese(II) and manganese(II)-EDTA complex ions were present, the wave showed a decrease in the current in the potential region more positive than about −1.25 V. as shown in Fig. 1, where the diffusion current observed in the absence of manganese(II)-EDTA is denoted by i_d, and the decrease in current by the addition of manganese(II)-EDTA, by i_k. The value of i_k was found to be proportional to the concentration of hexamminechromium(III) chloride. Table I gives the relation between the mercury height and i_k observed just before the mercury drop detaches the capillary. That i_k is independent of the mercury height indicates a kinetic nature of i_k. The value of i_k/i_d was dependent on the pH and concentrations of manganese(II) and manganese(II) - EDTA complex ions.

Table I. Values of i_k (at $t=t_d$)* at −1.06 V.vs. SCE at various heights of mercury reservoir**

Mercury height*** cm.	i_k (at $t=t_d$) μ amp.
68.5	0.168
58.5	0.173
48.5	0.163
38.5	0.173

* i_k observed just before the mercury drop detaches the capillary.

** Measurements were made in the solution of ionic strength 1.0 (NaCl), pH 4.94 containing 0.40 mM $Cr(NH_3)_6^{3+}$, 0.0079$_6$ M MnY^{2-}, 0.089$_2$ M Mn^{2+}, 0.005% gelatin and 0.1 M acetate buffer.

*** Corrected for the back pressure.

As manganese(II) and manganese(II)-EDTA complex ions are present in a large excess under the experimental condition, the apparent equilibrium constant of Reaction 1b is given as

$$K = \frac{l_f}{l_b} = \frac{[CrY^{2-}]_e}{[Cr^{2+}]_e} = \frac{K_{CrY}}{K_{MnY}} \frac{[MnY^{2-}]}{[Mn^{2+}]} \quad (17)$$

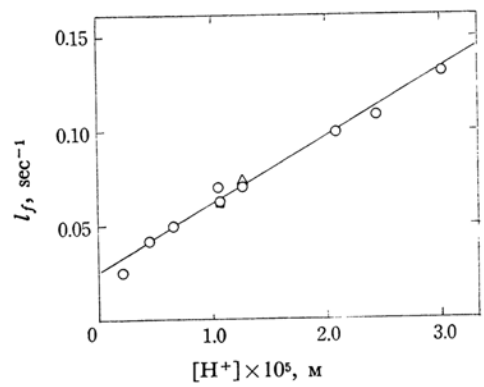

Fig. 2. Values of l_f as a function of the hydrogen ion concentration* in solutions of ionic strength 1.0 (NaCl) containing 0.4 mM $Cr(NH_3)_6^{3+}$, 0.1 M acetate buffer, 0.005% gelatin, a M Mn^{2+} and b M MnY^{2-}.

	○	△	□
a	0.089$_3$	0.179	0.044$_6$
b	0.0079$_5$	0.0159	0.0039$_8$

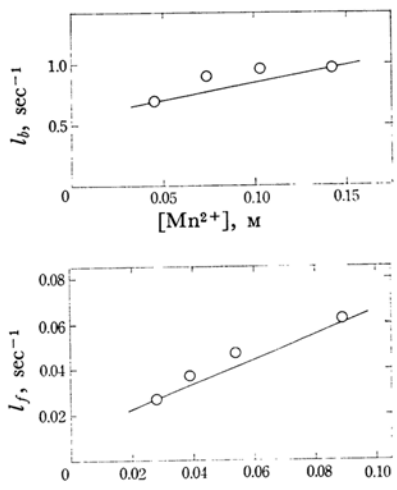

Fig. 3. Variation of l_f and l_b with the change of [Mn^{2+}] in solutions of ionic strength 1.0 (NaCl), pH 4.94 containing 0.4 mM $Cr(NH_3)_6^{3+}$, 0.0039$_8$ M MnY^{2-}, 0.1 M acetate buffer and 0.005% gelatin.

* The hydrogen ion concentration was assumed to be equal to antilog(−pH).

where K_{CrY} and K_{MnY} are the stability constants of CrY^{2-} and MnY^{2-} respectively. The values of the stability constants at ionic strength 0.1 at 20°C were reported to be $10^{13.61}$ for CrY^{2-} [7] and $10^{13.58}$ for MnY^{2-} [8], respectively. When it is assumed that the ratio K_{CrY}/K_{MnY} does not vary considerably with changes of ionic strength from 0.1 to 1.0 and of temperature from 20°C to 25°C, Eq. 17 becomes

$$K = 1.07[MnY^{2-}]/[Mn^{2+}] \quad (18)$$

As the ratio $[MnY^{2-}]/[Mn^{2+}]$ was less than 0.1 under the experimental condition, Eqs. 13 and 16 were employed for the calculation of the rate constants of Reaction 1b.* Rate constants l_f and l_b obtained at various pH's and concentrations of manganese(II) and manganese(II)-EDTA complex ions are plotted in Figs. 2 and 3.

Discussion

The following reaction paths can be assumed for Reaction 1b:

$$\text{(I)}\quad MnY^{2-} + jH^+ \rightleftharpoons Mn^{2+} + H_jY^{(j-4)+} \text{ (fast)} \quad (19a)$$

$$(j = 0, 1, 2, \cdots)$$

$$Cr^{2+} + H_jY^{(j-4)+} \underset{k_{Ijb}}{\overset{k_{Ijf}}{\rightleftharpoons}} CrY^{2-} + jH^+ \text{ (slow)} \quad (19b)$$

$$\text{(II)}\quad MnY^{2-} + jH^+ \rightleftharpoons MnH_jY^{(j-2)+} \text{ (fast)} \quad (20a)$$

$$Cr^{2+} + MnH_jY^{(j-2)+} \underset{k_{IIjb}}{\overset{k_{IIjf}}{\rightleftharpoons}} CrH_jY^{(j-2)+} + Mn^{2+} \text{ (slow)} \quad (20b)$$

$$CrH_jY^{(j-2)+} \rightleftharpoons CrY^{2-} + jH^+ \text{ (fast)} \quad (20c)$$

In Path I, Reaction 19a, the dissociation reaction of manganese(II)-EDTA, was assumed to be in equilibrium for the following reason. If Reaction 19a is rate-determining in Path I, it is expected that the rate of chromium(II)-EDTA formation, and hence i_k, is governed by the rate of Reaction 19a and is independent of the concentration of hexamminechromium(III). This is against the experimental result which showed a proportionality between i_k and the chromium(III) concentration.

When Reaction 1b proceeds via Paths I and II, the first-order rate constants of Reaction 1b with respect to Cr^{2+} and CrY^{2-} are given by

$$l_f = \frac{1}{K_{MnY}} \frac{[MnY^{2-}]}{[Mn^{2+}]} \sum_{j=0} \{k_{Ijf}[H^+]^j (\prod_{\nu=0}^{j} K_\nu)\} + [MnY^{2-}] \sum_{j=0} (k_{IIjf} K_{MnH_jY}[H^+]^j) \quad (22)$$

$$l_b = \sum_{j=0} (k_{Ijb}[H^+]^j) + [Mn^{2+}] \sum_{j=0} (k_{IIjb} K_{CrH_jY}[H^+]^j) \quad (23)$$

where K_{MnH_jY} and K_{CrH_jY} are the stability constants of protonated complexes, e. g.,

$$K_{MnH_jY} = \frac{[MnH_jY^{(j-2)+}]}{[MnY^{2-}][H^+]^j} \quad (24)$$

It is defined that K_{MnH_jY} and K_{CrH_jY} are equal to 1 for $j=0$. For $j=1$, the following values were reported at ionic strength 0.1 at 20°C: $K_{MnHY} = 10^{3.1}$;[8] $K_{CrHY} = 10^{3.00}$.[7] The symbol K_ν in Eq. 22 denotes a reciprocal of the acid dissociation constant of $H_\nu Y^{(\nu-4)+}$, and is defined to be equal to 1 for $\nu=0$; for $\nu=1, 2, 3$ and 4, the values of K_ν were reported to be $10^{10.26}$, $10^{6.16}$, $10^{2.67}$ and $10^{1.99}$ respectively at ionic strength 0.1 at 20°C.[9]

That l_f and hence l_b change linearly with the change in hydrogen ion concentration as shown in Fig. 2 indicates that j in Eqs. 22 and 23 takes only the values 0 and 1.

The first terms of Eqs. 22 and 23 correspond to rate constants for Path I and the second terms to those for Path II. Equations 22 and 23 indicate that if Path II is the predominant path of Reaction 1b, l_f should be constant as long as $[MnY^{2-}]$ is kept constant, and that l_b should be proportional to $[Mn^{2+}]$. They also indicate that, when Path I is predominant, l_b should be independent of concentrations of both manganese(II) and manganese(II)-EDTA complex ions, and l_f should be independent of $[Mn^{2+}]$ and $[MnY^{2-}]$ as long as the ratio $[MnY^{2-}]/[Mn^{2+}]$ is constant. The values of l_f and l_b obtained at different concentrations of manganese(II) and manganese(II)-EDTA complex ions with the same ratio of $[MnY^{2-}]/[Mn^{2+}]$ are given in Fig. 2, where all the values lie near a single straight line. Figure 3 shows that l_f is not constant by the change of $[MnY^{2-}]/[Mn^{2+}]$, but that it varies almost proportionally with the change of $[MnY^{2-}]/[Mn^{2+}]$, when $[MnY^{2-}]$ is kept constant. It is also shown that l_b is not proportional to $[Mn^{2+}]$. It may be concluded from these that the predominant path of Reaction 1b under conditions where the ratio $[MnY^{2-}]/[Mn^{2+}]$ is considerably large and pH is low is

$$MnY^{2-} + H^+ \rightleftharpoons Mn^{2+} + HY^{3-} \text{ (fast)} \quad (25a)$$

$$Cr^{2+} + HY^{3-} \underset{k_{1b}}{\overset{k_{1f}}{\rightleftharpoons}} CrY^{2-} + H^+ \text{ (slow)} \quad (25b)$$

The rate constants of Reaction 25b are obtained

7) R. L. Pecsok, L. D. Shields and W. P. Schaefer, *Inorg. Chem.*, **3**, 114 (1964).
8) G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 1503 (1951).
* The effect of mercury drop growth was neglected.
9) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).

Table II. Rate constants of reaction 26 (25°C)

M^{2+}	Ionic strength	k_{1f} l. mol^{-1} sec^{-1}	k_{1b} l. mol^{-1} sec^{-1}	Method	Investigators
Cr^{2+}	1.0	8×10^{7}	4×10^{4}	Polarographic kinetic current	The present authors
Co^{2+}	0.2	8×10^{6}	3×10	Polarographic diffusion current	Tanaka and Ogino[10]
Ni^{2+}	0.2	1.1×10^{4}	(5×10^{-5})	Polarographic diffusion current	Tanaka and Sakuma[11]
	1.25		8.0×10^{-4}	Spectrophotometry	Margerum and Bydalek[12]
Cu^{2+}	0.2	3×10^{9}	(9.5)	Polarographic diffusion current	Tanaka and Kato[13]
Zn^{2+}	0.2	$>10^{8}$		Polarographic diffusion current	Tanaka and Ogino[14]
	0.5	1.6×10^{9}	7×10^{2}	Polarographic kinetic current	Fujisawa and Tanaka[16]
Cd^{2+}	0.1	8.5×10^{8}	(4.0×10^{2})	Polarographic half-wave potential	Koryta and Zábransky[15]
	0.5	(2.3×10^{9})	1.1×10^{3}	Polarographic kinetic current	Fujisawa and Tanaka[16]
Pb^{2+}	0.2	1.1×10^{10}	(2.2×10^{2})	Polarographic diffusion current	Tanaka and Ogino[17]

Values in parentheses are those calculated from values of k_{1f} or k_{1b} and the equilibrium constant of Reaction 26[18] by the present authors.

from the plots in Figs. 2 and 3, and are given in Table II. Rate constants of other paths are not determined because of the rather large error.

The rate constants of Reaction 25b obtained here are compared with those of reactions similar to Reaction 25b involving other bivalent metal ions.

$$M^{2+} + HY^{3-} \underset{k_{1b}}{\overset{k_{1f}}{\rightleftharpoons}} MY^{2-} + H^{+} \qquad (26)$$

The values of k_{1f} and k_{1b} for several metal ions are also given in Table II. The dissociation rate constant k_{1b} for chromium(II) is larger than any of those for other metal ions given in the table.

It was reported by Eigen[19,20] that the rate-determining step of the complex-forming reaction of many metal ions is the substitution of a water molecule from the coordination sphere of the metal ions.

$$M(H_2O)_x\cdots L \overset{k_{H_2O}}{\rightleftharpoons} ML\cdot(H_2O)_{x-1}\cdots H_2O \qquad (27)$$

The values of k_{H_2O} for many bivalent metal ions are given in references 19 and 20. Reaction 26 can be considered to proceed in several consecutive steps

$$\begin{aligned} M(H_2O)_x^{2+} + HY^{3-} &\overset{K_{ass.}}{\rightleftharpoons} M(H_2O)_x^{2+}\cdots HY^{3-} \\ &\overset{k_{H_2O}}{\rightleftharpoons} M(HY)(H_2O)_{x-1}^{-}\cdots H_2O \\ &\rightleftharpoons \cdots \rightleftharpoons MY(H_2O)_y^{2-} + (x-y)H_2O + H^{+} \end{aligned} \qquad (28)$$

The first step, an outer-sphere association, and the steps following the substitution of a water molecule are more rapid than the substitution step, and hence the overall rate constant, k_{1f}, can be written as

$$k_{1f} = K_{ass.}k_{H_2O} \qquad (29)$$

The outer-sphere association constant, $K_{ass.}$, is not considered to vary considerably with different metal ions of the same charge according to the theory of the ion association by Bjerrum,[21] and therefore, a parallelism is expected to exist between values of k_{1f} and k_{H_2O}. Actually the order of Ni(II) $<$ Co(II) $<$ Cd(II) $<$ Cu(II) $<$ Pb(II) and that of Co(II) $<$ Zn(II) for k_{1f} are the same as those for k_{H_2O} reported by Eigen. These orders can be

10) N. Tanaka and H. Ogino, The 15 th Annual Symposium on Coordination Chemistry, Kanazawa, October 1965.
11) N. Tanaka and Y. Sakuma, This Bulletin, **32**, 578 (1959).
12) D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, **2**, 683 (1963).
13) N. Tanaka and K. Kato, This Bulletin, **32**, 1376 (1959).
14) N. Tanaka and H. Ogino, unpublished.
15) J. Koryta and Z. Zábranský, *Collection Czech. Chem. Commun.*, **25**, 3153 (1960).
16) T. Fujisawa and N. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, **87**, 965 (1966).
17) N. Tanaka and H. Ogino, This Bulletin, **36**, 175 (1963).
18) L. G. Sillén and A. E. Martell, "Stability Constants of Metal Ion Complexes," Chemical Society, London (1964).
19) M. Eigen, "Advances in the Chemistry of Coordination Compounds" Ed. by S. Kirschner, Macmillan, New York (1961), p. 371.
20) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).
21) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing, New York (1950), p. 42.

understood when the crystal field activation energies for the dissociation mechanism and the Jahn-Teller effect are considered.[20] Though the k_{H_2O} value for chromium(II) has not been reported, it is expected that k_{H_2O} for chromium(II) which has four d electrons is larger than those for nickel(II) and cobalt(II) from the view points of the crystal field activation energies and of the Jahn-Teller effect. Thus, it may be considered to be valid that the value of k_{1f} for chromium(II) obtained in this study is larger than those for cobalt(II) and nickel(II).