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ECE Mechanisms as a Tool for the Investigation of Unstable Metal Complexes. 3. Polarographic Studies of Ligand Dissociation of Dibromocobalt(II) and Dibromocobalt(III) Complexes[1]

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The electrode reaction of *trans*-$[CoBr_2(N)_4]^+$ ($(N)_4$ = $(en)_2$, $(pn)_2$, $(tn)_2$, and $(NH_3)_4$; en = ethylenediamine, pn = propylenediamine, tn = trimethylenediamine) has been examined in 0.1 M sodium acetate buffer solutions at mercury electrodes. All complexes exhibit the complicated electrode processes in which both the parallel ECE reaction and the Br^- dissociation of cobalt(III) complexes take place. The dissociation rates of Br^- from the Co(III) and Co(II) complexes are determined. The Br^--dissociation rate constant (s^{-1}) at 25 °C, ΔH^* (kcal mol^{-1}), and ΔS^* (cal K^{-1} mol^{-1}) for *trans*-$[Co^{III}Br_2(N)_4]^+$ complexes are as follows: en, 1.51×10^{-4}, 27.2, +15; pn, 3.30×10^{-4}, 19.1, −10; NH_3, 4.20×10^{-3}, 26.8, +20; tn, 2.12×10^{-2}, 15.2, −15. Also, the Br^--dissociation rate constant (s^{-1}) at 25 °C, ΔH^* (kcal mol^{-1}), and ΔS^* (cal K^{-1} mol^{-1}) for *trans*-$[Co^{II}Br_2(N)_4]$ complexes are as follows: en, 0.508, 1.3, −55; pn, 0.538, 2.9, −50; NH_3, 0.610, 1.3, −55; tn, 0.571, 6.5, −38.

Introduction

In recent years studies of unstable cobalt(II) complexes have progressed with the rapid growth of fast reaction techniques such as NMR techniques[2,3] conductometric pulse radiolysis.[4-6]

Previous work in this series has shown that the electrode reaction of a series of *trans*-$[CoBr_2(N)_4]^+$ type complexes proceeds in steps[7,8] (eq 1-3) where $k_{1,e}$ and $k_{3,e}$ are the heterogeneous rate constants for the electrode reactions 1 and 3, respectively, and k_2 is the homogeneous rate constant of the ligand dissociation of *trans*-$[Co^{II}Br_2(N)_4]$. The chemical reaction (eq 2) is interposed between the two electron transfers (eq 1 and 3). This mechanism is an important class of coupled chemical reactions and is referred to as the ECE (electrochemical, chemical, electrochemical) mechanism.[9]

$$trans\text{-}[Co^{III}Br_2(N)_4]^+ + e^- \xrightarrow{k_{1,e}} trans\text{-}[Co^{II}Br_2(N)_4] \quad (1)$$

$$trans\text{-}[Co^{II}Br_2(N)_4] + 6H_2O \xrightarrow{k_2} [Co^{II}(H_2O)_6]^{2+} + 2Br^- + (N)_4 \quad (2)$$

$$2Br^- + 2Hg \xrightarrow{k_{3,e}} Hg_2Br_2 + 2e^- \quad (3)$$

$$(N)_4 = (en)_2,\ (pn)_2,\ (tn)_2,\ \text{and}\ (NH_3)_4$$

The ECE currents due to the reaction sequence (1-3) depend on the dissociation rate (k_2) of reaction 2 and on the heterogeneous rates ($k_{1,e}$ and $k_{3,e}$) of reaction 1 and 3. If both electrode reactions proceed rapidly (diffusion controlled) at a given electrode potential, the ECE current is controlled by the dissociation rate of reaction 2. The reduction potential of *trans*-$[Co^{III}Br_2(N)_4]^+$ is far more positive than the oxidation potential of the electrode reaction 3, and the polarographic current (at potentials corresponding to the reduction of *trans*-$[Co^{III}Br_2(N)_4]^+$) is influenced only by the simultaneous oxidation of a portion of the Br^- produced by the dissociation reaction 2. It is, therefore, possible to calculate the rate constant of the dissociation reaction from the polarographic ECE current. The theoretical relationships have been discussed previously.[8]

Such an in situ generation technique (based on the analysis of the polarographic currents attributable to the ECE mechanism) is useful for the study of unstable species and is successfully applied to the determination of the dissociation rate constant of dibromobis(ethylenediamine)cobalt(II) complex formed by the electrochemical reduction of the Co(III) complex.[8] The present paper deals with extensive kinetic studies concerning the dissociation of Br^- from labile *trans*-$[Co^{II}Br_2(N)_4]$ complexes which are generated by the electrochemical reduction of *trans*-$[Co^{III}Br_2(N)_4]^+$ in aqueous solutions. Furthermore, the data for the dissociation (aquation) of *trans*-$[Co^{III}Br_2(N)_4]^+$ are present and compared with the literature values. The dissociation kinetics of both Co(II) and Co(III) complexes are discussed on the basis of the activation parameters.

Experimental Section

Reagents. *trans*-$[CoBr_2(en)_2]NO_3$,[10] *trans*-$[CoBr_2(pn)_2]ClO_4 \cdot 0.5H_2O$,[11] and *trans*-$[CoBr_2(NH_3)_4]ClO_4$[12] were prepared according to the literature with partial modifications. *trans*-$[CoBr_2(tn)_2]ClO_4$ was prepared by adding dilute hydrobromic acid into the solution of $[CoCO_3(tn)_2]ClO_4$, and the solution was concentrated. Corresponding divalent cobalt species were prepared in situ by a polarographic technique (ECE process) with a dropping mercury electrode. Other chemicals were analytical reagent grade and were used without further purification.

Apparatus. Polarograms were obtained with a Fuso Model 312 polarograph with use of a three-electrode system with a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the auxiliary electrode. Oxygen in solution was eliminated by purging the solutions with O_2-free nitrogen. The electrochemical cell was kept at a constant temperature [(5, 10, 15, 25) ± 0.1 °C] by pumping water through jackets surrounding the cell compartment.

Procedures. Bromide ions are released from both tervalent and divalent cobalt species, but the current extrapolated to time zero corresponds to the net current due to the ECE mechanism, which is controlled only by the rate of dissociation of divalent species. The electrochemical procedure in a series of determination of the dissociation rates of the cobalt complexes was as follows. After measurements were taken of the residual current of a 40-mL portion of

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the supporting electrolyte solution, a solid sample of the cobalt(III) complex being tested was added to the solutions. As soon as the complex had dissolved, the current attributable to the ECE mechanism and the bromide ions was measured at +0.25 V vs. SCE as a function of the time.

With the use of the working curve obtained with KBr, the concentration of Br^- at various time was obtained and used in the calculation of the modified log plot analysis (see Treatment of Data). The dissociation rate of divalent cobalt species can be obtained from the intercept of this log plot and that of tervalent cobalt species from the slope of the log plot.

The diffusion coefficients of the series of *trans*-$[CoBr_2(N)_4]^+$ type complexes, which are required for the calculation of the modified log plots, were determined by the electrochemical method previously reported.[13] The results are given in Table I, in which limiting currents were measured at −0.7 V vs. SCE for the complexes and +0.25 V vs. SCE for Br^-. The calculations for eq 5 and 6 were carried out with a TACC 1200M (NOVA 01) computer.[14]

Treatment of Data

Previous electrochemical studies[7,8,15] of *trans*-$[CoBr_2(N)_4]^+$ type complexes showed that they undergo electrode reactions according to the ECE mechanism represented by eq 1–3. Under the experimental conditions, the current due to the ECE mechanism depends on the dissociation rate of reaction 2: the current is controlled by the rate of bromide dissociation of the *trans*-$[Co^{II}Br_2(N)_4]$ species.

On the other hand, tervalent cobalt complexes also lose Br^- ligands in the solutions[15]

$$\textit{trans}\text{-}[Co^{III}Br_2(N)_4]^+ + 2H_2O \xrightarrow{k_4} [Co^{III}(H_2O)_2(N)_4]^{3+} + 2Br^- \quad (4)$$

$$(N)_4 = (en)_2,\ (pn)_2,\ (tn)_2,\ \text{and } (NH_3)_4$$

where k_4 is the rate constant for the ligand dissociation of *trans*-$[Co^{III}Br_2(N)_4]^+$. The liberated Br^- also give the anodic current according to eq 3.[16] The rate of reaction 4 is slow, but the ligand dissociation of the divalent cobalt complex in eq 2 is very rapid. Therefore, the anodic current at positive potentials consists of the sum of the reaction current due to the ECE electrode process (eq 1–3) and the current due to the homogeneous reaction (eq 4).

For the present heterogeneous and homogeneous reactions, the ligand dissociation 4 has been reported to be first order.[14] The modified kinetic equation for the series of reactions 1–4 is[8]

$$\ln\left(\frac{2c^0}{2c^0 - c}\right) = k_4t + \ln\,(1 - \tfrac{1}{2}z)^{-1} \qquad (5)$$

with

$$z = \left(\frac{D_A}{D_C}\right)^{1/2}\left(-1 + 2\left[\phi\left(\frac{D_Ck_2\tau}{D_C - D_B}\right)^{1/2} - \left(\frac{D_C}{D_B}\right)^{1/2}\exp(-k_2\tau)\,\phi\left(\frac{D_Bk_2\tau}{D_C - D_B}\right)\right]\right) \qquad (6)$$

and

$$\phi(x) = 2x\,\exp(-x^2)\int_0^x \exp(u^2)\,\mathrm{d}u \qquad (7)$$

where c^0 is the initial concentration of the cobalt(III) complex, c is the concentration of Br^- at time t, τ is the drop time, and D_A, D_B, and D_C are the diffusion coefficients of *trans*-$[Co^{III}Br_2(N)_4]^+$, *trans*-$[Co^{II}Br_2(N)_4]$, and Br^-, respectively.

If the diffusion coefficient of each complex is known, both the rate constants (k_2 and k_4) of the reactions 2 and 4 can be calculated from the slope and the intercept of the plot $\ln\,[2c^0/(2c^0 - c)]$ vs. t. So that the rate constant k_2, could be evaluated, the value of z was calculated against $k_2\tau$ for the given diffusion coefficients, and the working curve for calculation of rate constant was constructed.

Table I. Diffusion Coefficient of Co(III) Complexes and Br^- Obtained in 0.1 M Acetate Buffer (pH 5.0) and 0.005% Gelatin

complexes	diffusion coefficient 10^6D, cm² s⁻¹ 15 °C	 10 °C	 5 °C
trans-$[CoBr_2(en)_2]^+$	6.55	5.60	4.62
trans-$[CoBr_2(pn)_2]^+$	5.77	4.73	3.71
trans-$[CoBr_2(tn)_2]^+$	5.35	4.78	4.07
trans-$[CoBr_2(NH_3)_3]^+$	7.59	6.79	5.75
Br^-	19.5	16.4	13.7

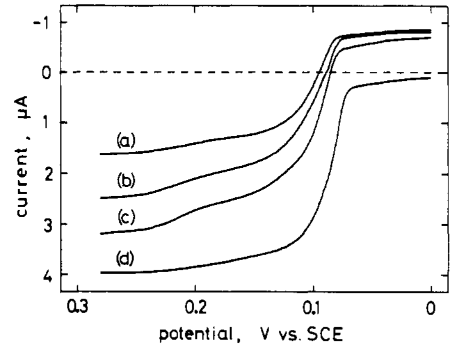

Figure 1. Current-potential curves of 0.5 mM *trans*-$[CoBr_2(tn)_2]^+$ obtained in 0.1 M sodium acetate buffer solutions (pH 5.0) containing 0.005% gelatin at 5 °C. Currents are measured (a) immediately after dissolving complex, (b) after 5 min, and (c) after 20 min. Curve d is the current-potential curve of 1 mM KBr.

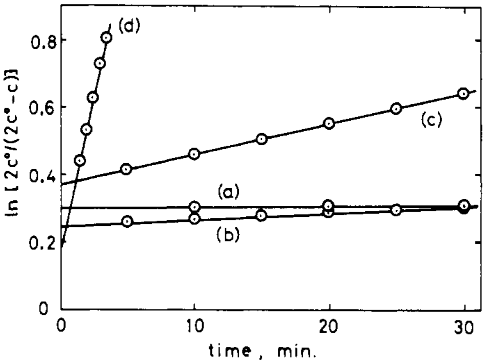

Figure 2. Relations of $\ln\,[2c^0/(2c^0 - c)]$ against time for (a) *trans*-$[CoBr_2(en)_2]^+$, (b) *trans*-$[CoBr_2(pn)_2]^+$, (c) *trans*-$[CoBr_2(NH_3)_4]^+$, and (d) *trans*-$[CoBr_2(tn)_2]^+$ obtained at 10 °C and ionic strength of 0.1.

Results and Discussion

Figure 1 shows an example of the polarogram of *trans*-$[CoBr_2(tn)_2]^+$ obtained in 0.1 M sodium acetic acid buffers at 5 °C. The polarogram appeared partly above and partly below the zero current line. The anodic current increased with the time, corresponding to the occurrence of reaction 4. The anodic current at time zero corresponds to that of reactions 1–3 (ECE process). Other cobalt(III) complexes ($(N)_4$ = $(en)_2$, $(pn)_2$ and $(NH_3)_4$) also gave similar polarographic waves.

With the use of the working curve obtained with KBr, the concentration of Br^- at various time was obtained and used

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Table II. Rate Data for the Br^- Dissociation of *trans*-$[Co^{III}Br_2(N)_4]^+$ and *trans*-$[Co^{II}Br_2(N)_4]$ Obtained at Various Temperatures and at an Ionic Strength of 0.1

			Co(III) complex k_4, s^{-1}	
$(N)_4$	*T*, °C	Co(II) complex (this study) k_2, s^{-1}	this study	other study
$(en)_2$	5.0	0.405 ± 0.004	$(5.19 \pm 0.08) \times 10^{-6}$	
	10.0	0.430 ± 0.004	$(1.18 \pm 0.06) \times 10^{-5}$	
	15.0	0.455 ± 0.004	$(2.98 \pm 0.06) \times 10^{-5}$	
	20.0		$(5.83 \pm 0.08) \times 10^{-5}$	
	25.0	0.508 ± 0.012[a]	$(1.51 \pm 0.06) \times 10^{-4}$	1.4×10^{-4} [17–19]
$(pn)_2$	5.0	0.354 ± 0.004	$(3.04 \pm 0.08) \times 10^{-5}$	
	10.0	0.396 ± 0.004	$(6.19 \pm 0.09) \times 10^{-5}$	
	15.0	0.440 ± 0.004	$(1.04 \pm 0.05) \times 10^{-4}$	
	20.0		$(1.86 \pm 0.06) \times 10^{-4}$	
	25.0	0.538 ± 0.011[a]	$(3.30 \pm 0.06) \times 10^{-4}$	3.13×10^{-4} [20]
$(NH_3)_4$	5.0	0.489 ± 0.004	$(1.53 \pm 0.08) \times 10^{-4}$	
	10.0	0.519 ± 0.004	$(3.50 \pm 0.08) \times 10^{-4}$	
	15.0		$(7.13 \pm 0.09) \times 10^{-4}$	
	20.0		$(2.07 \pm 0.09) \times 10^{-3}$	
	25.0	0.610 ± 0.015[b]	$(4.19 \pm 0.08) \times 10^{-3}$	ca. 7×10^{-3} [20]
$(tn)_2$	5.0	0.242 ± 0.006	$(3.14 \pm 0.06) \times 10^{-3}$	
	10.0	0.303 ± 0.007	$(5.10 \pm 0.06) \times 10^{-3}$	
	15.0	0.378 ± 0.006	$(8.43 \pm 0.08) \times 10^{-3}$	
	25.0	0.571 ± 0.018[a]	$(2.12 \pm 0.14) \times 10^{-2}$	9.49×10^{-2} [21]

[a] Extrapolated from 5–15 °C values. [b] Extrapolated from 5–10 °C values.

in the calculation of eq 5. log plots of eq 5 for the series of *trans*-$[CoBr_2(N)_4]^+$ complexes are shown in Figure 2. The Br^- dissociation rates of *trans*-$[Co^{III}Br_2(N)_4]^+$ and *trans*-$[Co^{II}Br_2(N)_4]$ complexes obtained in 0.1 M acetate buffer solutions are given in Table II. In the above calculation, the diffusion coefficients of *trans*-$[Co^{II}Br_2(N)_4]$ and *trans*-$[Co^{III}Br_2(N)_4]^+$ are assumed to be equal. The Br^- dissociation rate of *trans*-$[Co^{III}Br_2(N)_4]^+$ reported in the literature is also given in Table II.

Electrochemical investigations in our laboratory[7,8,15] of electroreduction in a series of dihalogenocobalt(III) complexes have shown that *trans*-$[CoBr_2(N)_4]^+$ type complexes follow the electrode reaction as represented by eq 1–3 at mercury electrodes. This type of reaction belongs to the so-called ECE mechanism[9] (a chemical reaction interposed between two electron-transfer reactions). The current characteristic for an ECE mechanism depends on the rate of chemical reaction 2.

According to Ruzic et al.,[22] an ECE mechanism is classified into two cases, i.e., consecutive ECE pathway and parallel ECE pathway. In the present case, the electroreduction of *trans*-$[CoBr_2(N)_4]^+$ is followed by subsequent oxidation of mercury so that the electrode reaction belongs to the parallel ECE pathway. Other better understood examples of parallel ECE pathway, the reduction of *trans*-$[CoCl_2(en)_2]^+$ in excess ethylenediamine[23] and the reduction of $[Cr(H_2O)(edta)]^-$ in ethylenediaminetetraacetic acid,[24,25] have been reported. The behavior is seen only in the presence of excess ligand, i.e., intermolecular type. On the other, in the case of the reduction of *trans*-$[CoBr_2(N)_4]^+$ complexes, the ECE pathway is produced by the dissociation of cobalt(II) complex itself, i.e., intramolecular type. An analogous example is seen for the reduction of *p*-nitrosophenol[26] in acidic media though this reaction belongs to the consecutive ECE pathway.

For the series of *trans*-$[CoBr_2(N)_4]^+$ complexes, all the rate data followed the first-order rate relation given by eq 5 with a satisfactory linearity (Figure 2). A good agreement between the data of *trans*-$[CoBr_2(N)_4]^+$ obtained in the present study and those in the literature[17-20] at 25 °C was obtained, except for *trans*-$[CoBr_2(NH_3)_4]^+$ and *trans*-$[CoBr_2(tn)_2]^+$ (Table II). The literature value[20] for *trans*-$[CoBr_2(NH_3)_4]^+$ was estimated to be 3.5 times the rate constant for the dichloro analogue, and the accuracy is not satisfactory. The literature value[21] for *trans*-$[CoBr_2(tn)_2]^+$ also seems to be fast.

At all temperatures, the bromide dissociation rates of *trans*-$[Co^{III}Br_2(N)_4]^+$ increase in the order $(tn)_2 > (NH_3)_4 > (pn)_2 > (en)_2$ (Table II). This order is essentially the same as the increasing order of chloride dissociation rates of *trans*-$[Co^{III}Cl_2(en)_2]^+$.[15] In the case of *trans*-$[Co^{II}Cl_2(en)_2]$ complexes, the rate constants in the rather narrow range of 0.2–0.6 s^{-1} were obtained depending upon the nature of the ligands. No rate constants are available for the bromide dissociation of *trans*-$[Co^{II}Br_2(N)_4]$. However, several intermediate reactions with analogous order of rate constants have been reported from the analysis of ECE mechanism. For example, a value of $k = 0.6$–1.3 s^{-1} has been measured for the dehydration of *p*-(hydroxylamino)phenol to *p*-benzoquinone imine in ethanol–water solutions.[26] Čukman and Pravdič[27] reported $k = 0.03$–0.34 s^{-1} for the cyanide dissociation $Ni^I(CN)_4^{3-} \rightarrow Ni^I(CN)_3^{2-} + CN^-$. Feldberg and Jeftic[28] studied the electrochemical reduction of hexacyanochromate(III) and reported $k = 11$ s^{-1} for $Cr^{II}(CN)_6^{4-} \rightarrow Cr^{II}(CN)_5^{3-} + CN^-$.

Lilie et al.[5] reported from the pulse radiolysis method that, for the dissociation of *trans*-$[Co^{II}Cl_2(en)_2]$ which is reduced by the hydrated electron, the two Cl^- ligands detach rapidly ($k_2 = 3 \times 10^5$ s^{-1}). According to their values, the currents due to the ECE mechanism (eq 1–3) should be diffusion controlled at all temperatures. The results of careful experiments on the *trans*-$[CoBr_2(N)_4]^+$ type complexes showed that the experimental intercepts of first-order plots (eq 5) at all temperatures studied were different from the calculated one for the diffusion-controlled case and beyond experimental error. The discrepancy between the rate constant obtained

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Table III. Activation Parameters for Br^- Dissociation of *trans*-$[Co^{III}Br_2(N)_4]^+$ and *trans*-$[Co^{II}Br_2(N)_4]$ Obtained at an Ionic Strength of 0.1

complex	$\Delta G^{\ddagger}$(25 °C), kcal mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}
Co(III) Complex			
trans-$[CoBr_2(en)_2]^+$	22.7 ± 0.1	27.2 ± 0.6	+15 ± 2
trans-$[CoBr_2(pn)_2]^+$	22.2 ± 0.1	19.1 ± 0.7	−10 ± 2
trans-$[CoBr_2(NH_3)_4]^+$	20.7 ± 0.1	26.8 ± 1.1	+20 ± 2
trans-$[CoBr_2(tn)_2]^+$	19.8 ± 0.1	15.2 ± 1.4	−15 ± 3
Co(II) Complex			
trans-$[CoBr_2(en)_2]$	17.9 ± 0.1	1.33 ± 0.05	−55 ± 3
trans-$[CoBr_2(pn)_2]$	17.8 ± 0.1	2.90 ± 0.05	−50 ± 3
trans-$[CoBr_2(NH_3)_4]$	17.8 ± 0.1	1.25 ± 0.05	−55 ± 3
trans-$[CoBr_2(tn)_2]$	17.8 ± 0.1	6.53 ± 0.08	−38 ± 2

by pulse radiolysis and that by the electrochemical method may be attributed to the environment around the coordination sphere.

In the pulse radiolysis experiemnts, the products will be formed in highly excited states, often in excited electronic states,[29] by means of the very high doses per pulse under experimental conditions. The unstable *trans*-$[Co^{II}Cl_2(en)_2]$ complex thus produced by the hydrated electron may decompose rather rapidly. On the other hand, the dissociation reaction 2 in the ECE mechanism occurs near the electrode and will be affected by the double-layer structure.[30] The concentration of charged species in the electrode field is different from that in the bulk of the solution, and the apparent rate may be influenced by the double-layer potential.[31] Sometimes, the activity of water molecules near the electrode may become smaller than that of the bulk solutions.[32] Thus, the apparent dissociation rate of eq 2 may be smaller than that obtained by pulse radiolysis. Such electrostatic effects from the double-layer structure acting upon the rate constant observed for the dissociation of $[Co(en)_3]^{2+}$[33] and $[Cd(CN)_4]^{2-}$.[34]

The activation data for the dissociation reaction of both *trans*-$[Co^{III}Br_2(N)_4]^+$ and *trans*-$[Co^{II}Br_2(N)_4]$ are given in Table III, which are calculated from the data in Table II.

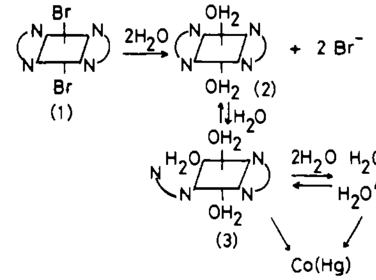
The free energy of activation for the series of *trans*-$[Co^{III}Br_2(N)_4]^+$ complexes decreases with changes of $(N)_4$ in the order $(en)_2 > (pn)_2 > (NH_3)_4 > (tn)_2$, while the enthalpy of activation decreases in the order $(en)_2 > (NH_3)_4 > (pn)_2 > (tn)_2$. This suggests that accelerations in Br^- dissociation rate are likely to occur in complexes with bulky ligands.

On the other hand, in the case of the divalent state of cobalt the free energy of activation for *trans*-$[Co^{II}Br_2(N)_4]$ does not differ significantly; the value was calculated to be ca 18 kcal/mol for all the complexes. The enthalpy of activation varied slightly in the order $(tn)_2 > (pn)_2 > (en)_2 > (NH_3)_4$, while the entropy of activation was found to be almost equal and small except for the $(tn)_2$ complex. The entropy of activation for the $(tn)_2$ complex is approximately 30% larger than that of the other three complexes. This may be caused by the structural change in the dissociation of Br^-. It is of interest to note that, for these four examples, the entropy of activation seems to play a important role in the ligand dissociation of divalent cobalt complexes, whereas the enthalpy of activation makes a large contribution to the ligand dissociation of tervalent cobalt complexes.

Table IV. Polarographic Half-Wave Potentials of Second Wave of Some Co(III) Complexes Obtained in 0.1 M Acetate Buffer (pH 5.0) and 0.005% Gelatin at 25 °C

complex	half-wave potential, V vs. SCE
trans-$[CoBr_2(en)_2]^+$	−1.183
trans-$[CoBr_2(pn)_2]^+$	−1.176
trans-$[CoBr_2(NH_3)_4]^+$	−1.219
$[Co(en)_3]^{3+}$	−1.190
$[Co(pn)_3]^{3+}$	−1.180
$[Co(NH_3)_6]^{3+}$	−1.225
$[Co(tn)_3]^{3+}$	−1.179
$[Co(H_2O)_2(en)_2]^{3+}$	−1.186
$[Co(H_2O)_2(NH_3)_4]^{3+}$	−1.223
$[Co(H_2O)_6]^{2+}$	−1.252

Scheme I



Although the electrode reaction of the divalent cobalt complexes is irreversible in nature, the structural information concerning the divalent cobalt complex immediately after dissociation of Br^- may be obtained[35] from the polarographic half-wave potentials corresponding to the reduction of Co(II) → Co(0). The half-wave potentials of the second wave (Co(II) → Co(0)) for several complexes are given in Table IV. The half-wave potentials of *trans*-$[CoBr_2(N)_4]^+$ type complexes were found to be less negative than that of $[Co(H_2O)_6]^{2+}$ and shifted to negative potential in the order $(pn)_2 > (en)_2 > (NH_3)_4$. The half-wave potentials of $[Co^{III}(H_2O)_2(N)_4]^{3+}$ type complexes were found to be nearly equal to those of corresponding *trans*-$[CoBr_2(N)_4]$ type complexes. Furthermore, $[Co(N)_6]^{3+}$ complexes gave more negative half-wave potentials than the corresponding bis-type complexes (Table IV). From these facts, two conclusions may be drawn. The rate of Br^- loss from the cobalt(II) complexes (see Scheme I) depends upon the nature of the diamine ligands. The extent of dissociation of the diamine nitrogens from the coordination sphere of cobalt(II) is also determined by the identity of the diamine ligand itself. At least one diamine nitrogen remains bound to cobalt until the cobalt is reduced to Co^0.[36]

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Registry No. *trans*-$[Co^{III}Br_2(en)_2]^+$, 15379-04-1; *trans*-$[Co^{III}Br_2(pn)_2]^+$, 18660-74-7; *trans*-$[Co^{III}Br_2(NH_3)_4]^+$, 36273-40-2; *trans*-$[Co^{III}Br_2(tn)_2]^+$, 56322-91-9; *trans*-$[Co^{II}Br_2(en)_2]$, 73946-19-7; *trans*-$[Co^{II}Br_2(pn)_2]$, 77210-80-1; *trans*-$[Co^{II}Br_2(NH_3)_4]$, 77210-81-2; *trans*-$[Co^{II}Br_2(tn)_2]$, 77210-82-3; $[Co(en)_3]^{3+}$, 14878-41-2; $[Co(pn)_3]^{3+}$, 16786-50-8; $[Co(NH_3)_6]^{3+}$, 14695-95-5; $[Co(tn)_3]^{3+}$, 16786-53-1; $[Co(H_2O)_2(en)_2]^{3+}$, 19314-32-0; $[Co(H_2O)_2(NH_3)_4]^{3+}$, 19394-99-1; $[Co(H_2O)_6]^{2+}$, 15276-47-8.

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(35) In the case of an irreversible electrode reaction, rigorous thermodynamic arguments are difficult for the stability of complexes. It may be, however, of value to compare half-wave potentials for reaction involving a series of related compounds at some convenient reference electrode.[30]

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