

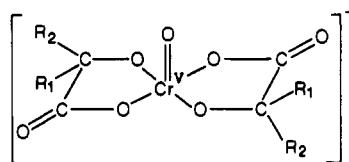
Electron Transfer. 80. Further Reductions of Carboxylato-Bound Chromium(V)¹

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The chelated chromium(V) complex sodium bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) (I) smoothly oxidizes Sn(II) to Sn(IV), IrCl_6^{3-} to IrCl_6^{2-} , and H_2O_2 to O_2 . Properties of the chromium product correspond in each case to those of a bischelated derivative of $(\text{H}_2\text{O})_2\text{Cr}^{\text{III}}$. In none of these reactions is the intervention of a Cr(IV) transient observed. Kinetics of the reaction of Sn(II) (in 0.2–0.4 M LiCl) point to participation of mono- and dichloro forms of the reductant (which react at nearly the same specific rate) and a deprotonated form as well. It is likely that this reaction proceeds by direct oxygen transfer. Rates of reaction of H_2O_2 and IrCl_6^{3-} are independent of both pH (in the range 2.5–4.5) and [ligand anion]. For the H_2O_2 reaction we favor an inner-sphere process involving initial coordination of peroxide to the axial position of the Cr(V) chelate. The reaction with IrCl_6^{3-} (which is substitution-inert) is almost certainly outer-sphere, necessarily proceeding through a Cr(IV) chelate, which, however, is reduced at least 20 times as rapidly as the Cr(V) reactant. An upper limit for $\text{Cr}^{\text{V/IV}}$ self-exchange in this system is estimated as $5 \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$, a value well below those reported for other high-valent transition-metal species in their oxygenated forms.

The reductions of chelated carboxylato complexes of chromium(V) (such as anion I) exhibit considerable mechanistic variety.²



I. $\text{R}_1 = \text{R}_2 = \text{C}_2\text{H}_5$
II. $\text{R}_1 = \text{CH}_3$, $\text{R}_2 = \text{C}_2\text{H}_5$

Evidence for both inner- and outer-sphere types has been presented, and depending upon the reductant, the rate-determining step may involve transfer of one, two, or four electrons. More than one ligation and/or protonation level of the oxidant may contribute to the overall sequence, and at least one system featuring strong autocatalysis has been reported.^{2b,3}

The present contribution deals mainly with further reductions of bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) (chelate I), each of which appears to be more straightforward than reductions by $\text{Fe}(\text{II})$,⁴ VO^{2+} ,⁵ $\text{U}(\text{IV})$,^{2a} or $\text{S}(\text{IV})$ ³ described previously.

Experimental Section

Materials. Sodium salts of the complexes bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) (I)⁶ and its 2-methyl analogue (II)^{6,7} were prepared as described. Lithium chloride and lithium perchlorate, for use in kinetic experiments, were prepared from lithium carbonate and the corresponding acid and were crystallized twice before use. Hydrogen peroxide (Fisher), sodium hexachloroiridate(III) (Na_2IrCl_6 , Alfa), tin(II) chloride (MCB), and the carboxylic acids used as ligands and in buffers (Aldrich) were used as received. Cation-exchange resin (Bio-Rad 50W-X2; 200–400 mesh) was pretreated before use as described.⁸

Stoichiometric Studies. The reaction between the bis(2-ethyl) chelate (I) and Sn(II) was carried out in a solution 0.20 M in NaCl and 0.10 M in the parent carboxylic acid, 2-ethyl-2-hydroxybutyric acid, with Sn(II) in excess. The quantity of Sn(II) remaining after 15 min was estimated by titration with KI_3 . Data are summarized in Table I.

The stoichiometry of the reaction between chelate I and excess H_2O_2 was determined by carrying out the reaction in a solution buffered by the parent acid and its anion (pH 3.7). After 30 min of reaction time, the

Table I. Stoichiometries of the Reactions of Chromium(V) Chelate I with Sn(II) and with H_2O_2 ^a

A. Sn(II) Reaction				
mmol of Cr^{V}	mmol of Sn^{II}	$\Delta\text{Sn}^{\text{II}}$, ^b mmol	$\Delta\text{Cr}^{\text{V}}/\Delta\text{Sn}^{\text{II}}$	
0.125	0.284	0.148	1.18	
0.098	0.195	0.117	1.19	
0.074	0.236	0.096	1.29	
B. H_2O_2 Reaction				
mmol of Cr^{V}	mmol of H_2O_2	$\Delta\text{H}_2\text{O}_2$, ^c mmol	$\Delta\text{Cr}^{\text{V}}/\Delta\text{H}_2\text{O}_2$	
0.104	0.200	0.099	1.06	
0.148	0.450	0.139	1.06	
C. Evolution of O_2				
mmol of Cr^{V}	mmol of H_2O_2	mmol of O_2	$\text{Cr}^{\text{V}}/\text{O}_2$	
0.111	0.30	0.108	0.97	
0.136	0.30	0.126	0.93	
0.154	0.30	0.137	0.90	

^a Chromium(V) was added as sodium bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) (I). Reactions were carried out in solutions buffered by the parent hydroxy acid and its sodium salt. ^b Determined by titration with KI_3 . ^c Determined by titration with KI and $\text{Na}_2\text{S}_2\text{O}_3$.

reaction was acidified with 1 M H_2SO_4 , KI added, and the liberated I_3^- titrated with standard $\text{Na}_2\text{S}_2\text{O}_3$. In addition, the volume of oxygen released when a known quantity of Cr(V) was treated with excess H_2O_2 was measured by carrying out the reaction in a gas buret. Solutions resulting from reactions with H_2O_2 gave negative tests for CrO_4^{2-} .

The reaction between IrCl_6^{3-} and the bis(2-methyl) chelate (II) was studied by spectrophotometric titration at 488 nm (λ_{max} for IrCl_6^{2-}). To a 0.0014 M solution of K_2IrCl_6 in 0.20 M NaCl was added small portions of chelate II in 0.20 M ligand acid. Optical densities were recorded 30 min after each addition. Plots of absorbance vs. added Cr^{V} featured a (relatively blunt) "break point" at $[\text{Ir}^{\text{III}}]/[\text{Cr}^{\text{V}}] = 1.73 \pm 0.10$.

Examination of the Cr(III) Reaction Products. The chromium(III) product from reaction of the Cr(V) chelate I with excess Sn^{II} or excess H_2O_2 (in a solution buffered at pH 3 with the ligand acid and its sodium salt) exhibited maxima at 590 ($\epsilon = 48 \text{ M}^{-1} \text{ cm}^{-1}$) and 418 nm ($\epsilon = 60 \text{ M}^{-1} \text{ cm}^{-1}$). When this solution was subjected to treatment on a cation-exchange column (length 7 cm; capacity 4 mequiv; H^+ form) at 2 °C, a green eluate passed through the column quickly, and an additional green band (constituting about half of the chromium taken) was eluted with 0.5 M NaClO_4 . Spectra of both fractions corresponded to that of the untreated solution.

The solution resulting from the reaction of the bis(2-methyl) chelate, II, with IrCl_6^{3-} was passed through an anion-exchange column to remove the iridium-containing anions. The resulting eluate showed maxima at 586 ($\epsilon = 50$) and 420 nm ($\epsilon = 59 \text{ M}^{-1} \text{ cm}^{-1}$). Its cation-exchange elution behavior resembled those of the products from reactions of the bis(2-ethyl) Cr(V) chelate with Sn^{II} and H_2O_2 .

Kinetic Studies. Rates were estimated from measurements of changes in absorbance by using a Cary 14 recording spectrophotometer or (for the more rapid reductions by Sn^{II}) a Durrum-Gibson stopped-flow spectrophotometer. Reductions by H_2O_2 and by Sn^{II} were monitored by

- (1) Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.
- (2) For summaries, see: (a) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 94. (b) Gould, E. S. *Acc. Chem. Res.* **1986**, *19*, 66.
- (3) Bose, R. N.; Rajasekar, N.; Thompson, D. M.; Gould, E. S. *Inorg. Chem.*, in press.
- (4) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832.
- (5) Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 4679.
- (6) Krumpal, M.; Roček, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.
- (7) Rajasekar, N.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 3798.
- (8) Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792.

Table II. Kinetic Data for Reduction of (Carboxylato)chromium(V) with Sn(II) (23 °C, $\mu = 0.40$ M)^a

$10^3 \times$ [Sn ^{II}], M	[Lig ⁻], ^b M	[HLig ⁻], ^c M	[Cl ⁻], M	$10^4 \times$ [H ⁺]	$10^{-3}k$, ^d M ⁻¹ s ⁻¹
4.7	0.100	0.100	0.30	1.10	4.4
9.5	0.055	0.055	0.345	1.02	4.9
9.5	0.100	0.100	0.30	1.10	4.2
9.5	0.20	0.20	0.20	1.18	4.4
9.5	0.100	0.055	0.30	0.62	6.5
9.5	0.055	0.100	0.345	3.5	2.9
9.5	0.055	0.20	0.345	7.2	1.98
9.5	0.030	0.20	0.370	9.5	1.88

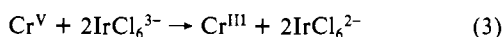
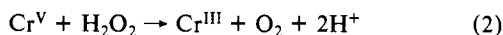
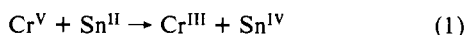
^aChromium(V) (0.001 25 M throughout) was added as sodium bis-(2-ethyl-2-hydroxybutyrate)oxochromate(V) (I); Sn(II) was added as SnCl₂. The supporting electrolyte was LiCl. ^b2-Ethyl-2-hydroxybutyrate. ^c2-Ethyl-2-hydroxybutyric acid. ^dSecond-order specific rates $-d(\ln [\text{Cr}^{\text{V}}])/dt[\text{Sn}^{\text{II}}]^{-1}$.

following the disappearance of Cr(V) at 510 nm; reductions by IrCl₆³⁻ were studied by measuring the appearance of IrCl₆²⁻ at 488 nm. Ionic strengths for the reactions with H₂O₂ were regulated by addition of LiClO₄ whereas those for the reactions with SnCl₂ and IrCl₆³⁻ were controlled by addition of LiCl.⁹ Reactions were first order each in Cr(V) and reductant but were generally carried out under pseudo-first-order conditions with the reductant in greater than fivefold excess. Conversions were followed for at least 4 half-lives. Rate constants calculated from successive half-life values within a run generally agreed to within 6%, and average values did not differ significantly from those obtained from slopes of logarithmic plots of absorbance differences against reaction time. Specific rates from replicate runs checked to better than 8%.¹⁰

Neither of the two Cr(V) chelates reacted, at an appreciable rate, with formic acid, formaldehyde, or phosphorous acid or with the metal complexes Rh₂(OAc)₂, Ru(NH₃)₆²⁺, or MoOCl₅²⁻. Reactions with Fe(CN)₆⁴⁻ were rapid but were complicated by the precipitation of Prussian blue. Reactions with sodium chlorite yielded Cl₂ and CrO₄²⁻.

Results and Discussion

The results of the stoichiometric experiments (Table I) and the Cr(V)-Ir(III) spectrophotometric titration indicate that the reactions at hand may be represented schematically as



The principal Cr(III) product formed in the reduction of Cr(V) chelate I with Sn(II) or with H₂O₂ corresponds to that formed when this chelate is reduced, in the presence of excess ligand, by V(IV),³ Eu(II),⁵ Fe(II),⁴ U(IV),^{2a} or Ti(III).¹¹ The relatively high extinction coefficients ($\epsilon_{418} = 60 \text{ M}^{-1} \text{ cm}^{-1}$, $\epsilon_{590} = 48 \text{ M}^{-1} \text{ cm}^{-1}$), in conjunction with a low affinity for sulfonate cation-exchange resin, indicate that here, as in earlier instances, we are dealing with a bischelated hydroxycarboxylato Cr(III) complex and that the principal coordinative features of the Cr(V) reactant are preserved in the Cr(III) product.¹² A similar conclusion

(9) When reductions by Sn^{II} or IrCl₆³⁻ were carried out with LiClO₄ or NaClO₄ (rather than LiCl) as the supporting electrolyte, erratic decay curves were obtained. The Sn^{II} reactions seemingly were complicated by the appearance of very slightly turbidity, whereas IrCl₆³⁻ curves were of the type resulting from the superposition of two kinetic components. The latter feature may reflect a ligand substitution reaction (on Ir^{III}) competitive with the redox reaction. These complications were minimized in the presence of excess Cl⁻, but even here, examination of the Cr(V)-Sn(II) system at higher pH values was ruled out by precipitation of one or more tin species.

(10) In reductions by excess SnCl₂, the primary reaction was followed by a much slower process constituting less than 10% of the total absorbance change. Since its rate constant was about 10⁻² that for the principal reaction, it did not interfere with analysis of the latter. The slow component was first order each in Cr(V) and Sn(II), but its rate did not vary systematically with pH or with the concentration of buffering species. This component was not observed when Cr(V) was in excess. This complication is similar to that described for Cr(V)-V(IV) systems.⁵

(11) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2645.

appears to apply to the reaction of the methyl-substituted Cr(V) chelate, II, with IrCl₆³⁻.

The persistence of the bis(chelate) in these reactions is not, in itself, informative as to mechanism, for similar behavior has been reported for reductions that are thought to utilize an outer-sphere path,^{2a,11} as well as those for which there is evidence implicating a bridged route.^{4,5} However, in the case of reduction by the 1e reagent IrCl₆³⁻, which must pass through a Cr(IV) intermediate, we may infer that reduction of such an intermediate is more rapid than disruption of its ligand sheath.^{13,14}

Representative kinetic data for the Cr(V)-Sn(II) reaction appear in Table II. From recorded association constants of the various chloro complexes of Sn(II), it may be shown that the predominant Sn^{II} species in our reaction mixtures are mono- and dichloro derivatives.¹⁵ With [Cl⁻] = 0.40, the ratio of monochloro to dichloro complex is 1.24, whereas with [Cl⁻] = 0.20, this ratio rises to 2.3. Since, however, the observed rate does not vary significantly with [Cl⁻] within this range, we must infer that individual specific rates for the mono- and dichloro species are nearly the same.

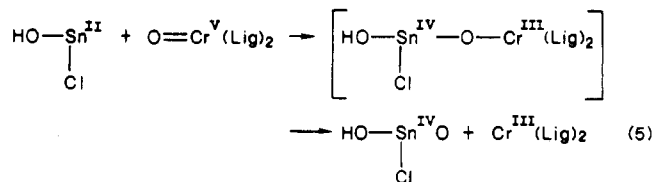
In contrast to reductions by IrCl₆³⁻ and by H₂O₂, which proceed at rates independent of acidity, the Sn(II) reaction is retarded by increasing [H⁺]. Plots of k_{obsd} vs. 1/[H⁺] are linear, conforming to eq 4. We are thus dealing with a two-path reaction. The

$$k_{\text{obsd}} = (1.6 \times 10^3 + 0.32[\text{H}^+]^{-1}) \text{ M}^{-1} \text{ s}^{-1} \quad (4)$$

(23 °C, $\mu = 0.4$ M)

inverse-acid term very probably arises from the deprotonation of a water molecule bound to Sn(II).¹⁶

In view of the general inaccessibility of Sn(III)¹⁷ and the absence of distortion attributable to Cr(IV) in the Sn(II)-Cr(V) kinetic curves, it is justifiable to assume that this reaction is a 2e transaction. If so, it must be assigned an inner-sphere route, for rapid outer-sphere transfer of two electrons between metal centers has not yet been documented. Kochi and co-workers^{18a,b} have shown that reductions of chelated oxochromium(V) complexes by olefins and substituted phosphines occur via direct transfer of the oxo oxygen, and a related mechanism, represented pictorially as (5), appears to be attractive in the present case as well.



The reduction of Cr(V) chelate I with H₂O₂, in analogy with the reaction of N₂H₅⁺^{18c} (which is isoelectronic with H₂O₂), would

(12) Partition of this product on a cation-exchange column in the presence of excess ligand anion suggests the operation of a relatively mobile equilibrium involving substitution of an additional carboxylate group for axial H₂O in the Cr(III) product. The resulting spectral difference appears to be too slight to allow a quantitative study of this transformation.

(13) Although reduction of the Cr(IV) intermediate is more rapid than ligand substitution about Cr(IV) in the reactions of Ti(III), V(IV), Fe(II), and U(IV), this does not appear to be the case when we are dealing with the less strongly reducing species Mn(II) and Ce(III).^{7,14}

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

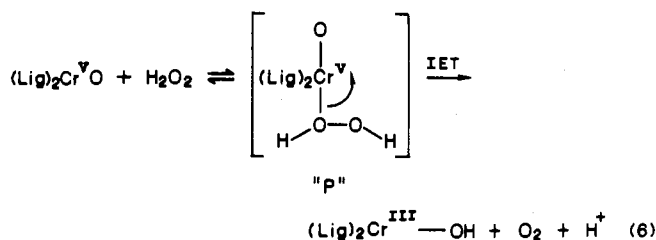
(15) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1982; Vol. 5, pp 395, 420. Association constants (25 °C, $\mu = 0.50$ M) for coordination of one, two, three, and four chlorides are 12 M⁻¹, 26 M⁻², 20 M⁻³, and ~100 M⁻⁴.

(16) Since substitution of chloride for coordinated water on Sn(II)_{aq} ($\text{p}K_{\text{a}} = 3.5$)¹⁵ would be expected to increase the acidity of this center, it is likely that the predominant Sn^{II} species in these systems are of the type Sn^{II}(OH)Cl and that the inverse-acid term in (4) represents contribution of species of the type Sn^{II}(OH)₂Cl.

(17) See, however: Higginson, W. C. E.; Leigh, R. T.; Nightingale, R. J. *Chem. Soc.* **1962**, 435.

(18) (a) Siddall, T. L.; Miyaura, N.; Huffman, J. C.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1983**, 1185. (b) Samsel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606. (c) Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 3176.

be expected to be a 2e transaction, and the straightforward stoichiometry and uncomplicated kinetic profiles found for this reaction are consistent with such an assignment (although they do not demand it). Unlike the $N_2H_5^+$ reduction, which is retarded by addition of both H^+ and the carboxylate ligand, the rate of the H_2O_2 reduction ($k = 5.5 \times 10^{-2} M^{-1} s^{-1}$, $25^\circ C$, $\mu = 0.40 M$)¹⁹ is affected by neither, indicating that neither deprotonation nor loss of ligand from the oxidant precedes the act of electron transfer. Although an inner-sphere route is again preferred, direct transfer of the Cr(V)-bound oxo groups, as proposed for the Sn(II) reduction, does not readily accommodate the observed transformation. Instead, we favor a path in which H_2O_2 becomes attached to an axial position of the Cr(V) chelate, prior to internal transfer (IET) of two electrons to form Cr(III) and O_2 :



Since there is no indication of kinetic saturation of H_2O_2 concentrations as great as 0.5 M, we may infer that the formation constant of the Cr(V)- H_2O_2 precursor complex ("P") lies below $10^{-1} M^{-1}$.

Reductions with $IrCl_6^{3-}$ are the most sluggish encountered among those involving action of a 1e reagent on Cr(V), reflecting the weakly reducing formal potential ($E^\circ = 0.93 V$)²⁰ of the reductant and its high negative charge. Specific rates ($25^\circ C$, $\mu = 0.4 M$)¹⁹ for reaction of the ethylbutyrate dichelate (I) and its methylbutyrate analogue (II) with this anion are found to be 3.4×10^{-2} and $1.11 \times 10^{-1} M^{-1} s^{-1}$ and are independent of added carboxylate and chloride.²¹ Although the reductant is necessarily a 1e donor, distortion of the Ir(III)-Cr(V) kinetic profiles attributable to intervention of a strongly absorbing^{4,5} Cr(IV) transient was not detected, bringing to mind the situation described for Ti(III)-Cr(V) systems.¹¹ It has been pointed out that such distortion should not be perceptible if the Cr(IV) intermediate reacts with the reductant at a specific rate greater than 20 times that for the Cr(V) reactant,¹¹ and such an inference may be drawn in the present case, as well as for the earlier Ti(III) reductions. Evidence has been presented that complexes of both Cr(V) and Cr(IV) undergo reduction by Ti(III) mainly through outer-sphere routes,¹¹ and the substitution-inert character of $IrCl_6^{3-}$ points to the same conclusion for this reductant. Note that the Marcus model for outer-sphere reactions²² implies that the ratio of specific rates, $k_{Cr(V)}/k_{Cr(IV)}$, should be very nearly the same for the two single-electron donors.

The formal potential for Ti(III)²³ is about 0.94 V more negative than that for $IrCl_6^{3-}$. This difference corresponds^{24,25} to a rate ratio, k_{Ti}/k_{Ir} , near 5×10^8 , which may be compared to the observed ratio, 2×10^7 , pertaining to the two 1e reductions of chelate I.²⁶⁻²⁸ An estimate of the self-exchange rate for $Cr^{V/IV}$ in this system requires knowledge of the potential associated with this couple. The value 0.43 V (vs. NHE), obtained from electrochemical measurements in the absence of added ligand,²⁹ is not applicable, for it does not take into account the marked stabilization of Cr(IV) by excess carboxylate ligand.^{4,5} Assuming, however, that this potential is at least as positive as that for the coreagent, $IrCl_6^{3-}$, we may use eq 7, which stems from Marcus'

$$k_{Cr,Ir} = (k_{Cr(5,4)}k_{Ir(4,3)}K_{Cr,Ir})^{1/2} \quad (7)$$

treatment,²² to approximate an upper limit. Taking $K_{Cr,Ir}$ (the equilibrium constant for the redox reaction) as at least unity, in conjunction with measured specific rates for this reaction ($k_{Cr,Ir}$) and for the $IrCl_6^{2-/3-}$ self-exchange ($k_{Ir(4,3)}$),²⁸ we calculate $k_{Cr(5,4)}$ to be less than $5 \times 10^{-9} M^{-1} s^{-1}$. This value falls well below reported rates for analogous exchanges involving other oxygenated forms of high-valent transition-metal centers ($VO_2H^{+2+} \geq 1 M^{-1} s^{-1}$; MnO_4^{-2-} , $2 \times 10^4 M^{-1} s^{-1}$; NpO_2^{+2+} , $10^2 M^{-1} s^{-1}$; AmO_2^{+2+} , $2.4 M^{-1} s^{-1}$)^{30,31} and suggests that the exchange in this $Cr^{V/IV}$ system entails considerable adjustment of the Cr=O bond length and/or twisting of the chelate rings.³²

Acknowledgment. We are grateful to Dr. D. H. Macartney for communication of his rate data prior to publication.

Registry No. I-Na⁺, 97042-89-2; Sn^{II}, 22541-90-8; $IrCl_6^{3-}$, 14648-50-1; H_2O_2 , 7722-84-1.

Supplementary Material Available: Table S-1, listing kinetic data for reductions of carboxylato-bound chromium(V) complexes with H_2O_2 and with $IrCl_6^{3-}$ (2 pages). Ordering information is given on any current masthead page.

- (19) Detailed kinetic data pertaining to reductions of these Cr(V) chelates with H_2O_2 and with $IrCl_6^{3-}$ appear in Supplementary Table S-1.
 (20) George, P.; Hanania, G. I. H.; Irvine, G. H. *J. Chem. Soc.* **1957**, 3048. This value pertains to $20.3^\circ C$ and $\mu = 0.2$.
 (21) Note that the ratio of rates for the methyl- and ethyl-substituted chelates lies close to that reported⁷ for the Ce(III)-catalyzed disproportionation of these Cr(V) complexes. These disproportionation rates are thought to be determined principally by oxidation of Ce(III) by the Cr(V) center.
 (22) (a) Marcus, R. A. *J. Phys. Chem.* **1963**, *67*, 853. (b) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

- (23) Brunschwig, B. S.; Sutin, N. *Inorg. Chem.* **1979**, *18*, 1731. The formal potential for Ti(III) ($-0.016 V$) recorded by these workers pertains to 1 M HCl.
 (24) See, for example: Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557. An adjustment of this ratio has been made to take into account the greater electrostatic work²⁵ associated with reduction by $IrCl_6^{3-}$.
 (25) (a) Phillips, J.; Haim, A. *Inorg. Chem.* **1980**, *19*, 76. (b) Singh, A. N.; Srinivasan, V. S.; Gould, E. S. *Ibid.* **1982**, *21*, 1236.
 (26) The specific rate for the reaction of $TiOH^{2+}$ with Cr(V) chelate I ($5 \times 10^5 M^{-1} s^{-1}$ at $23^\circ C$) has been calculated from the data of Bose.¹¹
 (27) The near agreement here suggests that the self-exchange rate for $TiOH^{3+/2+}$ is not greatly different from that for $IrCl_6^{2-/3-}$, which has been reported²⁸ as $2.3 \times 10^5 M^{-1} s^{-1}$ ($25^\circ C$, $\mu = 0.1 M$), and thus supports the suggestion by Brunschwig and Sutin²³ that a rate constant $\geq 10^{-2} M^{-1} s^{-1}$ for the titanium-exchange reaction is more reasonable than a much lower value (3×10^{-7}) calculated from consideration of the Ti(III) reductions of poly(pyridine)osmium(III) complexes.
 (28) Hurwitz, P.; Kustin, *Trans. Faraday Soc.* **1966**, *62*, 427.
 (29) Bose, R. N.; Neff, V. D.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 165.
 (30) (a) MacCartney, D. H.; McAuley, A.; Olubuyide, O. A. *Inorg. Chem.* **1985**, *24*, 307. (b) MacCartney, D. H. *Ibid.* **1986**, *25*, 2222.
 (31) Cannon, R. D. *Electron Transfer Reactions*; Butterworths: London, 1980; p 208.
 (32) A reviewer has asked whether the inverse- $[H^+]$ term in rate law 4 can be interpreted in terms of protonation of the $Cr^V=O$ function with partial loss of its reactivity. This possibility is consistent with the observed kinetics but is probably less satisfactory than the proposed alternative. In the large majority of known cases, protonation decreases, rather than increases, the effectiveness of an oxidant. Moreover, earlier examination of the electronic spectrum of the Cr(V) chelate at varying acidities^{18c} detected no change indicative of such an acid-base equilibrium.