

mosphere were recorded as a function of p[H] (Figure 8). In acidic solutions there is no absorption band between 300 and 400 nm, and the intensity and position of the band close to 360 nm change only slightly with p[H]. Dioxygen complex formation is detected by the appearance of a band at 360 nm with a small shoulder close to 310 nm. This band appears only in the spectra corresponding to p[H] values higher than 7.4, and its shape and position are similar to those previously observed for other dibridged μ -hydroxo- μ -peroxo complexes.²⁴ However, at p[H] 10.5, where the degree of dioxygen complex formation is high, the absorbance values at 360 nm agree well with the values expected from Figure 6, showing that dioxygen complexes of Co(II) with BISBAMP

have low stability and are formed only under basic conditions. Under the conditions employed for Figure 6, the concentrations of the dioxygen complexes (e.g., at p[H] values 9.0 and 11.0) indicated in Figure 7 may be employed to estimate their molar absorbances in solution. The values thus obtained for $\text{Co}_2\text{LO}_2(\text{OH})_2$ and $\text{Co}_2\text{LO}_2(\text{OH})_3$ are 4500 and 2800 $\text{M}^{-1} \text{cm}^{-1}$, which correlate well with reported values for other μ -hydroxo- μ -peroxo complexes.²⁴ A corresponding value could not be obtained for $\text{Co}_2\text{LO}_2\text{OH}$ because of its low concentration.

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Electron Transfer. 95. Reductions of Peroxide-Bound Chromium(IV)¹

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The peroxochromium(IV) derivative of diethylenetriamine $\text{Cr}^{\text{IV}}(\text{dien})(\text{O}_2)_2\cdot\text{H}_2\text{O}$ (chelate I) may be prepared with ease and forms aqueous solutions that, when suitably buffered, are stable for over 1 h. Aqueous solutions of this complex in glycine buffers react rapidly with vanadium(IV), hexacyanoferrate(II), and Ti(III). With VO^{2+} , the Cr(IV) center, but not the peroxo ligands, is reduced, but $\text{Fe}(\text{CN})_6^{4-}$ and Ti(III) reduce both functions. The chromium(III) products contain bound diethylenetriamine, and in the course of the reactions with Ti(III), carboxylate groups from the supporting media also enter the coordination sphere of chromium, with the extent of such intrusion greatest at highest carboxylate concentrations. Rate laws for reductions by $\text{Fe}(\text{CN})_6^{4-}$ and VO^{2+} feature both acid-independent and $[\text{H}^+]$ -proportional terms, the latter indicating involvement of a more reactive protonated form of the peroxo complex, for which the $\text{p}K_{\text{a}}$ is less than 0.5. Specific rates for these two reductants are remarkably similar despite the poorer oxidation potential and the slower self-exchange associated with VO^{2+} . Reductions with Ti(III) appear to proceed through a strongly absorbing intermediate ($\epsilon_{380} = 600 \text{ M}^{-1} \text{ s}^{-1}$), which is generated at a rate proportional to $[\text{Ti}^{\text{III}}]$ but decays unimolecularly ($k = 0.20 \text{ s}^{-1}$). The behavior of this species corresponds to that of a Cr(IV)-Ti(III) precursor complex, formed prior to the act of internal electron transfer. Attachment of external carboxylate to the chromium center does not occur before electron transfer nor does it take place after all redox processes are complete. We suggest rather that it is associated with homolytic reduction, by Ti(III), of an O-O bond in a Cr(III)-peroxy intermediate, yielding a $\text{Cr}^{\text{III}}\text{-O}^{\cdot}$ fragment, which is rapidly converted to a substitution-labile $\text{Cr}^{\text{IV}}\text{-OH}$ species. Reductions by VO^{2+} , which leave the peroxide group intact, are not accompanied by incorporation of external donors.

We have been interested since 1981 in the redox chemistry of the atypical states of chromium and have reported evidence that a variety of reductions of carboxylato-bound chromium(V) proceed through species having properties corresponding to complexes of the still less usual state chromium(IV).² However, this state appears to exist only transiently in carboxylate systems, for it is consumed by a combination of ligand oxidation, disproportionation, and rapid reaction with the added reductant. In contrast, several chromium(IV) diperoxo amines may be isolated by conventional procedures and form aqueous solutions that, when suitably buffered, are stable for several hours. Prototype members of this series, featuring ligated ammonia³ and ethylenediamine,⁴ were reported near the turn of the century and attracted relatively little subsequent attention, but more stable derivatives were more recently described by Garner and co-workers.⁵ Such complexes

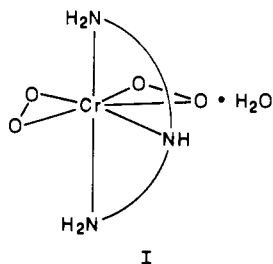
are attractive candidates for redox studies,⁶ despite (or perhaps because of) possible complications stemming from the presence of two different oxidizing functions in the same molecule. This report deals with the reactions of the most robust of these diperoxo complexes, chelate I,^{7,8} with the inorganic reductants vanadium(IV), titanium(III), and hexacyanoferrate(II).

Experimental Section

Materials. Diperoxo(diethylenetriamine)chromium(IV) monohydrate, $\text{Cr}(\text{dien})(\text{O}_2)_2\cdot\text{H}_2\text{O}$ (I), was prepared by the method of House and Garner.^{5a,b} The complex, which precipitated from aqueous solution, was washed with methanol at 0 °C and then dried over P_2O_5 for 10-12 h.

- (1) Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.
- (2) See, for example: (a) Gould, E. S. *Acc. Chem. Res.* **1986**, *19*, 66. (b) Ghosh, S. K.; Bose, R. N.; Laali, K.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 4737. (c) Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 899.
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- (4) Hoffman, K. A. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 3181.

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- (6) For recent studies of the reactions of these complexes, see: (a) Sriram, M.; Ramasami, T.; Ramaswamy, D. *Inorg. Chim. Acta* **1979**, *36*, L433. (b) Ranganathan, C. K.; Ramasami, T.; Ramaswamy, D.; Santappa, M. *Inorg. Chem.* **1986**, *25*, 915.
- (7) Structure I has been assigned by House and Garner^{5a} in analogy to that determined^{8a} for the ethylenediamine analogue, $\text{Cr}(\text{en})(\text{O}_2)_2\cdot\text{H}_2\text{O}$.
- (8) (a) Stomberg, R. *Ark. Kemi* **1965**, *24*, 47. For determinations of related structures, see: (b) Stomberg, R. *Ark. Kemi* **1964**, *22*, 29, 49. (c) Stomberg, R. *Ark. Kemi* **1965**, *23*, 401. (d) Stomberg, R. *Ark. Kemi* **1965**, *24*, 111. For an overview of these investigations, see: (e) Stomberg, R. *Ark. Kemi* **1965**, *24*, 282.



Warning! One example of this complex exploded violently when touched with a metal spatula on a sintered-glass crucible. Subsequent preparations were carried out on a small scale (less than 500 mg), and all manipulations were done with a plastic spatula.

Solutions of $\text{VO}(\text{ClO}_4)_2$ were prepared^{9a} from VOSO_4 and $\text{Ba}(\text{ClO}_4)_2$ (Alfa) as described, and solutions of $\text{Ti}(\text{III})$ were derived from TiCl_3 .^{9b} These were analyzed by literature methods.^{9b,10} Cation-exchange resin (Dowex 50-X2; 400 mesh; H^+ form) was pretreated as described¹¹ and converted to its Na^+ form by washing with saturated NaHCO_3 . Lithium perchlorate (used in kinetic experiments) was prepared by the method of Dockal¹² and recrystallized twice. Remaining reagents (Fisher, Alfa, or Baker and Adamson products) were used as received, as was catalase (Sigma Chemical; bovine liver; 11 000 units/mg) and BioGel P2 (Bio-Rad).

Measurements of Paramagnetic Susceptibility. Susceptibility of the peroxo complex was estimated by the procedure of Evans,¹³ in which the shift in the NMR frequency of the methyl hydrogens of added *t*-BuOH in the presence of a paramagnetic species was measured. This method was standardized by measurements on $\text{Ni}(\text{NO}_3)_2$ (effective magnetic moment 3.24 μ_B).¹⁴

Stoichiometric Studies. The stoichiometries of the reactions of the diperochromium(IV) complex (I) with vanadium(IV) and with $\text{Ti}(\text{III})$ were determined by spectrophotometric titrations at 382–385 nm. To measured quantities of $\text{Cr}(\text{IV})$ (0.004–0.014 mmol) in a buffered solution were added successive known quantities of reductant. Plots of absorbance vs [added reductant] showed sharp break points at $[\text{V}^{\text{IV}}]/[\text{Cr}^{\text{IV}}] = 1.04 \pm 0.02$ and $[\text{Ti}^{\text{III}}]/[\text{Cr}^{\text{IV}}] = 5.1 \pm 0.2$.¹⁵ The stoichiometry of the reaction of $\text{Cr}(\text{IV})$ with $\text{Fe}(\text{CN})_6^{4-}$, determined from the absorbance change at 418 nm (λ_{max} for $\text{Fe}(\text{CN})_6^{3-}$), was $[\text{Fe}^{\text{II}}]/[\text{Cr}^{\text{IV}}] = 4.79 \pm 0.16$, with both oxidant and reductant in excess.

In addition, a number of reactions were carried out in a gas buret, adding, in some cases, the enzyme catalase (0.5 mg/mL of solution), which catalyzes the disproportionation of H_2O_2 and some of its derivatives. The reaction with excess VO^{2+} quickly liberated 0.40 mol of O_2 /mol of $\text{Cr}(\text{IV})$ in the absence of catalase but 0.87 mol of O_2 in its presence. In contrast, no gas was evolved in the reactions with $\text{Fe}(\text{CN})_6^{3-}$ and with $\text{Ti}(\text{III})$, even upon addition of catalase. Treatment of the diperoxo complex with catalase in the absence of an external reductant released 1.02 mol of O_2 /mol of $\text{Cr}(\text{IV})$.

Examination of the $\text{Cr}(\text{III})$ Reaction Products. Reaction mixtures (volume 2–3 mL) were 0.02–0.06 M in $\text{Cr}(\text{IV})$ and were buffered with acetate, salicylate, or glycine, together with their respective acids. These were treated with a 4-fold excess of reductant, and the resulting mixture was subjected to column chromatography, either on Dowex 50-X2 (at 2 °C) or on BioGel P2 (at room temperature).¹⁶ Chromium(III) products were eluted slowly from BioGel with distilled water and from Dowex with water or perchlorate solutions. Better fractionation of products was achieved with Dowex, but loss of chromium (due to column-catalyzed polymerization)¹⁷ was more serious with this resin.

Table I. Magnetic Moments of Transition-Metal Compounds^a

compd	configuration	μ_{eff} , μ_B
$\text{VO}(\text{ClO}_4)_2$	d^1	1.50
CuSO_4	d^9	1.75
$\text{Na}^+[(\text{Lig})_2\text{Cr}^{\text{VO}}\text{O}]^{-b}$	d^1	1.88
$\text{Ni}(\text{NO}_3)_2$	d^8	3.24
$\text{Cr}(\text{H}_2\text{O})_6(\text{ClO}_4)_3$	d^3	3.9 ^c
$\text{Cr}^{\text{IV}}(\text{dien})(\text{O}_2)_2 \cdot \text{H}_2\text{O}$	d^2	2.71
$(\text{K}^+)_3[\text{Cr}^{\text{IV}}(\text{O}_2)_2(\text{CN})_3]^{3-}$	d^2	2.82 ^d

^a Measured in aqueous solution at 293 K by using the procedure of Evans.¹³ ^b Lig = $[-\text{OCEt}_2\text{C}(\text{=O})\text{O}]^{2-}$. ^c Rajasekar, N.; Subramaniam, R.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 971. ^d Reference 8c.

Spectra from the $\text{Ti}(\text{III})$ reactions, which were more informative than those with the other reductants,¹⁸ indicated that the identities of the $\text{Cr}(\text{III})$ complexes formed were dependent in part on the buffering species used in the supporting medium and on their concentrations (Table II).

Kinetic Measurements. Rates of the VO^{2+} and $\text{Fe}(\text{CN})_6^{4-}$ reactions were estimated from absorbance changes by using a Cary 14 or Beckman Model 5260 recording spectrophotometer. Reductions with VO^{2+} were monitored at 382 nm (λ_{max} for $\text{Cr}(\text{IV})$, $\epsilon = 460 \text{ M}^{-1} \text{ cm}^{-1}$), and those with $\text{Fe}(\text{CN})_6^{4-}$ were followed at 418 nm. Ionic strength was regulated by addition of LiClO_4 . Reactions were first order each in $\text{Cr}(\text{IV})$ and reductant but were generally carried out under pseudo-first-order conditions, with the reductant in greater than 10-fold excess. Conversions were followed for at least 5 half-lives. Rate constants from successive half-life values within a run generally agreed to within 4%, and average values did not differ significantly from those obtained from logarithmic plots of absorbance differences against reaction time. Specific rates from replicate runs agreed to better than 6%. With the $\text{Fe}(\text{CN})_6^{4-}$ reactions, the absorbance increase due to the primary transformation was followed by a much slower rise corresponding to only about 7% of the total change, due possibly to reaction with air or small quantities of H_2O_2 released after all $\text{Cr}(\text{IV})$ had been reduced.¹⁹ This lag did not seriously complicate our kinetic analysis.

The rapid reaction with excess $\text{Ti}(\text{III})$ in glycine buffer, which was monitored on a Durrum–Gibson stop-flow spectrophotometer, exhibited two kinetically separable components at 382 nm. A very rapid rise in absorbance (half-life less than 20 ms) was followed by a much slower fading ($t_{1/2} = 3$ s). The first of these components appeared to be first order in $\text{Ti}(\text{III})$, whereas the rate of the second was independent of reductant. Examination of the reaction with VO^{2+} during the first few milliseconds after mixing gave no indication of the intervention of an analogous intermediate.

The diperochromium(IV) complex was unreactive toward $\text{Ru}(\text{NH}_3)_6^{2+}$, IrCl_6^{3-} , $\text{Fe}(\text{bpy})_3^{2+}$, and $[(\text{AcO})_2\text{Rh}^{\text{II}}]_2$, whereas precipitation of $\text{Fe}(\text{OH})_3$ occurred during reaction with aqueous FeSO_4 . Reduction by Eu^{2+} was rapid but was complicated by a secondary reaction involving the $\text{Cr}(\text{III})$ product(s). Reaction with thiolactic acid was rapid but yielded kinetic profiles that thus far have not been tractable. Reactions with hydroxylamine and with ascorbic acid were very slow but were catalyzed strikingly by traces of dissolved iron ($\text{Fe}(\text{II})$ or $\text{Fe}(\text{III})$), even with the catalyst at the 10^{-7} M level. Further work is being carried out on these catalyzed systems. Reactions of the diperoxo complex with carboxylate species such as glycine, acetate, or EDTA in the absence of reducing agents, although perceptible, were not rapid enough to introduce complications in interpretation.²⁰

Results and Discussion

The magnetic susceptibility of our oxidant is compared to those of several transition-metal compounds in Table I and is seen to lie slightly below that of $\text{Ni}(\text{NO}_3)_2$, which has 2 unpaired electrons/metal center, thus confirming the formulation as a diperoxo complex of $\text{Cr}(\text{IV})$ (d^2) and ruling out such alternate possibilities as a mixed peroxo-superoxo complex of $\text{Cr}(\text{III})$. This result is

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- (10) (a) Telep, G.; Boltz, D. F. *Anal. Chem.* **1951**, *23*, 901. (b) Guenther, P. R.; Linck, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 3769.
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- (13) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.
- (14) Figgis, B. B.; Lewis, J. *Prog. Inorg. Chem.* **1964**, *6*, 37. (See Table III in this review.)
- (15) Reactions with $\text{V}(\text{IV})$ and $\text{Ti}(\text{III})$ were carried out in solutions buffered with glycine and its hydroperchlorate (pH 2.8) in the presence of 0.020 M Na_3HEDTA in a 1.00-cm cell. The (slower) reactions involving deficiencies of $\text{Fe}(\text{CN})_6^{4-}$ were run in a 0.20-cm cell in HOAc-OAc^- buffers.
- (16) For estimates of extinction coefficients of $\text{Cr}(\text{III})$ complexes, aliquots of the eluates were oxidized with basic H_2O_2 , and the chromium content was determined as chromate. See, for example: Haupt, G. W. *J. Res. Natl. Bur. Stand. (U.S.)* **1952**, *48*, 414.
- (17) See, for example: Gould, E. S. *J. Am. Chem. Soc.* **1968**, *90*, 1740.

- (18) Spectra from the $\text{Fe}(\text{CN})_6^{4-}$ reactions exhibited cyanoiron-related absorbance in the near-UV region that could be removed only in part by passage through anion-exchange resin or treatment with Cd^{2+} or Ag^+ . Solutions from the VO^{2+} reactions exhibited absorbance attributable to peroxovanadium(V) species.
- (19) In a separate experiment, the oxidation of $\text{Fe}(\text{CN})_6^{4-}$ (9×10^{-3} M) by H_2O_2 (6×10^{-4} M) was found to proceed at a specific rate of $0.048 \text{ M}^{-1} \text{ s}^{-1}$ under comparable conditions (25 °C, $\mu = 0.40$, 1:1 HOAc-OAc^- buffer) in the absence of dissolved chromium.
- (20) Because solutions of the diperoxo complex in carboxylate buffers were found to undergo slow change, kinetic runs in buffered media were carried out by mixing buffered solutions of the reductant with unbuffered solutions of the $\text{Cr}(\text{IV})$ complex.

Table II. Chromium(III) Products from Reactions of (dien)Cr^{IV}(O₂)₂

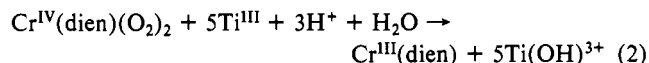
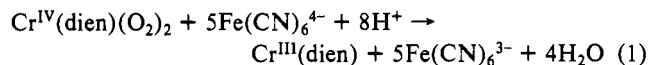
reagent	medium	eluant ^a	ε ₁ ^b	λ ₁ ^b	ε ₂	λ ₂	% Cr ^c
HClO ₄	0.1 M HClO ₄	1.5 M H ₂ SO ₄	37	518	23	388	94
VO ²⁺	0.1 M glycine	1 M NaClO ₄	49	520	33	387	93
Ti(III)	0.1 M TosH	2 M NaClO ₄	45	515	36	385	89
Ti(III)	0.1 M NaCl	1 M NaClO ₄	82	513	49	398	75
Ti(III)	0.2 M salicylate	<i>d</i>	55	512	150	360 ^e	<i>d</i>
Ti(III)	0.2 M glycine	water	68	507	57	395 ^e	58
		1 M NaClO ₄	75	507	47	387 ^e	26
Ti(III)	0.5 M glycine	water	70	507	78	390 ^e	33
		1 M NaClO ₄	81	502	50	390 ^e	55
Ti(III)	1.0 M glycine	water	78	510	86	390 ^e	13
		1 M NaClO ₄	83	500	56	392 ^e	81
Fe(CN) ₆ ⁴⁻	0.1 M OAc ⁻	water	44	527	<i>f</i>		

^a Eluted from Dowex X-2 at 2 °C. ^b Absorption maxima (λ values) are in nm; apparent ε values (in M⁻¹ cm⁻¹) were obtained by dividing absorbance by total Cr(III) in fraction.¹⁶ ^c Percent of Cr(IV) taken. ^d Extensive decomposition on ion-exchange column. ^e Shoulder. ^f High-energy maximum obscured by absorbance of cyanoferrate species.

in accord with a similar conclusion based on an earlier study^{8c} of the analogous tricyano derivative K₃Cr^{IV}(O₂)₂(CN)₃.

Spectrophotometric titration indicates that the stoichiometry of the reduction by VO²⁺ (when Cr(IV) is in excess) closely approaches 1:1. The net reaction is then, in this instance, a 1e transaction, generating Cr(III) and V(V) and releasing peroxide, the disproportionation of which (to O₂ and H₂O) need not affect the primary transformation. The formation of much less than 1 mol of O₂/mol of Cr(IV) is attributable to partial conversion of the H₂O₂ to a peroxovanadium(V) complex, which, however, releases further O₂ on treatment with catalase. With V(IV) in excess, a small fraction of the peroxide is lost in a competing process, most probably the oxidation of V(IV).

In contrast, the reactions with Ti(III) and Fe(CN)₆⁴⁻ consume nearly 5 mol of reductant/mol of Cr(IV). With these reagents, peroxide participates in the overall conversions



It is extremely unlikely that the oxidation of Fe(CN)₆⁴⁻ by peroxide occurs after the latter leaves the coordination sphere of chromium, for the reaction of uncomplexed H₂O₂ with this reductant proceeds much more slowly than the Cr^{IV}(O₂)₂ reaction¹⁹ and is not perceptibly catalyzed by the Cr^{III}(dien) product. The picture is less clear for Ti(III), which is known to reduce H₂O₂ very rapidly.²¹ In this system, consumption of peroxide may involve free or coordinated oxidant or a combination of both.

Spectral and elution characteristics of the principal products from several reactions of Cr^{IV}(dien)(O₂)₂ are summarized in Table II. Values of λ_{max} (510–530 and 370–390 nm) lie well below those for aquo- and carboxylato-substituted Cr(III) complexes,^{9a,22} reflecting incorporation of the N-donor sites of coordinated diethylenetriamine. When this ligand assumes its usual tridentate function, it is taken to occupy the 1,2,6-positions of the Cr(III) coordination octahedron (with the two end NH₂ groups trans), in line with the preferred structure (I) of the (O₂)₂Cr^{IV} precursor. This amine is known to “unwrap” itself from the Cr(III) center (slowly and in a stepwise manner) under hydrolytic conditions and during ion-exchange separations, yielding first a “doubly anchored” species such as (dienH)Cr(H₂O)₄⁴⁺,²³ and then a singly attached complex such as (dienH₂)Cr(H₂O)₅⁵⁺.²⁴

In addition, it is recognized^{5b,c,25} that conversion of these peroxo complexes to Cr(III) derivatives may entail intrusion of donor centers present in solution into the ligand sphere of Cr(III). The

Table III. Kinetic Data for Reduction of Diperoxo-chromium(IV) with Vanadium(IV)^a

10 ³ [H ⁺], M	<i>k</i> , M ⁻¹ s ⁻¹ ^b	10 ³ [H ⁺], M	<i>k</i> , M ⁻¹ s ⁻¹ ^b
1.55 ^c	1.28	6.5	3.1
1.62 ^d	1.35	8.5	4.0
1.66	1.33	11.2	5.1
0.57	1.06	12.9	5.3
3.31	1.88	1.74 ^e	1.28
5.01	2.5	1.74 ^f	1.34

^a Reactions were carried out at 25 °C; μ = 0.50 (LiClO₄). Chromium(IV) was added as Cr^{IV}(dien)(O₂)₂·H₂O (I). pH values were regulated by addition of measured amounts of glycine (0.04–0.20 M) and its hydroperchlorate (0.04–0.24 M). [Na₃HEDTA] = 0.2 M; [Cr^{IV}] = 4.5 × 10⁻⁴ M; [V^{IV}] = 4.5 × 10⁻³ M, unless otherwise indicated. ^b Second-order specific rates (-d[Cr^{IV}]/dt)/[Cr^{IV}][V^{IV}]. ^c [Cr^{IV}] = 4.5 × 10⁻⁴ M; [V^{IV}] = 2.25 × 10⁻⁴ M. ^d [Cr^{IV}] = 2.25 × 10⁻⁴ M; [V^{IV}] = 4.5 × 10⁻³ M. ^e [Cl⁻] = 0.01 M. ^f [Cl⁻] = 0.20 M.

Table IV. Kinetic Data for Reduction of Cr^{IV}(diene)(O₂)₂ with Fe(CN)₆⁴⁻ (25 °C, μ = 0.40 (LiClO₄))^a

Glycine Buffers				
10 ³ [Fe ^{II}], M	[GlyH ⁺], M	[Gly], M	pH	<i>k</i> , M ⁻¹ s ⁻¹ ^b
2.50	0.010	0.010	2.36	10.0
5.0	0.010	0.010	2.34	10.4
1.25 ^c	0.010	0.010	2.36	9.6
2.50	0.020	0.020	2.34	10.0
2.50	0.040	0.040	2.35	9.2
2.50	0.080	0.080	2.36	10.4
2.50	0.010	0.080	3.04	5.8
2.50	0.020	0.080	2.87	6.4
2.50	0.040	0.080	2.62	7.6
2.50	0.060	0.080	2.43	9.2
Acetate Buffers				
10 ³ [Fe ^{II}], M	[HOAc], M	[Ac ⁻], M	pH	<i>k</i> , M ⁻¹ s ⁻¹
9.0	0.010	0.010	4.28	2.1
9.0	0.040	0.040	4.28	2.2
9.0	0.005	0.040	5.10	2.0
9.0 ^d	0.010	0.010	4.31	1.60

^a [Cr^{IV}] = 1.50 × 10⁻⁴ M, unless otherwise indicated. ^b Second-order specific rates (-d[Fe^{II}]/dt)/[Fe^{II}][Cr^{IV}] = 5(-d[Cr^{IV}]/dt)/[Fe^{II}][Cr^{IV}]. ^c [Cr^{IV}] = 7.5 × 10⁻⁵ M. ^d Fe(NH₄)₂(SO₄)₂ (2 × 10⁻⁵ M) added.

elution behavior and the spectrum of the product arising from the decomposition of the diperoxo complex in HClO₄ correspond to a mixture of Cr(dienH)(H₂O)₄⁴⁺ and the fully aquated complex, Cr(H₂O)₆³⁺.²³ Reductions by Ti(III) in the poorly coordinating medium *p*-toluenesulfonate yield a complex having a spectrum closely resembling that of Cr(dienH)(H₂O)₄⁴⁺ (ε₅₂₁ = 46; ε₃₈₇ = 30),²³ and this appears to be the principal product from reduction by VO²⁺ in 0.1 M glycine (the buffer used in the kinetic experiments). When the Ti(III) reduction is carried out in 0.1 M Cl⁻, the high-energy maximum of the Cr(III) product shifts to 398 nm, suggesting partial incorporation of chloride. Ligation by added

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Table V. Kinetic Data for Reduction of Cr^{IV}(dien)(O₂)₂ with Ti(III) (23.5 °C, $\mu = 0.25$ M (LiClO₄), 380 nm)

10 ⁴ [Cr ^{IV}], M	10 ³ [Ti ^{III}], M	[GlyH ⁺], ^a M	[Gly], ^a M	pH	k ₁ , ^b s ⁻¹	k ₂ , ^c s ⁻¹
2.5	5.00	0.040	0.040	2.31	33	0.19
2.5	10.0	0.040	0.040	2.30	63	0.22
2.5	15.0	0.040	0.040	2.28	92	0.22
5.0	10.0	0.040	0.040	2.28	73	0.18
10.0	10.0	0.040	0.040	2.27	71	0.18
5.0	10.0	0.080	0.080	2.28	63	0.18
5.0	10.0	0.160	0.160	2.30	63	0.22
5.0	10.0	0.200	0.200	2.27	77	0.23
5.0	10.0	0.025	0.200	3.18	63	0.22
5.0	10.0	0.050	0.200	2.87	69	0.20
5.0	10.0	0.30	0.200	2.11	63	0.20

^aSolutions were buffered with glycine (Gly) and its conjugate acid (GlyH⁺). ^bRapid growth of strongly absorbing intermediate. ^cSlow decay of intermediate.

salicylate results in a further marked increase in absorbance near 360 nm.

Titanium(III) reductions in glycine are seen to yield two eluted fractions. Since the spectra of these fractions undergo variations with [glycine] in the generating solutions, we are again dealing, at least in part, with mixtures. The major portion of the product formed in 0.2 M glycine is eluted from sulfonate resin with water alone, but as the buffer concentration is increased to 1.0 M, a fraction eluted with 1 M NaClO₄ predominates. This trend suggests that the first unit of glycine entering the Cr(III) sphere is incorporated as a chelating (uninegative) ligand but that the second unit coordinates as a unidentate, leaving its positive -NH₃⁺ function free. Attempts at further separations of the fractions from the Ti(III) reductions were not successful.

Kinetic data for reduction of (O₂)₂Cr^{IV} complex I with VO²⁺ in glycine buffers are assembled in Table III. Reactions are seen to be accelerated by H⁺, with observed specific rates conforming to the binomial expression $a + b[H^+]$, where $a = 0.74 \pm 0.07$ M⁻¹ s⁻¹ and $b = 371 \pm 11$ M⁻² s⁻¹ (25 °C, $\mu = 0.50$ M). The [H⁺]-proportional term, which predominates throughout much of the pH range examined, cannot reflect protonation of V(IV) (pK_A = 6.1)²⁶ but may instead be attributed to partial conversion of the oxidant to a more reactive conjugate acid. Since there is no evidence of kinetic saturation above pH 2, the pK of this form must fall below 0.5, corresponding to a bimolecular rate constant greater than 10² M⁻¹ s⁻¹ for reduction of this protonated species.

An analogous picture appears to apply to the reductions by Fe(CN)₆⁴⁻ in glycine buffers (Table IV), which follow the same type of binomial rate law, i.e.

$$\frac{-d[\text{Cr}^{\text{IV}}]}{dt} = \frac{1}{5} \frac{-d[\text{Fe}^{\text{II}}]}{dt} = [\text{Fe}^{\text{II}}][\text{Cr}^{\text{IV}}](a + b[\text{H}^+]) \quad (3)$$

with $a = 0.94 \pm 0.07$ M⁻¹ s⁻¹ and $b = 236 \pm 19$ M⁻² s⁻¹ (25 °C, $\mu = 0.40$ M). A slightly lower limiting rate is observed in acetate buffers, suggesting a perceptible medium effect. No catalysis by Fe²⁺_{aq} at the 10⁻⁵ M level was noted. Specific rates pertaining to the two components are remarkably similar for the two reductants, whereas the Marcus model²⁷ indicates that reduction by Fe(CN)₆⁴⁻ should be favored by a factor of about 10⁹ if the rate-determining steps in both reactions were outer-sphere processes.^{28,29} The discrepancy is in the direction consistent with a preponderant inner-sphere path for the reduction by VO²⁺.^{30,31}

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(28) The difference in formal potentials for the two reductants (0.64 V)^{29a} corresponds to a kinetic advantage of 10^{5.5} for Fe(CN)₆⁴⁻. The estimated self-exchange rates (Fe(CN)₆^{4-/3-}, 7×10^4 M⁻¹ s⁻¹; V(IV/V), 10⁻³ M⁻¹ s⁻¹)^{29b,c} favor the ferrocyanide reduction by an additional factor of 10^{3.9}.

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(30) The protonation of Fe(CN)₆⁴⁻ (pK_A 2.7 at $\mu = 0.5$ M)³¹ appears to be without significant kinetic effect in this system. If the reactivities of the protonated and nonprotonated forms of this reductant differed appreciably, we should have seen an indication of kinetic saturation.

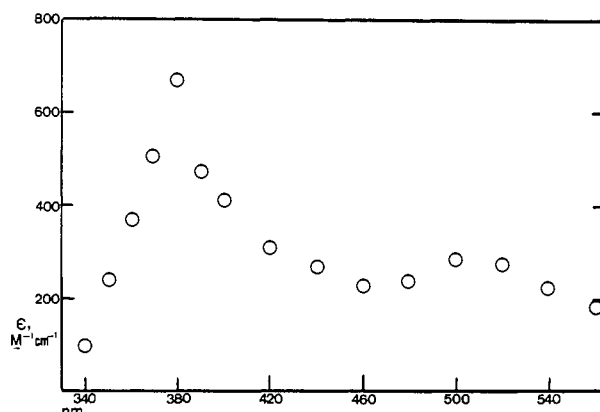
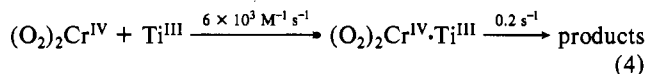


Figure 1. Spectrum of the intermediate species formed in the reduction of 0.00050 M Cr^{IV}(dien)(O₂)₂ (chelate I) with 0.010 M Ti(III) in glycine buffer (0.04 M each in Gly and GlyH⁺). Points were taken 60 ms after mixing (path length 2.0 cm; T = 24 °C).

The reactions of Cr^{IV}(dien)(O₂)₂ with Ti(III) in glycine buffers were carried out principally with the reductant in excess to avoid complications resulting from the formation of Ti(IV)-peroxo complexes.³² This reduction proceeds through a species absorbing strongly near 380 nm ($\epsilon = 660$ M⁻¹ cm⁻¹) (Figure 1), which is formed rapidly but decays much more slowly. Rate data for both components, which are kinetically separable, appear in Table V. The growth of the intermediate (k_1 values) is seen to be first order in Ti(III), whereas its decay (k_2) is independent of reductant. Neither transformation is acid-dependent within the (relatively narrow) pH range examined.

The kinetic behavior of this system is consistent with the intervention of a bimolecular Cr(IV)-Ti(III) complex, which decays unimolecularly to Cr(III) and Ti(IV)



and the spectrum of the intermediate features maxima that are characteristic of the two redox components. The estimated rate of formation of this precursor falls below the limit set by ligand substitution at the Ti(III) center, especially since ligation of Ti(III) by the carboxylate function of the glycine buffer is expected to facilitate such substitution.^{9b,33}

Undoubtedly, the most notable aspect of the present study is the ease with which ligands in the supporting electrolyte enter the coordination sphere of the Cr(III) product during the rapid reduction by Ti(III). Carboxylate incorporation at the Cr^{IV}(O₂)₂ center in the absence of redox is found here to be slow in the media at hand, and ligand exchange in the usual substitution-inert Cr(III)

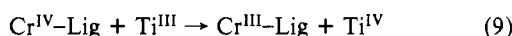
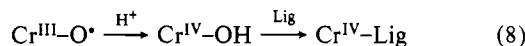
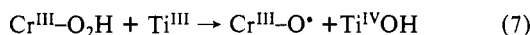
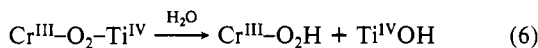
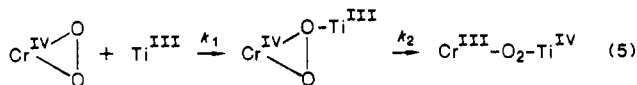
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centers should be still more sluggish. Our reaction conditions are somewhat milder than those used by Garner and co-workers,⁵ who found that as many as four halide anions can become attached to chromium when decompositions of $\text{Cr}^{\text{IV}}(\text{O}_2)_2$ complexes are carried out at high acidities, and we see no evidence in our systems that more than two carboxylate groups have become bonded to $\text{Cr}(\text{III})$.

Our observations appear to be consistent with the sequence (5)–(9), in which the steps (6)–(9) are taken to proceed after the



rate-determining steps. The initial act of electron transfer (eq 5) is probably accompanied by breakage of a chromium-peroxy bond as 7-coordinate $\text{Cr}(\text{IV})$ is converted to 6-coordinate $\text{Cr}(\text{III})$. The proposed $\text{Cr}(\text{III})$ -peroxy intermediate brings to mind related complexes described by King and co-workers,³⁴ who have emphasized the ease with which such species decompose in aqueous

media. However, such decompositions are reported to be much slower ($k = 10^{-5}$ – 10^{-4} s^{-1} at 25 °C) than the redox reactions under consideration. We suspect then that the subsequent attack by $\text{Ti}(\text{III})$ on the peroxy complex results in homolysis of the O–O bond (eq 7), that the resulting $\text{Cr}^{\text{III}}-\text{O}^\bullet$ fragment is rapidly converted, via internal electron transfer, to a $\text{Cr}^{\text{IV}}-\text{O}$ complex (eq 8), and that rapid ligand exchange involves the latter oxidation state, which is known to be substitution-labile³⁵ except when bound to strongly chelating groups.³⁶ Note that reduction by VO^{2+} , during which the O–O bonds remain unbroken, is not accompanied by intrusion of external glycine.

In sum, this work points to considerable versatility of peroxy-bound chromium(IV) species as oxidants. Although only three reductants have been examined, we see that in some cases both oxidizing functions react, whereas in others only the $\text{Cr}(\text{IV})$ center is reduced. Evidence has been obtained that both inner- and outer-sphere paths may operate. Moreover, we find that greatly increased substitution lability may be associated with reduction of the peroxy group with 1e reagents. Finally, the marked catalyses of the oxidations of hydroxylamine and ascorbic acid by $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$ are expected to add further detail to an already complicated picture. Examination of these catalyzed reactions is continuing.

Acknowledgment. We are grateful to Dr. James Espenson for valuable discussions and to Arla White for technical assistance.

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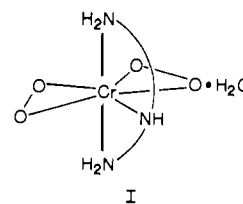
Electron Transfer. 96. Catalyzed Reduction of Peroxide-Bound Chromium(IV) with Hydroxylamine¹

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The diperoxo chromium(IV) derivative of diethylenetriamine, $\text{Cr}^{\text{IV}}(\text{dien})(\text{O}_2)_2$ (chelate I) reacts very slowly with hydroxylamine in acetate buffers, but the reaction is markedly catalyzed by $\text{Fe}(\text{II})$ or $\text{Fe}(\text{III})$ and, to a much lesser extent, by $\text{Cu}(\text{II})$. With excess NH_3OH^+ , products are N_2 , $\text{Cr}(\text{III})$, and O_2 (the latter arising from the disproportionation of peroxide). The $\text{Cr}(\text{III})$ products contain bound acetate groups from the supporting medium and chelating diethylenetriamine. The reaction is half-order in $\text{Fe}(\text{II})$ and exhibits kinetic saturation with respect to $[\text{NH}_3\text{OH}^+]$ (eq 2). The rate law suggests that catalytic iron exists predominantly in an inactive dimeric form with a small active monomeric fraction that forms a 1:1 complex ($K_{\text{assn}} = 10^3 \text{ M}^{-1}$) with NH_3OH^+ . The proposed catalytic sequence involves recycling of dissolved iron between the di- and tripositive states, the rapid oxidation of $\text{Fe}(\text{II})$ by $\text{Cr}(\text{IV})$ ($k = 3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at 22 °C), a rate-determining 1e oxidation of $\text{Fe}(\text{III})$ -bound hydroxylammonium ion by $\text{Cr}(\text{IV})$, and the rapid reaction of $\text{Fe}^{\text{III}}(\text{OHNH}_2^+)$ with excess NH_3OH^+ . Incorporation of external acetate at the $\text{Cr}(\text{III})$ center appears to occur during the iron-catalyzed disproportionation of $\text{Cr}(\text{III})$ -bound peroxide. The structural requirements for catalytic effectiveness in this reaction are briefly considered.

Although chromium(IV) diperoxo amines have been known since the beginning of the century,² interest in their detailed redox chemistry has developed more recently.³ The most robust of these diperoxo complexes, chelate I (derived from diethylenetriamine),⁴ has been found to be an unusually versatile oxidant, for both the $\text{Cr}(\text{IV})$ and peroxy functions are reduced rapidly by $\text{Ti}(\text{III})$ and



- (1) Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.
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by $\text{Fe}(\text{CN})_6^{4-}$, whereas VO^{2+} reduces only the $\text{Cr}(\text{IV})$ center.^{3d} We have reported evidence that both VO^{2+} and $\text{Ti}(\text{III})$ utilize inner-sphere paths in these reductions,^{3d} whereas the reaction by $\text{Fe}(\text{CN})_6^{4-}$ is probably initiated by an outer-sphere transfer. In addition, some (but not all) of these reductions are accompanied by incorporation of anions from the supporting media into the coordination sphere of the $\text{Cr}(\text{III})$ product.

A number of non-metal-derived reductants, among them hydroxylamine, ascorbic acid, and mercapto-substituted species, have