volume of ice-cold water, and charged onto a column of Sephadex SP-C25 at 4 °C. The products were eluted by using 0.10 M $HClO_4$ with increasing concentrations of $NaClO_4$. The total cobalt and chromium concentrations were determined in each fraction, and the electronic spectrum was recorded whenever possible. The observations are summarized in Table II.

The total chromium in bands 1 through 3 is 2.87×10^{-4} mol. This amount should equal the 2.3×10^{-4} mol required for iodide abstraction. The excess $Cr(OH_2)_6^{3+}$ is believed to come as a minor product of air oxidation of chromium(II). For the expected overall stoichiometry, $2 \times 2.3 \times 10^{-4}$ mol of chromium(II) should be consumed leaving an excess of 5.0×10^{-4} mol. Previous experience indicates that about 10% of the latter will appear as $Cr(OH_2)_6^{3+}$ after air oxidation. Therefore, the total chromium in bands 1 through 3 can be corrected to give $2.87 \times 10^{-4} - 0.5 \times 10^{-4} = 2.4 \times 10^{-4}$ mol of chromium consumed by the first reaction, in good agreement with the 2.3×10^{-4} mol expected.

Products of Acidolysis of II. Ion-exchange separation of the reaction products on Sephadex SP-C25 at 5 °C revealed two products. The first to elute with 0.1 M H^+ + 0.7 M $NaClO_4$ was pink and has absorbance maxima at 414 and 510 nm with absorption coefficients of 82.7 and 63.9 M^{-1} cm^{-1}, respectively (based on Cr analysis). The second product was eluted with 0.1 M $HClO_4$ and 1.1 M $NaClO_4$ and was greenish yellow. The absorbance maxima are at 340, 470, and 600 nm with absorption coefficients of 66.9, 70.4, and 34.4 M^{-1} cm^{-1}, respectively.

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Registry No. I, 111410-16-3; II, 111410-17-4; III, 111410-18-5; IV, 111410-19-6; V, 111410-20-9; VII, 42947-06-8; IX, 88157-86-2; $[(H_3N)_5CoNH_2C(O)CH_2I](ClO_4)_3$, 111410-15-2; $(H_2O)_5CrI^{2+}$, 18955-06-1; $Cr(H_2O)_6^{3+}$, 14873-01-9; $(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4^{4+}$, 23852-05-3; $(H_3N)_5CoNH(OH)CCH_3^{3+}$, 51538-47-7; Cr^{2+}, 22541-79-3; Hg^{2+}, 14302-87-5.

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Kinetics and Mechanism of Reduction of Pentaamminecobalt(III) Complexes, $[CoX(NH_3)_5]^{2+}$ (X = F, Cl, Br, N_3), by [*N*′-(2-Hydroxyethyl)ethylenediamine-*N*,*N*,*N*′-triacetato]aquavanadium(III)

Hiroshi Ogino,* Makoto Shimura, Noriko Yamamoto, and Nobuyuki Okubo

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[*N*′-(2-Hydroxyethyl)ethylenediamine-*N*,*N*,*N*′-triacetato]aquavanadium(III), $[V(hedtra)(H_2O)]$, was found to reduce $[CoX(NH_3)_5]^{2+}$ (X = F, Cl, Br, N_3) in acidic HEDTRA solutions to give $[VO(hedtra)]^-$ and $[Co(hedtra)(H_2O)]^-$. The reactions obeyed the pseudo-zeroth-order rate law in the presence of excess $[V(hedtra)(H_2O)]$, while the reactions were first order in the presence of excess $[CoX(NH_3)_5]^{2+}$. The kinetic measurements have suggested that the rate of the reaction is controlled by the conversion of $[V(hedtra)(H_2O)]$ to a species ($\{V(hedtra)\}$) that is either the deaquated species or an isomer of the parent $[V(hedtra)(H_2O)]$ and that only $\{V(hedtra)\}$ is reactive toward the electron transfer to the $[CoX(NH_3)_5]^{2+}$ complexes (X = F, Cl, Br, N_3). The averaged rate constant of the conversion of $[V(hedtra)(H_2O)]$ to $\{V(hedtra)\}$, determined by the $[CoX(NH_3)_5]^{2+}$ complexes, was $(3.5 \pm 1.3) \times 10^{-4}$ s^{-1} at $I = 0.10$ (NaCl) and 40.0 °C. For the reaction of $[CoF(NH_3)_5]^{2+}$, the reduction by $[V(hedtra)(H_2O)]$ ($(2.4 \pm 0.4) \times 10^{-2}$ M^{-1} s^{-1}) gives a minor contribution to the electron transfer in addition to the reduction by $\{V(hedtra)\}$. The effect of the halide ligands in the $[CoX(NH_3)_5]^{2+}$ complexes (X = F, Cl, Br) on the rates of reduction by $[V(hedtra)(H_2O)]$ indicates that these reactions form a system showing the so-called "inverse order" for the electron transfer. When excess $[CoX(NH_3)_5]^{2+}$ is allowed to react with $[V(hedtra)(H_2O)]$ in an acidic HEDTRA solution, the electron-transfer reaction between $[CoX(NH_3)_5]^{2+}$ and $[Co(hedtra)(H_2O)]^-$ also occurs in addition to the reaction of $[V(hedtra)(H_2O)]$ with $[CoX(NH_3)_5]^{2+}$. The relative rates of the reactions of $[CoX(NH_3)_5]^{2+}$ with $[Co(hedtra)(H_2O)]^-$ conform to the "normal order".

Introduction

In the course of our continuing efforts to investigate the reactions of transition-metal–polyamino polycarboxylate complexes,[1] we have found that the vanadium(III)–HEDTRA complex $[V(hedtra)(H_2O)]$[2] reduces pentaamminecobalt(III) complexes in acidic HEDTRA buffer solutions (eq 1), whereas the reduction

$$[V(hedtra)(H_2O)] + [CoX(NH_3)_5]^{2+} \rightarrow [VO(hedtra)]^- + Co(II) \quad (1)$$

$$X = F, Cl, Br, N_3$$

of cobalt(III) complexes with V^{3+} is immeasurably slow.[3] The kinetics of reaction 1 showed an anomaly: Reaction 1 obeyed the zeroth-order rate law when $[V(III)]_0 \gg [Co(III)]_0$. Since the zeroth-order reaction has been rarely encountered,[4-11] kinetic studies of reaction 1 were carried out. We also developed the rate equations for analyzing the pseudo-zeroth-order reactions, which have not been discussed in detail previously.[4]

Experimental Section

Materials. $[V(hedtra)(H_2O)]\cdot 2H_2O$. $H_3hedtra$ (3.1 g, 0.011 mol) in 25 mL of water was neutralized with Na_2CO_3 (1.6 g, 0.015 mol). Anhydrous VCl_3 (1.6 g, 0.010 mol) was added to the solution under nitrogen atmosphere. After the solution was stirred for a few minutes, brown $[V(hedtra)(H_2O)]\cdot 2H_2O$ crystallized. The crystals were collected and washed with cold water and acetone. Yield: 3.2 g (85%). Anal. Calcd for $C_{10}H_{21}N_2O_{10}V$: C, 31.59; H, 5.57; N, 7.37. Found: C, 31.54; H, 5.83; N, 7.35.

$K[VO(hedtra)]\cdot 0.25H_2O$. $H_3hedtra$ (2.8 g, 0.010 mol) in 10 mL of water was neutralized with $BaCO_3$ (2.0 g, 0.010 mol). A solution of $VOSO_4 \cdot nH_2O$ (2.9 g, 0.01 mol) in 10 mL of water was added dropwise with stirring to the solution at 80 °C. To this mixture was added 0.79 g of K_2CO_3 (5.0 mmol). After the solution was kept for 30 min at 80 °C, the $BaSO_4$ precipitated was removed by filtration. The filtrate was concentrated to small volume by a rotary evaporator. When ethanol was

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[1] Ogino, H.; Shimura, M. *Adv. Inorg. Bioinorg. Mech.* **1986**, *4*, 107 and references cited therein.

[2] Abbreviations: $edta^{4-}$, ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate; $hedtra^{3-}$, *N*′-(2-hydroxyethyl)ethylenediamine-*N*,*N*,*N*′-triacetate.

[3] Parker, O. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 1313.

[4] The following references (ref 5–11) deal with the zeroth-order or the mixed zeroth- and first-order reactions of metal complexes.

[5] Wilkins, R. G. *The Study of Kinetics and Mechanisms of Transition Metal Complexes*; Allyn and Bacon: Boston, MA, 1974; p 11.

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[7] Yamamoto, K.; Ohashi, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2433.

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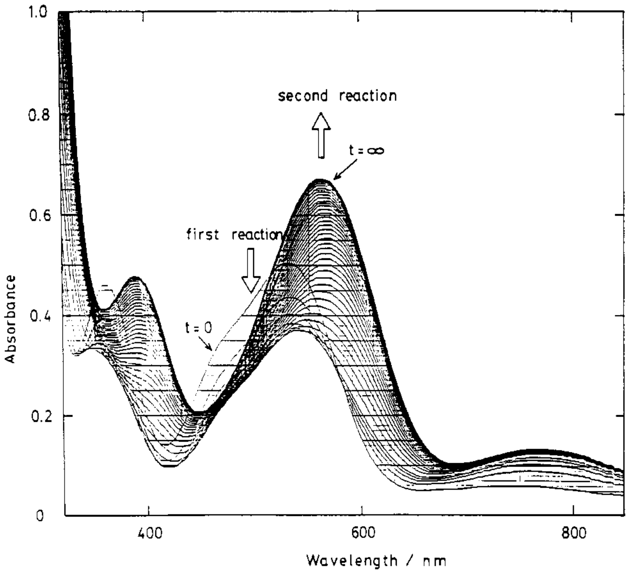

Figure 1. Spectral change of the reaction of $[V(hedtra)(H_2O)]$ with $[CoCl(NH_3)_5]^{2+}$. Time intervals are 10 min for the first reaction (five spectra) and 30 min for the second reaction. $[V(III)]_0 = 4.90 \times 10^{-3}$ M; $[Co(III)]_0 = 9.51 \times 10^{-3}$ M; pH = 3.10.

added, blue microcrystals of $K[VO(hedtra)]\cdot 0.25H_2O$ deposited. The crude product was recrystallized from water by the addition of ethanol. Yield: 2.7 g (70%). Anal. Calcd for $C_{10}H_{15.5}KN_2O_{8.25}V$: C, 31.13; H, 4.05; N, 7.26. Found: C, 31.08; H, 4.34; N, 7.41.

The $[V(hedtra)(H_2O)]$ solutions for kinetic measurements were prepared by dissolving VCl_3 in HEDTRA buffer solutions under nitrogen atmosphere. The concentrations of $[V(hedtra)(H_2O)]$ were determined spectrophotometrically.

Cobalt(III) complexes, $[CoF(NH_3)_5](ClO_4)_2$,[12] $[CoCl(NH_3)_5]Cl_2$,[13] $[CoBr(NH_3)_5](ClO_4)_2\cdot H_2O$,[14] and $[Co(N_3)(NH_3)_5]Cl_2$,[15] were prepared by literature methods. Other reagents were used as received.

Kinetic Measurements. Kinetic measurements were made at $I = 0.10$ (NaCl) and 40.0 °C under nitrogen atmosphere. The pH of the solutions was adjusted between 2.5 and 3.7 with 0.055–0.085 M HEDTRA buffer solutions and measured by a Toa HM-20B pH meter. In this pH range, the formation of the V(III)–HEDTRA dimer is negligible.[16] The reactions were initiated by the conventional syringe technique using Teflon or polyethylene tubings instead of stainless steel needles and followed spectrophotometrically by using a Hitachi 330 or a Union-Giken SM401 spectrophotometer. The reactions sometimes proceeded abnormally fast, when stainless steel needles were used to handle solutions. Therefore, care was taken to avoid contact of the reactant solutions with metallic parts. Even with this care, the fluctuations of the rate constants were larger than those obtained generally for many other reactions, though the origin of these fluctuations is not certain.

EPR Measurements. The reaction between $[V(hedtra)(H_2O)]$ and $[CoCl(NH_3)_5]^{2+}$ was followed also by EPR measurements of V(IV). The reaction was allowed to run at 40.0 °C, and the solution was sampled periodically while the visible absorption spectrum was monitored at the same time. The sampled solutions were sealed in EPR tubes (5-mm o.d.) under nitrogen. The EPR spectra were taken at 77 K on a Varian E112 spectrometer operating in the X-band.

Cobalt(II) Analyses. Cobalt(II) formed during the reaction of $[V(hedtra)(H_2O)]$ with $[CoCl(NH_3)_5]^{2+}$ was determined by Kitson's method[17] without the separation of cobalt(II) from the reaction mixture. Species other than cobalt(II) did not interfere with the spectrophotometric determination of cobalt(II).

Results and Discussion

Reaction Profile. When the reactions of $[V(hedtra)(H_2O)]$ with $[CoX(NH_3)_5]^{2+}$ were followed spectrophotometrically, two-step reactions were clearly observed. One example of the spectral changes for the reaction of $[V(hedtra)(H_2O)]$ with $[CoCl(NH_3)_5]^{2+}$ is shown in Figure 1. The two-step reactions can be explained by the occurrence of the consecutive reactions (2) and (3). The occurrence of these reactions was deduced from the

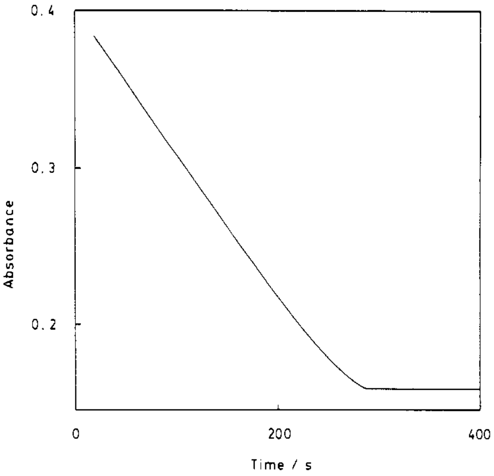

Figure 2. Change of absorbance at 526.5 nm with time for the reaction of $[Co(N_3)(NH_3)_5]^{2+}$ with $[V(hedtra)(H_2O)]$. $[V(III)]_0 = 1.45 \times 10^{-2}$ M; $[Co(III)]_0 = 1.02 \times 10^{-3}$ M; pH = 2.68.

$$\text{first reaction: } [V(hedtra)(H_2O)] + [CoX(NH_3)_5]^{2+} \xrightarrow{H_n(hedtra)^{(3-n)-}} [VO(hedtra)]^- + [Co^{II}(hedtra)(H_2O)]^- \quad (2)$$

$$\text{second reaction: } [Co^{II}(hedtra)(H_2O)]^- + [CoX(NH_3)_5]^{2+} \xrightarrow{H_n(hedtra)^{(3-n)-}} [Co^{III}(hedtra)(H_2O)] + [Co^{II}(hedtra)(H_2O)]^- \quad (3)$$

following observations: (i) Cobalt(II) is formed in the first reaction. (ii) The EPR measurements showed that $[VO(hedtra)]^-$ was the only V(IV) species formed, and the formation of $[VO(hedtra)]^-$ occurred in the first reaction. (iii) The absorption spectrum at the end of the first reaction is consistent with the occurrence of reaction 2. (iv) The spectrum at the end of the second reaction indicated the formation of $[Co(hedtra)(H_2O)]$. The occurrence of reaction 3 was confirmed from independent experiments: When $[Co(hedtra)(H_2O)]^-$ and $[CoX(NH_3)_5]^{2+}$ were mixed in HEDTRA buffer solutions, the spectral changes observed were the same as those obtained for the second reaction. (v) The second reaction becomes invisible with the increase of the initial concentrations of $[V(hedtra)(H_2O)]_0$, because the time to the completion of the first reaction becomes shorter with the increase of $[V(hedtra)(H_2O)]_0$.

The rates of the second reactions varied depending on the nature of the cobalt(III) complexes, as noted later. In this work, only the electron-transfer reactions of the vanadium(III) complex with $[CoX(NH_3)_5]^{2+}$ complexes (eq 2) were investigated in detail, since the reactions were our primary concern.

Reduction of $[Co(N_3)(NH_3)_5]^{2+}$. Reactions 2 and 3 are not perfectly separated from each other. Therefore, reaction 2 (the first reaction) was followed at the isosbestic point observed during the second reaction (526.5 nm). When excess Co(III) was present, the absorbance decreased exponentially with time and obeyed the rate equation (4), where A and A_∞ are the absorbances at time

$$\ln |A - A_\infty| = -k_{obsd}t + \text{const} \quad (4)$$

t and at the completion of the reaction and k_{obsd} is the observed first-order rate constant. When excess V(III) was present, however, the reaction became zeroth order, as depicted in Figure 2. The initial slope of the absorbance vs time curve was proportional to the initial concentrations of $[V(hedtra)(H_2O)]$, as shown in Figure S1.[18]

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(17) Kitson, R. E. *Anal. Chem.* **1950**, *22*, 664.
(18) Supplementary material.

These results can be explained by Scheme I, where k_1, k_{-1}, and k_β are the rate constants for the respective reactions in Scheme I. It is assumed, in Scheme I, that there are two V(III)–hedtra species, specified as [V(hedtra)(H$_2$O)] and {V(hedtra)}, and only {V(hedtra)} reacts with $[Co(N_3)(NH_3)_5]^{2+}$, where {V(hedtra)} denotes either the deaquated species or an isomer of the parent [V(hedtra)(H$_2$O)]. If steady-state approximation is applied to {V(hedtra)} and if $k_\beta[\mathrm{Co(III)}] \gg k_{-1}$, the rate equation

Scheme I

$$[\mathrm{V(hedtra)(H_2O)}] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{\mathrm{V(hedtra)}\}$$

$$\{\mathrm{V(hedtra)}\} + \mathrm{Co(III)} \xrightarrow{k_\beta} \mathrm{V(IV)} + \mathrm{Co(II)}$$

$$-\mathrm{d[Co(III)]}/\mathrm{d}t = k_1[\mathrm{V(III)}] \qquad (5)$$

is obtained. Equation 5 implies that the reaction becomes pseudo zeroth order, if [V(III)] is higher than [Co(III)]. Hence, the initial slope of the absorbance vs time plot should be proportional to $[\mathrm{V(III)}]_0$:

$$-\frac{1}{\Delta\epsilon}\left(\frac{\mathrm{d}A}{\mathrm{d}t}\right)_{t=0} = k_1[\mathrm{V(III)}]_0 \qquad (6)$$

Where

$$\Delta\epsilon = \epsilon_{\mathrm{V(III)}} + \epsilon_{\mathrm{Co(III)}} - \epsilon_{\mathrm{V(IV)}} - \epsilon_{\mathrm{Co(II)}}$$

Integration of eq 5 gives

$$\ln\,([\mathrm{Co(III)}] + [\mathrm{V(III)}]_0 - [\mathrm{Co(III)}]_0) = -k_1t + \ln\,[\mathrm{V(III)}]_0 \qquad (7)$$

which can be converted to

$$\text{for } [\mathrm{Co(III)}]_0 \geq [\mathrm{V(III)}]_0\text{: } \ln|A - A_\infty| = -k_1t + \ln\,(\Delta\epsilon[\mathrm{V(III)}]_0) \qquad (8)$$

$$\text{for } [\mathrm{Co(III)}]_0 \leq [\mathrm{V(III)}]_0\text{: } \ln|A - A_\infty + \Delta\epsilon([\mathrm{V(III)}]_0 - [\mathrm{Co(III)}]_0)| = -k_1t + \ln\,(\Delta\epsilon[\mathrm{V(III)}]_0) \qquad (9)$$

The kinetic traces fitted eq 8 and 9 excellently. The k_1 values determined under various conditions are given in Table S1.[18] The k_1 values did not depend apparently on pH between pH 2.58 and 3.63. The averaged k_1 value was determined to be (3.5 ± 1.1) × 10^{-4} s^{-1}. The value can also be determined by use of eq 6. The value determined from the slope of the plot given in Figure S1[18] was k_1 = (2.7 ± 0.1) × 10^{-4} s^{-1}. This is in good agreement with the value determined by use of eq 8 and 9.

Reduction of $[CoF(NH_3)_5]^{2+}$. As the reaction of $[Co(hedtra)(H_2O)]^-$ with $[CoF(NH_3)_5]^{2+}$ is very slow, the separation between the reactions 2 and 3 is perfect. However, the first reaction (eq 2) did not strictly obey the pseudo-zeroth-order rate law even in the presence of excess [V(hedtra)(H$_2$O)]: The absorbance vs time curve begins to deviate from a straight line at an early stage of the reaction. One example of the kinetic runs is shown in Figure 3. Furthermore, when $[\mathrm{Co(III)}]_0 > [\mathrm{V(III)}]_0$, the rate constants determined by eq 8 increased with the increase of $[\mathrm{Co(III)}]_0 - [\mathrm{V(III)}]_0$.

The first reaction of [V(hedtra)(H$_2$O)] with $[CoF(NH_3)_5]^{2+}$ may be explained by Scheme II, where k_α is the rate constant for the reduction of cobalt(III) complex by [V(hedtra)(H$_2$O)]. This scheme is different from Scheme I in that both [V(hedtra)(H$_2$O)] and {V(hedtra)} react with the cobalt(III) complex. The rate equation for Scheme II is

Scheme II

$$[\mathrm{V(hedtra)(H_2O)}] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{\mathrm{V(hedtra)}\}$$

$$[\mathrm{V(hedtra)(H_2O)}] + \mathrm{Co(III)} \xrightarrow{k_\alpha} \mathrm{V(IV)} + \mathrm{Co(II)}$$

$$\{\mathrm{V(hedtra)}\} + \mathrm{Co(III)} \xrightarrow{k_\beta} \mathrm{V(IV)} + \mathrm{Co(II)}$$

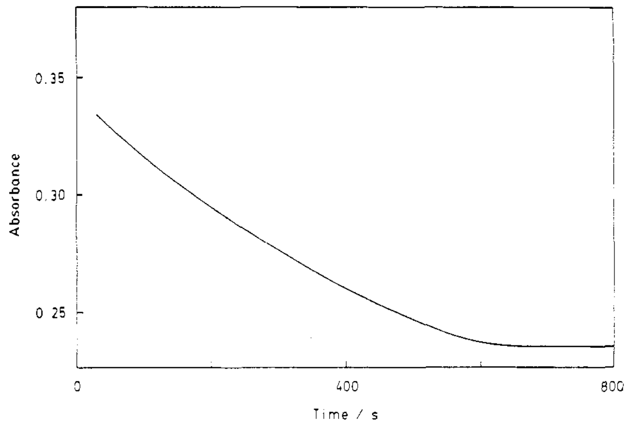

Figure 3. Change of absorbance at 460 nm with time for the reaction of $[CoF(NH_3)_5]^{2+}$ with [V(hedtra)(H$_2$O)]. $[\mathrm{V(III)}]_0 = 1.44 \times 10^{-2}$ M; $[\mathrm{Co(III)}]_0 = 3.01 \times 10^{-3}$ M; pH = 2.74.

$$-\frac{\mathrm{d[Co(III)]}}{\mathrm{d}t} = k_1[\mathrm{V(III)}] + k_\alpha[\mathrm{V(III)}][\mathrm{Co(III)}] \qquad (10)$$

Integration of eq 10 gives

for $[\mathrm{Co(III)}]_0 > [\mathrm{V(II)}]_0$:

$$\ln\frac{A - A_\infty}{A - A_\infty + \Delta\epsilon([\mathrm{Co(III)}]_0 - [\mathrm{V(III)}]_0 + k_1/k_\alpha)} = -\{k_1 + k_\alpha([\mathrm{Co(III)}]_0 - [\mathrm{V(III)}]_0)\}t + \ln\frac{[\mathrm{V(III)}]_0}{[\mathrm{Co(III)}]_0 + k_1/k_\alpha} \qquad (11)$$

for $[\mathrm{V(III)}]_0 > [\mathrm{Co(III)}]_0$:

$$\ln\frac{A - A_\infty + \Delta\epsilon([\mathrm{V(III)}]_0 - [\mathrm{Co(III)}]_0)}{A - A_\infty + \Delta\epsilon k_1/k_\alpha} = -\{k_1 + k_\alpha([\mathrm{Co(III)}]_0 - [\mathrm{V(III)}]_0)\}t + \ln\frac{[\mathrm{V(III)}]_0}{[\mathrm{Co(III)}]_0 + k_1/k_\alpha} \qquad (12)$$

Since eq 11 and 12 contain k_1 and k_α in a complicated way, the determinations of the k_1 and k_α values were carried out by a nonlinear-least-squares method.[19] The simultaneous determinations of the values of k_1 and k_α from each kinetic run did not always work well: In the analysis of the kinetic data obtained under the condition $[\mathrm{Co(III)}]_0 > [\mathrm{V(III)}]_0$, the k_1 value tends to converge to a negative value. Therefore, the k_1 value was determined first by use of the kinetic data obtained under the condition $[\mathrm{Co(III)}]_0 < [\mathrm{V(III)}]_0$, since the contribution of the k_α path to the overall reaction is minor. This procedure gave (1.3 ± 0.4) × 10^{-4} s^{-1} as the k_1 value (Table S2[18]). Then, by use of the k_1 value thus obtained, the k_α value was determined from the data obtained under the condition $[\mathrm{Co(III)}]_0 > [\mathrm{V(III)}]_0$, where the contribution of the k_α path to the overall reaction becomes major (Table S2[18]). The k_α value thus determined was (2.4 ± 0.4) × 10^{-2} M^{-1} s^{-1}.

Reduction of $[CoCl(NH_3)_5]^{2+}$ and $[CoBr(NH_3)_5]^{2+}$. The second reaction for $[CoCl(NH_3)_5]^{2+}$ (the reaction between $[Co(hedtra)(H_2O)]^-$ and $[CoCl(NH_3)_5]^{2+}$) was much slower than the first reaction (eq 2), though the reaction of $[Co(hedtra)(H_2O)]^-$ with $[CoCl(NH_3)_5]^{2+}$ was faster than that of $[Co(hedtra)(H_2O)]^-$ with $[CoF(NH_3)_5]^{2+}$. The first reaction for $[CoCl(NH_3)_5]^{2+}$ was followed at 780 nm, where the absorbance change due to the second reaction was minimal. The kinetic runs for the first reaction fitted eq 8 and 9. The kinetic data are listed in Table S3.[18] The averaged k_1 value was (3.3 ± 0.4) × 10^{-4} s^{-1}.

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[19] Nonlinear-least-squares calculations were made by the Gauss–Newton or the modified Marquardt method. The principles of the nonlinear-least-squares method are described in: Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969.

The second reaction for $[CoBr(NH_3)_5]^{2+}$ was so fast that this overlapped the first reaction. Furthermore, the spectral change observed during the second reaction did not show any isosbestic point. Therefore, the first reaction was followed only in the presence of excess $[V(hedtra)(H_2O)]$, where the second reaction did not take place appreciably. The kinetic runs were analyzed by eq 9. The kinetic data are given in Table S4.[18] The averaged value of k_1 was $(6 \pm 1) \times 10^{-4}$ s^{-1}.

Reaction Scheme and Rate Equation. The reaction of $[V(hedtra)(H_2O)]$ with $[Co(N_3)(NH_3)_5]^{2+}$ is a typical case to which Scheme I is applicable. Hence, the k_α value is negligibly small. The reaction of $[V(hedtra)(H_2O)]$ with $[CoBr(NH_3)_5]^{2+}$ also appears to follow Scheme I, and the k_α value is very small. On the other hand, the reaction of $[V(hedtra)(H_2O)]$ with $[CoF(NH_3)_5]^{2+}$ consists of the mixed zeroth- and first-order reactions with respect to the concentration of the cobalt(III) complex (Scheme II). In the reaction of $[CoCl(NH_3)_5]^{2+}$, the shape of the kinetic traces indicates that the k_α path may not be negligible. However, the contribution of the k_α path to the overall reaction is so small that the k_α value could not be determined. The upper limit of the k_α value was estimated to be less than 2×10^{-3} M^{-1} s^{-1} for $[CoCl(NH_3)_5]^{2+}$.

The rate constant values, k_1, determined for different cobalt(III) complexes were $(3.5 \pm 1.1) \times 10^{-4}$ s^{-1} for $[Co(N_3)(NH_3)_5]^{2+}$, $(1.3 \pm 0.4) \times 10^{-4}$ s^{-1} for $[CoF(NH_3)_5]^{2+}$, $(3.3 \pm 0.4) \times 10^{-4}$ s^{-1} for $[CoCl(NH_3)_5]^{2+}$, and $(6 \pm 1) \times 10^{-4}$ s^{-1} for $[CoBr(NH_3)_5]^{2+}$ at $I = 0.10$ (NaCl) and 40.0 °C. If the rather large fluctuations of kinetic data are considered, these values are essentially the same and support the validity of the mechanism presented in Schemes I and II.

Most of the zeroth-order reactions so far reported consist of two-step reactions similar to Scheme I.[4] Kinetic analyses of the pseudo-zeroth-order reactions have been made by the initial rate method in the previous literature.[4] However, the rate equations (8) and (9) can be applied to any combinations of the $[V(III)]_0$ and $[Co(III)]_0$ values. Therefore, it becomes possible by use of eq 8 and 9 to analyze kinetic traces under conditions that are not of ideal zeroth order.

Close inspection of eq 7 reveals the interesting kinetic nature of Scheme I. Equation 7 can be rewritten as

$$[Co(III)] = [V(III)]_0 \exp(-k_1 t) + [Co(III)]_0 - [V(III)]_0 \tag{13}$$

Equation 13 indicates that $[Co(III)]$ decreases with time exponentially to approach the final value of $[Co(III)]_0 - [V(III)]_0$. Since $[Co(III)]_0 - [V(III)]_0$ is negative under the condition $[Co(III)]_0 < [V(III)]_0$, the monotonic decrease of $[Co(III)]$ is interrupted abruptly at the entire consumption of Co(III). This situation is illustrated in Figure 4, by using a model system. If $[Co(III)]_0 \ll [V(III)]_0$, the decrease of $[Co(III)]$ with time can be approximated by a straight line. These are what we observed in this study. An example similar to this situation has also been reported in a figure of ref 3, although the rate constant was determined by the Guggenheim method.[20]

Conversion-controlled electron-transfer reactions similar to those presented here have been reported for related systems: Kristine and Shepherd reported that there are two isomeric structures of $[Ti(hedtra)(H_2O)]$ and only one of the two isomers reduces $[VO(hedtra)]^-$.[21] It was pointed out that the rearrangement of the $hedtra^{3-}$ chelate around the metal centers limits the rates of the intramolecular electron transfer in $V^{II}V^{IV}(hedtra)_2$ and $[(NH_3)_5RuOV(hedtra)]^+$ complexes.[22,23]

Ahmad and Higginson reported the kinetic study of the electron-transfer reaction between $[V(edta)]^-$ and $[Fe(edta)]^-$.[24] This reaction is first order in both V(III) and Fe(III) complexes. Therefore, the conversion-controlled electron transfer is not operative in this sytem. The kinetic difference between the reactions of the HEDTRA and the EDTA complexes might support the idea that the V(III)–EDTA complex is predominantly sexidentate in solution.

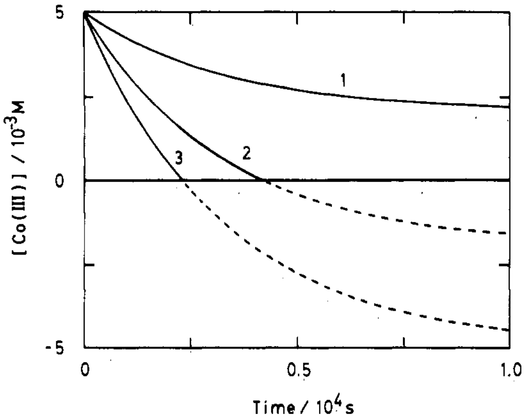

Figure 4. Concentration change of a cobalt(III) complex with time for the reaction given in Scheme I. The solid lines are those given by the following set of parameters: $k_1 = 3 \times 10^{-4}$ s^{-1}; $[Co(III)]_0 = 5 \times 10^{-3}$ M; $[V(III)]_0 = 3 \times 10^{-3}$ M (curve 1), 7×10^{-3} M (curve 2), 1×10^{-2} M (curve 3).

Effects of Halide Ligands in $[CoX(NH_3)_5]^{2+}$ on the Electron-Transfer Rates. The rate constants for the electron-transfer reactions between $[V(hedtra)(H_2O)]$ and $[CoX(NH_3)_5]^{2+}$ (k_α) decrease in the order $[CoF(NH_3)_5]^{2+} > [CoCl(NH_3)_5]^{2+} > [CoBr(NH_3)_5]^{2+}$. The trend indicates that these reactions can be classified as "inverse order".[25] The reactivity pattern belonging to the inverse order has been known for only a few reactions.[26-28] Our present work adds another example of the inverse-order redox reactions.

Qualitative kinetic data obtained in this work indicate that the rates of the electron-transfer reactions between $[Co(hedtra)(H_2O)]^-$ and $[CoX(NH_3)_5]^{2+}$ increase with the order of X: F < Cl < Br. In other words, these reactions obey the "normal order".

Burdett made a theoretical study of the electron-transfer reactions of transition-metal complexes based on molecular orbital calculations and presented a diagnostic method for classification of normal vs inverse order.[29] It should be noted that the reactivity orders found in this study accord with Burdett's conclusion. The transfer of a t_{2g} electron of a reductant to the d_{z^2} orbital of an oxidant permits the inverse-order reactivity.[29] This is the case for the reactions between $[V(hedtra)(H_2O)]$ and $[CoX(NH_3)_5]^{2+}$. The transfer of a d_{z^2} electron of a reductant to the d_{z^2} orbital of an oxidant should result in the normal order.[29] This is the case for the reduction of $[CoX(NH_3)_5]^{2+}$ by $[Co(hedtra)(H_2O)]^-$.

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Registry No. $[V(hedtra)(H_2O)]$, 75431-42-4; $[CoF(NH_3)_5]^{2+}$, 15392-06-0; $[CoCl(NH_3)_5]^{2+}$, 14970-14-0; $[CoBr(NH_3)_5]^{2+}$, 14970-15-1; $[Co(N_3)(NH_3)_5]^{2+}$, 14403-83-9.

Supplementary Material Available: Figure S1 (relation between the initial slope of the absorbance–time curve and the initial concentration of $[V(hedtra)(H_2O)]$ for the reaction of $[V(hedtra)(H_2O)]$ with $[Co(N_3)(NH_3)_5]^{2+}$) and kinetic data for the $[V(hedtra)(H_2O)]$ reductions of $[Co(N_3)(NH_3)_5]^{2+}$ (Table S1), $[CoF(NH_3)_5]^{2+}$ (Table S2), $[CoCl(NH_3)_5]^{2+}$ (Table S3), and $[CoBr(NH_3)_5]^{2+}$ (Table S4) (5 pages). Ordering information is given on any current masthead page.

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