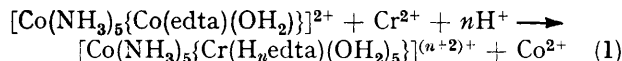


Kinetics of the Reduction of (Ethylenediaminetetra-acetato)cobaltate(III) and Related Complexes by Chromium(II) Ions

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Rate constants of the electron-transfer reactions of three cobalt(III)-edta (edta = ethylenediaminetetra-acetate) complexes with Cr^{2+} have been determined by a stopped-flow spectrophotometric method at 25 °C and an ionic strength of 1.0 mol dm⁻³ (Na[ClO₄]). The values are $(6.6 \pm 1.0) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $[\text{Co}(\text{edta})]^-$, $(7.6 \pm 0.4) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $[\text{Co}(\text{Hedta})(\text{OH}_2)]$, and $>2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $[\text{CoCl}(\text{Hedta})]^-$. A comparison with other reducing agents { Fe^{2+} , $[\text{Fe}(\text{CN})_6]^{4-}$, and Ti^{III} } indicates that titanium (III) reduction of the same series of cobalt(III)-edta complexes, studied by Marčec and Orhanović, proceeds *via* an outer-sphere mechanism.

RECENTLY, we have investigated the reactions of some cobalt(III) complexes containing ethylenediamine-*NNN'*-tetra-acetate (edta) with Cr^{2+} ,^{1,2} and found that the reduction of $[\text{Co}(\text{NH}_3)_5\{\text{Co}(\text{edta})(\text{OH}_2)\}]^{2+}$ † proceeds *via* an inner-sphere mechanism as expressed by reaction (1). From the identification of the $[\text{Co}(\text{NH}_3)_5$ -



$\{\text{Cr}(\text{H}_n\text{edta})(\text{OH}_2)_5\}^{(n+2)+}$ product, it was inferred that Cr^{2+} attacks the carbonyl oxygen atom at the $[\text{Co}(\text{edta})(\text{OH}_2)]^-$ moiety. The rate constant for reaction (1) was $(2.55 \pm 0.15) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ($\text{M} = \text{mol dm}^{-3}$) at 25 °C and an ionic strength (*I*) of 0.2 M (Li[ClO₄]). Reaction (1) is analogous to the reaction of $[\text{Co}(\text{edta})]^-$ {or $[\text{Co}(\text{Hedta})(\text{OH}_2)]$ } with Cr^{2+} ,³ because the $[\text{Co}(\text{edta})(\text{OH}_2)]^-$ moiety has almost the same environment as that of $[\text{Co}(\text{edta})]^-$ or $[\text{Co}(\text{Hedta})(\text{OH}_2)]$ and, in each complex, the Cr^{2+} attacks the carbonyl oxygen atom of the quinquedentate or sexidentate edta.‡ Therefore, it is expected that the rate for reaction (1) is similar to those for the reduction of $[\text{Co}(\text{edta})]^-$ and $[\text{Co}(\text{Hedta})(\text{OH}_2)]$. The reduction of $[\text{Co}(\text{NH}_3)_5\{\text{Co}(\text{edta})(\text{OH}_2)\}]^{2+}$ by Cr^{2+} is, however, much slower than the reduction of $[\text{Co}(\text{edta})]^-$ and $[\text{Co}(\text{Hedta})(\text{OH}_2)]$, which have been reported by Wood and Higginson;³ the rate constants were $1.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for $[\text{Co}(\text{edta})]^-$ and $1.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for $[\text{Co}(\text{Hedta})(\text{OH}_2)]$ at 20 °C and *I* = 1.0 M (Na[ClO₄]). It is difficult to accept that such a large difference in rate constants arises from the difference in the charge of the respective cobalt(III) complexes, since the attacking site of Cr^{2+} in the $[\text{Co}(\text{edta})(\text{OH}_2)]^-$ moiety is separated by a O₂CCH₂N chain from the tripisitive $[\text{Co}(\text{NH}_3)_5]^{3+}$ moiety. These considerations motivated us to reinvestigate the kinetics of the reactions of $[\text{Co}(\text{edta})]^-$, $[\text{Co}(\text{Hedta})(\text{OH}_2)]$, and $[\text{CoCl}(\text{Hedta})]^-$ with Cr^{2+} .

EXPERIMENTAL

Materials.—The compounds Na[Co(edta)]·4H₂O⁴ and H[CoCl(Hedta)]·2H₂O⁵ were prepared as reported in the

† The edta acts as a quinquedentate ligand in the $[\text{Co}(\text{edta})(\text{OH}_2)]^-$ moiety, and as a unidentate ligand for the $[\text{Co}(\text{NH}_3)_5]^{3+}$ moiety.

literature. The compound $[\text{Co}(\text{Hedta})(\text{OH}_2)]$ was prepared *in situ* by overnight equilibration of $[\text{Co}(\text{edta})]^-$ solution containing the requisite amount of HClO₄ at 25 °C. The concentration of $[\text{Co}(\text{Hedta})(\text{OH}_2)]$ was calculated from the equilibrium constant $K = [\text{Co}(\text{Hedta})(\text{OH}_2)]/[\text{Co}(\text{edta})]^- [\text{H}_3\text{O}^+] = 1.28 \text{ M}^{-1}$ at 25 °C and *I* = 1.0 M.⁶ Chromium(II) perchlorate solutions were prepared as described previously.⁷

Kinetic Measurements.—Kinetic measurements were made with a Union-Giken RA-401 stopped-flow spectrophotometer under a nitrogen atmosphere. The temperature was controlled at 25.0 ± 0.1 °C and the ionic strength was adjusted to 1.0 M with Na[ClO₄] and HClO₄.

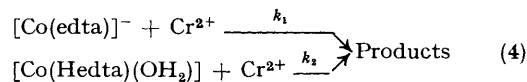
The reaction of $[\text{Co}(\text{edta})]^-$ with Cr^{2+} was followed at 535 nm and at various hydrogen-ion concentrations. In order to avoid the formation of $[\text{Co}(\text{Hedta})(\text{OH}_2)]$,^{6,8} the reaction was initiated by mixing a chromium(II) solution containing the requisite amount of HClO₄ with a neutral solution of $[\text{Co}(\text{edta})]^-$. The rate constants were determined from the second-order rate equation (2) where $[\text{R}_1]_0$ and $[\text{R}_2]_0$ denote

$$\ln\left\{1 + \frac{([\text{R}_1]_0 - [\text{R}_2]_0)(A_0 - A_\infty)/[\text{R}_2]_0(A_t - A_\infty)}{k_1([\text{R}_1]_0 - [\text{R}_2]_0)t} + \ln\left(\frac{[\text{R}_1]_0}{[\text{R}_2]_0}\right)\right\} =$$

the initial concentrations of each reactant ($[\text{R}_1]_0 > [\text{R}_2]_0$), and A_0 , A_t , and A_∞ , the absorbances at time zero, *t*, and infinity respectively. The reaction of $[\text{CoCl}(\text{Hedta})]^-$ with Cr^{2+} was too rapid to be followed.

To determine the rate constant for the reduction of $[\text{Co}(\text{Hedta})(\text{OH}_2)]$ by Cr^{2+} , the cobalt(III) solutions containing $[\text{Co}(\text{edta})]^-$ and $[\text{Co}(\text{Hedta})(\text{OH}_2)]$ were allowed to react with Cr^{2+} , and the absorbance against time trace was analyzed by the treatment of Marčec and Orhanović.⁹ Since their equation contains typographic errors, the rate

$$\ln\left\{\frac{(A_t - A_\infty)}{(A_0 - A_\infty)} - \frac{[\text{Co}(\text{edta})]_0}{[\text{Co}(\text{edta})]_0 + [\text{Co}(\text{Hedta})(\text{OH}_2)]_0}\right\} \exp(-k_1[\text{Cr}^{2+}]_0 t) = -k_2[\text{Cr}^{2+}]_0 t + \ln\left(\frac{[\text{Co}(\text{Hedta})(\text{OH}_2)]_0}{[\text{Co}(\text{edta})]_0 + [\text{Co}(\text{Hedta})(\text{OH}_2)]_0}\right) \quad (3)$$



equation is rewritten here [equation (3)] where the rate constants, k_1 and k_2 , are designated in reaction (4). The

‡ $[\text{Cr}(\text{H}_n\text{edta})(\text{OH}_2)_5]^{(n-1)+}$ is the main product of the reaction of $[\text{Co}(\text{edta})]^-$ with Cr^{2+} .³

kinetic measurements were made at 579 nm, the isosbestic wavelength of $[\text{Co}(\text{edta})]^-$ and $[\text{Co}(\text{Hedta})(\text{OH}_2)]$, and under the condition $[\text{Cr}^{2+}]_0 > 50 [\text{Co}^{\text{III}}]_0$.

RESULTS AND DISCUSSION

Kinetic data for the reaction of $[\text{Co}(\text{edta})]^-$ are listed in Table 1. The second-order rate constants appear to be independent of the hydrogen-ion concentrations and the initial concentrations of cobalt(III) and Cr^{2+} , although the fluctuations of the rate-constant values are somewhat larger than those for the reactions of many other cobalt(III) complexes with Cr^{2+} . The origin of this

TABLE 1

Rate constants for the reduction of $[\text{Co}(\text{edta})]^-$ by Cr^{2+} at $25.0 \pm 0.1^\circ\text{C}$ and $I = 1.0 \text{ M}$ ($\text{Na}[\text{ClO}_4]$)

$[\text{Co}^{\text{III}}]_0/$ mM	$[\text{Cr}^{2+}]_0/$ mM	$[\text{H}^+]/\text{M}$	$10^{-3}k_1/$ $\text{M}^{-1}\text{s}^{-1}^a$
0.251	1.98	0.442	5.7
0.501	1.98	0.442	5.2
1.00	1.98	0.442	5.1
2.51	1.98	0.442	8.2
5.01	1.98	0.442	7.4
5.01	0.980	0.456	6.1
5.01	3.06	0.427	5.8
5.01	1.98	0.111	6.5
5.01	1.98	0.221	7.0
5.01	1.98	0.663	7.6
5.01	1.98	0.883	8.2
5.01	1.98	0.221	12 ^b

^a Average of 3–5 determinations. ^b $I = 0.24 \text{ M}$.

fluctuation is not certain at present. The average of the rate constant values obtained at $I = 1.0 \text{ M}$ was $(6.6 \pm 1.0) \times 10^3 \text{ M}^{-1}\text{s}^{-1}$. The rate constant obtained at $I = 0.24 \text{ M}$ is larger than that at $I = 1.0 \text{ M}$ and this

$(\text{OH}_2)]$ are nearly the same as that for $[\text{Co}(\text{NH}_3)_5\text{Co}(\text{edta})(\text{OH}_2)]^{2+}$. This is consistent with our expectation. The rate constants determined here are much smaller than the values of Wood and Higginson which

TABLE 2

Rate constants for the reduction of $[\text{Co}(\text{Hedta})(\text{OH}_2)]$ by Cr^{2+} ^a at $25.0 \pm 0.1^\circ\text{C}$ and $I = 1.0 \text{ M}$ ($\text{Na}[\text{ClO}_4]$)

$[\text{Co}^{\text{III}}]_0/$ mM	$[\text{H}^+]/\text{M}$	$10^{-3}k_2/$ $\text{M}^{-1}\text{s}^{-1}^b$
0.501	0.541	7.2
0.501	0.673	7.1
0.501	0.849	8.0
0.251	0.849	8.0

^a $[\text{Cr}^{2+}]_0 = 28.8 \text{ mM}$. ^b Average of 4–5 determinations.

were determined by the competition reaction method, measuring the consumption of two cobalt(III) complexes $\{[\text{CoCl}(\text{NH}_3)_5]^{2+}$ and one of the cobalt(III) complexes in question $\}$ competing for a limited amount of Cr^{2+} . We suggest that the discrepancy is possibly due to incomplete mixing in their experimental method. When the time taken to mix the reagents is long in comparison with the half-life of the reaction, selectivity of Cr^{2+} toward the two cobalt(III) ions is lost. If this is the case, the rate-constant values obtained for $[\text{Co}(\text{edta})]^-$ and $[\text{Co}(\text{Hedta})(\text{OH}_2)]$ will be larger than the true values, because $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ has been known to react with Cr^{2+} very rapidly ($2.6 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ at 25°C and $I = 1.0 \text{ M}$).¹⁰

The data revised here may offer some clues to the mechanism of the titanium(III) reduction of cobalt(III) complexes. In order to elucidate this mechanism in the case of cobalt(III)–edta complexes, Marčec and Orhanović

TABLE 3

Rate constants for the reduction of cobalt(III)–edta complexes at 25°C and $I = 1.0 \text{ M}$, and their rate ratios

	Reducing agent				
	Cr^{2+} ^a $k/\text{M}^{-1}\text{s}^{-1}$	Cr^{2+} ^b $k/\text{M}^{-1}\text{s}^{-1}$	Fe^{2+} ^c $k/\text{M}^{-1}\text{s}^{-1}$	$[\text{Fe}(\text{CN})_6]^{4-}$ ^d $k/\text{M}^{-1}\text{s}^{-1}$	Ti^{III} ^e a/s^{-1}^f
(a) Rate constants					
k_{I} $[\text{Co}(\text{edta})]^-$	1.6×10^5	6.6×10^3	6.0×10^{-4}	0.21	0.29
k_{II} $\{[\text{Co}(\text{Hedta})(\text{OH}_2)]$ $\text{or } [\text{Co}(\text{edta})(\text{OH}_2)]^-\}$	1.3×10^5	7.6×10^3	8.5×10^{-3}	3.4	3.0
k_{III} $\{[\text{CoCl}(\text{Hedta})]^-$ $\text{or } [\text{CoCl}(\text{edta})]^{2-}\}$	2.5×10^6	$> 2 \times 10^6$	1.36	7.0	9.0
(b) Ratio of rate constants					
$k_{\text{II}}/k_{\text{I}}$	0.8	1.2	14	16	10
$k_{\text{III}}/k_{\text{I}}$	16	$> 3 \times 10^2$	2×10^3	33	31

^a Ref. 3, 20°C . ^b This work. ^c Refs. 12 and 13. ^d Ref. 11, $I = 0.59 \text{ M}$. ^e Ref. 9. ^f See text for definition of a .

effect is consistent with reaction between reactants having opposite charges.

Kinetic data for the reaction of $[\text{Co}(\text{Hedta})(\text{OH}_2)]$ are listed in Table 2. The rate constants again appear to be independent of the hydrogen-ion concentration. The rate of the reaction between $[\text{CoCl}(\text{Hedta})]^-$ and Cr^{2+} was immeasurably rapid and only the lower limit of the rate constant, $2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$, was estimated. The rate constants obtained in this work are summarized in Table 3 along with the values of Wood and Higginson.³

The rate constants for $[\text{Co}(\text{edta})]^-$ and $[\text{Co}(\text{Hedta})-$

have studied the reactions, and compared the rate constants with those of the reactions with other reducing agents, Fe^{2+} , $[\text{Fe}(\text{CN})_6]^{4-}$, and Cr^{2+} .⁹ These rate constants are also included in Table 3. The reactions

$$-d[\text{Co}^{\text{III}}]/dt = \left\{ \frac{a/[\text{H}^+]}{1 + (K_h/[\text{H}^+])} \right\} [\text{Co}^{\text{III}}][\text{Ti}^{\text{III}}] \quad (5)$$

of cobalt(III)–edta complexes with titanium(III) conform to rate equation (5)^{9,*} where K_h denotes the acid dis-

* In the reaction of $[\text{Co}(\text{edta})]^-$ with titanium(III), there is an additional term involving a second-order dependence on $[\text{Ti}^{\text{III}}]$.⁹

sociation constant of $\text{Ti}^{3+}(\text{aq})$ and a denotes the rate constants in Table 3.*

It was disclosed that $[\text{Fe}(\text{CN})_6]^{4-}$ reduces cobalt(III)-edta complexes by an outer-sphere mechanism,¹¹ while an inner-sphere reduction of the same cobalt(III) complexes by Fe^{2+} was suggested.^{12,13} From product criterion, it is apparent that Cr^{2+} reduces the cobalt(III) complexes by an inner-sphere mechanism.^{2,3} In the rate comparison made by Marčec and Orhanović, the data reported by Wood and Higginson³ were used. The reactivity pattern of the Fe^{2+} reduction is quite different from that of Cr^{2+} reduction, although an inner-sphere mechanism is considered to operate for each system. However, when the values revised here are compared with those of the Fe^{2+} system, it is apparent that the reactivity patterns of both systems are reasonably similar to each other and quite different from those of $[\text{Fe}(\text{CN})_6]^{4-}$ and titanium(III) systems. This therefore implies that the titanium(III) reduction of the cobalt(III) complexes proceeds *via* an outer-sphere mechanism. It should also be noted that rate equation (5) has often been observed for an outer-sphere reduction by $[\text{Ti}(\text{OH})]^{2+}$.¹⁴ The present inference that titanium(III) reduces cobalt(III)-edta complexes by an outer-sphere mechanism raises the question of why the reactions proceed *via* an outer-sphere path, since a variety of cobalt(III) complexes containing the carboxylato-ligand are reduced by titanium(III) *via* an inner-sphere mechanism.¹⁵⁻¹⁸ However, Marčec and Orhanović¹⁹ reported quite recently that the reduction of $[\text{Co}(\text{O}_2\text{CCl}_3)(\text{NH}_3)_5]^{2+}$ and $[\text{Co}(\text{O}_2\text{CCF}_3)(\text{NH}_3)_5]^{2+}$ by titanium(III)

* If an outer-sphere mechanism operates, the term a corresponds to the product of K_b and the second-order rate constant of the reduction of cobalt(III) with $[\text{Ti}(\text{OH})]^{2+}$.

proceeds *via* an outer-sphere mechanism. The mechanism of the titanium(III) reduction of cobalt(III) complexes containing the carboxylato-ligand (L) seems to be affected subtly by the nature of L. For further elucidation of the factors controlling the mechanism of the titanium(III) reduction, additional studies must be undertaken.

[0/1412 Received, 12th September, 1980]

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