

perature, CO addition caused no change. However, for CeO<sub>2</sub>-873 the A1, A2, and B species all disappeared almost completely upon CO treatment. Interestingly, no selectivity for A1, A2, or B was observed.

After the CeO<sub>2</sub>-873 sample had been treated with CO, and almost all ESR signals had disappeared, this sample was evacuated at room temperature for 10 min and then treated with O<sub>2</sub> again. Species A1, A2, and B reappeared (Figure 6) at lower overall intensities, but the peaks for B were the weakest. This is additional evidence that species B resides at a site significantly different from those of A1 and A2.

It is difficult to understand the dependence of CO reactivity on CeO<sub>2</sub> heat treatment temperature. However, it is perhaps not surprising that A1, A2, and B cannot be differentiated by CO reactivity. Although these species can be differentiated by ESR spectroscopy at 77 K, the energy differences between them must be very small compared to the  $E_a$  of reaction with CO. Furthermore, the stabilities/lifetimes of the three species depend on each other on the ceria surface. Thus, destruction of B by heating led to a greater instability of A1.

The reappearance of A1, A2, and B when the sample was again treated with O<sub>2</sub> is very interesting. It implies that CO does not destroy the active sites. Further investigations are needed in order to better understand this interesting chemistry.

#### Further Discussion of Structural Assignments

As stated earlier, we believe species A1 and A2 are side-on bonded superoxide species on the surface of nonstoichiometric ceria. On the basis of stability, rotational behavior, and relative abundance on the surface, we believe species B may be superoxide,

inserted into an oxygen vacancy, and therefore an intermediate in the re-formation of a lattice O<sup>2-</sup> by further reduction.

At this point we should discuss why we do not believe other paramagnetic species are responsible for these signals, for example O<sup>-</sup> or O<sub>3</sub><sup>-</sup>. Although it is difficult to distinguish O<sup>-</sup>, O<sub>2</sub><sup>-</sup>, and O<sub>3</sub><sup>-</sup> by  $g$  value and line shape (without the use of <sup>17</sup>O labeling), it should be possible to differentiate them on the basis of stability and reactivity.

It is known that O<sub>3</sub><sup>-</sup> is formed from surface O<sup>-</sup> reacting with O<sub>2</sub> and that O<sub>3</sub><sup>-</sup> usually decomposes back to O<sup>-</sup> and gaseous O<sub>2</sub> during sample evacuation at room temperature.<sup>24</sup> Our species A1, A2, and B do not behave in this way. It is also known that O<sup>-</sup> is extremely reactive, and it has been reported that it reacts with CO at room temperature.<sup>25</sup> Our results show that A1, A2, and B react with similar rates with CO. Actually, they did not react when CeO<sub>2</sub>-673 was employed, but all reacted when CeO<sub>2</sub>-873 was employed. This result does not support the idea that we are dealing with O<sup>-</sup> species. However, it should be pointed out that we do not understand this striking difference between CeO<sub>2</sub>-673 and CeO<sub>2</sub>-873. It seems likely that these differences are due to a higher population of bulk oxygen vacancies in CeO<sub>2</sub>-873 and their ability to migrate to the surface. However, further work is necessary in order to gain a better understanding.

**Acknowledgment.** The support of the Army Research Office is acknowledged with gratitude.

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Kent State University, Kent, Ohio 44242

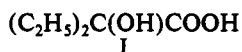
## Electron Transfer. 112. Reactions of Chromium(IV) with Tin(II) and Cerium(III)<sup>1</sup>

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Aqueous solutions of Cr(IV) may be stabilized through ligation by anions of branched  $\alpha$ -hydroxy acids. This atypical oxidation state, prepared at pH 2.5-3.5 in solutions buffered by 2-ethyl-2-hydroxybutanoic acid (HLig) and its anion (Lig<sup>-</sup>), is readily reduced to bischelated Cr(III) using Sn(II). Kinetic pH and ligand dependencies point to partial conversion of the oxidant to a less reactive deprotonated form and an unreactive "extraligated" form. The pattern of inhibition of the Cr(IV)-Sn(II) reaction by a series of (NH<sub>3</sub>)<sub>5</sub>Co<sup>III</sup> cations points to the intervention of a Cr(II) species which reacts with the halogeno-substituted "traps" about 3 times as rapidly as with Cr(IV) in our media. Reactions in the Cr(IV)-Ce(III) system result from superposition of an uncatalyzed bimolecular process and a Ce(III)-catalyzed contribution. The first of these is a disproportionation (2Cr<sup>IV</sup> → Cr<sup>III</sup> + Cr<sup>V</sup>), whereas the Ce(III)-catalyzed component features competition between oxidative cleavage of the Cr(IV)-bound ligand (to CO<sub>2</sub> and 3-pentanone) and Ce(III)-catalyzed disproportionation. Rate dependence on [Ce<sup>III</sup>] indicates partition of this catalyst between monomeric and dimeric forms, with the latter much less reactive. The observed rate behavior, in conjunction with measured yields of Cr(V), supports a sequence in which the active intermediate, Ce(IV), may undergo a 1e reduction by Cr(IV) or, alternatively, may collaborate with ligand-bound Cr(IV) in an induced electron-transfer process which results in concerted scission of a C-C bond in the ligand and reduction of both quadripotential centers. Differences in the catalytic behavior of Mn(II,III) and Ce(III,IV) are attributed to the recognized specific affinity of Ce(IV) for the alcoholic -OH function.

Solutions of chromium(IV) may be stabilized through ligation by anions of branched  $\alpha$ -hydroxy acids such as 2-ethyl-2-hydroxybutanoic acid (I) and may be generated by reductions of



Cr(VI), in media buffered by these acids, using the 2e donors As(III) and Sb(III).<sup>2</sup> The convenient preparation of this less usual d<sup>2</sup> state has facilitated the investigation of its behavior toward a variety of metal-center reagents, and the kinetic characteristics

of the systems Cr(IV)-Mo<sub>2</sub>O<sub>4</sub><sup>2+</sup>, Cr(IV)-U(IV), and Cr(IV)-Mn(II) have been found<sup>2,3</sup> to exhibit unexpected facets.

The present contribution deals with the reactions of carboxylato-bound chromium(IV) with tin(II) and cerium(III). The Cr(IV)-Sn(II) system is of interest because it has yielded evidence for the intervention of chromium(II), whereas the lanthanide center has been found to catalyze the reaction of Cr(IV) with the stabilizing ligand. The two systems, viewed together, exemplify contrasting paths by which noncomplementary redox reactions (involving the net 1e oxidant Cr(IV) in conjunction with 2e reductants) may proceed.

(1) Sponsorship of this work by the National Science Foundation (Grant 9019840) is gratefully acknowledged.

(2) Ghosh, M. C.; Gould, E. S. *Inorg. Chem.* 1990, 29, 4258.

(3) (a) Ghosh, M. C.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* 1991, 30, 1039. (b) *Idem.* *Inorg. Chem.* 1992, 31, 702.

### Experimental Section

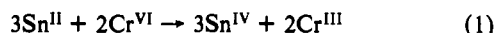
**Materials.** Sodium dichromate (MCB, Reagent Grade), 3-pentanone (Fisher), cerium(III) perchlorate (G. F. Smith), and the "ligand acid", 2-ethyl-2-hydroxybutanoic acid ("HLig", I), (Aldrich) were used as received. Solutions of As(III) were prepared by suspending reagent grade  $\text{As}_2\text{O}_3$  (Fisher) in water and then adding 1.0 M NaOH dropwise, with stirring, until solution was complete. Solutions of tin(II) were prepared by dissolving crystalline  $\text{SnCl}_2$  (MCB) in deaerated 1.0 M HCl and then diluting with deaerated aqueous NaCl; Sn(II) content was checked by titration with  $\text{KI}_3$ . Solutions of  $\text{NaClO}_4$  were prepared by neutralizing  $\text{HClO}_4$  with  $\text{NaHCO}_3$ . Chromium(IV) solutions were generated by treating known deficiencies of Cr(VI) with excess (0.01 M) As(III) in ligand buffer (HLig + Lig<sup>-</sup>) or, for the study of the Sn(II)-Cr(IV) system, with excess Sn(II) in ligand buffer.<sup>4,5a</sup> Cobalt(III) complexes (used in competition experiments) were available from previous studies.<sup>5b-d</sup>

**Analyses of Reaction Products.** 3-Pentanone, a product from the Cr(IV)-Ce(III) reaction in ligand buffer, was estimated using gas-liquid chromatography. After 4-min reaction time, the aqueous mixture was acidified with concentrated HCl and was extracted with a known volume of *p*-xylene. The xylene extracts were dried with anhydrous  $\text{Na}_2\text{SO}_4$ , and aliquots were subjected to GLC.<sup>6</sup> Comparisons with known samples of this ketone in xylene indicated that mixtures 0.005 M in Cr(IV), 0.05 M in As(III), 0.040 M in Ce(III), and 0.050-0.30 M in the ligand acid (I) and its anion yielded  $0.24 \pm 0.02$  mol of ketone/mol of Cr(IV) consumed and that the yield of ketone did not vary significantly with the concentration of ligand taken. Such reaction mixtures also gave strong qualitative tests for  $\text{CO}_2$  (precipitation of  $\text{BaCO}_3$  from aqueous  $\text{Ba}(\text{OH})_2$ ).

Chromium(V) content in Cr(IV)-Ce(III) systems was estimated at 510 nm ( $\epsilon = 181 \text{ M}^{-1} \text{ cm}^{-1}$ ), correcting for the slight absorbance of Cr(III) at this wavelength,<sup>7</sup> or alternatively, from its ESR signal at  $g = 1.98$  as described.<sup>3a</sup>

The predominant (>80%) Cr(III) product from each reaction in ligand buffer was adsorbed by neither cation- nor anion-exchange resin and exhibited maxima at 418 ( $\epsilon = 68 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 590 nm ( $\epsilon = 53$ ). On prolonged standing, this species was converted to a +1 charged complex,  $\epsilon_{\text{max}}^{570} = 36$ ,  $\epsilon_{\text{max}}^{412} = 46 \text{ M}^{-1} \text{ cm}^{-1}$ .

Although the stoichiometry of the Cr(IV)-Sn(II) reaction under kinetic conditions could not be evaluated directly, due to the competing bimolecular disproportionation of Cr(IV),<sup>3b</sup> the overall stoichiometry of the Cr(VI)-Sn(II) reaction in 0.05 M ligand buffer was determined by adding Cr(VI) to a known excess of Sn(II) (0.032 M) under  $\text{N}_2$ , waiting 2 min for complete reaction, and then titrating the unreacted Sn(II) with  $\text{KI}_3$ . Estimated ratios,  $\Delta[\text{Sn}^{\text{II}}]/\Delta[\text{Cr}^{\text{VI}}]$ , were  $1.48 \pm 0.05$ , confirming very nearly quantitative formation of Sn(IV) and Cr(III).<sup>8</sup>



Since the complete reaction has been shown to proceed mainly

through Cr(IV), quantitative conversion of the latter species to Cr(III) must likewise be inferred.

**Kinetic Experiments.** Reactions were followed by measuring absorbance changes at 510 nm, employing either a Beckman Model 5260 or a Cary 14 recording spectrophotometer. Solutions were buffered with measured quantities of the ligand acid, 2-ethyl-2-hydroxybutanoic acid (HLig, I), and its sodium salt ( $\text{Na}^+\text{Lig}^-$ ). Ionic strength was regulated by the addition of NaCl for the Cr(IV)-Sn(II) reaction and by added  $\text{NaClO}_4$  in the case of the Cr(IV)-Ce(III) reaction. Chromium(IV) was generated by adding the required quantity of Cr(VI) to a known excess of buffered As(III) or buffered Sn(II).<sup>9</sup>

Reactions with Sn(II) were examined in the pH range 2.5-3.4, and [Lig<sup>-</sup>] was allowed to vary between 0.02 and 0.16 M. However, almost all experiments in the Cr(IV)-Ce(III) system were carried out at pH  $3.30 \pm 0.03$ , with [Lig<sup>-</sup>] held at 0.20 M. At appreciably lower concentrations of  $\text{H}^+$  or Lig<sup>-</sup>, kinetic complications due to the Ce(III)-catalyzed disproportionation of the product Cr(V)<sup>10</sup> became troublesome. In addition, the solubility of the ligating acid in water imposed an upper limit on [HLig] taken and, therefore, on [ $\text{H}^+$ ] obtainable with this buffer.

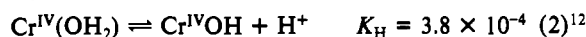
The Cr(IV)-Sn(II) reactions, which were carried out with the reductant in at least a 6-fold excess,<sup>11</sup> gave very nearly exponential profiles. Such conversions were followed for at least 4 half-lives. Pseudo-first-order rate constants from successive half-lives within a single run agreed to within 4%, and average values did not differ significantly from those estimated by nonlinear least-squares fitting of data points to the relationship describing first-order transformations. Specific rates from replicate runs checked to better than 6%. These reactions were retarded measurably (while retaining their exponential character), by addition of  $10^{-5}$ - $10^{-3}$  M [ $(\text{NH}_3)_5\text{CoCl}$ ]<sup>2+</sup>, by the analogous bromo, fluoro, and azido complexes, and by a number of organic derivatives of  $(\text{NH}_3)_5\text{Co}^{\text{III}}$ , but not by the corresponding acetate and pyridine complexes.

For the Cr(IV)-Ce(III) reactions, decay patterns generally corresponded to a combination of competing first- and second-order processes, and a more elaborate treatment (see Results Section) was used to obtain contributing specific rates.

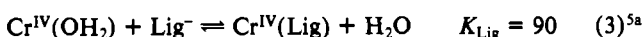
**Additional Observations and Control Experiments.** Solutions of Cr(IV) were not reduced at a detectable rate with excess quantities of  $\text{PtCl}_4^{2-}$ , Sb(III), Tl(I), or  $\text{H}_3\text{PO}_2$  under conditions where Sn(II) reacted readily. Moreover, no catalytic effects analogous to those noted for Ce(III) were observed with comparable concentrations of Fe(III), Cu(II), Ni(II), Ag(I), La(III), Tb(III), or V(V). Cerium(IV) oxidizes ligated Cr(IV) in our medium, but the resulting yield of Cr(V) corresponds to only a portion of the Ce(IV) taken (see Results Section). Sodium oxalate reacts very rapidly with Cr(IV) in the buffer used, yielding a product showing a broad maximum at 525 nm ( $\epsilon = 1.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ); the spectrum of the latter species suggests that it is an oxalato derivative of Cr(IV), i.e., that an exchange of ligands rather than a redox reaction had occurred.

### Results

Earlier studies yielded evidence that chelated Cr(IV) in our buffer system undergoes partial deprotonation



as well as partition between "ligation levels"



(4) Reduction of Cr(VI) to Cr(IV) using As(III) was virtually complete after 30-200 s, depending on [ $\text{H}^+$ ] and [Lig<sup>-</sup>],<sup>5</sup> but reduction using Sn(II) was much more rapid. Despite the recognized<sup>3a</sup> contamination of the latter preparation with Cr(V), specific redox rates measured with Cr(IV) generated from Sn(II) were not significantly different from those measured with Cr(IV) generated from As(III), provided the coreagent was kept in large excess.

(5) (a) Ghosh, M. C.; Gould, E. S. *Inorg. Chem.* **1991**, *30*, 491. (b) Fan, F.-R. F.; Gould, E. S. *Ibid.* **1974**, *13*, 2639. (c) Wu, M.-Y.; Paton, S. J.; Fanchiang, Y.-T.; Gelerinter, E.; Gould, E. S. *Ibid.* **1978**, *17*, 326. (d) Gould, E. S.; Johnson, N. A.; Morland, R. B. *Ibid.* **1976**, *15*, 1929.

(6) Separations were accomplished on a Hewlett-Packard 5890 instrument, using a HP Series 530- $\mu\text{m}$  capillary column. We thank Dr. C. Fenk and Mr. K. B. Chai for help in these determinations.

(7) The relationship used here was  $[\text{Cr}^{\text{V}}] = (A - \epsilon_3[\text{Cr}]_{\text{T}})/(\epsilon_5 - \epsilon_3)$ , where  $A$  is the absorbance,  $[\text{Cr}]_{\text{T}}$  designates the total chromium taken, and  $\epsilon_3$  and  $\epsilon_5$  are the molar absorbances of the two oxidation states in the mixture of products.

(8) In more dilute solutions with air not excluded, much higher ratios,  $\Delta[\text{Sn}^{\text{II}}]/\Delta[\text{Cr}^{\text{VI}}]$ , were observed, suggesting competition between  $\text{O}_2$  and one or more oxidizing chromium species for a very reactive oxidizable intermediate.

(9) A kinetic study of the generation of Cr(IV) using As(III) has been described.<sup>5a</sup> The much more rapid reaction of Sn(II) with Cr(VI) in our buffer system, which yields minor amounts of Cr(V) and Cr(III) as well as Cr(IV),<sup>3a</sup> was found to be kinetically complex. Although reaction profiles, both at 350 and 510 nm, were highly reproducible, several unexplained facets, including a delay between the disappearance of Cr(VI) and the formation of a portion of Cr(IV), were noted.

(10) Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 3798.

(11) Reductions with [ $\text{Sn}^{\text{II}}$ ] > 0.005 M could not be monitored successfully due to the formation of slight Sn(IV) turbidity as the reaction proceeded.

(12) Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 4679.

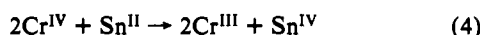
**Table I.** Kinetic Data for the Reaction of Chromium(IV) with Tin(II)<sup>a</sup>

$10^4[\text{Sn}^{II}]$ , M	$[\text{LigH}]$ , M <sup>b</sup>	$[\text{Lig}^-]$ , M <sup>c</sup>	pH	$10^2k$ , s <sup>-1 d</sup>
6.0	0.120	0.080	3.12	2.0 (2.1)
12.0	0.120	0.080	3.13	4.2 (4.3)
18.0	0.120	0.080	3.12	5.6 (6.5)
24	0.120	0.080	3.14	8.6 (8.6)
48	0.120	0.080	3.13	16.5 (17.3)
6.0	0.030	0.020	3.12	6.9 (5.7)
6.0	0.060	0.040	3.13	3.7 (3.7)
6.0	0.090	0.060	3.15	2.8 (2.8)
6.0	0.180	0.120	3.15	1.47 (1.54)
6.0	0.24	0.160	3.15	1.24 (1.19)
6.0	0.52	0.080	2.50	2.2 (2.0)
6.0	0.03	0.080	2.75	2.0 (2.0)
6.0	0.180	0.080	2.97	2.1 (2.1)
6.0	0.080	0.080	3.35	2.6 (2.3)

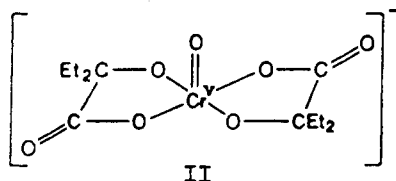
<sup>a</sup>Reactions were carried out at 25 °C,  $\mu = 0.50$  M (NaCl);  $[\text{Cr}^{IV}]_0 = (1.0\text{--}2.0) \times 10^{-4}$  M;  $\lambda = 510$  nm. <sup>b</sup>2-Ethyl-2-hydroxybutanoic acid (I). <sup>c</sup>Sodium 2-ethyl-2-hydroxybutanoate. <sup>d</sup>Pseudo-first-order specific rates; parenthetical values were calculated from eq 5, taking  $k_{\text{Cr}}$  as  $263 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_{\text{CrOH}}$  as  $102 \text{ M}^{-1} \text{ s}^{-1}$ ,  $K_{\text{Lig}}$  as  $90 \text{ M}^{-1}$  (ref 5a), and  $K_{\text{H}}$  as  $3.8 \times 10^{-4} \text{ M}$  (ref 12).

Both equilibria enter the picture when we consider the Cr(IV)–Sn(II) system.

The very close approach to 3:2 stoichiometry observed for the reaction of Cr(VI) with excess Sn(II) (eq 1) in the medium at hand points to the quantitative formation of Cr(III), not only from Cr(VI) but also from the intermediate state, Cr(IV) (eq 4).



The spectrum ( $\epsilon_{590} = 53$ ,  $\epsilon_{418} = 68 \text{ M}^{-1} \text{ cm}^{-1}$ ) of the principal Cr(III) product from both the Sn(II) and Ce(III) reactions corresponds to that of the species resulting when the Cr(V) chelate (II) derived from our ligand is reduced with ascorbic acid in the



same buffer.<sup>13</sup> The structure assigned to this product features a pair of chelate rings formed from the buffering carboxylate anion, as well as an additional monodentate carboxylate group, a picture consistent with the observed slow decomposition in solution, via partial aquation, with loss of the unidentate ligand.

Kinetic data for the Cr(IV)–Sn(II) reaction appear in Table I. The reaction is seen to be first order in Sn(II) with no hint of kinetic saturation within the range of relatively low concentrations<sup>11</sup> of reductant taken. Marked inhibition by excess ligand may be attributed to partial conversion of Cr(IV) to a very much less reactive “extraligated” form, Cr<sup>IV</sup>(Lig) (eq 3). If equilibria (2) and (3) are taken into consideration and the kinetic contribution of Cr<sup>IV</sup>(Lig) is assumed to be negligible, variation in rates should conform to (5), where  $k_{\text{Cr}}$  and  $k_{\text{CrOH}}$  pertain to the con-

$$k_{\text{obsd}} = \frac{[\text{Sn}^{II}](k_{\text{Cr}}[\text{H}^+] + k_{\text{CrOH}}K_{\text{H}})}{K_{\text{H}} + [\text{H}^+] + K_{\text{Lig}}[\text{H}^+][\text{Lig}^-]} \quad (5)$$

tributions from the protonated and deprotonated oxidant. Refinement of rate data in terms of (5) yields  $k_{\text{Cr}} = 263 \pm 20 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{\text{CrOH}} = 102 \pm 42 \text{ M}^{-1} \text{ s}^{-1}$ . Specific rates calculated from (5) are compared with observed values in the same table. Note that reactions with Sn(II) are rapid enough to allow us to neglect the loss of Cr(IV) by bimolecular decay.<sup>3b</sup>

Table II summarizes the results of experiments in which various  $(\text{NH}_3)_5\text{Co}^{III}$  complexes were added, as possible traps for a re-

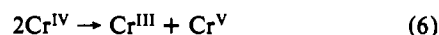
**Table II.** Effect of Added Cobalt(III) Complexes,  $[(\text{NH}_3)_5\text{Co}^{III}\text{X}]^{2+/3+}$ , on the Reduction of Chromium(IV) by Tin(II)<sup>a</sup>

$10^5[\text{Co}^{III}]$ , M	$10^2k_{\text{obsd}}$ , s <sup>-1</sup>						
	X						
	Cl	Br	F	N <sub>3</sub>	pyrazine	4-AcPy	pyruvato
0.0	7.9	7.8	8.0	8.0			7.8
1.0	7.2						
2.0	6.9	6.9	6.7	7.1			
3.0	6.6						
6.0	6.1	6.1	6.1	6.2	7.5	7.7	7.9
20	5.1	5.2	5.4	5.5	6.3		8.0
50	4.9			5.3	6.0		
100	4.7			5.2	5.7		
500			4.7	4.7	5.3	6.6	6.8
$k_{16}/k_{17}$ <sup>b</sup>	3.3	3.3	3.5	2.5	0.40	0.020	0.016
$10^{-5}k_{\text{Cr(III)}}^c$	6.0	14	2.5	3.0	1.0	0.95	0.10

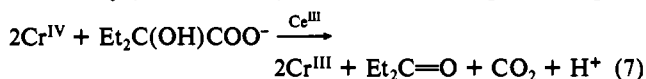
<sup>a</sup>Reactions were carried out at 25 °C,  $\mu = 0.50$  M (NaCl);  $[\text{Cr}^{IV}]_0 = 2.0 \times 10^{-4}$  M;  $[\text{Sn}^{II}] = 2.2 \times 10^{-3}$  M;  $[\text{LigH}] = 0.120$  M;  $[\text{Lig}^-] = 0.080$  M; pH = 3.1;  $\lambda = 510$  nm. No inhibition was observed with  $(\text{NH}_3)_5(\text{OAc})^{2+}$  or  $(\text{NH}_3)_5\text{CoPy}^{3+}$  ( $2 \times 10^{-4}$  M). <sup>b</sup>Selectivity of the redox intermediate toward Co(III) and Cr(IV) (see eq 18 and text). <sup>c</sup>Specific rates ( $\text{M}^{-1} \text{ s}^{-1}$ ) for reaction of the Co(III) complex with  $\text{Cr}^{2+}(\text{aq})$  (1.0 M  $\text{HClO}_4$ , 25 °C; see ref 5b–d).

ductive intermediate, to the Sn(II)–Cr(IV) reaction. Retardation is observed with the halide and azido complexes as well as with several heterocyclic (pyridine and pyrazine) complexes having ligands which are known to mediate inner-sphere reductions by  $\text{Cr}^{2+}$  unusually effectively,<sup>5d</sup> but not with the acetate or pyridine derivatives. At low concentrations, the effect becomes more pronounced with increasing  $[\text{Co}^{III}]$ , but there is a leveling off at higher concentrations, suggesting association (ion-pairing) with the trapped species. No differences are apparent in the effects associated with the three halide complexes.

The reactions observed in the Cr(IV)–Ce(III) system are much slower than those with Sn(II) and feature competition between the uncatalyzed bimolecular process and a Ce(III)-catalyzed contribution. The first of these has been shown<sup>3b</sup> to be a disproportionation to Cr(III) and Cr(V)



whereas the Ce(III)-catalyzed component involves partially, but not entirely (see Discussion), an oxidative cleavage of the ligand:



Cr(IV)-decay curves for the Cr(IV)–Ce(III) reaction, particularly at low  $[\text{Ce}^{III}]$ , reflect the superposition of uncatalyzed bimolecular ( $k_u$ ) and Ce(III)-catalyzed ( $k_c$ ) processes

$$-d[\text{Cr}^{IV}]/dt = k_u[\text{Cr}^{IV}]^2 + k_c[\text{Cr}^{IV}] \quad (8)$$

Integration of (8), expression of concentrations in terms of absorbances ( $A$  values), and rearrangement of terms gives (9), where  $\Delta\epsilon = (A_0 - A_\infty)/[\text{Cr}^{IV}]_0$ .

$$A_t = \frac{[e^{k_c t}(k_u A_\infty^2 - k_c \Delta\epsilon A_\infty - k_u A_0 A_\infty) + A_\infty(k_c \Delta\epsilon + k_u A_0 - k_u A_\infty) - k_c A_0 \Delta\epsilon]}{[e^{k_c t}(k_u A_\infty - k_c \Delta\epsilon - k_u A_0) + k_u(A_0 - A_\infty)]} \quad (9)$$

Treatment of data for runs in which  $[\text{Ce}^{III}]$  is allowed to vary yields the kinetic components given in Table III. Close correspondence between observed and calculated profiles was achieved using previously determined<sup>3b</sup>  $k_u$  values (which were shown to be markedly dependent on  $[\text{Lig}^-]$ ), and in cases where  $k_u$  was determined from the present data, agreement is satisfactory. Variation of  $k_c$  with  $[\text{Ce}^{III}]$  is seen to be less severe than that corresponding to unit order, pointing to partial conversion of this lanthanide center to a less active di- or polynuclear species analogous to that proposed by Biedermann<sup>14</sup> to correlate potentiometric data taken in carboxylate-free systems. If we assume

**Table III.** Kinetic Data for the Reaction of Chromium(IV) with Cerium(III)<sup>a</sup>

$10^3[\text{Ce}^{III}]$ , M	$[\text{Lig}^-]$ , <sup>b</sup> M	pH	$k_{\text{app}}^c$ , $\text{M}^{-1} \text{s}^{-1}$	$10^3 k_c^d$ , <sup>d</sup> $\text{s}^{-1}$
0.10	0.20	3.33	$0.88 \pm 0.08$	$0.28 \pm 0.01$ (0.27)
0.20	0.20	3.33	$0.78 \pm 0.07$	$0.40 \pm 0.02$ (0.41)
0.40	0.20	3.33	0.88 <sup>e</sup>	$0.63 \pm 0.04$ (0.63)
0.60	0.20	3.31	0.88 <sup>e</sup>	$0.75 \pm 0.04$ (0.81)
1.20	0.20	3.33	0.88 <sup>e</sup>	$1.20 \pm 0.05$ (1.24)
1.20	0.050	3.34	3.4 <sup>e</sup>	$2.4 \pm 0.1$
2.5	0.20	3.29	0.88 <sup>e</sup>	$2.1 \pm 0.1$ (2.0)
5.0	0.20	3.31	0.88 <sup>e</sup>	$3.2 \pm 0.1$ (3.1)
10.0	0.20	3.28	0.88 <sup>e</sup>	$5.5 \pm 0.2$ (5.0)
10.0	0.050	3.30	3.0 <sup>e</sup>	$10.1 \pm 0.3$
20	0.20	3.32	0.88 <sup>e</sup>	$8.6 \pm 0.2$ (8.3)
30	0.20	3.27	0.88 <sup>e</sup>	$10.8 \pm 0.3$ (11.2)
40	0.20	3.30	0.88 <sup>e</sup>	$13.3 \pm 0.5$ (14.0)
50	0.20	3.27	0.88 <sup>e</sup>	$16.8 \pm 0.5$ (16.8)

<sup>a</sup>Reactions were carried out at 25 °C,  $\mu = 0.50 \text{ M}$  ( $\text{NaClO}_4$ );  $[\text{Cr}^{IV}]_0 = 8.0 \times 10^{-4} \text{ M}$ ;  $\lambda = 510 \text{ nm}$ . <sup>b</sup>Sodium 2-ethyl-2-hydroxybutanoate, added with an equal concentration of the ligand acid (I). <sup>c</sup>Specific rate of the uncatalyzed bimolecular component. <sup>d</sup>Cerium(III)-catalyzed rates, obtained from refinement of the kinetic data in terms of (9). Parenthetical values were calculated from (11), using parameters in text. <sup>e</sup>Calculated from data in ref 3b.

operation of a rapid equilibrium (eq 10) entailing a dimeric

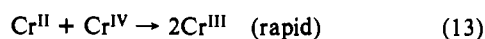
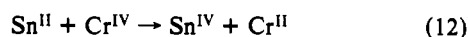


$$k_c = \frac{k_m[\text{Ce}^{III}] + k_d[\text{Ce}^{III}_2]}{(2k_m - k_d)(\sqrt{1 + 8K_D[\text{Ce}]_T} - 1) + 4k_dK_D[\text{Ce}]_T} \quad (11)$$

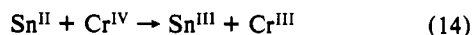
complex,<sup>15</sup> the composite specific rate ( $k_c$ ) for the catalyzed reaction is given by (11),<sup>16</sup> where  $k_m$  and  $k_d$  are bimolecular rate constants for catalysis by monomeric and dimeric Ce(III) and  $[\text{Ce}]_T$  is the total concentration of added cerium. Least-squares treatment of  $k_c$  values in terms of (11) yields  $k_m = 7.0 \pm 2.9 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_d = 0.40 \pm 0.04 \text{ M}^{-1} \text{ s}^{-1}$ , and  $K_D = (2.4 \pm 1.6) \times 10^4 \text{ M}^{-1}$ .

## Discussion

The reactivity of Sn(II) toward Cr(IV) stands in contrast to the behavior observed for the 2e reductants As(III) (which is consumed immeasurably slowly)<sup>3a</sup> and  $\text{Mo}^{V}(\text{aq})$  (which requires unimolecular activation prior to oxidation).<sup>2</sup> Aside from complications reflecting speciation of the oxidant, two mechanisms for this transformation come to mind, each featuring an initial slow step and a rapid follow-up step. The first, (12)–(13), entails



the intervention of the familiar state, Cr(II), whereas the second, (14)–(15), passes through the unusual state, Sn(III).<sup>17</sup> The



(15) In addition, modest but reproducible negative deviations from Beer's law observed for 0.0001–0.0150 M Ce(III) solutions at  $\lambda_{\text{max}}$  for Ce(III) (296 nm) in the buffer system used ( $[\text{Lig}^-] = [\text{HLig}] = 0.20 \text{ M}$ ) are consistent with the proposed monomer–dimer equilibrium (10). Refinement of absorbance data yielded  $K_D = (2.2 \pm 1.2) \times 10^4$ ,  $\epsilon_{\text{monomer}} = 239 \pm 32$ , and  $\epsilon_{\text{dimer}} = 146 \pm 6 \text{ M}^{-1} \text{ cm}^{-1}$  (per Ce(III)).

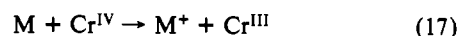
(16) Derivation of (10) is analogous to development of the expression pertaining to the reduction of a diperoxo complex of Cr(IV) by cysteine as catalyzed by iron(III). See: Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1989**, *28*, 3651.

(17) Of the relatively few reports presenting evidence for the intervention of Sn(III) in aqueous reactions, the most persuasive is probably that by: Higginson, W. C. E.; Leigh, R. T.; Nightingale, R. *J. Chem. Soc.* **1962**, 435.

potential for the  $\text{Cr}^{IV} \rightarrow \text{Cr}^{II}$  conversion (12) is presumably favorable.<sup>18–20</sup> Moreover, the pattern of inhibition (Table II) by a series of  $(\text{NH}_3)_5\text{Co}^{III}$  complexes which are known<sup>5d</sup> to react very rapidly with  $\text{Cr}^{2+}(\text{aq})$  strongly supports the intermediacy of a Cr(II) species.

The rates for the Cr(II)–Cr(IV) reaction (13) are too great to measure by our methods, but that for the Fe(II)–Cr(IV) reaction in a similar medium has been reported<sup>21</sup> as  $3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  (21 °C). Since Cr(II) reductions of metal complexes featuring a variety of mediating ligands have been found<sup>22</sup> to proceed  $10^7$ – $10^{10}$  as rapidly as reductions by Fe(II), it is likely that (13) proceeds at or near the diffusion-controlled limit. Values of  $k_{\text{Cr(II)}}$  for the “trapping reagents” in 1 M  $\text{HClO}_4$  lie between  $10^4$  and  $10^6 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>5d</sup> but much greater specific rates would be anticipated in the medium at hand.<sup>23</sup>

The relative rates at which the active intermediate, M, reacts with the Co(III) trap (eq 16) and Cr(IV) (eq 17) may be estimated



from the observed rate decreases, using, where possible, values at low  $[\text{Co}^{III}]$ , where inhibition is most nearly linear. If the steady-state approximation is applied to  $[\text{M}]$ , the specific rate for the Cr(IV)–Sn(II) reaction as inhibited by Co(III) ( $k_{\text{inh}}$ ) may be shown to be

$$k_{\text{inh}} = k_M[\text{Cr}^{IV}][\text{Sn}^{II}] \left( 1 + \frac{k_{17}[\text{Cr}^{IV}]}{k_{17}[\text{Cr}^{IV}] + k_{16}[\text{Co}^{III}]} \right) \quad (18)$$

where  $k_M$  is the specific rate of formation of M. The ratio of inhibited to uninhibited rates ( $k_{\text{inh}}/k$ ) may be expressed as (19).

$$\frac{k_{\text{inh}}}{k} = \frac{1}{2} + \frac{k_{17}[\text{Cr}^{IV}]}{2(k_{17}[\text{Cr}^{IV}] + k_{16}[\text{Co}^{III}])} \quad (19)$$

Values of the ratio  $k_{16}/k_{17}$  calculated from inhibition data are compared with  $k_{\text{Cr(II)}}$  (in 1 M  $\text{HClO}_4$ ) in Table II. Correspondence between patterns is remarkably close, considering especially that the Cr(II)–Co(III) reactions are subject to large medium effects that need not be precisely the same for all oxidants. Inhibition by the pyrazine complex is particularly informative, for this heterocyclic ligand is thought to be an effective redox bridge only for d-block centers.<sup>5d</sup>

Is it reasonable also to attribute to Cr(II) the formation of sizable quantities of Cr(V) from the very rapid Cr(VI)–Sn(II) reaction in our medium with the oxidant in excess?<sup>3a,9</sup> We think not—for although the Cr(VI)–Cr(II) reaction is rapid, it is necessarily delayed by the production of Cr(II), from Cr(IV) (eq 12), a reaction here shown to be slow. In this case, we favor a sequence in which Sn(III) is generated along with Cr(V), after which it is consumed rapidly by the major product, Cr(IV).

Oxidation of the ligand by Cr(IV) (reaction 7) is catalyzed by Ce(III), but by none of the other metal centers examined, pointing to the catalytic intervention of Ce(IV), a view in accord with the

(18) The estimated<sup>19</sup> formal potential for Cr(III,IV), in our medium, 0.96 V, in conjunction with that for Cr(II,III),  $-0.424 \text{ V}$ ,<sup>20</sup> leads to  $E^\circ = 0.27 \text{ V}$  for Cr(II,IV).  $E^\circ$  for Sn(II,IV) is listed as 0.070 V.<sup>20</sup> Note, however, that the older tabulated values apply to 1 M  $\text{H}^+$ ; each is expected to be pH-dependent and ligand-dependent, but the patterns of variation need not be the same.

(19) Ghosh, M. C.; Gould, E. S. *J. Chem. Soc., Chem. Commun.* **1992**, 195.

(20) Bard, A. J.; Parsons, R.; Jordan, J., Eds. *Standard Potentials in Aqueous Solution*; Marcel Dekker: New York, 1985; pp 218, 458, 620.

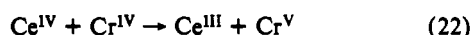
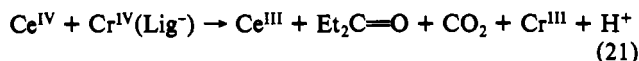
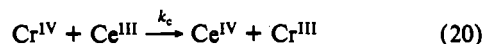
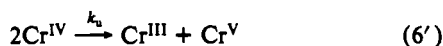
(21) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832.

(22) Compare, for example: (a) Candlin, J. P.; Halpern, J. *Inorg. Chem.* **1965**, *4*, 766. (b) Espenson, J. H. *Ibid.* **1965**, *4*, 121. See also: Basolo, F.; Pearson, R. J. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1968; p 481.

(23) We find, for example, that the Cr(II) reduction of the benzoate derivative of  $(\text{NH}_3)_5\text{Co}^{III}$  ( $k = 0.15 \text{ M}^{-1} \text{ s}^{-1}$ ) in 1 M  $\text{HClO}_4$  is accelerated 200-fold ( $k = 35 \text{ M}^{-1} \text{ s}^{-1}$ ) when carried out in a medium corresponding to that used for our Cr(IV)–Sn(II) experiments ( $[\text{LigH}] = 0.12 \text{ M}$ ,  $[\text{Lig}^-] = 0.08 \text{ M}$ ,  $\text{pH} = 3.16$ ,  $\mu = 0.50 \text{ M}$  ( $\text{NaCl}$ )).

recognized ease with which this tetravalent lanthanide oxidizes  $\alpha$ -hydroxy acids.<sup>24</sup> Since, however, Ce(IV) also oxidizes Cr(IV), some catalysis of the Cr(IV) disproportionation (as reported for Mn(II))<sup>3b</sup> would be anticipated, resulting in the formation of more Cr(V) than can be accounted for solely on the basis of the bimolecular process (6).

A simplified sequence applicable to Cr(IV)–Ce(III) in our medium is as follows:



Expression of this sequence as differential kinetic equations and application of the steady-state approximation to [Ce<sup>IV</sup>] yield (23) and (24). Employment of a numerical integration procedure<sup>26</sup>

$$-\frac{d[\text{Cr}^{\text{IV}}]}{dt} = k_u[\text{Cr}^{\text{IV}}]^2 + 2k_c[\text{Cr}^{\text{IV}}] \quad (23)$$

$$\frac{d[\text{Cr}^{\text{V}}]}{dt} = (1/2)k_u[\text{Cr}^{\text{IV}}]^2 + \frac{k_c[\text{Cr}^{\text{IV}}]}{1 + k_{21}/k_{22}} \quad (24)$$

to this system involved selection of  $k_u$  and  $k_c$  values from our kinetic experiments while the ratio  $k_{21}/k_{22}$  was allowed to vary. Integration then yields the concentration Cr(V) at the conclusion of the reaction. Values of [Cr<sup>V</sup>]<sub>∞</sub> calculated by taking  $k_{21}/k_{22}$  as 0.75 are compared with observed yields in Table III. Agreement is seen to be satisfactory over a range of reagent and catalyst levels, indicating that the Ce(IV)–Cr(IV) pair is 0.75 times as likely to attack the ligand as to undergo single-electron transfer to yield Ce(III) and Cr(V).

The proposed sequence stipulates that Cr(IV), as well as Ce(IV), is required for oxidation of the ligand (reaction 21). This oxidation is a net 2e transaction; both quadrivalent metal centers are 1e oxidants, and neither presumably can accomplish this alone. Moreover, we find that an alternate kinetic treatment in terms of a modified sequence, in which Cr(IV) is omitted from step 21, fails to reproduce the pattern of Cr(V) yields indicated in Table IV. Note also that the observed yields of 3-pentanone are very nearly independent of [Lig<sup>-</sup>] within the range 0.050–0.30 M, indicating that (21) involves the complex Cr<sup>IV</sup>(Lig<sup>-</sup>), the concentration of which, under near-saturation conditions, is determined mainly by [Cr<sup>IV</sup>] taken, rather than by unattached [Lig<sup>-</sup>].

Of the d- and f-block metal species considered here and in a previous study,<sup>3b</sup> only Mn(II,III) and Ce(III,IV) have been seen

Table IV. Yields of Chromium(V) from the Cr(IV)–Ce(III) Reaction<sup>a</sup>

method	[Cr <sup>IV</sup> ], mM	[Ce <sup>III</sup> ], mM	$k_u^b$ , M <sup>-1</sup> s <sup>-1</sup>	$10^4 k_c^c$ , s <sup>-1</sup>	[Cr <sup>V</sup> ] <sub>calcd.</sub> <sup>d</sup> , mM	[Cr <sup>V</sup> ] <sub>obsd.</sub> , mM
ESR	0.80	0.40	3.0	13.5	0.28	0.28
UV-vis <sup>e</sup>	2.3	0.40	3.0	13.5	0.91	0.96
UV-vis	2.5	0.50	3.0	15.4	0.98	1.04
UV-vis	2.5	1.00	3.0	24	0.93	0.95
UV-vis	2.3	2.0	3.0	36	0.80	0.81
ESR	2.3	2.0	3.0	36	0.80	0.82
UV-vis	2.3	10.0	3.0	105	0.72	0.60

<sup>a</sup>Reactions were carried out at 25 °C,  $\mu = 0.50$  M (NaClO<sub>4</sub>). Solutions were buffered with 0.05 M each of 2-ethyl-2-hydroxybutanoic acid (HLig) and its sodium salt. <sup>b</sup>Specific rate for uncatalyzed disproportionation at pH 3.32 and [Lig<sup>-</sup>] = 0.05 M, calculated from data in ref 3b. <sup>c</sup>Pseudo-first-order specific rate for the Ce<sup>III</sup>-catalyzed decay of Cr(IV), calculated using (11), and further adjusted by the factor 1.90 to apply to [Lig<sup>-</sup>] = 0.50 M (Table III). <sup>d</sup>Values were calculated by numerical integration of (24), taking the ratio  $k_{21}/k_{22}$  as 0.75 (see text). <sup>e</sup>Absorbance at 510 nm.

to be effective in catalyzing the disproportionation of Cr(IV). It has been noted<sup>3b</sup> that both catalytic systems feature formal potentials lying within or near the interval between Cr(III,IV) and Cr(IV,V)<sup>18,20</sup> and that the two systems are highly substitution-labile at both oxidation levels. Evidence has been presented that the Cr(IV)–Mn(II) reaction proceeds mainly through a OH-bridged activated complex of the type Cr<sup>IV</sup>–OH–Mn<sup>III</sup>, and it is likely that the Ce-catalyzed disproportionation utilizes an analogous transition state (Cr<sup>IV</sup>–OH–Ce<sup>IV</sup>). We suspect, however, that the ligand oxidation by Cr(IV)/Ce(IV), like that by Co(III)/Ce(IV),<sup>24b</sup> is an induced electron-transfer process requiring quite a different configuration and that it is initiated by attachment of Ce(IV) to the hydroxy group of a Cr(IV)-bound ligand before being consummated by C–C fragmentation and the two acts of electron transfer to the metal centers, with the three concluding events synchronous, or very nearly so. Catalytic complexity in the Cr(IV)–Ce(III) system may then be attributed, at least in part, to the long-recognized<sup>27</sup> strong affinity between Ce(IV) and the alcoholic hydroxyl function.

In sum, our results illustrate two routes which carboxylato-bound chromium(IV) may use to bypass the kinetic barrier thought to impede noncomplementary redox reactions. With Sn(II), an effective metal center reductant, 2e conversion to Cr(II) precedes a rapid bimolecular Cr(II)–Cr(IV) reaction. In contrast, net 2e oxidation of our difunctional ligand anion (Lig<sup>-</sup>) appears to require cooperative action with a second 1e acceptor, in this case cerium(IV).

**Acknowledgment.** We are grateful to Dr. J. H. Espenson for valuable discussions and to Ms. Arla McPherson for technical assistance.

**Registry No.** [(NH<sub>3</sub>)<sub>5</sub>Co<sup>III</sup>Cl]<sup>2+</sup>, 14970-14-0; [(NH<sub>3</sub>)<sub>5</sub>Co<sup>III</sup>Br]<sup>2+</sup>, 14970-15-1; [(NH<sub>3</sub>)<sub>5</sub>Co<sup>III</sup>F]<sup>2+</sup>, 15392-06-0; [(NH<sub>3</sub>)<sub>5</sub>Co<sup>III</sup>N<sub>3</sub>]<sup>2+</sup>, 14403-83-9; [(NH<sub>3</sub>)<sub>5</sub>Co<sup>III</sup>(pyrazine)]<sup>3+</sup>, 59389-55-8; [(NH<sub>3</sub>)<sub>5</sub>Co<sup>III</sup>(4-AcPy)]<sup>3+</sup>, 59389-47-8; [(NH<sub>3</sub>)<sub>5</sub>Co<sup>III</sup>(pyruvato)]<sup>2+</sup>, 19306-91-3; 3-pentanone, 96-22-0.

(24) See, for example: (a) Krishna, B.; Tewari, K. C. *J. Chem. Soc.* **1961**, 3097. (b) Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 208.

(25) Note that we have used [Ce<sup>III</sup>]-dependent pseudo-first-order rate constants for (24) to accommodate the observed departures from second-order behavior (eq 11).

(26) (a) Margenau, H.; Murphy, G. M. *The Mathematics of Physics and Chemistry*; Van Nostrand: New York, 1943; p 469. (b) Wiberg, K. *Tech. Chem. (N.Y.)* **1974**, *6*, 764. (c) Bose, R. N.; Rajasekar, N.; Thompson, D. M.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3349.

(27) Specific interaction between Ce(IV) and alcoholic –OH is almost certainly involved in the classical qualitative cerium(IV) nitrate test for alcohols. See, for example: Duke, F. R.; Smith, G. F. *Ind. Eng. Chem., Anal. Ed.* **1940**, *12*, 201.