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Reactions of Amino Polycarboxylic Acids with High-Valent Transition-Metal Ions: EDTA-Assisted Decomposition of Carboxylato-Bound Chromium(V) Complexes

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Ethylenediaminetetraacetic acid (EDTA) reacts with sodium bis(2-hydroxy-2-ethylbutyrato)oxochromate(V) to form $Cr^{III}(EDTA)$ and $Cr^{III}(EDTRI)$ (EDTRI = ethylenediamine-N,N',N'-triacetic acid) complexes and carbon dioxide in the pH range 3–4 in 0.5 M sodium perchlorate. In the presence of appreciable ligand anion (2-hydroxy-2-ethylbutyrate; >0.05 M) the reaction proceeds through the formation of an intermediate. Substitution of EDTA on the Cr(V) center, followed by rapid electron transfer to form a Cr(III)–Cr(V) binuclear intermediate, is consistent with the rate data. The rate of formation of the intermediate is not affected by the addition of ligand anion. The second-order rate constant, 2.2×10^{-3} M^{-1} s^{-1} at 25 °C (first order with respect to both Cr(V) and EDTA), and the enthalpy and entropy of activations, 75 kJ mol^{-1} and –44 J deg^{-1} mol^{-1}, were evaluated. The activation parameters are in accord with an associative mechanism for the substitution reactions of oxo–Cr(V) complexes. The second step of the reaction has been identified as the formation of a $Cr^{III}(EDTA)$ complex by the reaction of bisligated chromium(III) with EDTA, which is retarded by the addition of extra ligand anion. The enthalpy and the entropy of activations for the Cr(III) substitution reaction were calculated to be 90 kJ mol^{-1} and 25 J deg^{-1} mol^{-1}.

Introduction

Recent synthesis of stable water-soluble bis(α-hydroxy carboxylato)oxochromium(V) complexes by Krumpolc and Roček[1] has provided opportunities to explore the chemistry of this rare oxidatin state in aqueous solution. These authors have also demonstrated that the stable chromium(V) complexes oxidize many organic substrates at a much greater rate than the corresponding Cr(VI) oxidants.[2] Gould and co-workers[3-6] have investigated many redox reactions utilizing these (carboxylato)-oxochromium(V) complexes and a variety of metal and non-metal reductants. For example, cerium(III) catalyzes the disproportionation of Cr(V),[3] titanium(III) reduces Cr(V) with the reduction of Cr(V) to Cr(IV) being the rate-limiting step,[4] and reductions by iron(II), vanadium(IV), and uranium(IV) proceed through the formation of long-lived chromium(IV) intermediates.[5] The reactions of Cr(V) with non-metal reductants exhibit a "clock reaction" in which autocatalysis by Cr(IV) has shown to operate.[6] Strong autocatalysis was observed in the reductions by sulfite, iodide, and ascorbate ion.[6a] However, the reductions by other non-metals, such as nitrite, hypophosphorus acid, and mercapto acids, exhibit weak autocatalysis.[6b]

Results obtained from Roček's and Gould's laboratories show many mechanistic diversities. More studies are therefore needed in order to explore the further chemistry of chromium(V). Since ethylenediaminetetraacetic acid (EDTA) forms stable complexes with many metal ions, we have investigated the reaction of bis-(2-hydroxy-2-ethylbutyrato)oxochromate(V) (I; $R_1 = R_2 = C_2H_5$)
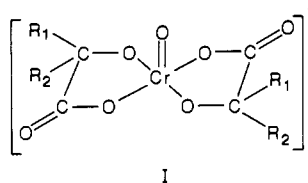
I

with EDTA. The results of this study point toward a sluggish substitution reaction of Cr(V) toward EDTA, followed by rapid intramolecular electron transfer within the substituted Cr(V)–EDTA complex to form Cr(III) complexes.

(1) Krumpolc, M.; Roček, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.
(2) Krumpolc, M.; Roček, J. *Inorg. Chem.* **1986**, *24*, 617.
(3) Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 338.
(4) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2645.
(5) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832. Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 4679. Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 94.
(6) Bose, R. N.; Rajasekar, N.; Thompson, D. M.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3349. Ghosh, S. K.; Bose, R. N.; Laali, K.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 4737. Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 899, 2684, 2688.

Experimental Section

Physical Measurements. A computer-interfaced double-beam spectrophotometer (Varian DMS-100) was employed for UV-visible spectroscopic measurements. The temperature of the cell compartment was thermostated at a desired temperature by using a water bath equipped with a pump. Gas chromatographic data were collected on a GC instrument (Perkin-Elmer 900) attached to a X-Y recorder (Perkin-Elmer 56) using a Golay column. A digital pH meter (Orion 701 A) was employed for pH measurements utilizing a combination electrode.

Materials. Stock solutions of NaOH were standardized against potassium hydrogen phthalate (Thorn Smith). Solutions of 2-hydroxy-2-ethylbutyric acid (HEBA) (Aldrich) were standardized against NaOH. Stock solutions of disodium salt of EDTA (Fisher) were prepared by using primary standard grade material and were used as such. Solutions of sodium perchlorate were prepared by dissolving desired anhydrous material (Aldrich) and were used to adjust the ionic strength of all reaction mixtures. Standard solutions of 3-pentanone (Baker) were prepared by appropriate dilutions. Vanadium(IV) solutions were made by dissolving $VOSO_4 \cdot xH_2O$ (Alfa Products) in 0.1 M perchloric acid and were standardized at the 760-nm absorption maximum by using 17.2 M^{-1} cm^{-1} as the molar absorptivity.[7] Chromium(III) contents were determined as Cr(VI) by using basic hydrogen peroxide.[8]

Anion- (Dowex 1-X8. 100–200 mesh, chloride form) and cation-exchange (Dowex 50W-X8, 100–200 mesh, H$^+$ form) resins were washed properly before use.[9] Usually more than 3 mequiv of resin was packed in narrow columns (internal diameter 1 cm) for the separation of chromium(III) products.

Sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) monohydrate was synthesized by the method of Krumpolc and Roček[1] and recrystallized from a 1:1 acetone–hexane mixture. Sodium aqua(ethylenediaminetetraacetato)chromate(III) was prepared from the method reported by Hamm.[10] Diaqua(ethylenediamine-N,N'-diacetato)chromium(III) chloride was generated in situ by following the method of Weyh and Pierce.[11]

Reaction of EDTA with Bis(2-hydroxy-2-ethylbutyrato)oxochromate-(V) and Characterization of Products. The reaction of the Cr(V) complex with EDTA by using a fixed concentration of Cr(V) (5 mM) and various EDTA concentrations (1–50 mM) at pH 3.3 maintained by the equimolar (0.05 M) composition of HEBA and its sodium salt was monitored spectrophotometrically in the wavelength region 750–350 nm. Absorbance measurements at the end of the reaction at several wavelengths as a function of EDTA concentrations show that 1 mol of EDTA/mol of Cr(V) is required for complete decomposition of the Cr(V) complex.

The various chromium(III) products were characterized by reacting the chromium(V) complex with excess EDTA and separating the prod-

(7) Furman, S.; Garner, C. S. *J. Am. Chem. Soc.* **1950**, *72*, 1785.
(8) Haupt, G. W. *J. Res. Natl. Bur. Stand., Sect. A*, **1952**, *48*, 414.
(9) Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792. The anion-exchange resin was pretreated exactly the same way except HCl was used instead of $HClO_4$.
(10) Hamm, R. E. *J. Am. Chem. Soc.* **1953**, *75*, 5670.
(11) Weyh, J. A.; Pierce, R. L. *Inorg. Chem.* **1971**, *10*, 858.

Table I. Stoichiometry between Cr(V) and Carbon Dioxide for the Reaction of EDTA with the Cr(V) Complex

mol ($\times 10^4$) of Cr(V) taken	mol ($\times 10^4$) of CO_2 produced	$[CO_2]/[Cr(V)]$
2.49	1.74	0.70
2.53	1.82	0.72
2.50	1.67	0.67

ucts by cation- and anion-exchange column chromatographic techniques. In a typical experiment, 0.25 mmol of the Cr(V) complex was reacted with 0.50 mmol of EDTA in 0.1 mmol of EBA⁻ (as sodium salt of HEBA) and 0.1 mmol of HEBA. At the end of the reaction, the products (10 mL) were charged to an anion-exchange column. A portion of the violet solution passed through the column quickly. The remaining portion was adsorbed on the column and appeared as violet band. The eluate that passed through the anion exchanger was poured onto a cation-exchange column. The compound passed through the column also without being adsorbed to the cation exchanger. The violet band on the anion-exchange column was eluted easily with 0.5 M HCl or 0.5 M NaCl.

The visible spectra of both the chromium(III) species as separated by the cation- and anion-exchange resins were recorded. The compound eluted with 0.5 M HCl (compound I) exhibited two absorption bands at 543 and 390 nm, while the species that adsorbed on neither exchanger (compound II) showed absorption bands at 540 and 384 nm.

A 5-mL aliquot of each of the compounds was then subjected to chromium analysis as outlined earlier.[8] In a typical analysis, a 5-mL aliquot of the compound, 20 mL of NaOH (1 M), and 3 mL of H_2O_2 (30%) were mixed. After excess H_2O_2 was removed by heating, each solution was diluted to a known volume and the spectrum was recorded. The extinction coefficients for the absorption maxima were then calculated from the estimated chromium concentration. Compound I and compound II constituted 81% and 18% of the total chromium. In an another identical experiment, hexaaquachromium(III) chloride was added after the reaction was complete. This reaction mixture was allowed to stand for 2 days at room temperature. The mixture was then subjected to ion-exchange chromatographic separation as outlined earlier. Compound II was analyzed to be 34% of the initial chromium(V) invested in the reaction.

The carbon dioxide produced by the reaction was determined by passing argon through a closed reaction vessel and collecting the CO_2 in NaOH traps (Table I). In a representative experiment, a solution (10 mL) that was 0.25 mmol in Cr(V) and 0.50 mmol in EDTA was placed in a closed reaction vessel, equipped with a stir bar, and argon was bubbled into the liquid. Two traps containing 10 mL each of approximately 0.1 M NaOH were connected to the reaction flask to collect the CO_2 as it evolved. Upon completion of the reaction, the traps were disconnected and the NaOH was titrated with standardized HCl (0.05 M) to phenophthalein and then to bromocresol green end points. An aliquot of stock NaOH solution was titrated in the same manner. The difference in the amount of HCl used to reach the second end point for the stock NaOH and that from the traps was indicative of the amount of CO_2 produced.

The amount of 3-pentanone in the products was estimated by gas chromatographic method after extraction with *p*-xylene.[12] In a typical experiment, 0.05 mmol of the Cr(V) complex in 0.1 mmol each of HEBA and EBA⁻ was allowed to react with 0.5 mmol of EDTA. After completion of the reaction, the products were extracted with *p*-xylene to a known volume. Similar xylene extraction was performed on a blank sample consisting of an identical concentration of the Cr(V) complex in the absence of EDTA. These two extracts were then subjected to GC analysis. When signal intensities of these two samples were compared with the signals of standard 3-pentanone solution in xylene, it was found that the amount of 3-pentanone in the extracts was less than 1% of the initial Cr(V) concentration. Moreover, the amount of ketone in the products was no more than in the blank sample.

Rate Measurements. The reaction between Cr(V) and EDTA was monitored at various Cr(V) and EDTA concentrations, buffer strengths, and temperatures by following the decrease in Cr(V) absorbance at 378 and 395 nm. The absorbance at 5-min intervals was recorded until no further changes in absorbance were observed. The substitution reaction of the HEBA complex of Cr(III) with EDTA was followed at 540 nm after reducing Cr(V) with V(IV).

The first order rate constants were evaluated from semilogarithmic $(D - D_\infty)$ vs time plots. The rate constant for biphasic absorbance–time profiles are computed from[13]

$$D = D_0 e^{-k_1 t} + \frac{[A]\epsilon k_1}{k_1 - k_2}(e^{-k_1 t} - e^{-k_2 t}) + \frac{D_\infty}{k_1 - k_2}(e^{-k_1 t} - e^{-k_2 t}) + D_\infty \quad (1)$$

where D_0, D, and D_∞ are the absorbances at zero time, at time t, and at infinite time. $[A]$ represents the initial concentration of the Cr(V) complex, ϵ is the extinction coefficient of the intermediate, and k_1 and k_2 are the two rate constants. A nonlinear least-squares computer program[14] was used to calculate the rate constants and the extinction coefficient of the intermediate. In this computation, the experimentally known parameters such as $[A]$, D_0, and D_∞ were held invariant and initial estimates of the other parameters were provided to the computer. In every cycle, the program generated a new set of parameters by minimizing the square of the deviation of the observed and calculated absorbance values. This iterative procedure was continued until the change in each parameter in two consecutive cycles divided by the magnitude of the parameter was equal to or less than 5×10^{-5} and an excellent agreement between the observed and calculated absorbances was achieved.

Results and Discussion

Characterization of Products. The visible spectrum of sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) exhibits two bands at 750 ($\epsilon = 44$ M⁻¹ cm⁻¹) and 510 nm ($\epsilon = 180$ M⁻¹ cm⁻¹) in aqueous solution buffered (pH 3.3) by equilmolar (0.05 M) HEBA and its sodium salt. No detectable changes in the spectrum at 25 °C over a period of 24 h were observed, indicating that the chromium(V) complex does not decompose under our experimental conditions.[15] In the presence of EDTA under the identical conditions, distinct changes in the absorption spectra were observed. The absorption bands at 750 and 510 nm disappeared, and new bands at 540 and 390 nm appeared. At 25 °C, after 10 h, no further changes in the absorption spectra were recorded. The two bands at 540 nm and 390 nm in the final products are characteristic of the chromium(III)-EDTA complex.[10,16]

Although the absorption bands closely resemble those of the Cr^{III}EDTA complex, the molar absorptivities of 187 and 103 M⁻¹ cm⁻¹ at 540 and 390 nm, which can be calculated from the initial Cr(V) concentration, are slightly low in comparison to the reported values of 213 and 114 M⁻¹ cm⁻¹ at the above two wavelengths.[16] The ion-exchange experiments revealed that a minor product consisting of 18% of the total chromium was not adsorbed by either the cation- or the anion-exchange columns. The visible spectrum of this neutral species consists of two bands at 540 ($\epsilon = 129$ M⁻¹ cm⁻¹) and 384 nm ($\epsilon = 111$ M⁻¹ cm⁻¹), which is not entirely different from the Cr^{III}EDTA spectrum except that the extinction coefficient for the 540-nm band is much lower. The neutral species cannot be a Cr(III) bis chelate of HEBA, the spectrum of which consists of two absorption bands at 585 ($\epsilon = 61$ M⁻¹ cm⁻¹) and 415 nm ($\epsilon = 49$ M⁻¹ cm⁻¹).[4,5] Moreover, such a chelate undergoes aquation in contact with cation-exchange resin[4,5] even at 2 °C to produce slowly hexaaquochromium(III), which was not observed for the chromium(III) product at hand. A mixed chelate consisting of ethylenediamine-*N,N'*-diacetic acid (EDDA) and HEBA in an α-cis configuration can also be ruled out. Such a complex would also suffer a loss of HEBA in a cation-exchange column. Also, the spectrum of α-*cis*-Cr(EDDA)(H₂O)₂⁺ in the presence of a large excess of HEBA and EBA⁻ at pH 3.4 did not change at room temperature even when the reaction mixture was allowed to stand for 3 days. The band maxima and the molar absorptivity of the neutral species correspond to Cr^{III}(EDTRI) (EDTRI = ethylenediamine *N,N',N'*-triacetic acid) reported by Ogino and co-workers.[16] An additional 16% of Cr^{III}(EDTRI) complex was recovered when the reaction products were further treated with hexaaquachromium(III) chloride. This result indicates that some of the EDTRI that was formed during the redox reaction was not

(12) Krumpolc, M.; Rocek, J. *J. Am. Chem. Soc.* **1977**, *99*, 137.

(13) Bose, R. N.; Viola, R. E.; Cornelius, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3336.
(14) The nonlinear least-squares program is written in BASIC for the Apple IIe computer. The program was kindly supplied by Professor James H. Espenson of Iowa State University.
(15) In the absence of extra HEBA, the Cr(V) complex undergoes a disproportionation reaction.[2]
(16) Ogino, H.; Watanabe, T.; Nobuyuki, T. *Inorg. Chem.* **1975**, *9*, 2093.
(17) Guardalabene, J.; Gulnak, S.; Keder, N.; Shepherd, R. E. *Inorg. Chem.* **1979**, *18*, 22.

Table II. Absorption Maxima (nm) and Molar Absorptivities (M^{-1} cm^{-1}) for (Amino polycarboxylato)chromium(III) Complexes in Aqueous Solution

complex	λ_1 (ϵ)	λ_2 (ϵ)	ref
Cr(EDTA)(H$_2$O)$^-$	543 (213)	392 (114)	10
	545 (200)	395 (104)	16
	545 (205)	392 (107)	f
compound I[a]	544 (202)	392 (105)	f
Cr(EDTRI)(H$_2$O)	540 (133)	386 (107)	16
compound II[a]	540 (129)	384 (111)	f
Cr(EDDA)(H$_2$O)$_2$	529 (77)[b]	401 (47)[b]	11
	527 (119)[c]	392 (72)[c]	11
Cr(EDDA)(acac)[d]	532 (65)	380 (168)	17
Cr(HEDTA)[e]	538 (85)	387 (253)	17
Cr(EBA)$_2$(H$_2$O)	587 (50)	415 (61)	5b

[a]Compounds I and II were separated from the products of the reaction of Cr(V) and EDTA. [b]α-Cis isomer. [c]β-Cis isomer. [d]acac represents 2,4-pentanedione. [e]HEDTA represents N-(hydroxyethyl)-ethylenediamine-N,N',N'-triacetic acid.

coordinated to Cr(III) and was released in solution. The absorption spectrum and the extinction coefficients of the major species that was eluted with 0.5 M HCl from the anion-exchange column are consistent with the [Cr(EDTA)H$_2$O]$^-$ complex. Table II reports the molar absorptivities of various chromium(III) amino polycarboxylato chelates.

Redox Reaction. The reaction of the chromium(V) complex with EDTA yielded 0.7 mol of CO_2/mol of Cr(V) as reported in Table I. The absence of 3-pentanone in the products suggests that HEBA was not involved in the reduction of chromium(V) to chromium(III) for which the ketone is expected to form.[18] The reduction must therefore be accomplished by EDTA. There are a few examples in which EDTA acts as a reductant. The Mn^{III}EDTA complex is prepared by reaction of manganese dioxide with the amino polycarboxylic acid.[19] The EDTA oxidation products in this reaction were not characterized, however. Ogino and co-workers[20] have reported that the Mn^{III}EDTA complex decomposes to Mn(II), ethylenediamine-N,N',N'-triacetic acid, and ethylenediamine-N,N'-diacetic acid. We did not observe any detectable amount of EDDA.
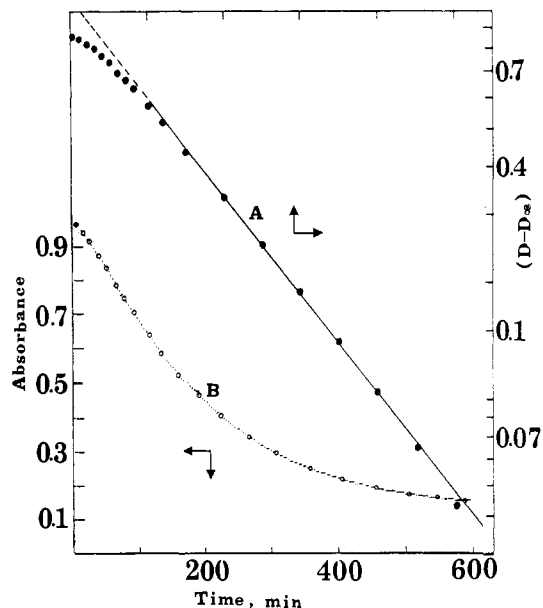
Since we have detected CO$_2$ and EDTRI in our system, EDTA is oxidized to EDTRI and CO$_2$, and concomitantly Cr(V) is reduced to Cr(III). Such a redox reaction

$$3Cr(V) + EDTA = 3Cr(III) + EDTRI + 2CO_2 \qquad (2)$$

would be consistent with observed amounts of CO$_2$ and EDTRI. A maximum of 33% of the Cr^{III}(EDTRI) complex is expected if all the EDTRI is coordinated to chromium during the redox reaction. However, some of the bound EDTRI that was released in solution during one of the intermediate steps (as discussed in the mechanism section) was recovered by adding extra chromium(III) in the products. The remaining chromium(III) species that may be coordinated to EBA$^-$ on further reaction with excess EDTA forms the Cr^{III}EDTA complex. The overall stoichiometry of the reaction of Cr(V) with EDTA would be 1:1 as observed spectrophotometrically at 750 nm although the primary redox reaction requires three molecules of chromium(V) per molecule of EDTA.

Kinetics and Mechanism. The absorbance–time profile in the presence of low ligand concentrations (<0.025 M) under pseudo-first-order conditions using excess EDTA exhibits very nearly an exponential decay. Semilogarithmic ($D - D_\infty$) vs time plots

Figure 1. Absorbance–time profile for the reaction of sodium bis(2-hydroxy-2-ethylbutyrato)oxochromate(V) (1.01 mM) with EDTA (0.05 M) at 378 nm in the presence of 0.075 M HEBA and 0.075 M NaEBA at 25.0 °C. The ionic strength was maintained at 0.5 M (NaClO$_4$). Curve A is the semilogarithmic plot of ($D - D_\infty$) vs time, indicating the deviation from a first-order reaction. Curve B is the absorbance–time plot; the dotted line is the computer-simulated profile according to eq 1. The values of the various parameters are D_0 = 0.98, k_1 = 9.8 × 10^{-5} s^{-1}, k_2 = 3.2 × 10^{-4} s^{-1}, ϵ = 640 M^{-1} cm^{-1}, D_∞ = 0.105. The closed circles are the experimentally determined absorbance values.

Table III. Rate Data for the Reaction of Bis(2-hydroxy-2-ethylbutyrato)oxochromate(V) Anion with EDTA[a]

[EDTA], mM	[EBA$^-$], mM	[HEBA], mM	T, °C	$10^4 k_1$,[b] s^{-1}	k_2,[b] s^{-1}
50.0	5.0	5.0	25	1.2	
50.0	10.0	10.0	25	1.1	
50.0	15.0	15.0	25	1.1	
50.0	25.0	25.0	25	1.1	
25.0	50.0	50.0	25	0.49	2.7
50.0	50.0	50.0	25	1.1	5.9
75.0	50.0	50.0	25	1.5	9.0
50.0	75.0	75.0	25	0.98	3.2
50.0	25.0	25.0	27	1.4	
50.0	25.0	25.0	30	1.8	
50.0	25.0	25.0	40	4.6	

[a]Ionic strength = 0.5 M; [Cr(V)] = 1–2 mM; the pH values were in the range 3.6–3.9. [b]The values of k_1 and k_2 were obtained from the nonlinear least-squares fit of eq 1 or from the first-order semilogarithmic plots.

Table IV. Comparison of the Second-Order Rate Constants for the Decomposition of the Intermediate (k_4) and the Formation of the Cr^{III}(EDTA) (k_5) Complex at 25 °C[a]

[EDTA], mM	[EBA$^-$], mM	[HEBA], mM	$10^2 k_4$,[b] M^{-1} s^{-1}	$10^5 k_5$,[c] M^{-1} s^{-1}
25.0	15.0	15.0		1.9
25.0	25.0	25.0		1.4
25.0	50.0	50.0	1.2	1.1
50.0	50.0	50.0	1.1	1.0
75.0	50.0	50.0	1.2	1.1
50.0	60.0	60.0		0.84
50.0	75.0	75.0	0.66	0.66

[a]Ionic strength = 0.5 M, the pH values were in the range 3.6–3.9. [b]k_4 = k_2/[EDTA]. [c]Second-order rate constant for the reaction of Cr^{III}(EBA)$_2$(H$_2$O)$_2$ and EDTA.

were linear up to 4 half-lives. A small deviation from linearity can be observed within the first half-life of the reaction when 0.05 M EBA$^-$ was used. This deviation was more pronounced when higher [EBA$^-$] was employed. Figure 1 is a typical absor-

(18) 3-Pentanone is formed by the reaction of Cr(VI) and 2-hydroxy-2-ethylbutyric acid[1]. The same ketone was observed when electrochemically generated Cr(IV) was reduced to Cr(III) by the hydroxy acid; see, for example: Bose, R. N.; Neff, V. D.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 165.

(19) Yoshino, Y.; Ouchi, A.; Tsunoda, Y.; Kojima, M. *Can. J. Chem.* **1962**, *40*, 775. Hamm, R. E.; Suwyn, M. A. *Inorg. Chem.* **1967**, *6*, 139.

(20) Shirakashi, T.; Ogino, H.; Tanaka, N. *Nippon Kagaku Kaishi* **1972**, 1658. Shirakashi, T.; Tanaka, N. *Nippon Kagaku Kaishi* **1974**, 1061; *Chem. Abstr.* **1975**, *82*, 3650r.

bance–time trace and first-order plot for the reaction at 0.075 M [EBA⁻].

The absorbance–time profiles at higher ligand anion concentrations (>0.025 M) can adequately be described by a pair of consecutive first-order processes.[21] Figure 1 also incorporates the simulated kinetic curve using the rate expression. Table III reports the computed rate data at various experimental conditions. The magnitudes of k_1 and k_2 linearly increase with the increase in [EDTA]. The values of $k_1/$[EDTA] do not change with the change in buffer concentrations while $k_2/$[EDTA] decreases with the increase in the ligand anion concentration.

In order to identify the rate processes dealing with the formation and decomposition of intermediate, we have compared the rate constants of the reaction of $Cr^{III}(EBA)_2(H_2O)_2$ and EDTA with those obtained from a biphasic kinetic profile. Table IV reports such rate data. The value of the rate constant at 0.05 M [EBA⁻] concentration is in excellent agreement with $k_2/$[EDTA] obtained from the biphasic curve. This result suggests that k_2 most likely is the rate constant for the substitution reaction of bisligated-Cr(III) species with EDTA. We also note that the rate constants increase with the decrease in the ligand anion concentration. The ratio of k_2/k_1 at 0.05 M EBA⁻ is 5.3. The same ratio can be calculated as 9 at 0.015 M [EBA⁻] (under identical EDTA concentration) by taking the observed rate constant for the Cr^{III}EDTA complex formation as k_2. This is consistent with the observation of single exponential kinetic curves for the Cr(V)–EDTA reaction at low ligand anion concentrations.

Since k_4 ($k_2/$[EDTA]) is the substitution rate constant for the bisligated-Cr(III) complex plus EDTA, k_3 ($k_1/$[EDTA]) must then represent the formation of such Cr(III) species.[22] Since Cr^{III}(EDTRI) was detected in the products, formation of such a complex cannot take place at the Cr(III) level, for [EDTA] is much higher (75–150 fold) than [EDTRI] even if both complexations occur at the same specific rate. The same argument can be applied to rule out the substitution at the Cr(IV) level by the EDTRI ligand if the redox reaction were to proceed by the formation of a transient Cr(IV) intermediate. The preceeding argument excludes the possibility of an outer-sphere mechanism between the Cr(V) complex and EDTA but points to an inner-sphere path. The rate-limiting substitution of EDTA onto Cr(V), followed by rapid electron transfer to form Cr(III), would be consistent with our data.

In the presence of added HEBA, the Cr(V) complex is known to equilibrate into two forms,[5b] Cr^VL_2 and Cr^VL_3, where L represents the EBA anion (eq 3). Since the rate constant, k_3, was unaffected by the addition of extra ligand, both forms of chromium(V) are very nearly equally reactive toward EDTA. The overall reaction can then be represented by Scheme I. We note that only 18% of the EDTRI was bound to Cr(III) and 16% was set free in solution. Once substitution on Cr(V) through a single carboxylic acid arm takes place, two competing processes, reduction by the –COO⁻ and ring closure by the other carboxylic acid groups, may proceed. Fast ring closure by the amino polycarboxylic acids and other multidentate ligands are documented.[23]
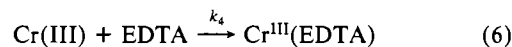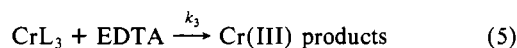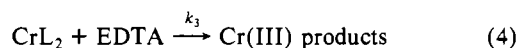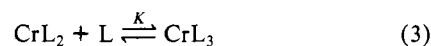
Table V. Second-Order Rate Constants for the Formation of the Intermediate and Substitution of EDTA on the Bisligated-Cr(III) Complex and Activation Parameters[a]

T, °C	k, M⁻¹ s⁻¹	$\Delta H^{\ddagger}$, kJ mol⁻¹	$\Delta S^{\ddagger}$, J mol⁻¹ deg⁻¹
	Formation of the Intermediate (k_3^b)		
25.0	2.2×10^{-3}		
27.0	2.8×10^{-3}	75[c]	−44[c]
30.0	3.6×10^{-3}		
40.0	9.2×10^{-3}		
	Substitution on Chromium(III) (k_5^d)		
24.2	2.0×10^{-2}		
31.0	5.7×10^{-2}	90[c]	25[c]
35.0	8.9×10^{-2}		
40.0	0.13		

[a] Ionic strength = 0.5 M; pH 3.6–3.9. [b] $k_3 = k_1/$[EDTA]. [c] The activation parameters were obtained from the least-squares fit of the equation $\ln (k_3/T) = -\Delta H^{\ddagger}/RT + \ln (k/h) + \Delta S^{\ddagger}/R$, utilizing the rate constants and the temperature listed in the first two columns. [d] Second-order rate constant for the reaction of the HEBA complex of Cr(III) with EDTA at [EBA⁻] = [HEBA] = 0.012 M.

If the ring closure is faster than the redox rection, all (33%) of the EDTRI is expected to be coordinated to chromium atom. In the presence of added ligand due to the formation of an extra-ligated complex, the ring closure may be retarded as compared to the electron-transfer reaction and consequently some of the EDTRI may be released in solution.

Scheme I

$$CrL_2 + L \xrightleftharpoons{K} CrL_3 \qquad (3)$$

$$CrL_2 + EDTA \xrightarrow{k_3} Cr(III)\ products \qquad (4)$$

$$CrL_3 + EDTA \xrightarrow{k_3} Cr(III)\ products \qquad (5)$$

$$Cr(III) + EDTA \xrightarrow{k_4} Cr^{III}(EDTA) \qquad (6)$$

Our results discussed above suggest that substitution reactions of these oxochromium(V) complexes toward amino polycarboxylic acid ligands are slow. A similar conclusion can also be arrived from the reaction of oxalic acid and other carboxylic acids with the Cr(V) complex reported by Krumpolc and Roček.[2] A slow reaction for the reduction of Cr(V) with lactic acid has also been reported by Haight and co-workers.[24]

The enthalpy and entropy of activations associated with k_3 were calculated to be 75 ± 5 kJ mol⁻¹ and −44 ± 3 J deg⁻¹ mol⁻¹ and for k_5 were 90 ± 6 kJ mol⁻¹ and 25 ± 2 J deg⁻¹ mol⁻¹. The activation parameters for k_5 are within the range of values reported for the substitution reactions for many Cr(III) complexes[25] and markedly different[26] from that of k_3 (Table V). According to our kinetic analysis, k_3 is the rate constant for EDTA substitution onto the Cr(V) complex. The moderately high negative entropy of activation would then indicate an associative or at least an I_a mechanism for the Cr(V) substitution reactions.

(21) Kinetic profiles dealing with a formation and decomposition of an absorbing intermediate by first-order rate processes can be described by two solutions having the identical numerical values for the rate constants except that the sequence is reversed. The computed extinction coefficients for the intermediate are different, however. The assignment of the rate constant in this work was based on the identification of one of the rate processes by separate experiments as discussed in the text.

(22) Although the values of k_4 ($k_2/$[EDTA]), under identical experimental conditions, match with the second-order rate constant for the formation of the Cr^{III}EDTA complex using bisligated-Cr(III) and EDTA, we are puzzled by the high extinction coefficient (700 ± 50 M⁻¹ cm⁻¹) of the intermediate. The high extinction coefficient may be due to the formation of a Cr(V)–Cr(III) binuclear species.

(23) Earley, J. E.; Surd, D. J.; Crone, L.; Quane, D. *J. Chem. Soc., Chem. Commun.* **1970,** 1401. Choi, S. N.; Carlyle, D. W. *Inorg. Chem.* **1974,** *13,* 1818. G. Guastalla, G.; Swaddle, T. W. *Inorg. Chem.* **1974,** *13,* 61.

(24) Haight, G. P.; Jursich, G. M.; Kelso, M. T.; Merrill, P. J. *Inorg. Chem.* **1985,** *24,* 2740.

(25) For example: Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, CA, 1985; pp 84–85 and references therein.

(26) We are grateful to a reviewer for suggesting that we compare the activation parameters of the substitution reactions pertaining to the Cr(III) and Cr(V) complexes.