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Electron Transfer. 97. The Iron-Catalyzed Reduction of Peroxide-Bound Chromium(IV) with Ascorbic Acid[1]

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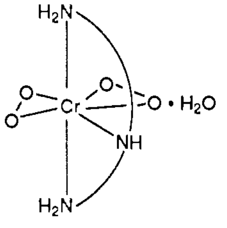
Received September 29, 1988

The diperoxochromium(IV) derivative of diethylenetriamine, $Cr^{IV}(dien)(O_2)_2$ (chelate I), reacts slowly with ascorbic acid (H_2A) in acetate buffers, but the reaction is strongly catalyzed by Fe(II) or Fe(III), in both the absence and the presence of EDTA. The observed stoichiometry (H_2A/Cr^{IV}) approaches 5/2; both the Cr(IV) center and the peroxo ligands are reduced. The Cr(III) products contain bound ascorbate groups and, at high acetate concentrations, bound acetate as well. With EDTA absent, the reaction is first order each in Cr(IV) and iron catalyst but exhibits kinetic saturation with respect to ascorbate (eq 2). Iron in these reaction mixtures is recycled between the di- and tripositive states but exists predominantly as Fe(III). The proposed catalytic sequence involves the formation of an Fe(III)–ascorbate complex ($K_{assn} = 5 \times 10^3\ M^{-1}$ at 25 °C) that reacts, in the rate-determining step, with the Cr(IV) oxidant (eq 9; $k = 1.5 \times 10^3\ M^{-1}\ s^{-1}$), yielding peroxide-bound Cr(III) and the ascorbate radical ($HA^\bullet$); the latter then reacts rapidly with a second Cr(IV) center. Subsequent reactions of ascorbate with coordinated peroxide are likewise taken to be rapid. The less effectively catalyzed reaction in the presence of EDTA is very nearly zero order in Cr(IV), is first order in iron, and, at low ascorbate concentrations, is first order in reductant. Here, Cr(IV) functions as a scavenger, reacting rapidly with an intermediate, almost certainly the ascorbate radical ($HA^\bullet$), formed by 1e oxidation of ascorbate by $Fe^{III}(EDTA)$. An approach to kinetic saturation at high reductant concentration points to the formation of a weakly associated ($K_{assn} = 88\ M^{-1}$) complex between $Fe^{III}(EDTA)$ and ascorbate. The effective bimolecular rate constant for the $Fe^{III}(EDTA)$–ascorbate electron-transfer reaction agrees with that earlier reported for chromium-free systems. The incorporation of ascorbate and acetate into the Cr(III) products is attributed to the intervention, during reduction of bound peroxide, of a $Cr^{III}–O^\bullet$ fragment having the character of a substitution-labile $Cr^{IV}–O$ species. Catalyses of the $Cr^{IV}(dien)(O_2)_2$–ascorbic acid reaction by Cu^{2+} and by VO^{2+}, in contrast to Fe^{2+} catalysis, are blocked by addition of EDTA. It is proposed that the weakly oxidizing Cu(II), when sequestered, is no longer able to oxidize ascorbate, whereas the weakly reducing VO^{2+}, when complexed, is no longer able to reduce Cr^{IV} effectively. In related noncatalytic systems, buffered by $HOAc–OAc^-$, $Cr^{IV}(dien)(O_2)_2$ oxidizes Fe(II) at a bimolecular specific rate of $4 \times 10^3\ M^{-1}\ s^{-1}$ (25 °C) and oxidizes $Fe^{II}(EDTA)$ with a specific rate of $1.4 \times 10^4\ M^{-1}\ s^{-1}$ (19 °C). The Fe(III)–ascorbate redox reaction proceeds through a blue complex ($\lambda_{max} = 550$ nm, $\epsilon = 1.0 \times 10^4\ M^{-1}\ cm^{-1}$), formed at a specific rate of 34 $M^{-1}\ s^{-1}$ at 19 °C and decaying by a combination of internal electron transfer ($k = 1.3\ s^{-1}$) and bimolecular attack by another unit of ascorbate ($k = 260\ M^{-1}\ s^{-1}$ at 19 °C).

Among the diperoxo complexes of the atypical oxidation state chromium(IV),[2] the derivative of diethylenetriamine (chelate I)[3] may be prepared, stored, and handled with particular ease. We have found that both the Cr(IV) and peroxo functions are reduced readily by $Fe(CN)_6^{4-}$ and Ti(III), whereas V(IV) reduces only Cr(IV).[4] Additional mechanistic versatility is demonstrated in the presence of dissolved iron. A number of reductants (among them, mercapto-substituted species and hydroxylamine) react with peroxide-bound Cr(IV) sluggishly or imperceptibly but are consumed rapidly when small concentrations ($<10^{-6}$ M) of Fe(II) or Fe(III) salts are added.[5]



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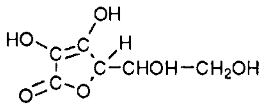

II

The present report deals with the reaction of the diperoxochromium(IV) complex I with the organic reductant ascorbic acid (II), a reagent selected in view of its capacity to undergo single-electron, as well as two-electron, changes.[6] This reaction is also catalyzed strongly by dissolved iron and proceeds at a measurable rate (albeit with altered kinetic character) even when iron has been sequestered by the very effective complexing agent EDTA.

Experimental Section

Materials. Diperoxo(diethylenetriamine)chromium(IV) hydrate, $Cr(dien)(O_2)_2 \cdot H_2O$ (I), was prepared by the method of House and Garner.[2b,3b] The complex, which precipitated from aqueous solution, was washed with methanol at 0 °C and then dried over P_2O_5 for 12 h.

Warning! A sample of this complex exploded violently when touched with a metal spatula on a sintered-glass surface. Subsequent preparations were carried out, without incident, on a small scale (less than 500 mg), and all manipulations were performed with a plastic spatula.

L-Ascorbic acid (Aldrich 99+%) was used as received, but all solutions of this reductant were prepared in distilled water that had been previously boiled and sparged with N_2 for 4 h to remove O_2; concentrations were checked by iodometry. Solutions of $(NH_4)_2Fe(SO_4)_2$ (Aldrich 99.9%) were prepared and stored in the dark; Fe(II) content was confirmed by titration with standard $Cr_2O_7^{2-}$, using diphenylamine as indicator.[7] The cation-exchange resin (Dowex 50-X2, 400 mesh, H^+ form) was pretreated as described.[8] Lithium perchlorate (for kinetic experiments) was prepared by the method of Dockal[9] and was recrystallized twice. Catalase (Sigma Chemical; bovine liver; 11 000 units/mg) was used as received.

Stoichiometric Studies. The stoichiometry of the reaction of the Cr(IV) complex (I) with ascorbic acid was determined by spectrophotometric titration at 382 nm (λ_{max} for $Cr(dien)(O_2)_2$; $\epsilon = 460\ M^{-1}\ cm^{-1}$). To measured quantities of Cr(IV) (0.002–0.020 mmol) in HOAc–OAc buffer were added successive known quantities of ascorbic acid. Plots of absorbance vs [added reductant] exhibited break points at [ascorbate]/[Cr^{IV}] near 2.50, both in the presence and absence of added Fe^{II} (Table I).[10] Addition of the enzyme catalase (0.5 mg/mL of solution), which catalyzes the disproportionation of H_2O_2 to H_2O and O_2, released no gas. Treatment of the diperoxo complex with catalase in the absence of ascorbic acid released 1.02 mol of O_2/mol of Cr(IV). In the absence of added transition-metal species, the (slow) reaction of ascorbic acid with

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[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) Hoffman, K. A. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 3181. (b) House, D. A.; Garner, C. S. *Inorg. Chem.* **1966**, *5*, 840. (c) House, D. A.; Hughes, R. G.; Garner, C. S. *Inorg. Chem.* **1967**, *6*, 1077.

[3] (a) Stomberg, R. *Ark. Kemi.* **1965**, *24*, 47. (b) House, D. A.; Garner, C. S. *Nature* **1965**, *208*, 776.

[4] Ghosh, S. K.; Laali, K.; Gould, E. S. *Inorg. Chem.* **1988**, *27*, 4224.

[5] Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1988**, *27*, 4228.

[6] See, for example: (a) Pelizzetti, E.; Mentasti, E.; Pramauro, E. *Inorg. Chem.* **1976**, *15*, 2898; **1978**, *17*, 1181. (b) Lannon, A. M.; Lappin, A. G.; Segal, M. G. *J. Chem. Soc., Dalton Trans.* **1986**, 619. (c) Akhtar, M. J.; Haim, A. *Inorg. Chem.* **1988**, *27*, 1608.

[7] Pierce, W. C.; Haenisch, E. L. *Quantitative Analysis*, 3rd ed.; Wiley: New York, 1948; p 259.

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

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

[10] Reactions catalyzed by added Fe^{II} were run in a 1.00-cm cell. The slower reactions with no added iron were carried out in a 0.20-cm cell.

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Table I. Stoichiometry of the Reaction of $Cr^{IV}(dien)(O_2)_2$ with Ascorbic Acid (H_2A)[a]

mmol			
Cr^{IV}	H_2A	$[Fe^{II}]$, M	$\Delta[H_2A]/\Delta[Cr^{IV}]$
0.0150	0.0381	0	2.54
0.0120	0.0282	0	2.35
0.0200	0.0510	0	2.55
0.0020	0.0051	5×10^{-5}	2.6
0.0040	0.0099	5×10^{-5}	2.5
0.0060	0.0153	5×10^{-5}	2.6

[a] Determined by spectrophotometric titration at 382 nm in HOAc–OAc⁻ buffers. See Experimental Section and footnote 10.

excess H_2O_2 (at pH 4.4) was shown to consume 1.03 ± 0.02 mol of peroxide/mol of ascorbic acid.

Examination of the Cr(III) Reaction Products. Reaction mixtures (volume 2–3 mL) were 0.02 M in Cr(IV), were 0.10–0.15 M in ascorbic acid, and were generally buffered with equimolar concentrations (0.05–1.0 M) of HOAc and OAc⁻. These were subjected to column chromatography on Dowex 50-X2 at 2 °C.[11] A portion of the chromium was eluted by water alone and exhibited an absorption maximum at 550 nm ($\epsilon = 65\ M^{-1}\ cm^{-1}$) and a shoulder near 375 nm ($\epsilon = 150$). A more tightly held fraction, eluted with 1–2 M $NaClO_4$, showed a maximum at 530 nm ($\epsilon = 68$) and a shoulder near 375 nm ($\epsilon = 150$). The fraction eluted with water constituted 70% of the recovered chromium when the acetate buffer was 1.0 M but dropped to 33% when [OAc⁻] was 0.1 M. The spectral characteristics of these fractions appeared to be the same for reactions catalyzed by iron as for those carried out in its absence and were not significantly altered by addition of 1.0 M Cl⁻ to the reaction medium. Chromium-bound ascorbate in the $NaClO_4$ eluate was estimated by acidifying with 0.1 M H_2SO_4, adding a known excess of KI_3, waiting 30 min, and then titrating the unreacted I_3^- with standard $Na_2S_2O_3$. The ascorbate/chromium ratio so obtained was 0.85–0.95.[12a] Recovery of total chromium was 75–90%, with the loss due mainly to column-catalyzed polymerization.[12b]

Kinetic Measurements. Rates were estimated from absorbance changes at 382 nm, by using a Beckman Model 5260 or a Cary 14 recording spectrophotometer. Ionic strength was regulated by addition of $LiClO_4$. Reactions were carried out with ascorbate in greater than 10-fold excess. Conversions were followed to at least 98% completion. Both in the absence and in the presence of added iron, reactions were first order in Cr(IV), and rate constants from successive half-life values generally agreed to within 5%; average values did not differ significantly from those obtained from logarithmic plots of absorbance differences against reaction time. For reactions of this type, specific rates from replicate runs agreed to better than 8%.

Reactions carried out in the presence of EDTA were much slower and exhibited quite different kinetic patterns. Rates were very nearly constant during the first 80% reaction, after which the decay curves assumed the more usual exponential character. Rates for these reactions, estimated from slopes during the first 50% conversion, were more poorly reproducible than specific rates obtained in the absence of EDTA. Variations as great as 15% between replicate runs persisted despite several modifications in technique.

The $Cr^{IV}(dien)(O_2)_2$–ascorbate reaction is catalyzed, although less strikingly, by Cu^{2+} and VO^{2+}; kinetic examinations of these catalytic systems are continuing. Additions of Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, $Co(en)_3^{3+}$, $Ru(NH_3)_6^{3+}$, $IrCl_6^{3-}$, Al^{3+}, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, or TiO^{2+} (each at the 10^{-4} M level) were without significant catalytic effect.

Two uncatalyzed reactions related to the catalytic system of interest were examined briefly. The reaction of the diperoxochromium(IV) complex (2.0×10^{-4} M) with excess Fe(II) (0.002–0.004 M) in the presence of 0.02 M EDTA (with ascorbate absent) was rapid and first order in both redox components. Stop-flow measurements at 400 nm in equimolar HOAc–OAc⁻ (0.10 M each) buffers yielded a bimolecular rate constant $1.4 \times 10^4\ M^{-1}\ s^{-1}$ (19 °C, $\mu = 0.4$ M). The reaction between Fe^{III} (2×10^{-4} M) and excess ascorbate in a similar medium (with Cr^{IV} absent) featured the formation and destruction of an intermediate strongly absorbing at 550 nm, similar to that reported by Laurence and Ellis.[13] The resulting biphasic kinetic curves, recorded at this wavelength, were separated into component pseudo-first-order processes as described by Bose.[14] Specific rates for both components (Table III) were found to increase with increasing ascorbate concentrations.

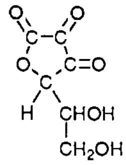
Table II. Kinetic Data for the Reduction of $Cr^{IV}(dien)(O_2)_2$ with Ascorbic Acid (H_2A), As Catalyzed by Fe(II)[a]

$10^3[H_2A]$, M	$10^5[Fe^{II}]$, M	[HOAc], M	[OAc⁻], M	10^2k, s^{-1}
8.0	0	0.010	0.010	0.012
8.0	0.10	0.010	0.010	0.24
8.0	0.20	0.010	0.010	0.64
8.0	0.40	0.010	0.010	1.30
8.0	0.60	0.010	0.010	1.65
8.0	0.80	0.010	0.010	2.1
8.0	1.00	0.010	0.010	2.7
0.25	1.00	0.010	0.010	1.58
0.50	1.00	0.010	0.010	1.70
1.00	1.00	0.010	0.010	2.0
2.0	1.00	0.010	0.010	2.7
4.0	1.00	0.010	0.010	3.0
16.0	1.00	0.010	0.010	3.4
8.0	1.00	0.025	0.025	3.0
8.0	1.00	0.050	0.050	3.5
8.0	1.00	0.10	0.100	4.1
8.0[b]	1.00	0.025	0.100	4.4
8.0[c]	1.00	0.200	0.100	4.4
8.0	0[d]	0.050	0.050	2.8

[a] Reactions were carried out at 25 °C; $\mu = 0.40$ ($LiClO_4$); $[Cr^{IV}] = 2.0 \times 10^{-4}$ M. The pH was 4.41 ± 0.03 unless otherwise indicated. [b] pH 4.98. [c] pH 4.19 [d] Reaction was catalyzed by Fe^{III} (1.0×10^{-5} M).

Results and Discussion

Spectrophotometric titration of the diperoxochromium(IV) complex I with ascorbic acid (at 382 nm) indicates that very nearly five molecules of the reductant (H_2A) are consumed by two molecules of the oxidant (Table I). No detectable O_2 is released, and at the end of the reaction no peroxide remains in solution. If, as with earlier ascorbate oxidations,[6,15] the organic product is taken to be dehydroascorbic acid (A),[16] the overall conversion may be represented as (1). Moreover, it is extremely unlikely



A

$$5H_2A + 2(dien)Cr^{IV}(O_2)_2 + 6H^+ \rightarrow 5A + 2(dien)Cr^{III} + 4H_2O \quad (1)$$

that the reduction of peroxide occurs after it leaves the coordination sphere of chromium, for reaction of uncomplexed H_2O_2 with ascorbate proceeds much more slowly than the $Cr^{IV}(O_2)_2$ reaction[17,18] and is not significantly catalyzed by the Cr^{III}(dien) product.

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(11) For estimates of the extinction coefficients of Cr(III) complexes, aliquots of the eluates were oxidized with basic H_2O_2, and the chromium content was determined as CrO_4^{2-}. See, for example: Haupt, G. W. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1952**, *48*, 414.

(12) (a) This determination could not be extended to that fraction eluted with water alone, for this contained unbound ascorbate. It was likewise found to be inapplicable to reaction mixtures in which ascorbate was taken in deficiency, due probably to the presence of peroxidic species. (b) See, for example: Gould, E. S. *J. Am. Chem. Soc.* **1968**, *90*, 1740.

(13) Laurence, G. S.; Ellis, K. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1667.

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

(15) See, for example: (a) Mushran, S. P.; Agrawal, M. C.; Mehrotra, R. M.; Sanehi, R. *J. Chem. Soc., Dalton Trans.* **1974**, 1460. (b) Kustin, K.; Toppen, D. L. *Inorg. Chem.* **1973**, *12*, 1404.

(16) For a critical consideration of the usual triketo structure for dehydroascorbic acid, see: Hvoslef, J. *Acta Crystallogr., Sect. B: Crystallogr. Cryst. Chem.* **1972**, *B28*, 916.

(17) A number of workers have studied the oxidation of ascorbic acid with H_2O_2, as catalyzed by transition-metal species, but there appears to be no general agreement concerning the specific rate of the uncatalyzed reaction, which is usually described as "slow".[18] Our experiments with $[H_2O_2] = 0.002$ M, [ascorbate] = 2×10^{-4} M, and [EDTA] = 0.015 M in acetate buffer indicate an upper limit of $4 \times 10^{-3}\ M^{-1}\ s^{-1}$ (25 °C, $\mu = 0.5$ M) for k_{uncat}.

(18) See, for example: (a) Kremer, M. L. *Trans. Faraday Soc.* **1967**, *63*, 1208. (b) Barteri, M.; Pispisa, B. *Biopolymers* **1982**, *21*, 1093. (c) Travin, S. O.; Travin, O. A.; Purmal, A. P.; Shurlatov, Y. I. *Khim. Fiz.* **1983**, 1247; *Chem. Abstr.* **1983**, *99*, 164617b. (d) Grinsted, R. R. *J. Am. Chem. Soc.* **1960**, *82*, 3464. (e) Shurlatov, Y. *Int. J. Chem. Kinet.* **1980**, *12*, 347.

Table III. Reaction of Fe(III) with Ascorbic Acid (H_2A): Formation and Decay of the Fe(III)–Ascorbate Complex (λ_{max} = 550 nm)[a]

$10^3[H_2A]$, M	k_1, s^{-1} [b]	k_2, s^{-1} [b]	$10^{-3}\epsilon$, M^{-1} cm^{-1} [c]
1.0	0.041	1.42	7.2
2.5	0.095	1.95	6.5
5.0	0.159	2.7	6.8
10.0	0.30	3.8	7.8
20.0	0.63	6.5	7.3

[a] Reactions were carried out at 19 °C; μ = 0.40 M ($LiClO_4$); [HOAc] = [OAc^-] = 0.050 M; pH = 4.37–4.41; [Fe^{III}] = 2×10^{-4} M; optical path length = 2.0 cm. Conversions were monitored at 550 nm. [b] Pseudo-first-order specific rates for formation (k_1) and decay (k_2) of the reaction intermediate (see text and ref 14). [c] Apparent extinction coefficient of the intermediate (see ref 14 and 24).

The low-energy absorption maxima of the Cr(III) products from the Cr(IV)–ascorbate reaction lie at 540–550 nm, i.e., well below those for aquo- and carboxylato-substituted Cr(III) species,[19] mirroring ligation by the N-donor sites of diethylenetriamine.[20] As in earlier work,[4] this ligand, when tridentate, is taken to occupy the 1-, 2-, and 6-positions of the coordination octahedron about Cr(III), with the two ligating NH_2 groups occupying trans positions. This configuration is closely related to the preferred structure (I) of the $Cr^{IV}(O_2)_2$ chelate used in the redox reaction. The observed shoulder at 375 nm, an appendage to a much stronger peak at 270 nm ($\epsilon = 4 \times 10^4$), is diagnostic of conjugation in the ligand sheath and is best ascribed to coordinated ascorbate, in accord with the ascorbate/Cr(III) ratio near unity which was determined analytically. Although the appearance of this shoulder is very similar in the two recovered Cr(III) fractions, that fraction eluted with water should have a net positive charge below that eluted with 1–2 M $NaClO_4$. We then attribute the difference in ion-exchange behavior to the incorporation of acetate in the lower charged (presumably +1) component. The yield of this fraction is seen to be highest at the highest acetate concentration, suggesting a competition between acetate and solvent water for a chromium intermediate.

Kinetic data are summarized in Tables II and III. Reactions are catalyzed by Fe(II), both in the absence of EDTA and in its presence. With EDTA absent (Table II), reactions are first order in Cr^{IV}, are first order in added iron, and exhibit kinetic saturation with respect to ascorbic acid (H_2A). Rates for disappearance of Cr^{IV} (in 0.010 M acetate buffers) conform to eq 2. Nonlinear

$$\text{rate} = [Cr^{IV}][Fe]_{added}\frac{kK[H_2A]}{1 + K[H_2A]} \qquad (2)$$

least-squares refinement of the rate data yields a rate constant, $k = (3.0 \pm 0.1) \times 10^3$ M^{-1} s^{-1}, and an association constant, $K = (3.7 \pm 0.8) \times 10^3$ M^{-1} (25 °C, μ = 0.4 M). From the observed rate of reaction in the absence of added reagent iron, we estimate a dissolved iron concentration of 5×10^{-8} M in our medium.

The ratio of tripositive to dipositive iron in these systems should depend upon the specific rates of two redox processes, the first involving $Cr^{IV}(dien)(O_2)_2$ + Fe(II) and the second involving ascorbate + Fe(III). The Cr(IV)–Fe(II) reaction has been found to proceed in a straightforward bimolecular manner ($k = 4 \times 10^3$ M^{-1} s^{-1} at 25°)[5] but the Fe(III)–ascorbate redox reaction goes through a blue complex (λ_{max} = 550 nm).[13]

Table III summarizes kinetic data for the formation and destruction of the latter complex at 19 °C. The usual ambiguity associated with the assignment of rate constants to components in such biphasic systems[21] is resolved in this case by comparing experiments at various ascorbate concentrations, for the alternate assignment ($k_1 > k_2$) yields ϵ values varying between 200 and 800 M^{-1} cm^{-1} for the complex. The implication here is somewhat surprising—that the specific rate for formation of the complex (entailing ligand substitution at the Fe^{III} center) is much less than that for electron transfer, which destroys the complex.[22] With [ascorbate] in the range 0.001–0.020 M, the formation of the complex is, as expected, first order in ascorbate (bimolecular specific rate 34 ± 4 M^{-1} s^{-1} at 19 °C) whereas its decay conforms to eq 3, where $k_0 = 1.27 \pm 0.08$ s^{-1} and $a = 260 \pm 8$ M^{-1} s^{-1}.[23]

$$-d[\text{complex}]/dt = [\text{complex}](k_0 + a[H_2A]) \qquad (3)$$

Rate law 3 indicates that destruction of the complex occurs by a combination of (unimolecular) internal electron transfer and bimolecular attack by a second unit of ascorbate.[24,25] Despite this complexity, it is clear that the iron in our catalytic systems exists chiefly in the tripositive state after the first few seconds of reaction. Moreover, added Fe(III) is seen to be catalytically equivalent to Fe(II) at the 10^{-5} M level (Table II).

Kinetic saturation with respect to ascorbate, observed here for the iron-catalyzed reaction (eq 2), in conjunction with the recognized predominance of trivalent iron in our systems, suggests the intervention of an Fe(III)–ascorbate complex in the catalytic sequence. However, it is not the complex observed in our Cr(IV)-free experiments, for the latter (blue) species is formed at a specific rate only about 10^{-2} times that for the catalyzed reaction and hence cannot contribute significantly to the overall conversion. We thus have at hand evidence for two ascorbate complexes. The first, formed rapidly, is catalytically active, whereas the second, found to form slowly, is not. We suspect that the catalytically active complex is a monoligated species, whereas the blue transient (the growth of which dominates the stop-flow profiles) is a dichelate.

The apparent association constant of the reactive complex at pH 4.40, when adjusted for the partial conversion of ascorbate to its parent acid,[24] is 5.2×10^3 M^{-1} (μ = 0.40 M). Rate law 2 points to a rate-determining step involving the Cr(IV) oxidant and this Fe(III)–ascorbate complex. In analogy with the known reaction of $Cr^{IV}(dien)(O_2)_2$ with VO^{2+},[4] reduction of the Cr^{IV} center is assumed to precede reduction of peroxide. Since kinetic profiles give no indication that a reaction intermediate accumulates, peroxide reduction may be taken to entail two or more rapid subsequent steps (about which our kinetic data yield no direct information) triggered by electron transfer to chromium. The kinetic picture is consistent with the oxidation of bound ascorbate in single-electron steps, first to the radical $HA^\bullet$ and then (more rapidly) to dehydroascorbate (A).

The proposed sequence may thus be represented schematically by eq 4–8, with reaction 4 contributing only during the first few

$$\begin{gathered} Fe^{II} + Cr^{IV}(O_2)_2 \rightarrow Fe^{III} + Cr^{III}(O_2)_2^- \\ k = 4 \times 10^3 \text{ M}^{-1}\text{ s}^{-1} \end{gathered} \qquad (4)$$

$$Fe^{III} + HA^- \rightleftharpoons Fe^{III}(HA^-) \qquad K = 5 \times 10^3 \text{ M}^{-1} \qquad (5)$$

$$\begin{gathered} Fe^{III}(HA^-) + Cr^{IV}(O_2)_2 \rightarrow Fe^{III} + HA^\bullet + Cr^{III}(O_2)_2^- \\ k = 1.5 \times 10^3 \text{ M}^{-1}\text{ s}^{-1} \end{gathered} \qquad (6)$$

$$HA^\bullet + Cr^{IV}(O_2)_2 \rightarrow A + Cr^{III}(O_2)_2^- + H^+ \quad \text{(rapid)} \qquad (7)$$

$$Cr^{III}(O_2)_2^- + 2H_2A + 4H^+ \rightarrow\rightarrow Cr^{III} + 4H_2O + 2A \quad \text{(rapid)} \qquad (8)$$

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(19) See, for example: (a) Butler, R. D.; Taube, H. *J. Am. Chem. Soc.* **1965**, *87*, 5597. (b) Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 4679.

(20) Garner, C. S.; House, D. A. *Transition Met. Chem.* (*N.Y.*) **1970**, *7*, 59 (Table 12).

(21) See, for example: Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; Chapter 4.

(22) For additional examples of measurably slow substitution reactions at metal centers that are generally considered to be substitution-labile, see, for example: (a) Dash, A. C.; Nanda, R. K. *Inorg. Chem.* **1973**, *12*, 2024 (Al^{III}). (b) Paquette, G.; Zador, M. *Inorg. Chim. Acta* **1978**, *26*, L23 (Zn^{II}). (c) Ram, M. S.; Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 1103 (Ti^{III}).

(23) At ascorbate concentrations above 0.02 M, the kinetic picture becomes less straightforward, possibly reflecting the increased importance of a 3/1 complex, $Fe^{III}(HA^-)_3$. Analogous complications have been reported by Laurence.[13]

(24) The pK_a for ascorbic acid is 4.01 at 25 °C.[25] The apparent extinction coefficient of the ascorbate complex, determined at pH 4.40 (where 71% of the added ascorbic acid exists as the anion, HA^-), may then be converted to the limiting value, 1.0×10^4 M^{-1} cm^{-1}, applying to HA^- at higher pH, by dividing by 0.71.

(25) Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 2684.

Table IV. Kinetic Data or the Reduction of $Cr^{IV}(dien)(O_2)_2$ with Ascorbic Acid (H_2A) As Catalyzed by Dissolved Iron in the Presence of EDTA[a]

$10^4[Cr^{IV}]$, M	$10^3[H_2A]$, M	$10^5[Fe^{II}]$, M	10^3[EDTA],[b] M	rate, M $s^{-1} \times 10^4$ [c]
1.0	0	2.5	1.0	0.3 (0.4)
1.0	1.0	2.5	1.0	0.9 (1.1)
2.0	2.0	2.5	1.0	1.7 (1.7)
2.0	4.0	2.5	1.0	3.2 (2.8)
2.0	8.0	2.5	1.0	4.4 (4.3)
2.0	16.0	2.5	1.0	5.9 (6.2)
2.0	32.0	2.5	1.0	7.2 (7.9)
2.0	8.0	0	1.0	0.9 (0.4)
2.0	8.0	1.0	1.0	2.4 (1.9)
2.0	8.0	5.0	1.0	8.8 (8.3)
2.0	8.0	10.0	1.0	15.2 (16.2)
1.0	8.0	1.0	1.0	2.2 (1.9)
4.0	8.0	1.0	1.0	2.4 (1.9)
2.0	8.0	2.5	0.5	3.6 (4.3)
2.0	8.0	2.5	2.5	4.2 (4.3)

[a] Reactions were carried out at 25 °C; $\mu = 0.40$ M ($LiClO_4$); [HOAc] = $[OAc^-]$ = 0.050 M; pH 4.40. Conversions were monitored at 382 nm. [b] Added as Na_2EDTA. [c] Initial rates, $-d[Cr^{IV}]/dt$, obtained from slopes of nearly linear decay traces early in the reaction (see text). Values in parentheses were calculated by using eq 11 and taking k as 43 s^{-1}, $K = 88$ M^{-1}, and $b = 3.6 \times 10^{-5}$ M s^{-1}.

seconds of the Fe(II)-catalyzed reaction.[26] Note that the specific rate assigned to step 6 is half the rate constant generated from refinement of (2) since the rapid follow-up step, (7), consumes a second unit of Cr(IV).

Addition of the powerful sequestrant EDTA retards the reaction greatly but does not halt it. Moreover, kinetic profiles are markedly altered, for the decay of Cr^{IV} proceeds at a constant speed (independent of $[Cr^{IV}]$) during the major portion of each reaction. Under these conditions, rates conform to eq 11, where

$$\text{rate} = \frac{-d[Cr^{IV}]}{dt} = \frac{kK[H_2A][Fe]}{1 + K[H_2A]} + b \tag{11}$$

$k = 43 \pm 11$ s^{-1}, $K = 88 \pm 37$ M^{-1}, and b = $(3.6 \pm 0.6) \times 10^{-5}$ M s^{-1}. Observed rates are compared to those calculated by (11) in Table IV. The absence of dependence on $[Cr^{IV}]$ indicates that this oxidant is functioning as a scavenger, reacting rapidly with an intermediate that is formed in the reaction of chelated iron with ascorbate.

Since the specific rate at which Fe^{II}(EDTA) is oxidized by $Cr^{IV}(dien)(O_2)_2$ in our media ($\sim 10^5$ M^{-1} s^{-1} at 25 °C)[27] exceeds that at which Fe^{III}(EDTA) is reduced by ascorbate (2.8×10^3 M^{-1} s^{-1}),[28] dissolved iron in the presence of EDTA, as in its absence, exists predominantly in the tripositive state during the major part of the reaction. At low ascorbate concentrations, the reactive intermediate is formed at a rate proportional to both [catalyst] and [ascorbate], but at higher concentrations of the reductant, kinetic saturation is evident, pointing to the formation of a 1/1 complex between catalyst and reductant. This adduct, which is weakly associated ($K_{assn} = 88$ M^{-1} at 25 °C), is of the type proposed by Taqui Khan and Martell,[28] who, however, presented no kinetic evidence for its intervention. The final small term, b in (11), may reasonably be attributed to the slow decomposition of $Cr^{IV}(dien)(O_2)_2$ (by disproportionation)[29] in the absence of ascorbate.

We suggest the sequence (12)–(15) for the iron-catalyzed reduction of Cr(IV) in the presence of excess EDTA. Since the

$$Fe^{III}(EDTA) + HA^- \rightleftharpoons Fe^{III}(EDTA)(HA^-) \qquad K = 88\ M^{-1} \tag{12}$$

$$Fe^{III}(EDTA)(HA^-) \rightarrow Fe^{II}(EDTA) + HA^\bullet \qquad k = 43\ s^{-1} \tag{13}$$

$$HA^\bullet + Cr^{IV}(O_2)_2 \rightarrow Cr^{III}(O_2)_2 + A + H^+ \quad \text{(rapid)} \tag{14}$$

$$Fe^{II}(EDTA) + Cr^{IV}(O_2)_2 \rightarrow Cr^{III}(O_2)_2 + Fe^{III}(EDTA) \quad \text{(rapid)} \tag{15}$$

overall rate of reaction is governed by the generation of the ascorbate radical, $HA^\bullet$, in step 13, we are, in effect, measuring the rate at which this reactive species if formed. At low ascorbate concentrations, the effective bimolecular rate constant for the $Fe^{III}(EDTA)–HA^-$ reaction may then be calculated as $K_{12}k_{13}$ or 3.2×10^3 M^{-1} s^{-1} at $\mu = 0.4$ M, a value which that be compared with 2.8×10^3 ($\mu = 0.1$ M) obtained from the experiments of Taqui Khan[28] in chromium-free systems. Departures from linearity during the final stages of reaction may reflect the falloff of the $[Fe^{III}]/[Fe^{II}]$ ratio as Cr^{IV} becomes nearly depleted. As in the absence of EDTA, kinetic behavior is uninformative as to the rapid reduction of peroxide, which is again presumed to follow reduction of Cr^{IV}.

The incorporation of ascorbate from the reaction mixture into the Cr(III) products is a prominent feature of this system. The reported[5] analogous intrusion of acetate during the Fe(III)-catalyzed reduction of $Cr^{IV}(dien)(O_2)_2$ by hydroxylamine in acetate buffer has been attributed to the intervention, during reduction of bound peroxide, of a $Cr^{III}–O^\bullet$ fragment having the character of a substitution-labile $Cr^{IV}–O$ species. Extension of this rationale to the case at hand (eq 16–19) requires coordination of such a

$$Cr^{III}–OOH + Fe^{III}(HA^-) \rightarrow Cr^{III}–O^\bullet + Fe^{III}(OH) + HA^\bullet \tag{16}$$

$$Cr^{III}–O^\bullet \xrightarrow{H^+} Cr^{IV}(OH) \tag{17}$$

$$Cr^{IV}(OH) + HA^- \xrightarrow{H^+} Cr^{III}(HA^\bullet) + H_2O \tag{18}$$

$$Cr^{III}(HA^\bullet) + HA^- \rightarrow Cr^{III}(HA) + HA^\bullet \tag{19}$$

transient to ascorbate, an act that would surely be accompanied by internal electron transfer (eq 18). Reduction of the resulting Cr(III)-bound ascorbate radical by external ascorbate (eq 19) would then yield the observed Cr(III)–ascorbate product. Electron transfer constituting step 19 should proceed in the direction indicated, for attachment of a tripositive chromium center to the ascorbate radical should make it a more effective oxidant than the unbound radical, $HA^\bullet$.

Note finally that catalysis of the $Cr^{IV}(dien)(O_2)_2$–ascorbate reaction by Cu^{2+} or VO^{2+} is virtually eliminated by addition of EDTA, whereas catalysis by the Fe(II,III) couple survives, although its nature is altered. We have proposed that the iron-catalyzed reaction in the absence of the sequestrant is initiated by the coordination of Fe^{III} to ascorbate, and it is likely that the first step in the presence of EDTA is also an inner-sphere event.

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(26) An alternate catalytic sequence, involving the recycling iron between the 2+ and 3+ states, is in accord with the absence of catalysis when the nonoxidizing metal centers Al(III) and Zn(II) are substituted for Fe(III). Substitution of reaction 9, an act of induced electron transfer,

$$Fe^{III}(HA^-) + Cr^{IV}(O_2)_2 \rightarrow Fe^{II} + A + H^+ + Cr^{III}(O_2)_2^- \tag{9}$$

for steps 6 and 7 yields a sequence that is consistent with rate law 2 at high ascorbate, but not at low. Moreover, such a sequence would require a net specific rate of reduction of Cr(IV) twice that recorded for step 4, contrary to experiment. Substitution of (10) for (7), yielding a

$$Fe^{III} + HA^\bullet \rightarrow Fe^{II} + H^+ + A \quad \text{(rapid)} \tag{10}$$

sequence kinetically equivalent to that which incorporates (9), is open to the same objection. Still another sequence, initiated by the formation of a complex of $Cr^{IV}(O_2)_2$ with nonligated Fe^{III}, which then undergoes attack by ascorbate, is in agreement with rate law 2 but implies an unusually large specific rate (ca. 10^7 M^{-1} s^{-1}) for the electron-transfer step. It is therefore considered less likely.

(27) The measured specific rate, 1.4×10^4 M^{-1} s^{-1} at 19 °C, for the $Fe^{II}(EDTA)–Cr^{IV}(dien)(O_2)_2$ reaction, after adjustment to 25 °C, has been multiplied by 5 since 1 mol of $Cr^{IV}(O_2)_2$ consumes 5 mol of Fe(II).

(28) Taqui Khan, M. M.; Martell, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 2286. The indicated specific rate is 71% of the value calculated by these workers for oxidation of the ascorbate anion by Fe^{III}(EDTA) at high pH.[24]

(29) See, for example: Ranganathan, C. K.; Ramasami, T.; Ramaswami, D.; Santappa, M. *Inorg. Chem.* **1986**, *25*, 915.

The association constant obtained for the Fe^{III}(EDTA)–ascorbate complex is probably too large for an outer-sphere complex between two negatively charged species,[30] and there is considerable evidence that EDTA, although nominally sexadentate, occupies, on coordination with transition-metal ions, only five positions, leaving the sixth bound to donor water,[31] which is easily lost. It appears then that EDTA-bound Fe^{III} is less effective than aquo-bound Fe^{III} in polarizing ligating ascorbate prior to attack by Cr^{IV}(O$_2$)$_2$. When that ordinarily preferred path becomes disfavored, electron transfer from ascorbate to Fe^{III} assumes the catalytic burden (albeit less efficiently). Persistence of a less advantageous route may be linked to a formal potential of Fe(II,III) in the proper range. When Cu^{II}, a much weaker oxidant than Fe^{III}, is sequestered, it is no longer able to oxidize ascorbate effectively. With the V(IV,V) couple, on the other hand, complexation of the more poorly reducing VO^{2+} appears to halt its reduction of Cr^{IV}, a reaction for which an inner-sphere route has been shown to operate.[4]

Acknowledgment. We are grateful to Professors Henry Taube and Rathindra Bose for valuable discussions and to Arla White for technical assistance.

Registry No. EDTA, 60-00-4; Fe, 7439-89-6; Cr^{IV}(dien)(O$_2$)$_2$, 59419-71-5; ascorbic acid, 50-81-7.

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(30) We thank a reviewer for calling our attention to this point.

(31) See, for example: (a) Gerdom, L. E.; Baenziger, N. A.; Goff, H. M. *Inorg. Chem.* **1981**, *20*, 1606. (b) Hoard, J. L.; Kennard, C. H. L.; Smith, G. S. *Inorg. Chem.* **1963**, *2*, 1316.

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Stereoselectivity in the Reduction of [Co(ox)$_3$]$^{3-}$ by [Co(en)$_3$]$^{2+}$ and Its Derivatives

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Received September 14, 1988

The oxidation of cobalt(II) by [Co(ox)$_3$]$^{3-}$ in 1,2-diaminoethane solutions proceeds by both inner-sphere and outer-sphere pathways leading to formation of [Co(en)$_2$(ox)]$^+$ and [Co(en)$_3$]$^{3+}$ with rate constants 3300 and 390 M^{-1} s^{-1}, respectively, at 25.0 °C and 0.10 M ionic strength. When optically active [Co(ox)$_3$]$^{3-}$ is used, both pathways show stereoselectivity. In the inner-sphere pathway, stereoselectivity is small, 1.5% ΔΔ, a consequence of the separation of the reacting centers by the oxalate bridge. In the outer-sphere pathway, stereoselectivity is 9% ΔΛ. The effect on the stereoselectivity of varying the structure of the reductant for the series [Co(sep)]$^{2+}$, [Co(sen)]$^{2+}$, [Co(en)$_3$]$^{2+}$, [Co((±)-bn)$_3$]$^{2+}$, and [Co((±)-chxn)$_3$]$^{2+}$ has been investigated for this pathway. Outer-sphere stereoselectivity has also been examined in the reactions of [Co(mal)$_3$]$^{3-}$ with [Co(en)$_3$]$^{2+}$ and [Co((±)-chxn)$_3$]$^{2+}$. The stereoselectivity data are consistent with a mechanism in which the carboxylate faces of [Co(ox)$_3$]$^{3-}$ or [Co(mal)$_3$]$^{3-}$ are presented to various orientations of the reductants in strong precursor ion pairs and are dependent on the relative importance of hydrogen-bonding and electrostatic interactions between the complexes.

Introduction

Stereoselectivity in the oxidation of [Co(en)$_3$]$^{2+}$ (en = 1,2-diaminoethane) and its derivatives by [Co(edta)]$^-$, [Co(pdta)]$^-$, and [Co(cdta)]$^-$ (edta^{4-} = 1,2-diaminoethane-*N*,*N*,*N*′,*N*′-tetraacetate(4−)) has been investigated in considerable detail.[1-3] A picture of the complex that is the precursor to electron transfer has been deduced in which the pseudo-C_3 carboxylate face of [Co(edta)]$^-$ is strongly hydrogen bonded to amine hydrogens on the reductants. It is of considerable interest to know if other oxidants possessing a C_3 carboxylate face behave similarly, and so studies with [Co(ox)$_3$]$^{3-}$ (ox^{2-} = oxalate(2−)) were initiated with the hope that the higher symmetry of the complex might simplify the interpretation of the stereoselectivity data. Previously, it was noted that chiral discrimination in interactions with tris-bidentate chelates is thought to arise from the different helicities described by the C_2 and C_3 axes.[4,5] For example, in [Δ-Co(ox)$_3$]$^{3-}$, the complex has C_3 axes and C_2 axes of differing helicities, each capable of sustaining hydrogen bonding interactions between carboxylate groups and the amine hydrogen atoms on the reductants. In this example, these can be described as $P(C_3)M(C_2)$ where P indicates a plus or clockwise helical arrangement and M a minus arrangement.

A feature of previous work with [Co(edta)]$^-$ as oxidant was the investigation of the effects of chelate ring conformation in the reductants on the electron-transfer stereoselectivity.[2] Chelate ring conformation in [Co(en)$_3$]$^{3+}$ and its derivatives may be described as *lel* if the C–C bond in the five-membered ring lies parallel to the C_3 axis and *ob* if the C–C bond lies oblique to this axis. Four conformational isomers are possible, *lel*$_3$, *lel*$_2$*ob*, *lel ob*$_2$, and *ob*$_3$, where each of the three chelate rings is designated.[6] Coformational isomers in [Co(en)$_3$]$^{3+}$ are interconvertible by low-energy rotations, but in the complexes [Co((±)-bn)$_3$]$^{3+}$ and [Co((±)-chxn)$_3$]$^{3+}$ ((±)-bn = *rac*-2,3-diaminobutane, (±)-chxn = *rac*-1,2-diaminocyclohexane), they are diastereomers and can be separated readily.[2,7] With [Co(edta)]$^-$ there is a strong trend[2] in stereoselectivity with a preference for ΔΔ interactions for *lel*$_3$ isomers and ΔΛ interactions for *ob*$_3$ isomers, although the trend is markedly solvent dependent.[8]

The oxidant [Co(ox)$_3$]$^{3-}$ is readily resolved.[9,10] It has a reduction potential of 0.57 V[11] (vs NHE) and an electronic self-exchange rate estimated variously as 3 × 10^{-7} [12] or 1.4 × 10^{-12} M^{-1} s^{-1},[13] ideal for stereoselectivity studies since self-exchange racemization is slow. However, the complex is heat and light sensitive and is prone to rapid racemization, even in the solid state.[10,14] The reactions of [Co(ox)$_3$]$^{3-}$ with [Co(en)$_3$]$^{2+}$ and its

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