slowly. The exchange of pyridine occurs with the same rate as the interconversion between planar and octahedral complexes. This implies that any five-coordinate intermediate is a high-energy unstable species. In contrast, water exchange on $Ni([12]aneN_4)(H_2O)_2^{2+}$ occurs much more rapidly than conversion to the planar complex.[23] This is clear evidence that the conversion of the planar species to a five-coordinate intermediate is the rate-determining step in this case, which probably involves a cis-trans rearrangement of the macrocyclic ligand. In the present study it would be necessary to determine independently the rate of the piperidine ligand dissociation from the octahedral complex to establish the rate-determining step in the planar-octahedral equilibrium.

Acknowledgment. This work was supported by the Australian Research Grants Committee. We gratefully acknowledge the skilled machine work of Peter Watson.

Registry No. $Ni(salpip)_2$, 87555-37-1.

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[23] Coates, J. H.; Hadi, D. A.; Lincoln, S. F.; Dodgen, H. W.; Hunt, J. P. *Inorg. Chem.* **1981**, *20*, 707.

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Electron Transfer. 65. Cerium Catalysis of the Disproportionation of Carboxylato-Bound Chromium(V)[1]

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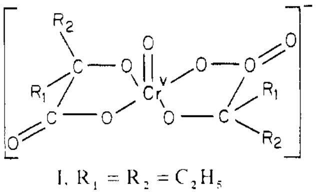
Among the tripositive metal ions, Ce(III) is uniquely effective in catalyzing the disproportionation of chelated 2-hydroxy carboxylato complexes of chromium(V): $3Cr^V \xrightarrow{Ce(III)} 2Cr^{VI} + Cr^{III}$. When these reactions are carried out in acetate buffers in the presence of the parent hydroxy carboxylic acid, the Cr(III) product is the nonchelated monocarboxylato derivative of $(H_2O)_5Cr^{III}$. Reaction rates are inversely proportional to the concentration of added parent carboxylate, directly proportional to $[OAc^-]^2$, and inversely proportional to the binomial expression $(1 + a[H^+])$. Kinetic results are consistent with a mechanism initiated by rapid and reversible loss of one carboxylato group from the Cr(V) complex, followed by formation of a Cr^V-$Ce^{III}(OAc)_2$ precursor complex and attendant deprotonation, then an internal electron transfer to form Cr(IV) and Ce(IV), and, finally, parallel oxidations of Cr(V) by the two tetrapositive centers. It appears further that breakage of the second chelate ring occurs at the Cr(IV) level, implying that Cr(IV) is more substitution labile than either Cr(III) or Cr(V) but less so than Cr(VI).

2-Hydroxy carboxylato complexes of chromium in its unusual pentapositive (Cr^V) state were characterized by Krumpolc and Roček[2] in 1979 and were reported by these workers to undergo slow disproportionation

$$3Cr^V \rightarrow 2Cr^{VI} + Cr^{III} \qquad (1)$$

in aqueous solution. This mode of decomposition appears to be minimal at pH 3.3-4.7 and may be further retarded by addition of the parent hydroxy acid.[2,3] We find, on the other hand, that this reaction is promoted by several polyvalent metal ions, by far the most effective of which is Ce^{3+}. Since this center differs from the others (Al^{3+}, La^{3+}, Pr^{3+}, and Gd^{3+}) in the accessibility, in solution, of an oxidation state 1 unit higher, we suspect that electron transfer plays a part in this acceleration, although no net oxidation of the lanthanide is detectable. The present paper deals with the Ce(III) catalysis of the disproportionation of bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) and its 2-methyl analogue (II).



I. $R_1 = R_2 = C_2H_5$
II. $R_1 = CH_3$, $R_2 = C_2H_5$

Experimental Section

Materials. Lithium perchlorate was prepared as described[4] and was recrystallized three times before use in kinetic runs. The remaining perchlorates (G. F. Smith products) were used as received; $Ce(ClO_4)_3$ contained 0.28% $Pr(ClO_4)_3$ and 0.65% $Nd(ClO_4)_3$ as impurities.[5] Other lanthanide perchlorates had been derived from the corresponding oxides to which purities of 99.9% were assigned. Sodium salts of the complexes bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) and its 2-methyl analogue (II) were prepared as monohydrates as described by Krumpolc[2,6] and were stored at 0 °C. Cation-exchange resin (Bio-Rad 50W-X2, 200-400 mesh) used in separations was pretreated as described.[7]

Stoichiometric Studies. The quantity of Cr(VI) formed from a known amount of Cr(V) was estimated, after allowing the Ce(III)-catalyzed reaction to proceed for 4-5 h in a $HOAc$-OAc^- buffer, by measuring the absorbance at 350 nm ($\epsilon_{Cr(VI)} = 1750$ M^{-1} cm^{-1} in this buffer). To estimate Cr(III) in such reaction mixtures, a slight excess of $Ba(ClO_4)_2$ was added, the mixture allowed to stand for 10 h, the precipitated $BaCrO_4$ filtered off, the filtrate adjusted to pH 0 with $HClO_4$, the mixture kept at 90 °C for 10 h to convert all Cr(III) to $Cr(H_2O)_6^{3+}$, the slight turbidity removed by centrifugation, and the concentration of $Cr(H_2O)_6^{3+}$ estimated at 574 nm ($\epsilon = 13.4$ M^{-1} cm^{-1}).[8] Results are summarized in Table I. The absence of measurable quantities of Ce(IV) in the reaction mixtures was confirmed by examination in the range 390-320 nm.

Examination of the Chromium(III) Product. A reaction mixture (5 mL) that was 0.0130 M in the 2-ethyl-2-hydroxybutyrato complex of Cr(V) (I), 0.035 M in the parent carboxylic acid, 0.20 M in acetic

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[1] Joint sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (Grant 8022881) is gratefully acknowledged.

[2] Krumpolc, M.; Roček, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.

[3] Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 3176.

[4] Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.

[5] Determinations of Pr^{3+} and Nd^{3+} were carried out spectrophotometrically, the former at 482 nm ($\epsilon = 4.0$ M^{-1} cm^{-1}), the latter at 575 nm ($\epsilon = 7.1$ M^{-1} cm^{-1}). See, for example: Holleck, L.; Hartinger, L. *Angew. Chem.* **1955**, *67*, 648.

[6] In our hands, Krumpolc's procedure[2] for preparing the 2-methyl-2-hydroxybutyrato complex, which calls for a 6:1 mole ratio of hydroxy acid to $Na_2Cr_2O_7$, yielded product significantly contaminated with Cr(VI) unless this ratio was increased to 7:1. Preparation of the 2-ethyl-2-hydroxybutyrato complex proceeded free of difficulty with the specified 6:1 ratio of reactants.

[7] Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792.

[8] Laswick, J. A.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3465. The second $Cr(H_2O)^{3+}$ peak at 408 nm, ($\epsilon = 15.6$) is not suited for determination of Cr(III) in these systems since there is some distortion of this peak from the "tail" of the absorbance resulting from the small quantity of Cr(VI) remaining after precipitation.

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Table I. Stoichiometry of the Cr^{V}-Ce^{III} Reaction[a]

complex	$10^4[Cr^{V}]$ taken	$[Ce^{III}]$	$10^3[HLig]$[b]	$10^4[Cr^{VI}]$ formed[c]	$[Cr^{VI}]/[Cr^{V}]$	$10^4[Cr^{III}]$ formed[d]	$[Cr^{III}]/[Cr^{V}]$
I	5.00	0.087	1.81	3.43	0.68		
	5.00[e]	0.087	1.99	3.43	0.68		
	7.78	0.080	3.01	5.17	0.66		
	7.78	0.080	4.82	5.20	0.67		
	3.82[f]	0.080	1.81	2.51	0.66		
	124	0.30	112			42.5	0.34
II	9.0	0.116	6.28	5.94	0.66		
	9.0	0.050	6.28	5.81	0.65		
	18.0	0.050	6.28	11.50	0.64		
	9.1	0.080	5.02	6.06	0.67		
	9.1	0.080	14.4	5.98	0.65		
	9.0[e]	0.087	7.66	5.50	0.61		
	97.8	0.080	62.8			33.6	0.34

[a] All concentrations are in molar units. Chromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) or as its 2-methyl analogue (II) ($[H^+] = 1.23 \times 10^{-5}$ M ($HOAc$-OAc^- buffer); $[OAc^-] = 0.40$ M unless otherwise indicated). [b] "HLig" is the parent 2-hydroxy acid. [c] Estimated at 350 nm (see text). [d] Estimated at 574 nm (see text). [e] $[H^+] = 6.4 \times 10^{-5}$ M. [f] $[OAc^-] = 0.24$ M.

acid, and 0.040 M in sodium acetate was allowed to stand at room temperature for 7 h, after which is was subjected to cation-exchange chromatography at 2 °C (Bio-Rad 50W-X2 sulfonate resin, H^+ form, 200–400 mesh) as described.[9] The major fraction of dissolved chromium ws eluted rapidly with water as CrO_4^{2-}; the remaining fraction appeared to be a single pink band, eluted in 90 min by using a solution 1.20 M in $NaClO_4$ and 0.04 M in $HClO_4$ [λ_{max} 572 nm ($\epsilon = 31$), 412 nm ($\epsilon = 28$)]. After the latter elution, no detectable chromium remained on the column. Prolonged treatment of the second fraction with excess $HClO_4$ converted it to $Cr(H_2O)_6^{3+}$.

Rate Measurements. Rates were estimated from measurements of decreases in absorbance at 510 nm, a Cr(V) absorption maximum, using a Beckman 5260 recording spectrophotometer.[3] Ionic strength was regulated with $LiClO_4$. Kinetic runs were carried out in the pH range 4.0–5.6 (using $HOAc$–OAc^- buffers). Reactions were first order each in Cr(V) and Ce(III). Conversions were followed for at least 5 half-lives. Rate constants from successive half-lives within a single run agreed to within 6%, and average values did not differ significantly from those obtained from the slopes of logarithmic plots of absorbance difference against reaction times. Specific rates from replicate runs checked to better than 10%. Temperatures were kept at 25.0 ± 0.2 °C during all kinetic experiments.

Several reaction mixtures in which other trivalent metal perchlorates were substituted for $Ce(ClO_4)_3$ were examined. The loss of Cr(V) in all such mixtures was much slower than that in the presence of Ce(III). Reaction rates, estimated from slopes in absorbance during the first 5% of reaction,[10] are compared in Table II. In addition, the primary reaction was not perceptibly catalyzed by Mn^{2+}.

Results and Discussion

Determinations of stoichiometry (Table I) allow us to represent the predominant reaction in the Ce(III)–Cr(V) system as (1). In particular, the conversion of almost exactly two thirds of the added Cr(V) to Cr(VI), in conjunction with the absence of growth of absorbance in 290–320 nm, rules out appreciable net conversion of Ce(III) to Ce(IV).[11,12] The ion-exchange elution behavior of the Cr(III) product from I corresponds to that of a dipositive species, and the spectral properties of this product [λ_{max} 572 nm (ϵ 31), 412 nm ($\epsilon = 28$)] indicate it to be a nonchelated 2-ethyl-2-hydroxybutyrato complex of $(H_2O)_5Cr^{III}$, rather than the corresponding acetato complex [λ_{max} 568 nm ($\epsilon = 22$), 406 nm (ϵ 21)[13a]] or the chelated carboxylato species thought to result from reduction of the parent chromium(V) complex with hydrazine [λ_{max} 564 nm (ϵ 35), 435 nm (ϵ 47)].[3]

Table II. Disproportionation of Carboxylato-Bound Chromium(V) As Catalyzed by Tripositive Metal Ions[a]

	rate[b]	
metal ion (M)[c]	ethylbutyrato complex (I)[d]	methylbutyrato complex (II)[e]
Ce^{3+} (0.075)	2.9	17
La^{3+} (0.071)	0.07	0.24
Pr^{3+} (0.073)	0.08	0.22
Gd^{3+} (0.076)	0.11	0.33
Tb^{3+} (0.082)	0.08	0.18[f]
Al^{3+} (0.078)	0.08	0.12
none	0.02	0.06

[a] Reactions were carried out at 25 °C in 0.60 M $LiClO_4$; $[HOAc^-] = 0.20$ M; $[OAc^-] = 0.40$ M. [b] Loss of Cr(V) (M $s^{-1} \times 10^6$); estimated from initial slopes (see Experimental Section). [c] Added as metal perchlorates. [d] $[Cr^{V}] = 6.4 \times 10^{-4}$ M; [excess ligand] $= 9.6 \times 10^{-4}$ M. [e] $[Cr^{V}] = 1.04 \times 10^{-3}$ M; [excess ligand] $= 6.3 \times 10^{-3}$ M. [f] $[Tb^{3+}] = 0.040$ M.

Representative kinetic data for the disproportionation of the 2-ethyl-2-hydroxybutyrato complex (I), as catalyzed by Ce(III), are assembled in Table III. The reaction is first order in Ce(III) and is seen to be retarded by increasing acidity and, more markedly, by addition of unbound carboxylato ligand. (The latter is designated as $HLig^-$ to differentiate it from the dinegative form Lig^{2-} bound to Cr^V in the chelated reactant). Moreover, it is strongly accelerated by addition of acetate. Within the range of concentrations indicated in Table III, rates conform to eq 2. An iterative nonlinear least-squares refinement,[14] minimizing the function $(k_{obsd} - k_{calcd})^2$ (where the k's represent pseudo-first-order rate constants with Ce^{III} in excess) yielded the parameters $k = (7.84 \pm 0.21) \times 10^{-4}$ M^{-1}

$$\text{rate} = \frac{k[Ce^{III}][Cr^{V}][OAc^-]^2}{[HLig^-](1 + a[H^+])} \tag{2}$$

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(9) Wu, M.-Y.; Paton, S. J.; Fanchiang, Y.-T.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 326.

(10) In a number of cases, a slight but sharp absorbance drop of unknown origin, corresponding the loss of only a few percent of the added Cr(V), was observed immediately after mixing. Initial rates listed in Table II were measured after this drop had occurred.

(11) Recorded reduction potentials[12] for Cr^{VI} and Ce^{IV} allow us to estimate the equilibrium ratio $[Ce^{IV}]/[Ce^{III}]$ in a 1 M $HClO_4$ solution in which $[Cr^{VI}]/[Cr^{III}] = 2$. The calculated ratio, 7×10^{-7}, may be taken as an upper limit for the systems at hand if it is assumed that the Ce^{IV} potential is no more sensitive to variation in $[H^+]$ than is that for Cr^{VI}.

(12) See, for example: Latimer, W. M. "Oxidation Potentials", 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1952; pp 249, 294.

(13) (a) Hamm, R. E.; Johnson, R. L.; Perkins, R. H.; Davis, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 4469. For further comparisons of spectra of carboxylato derivatives of $(H_2O)_5Cr^{III}$, see: (b) Gould, E. S.; Taube, H. *Ibid.* **1964**, *86*, 1318. (c) Butler, R. D.; Taube, H. *Ibid.* **1965**, *87*, 5597. (d) Schlafer, H. L. *Z. Phys. Chem.* (*Wiesbaden*) **1967**, *11*, 65.

(14) Trial values of k and a for this refinement were obtained by plotting value of $(k_{obsd})^{-1}[Ce^{III}][OAc^-]^2[HLig^-]^{-1}$ vs. $[H^+]$. Individual data points were unweighted for this refinement, which converged after three cycles.

Table III. Representative Kinetic Data for the Disproportionation of Sodium Bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I), As Catalyzed by Cerium(III)[a]

$[Ce^{III}]$	$10^4[Cr^V]$[b]	$10^3[HLig^-]$[c]	$10^5[H^+]$[c]	$[OAc^-]$	10^3k_{obsd}	10^3k_{calcd}[e]
0.10	7.79	1.76	1.23	0.40	6.1	6.3
0.087	7.79	1.76	1.23	0.40	5.6	5.6
0.060	7.79	1.76	1.23	0.40	3.6	3.8
0.030	7.79	1.76	1.23	0.40	1.93	1.91
0.087	10.80	1.76	1.23	0.40	5.5	6.3
0.087	3.82	1.76	1.23	0.40	5.5	6.3
0.087	4.61	1.17	1.23	0.40	7.2	8.3
0.087	4.61	2.95	1.23	0.40	3.2	3.3
0.087	4.61	4.13	1.23	0.40	2.3	2.4
0.087	4.61	5.90	1.23	0.40	1.49	1.65
0.087	4.61	8.85	1.23	0.40	1.13	1.10
0.087	7.89	1.76	0.49	0.40	5.8	5.9
0.087	7.89	1.76	0.98	0.40	5.3	5.7
0.087	7.89	1.76	1.97	0.40	4.7	5.2
0.087	5.00	1.76	10.71	0.40	3.1	3.1
0.087	3.82	1.76	1.23	0.32	3.5	3.5
0.087	3.82	1.76	1.23	0.24	2.2	2.0
0.087	3.82	1.76	1.23	0.16	0.91	0.90

[a] All concentrations are in molar units. Reactions were carried out at 25 °C in 0.60 M $LiClO_4$. [b] Sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I). [c] Concentrations of H^+ and 2-ethyl-2-hydroxybutyrate ($HLig^-$) were controlled by addition of measured quantities of the parent acid ($pK_A = 3.32$),[3] acetic acid ($pK_A = 4.61$), and acetate. [d] Pseudo-first-order rate constants (in s^{-1}) = $-d \ln [Cr^V]/dt$. [e] Calculated from rate law 2 in text with k taken as 7.84×10^{-4} M^{-1} s^{-1} and a as 9.6×10^3 M^{-1}.

s^{-1} and $a = (9.6 \pm 1.9) \times 10^3$ M^{-1}).[15] Table III also compares observed rates with those calculated by using rate law 2. The more rapid disproportionation of the 2-methyl-2-hydroxybutyrato complex (II), for which kinetic data exhibit somewhat more scatter than do the data for complex I, follows an analogous rate law with $k = (8.05 \pm 0.46) \times 10^{-3}$ M^{-1} s^{-1} and $a = (11.5 \pm 2.3) \times 10^3$ M^{-1}.

Rate law 2 implies an activated complex that includes, in addition to the Ce^{III} and Cr^V centers, two acetate units. The latter are taken to be associated with Ce^{III}, since analogous acetate dependencies are not observed for the reductions of the same Cr^V complex with hydrazine[3] or hydroxylamine[16] under very similar conditions. The inverse first-order dependence on ligand, $HLig^-$, must, on the other hand, pertain to a preliminary equilibrium about the Cr(V) center, for inhibition by $HLig^-$ is effective at concentrations of the latter that are far below $[Ce^{III}]$ added.

The $a[H^+]$ term suggests partition of one of the reactants between two protonation levels, of which only the deprotonated form is measurably reactive, with the reciprocal $1/a = 1.0 \pm 10^{-4}$ M corresponding to the acidity constant governing this equilibrium. The latter inference, however, is untenable here, for neither Ce^{3+} (for which pK_A lies near 9)[17] nor the Cr(V) complex[18] features a pK_A value near 4.

Our results appear to be consistent instead with a mechanism analogous to those suggested for earlier reactions[3,16] of this Cr(V) derivative, featuring, in each case, intervention of an intermediate formed reversibly from Cr(V) and the reductant with expulsion of H^+. Since, among the tripositive ions examined (Table I), only Ce forms a +4 state stable in aqueous solution,[19] we suspect also that recycling between Ce^{III} and Ce^{IV} is occurring, as has been proposed for the cerium-catalyzed disproportionation of Cr(IV).[20] We thus favor the sequence represented as eq 3–9, in which the Cr(V)–Ce(III) intermediate is designated as the precursor complex ("P") for an initial act of electron transfer. If the sequence indicated is applicable, the observed rate law can give no information about steps 7–9, which are formulated to occur after internal electron transfer within precursor P (step 6) and are taken to be rapid.

$$Ce^{3+} + 2OAc^- \overset{K_1}{\rightleftharpoons} Ce(OAc)_2^+ \tag{3}$$

$$\underset{\text{“Cr}^{\text{V}}\text{L}_2\text{”}}{[(Lig^{2-})_2Cr^VO(OH_2)]^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (Lig^{2-})Cr^VO(OH) + HLig^- \tag*{(4)[21]}$$

$$(Lig^{2-})Cr^VO(OH) + Ce(OAc)_2^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{“P”}}{(Lig^{2-})Cr^V(O)\text{-}\underline{O}\text{-}Ce(OAc)_2} + H^+ \tag{5}$$

$$P \xrightarrow{k_3} (Lig^{2-})Cr^{IV}O + Ce^{IV}(O)(OAc)_2 \tag{6}$$

$$(Lig^{2-})Cr^{IV}O + H_2O + 3HOAc \xrightarrow{\text{rapid}} [(HLig^-)Cr^{IV}(H_2O)_2]^{3+} + 3OAc^- \tag{7}$$

$$[(HLig^-)Cr^{IV}(H_2O)_2]^{3+} + Cr^V \xrightarrow{\text{rapid}} [(HLig^-)Cr^{III}(H_2O)_2]^{2+} + Cr^{VI} \tag{8}$$

$$Ce^{IV} + Cr^V \xrightarrow{\text{rapid}} Ce^{III} + Cr^{VI} \tag{9}$$

Application of the steady-state approximation to the precursor, P, and to the monocarboxylato intermediate, $(Lig^{2-})Cr^VO(OH)$, leads to the rate expression (10). If the k_{-1} term in the denominator of (10) is taken to be much larger than the k_2k_3 term and the resulting simplified expression is rewritten in terms of the total concentrations of chromium(V),

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(15) The relatively large uncertainty in the derived parameter a reflects the circumstance that rates are much less sensitive to $[H^+]$ than to $[Ce^{III}]$, $[LigH^-]$, and $[OAc^-]$.

(16) Rajasekar, N.; Subramaniam, R.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 971.

(17) The pK_A for Ce^{3+} is taken to fall between the recorded values for La^{3+} (9.33) and Pr^{3+} (8.82). See, for example: Smith, R. H.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York, 1976; Vol. 4, p 2.

(18) The spectrum of the Cr(V) complex has been found[3] to be invariant between pH 3 and 5. Attempted determinations of the pK_A for this derivative in the absence of an excess of the parent ligand are complicated by disproportionation at pH values above 5.

(19) See, for example: Moeller, T. "The Chemistry of the Lanthanides"; Pergamon Press: Oxford, 1973; p 5.

(20) Doyle, M.; Swedo, R. J.; Roček, J. *J. Am. Chem. Soc.* **1973**, *95*, 8352.

(21) We suggest that the proton lost during this dissociation arises from the hydrated form of the original Cr(V) chelate. A number of carboxy complexes of this type, including the two considered in this study, are known to be strongly hydrated.[2]

$$\text{rate} = \frac{[\mathrm{Cr^VL_2}][\mathrm{Ce(OAc)_2}^+]}{\dfrac{k_2k_3[\mathrm{Ce(OAc)_2}^+]}{k_{-2}[\mathrm{H^+}] + k_3} + k_{-1}[\mathrm{HLig^-}]} \times \frac{k_1k_2k_3}{k_{-2}[\mathrm{H^+}] + k_3} \quad (10)$$

$[\mathrm{Cr^V}]_\mathrm{T}$, and cerium(III), $[\mathrm{Ce^{III}}]_\mathrm{T}$, expression 11 is obtained.

$$\text{rate} = \frac{K_1k_2[\mathrm{Cr^V}]_\mathrm{T}[\mathrm{Ce^{III}}]_\mathrm{T}[\mathrm{OAc^-}]^2}{\left(\dfrac{k_{-1}}{k_1}[\mathrm{Hlig^-}] + 1\right)\left(1 + \dfrac{k_{-2}}{k_3}[\mathrm{H^+}]\right)} \quad (11)$$

Finally, if $(k_{-1}/k_1)[\mathrm{HLig^-}]$ is assumed to be much greater than unity (implying that the extent of dissociation of the chelate is small), (11) may be further simplified to (12). The latter

$$\text{rate} = \frac{K_1k_1k_2[\mathrm{Cr^V}]_\mathrm{T}[\mathrm{Ce^{III}}]_\mathrm{T}[\mathrm{OAc^-}]^2}{k_{-1}[\mathrm{HLig^-}]\left(1 + \dfrac{k_{-2}}{k_3}[\mathrm{H^+}]\right)} \quad (12)$$

is seen to be equivalent to the observed rate law (2), with $a = k_{-2}/k_3$ (a measure of the competition between reactions of precursor, P). Individual values of k_{-2} and k_3 cannot be determined from steady-state experiments alone.

Of the three proposed rapid steps following the rate-determining sequence, step 7, which represents opening of a chelate ring in the $\mathrm{Cr^{IV}}$ intermediate, is inserted to accommdate our evidence that the observed $\mathrm{Cr^{III}}$ product is carboxyl bound but unchelated. By suggesting that such breakage occurs at the tetrapositive level, we are implying that ligand substitution at the Cr(IV) center is substantially more rapid than that at either Cr(III) (which has been shown to undergo dechelation slowly[13c]) or Cr(V). This conclusion is in accord with that arising from earlier studies[22] of reactions that appear to proceed through Cr(IV).

The final two steps, (8) and (9), are taken to be rapid parallel oxidations of the Cr(V) reactant with the two powerful oxidants, $\mathrm{Cr^{IV}}$ and $\mathrm{Ce^{IV}}$. Both are highly favored thermodynamically. Although we have been unable to find a precedent for the first of these, reaction 9 has been previously proposed as a rapid step in transformations occurring in Ce–Cr redox systems both by Doyle and co-workers[20] and by Tong and King.[23,24] Note further that Mn(II) is ineffective as a catalyst for the disproportionation reaction at hand, despite the ease with which it undergoes oxidation to carboxylate-bound Mn(III); the difficulty here is probably that the latter is too weak an oxidant to oxidize Cr(V) in a rapid step analogous to (8).

To summarize, the Ce(III)-catalyzed disproportionation of carboxylato-bound chromium(V) is seen to be initiated in the same manner as reductions by hydrazine[3] and by hydroxylamine;[16] i.e., all three reactions require preliminary loss of one ligand per Cr(V) and all provide evidence that they proceed through a difunctional precursor formed by loss of a proton. Beyond that point, however, paths diverge markedly since the Ce(III) reaction necessarily features a series of 1e transactions, whereas reactions of the nitrogen-derived reductants are consummated with 2e changes.[25]

Acknowledgment. The authors are indebted to Dr. M. S. Ram for his help in carrying out the nonlinear least-squares treatment of kinetic data and to Professor Jan Roček for valuable discussions.

Registry No. I, 75476-70-9; II, 87509-55-5; Ce, 7440-45-1; Cr, 7440-47-3.

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(22) (a) Plane, R. A.; Taube, H. *J. Phys. Chem.* **1952**, *56*, 33. (b) Ogard, A. E.; Taube, H. *Ibid.* **1958**, *62*, 357.

(23) Tong, J. Y.-P; King, E. L. *J. Am. Chem. Soc.* **1960**, *15*, 3805. Note, however that this study was carried out in strong acid, rather than in a buffered medium.

(24) Preliminary experiments in this laboratory indicate that Ce(IV) oxidizes Cr(V) chelate I to Cr(VI) at a specific rate near 1.93 $\mathrm{M^{-1}\,s^{-1}}$ (25 °C; [HOAc] = 0.2 M; $[\mathrm{OAc^-}]$ = 0.4 M; $[\mathrm{HLig^-}]$ = 0.0018 M); i.e., this reaction is much more rapid than the primary reaction considered in the present study.

(25) Two suggestions by a reviewer for modification of the mechanistic sequence (3)–(9) merit response. First, it is proposed that the two acetate ions appearing in the activated complex might have been coordinated originally with $\mathrm{Cr^V}$, rather than with $\mathrm{Ce^{III}}$. Although our experiments do not exclude this possibility, we believe it to be unlikely since similar catalysis by acetate has been observed neither in other reductions of carboxylato complexes of Cr(V)[3,16] nor in the disproportionation of Cr(V) in aqueous solutions in the absence of metal ions. Acetate catalysis than appears to be characteristic of the Ce(III) center. It has also been asked whether we have considered the oxidation of $\mathrm{Ce^{III}}$ with $\mathrm{Cr^{IV}}$

$$\mathrm{Ce^{III} + Cr^{IV} \rightarrow Ce^{IV} + Cr^{III}} \quad (13)$$

as an alternative to (8). We doubt that (13) contributes significantly to the overall transformation, for addition of (7), (9), and (13) yields

$$\mathrm{2Cr^{V} + Ce^{III} \rightarrow Ce^{IV} + Cr^{III} + Cr^{VI}} \quad (14)$$

which is in accord with neither the observed stoichiometry nor the absence of $\mathrm{Ce^{IV}}$ in the final products.