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Kinetics and Mechanisms of the Reduction of Cobalt(III) Complexes by the Chromium(II) Complex Ligating *N*-(2-Hydroxyethyl)-ethylenediamine-*N*,*N′*,*N′*-triacetate

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The reduction of the cobalt(III) complexes, $CoX(NH_3)_5^{(3-m)+}$ ($X^{m-}=Cl^-$, Br^-, NCS^-, and H_2O) and $Co(en)_3^{3+}$, by Cr(II)–HEDTRA was studied by the stopped-flow method, where en and HEDTRA denote ethylenediamine and *N*-(2-hydroxyethyl)ethylenediamine-*N,N′,N′*-triacetatic acid respectively. From the kinetic behavior and the spectral properties of the immediate chromium(III) products, it is concluded that the Cr(II)–HEDTRA reductions of $CoX(NH_3)_5^{2+}$ ($X^-=Cl$,$^-$ Br^-, and NCS^-) are of an inner-sphere type. The effect of the HEDTRA coordinated to chromium(II) on the rates of the electron-transfer reactions is discussed.

There has been much interest in the mechanisms of the electron-transfer reactions of $MX(NH_3)_5^{(3-m)+}$ ($M=Co^{III}$ or Cr^{III}) with $Cr^{II}L(H_2O)^{(n-2)-}$, where X^{m-} denotes a potential bridging ligand.[1–7] The present authors proposed an inner-sphere mechanism for the reactions of $CrX(NH_3)_5^{2+}$ ($X=F^-$, Cl^-, Br^-, NCS^-, and OH^-) with $Cr^{II}(edta)(H_2O)^{2-}$ on the basis of the reactivity pattern.[2,3] A similar proposal has been made by Earley and Davies for the reactions of $CrX(NH_3)_5^{2+}$ ($X=Cl^-$ and OH^-) with several chromium(II)–amino polycarboxylates by considering the linear free energy relationship.[4,5] Diebler *et al.* reported that, from the findings on the isotopic fractionation effects, the reaction of $Co(OH)(NH_3)_5^{2+}$ with $Cr^{II}(edta)(H_2O)^{2-}$ is of an inner-sphere type.[6] Thorneley *et al.* investigated the reactions of several oxidants containing potential halide bridges with $Cr^{II}(edta)(H_2O)^{2-}$ and found that the final spectra recorded within 3 min of mixing always agreed with that of $Cr^{III}(edta)(H_2O)^-$.[7] Therefore, they proposed an outer-sphere mechanism for these reactions, because it was difficult to accept the idea the aquation of $Cr^{III}X(edta)^{2-}$ is rapid and complete within 3 min in view of the substitution inertness of chromium(III) complexes.

Quite recently, the present authors presented evidence that the reaction of $Co(OAc)(NH_3)_5^{2+}$ with $Cr^{II}L(H_2O)^{(n-2)-}$ is of an inner-sphere type, because the immediate chromium(III) product was $Cr^{III}(OAc)L^{(n-2)-}$ and aquated rapidly.[8] Therefore, the over-all reaction can be expressed in the following two stages:

$$Co(OAc)(NH_3)_5^{2+} + Cr^{II}L(H_2O)^{(n-2)-} \xrightarrow{k_{et}} Co^{2+} + 5NH_3 + Cr^{III}(OAc)L^{(n-2)-} + H_2O, \quad (1)$$

$$Cr^{III}(OAc)L^{(n-2)-} + H_2O \rightleftharpoons Cr^{III}L(H_2O)^{(n-3)-} + OAc^-. \quad (2)$$

It is also known that Reaction 3, involving OAc^-,[9] N_3^-,[10,11] or some other anions[12] as X^-, is reversible and extremely rapid:

$$Cr^{III}L(H_2O)^{(n-3)-} + X^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Cr^{III}XL^{(n-2)-} + H_2O. \quad (3)$$

These observations indicate that the detection of the immediate chromium(III) product after the electron-transfer is the key to distinguishing the mechanisms. In order to ascertain the role of the coordinated amino polycarboxylates in the electron-transfer reactions and to elucidate the mechanism of the reactions, the previous work[8] has now been extended to the electron-transfer reactions of $CoCl(NH_3)_5^{2+}$, $CoBr(NH_3)_5^{2+}$, $Co(NCS)(NH_3)_5^{2+}$, $Co(NH_3)_5(H_2O)^{3+}$, and $Co(en)_3^{3+}$ ions with $Cr^{II}(hedtra)(H_2O)^-$. The findings on the reaction of $Co(en)_3^{3+}$ with $Cr^{II}(edta)(H_2O)^{2-}$ will also be given in this paper.

Experimental

Materials. The cobalt(III) complexes, $[CoCl(NH_3)_5](ClO_4)_2$,[13] $[CoBr(NH_3)_5](ClO_4)_2$,[14] $[Co(NCS)(NH_3)_5](ClO_4)_2$,[15] $[Co(NH_3)_5(H_2O)](ClO_4)_3$,[14] and $[Co(en)_3](ClO_4)_3$,[16] were prepared according to the literature. The solutions of $[Cr(H_2O)_6](ClO_4)_3$ and $[Cr(H_2O)_6](ClO_4)_2$ were prepared as has been described previously.[2] The $Cr^{II}(hedtra)(H_2O)^-$ and $Cr^{II}(edta)(H_2O)^{2-}$ were generated *in situ* by the injection of $Cr(H_2O)_6^{2+}$ solutions into excess HEDTRA and EDTA solutions respectively. All the solutions were prepared with redistilled water.

Kinetic Procedure. Many of the kinetic measurements were made with a Union-Giken RA 401 stopped-flow spectrophotometer and a Hitachi RSP-2 rapid scanning spectrophotometer. The dead time of mixing was approximately 0.5 ms for the former instrument and 20 ms for the latter instrument. Slow kinetic measurements were made with a Union-Giken SM 401 and a Hitachi EPS-3 recording spectrophotometer. All the kinetic measurements were made at $I=1.0$ ($NaClO_4$) under an atmosphere of nitrogen. The temperature was kept at 25.0 °C, unless otherwise stated. The hydrogen-ion concentrations of the solutions were adjusted with HEDTRA solutions as buffers, except for the reactions of $Co(en)_3^{3+}$ with $Cr^{II}(hedtra)(H_2O)^-$ and $Cr^{II}(edta)(H_2O)^{2-}$, which were performed in acetate buffer solutions. A Hitachi F-5 pH meter was used for the determination of the hydrogen-ion concentrations; the meter readings were calibrated against standard perchloric acid solutions.

The kinetics of the electron-transfer reactions was studied under the condition of $[Co(III)]_0 > [Cr(II)]_0$, where $[\ ]_0$ represents the initial concentration of the given species. The reactions were usually monitored by the appearance of the Cr(III)-HEDTRA or -EDTA complex at 545—550 nm. On the assumption that the electron-transfer reaction:

$$Co(III) + Cr(II)\text{-}L \xrightarrow{k_{et}} Co(II) + Cr(III)\text{-}L \quad (4)$$

proceeds by means of the second order rate law;

$$\frac{d[Cr(III)\text{-}Y]}{dt} = k_{et}[Co(III)][Cr(II)\text{-}L], \quad (5)$$

the following equation was derived:

$$\ln\left\{1+\frac{\varepsilon_{\mathrm{Co(III)}}+\varepsilon_{\mathrm{Cr(II)}}-\varepsilon_{\mathrm{Co(II)}}-\varepsilon_{\mathrm{Cr(III)}}}{A_t-A_\infty}[\mathrm{Co(III)}]_\infty\right\} = [\mathrm{Co(III)}]_\infty k_{\mathrm{et}}t + \ln\frac{[\mathrm{Co(III)}]_0}{[\mathrm{Cr(II)}]_0}, \tag{6}$$

where A_t and A_∞ denote the absorbancies at time t and infinity respectively; $\varepsilon_{\mathrm{Co(III)}}$, $\varepsilon_{\mathrm{Cr(II)}}$, $\varepsilon_{\mathrm{Co(II)}}$, and $\varepsilon_{\mathrm{Cr(III)}}$, the molar absorption coefficients of the given species, and $[\mathrm{Co(III)}]_\infty$, the concentration of Co(III) after the completion of the reaction. The value of the $\varepsilon_{\mathrm{Cr(II)}}$ is so small that it can be neglected. The $[\mathrm{Co(III)}]_\infty$ quantity was determined as follows. A known volume of the product solution was poured into an SP-Sephadex C-25 cation exchanger column in the Na^+ form. When the column was washed with water, only the unreacted cobalt(III) ions remained in the column, and they were eluted with 0.5—1.0 M NaCl solutions. The eluate was then acidified with hydrochloric acid. After the cobalt(III) ions in the solution has been reduced to cobalt(II) ions with amalgamated zinc, the cobalt(II) content was determined by Kitson's method.[17] The subtraction of $[\mathrm{Co(III)}]_\infty$ from $[\mathrm{Co(III)}]_0$ left $[\mathrm{Cr(II)}]_0$. The plots of the left-hand side of Eq. 6 *vs.* the time gave straight lines for all the electron-transfer reactions within three half-lives.

The dependence of the observed rate constants on the hydrogen-ion concentrations was examined for all the electron-transfer reactions studied. Except for the reaction of $\mathrm{Co(NH_3)_5(H_2O)^{3+}}$ with $\mathrm{Cr^{II}(hedtra)(H_2O)^-}$, the observed rate constants were found to be independent of the hydrogen-ion concentrations under the present experimental conditions.

Results

Reaction of $\mathrm{Co(NH_3)_5(H_2O)^{3+}}$ *with* $\mathrm{Cr^{II}(hedtra)(H_2O)^-}$. The observed rate constants(k_{obsd}) of the electron-transfer reaction were dependent on the hydrogen-ion concentrations, as is shown in Table 1. The plots of k_{obsd} *vs.* $[\mathrm{H^+}]^{-1}$ give a good linear relation. Therefore, the reaction obeys the rate law given in Eqs. 7 and 8:

$$\frac{d[\mathrm{Cr(III)\text{-}HEDTRA}]}{dt} = k_{\mathrm{obsd}}[\mathrm{Co(III)}][\mathrm{Cr(II)}], \tag{7}$$

$$k_{\mathrm{obsd}} = \frac{a}{[\mathrm{H^+}]} + b. \tag{8}$$

The values of a and b were determined to be 12.5± 0.5 s^{-1} and (1.30±0.10) × 10^5 M^{-1} s^{-1} respectively. No absorbance change subsequent to the electron-transfer reaction was observed.

TABLE 1. THE ACID DEPENDENCE OF THE OBSERVED SECOND-ORDER RATE CONSTANT FOR THE REACTION OF $\mathrm{Co(NH_3)_5(H_2O)^{3+}}$ WITH $\mathrm{Cr^{II}(hedtra)(H_2O)^-}$

$[\mathrm{Co(III)}]_0$ / 10^{-3} M	$[\mathrm{Cr(II)}]_0$ / 10^{-3} M	$[\mathrm{H^+}]$ / 10^{-5} M	k_{obsd} / 10^5 M^{-1} s^{-1}
2.36	1.52	1.99	7.51±0.17
2.37	1.76	3.15	5.40±0.25
2.32	1.53	5.73	3.98±0.18
2.34	1.60	6.14	3.43±0.10
2.30	1.25	7.21	3.01±0.09
4.73	4.02	7.21	2.60±0.11
2.37	1.23	37.8	1.60±0.04
2.29	1.39	47.6	1.51±0.10

Reactions of $\mathrm{Co(en)_3^{3+}}$ *with* $\mathrm{Cr^{II}(hedtra)(H_2O)^-}$ *and* $\mathrm{Cr^{II}(edta)(H_2O)^{2-}}$. The rate constants of the electron-transfer reactions(k_{et}) are given in Table 2.

Reaction of $\mathrm{Co(NCS)(NH_3)_5^{2+}}$ *with* $\mathrm{Cr^{II}(hedtra)(H_2O)^-}$. The rate constant of the electron-transfer reaction of $\mathrm{Co(NCS)(NH_3)_5^{2+}}$ with $\mathrm{Cr^{II}(hedtra)(H_2O)^-}$ was determined and is given in Table 2. The electron-transfer reaction was found to be practically completed within 50 ms under the present experimental conditions. After this rapid reaction had been completed, the spectrum changed slowly, as is shown in Fig. 1. The absorption maxima of the immediate chromium(III) species produced by the electron-transfer reaction initially shifted to shorter wavelengths and then to longer wavelengths. These spectral changes indicate that the immediate chromium(III) species is converted to some other species in a complicated manner.

Reaction of $\mathrm{CoBr(NH_3)_5^{2+}}$ *with* $\mathrm{Cr^{II}(hedtra)(H_2O)^-}$. The electron-transfer reaction of this system was found to be completed within the time of mixing (<0.5 ms), so the k_{et} value was estimated to be more than 1 × 10^6 M^{-1} s^{-1}. The spectrum obtained immediately after the electron-transfer reaction (Curve A in Fig. 2) changed to that of $\mathrm{Cr^{III}(hedtra)(H_2O)}$ (Curve B in Fig. 2) with the time scale of s, and the reaction was practically completed within 4 s. This spectral change obeyed the first-order kinetics; hence, the conventional plots, $\ln|A_t-A_\infty|$ *vs.* t at 430 nm, gave a linear relation

TABLE 2. THE SECOND-ORDER RATE CONSTANTS ($k_{\mathrm{et}}/M^{-1}\,s^{-1}$) FOR THE ELECTRON-TRANSFER REACTIONS OF COBALT(III) COMPLEXES WITH CHROMIUM(II) COMPLEXES

Oxidant	Reductant			Rate ratio	
	$\mathrm{Cr^{II}(hedtra)(H_2O)^-}$	$\mathrm{Cr^{II}(edta)(H_2O)^{2-}}$	$\mathrm{Cr(H_2O)_6^{2+}}$	$\frac{k(\mathrm{Cr\text{-}hedtra})}{k(\mathrm{Cr})}$	$\frac{k(\mathrm{Cr\text{-}edta})}{k(\mathrm{Cr})}$
$\mathrm{Co(en)_3^{3+}}$	$(3.14\pm0.16)\times10^{3}$ a)	$(4.24\pm0.22)\times10^{3}$ a)	3.4×10^{-4} b)	9×10^{6}	1×10^{7}
$\mathrm{Co(OAc)(NH_3)_5^{2+}}$	$(3.06\pm0.18)\times10^{4}$ c)	1.0×10^{4} c)	0.35 d)	9×10^{4}	3×10^{4}
$\mathrm{Co(NCS)(NH_3)_5^{2+}}$	$(1.19\pm0.08)\times10^{5}$ a)	—	19 e)	6×10^{3}	—
$\mathrm{Co(NH_3)_5(H_2O)^{3+}}$	$(1.3\pm0.1)\times10^{5}$ a)	—	<0.1 f)	$>1\times10^{6}$	—
$\mathrm{Co(OH)(NH_3)_5^{2+}}$	$(2.06\pm0.13)\times10^{7}$ a)	—	5.2×10^{6} f)	4	—
$\mathrm{CoCl(NH_3)_5^{2+}}$	$>1\times10^{6}$ a)	—	$(2.6\pm0.5)\times10^{6}$ g)	>0.4	—
$\mathrm{CoBr(NH_3)_5^{2+}}$	$>1\times10^{6}$ a)	—	$(1.4\pm0.4)\times10^{6}$ g,h)	>0.7	—

a) This work. b) Ref. 18. c) Ref. 8. d) Ref. 19. e) Ref. 20. f) Ref. 21. g) Ref. 22. h) at I=0.1 ($\mathrm{NaClO_4}$).

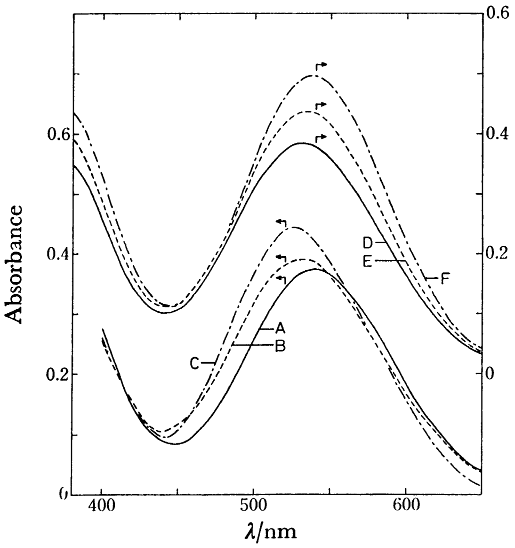

Fig. 1. Spectral changes after the electron-transfer reaction of $\mathrm{Co(NCS)(NH_3)_5^{2+}}$ with $\mathrm{Cr^{II}(hedtra)(H_2O)^-}$ at $[\mathrm{H^+}]=1.99\times10^{-4}$ M, $[\mathrm{Co(NCS)(NH_3)_5^{2+}}]_0=2.25\times10^{-3}$ M, $[\mathrm{Cr^{II}(hedtra)(H_2O)^-}]_0=1.76\times10^{-3}$ M, and cell length = 1 cm. Curves A, B, C, D, E, and F show the spectra obtained at $t=0.25$ s, 60 s, 120 s, 5 h, 49 h, and 147 h after the mixing respectively. The absorptions due to $\mathrm{Co(NCS)(NH_3)_5^{2+}}$ unreacted and $\mathrm{Co^{II}(hedtra)(H_2O)^-}$ produced are subtracted.

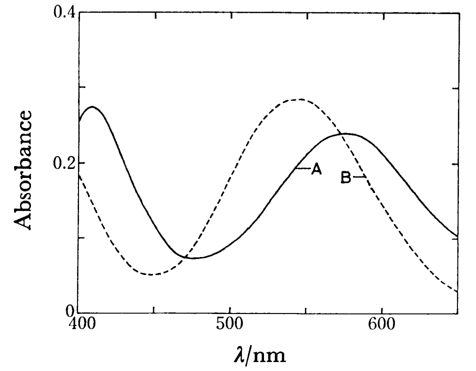

Fig. 2. Spectra obtained after the electron-transfer reaction of $\mathrm{CoBr(NH_3)_5^{2+}}$ with $\mathrm{Cr^{II}(hedtra)(H_2O)^-}$ at $[\mathrm{H^+}]=1.73\times10^{-5}$ M, $[\mathrm{CoBr(NH_3)_5^{2+}}]_0=4.00\times10^{-3}$ M, $[\mathrm{Cr^{II}(hedtra)(H_2O)^-}]_0=1.89\times10^{-3}$ M, and cell length = 1 cm. Curves A and B show the spectrum extraporated to $t=0$ and that obtained at $t=25$ s after the mixing respectively. The absorptions due to $\mathrm{CoBr(NH_3)_5^{2+}}$ unreacted and $\mathrm{Co^{II}(hedtra)(H_2O)^-}$ produced are subtracted.

within two half-lives. The observed rate constant was 2.0 s^{-1}. Therefore, the over-all reactions can be expressed in two stages given in Eqs. 9 and 10:

$$\mathrm{CoBr(NH_3)_5^{2+} + Cr^{II}(hedtra)(H_2O)^-} \xrightarrow[\text{immeasurably fast}]{k_{\mathrm{et}}} \mathrm{Co(II)} + \text{Intermediate of }\mathrm{Cr(III)}, \tag{9}$$

$$\text{Intermediate of }\mathrm{Cr(III)} \xrightarrow[2.0\,\mathrm{s^{-1}}]{} \mathrm{Cr^{III}(hedtra)(H_2O)}. \tag{10}$$

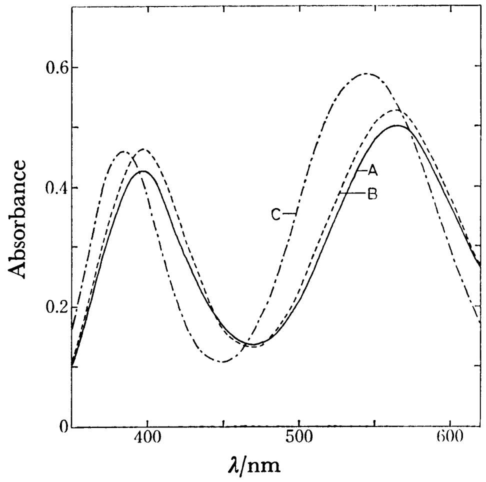

Fig. 3. Spectra obtained after the electron-transfer reaction of $\mathrm{CoCl(NH_3)_5^{2+}}$ with $\mathrm{Cr^{II}(hedtra)(H_2O)^-}$ at $[\mathrm{H^+}]=1.14\times10^{-5}$ M, $[\mathrm{CoCl(NH_3)_5^{2+}}]_0=4.83\times10^{-3}$ M, $[\mathrm{Cr^{II}(hedtra)(H_2O)^-}]_0=3.91\times10^{-3}$ M, and cell length = 1 cm. Curves A, B, and C show the spectra obtained at $t=0$, 0.12, and 10 s after the mixing. The absorptions due to $\mathrm{CoCl(NH_3)_5^{2+}}$ unreacted and $\mathrm{Co^{II}(hedtra)(H_2O)^-}$ produced are subtracted.

Reaction of $\mathrm{CoCl(NH_3)_5^{2+}}$ *with* $\mathrm{Cr^{II}(hedtra)(H_2O)^-}$. The electron-transfer reaction of this system was found to be completed within the time of mixing. The spectrum obtained immediately after the electron-transfer reaction did not change to that of $\mathrm{Cr^{III}(hedtra)(H_2O)}$ directly. Figure 3 shows the spectral changes subsequent to the electron-transfer reaction of $\mathrm{CoCl(NH_3)_5^{2+}}$ with $\mathrm{Cr^{II}(hedtra)(H_2O)^-}$. The final spectrum, obtained 10 s after the electron-transfer reaction, was found to correspond to the absorption of $\mathrm{Cr^{III}(hedtra)(H_2O)}$. The spectral changes shown in Fig. 3 can be reasonably explained by the occurrence of the following reactions:

$$\mathrm{CoCl(NH_3)_5^{2+} + Cr^{II}(hedtra)(H_2O)^-} \xrightarrow[\text{immeasurably fast}]{k_{\mathrm{et}}} + \text{Intermediate (A) of }\mathrm{Cr(III)}\ (\mathrm{Int_A}), \tag{11}$$

$$\mathrm{Int_A} \xrightarrow{k_{\mathrm{A}}} \text{Intermediate (B) of }\mathrm{Cr(III)}\ (\mathrm{Int_B}), \tag{12}$$

$$\mathrm{Int_B} \xrightarrow{k_{\mathrm{B}}} \mathrm{Cr^{III}(hedtra)(H_2O)}. \tag{13}$$

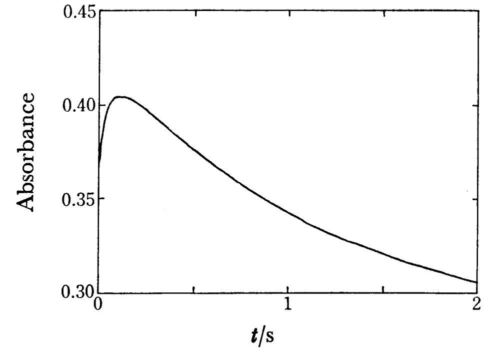

Fig. 4. The change of absorbance with time for the reactions subsequent to the electron-transfer reaction of $\mathrm{CoCl(NH_3)_5^{2+}}$ with $\mathrm{Cr^{II}(hedtra)(H_2O)^-}$ at 420 nm, $[\mathrm{H^+}]=1.14\times10^{-5}$ M, $[\mathrm{CoCl(NH_3)_5^{2+}}]_0=4.83\times10^{-3}$ M, $[\mathrm{Cr^{II}(hedtra)(H_2O)^-}]_0=3.91\times10^{-3}$ M, and cell length = 1 cm.

TABLE 3. THE RATE CONSTANTS OF REACTION 12 ($k_{\rm A}$) AND REACTION 13 ($k_{\rm B}$)

$[{\rm Cr}]_{\rm T}$ / 10^{-3} M	$[{\rm H}^+]$ / 10^{-5} M	T / °C	$k_{\rm A}$ / $\rm s^{-1}$	$k_{\rm B}$ / $\rm s^{-1}$
1.32	2.23	20.7	14.0 ± 1.3	0.469 ± 0.016
1.77	0.635	25.0	—	0.741 ± 0.012
2.01	2.81	25.0	13.0 ± 1.0	0.670 ± 0.036
2.18	7.91	25.0	—	0.681 ± 0.015
1.89	3.15	34.8	29.7 ± 4.3	$1.44\ \pm0.03$
2.24	3.15	47.1	65 ± 16	$3.14\ \pm0.11$

The change in the absorbance against time at 420 nm is exemplified in Fig. 4. The initial increase in the absorbance was assigned to the occurrence of Reaction 12, and the subsequent decrease in the absorbance, to that of Reaction 13. In accordance with these assignments, both the absorbance changes fit the first-order kinetics. The rate constant of Reaction 12 ($k_{\rm A}$) was determined at 390 and 567 nm, while that of Reaction 13 ($k_{\rm B}$) was determined at 420 and 510 nm. The values thus obtained are given in Table 3.

Discussion

Mechanism of the Reaction of $Co(NH_3)_5(H_2O)^{3+}$ with $Cr^{II}(hedtra)(H_2O)^-$. The observed second-order rate constants were considerably dependent on $[{\rm H}^+]$, as is expressed in Eq. 8. If the acid-base equilibria for $\rm Cr^{II}(hedtra)(H_2O)^-$ and $\rm Co(NH_3)_5(H_2O)^{3+}$ are taken into consideration, the reaction in question can be expressed as the following four parallel reactions:

$$\rm Co(OH)(NH_3)_5{}^{2+} + Cr^{II}(hedtra)(H_2O)^- \xrightarrow{k_1} products, \tag{14}$$

$$\rm Co(NH_3)_5(H_2O)^{3+} + Cr^{II}(hedtra)(H_2O)^- \xrightarrow{k_2} products, \tag{15}$$

$$\rm Co(OH)(NH_3)_5{}^{2+} + Cr^{II}(Hhedtra)(H_2O)_2 \xrightarrow{k_3} products \tag{16}$$

$$\rm Co(NH_3)_5(H_2O)^{3+} + Cr^{II}(Hhedtra)(H_2O)_2 \xrightarrow{k_4} products. \tag{17}$$

Then, the following equation can be derived for the observed rate constant:

$$k_{\rm obs} = \frac{\dfrac{k_1K^{\rm H}_{\rm Co}}{[{\rm H}^+]} + k_2 + \dfrac{k_3K^{\rm H}_{\rm Co}}{K^{\rm H}_{\rm Cr}} + \dfrac{k_4[{\rm H}^+]}{K^{\rm H}_{\rm Cr}}}{\left(1+\dfrac{K^{\rm H}_{\rm Co}}{[{\rm H}^+]}\right)\left(1+\dfrac{[{\rm H}^+]}{K^{\rm H}_{\rm Cr}}\right)}, \tag{18}$$

where k_1—k_4 denote the rate constants of Reactions 14—17 and where $K^{\rm H}_{\rm Co}$ and $K^{\rm H}_{\rm Cr}$ are defined as the equilibrium constants given by Eqs. 19 and 20 respectively:

$$K^{\rm H}_{\rm Co} = \frac{[{\rm H}^+][{\rm Co(OH)(NH_3)_5{}^{2+}}]}{[{\rm Co(NH_3)_5(H_2O)^{3+}}]}, \tag{19}$$

$$K^{\rm H}_{\rm Cr} = \frac{[{\rm H}^+][{\rm Cr^{II}(hedtra)(H_2O)^-}]}{[{\rm Cr^{II}(Hhedtra)(H_2O)_2}]}. \tag{20}$$

Although the value of $K^{\rm H}_{\rm Cr}$ has not been reported, it may be estimated to be approximately $10^{-2.5}$ M from the corresponding values of the related complexes.[23] The value of $K^{\rm H}_{\rm Co}$ has been reported to be $10^{-6.22}$ M at $I=0.3$ and 25 °C.[24] If the range of $[{\rm H}^+]$ values employed in this work ($2\times10^{-5}\ {\rm M}<[{\rm H}^+]<5\times10^{-4}$ M) and the magnitudes of $K^{\rm H}_{\rm Cr}$ and $K^{\rm H}_{\rm Co}$ values are taken into consideration, Eq. 18 can be simplified to

$$k_{\rm obs} = \frac{k_1K^{\rm H}_{\rm Co}}{[{\rm H}^+]} + k_2 + \frac{k_3K^{\rm H}_{\rm Co}}{K^{\rm H}_{\rm Cr}} + \frac{k_4[{\rm H}^+]}{K^{\rm H}_{\rm Cr}}. \tag{21}$$

When Eq. 21 is compared with Eq. 8, it is evident that the last term on the right-hand side of Eq. 21 is negligibly small. The value of k_1 is calculated to be $(2.06\pm0.13)\times10^7\ \rm M^{-1}\,s^{-1}$. The value of b in Eq. 8 corresponds to the relation

$$b = k_2 + \frac{k_3K^{\rm H}_{\rm Co}}{K^{\rm H}_{\rm Cr}}. \tag{22}$$

This provides an example of a so-called proton ambiguity.[25,26] It would be reasonable to assume that the rate constant of the reaction of $\rm Co(OH)(NH_3)_5{}^{2+}$ with $\rm Cr^{II}(hedtra)(H_2O)^-$ (k_1) is larger than that with $\rm Cr^{II}(Hhedtra)(H_2O)_2$ (k_3), because, in a closely related system, it has been shown that $\rm Cr^{II}Y(H_2O)^{(n-2)-}$ is more reactive than its protonated form, $\rm Cr^{II}(HY)(H_2O)^{(n-3)-}$; that is, the reaction of $\rm Cr(OH)(NH_3)_5{}^{2+}$ with $\rm Cr^{II}(edta)(H_2O)^{2-}$ has been found to proceed much faster than that with $\rm Cr^{II}(Hedta)(H_2O)^-$.[3] Even if k_3 is equal to k_1, the value of $k_3K^{\rm H}_{\rm Co}/K^{\rm H}_{\rm Cr}$ amounts to $4\times10^3\ \rm M^{-1}\,s^{-1}$, whose contribution to the b value of Eq. 22 is only a small percentage. Hence the b value is considered to represent k_2 value itself.

Mechanisms of the Electron-transfer Reactions. The rate constants of the electron-transfer reactions of Co(III) complexes with $\rm Cr^{II}Y(H_2O)^{(n-2)-}$ are summarized in Table 2, together with those with $\rm Cr(H_2O)_6{}^{2+}$. Among them, the reactions of $\rm Co(en)_3{}^{3+}$ with Cr(II) complexes are considered to proceed through an outer-sphere mechanism, because $\rm Co(en)_3{}^{3+}$ has no bridging ligand.

On the bases of the extremely low basicity of a coordinated water molecule and a consideration of Marcus' cross reaction equation,[27] it has been proposed that water coordinated to a metal ion does not act as a bridging ligand in reduction by $\rm Cr(H_2O)_6{}^{2+}$.[21] This proposal can be tested by a similar consideration of whether or not the electron-transfer reaction of $\rm Co(NH_3)_5(H_2O)^{3+}$ with $\rm Cr^{II}(hedtra)(H_2O)^-$ is of an outer-sphere type. According to Marcus' theory, the rate constant (k_{12}) of a cross reaction

$$\rm Oxidant_1 + Reductant_2 \xrightarrow{k_{12}} Reductant_1 + Oxidant_2 \tag{23}$$

can be given as

$$k_{12} = \sqrt{k_{11}k_{22}K_{12}f}, \tag{24}$$

where k_{11} and k_{22} denote the rate constants of the exchange reactions; K_{12}, the equilibrium constant of Reaction 23; $\ln f = (\ln K_{12})^2/\{4\ln(k_{11}k_{22}/Z^2)\}$, and Z, the collision frequency. If Eq. 24 is compared for the two oxidants 1 and 1′, say $\rm Co(NH_3)_5(H_2O)^{3+}$ and $\rm Co(en)_3{}^{3+}$, and a common reductant 2, the ratio of the rate constants can be expressed as

$$\frac{k_{12}}{k_{1'2}} = \sqrt{\frac{k_{11}}{k_{1'1'}}K_{11'}}, \tag{25}$$

TABLE 4. COMPARISON OF THE RATE CONSTANTS OF THE ELECTRON-TRANSFER REACTIONS OF $Co(NH_3)_5(H_2O)^{3+}$ AND $Co(en)_3^{3+}$ WITH VARIOUS REDUCTANTS

Reductant	$k_{et}/M^{-1}\,s^{-1}$		Rate ratio
	$Co(NH_3)_5(H_2O)^{3+}$	$Co(en)_3^{3+}$	$k(Co(NH_3)_5(H_2O)^{3+})/k(Co(en)_3^{3+})$
$Cr^{II}(hedtra)(H_2O)^-$	1.3×10^5 a)	3.14×10^3 a)	41
$Cr(bpy)_3^{2+}$	5×10^4 b,c)	1.8×10^2 b,c)	2.8×10^2
$Eu(H_2O)_6^{2+}$	1.5×10^{-1} b)	$\approx5\times10^{-3}$ b)	≈30
$V(H_2O)_6^{2+}$	5.3×10^{-1} d)	7.2×10^{-4} e)	7.4×10^2

a) This work. b) Ref. 20. c) at $I=0.1$ ($NaClO_4$). d) Ref. 28. e) Ref. 18.

where the f terms are ignored or considered to be cancelled. Equation 25 indicates that the rate ratio of $k_{12}/k_{1'2}$ is dependent only on the properties of the two oxidants 1 and 1′. The values of the rate ratios for the reductions of $Co(NH_3)_5(H_2O)^{3+}$ and $Co(en)_3^{3+}$ with various reductants are summarized in Table 4; they are quite similar to one another. This may support the thought that the $Cr^{II}(hedtra)(H_2O)^-$ reduction of $Co(NH_3)_5(H_2O)^{3+}$ is of an outer-sphere type.

It has been reported previously that the immediate chromium(III) product of the electron-transfer reaction of $Co(OAc)(NH_3)_5^{2+}$ with $Cr^{II}(hedtra)(H_2O)^-$ is $Cr^{III}(OAc)(hedtra)^-$ and that the inner-sphere electron-transfer is the dominant path of this reaction.[8] It would be reasonable to consider that the intermediate given in Eq. 9 is $Cr^{III}Br(hedtra)^-$. When it is assumed that the reaction proceeds exclusively through an inner-sphere mechanism, the absorption spectrum of $Cr^{III}Br(hedtra)^-$ can be estimated from the spectrum measured immediately after the electron-transfer reaction (see Fig. 2). The spectral data thus obtained and those of the related chromium(III) and cobalt(III) complexes are listed in Table 5. It is well known that the spectral shapes and absorption positions of the d-d bands of chromium(III) complexes are quite similar to those of the corresponding cobalt(III) complexes. The d-d absorption bands of the intermediate in question shift to longer wavelengths than those of $Cr^{III}(hedtra)(H_2O)$. A comparison of the data given in Table 5 will indicate that the assignment of the intermediate to $Cr^{III}Br(hedtra)^-$ is reasonable.

The intermediate formed by the reaction of $CoCl(NH_3)_5^{2+}$ with $Cr^{II}(hedtra)(H_2O)^-$(Int_A) was found to be converted into another intermediate, Int_B, and finally into $Cr^{III}(hedtra)(H_2O)$ (see Eqs. 11—13). The spectral data of Int_A and Int_B, both given in Table 5, are very similar to each other, and so it is not unreasonable to conclude that both of the intermediates are $Cr^{III}Cl(hedtra)^-$. However, data sufficient to characterize the structural difference between these two intermediates are not available at present.

TABLE 5. ABSORPTION MAXIMA (λ) AND MOLAR ABSORPTION COEFFICIENTS (ε) OF CHROMIUM(III) AND COBALT(III) COMPLEXES OF THE $M^{III}X(hedtra)^{n-}$ TYPE

Complex	$\lambda/nm(\varepsilon/M^{-1}\,cm^{-1})$		Ref.
	First band	Second band	
$Cr(hedtra)(H_2O)$	545 (151)	385 (117)	9
$Co(hedtra)(H_2O)$	544 (245)	383 (197)	29
$Cr(NCS)(hedtra)^-$	535 (187)	392 (110)	12
$Cr(N_3)(hedtra)^-$	552 (207)	407 (130)	10
$Cr(OAc)(hedtra)^-$	556 (162)	394 (113)	9
$CrCl(hedtra)^-$ (Int_A)a)	565 (128)	397 (109)	This work
$CrCl(hedtra)^-$ (Int_B)a)	563 (136)	398 (121)	This work
$CoCl(hedtra)^-$	585 (278)	403 (251)	30
$CrBr(hedtra)^-$ a)	575 (127)	408 (145)	This work
$CoBr(hedtra)^-$	588 (241)	400 (243)	30

a) The spectral data were estimated on the assumption that the electron-transfer reaction of $CoCl(NH_3)_5^{2+}$ or $CoBr(NH_3)_5^{2+}$ with $Cr^{II}(hedtra)(H_2O)^-$ proceeds exclusively through the inner-sphere mechanism.

If the electron-transfer reaction of $Co(NCS)(NH_3)_5^{2+}$ with $Cr^{II}(hedtra)(H_2O)^-$ is of an outer-sphere type, the immediate product should be $Cr^{III}(hedtra)(H_2O)$. However, the spectrum of the immediate chromium(III) product in the electron-transfer reaction does not agree with that of $Cr^{III}(hedtra)(H_2O)$. This suggests that the possibility of an outer-sphere mechanism can be ruled out. The reactions of $Co(NCS)(NH_3)_5^{2+}$ and $Co(SCN)(NH_3)_5^{2+}$ with $Cr(H_2O)_6^{2+}$ have been observed to give $Cr(SCN)(H_2O)_5^{2+}$ and a mixture of $Cr(SCN)(H_2O)_5^{2+}$ and $Cr(NCS)(H_2O)_5^{2+}$ respectively.[31] Therefore, if the electron-transfer reaction of the present system proceeds through only an inner-sphere mechanism, it would be possible to assume the formation of $Cr^{III}(SCN)(hedtra)^-$ and/or $Cr^{III}(NCS)(hedtra)^-$. From independent experiments,[12] the reaction of $Cr^{III}(hedtra)(H_2O)$ with NCS^- was found to occur quite rapidly and reversibly as

$$Cr^{III}(hedtra)(H_2O) + NCS^- \rightleftharpoons Cr^{III}(NCS)(hedtra)^- + H_2O. \qquad (26)$$

The absorption positions and intensities of the $Cr^{III}(NCS)(hedtra)^-$, which were determined from the equilibrium study of Reaction 26, are also given in Table 5. The spectrum of the immediate chromium(III) product in the present system does not agree with that of $Cr^{III}(NCS)(hedtra)^-$. The spectral changes after the electron-transfer reaction shown in Fig. 1 are very slow. This also indicates that the immediate product is not $Cr^{III}(NCS)(hedtra)^-$. Although the complicated spectral changes after the electron-transfer reaction cannot be explained thoroughly, the over-all features of the reaction of $Co(NCS)(NH_3)_5^{2+}$ with $Cr^{II}(hedtra)(H_2O)^-$ suggest that the reaction proceeds through an inner-sphere mechanism to give $Cr^{III}X(hedtra)^{n-}$, where X is an unidentified ligand.

Rate Constants of the Electron-transfer Reactions. In the previous papers,[2,3] it was reported that Cr^{II}-

(edta)$(H_2O)^{2-}$ reacts with $CrX(NH_3)_5^{2+}$ ($X=F^-$, Cl^-, Br^-, NCS^-, and OH^-) much faster than $Cr(H_2O)_6^{2+}$ does, and this was explained by considering the change in the standard oxidation-reduction potentials of the Cr(II)–Cr(III) couples. Recently, Davies and Earley reported that the electron-transfer reactions of $CrCl(NH_3)_5^{2+}$ with some Cr(II)–amino polycarboxylate complexes followed the linear free-energy relationship with the slope ($\Delta\Delta G^{*}/\Delta\Delta G^{\circ}$) of 0.48, where $\Delta\Delta G^{*}$ and $\Delta\Delta G^{\circ}$ denote the change in the free energy of activation of the electron-transfer reactions and the free-energy difference between the chromium(II) and chromium(III) species respectively.[5] The data given in Table 2 show that the rate constants of the electron-transfer reactions of the cobalt(III) complexes with $Cr^{II}(hedtra)(H_2O)^-$ and $Cr^{II}(edta)(H_2O)^{2-}$ are larger than those of the corresponding reactions with $Cr(H_2O)_6^{2+}$. This rate enhancement may also be understood qualitatively by considering the free-energy change in the reactions. If the electron-transfer reactions of a common cobalt(III) complex with $Cr^{II}L(H_2O)^{(n-2)-}$ and $Cr(H_2O)_6^{2+}$ follow the linear free-energy relationship with the slope of 0.5, 6×10^4 and 7×10^4 may be expected for the values of k(Cr-hedtra)/k(Cr) and k(Cr-edta)/k(Cr) respectively. Among the data shown in Table 2, the observed values of $Co(en)_3^{3+}$, $Co(NH_3)_5(H_2O)^{3+}$, and $Co(OH)(NH_3)_5^{2+}$ deviate considerably from the expected values. This may suggest that the assumption mentioned above is not satisfied for, at least, these systems, and that the other factors controlling the rates should be considered. The observed value for $Co(OH)(NH_3)_5^{2+}$ may be nearly a rate limit in the inner-sphere electron-transfer reactions containing Cr(II) ions as reductants.[32] This leads to the understanding that the free-energy change in the reaction by the coordination of HEDTRA to Cr(II) affects only slightly the rate of electron-transfer for, at least, the $Co(OH)(NH_3)_5^{2+}$ system.

Aquation Reactions of $Cr^{III}Cl$(hedtra)$^-$ and $Cr^{III}Br$(hedtra)$^-$ Subsequent to the Electron-transfer Reactions. It has been shown previously that the water position in the Cr^{III}(hedtra)(H_2O) is a substitution-labile site.[9,10] This has been so postulated that the free $-CH_2CH_2OH$ existing in the complex ion acts as a nucleophile and catalyzes the substitution. It was found in this work that $Cr^{III}Cl$(hedtra)$^-$ and $Cr^{III}Br$(hedtra)$^-$ also aquate rapidly to give Cr^{III}(hedtra)(H_2O). However, no formation of $Cr^{III}Cl$(hedtra)$^-$ or $Cr^{III}Br$(hedtra)$^-$ was observed upon the addition of an NaCl or NaBr solution up to a 1 M to Cr^{III}(hedtra)(H_2O) solution. This may allow one to estimate that the formation constants of these mixed ligand complexes are less than 0.1 M^{-1}. The Eyring plot for the rate constants of the aquation reaction of $Cr^{III}Cl$(hedtra)$^-$ (the k_2 values are given in Table 3) gives activation parameters of $\Delta H^{*}=53.9\pm3.3$ kJ mol^{-1} and $\Delta S^{*}=-68\pm11$ J K^{-1} mol^{-1}. The large negative entropy of activation suggests an associative nature in the mechanism of this aquation reaction.

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1) The following abbreviations are used throughout the paper: HEDTRA=*N*-(2-hydroxyethyl)ethylenediamine-*N,N′,N′*-triacetic acid, EDTA=ethylenediamine-*N,N,N′,N′*-tetraacetic acid, L=hedtra^{3-} or edta^{4-}, OAc^-=acetate, and en=ethylenediamine.

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