942 © 1980 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 53, 942—946 (1980) [Vol. 53, No. 4

A Polarographic Rate Study on the Acid Hydrolysis of Several Halogeno Cobalt(III) Complexes

Akifumi YAMADA,* Tadatsugu YOSHIKUNI, Yoshikiyo KATO, and Nobuyuki TANAKA
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

(Received September 10, 1979)

A polarographic rate study of the acid hydrolysis of $[CoX(NH_3)_5]^{2+}$- and *trans*-$[CoX_2(N)_4]^+$-type complexes ($X = Cl^-$ and Br^-; $(N)_4 = (NH_3)_4$, (ethylenediamine)$_2$, (propylenediamine)$_2$ and (1,2-cyclohexanediamine)$_2$) has been carried out in 0.1 M acetate buffer solutions. These complexes gave two polarographic waves; the first wave corresponds to the reduction of Co(III) to Co(II) and the second one, to the reduction of Co(II) to Co(0). The relation between the current and the time of the first wave in a positive potential was dependent on the dissolution wave caused by halogenide ions produced by acid hydrolysis and also on the parallel ECE mechanism. The acid-hydrolysis rate of tervalent cobalt complexes was determined from the variation in the current of the first wave. The rates are: 1.31×10^{-6} s^{-1} for $[CoCl(NH_3)_5](NO_3)_2$, 6.25×10^{-4} s^{-1} for *trans*-$[CoCl_2(NH_3)_4]ClO_4$, 3.20×10^{-5} s^{-1} for *trans*-$[CoCl_2(en)_2]NO_3$, 4.28×10^{-5} s^{-1} for *trans*-$[CoCl_2(pn)_2]ClO_4$, 1.53×10^{-4} s^{-1} for *trans*-$[CoCl_2(chxn)_2]ClO_4 \cdot H_2O$, 5.80×10^{-6} s^{-1} for $[CoBr(NH_3)_5](NO_3)_2$, 4.19×10^{-3} s^{-1} for *trans*-$[CoBr_2(NH_3)_4]ClO_4$, 1.51×10^{-4} s^{-1} for *trans*-$[CoBr_2(en)_2]NO_3$, 3.30×10^{-4} s^{-1} for *trans*-$[CoBr_2(pn)_2]ClO_4 \cdot 0.5H_2O$ and 5.10×10^{-4} s^{-1} for *trans*-$[CoBr_2(chxn)_2]NO_3$ at 25 °C and an ionic strength of 0.1.

The acid hydrolysis of several halogeno cobalt(III) complexes, such as $[CoX(NH_3)_5]^{2+}$ and $[CoX_2(N)_4]^+$, where X is Cl^- and Br^-, and where $(N)_4$ represents $(NH_3)_4$, $(en)_2$ and $(pn)_2$, has been studied by chemical and spectrophotometric methods.[1-6] There have, however, been only a few papers on the determination of the acid-hydrolysis rate constant under the same conditions. The accuracy is not yet satisfactory.

When the acid hydrolysis of a halogeno cobalt(III) complex proceeds, one mole or two moles of halogenide ions are liberated. It is well known that the halogenide ions, such as chloride and bromide ions, give a well-defined diffusion-controlled polarographic wave.[7] Therefore, by monitoring these liberated halogenide ions polarographically, the rate of the acid hydrolysis of such complexes can be obtained very accurately.

This paper will describe the polarographic determination of the acid-hydrolysis rate of halogeno cobalt(III) complexes, since we have obtained more satisfactory results.

Experimental

The electrolysis cell was of a conventional design, comprising a 50-ml cell, a platinum wire anode, and a saturated calomel electrode. The dropping mercury electrode (flow rate, 1.17 mg s^{-1} and drop time, 3.97 s in 0.1 M acetate buffer solutions (1M = 1 mol dm^{-3})) served as a working electrode. The current-time curves during aquation were recorded by the use of a Fuso Model 312 polarograph with a Watanabe Model WX441 x-y recorder.

The complexes used were prepared according to the literature,[8-19] with partial modifications. The analytical data for all the complexes obtained are summarized in Table 1, together with the literature of the syntheses.

In a series of determinations of the acid-hydrolysis rates of various halogeno cobalt(III) complexes, the electrochemical procedure was as follows. After measurements of the residual current of a 40-ml portion of the supporting electrolyte solution, a solid sample of the cobalt complex being tested was added to the solutions. As soon as the complex had been dissolved by bubbling in nitrogen gas, the current attributable to the halogenide ions was measured against the time. All the measurements were carried out at 25 °C. A small amount of gelatin was added as a maximum suppressor.

TABLE 1. ANALYTICAL DATA FOR Co(III) COMPLEXES

Complex	C(%)		H(%)		N(%)	
	Found	Calcd	Found	Calcd	Found	Calcd
$[CoCl(NH_3)_5](NO_3)_2$[8]	—	—	5.04	4.98	32.84	32.30
trans-$[CoCl_2(en)_2]NO_3$[9]	15.25	15.40	5.21	5.17	22.36	22.44
trans-$[CoCl_2(pn)_2]ClO_4$[10]	19.12	19.09	5.49	5.34	14.91	14.84
trans-$[CoCl_2(chxn)_2]ClO_4 \cdot H_2O$[11]	29.77	30.30	6.11	6.36	11.65	11.78
trans-$[CoCl_2(NH_3)_4]ClO_4$[12]	—	—	4.33	4.07	19.38	18.84
$[CoBr(NH_3)_5](NO_3)_2$[13]	—	—	4.59	4.34	28.02	28.17
trans-$[CoBr_2(en)_2]NO_3$[14]	11.90	11.98	4.15	4.02	17.66	17.47
trans-$[CoBr_2(pn)_2]ClO_4 \cdot 0.5H_2O$[15]	15.14	15.16	4.62	4.45	11.65	11.78
trans-$[CoBr_2(chxn)_2]NO_3$[11]	28.10	28.31	5.67	5.54	13.46	13.76
trans-$[CoBr_2(NH_3)_4]ClO_4$[16]	—	—	3.42	3.13	14.85	14.50
cis-$[Co(H_2O)_2(en)_2](ClO_4)_3$[17]	10.00	9.36	4.58	3.93	10.74	10.91
cis-$[Co(AcO)_2(en)_2]ClO_4$[18]	24.28	24.22	5.51	5.59	13.85	14.12
cis-$[Co(AcO)_2(pn)_2]ClO_4$[18]	28.43	28.28	6.41	6.17	12.44	13.19
cis-$[Co(H_2O)_2(NH_3)_4](ClO_4)_3$[19]	—	—	3.97	3.50	11.90	12.14

Results

The series of $[CoCl(NH_3)_5]^{2+}$, $[CoBr(NH_3)_5]^{2+}$, *trans*-$[CoCl_2(N)_4]^+$ and *trans*-$[CoBr_2(N)_4]^+$ complexes (where $(N)_4$ represents $(NH_3)_4$, $(en)_2$, $(pn)_2$ and $(chxn)_2$) gave two polarographic waves. Figure 1 shows examples of the current-potential curves of these halogeno cobalt(III) complexes obtained in 0.1 M acetate buffer solutions at 25 °C.

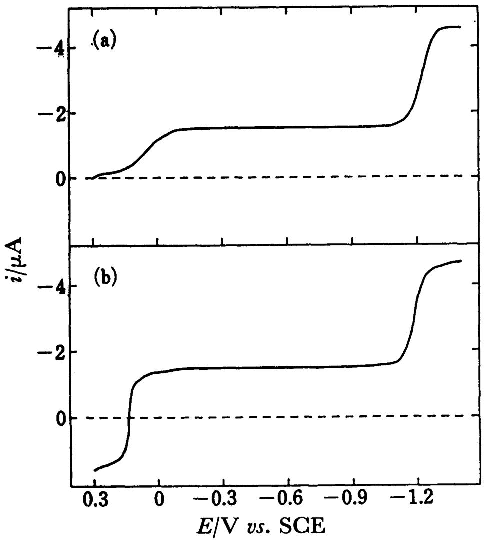

Fig. 1. Current-potential curves of 0.5 mM halogeno cobalt(III) complexes obtained in 0.1 M sodium acetate buffer solutions (pH 5.0) containing 0.005% gelatin at 25 °C. (a) $[CoCl(NH_3)_5](NO_3)_2$, (b) *trans*-$[CoBr_2(en)_2]NO_3$.

The first wave appeared in the field of the cathodic current for the monohalogeno cobalt(III) complex or in the field of the anodic and cathodic currents for the dihalogeno cobalt(III) complex. The first wave was considered to be a one-electron reduction of Co(III) to Co(II). Since the limiting current of the second wave was twice that of the first one, the second wave was considered to be a two-electron reduction, that is, Co(II)→Co(0), in analogy with the electrode reaction of other cobalt complexes.[20)]

The cathodic limiting current of the first wave was diffusion-controlled and was proportional to the concentration of the complex. The anodic limiting current of the first wave was also diffusion-controlled, but increased gradually with the time elapsed corresponding to the acid hydrolysis of the tervalent cobalt complex, as is seen in Fig. 2. When the anodic current increased with the time, the cathodic current decreased slightly.

The polarographic characteristics, such as the diffusion current(i_d), the half-wave potential ($E_{1/2}$), and the reciplocal slope of the log-plot, are given in Table 2; they were obtained immediately after dissolving 0.5 mM of the complex in 0.1 M sodium acetate buffer solutions

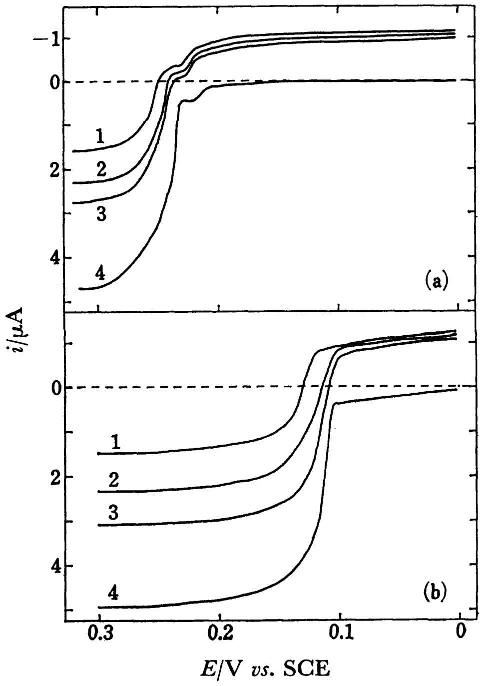

Fig. 2. Current-potential curves of (a) 0.5 mM *trans*-$[CoBr_2(chxn)_2]ClO_4 \cdot H_2O$ and (b) 0.5 mM *trans*-$[CoBr_2(pn)_2]ClO_4 \cdot 0.5H_2O$ obtained in 0.1 M sodium acetate buffer solutions (pH 5.0) containing 0.005% gelatin at 25 °C. Currents are measured (1) immediately after dissolving complex, (2) after 20 min and (3) after 40 min. Curves 4 are the current-potential curves of (a) 1 mM KCl and (b) 1 mM KBr, respectively.

TABLE 2. POLAROGRAPHIC CHARACTERISTICS OF 0.5 mM HALOGENOCOBALT(III) COMPLEXES OBTAINED IN A 0.1 M SODIUM ACETATE BUFFER (pH 5.0) CONTAINING 0.005% GELATIN AT 25 °C

Complex	First wave		Second wave		
	$\frac{i_d}{\mu A}$	$\frac{E_{1/2}}{V\ vs.\ SCE}$	$\frac{i_d}{\mu A}$	$\frac{E_{1/2}}{V\ vs.\ SCE}$	$\frac{slope}{(mV)}$
$[CoCl(NH_3)_5](NO_3)_2$	1.51	0.05_6	3.04	−1.219	65
trans-$[CoCl_2(en)_2]NO_3$	1.49	0.24_1	3.04	−1.181	54
trans-$[CoCl_2(pn)_2]ClO_4$	1.43	0.23_8	2.96	−1.176	53
trans-$[CoCl_2(chxn)_2]ClO_4 \cdot H_2O$	1.20	0.22_5	2.69	−1.163	60
trans-$[CoCl_2(NH_3)_4]ClO_4$	1.59	0.22_9	3.10	−1.224	74
$[CoBr(NH_3)_5](NO_3)_2$	1.55	0.15_1	3.20	−1.221	72
trans-$[CoBr_2(en)_2]NO_3$	1.44	0.12_2	2.94	−1.183	56
trans-$[CoBr_2(pn)_2]ClO_4 \cdot 0.5H_2O$	1.37	0.12_2	2.88	−1.176	55
trans-$[CoBr_2(chxn)_2]NO_3$	1.31	0.06_6	2.92	−1.154	51
trans-$[CoBr_2(NH_3)_4]ClO_4$	1.50	0.10_5	2.99	−1.219	73

at 25 °C.

It has been reported that halogeno cobalt(III) complexes undergo acid hydrolysis with first-order kinetics and liberate halogenide ions:[1–4,6,21]

$$[\mathrm{Co^{III}X(NH_3)_5}]^{2+} + \mathrm{H_2O} \longrightarrow [\mathrm{Co^{III}(H_2O)(NH_3)_5}]^{3+} + \mathrm{X^-}, \quad (1)$$

$$\textit{trans}\text{-}[\mathrm{Co^{III}X_2(N)_4}]^{+} + 2\mathrm{H_2O} \longrightarrow [\mathrm{Co^{III}(H_2O)_2(N)_4}]^{3+} + 2\mathrm{X^-} \quad (2)$$

$(\mathrm{X^-} = \mathrm{Br^-}$ and $\mathrm{Cl^-}$;
$(\mathrm{N})_4 = (\mathrm{NH_3})_4$, $(\mathrm{en})_2$, $(\mathrm{pn})_2$ and $(\mathrm{chxn})_2)$.

Thus, by monitoring the concentration of halogenide ions, the acid-hydrolysis rate can be measured.

Halogenide ions give a well-defined polarographic wave in the presence of gelatin:[7]

$$2\mathrm{Cl^-} + 2\mathrm{Hg} \longrightarrow \mathrm{Hg_2Cl_2} + 2\mathrm{e^-}, \quad (3)$$

$$2\mathrm{Br^-} + 2\mathrm{Hg} \longrightarrow \mathrm{Hg_2Br_2} + 2\mathrm{e^-}. \quad (4)$$

An example of the polarogram of the halogenide ions is also shown in Fig. 2. The anodic limiting current around *ca.* +0.25—+0.30 V *vs.* SCE is, therefore, given as the sum of the current attributable to the remaining halogeno cobalt(III) complex (i_{complex}) and the liberated halogenide ions (i_{halogen}). Assuming a first-order kinetics, the concentration of the liberated halogenide ions and that of remaining halogeno complex are represented[22] as $pc^\circ(1-\exp(-kt))$ and $c^\circ\exp(-kt)$, where c° is the initial concentration of the complex and where k is the first-order rate constant of acid hydrolysis given by Eq. 1 or 2. The anodic current can, therefore, be expressed as:

$$\begin{aligned} i_{\mathrm{a}} &= i_{\mathrm{complex}} + i_{\mathrm{halogen}} \\ &= \alpha_1 c_{\mathrm{complex}} + \alpha_2 c_{\mathrm{halogen}} \\ &= \alpha_1 c^\circ \exp(-kt) + \alpha_2 pc^\circ(1-\exp(-kt)), \end{aligned} \quad (5)$$

where α_1 and α_2 are the proportional constant with respect to the concentration and where p is the number of halogenide ions liberated. In the present case, $p=1$ for the monohalogeno complex and $p=2$ for the dihalogeno complex.

The first-order rate constant of the acid hydrolysis of tervalent cobalt complex can be determined from the time variation of the current given by Eq. 5. The rearrangement of Eq. 5 yields:

$$\ln\frac{pc^\circ}{pc^\circ - c} = kt + \ln\left(1 - \frac{1}{p}\frac{\alpha_1}{\alpha_2}\right)^{-1}, \quad (6)$$

with:

$$c = \frac{i}{\alpha_2}. \quad (7)$$

Equation 6 shows that, if the values of α_1 and α_2 are constant with the time, the plot of $\ln[pc^\circ/(pc^\circ - c)]$ against the time should be a straight line. From the slope of this plot, the rate constant of acid-hydrolysis can be obtained.

The rate constant for the acid-hydrolysis of tervalent cobalt complexes was determined according to Eq. 5 with the concentrations obtained from the working curve prepared with the standard solutions of potassium chloride or potassium bromide. Examples of these plots are shown in Fig. 3, while the rate constants obtained are given in Table 3. The relation between $\ln[pc^\circ/(pc^\circ - c)]$ and the time gave a straight line with an intercept.

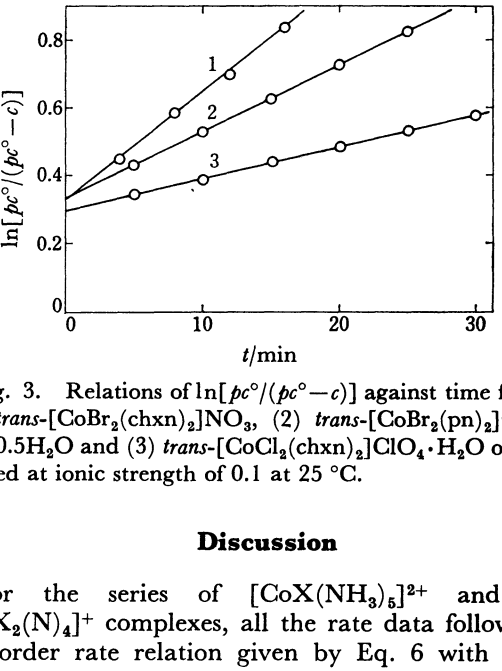

Fig. 3. Relations of $\ln[pc^\circ/(pc^\circ - c)]$ against time for (a) *trans*-$[\mathrm{CoBr_2(chxn)_2}]\mathrm{NO_3}$, (2) *trans*-$[\mathrm{CoBr_2(pn)_2}]\mathrm{ClO_4}\cdot 0.5\mathrm{H_2O}$ and (3) *trans*-$[\mathrm{CoCl_2(chxn)_2}]\mathrm{ClO_4}\cdot\mathrm{H_2O}$ obtained at ionic strength of 0.1 at 25 °C.

Discussion

For the series of $[\mathrm{CoX(NH_3)_5}]^{2+}$ and *trans*-$[\mathrm{CoX_2(N)_4}]^{+}$ complexes, all the rate data followed the first-order rate relation given by Eq. 6 with a satisfactory linearity. A good agreement between the data obtained in the present study and those in the literature was obtained except for *trans*-$[\mathrm{CoCl_2(NH_3)_4}]^{+}$ and *trans*-$[\mathrm{CoBr_2(NH_3)_4}]^{+}$ (Table 3). This suggests that the polarographic method based on the measurement of the dissolution wave can be applied for the determination of the acid hydrolysis of complexes by analogy with the chemical[2,3] and the spectrophotometric method.[2,3,6]

As for *trans*-$[\mathrm{CoCl_2(NH_3)_4}]^{+}$, the value of 2.05×10^{-3} $\mathrm{s^{-1}}$ has been reported.[5] From our results, however, this value seems to be fast: if it is ture, aquation should proceed to an extent of 22% 2 min after the complex

Table 3. Rate data for the acid hydrolysis of Co(III) complexes obtained at 25 °C and an ionic strength of 0.1

Complex	$\mathrm{X^-}=\mathrm{Cl^-}$		$\mathrm{X^-}=\mathrm{Br^-}$	
	This study $k/\mathrm{s^{-1}}$	Other studies $k/\mathrm{s^{-1}}$	This study $k/\mathrm{s^{-1}}$	Other studies $k/\mathrm{s^{-1}}$
$[\mathrm{CoX(NH_3)_5}]^{2+}$	1.31×10^{-6}	1.7×10^{-6} [1]	5.80×10^{-6}	6.3×10^{-6} [1]
trans-$[\mathrm{CoX_2(en)_2}]^{+}$	3.20×10^{-5}	3.5×10^{-5} [6]	1.51×10^{-4}	1.4×10^{-4} [2–4]
trans-$[\mathrm{CoX_2(pn)_2}]^{+}$	4.28×10^{-5}	6.2×10^{-5} [6]	3.30×10^{-4}	3.13×10^{-4} [6]
trans-$[\mathrm{CoX_2(chxn)_2}]^{+}$	1.53×10^{-4}	2.16×10^{-4} [21]	5.10×10^{-4}	—
trans-$[\mathrm{CoX_2(NH_3)_4}]^{+}$	6.25×10^{-4}	2.05×10^{-3} [5,6]	4.19×10^{-3}	*ca.* 7×10^{-3} [6]

is dissolved. Our results clearly indicate that this is not so. The literature values[6] for *trans*-$[CoBr_2(NH_3)_4]^+$ were estimated to be 3.5 times the rate constant for the dichloro analog; also the accuracy is not satisfactory. The acid-hydrolysis rate of *trans*-$[CoBr_2(chxn)_2]^+$ has not yet been reported, but the present value seems valid in comparison with the other halogeno analog.

The extinction coefficients of the halogeno complex are *ca.* 30—100 $mol^{-1}\,cm^{-1}$. Therefore, if a number of products with the same order of the extinction coefficient are produced, it seems difficult to determine the rate constant with any accuracy. On the other hand, in the polarographic method, only halogenide ions gave an anodic wave; furthermore, the diffusion coefficients of halogenide ions are about 3 times those of complexes. Therefore, the present polarographic method is very useful in the determination of the acid hydrolysis of such halogeno cobalt(III) complexes.

It is a well-known fact that the presence of excess mercuric ions accelerates the rate of the acid hydrolysis of several kinds of complexes.[23–25] In the case of the dropping mercury electrode, however, since mercurous and mercuric ions are in equilibrium, and since the mercuric ions amount to less than 1/120 of the mercury(I) ions,[26–28] the influence of the mercury(II) ions on the acid-hydrolysis of complex may be neglected compared with the large quantity of the bulk concentration of the complexes.

With the advance in acid hydrolysis, the cathodic limiting current decreased slightly. There are many factors to account for this: the effects of an ionic radius,[29] an increase or decrease in the charge,[30] a complex formation,[31] and an ion-pair formation.[32,33] However, those effects can not explain the present decrease in the current with the time. The decrease in the cathodic limiting current can be expected from the discussion given in connection with the change in the diffusion coefficient. The cathodic current of the first wave may be written as the sum of the current due to the remaining halogeno cobalt(III) and the aquated cobalt(III) complexes. Thus,

$$\begin{aligned} i_c &= i_{\text{complex}} + i_{\text{aquated}} \\ &= \alpha_1 c_{\text{complex}} + \alpha_3 c_{\text{aquated}}, \end{aligned} \tag{8}$$

where α_3 is the proportional factor of the aquated complex with respect to the concentration. If the current is diffusion controlled, α_1 and α_3 are related to the diffusion coefficient thus:[34]

$$\alpha_3 = An_1\sqrt{D_{\text{Co(III)}}}, \tag{9}$$

$$\alpha_3 = An_1\sqrt{D_{\text{Co(III)aq}}}, \tag{10}$$

where $D_{\text{Co(III)aq}}$ is the diffusion coefficient of the aquated cobalt(III) complex and where A is the constant including the flow rate of mercury and the drop time. Thus, the cathodic current is;

$$\begin{aligned} i_c &= An_1\sqrt{D_{\text{Co(III)}}}\,c^\circ \exp(-kt) \\ &\quad + An_1\sqrt{D_{\text{Co(III)aq}}}\,c^\circ(1-\exp(-kt)). \end{aligned} \tag{11}$$

If the diffusion coefficient of the aquated complex is smaller than that of the original complex, the current will decrease with the time.

This speculation was confirmed by ascertaing the diffusion coefficients of the halogeno and aqua complexes. Some of the observed and reported values for the diffusion coefficient are listed in Table 4. The method for the precise determination of the diffusion coefficient has been described previously.[29] In this determination, the diffusion-controlled currents of the cobalt complex, Cl^- ions, and Br^- ions were measured at −0.70, +0.30 and +0.25 V *vs.* SCE respectively.

TABLE 4. DIFFUSION COEFFICIENT OF Co(III) COMPLEXES AND HALOGENIDE IONS OBTAINED IN A 0.1 M SODIUM ACETATE BUFFER (pH 5.0) CONTAINING 0.005% GELATIN AT 25 °C

Complex	Diffusion coefficient ($D/10^{-6}\,cm^2\,s^{-1}$)
$[CoCl(NH_3)_5]^{2+}$	9.13
trans-$[CoCl_2(en)_2]^+$	8.56
trans-$[CoCl_2(pn)_2]^+$	8.13
trans-$[CoCl_2(chxn)_2]^+$	6.79
trans-$[CoCl_2(NH_3)_4]^+$	9.37
$[CoBr(NH_3)_5]^{2+}$	9.11
trans-$[CoBr_2(en)_2]^+$	8.32
trans-$[CoBr_2(pn)_2]^+$	7.93
trans-$[CoBr_2(chxn)_2]^+$	6.56
trans-$[CoBr_2(NH_3)_4]^+$	9.18
cis-$[Co(H_2O)_2(en)_2]^{3+}$	6.18
cis-$[Co(AcO)_2(en)_2]^+$	6.15
cis-$[Co(AcO)_2(pn)_2]^+$	5.63
cis-$[Co(H_2O)_2(NH_3)_4]^{3+}$	7.11
Cl^-	22.31
Br^-	25.14

Although the aqua and acetato complexes are *cis*-type, the diffusion coefficients of the aqua and acetato complexes are smaller than those of the halogeno complexes. By using these diffusion coefficients, the cathodic limiting current at −0.7 V *vs.* SCE was calculated from Eq. 11 for various times elapsed. The calculated values agreed with the experimental ones within the limits of experimental error.

In the present study, the plot for first-order kinetics, $\ln[pc^\circ/(pc^\circ - c)]$ *vs.* t, has the intercept to be seen in Eq. 6, whereas the conventional plot has no intercept.[22] This arises from the parallel ECE pathway represented by the reaction:[35]

$$[Co^{III}X(NH_3)_5]^{2+} + e^- \longrightarrow [Co^{II}X(NH_3)_5]^+, \tag{12a}$$

$$[Co^{II}X(NH_3)_5]^+ + 6H_2O \longrightarrow [Co^{II}(H_2O)_6]^{2+} + X^- + 5NH_3, \tag{12b}$$

$$X^- + \frac{1}{2}Hg \longrightarrow \frac{1}{2}Hg_2X_2 + e^-, \tag{12c}$$

$(X^- = Cl^-$ and $Br^-)$

or:

$$trans\text{-}[Co^{III}X_2(N)_4]^+ + e^- \longrightarrow trans\text{-}[Co^{II}X_2(N)_4], \tag{13a}$$

$$trans\text{-}[Co^{II}X_2(N)_4] + 6H_2O \longrightarrow [Co^{II}(H_2O)_6]^{2+} + 2X^- + (N)_4, \tag{13b}$$

$$2X^- + 2Hg \longrightarrow Hg_2X_2 + 2e^-. \tag{13c}$$

$(X^- = Cl^-$ and Br^-;
$(N)_4 = (NH_3)_4$, $(en)_2$, $(pn)_2$, and $(chxn)_2)$

When the tervalent cobalt complex is reduced to the bivalent one, the bivalent complex, which is substitutionlabile, liberates one mole or two moles of halogenide ions and the dissolution wave of mercury attributable to halogenide ions appears. This results in a net current anodic for dihalogeno complexes and in a net current cathodic for monohalogeno complexes. As the potential becomes negative, dissolution ceases, and a wave with a half-wave potential nearly equal to that of the dissolution wave in the presence of bromide ions appears (Fig. 1).

At 25 °C, Reaction 13b for the acid hydrolysis of dibromo cobalt(II) may proceed very rapidly, and the net current for the parallel ECE pathway becomes diffusion-controlled. From the theory of parallel ECE pathway,[35,36)]

$$\alpha_1 = A(n_1+n_2)\sqrt{D_{\mathrm{Co(III)}}}, \qquad (14)$$

and:

$$\alpha_2 = An_2\sqrt{D_{\mathrm{Br}^-}}, \qquad (15)$$

where n_1 and n_2 are the number of electrons involved in Reactions 12a and 13c respectively. The intercept (the second term on the right-hand side in Eq. 6) was calculated from the diffusion coefficients given in Table 3, and $n_1 = -1$ and $n_2 = +1$. The values are: 0.360 for *trans*-$[\mathrm{CoBr_2(NH_3)_4}]^+$, 0.339 for *trans*-$[\mathrm{CoBr_2(en)_2}]^+$, and 0.330 for *trans*-$[\mathrm{CoBr_2(pn)_2}]^+$, while the observed values are 0.36, 0.34, and 0.33 respectively.

As for other complexes, α_1 was dependent on the electrode potential because the current-potential curve did not give a diffusion plateau. No kinetic parameters of the two electrode reactions 12a and 13a have been reported, and so no further calculation was made for these cases.

The authors wish to thank the Ministry of Education for the financial support granted for this research. A part of the work was supported by a Grant-in-Aid for Scientific Research, No. 364205.

References

1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions. A Study of Metal Complexes in Solution," John Wiley & Sons, New York (1967), pp. 158—177.

2) R. G. Pearson, R. M. Meeker, and F. Basolo, *J. Am. Chem. Soc.*, **78**, 709 (1956).

3) F. Basolo, W. R. Matoush, and R. G. Pearson, *J. Am. Chem. Soc.*, **78**, 4883 (1956).

4) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, **1963**, 5700.

5) R. G. Linck, *Inorg. Chem.*, **8**, 1016 (1969).

6) L. M. Eade, G. A. Rodley, and D. A. House, *J. Inorg. Nucl. Chem.*, **37**, 1049 (1975).

7) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, New York (1964), Vol. 2, pp. 577—581.

8) G. G. Schlessinger, "Inorganic Syntheses," ed. by S. Y. Tyree, McGraw-Hill, New York (1939), Vol. 9, p. 160.

9) J. Springbørg and C. E. Schäffer, "Inorganic Syntheses," ed by A. Wold and J. K. Ruff, McGraw-Hill, New York (1973), Vol. 14, p. 68.

10) A. Werner and A. Fröhlich, *Ber.*, **40**, 2225 (1907).

11) R. S. Treptow, *Inorg. Chem.*, **5**, 1593 (1966).

12) S. M. Jørgensen, *Z. Anorg. Chem.*, **14**, 415 (1897).

13) H. Diehl, H. Clark, and H. H. Willard, "Inorganic Syntheses," ed by H. S. Booth, McGraw-Hill, New York (1939), Vol. 1, p. 186.

14) A. Werner, L. Gerb, S. Lorie, and J. Rapiport, *Ann.*, **386**, 111 (1912).

15) R. Tsuchiya, Y. Natsume, A. Uehara, and E. Kyuno, *Thermochim. Acta*, **12**, 147 (1975).

16) A. Werner and A. Wolberg, *Ber.*, **38**, 993 (1905).

17) A. Werner and G. Jantsch, *Ber.*, **40**, 265 (1907).

18) M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **264**, 321 (1951).

19) R. G. Jørgensen, *Z. Anorg. Chem.*, **2**, 294 (1892).

20) N. Maki and N. Tanaka, "Encyclopedia of Electrochemistry of the Elements," ed by A. J. Bard, Mercel Dekker Inc., New York (1975), Vol. 3, pp. 43—210.

21) S. C. Chan and F. K. Chan, *Aust. J. Chem.*, **23**, 1477 (1970).

22) K. J. Laidler, "Chemical Kinetics," McGraw-Hill, New York (1965), Chap. 1.

23) J. N. Brønsted and R. Livingston, *J. Am. Chem. Soc.*, **49**, 435 (1927).

24) A. M. Sargeson, *Aust. J. Chem.*, **17**, 385 (1964).

25) J. H. Espenson and J. P. Birk, *Inorg. Chem.*, **4**, 527 (1965).

26) A. Ogg, *Z. Phys. Chem.*, **27**, 293 (1898).

27) E. Abel, *Z. Anorg. Chem.*, **26**, 375 (1901).

28) J. Revenda, *Collect. Czech. Chem. Commun.*, **6**, 453 (1934).

29) A. Yamada, Y. Kato, T. Yoshikuni, Y. Tanaka, and N. Tanaka, *Anal. Chim. Acta*, **112**, 55 (1979).

30) K. Asada, P. Delahay, and A. K. Sundarm, *J. Am. Chem. Soc.*, **83**, 3396 (1961).

31) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 589 (1943).

32) N. Tanaka, K. Ogino, and G. Sato, *Bull. Chem. Soc. Jpn.*, **39**, 366 (1966).

33) N. Tanaka and A. Yamada, *Z. Anal. Chem.*, **224**, 117 (1967).

34) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, New York (1964), Vol. 1. pp. 63—98.

35) N. Tanaka, T. Yoshikuni, Y. Kato, and A. Yamada, *J. Electroanal. Chem.*, **107**, 95 (1980).

36) A. Yamada, T. Yoshikuni, Y. Kato, and N. Tanaka, *Bull. Chem. Soc. Jpn.*, **53**, 936 (1980).