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Electron Transfer. 98. Copper(II) and Vanadium(IV) Catalysis of the Reduction of Peroxide-Bound Chromium(IV) with Ascorbic Acid[1]

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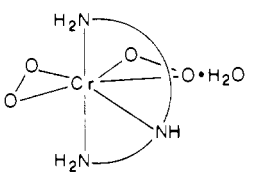
The very slow reduction of the diperoxochromium(IV) derivative of diethylenetriamine, $Cr^{IV}(dien)(O_2)_2$ (chelate I), with ascorbic acid (H_2A) is markedly catalyzed by copper(II), vanadium(IV), and vanadium(V) in acetate buffers. Both the Cr(IV) center and the peroxo ligands are reduced, resulting in a 5:2 ($H_2A:Cr^{IV}$) stoichiometry. Ascorbate and acetate from the reaction medium are incorporated into the Cr(III) products. Reactions are first order in Cr(IV) and exhibit kinetic saturation with respect to ascorbate. Copper-catalyzed reactions are retarded by increased acidity, whereas vanadium-catalyzed reactions are inhibited by added acetate. Rate law 2 for the Cu(II)-catalyzed reaction is consistent with the formation of a Cu(II)–ascorbate complex ($K_{assn} = 3 \times 10^2$ M^{-1}) that undergoes deprotonation ($K_A = 4 \times 10^{-5}$ M) to yield the kinetically active species. The latter reacts with Cr(IV) ($k = 8 \times 10^2$ M^{-1} s^{-1}). Rate law 9 for the V(IV,V)-catalyzed reaction points to intervention of a VO^{2+}–ascorbate complex ($K_{assn} = 4 \times 10^2$ M^{-1}), which reduces Cr(IV) ($k = 1 \times 10^3$ M^{-1} s^{-1}). The predominant oxidation states are Cu(II) in the copper system and V(IV) in the vanadium systems. Comparisons of rates of catalyzed reactions with those of uncatalyzed reductions of Cu(II) and VO_2^+ by ascorbate and reductions of Cr(IV) by Cu(I) and VO^{2+} lead to the conclusion that recycling of catalyst between oxidation states (which occurs in Fe(II,III)–EDTA catalysis) is of importance for neither copper nor vanadium. It is proposed instead that both Cu(II) and VO^{2+} polarize the ascorbate anion through chelation, that the resulting ascorbate complexes suffer 1e oxidation by Cr(IV), yielding the ascorbate radical anion, $A^{\bullet-}$, and that the latter is in turn rapidly oxidized to dehydroascorbate. Subsequent reductions of coordinated peroxide are also taken to be rapid. The inclusion of ascorbate and acetate into the Cr(III) products points to the intermediacy, during reduction of bound peroxide, of a Cr^{III}–$O^{\bullet}$ transient that is rapidly converted to a substitution-labile Cr^{IV}–OH species. Catalysis by neither copper nor vanadium is observed in the presence of excess EDTA. The latter sequestrant is thought to occupy five of the six coordination positions about the metal centers, thus preventing the formation of catalytically active metal–ascorbate chelates.

The unusual oxidation state chromium(IV) is strikingly stabilized through coordination by combinations of peroxo groups and various nitrogenous bases, forming a series of diperoxo derivatives,[2] the most robust of which is the complex of diethylenetriamine (chelate I).[2d,e] The metal-based single electron



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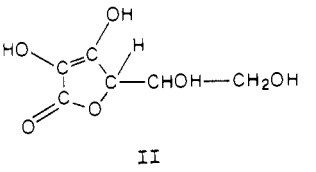

II

donors Ti(III) and Fe(II) rapidly reduce both the Cr(IV) center and the peroxo groups of this chelate,[3,4] whereas vanadium(IV) reduces only Cr(IV).[3] In contrast, a variety of metal-free reductants (mercapto compounds, hydroxylamine, and ascorbic acid) reduce peroxide-bound Cr(IV) very sluggishly, but their reactions are accelerated dramatically by traces of Fe(II), Fe(III), or Cu(II).[4,5]

Results of an earlier study[4] dealing with the oxidation of ascorbic acid (II) to dehydroascorbic acid using $Cr^{IV}(dien)(O_2)_2$ (chelate I) in the presence of dissolved iron suggested the operation of two modes of catalysis. A rapid route, involving Fe(III), is initiated by the formation of a complex from ascorbate and $Fe(III)_{aq}$, whereas a slower sequence, which becomes evident in the presence of a strongly chelating external species, requires recycling of the catalyst between di- and tripositive states and appears to entail a rate-determining generation of an ascorbate radical ($HA^{\bullet}$).

The present investigation deals with catalysis of the $Cr^{IV}(dien)(O_2)_2$–ascorbate reaction using Cu^{2+} and VO^{2+}. The resulting picture is similar to that for the iron-catalyzed system, but there are significant differences in detail.

Table I. Stoichiometry of the Reaction of $Cr^{IV}(dien)(O_2)_2$ with Ascorbic Acid (H_2A), As Catalyzed by Transition-Metal Ions[a]

catalyst	mmol of Cr^{IV}	mmol of H_2A	$\Delta[H_2A]/\Delta[Cr^{IV}]$
Cu^{2+}	0.0020	0.0049	2.5
	0.0040	0.0092	2.3
	0.0060	0.0144	2.4
VO^{2+}	0.0020	0.0049	2.5
	0.0040	0.0101	2.5
	0.0060	0.0155	2.6
Fe^{2+} [b]	0.0060	0.0153	2.6
none[b]	0.0200	0.0510	2.55

[a] Determined by spectrophotometric titration at 382 nm in buffered solutions 0.1 M each in HOAc and Na^+OAc^- (pH = 4.73); metal ion catalysts, when added, were 5×10^{-5} M (see Experimental Section). [b] Reference 4.

Experimental Section

Materials. Diperoxo(diethylenetriamine)chromium(IV) hydrate, $Cr(dien)(O_2)_2 \cdot H_2O$, chelate I, was prepared as described.[2b,e] 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 material exploded 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.

In accord with the reports of House,[2b,c] solutions of this complex in distilled water are stable for at least 12 h at room temperature, whereas solutions in aqueous acetate buffers undergo no measurable decomposition in 60 min.

L-Ascorbic acid (Aldrich 99+%) was used as received, but all solutions were prepared in deionized water that had been previously boiled and purged with N_2 for at least 4 h to remove dissolved O_2; concentrations were checked by iodimetry. Solutions of $VO(ClO_4)_2$ were prepared and standardized by the method of Fanchiang,[6] whereas $Cu(ClO_4)_2$ was prepared by the reaction of $CuCO_3$ (Baker and Adamson) with $HClO_4$. Lithium perchlorate (for kinetic experiments) was prepared by the method of Dockal[7] and was recrystallized twice. Cation-exchange resin (Dowex 50-X2, 400 mesh, H^+ form) was pretreated as described.[8]

Stoichiometric Studies. The stoichiometry of the reaction of ascorbic acid with $Cr^{IV}(dien)(O_2)_2$, as catalyzed by Cu^{2+} and VO^{2+}, was deter-

(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. (d) Stomberg, R. *Ark. Kemi*, **1965**, *24*, 47. (e) House, D. A.; Garner, C. S. *Nature* **1965**, *208*, 776.

(3) Ghosh, S. K.; Laali, K.; Gould, E. S. *Inorg. Chem.* **1988**, *27*, 4224.

(4) Ghosh, S. K.; Gould, E. S. *Inorg. Chem.*, in press.

(5) Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1988**, *27*, 4228.

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

(7) Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.

(8) Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792.

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mined by spectrophotometric titration at 382 nm. To measured quantities of Cr(IV) (0.002–0.006 mmol) in a buffered solution (HOAc–OAc^-) containing known concentrations of catalyst were added successive known quantities of ascorbic acid. Plots of absorbance vs added reductant showed break points at [ascorbate]/[Cr^{IV}] near 2.50 (Table I).

Examination of the Cr(III) Reaction Products. Reaction mixtures (volume of 3 mL) were 0.018–0.025 M in Cr(IV), 0.10–0.13 M in ascorbic acid, and 5×10^{-5} M in Cu(II) or VO^{2+} and were buffered with equimolar concentrations of HOAc and OAc^-. These were subjected to column chromatography on Dowex 50X-2 at 2 °C.[9] As was the case with iron-catalyzed reactions,[4] a portion of the Cr(III) product was eluted by water alone and exhibited an absorption maximum at 548 nm (ϵ = 71 M^{-1} cm^{-1}) and a shoulder near 375 nm (ϵ = 131). A more tightly held fraction, eluted with 0.5 M $NaClO_4$ + 0.1 M $HClO_4$, showed a maximum at 531 nm (ϵ = 75) and a shoulder near 375 nm (ϵ = 128). The fraction eluted with water constituted 45% of the recovered chromium when [OAc^-] was 0.1 M but rose to near 70% when [OAc^-] was 1.0 M. Recovery of total chromium was 90–93%, with the loss due pricipally to column-catalyzed polymerization.[10]

Kinetic Measurements. Rates were estimated from absorbance changes at 382 nm, observed on a Cary 14 or Beckman 5260 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 97% completion. All 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. Specific rates from replicate runs agreed to better than 8%.

In contrast to the results with Cu^{2+}, VO^{2+}, and (earlier)[4] with Fe^{2+}, the $Cr^{IV}(dien)(O_2)_2$–ascorbate reaction was not catalyzed significantly by Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $IrCl_6^{3-}$, $Co(en)_3^{3+}$, Eu^{3+}, or $Ru(NH_3)_6^{3+}$ (each at the 10^{-4} M level). Catalysis by both Cu^{2+} and VO^{2+} was strongly inhibited by addition of excess EDTA.

Five additional reactions related to the catalytic systems of interest were examined briefly. The reaction of vanadium(V) (from dissolved NH_4VO_3) with excess ascorbic acid in acetate buffer was found to be rapid and first order in both redox components. Stop-flow measurements at 360 nm yielded a bimolecular rate constant (1.0 ± 0.1) $\times 10^2$ M^{-1} s^{-1} (pH 4.4, 24 °C),[11] whereas the reaction of $Cr^{IV}(dien)(O_2)_2$ with Cu^I exhibited a bimolecular specific rate near 60 M^{-1} s^{-1} (pH 4.4, 25 °C).[12] The reduction of Cu(II) by ascorbic acid in aqueous $LiClO_4$ was sluggish. At pH 2.5, with ascorbic acid in excess at 0.10 M, less than 15% of the added Cu(II) was reduced in 1900 s, corresponding to a bimolecular rate constant below 8×10^{-4} M^{-1} s^{-1}. Oxidations of ascorbate by H_2O_2, as catalyzed by Cu^{2+} or VO^{2+} in acetate buffers (in the absence of chromium), generally featured nonexponential decay curves and less-than-unit orders in peroxide, ascorbate, and metal catalyst. Although detailed rate laws were not obtained, consumption of ascorbate was found to be as much as 10^2 times as rapid as occurs in the presence of an equivalent concentration of $Cr^{IV}(dien)(O_2)_2$ under analogous conditions.

Results and Discussion

Our spectrophotometric titrations of $Cr^{IV}(dien)(O_2)_2$ (I) with ascorbic acid at 382 nm (Table I) indicate the consumption of nearly five molecules of the reductant (H_2A) by two molecules of the oxidant. As with reported ascorbate oxidations,[11,13] the organic product is taken to be dehydroascorbic acid (A), and we thus summarize the overall conversion as (1) in obvious analogy to the iron-catalyzed systems described previously.[4]

$$5H_2A + 2Cr^{IV}(dien)(O_2)_2 + 6H^+ \rightarrow 2(dien)Cr^{III} + 5A + 8H_2O \quad (1)$$

Although the reaction of ascorbate with uncomplexed H_2O_2 is known to be much slower than its oxidation by peroxochromium(IV) species,[4,14] this reaction has likewise been found to be catalyzed strongly by both Cu^{2+} and VO^{2+}, and H_2O_2, if present in our systems, may compete effectively with bound peroxide for ascorbate. Neither our kinetic experiments nor our stoichiometric determinations tell us whether the peroxo groups from $Cr^{IV}(O_2)_2$ are reduced while bound to chromium or whether they are first liberated as H_2O_2. However, two considerations lead us to suspect that peroxide is reduced mainly as a Cr(III)-bound species. The first is the recognized substitution-inert character of Cr(III) complexes, which implies that aquation of a peroxochromium(III) complex will be much slower than the primary redox reaction under consideration. In addition, the extensive incorporation of anionic ligands from the reaction medium into the observed Cr(III) products is best rationalized in terms of a $Cr^{III}(OOH)$ intermediate (vide infra).

The predominant Cr(III) products from the reactions catalyzed by Cu^{2+} and VO^{2+} correspond closely to those obtained from reactions catalyzed by Fe^{2+}. The positions of the low-energy maxima (531 and 548 nm) point to coordination by the nitrogen atoms of diethylenetriamine,[3,6,15] whereas the shoulder at 375 nm is diagnostic of incorporation of ascorbate as well. The properties of the water-eluted fraction and its increased yield at higher acetate concentrations are indicative of ligation by acetate, as well as by ascorbate, in this species.

Kinetic data for the Cu^{2+}-catalyzed reaction appear in Table II. Rates are seen to be proportional to the concentration of Cu(II) and to rise with increases in pH and in [ascorbate] with the latter two dependencies subject to kinetic saturation. Since the pK_A of ascorbic acid in this medium (4.01)[16] lies close to the

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

$10^4[Cr^{IV}]$, M	$10^3[H_2A]$, M	$10^5[Cu^{II}]$, M	$10^5[H^+]$, M	10^3k,[b] s^{-1}
2.0	8.0	0.25	3.8	1.00 (0.80)
2.0	8.0	0.50	4.2	1.62 (1.49)
2.0	8.0	1.00	3.9	3.1 (3.1)
2.0	8.0	2.5	4.1	9.2 (7.6)
2.0	8.0	5.0	3.9	16.9 (15.7)
4.0	8.0	7.5	3.8	31 (24)
4.0	8.0	10.0	3.8	38 (31)
2.0	4.0	0	3.8	0.08 (0)
2.0	4.0	1.0	3.8	0.05[c]
1.0	8.0	5.0	3.7	14.8 (16.3)
4.0	8.0	5.0	4.2	14.5 (14.9)
8.0	8.0	5.0	4.2	15.0 (14.9)
1.0	1.0	5.0	3.9	5.4 (5.6)
2.0	2.0	5.0	3.9	7.8 (8.9)
2.0	4.0	5.0	3.9	11.7 (12.3)
2.0	8.0	5.0	4.0[d]	16.3 (15.7)
2.0	8.0	5.0	4.0[e]	14.7 (15.2)
2.0	16.0	5.0	4.2	22 (17)
2.0	24.0	5.0	4.2	23 (19)
2.0	8.0	5.0	0.55	30 (34)
2.0	8.0	5.0	0.98	25 (30)
2.0	8.0	5.0	1.82	18.2 (24.2)

[a] Reactions at 25 °C in HOAc–OAc^- buffers; [HOAc] = 0.025–0.20 M; [OAc^-] = 0.20–0.025 M; μ = 0.40 M ($LiClO_4$). [b] Parenthetical values calculated by using eq 2 and parameters listed in the Text [c] [HOAc] = [OAc^-] = 0.20 M.

(9) For estimates of the extinction coefficients of the Cr(III) products, 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.
(10) See, for example: Gould, E. S. *J. Am. Chem. Soc.* **1968**, *90*, 1740.
(11) For an earlier study of this reaction in strongly acid media, see: Kustin, K.; Toppen, D. L. *Inorg. Chem.* **1973**, *12*, 1304.
(12) For this determination, Cu(I) was generated by addition of a deficiency (0.002 M) of ascorbate to Cu(II) (0.004 M) in aqueous NaCl. The use of this chloride medium greatly accelerates the Cu(II)–ascorbate reaction and minimizes complications due to precipitation of Cu_2O. An attempt was made to examine the corresponding reaction in the absence of chloride, generating Cu(I) from the reduction of Cu(II) with a deficiency of Cr(II)[7] at pH 2.6. The Cr(IV)–Cu(I) reaction appeared to be much slower in perchlorate media ($k \sim 1$ M^{-1} s^{-1}), and interpretation was clouded by the competing disproportionation of the Cr(IV) complex in this acidic solution.
(13) See, for example: (a) Mushran, S. P.; Agrawal, M. C.; Mehrotra, R. M.; Sanehi, R. *J. Chem. Soc., Dalton Trans.* **1974**, 1460. (b) Pelizzeti, E.; Mentasti, E.; Pramauro, E. *Inorg. Chem.* **1976**, *15*, 2898. (c) Akhtar, M. J.; Haim, A. *Inorg. Chem.* **1988**, *27*, 1608. (d) Lannon, A. M.; Lappin, A. G.; Segal, M. G. *J. Chem. Soc., Dalton Trans.* **1986**, 619.
(14) See, for example: (a) Barteri, M.; Pispisa, B. *Biopolymers* **1982**, *21*, 1093. (b) Skurlatov, Y. *Int. J. Chem. Kinet.* **1980**, *XII*, 347.
(15) Garner, C. S.; House, D. A. *Transition Met. Chem.* (*N.Y.*) **1970**, *7*, 59 (Table 12).

acidity range examined, partial dissociation of the reductant must be taken into account. Saturation with respect to ascorbate indicates formation of a complex of ascorbate with copper. Moreover, the observed rate increases near pH 5 are too steep to be attributed solely to ionization of ascorbic acid. Our observations support an additional deprotonation equilibrium, presumably involving the copper–ascorbate complex. Rates are correlated by eq 2, in which $[Cu]_T$ and $[H_2A]_T$ are the total added

$$\text{rate} = \frac{k[Cr^{IV}][Cu]_T[H_2A]_T K_A K_L K_A'}{(K_A' + [H^+])(K_L K_A [H_2A]_T) + [H^+]([H^+] + K_A)} \quad (2)$$

concentrations of copper and ascorbic acid, K_A is the acidity constant of ascorbic acid, K_L is the association constant of the ascorbate complex, and K_A' is the acidity constant of this complex. This relationship is consistent with a mechanism involving interaction of Cr(IV) with the deprotonated form of the complex. Nonlinear least-squares refinement of rate data in terms of (2) yields[17] a rate constant $k = (8.3 \pm 0.7) \times 10^2$ M^{-1} s^{-1} and equilibrium constants $K_L = (2.6 \pm 0.7) \times 10^2$ M^{-1} and $K_A' = 4 \times 10^{-5}$ M.[18,19] Table II also compares observed rates with those calculated by eq 2.

Dissolved copper in these solutions exists predominantly in the dipositive state since the oxidation of Cu(I) by our Cr(IV) complex ($k = 60$ M^{-1} s^{-1}) is much more rapid than the reduction of Cu(II) by ascorbate ($k < 0.03$ M^{-1} s^{-1} in aqueous perchlorate).[20]

The catalytically active species in this reaction may thus be formulated as a Cu(II)–ascorbate complex from which an additional proton has been removed (presumably from a Cu(II)-bound water). As with the known reaction of $Cr^{IV}(dien)(O_2)_2$ with VO^{2+},[3] reduction of the Cr(IV) center is taken to precede reduction of peroxide. Since there is no evidence of the buildup of a reaction intermediate, peroxide reduction may be assumed to involve rapid subsequent steps about which rate data are uninformative.[21]

Rate law 2 brings to mind a related (although somewhat simpler) kinetic pattern observed for the Cr(IV)–ascorbate reaction as catalyzed by dissolved iron in the absence of powerfully chelating species.[4] Although the catalytic sequence operating in the presence of excess EDTA almost certainly features the recycling of iron between the 2+ and 3+ states, catalysis by nonsequestered iron appears to involve only Fe(III). In the case of catalysis by copper, it is again most unlikely that recycling between states plays a significant role, for both the Cr(IV)–Cu(I) reaction in our medium ($k \sim 1$ M^{-1} s^{-1}) and the reduction of Cu(II) by ascorbate ($k < 10^{-3}$ M^{-1} s^{-1}) are much slower than the primary reaction.

We suggest a sequence, in accord with eq 2, initiated by the single electron oxidation of the deprotonated form of Cu(II)-bound ascorbate, $Cu^{II}(HA^-)(OH^-)$, to the radical anion, $HA^{\bullet -}$, which then undergoes further (rapid) oxidation to dehydroascorbate (A). This mechanism is then summarized as eq 3–8.

$$H_2A \rightleftharpoons H^+ + HA^- \qquad K_A = 9.8 \times 10^{-5} \text{ M} \quad (3)$$

$$Cu^{2+}_{aq} + HA^- \rightleftharpoons Cu^{II}(HA^-) \qquad K_L = 3 \times 10^2 \text{ M}^{-1} \quad (4)$$

$$Cu^{II}(HA^-) + H_2O \rightleftharpoons Cu^{II}(HA^-)(OH^-) + H^+ \qquad K_A' = 4 \times 10^{-5} \text{ M} \quad (5)$$

$$Cu^{II}(HA^-)(OH^-) + Cr^{IV}(O_2)_2 \rightarrow Cu^{II} + A^{\bullet -} + Cr^{III}(O_2)_2^- + H_2O \qquad k = 8 \times 10^2 \text{ M}^{-1} \text{ s}^{-1} \quad (6)$$

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

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

An analogous picture appears to apply to the vanadium-catalyzed reaction, for which added V(IV) and V(V) have been found to be equally effective. In this instance, reduction of the pentapositive state by ascorbate ($k = 1.0 \times 10^2$ M^{-1} s^{-1} at pH 4.4) is much more rapid than oxidation of VO^{2+} by Cr(IV) ($k \sim 1$ M^{-1} s^{-1} under similar conditions).[3] Hence, the tetrapositive state predominates in our media.[22,23]

Rate data for vanadium catalysis are assembled in Table III. Kinetic saturation with respect to ascorbate is again evident, and some inhibition by added acetate is perceptible. Variation in rates follows eq 9, in which K_L and K_{Ac} are the association constants

$$\text{rate} = \frac{k[Cr^{IV}][V]_T[H_2A]_T K_A K_L}{K_L K_A [H_2A]_T + (1 + K_{Ac}[Ac^-])([H^+] + K_A)} \quad (9)$$

of complexes of V(IV) with ascorbate and acetate and the remaining symbols correspond to those used in (2). This rate law is in accord with a reaction of Cr(IV) with a 1:1 vanadium–ascorbate complex, the formation of which is subject to modest

Table III. Kinetic Data for Reduction of $Cr^{IV}(dien)(O_2)_2$ with Ascorbic Acid (H_2A) As Catalyzed by Vanadium(IV/V)[a]

$10^3[H_2A]$, M	$10^5[cat]$, M	$10^5[H^+]$, M	$[OAc^-]$, M	10^3k,[b] s^{-1}
4.0	0.50[c]	3.9	0.010	2.8 (2.4)
4.0	1.00[c]	3.7	0.010	5.4 (4.9)
4.0	2.5[c]	4.1	0.010	12.8 (12.1)
4.0	5.0[c]	3.8	0.010	26 (24)
4.0	7.5[c]	4.1	0.010	39 (36)
4.0	10.0[c]	4.0	0.010	51[e] (49)
4.0	0	3.9	0.010	0.08 (0)
4.0	1.0[c]	4.0	0.010	0.06[f]
4.0	10.0[c]	4.0	0.010	46[e] (49)
4.0	10.0[c]	3.9	0.025	39[e] (46)
4.0	10.0[c]	3.7	0.050	33[e] (42)
4.0	10.0[c]	4.1	0.100	29[e] (35)
4.0	10.0[c]	4.2	0.20	23[e] (27)
1.0	5.0[d]	4.2	0.0050	7.8 (7.6)
2.0	5.0[d]	3.7	0.050	14.1 (13.2)
4.0	5.0[d]	4.1	0.050	23 (21)
8.0	5.0[d]	3.8	0.050	30 (29)
16.0	5.0[d]	4.1	0.050	37 (37)
4.0	1.00[c]	1.4	0.20	38 (31)
4.0	1.00[c]	7.8	0.20	23 (23)
4.0	1.00[c]	15.1	0.20	17.8 (17.1)

[a] Reactions at 25 °C in HOAc–OAc^- buffers; $\mu = 0.40$ M ($LiClO_4$); $[Cr^{IV}] = 2.0 \times 10^{-4}$ M unless otherwise indicated. [b] Values in parentheses calculated by using eq 9 and taking $k = 981$ M^{-1} s^{-1}, $K_{Lig} = 375$ cm^{-1}, $K_{Ac} = 9.0$ M^{-1}, and $K_A = 1 \times 10^{-4}$ M. [c] $VO(ClO_4)_2$. [d] NH_4VO_3. [e] $[Cr^{IV}] = 4.0 \times 10^{-4}$. [f] [EDTA] = 0.0010 M

(16) Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 2684.
(17) In this case data were too few and of insufficient precision to allow refinement of all four parameters in a single stage. Instead, K_A was held at the recorded[16] experimental value, 9.8×10^{-5} M, K_A' was initially set at 10^{-5} M, and k and K_L were allowed to vary. The resulting refined values of k and K_L were then kept fixed, and K_A' was allowed to float. Finally, the resulting value of K_A' was held constant, and k and K_L were refined once more. This tactic was unnecessary for treatment of the data pertaining to catalysis by vanadium, which underwent refinement without complication.
(18) The calculated value for log K_L (2.41), pertaining to the stability constant for the Cu(II)–ascorbate complex, differs from an earlier value (1.57; 0 °C, $\mu = 0.1$ M) obtained potentiometrically, but reported without supporting data.[19]
(19) Sillen, L. G.; Martell, A. E. *Stability Constants of Metal-Ion Complexes*; Special Publication 17; The Chemical Society: London, 1964; p 477.
(20) The indicated figure was calculated by multiplying the upper limit recorded for this rate at pH 2.5 by 30 since only $^1/_{30}$th of the added ascorbic acid is present as its monoanion at that pH. Note that the Cu(II)–ascorbate reaction in perchlorate medium is slower (by a factor of at least 10^5) than that in aqueous chloride, for which a specific rate near 3×10^3 M^{-1} s^{-1} has been reported: Martinez, P.; Zuluaga, J.; Dieiro, C. *Z. Phys. Chem. (Leipzig)* **1984**, *265*, 1225.
(21) The activation of Cr(III)-bound peroxide has been described: Adams, A. C.; Crook, J. R.; Bockhoff, F.; King, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 5761.
(22) The low formal potential for V(III,IV) (0.361 V)[23a] allows us to disregard reduction of VO^{2+} to V(III) by ascorbate ($E^\circ = 0.412$ V)[23b] in these systems.
(23) (a) Jones, G.; Colvin, J. H. *J. Am. Chem. Soc.* **1944**, *66*, 1563. (b) Clark, W. M. *Oxidation-Reduction Potentials of Organic Systems*; Williams and Wilkins: Baltimore, MD, 1960; p 469.

inhibition by acetate. Refinement of catalytic data[16] in terms of (9) yields a rate constant $k = (9.8 \pm 1.8) \times 10^2\ M^{-1}\ s^{-1}$ and equilibrium constants $K_L = (3.7 \pm 1.3) \times 10^2\ M^{-1}$ and $K_{Ac} = 9 \pm 3\ M^{-1}$.

As with catalysis by Cu(II), the low specific rate for the direct oxidation of VO^{2+} by Cr(IV) rules out a recycling between V(IV) and V(V) in the catalytic process. The preferred sequence for vanadium catalysis then differs from that for Cu(II) in the initial steps (10)–(13). Rapid oxidation of the radical anion $A^{\bullet-}$ (eq 7) and reduction of Cr(III)-bound peroxide (eq 8) are taken to be common to the two catalytic systems. Note that both the specific rate, k_{13}, and the ligation constant, K_L, lie close to the corresponding values for the Cu(II)-catalyzed reaction, whereas the derived association constant for the vanadium(IV)–acetate complex is, as expected, somewhat less than that recorded for the analogous formato complex (95 M^{-1} at 18 °C).[24]

$$2VO_2^+ + H_2A + 2H^+ \rightarrow 2VO^{2+} + A + 2H_2O \qquad k = 1.0 \times 10^2\ M^{-1}\ s^{-1} \tag{10}$$

$$VO^{2+} + HA^- \rightleftharpoons VO^{2+}(HA^-) \qquad K_L = 4 \times 10^2\ M^{-1} \tag{11}$$

$$VO^{2+} + OAc^- \rightleftharpoons VO(OAc)^+ \qquad K_{Ac} = 9\ M^{-1}\ \text{(inhibition)} \tag{12}$$

$$VO^{2+}(HA^-) + Cr^{IV}(O_2)_2 \rightarrow VO^{2+} + A^{\bullet-} + Cr^{III}(O_2)_2^- + H^+ \qquad k = 9.8 \times 10^2\ M^{-1}\ s^{-1} \tag{13}$$

As is the case with iron catalysis,[4] ascorbate from the reaction medium is found to make its way into the coordination sphere of Cr(III) in the reaction products. This anion intrusion, which occurs after the original Cr(IV) chelate has been consumed but before all redox processes are complete, has been attributed[3,4] to the intercession, during reduction of bound peroxide, of a Cr^{III}–$O^{\bullet}$ transient having the character of substitution-labile Cr^{IV}–O^-. Because the predominant metal centers in the catalytic systems at hand are poorly reducing, we suspect that generation of this intermediate entails reduction by free or bound ascorbate (eq 14).

$$Cr^{III}\text{–}OOH + M(HA^-) \rightarrow Cr^{III}\text{–}O^{\bullet} + M(OH) + A^{\bullet} \tag{14}$$

$$Cr^{III}\text{–}O^{\bullet} + H^+ \rightarrow Cr^{IV}(OH) \tag{15}$$

$$Cr^{IV}(OH) + HA^- \xrightarrow{H^+} Cr^{III}(HA^{\bullet}) + H_2O \tag{16}$$

$$Cr^{III}(HA^{\bullet}) + HA^- \rightarrow Cr^{III}(HA) + HA^{\bullet} \tag{17}$$

$$Cr^{III}\text{–}OOH + HA^{\bullet} \rightarrow Cr^{III}\text{–}O^{\bullet} + H_2O + A \tag{18}$$

Coordination of this fragment to a second unit of ascorbate would be accompanied by internal electron transfer, yielding a Cr(III)-bound ascorbate radical (eq 16). The latter may then undergo reduction by still another (external) ascorbate (eq 17).

A key point of divergence between the systems at hand and catalysis of the Cr(IV)–ascorbate reaction by Fe(II,III)[4] is that the action of Cu^{2+} and VO^{2+} disappears on addition of the sequestrant EDTA, whereas catalysis by iron persists, although its kinetic nature is altered. This contrast may be interpreted in view of the evidence that EDTA, although potentially sexadentate, occupies, on coordination with the usual octahedral metal centers, only five positions, leaving the sixth bound to donor water.[25] In iron systems, ligation by EDTA, although lowering the 2+/3+ formal potential,[26] leaves open a path for the inner-sphere oxidation of ascorbate,[27,28] since this anion can rapidly replace Fe(III)-bound water. Both Cu(II) and VO^{2+} are presumed to operate, at least in part, by polarization of ascorbate, and this is probably favored by chelation, an act that cannot proceed if only a single labile position remains at the metal center. An alternate path for copper catalysis, entailing oxidation by Cu(II), cannot function in the presence of EDTA, since the weakly positive $Cu^{+/2+}$ potential (0.16 V) is further lowered to about −0.90 V by formation of the Cu^{II}(EDTA) complex ($K_{assn} = 10^{18}\ M^{-1}$).[24] In the case of VO^{2+}, which appears to reduce Cr(IV) by an inner-sphere route,[3] electron-transfer processes do not survive treatment with EDTA, for chelation by this ligand (K_{assn}) = $10^{19}\ M^{-1}$ for VO^{2+}) blocks off five available coordination positions, leaving only the substitution-inert "oxo" function.[29]

Finally, it may be asked why other substitution-labile transition-metal centers, among them Mn^{2+}, Co^{2+}, and Ni^{2+}, are devoid of catalytic activity in the reaction at hand, for each of these should, in principle, polarize coordinated ascorbate about as effectively as does Cu^{2+} or VO^{2+}. Although the ascorbate complexes of these inactive ions are less strongly associated than that of Cu^{2+},[24] the differences are not great (approximately 1 pK unit), suggesting the operation of an additional factor. We suspect that peroxide–catalyst interaction may be playing a part. It is recognized that both vanadium(IV)[30] and copper(II)[31] readily form peroxo-coordinated adducts, and the reduction of $Cr^{IV}(dien)(O_2)_2$ with Ti(III)[3] has been found to proceed through a transient having properties expected for a peroxo-bridged precursor complex. It thus appears that peroxo-bridged intermediates cannot be ruled out in the present catalytic systems, although their concentrations would undoubtedly fall below detectable limits.

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(24) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1974, 1977: Vol. 1, pp 206, 207 (EDTA complexes); Vol. 3, p 1 (formato complexes); Vol. 3, p 265 (ascorbato complexes). We find no reported value for the stability constant of the weakly associated VO^{2+}–acetate complex.

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

(26) Reported[24] association constants for the EDTA complexes of Fe(III) ($1 \times 10^{25}\ M^{-1}$) and Fe(II) (5×10^{14}), in conjunction with $E°$ for $Fe^{2+/3+}$ (0.77 V), allow us to estimate a Fe(II,III) potential of 0.11 V in the presence of excess EDTA.

(27) Note that $Ru(NH_3)_6^{3+}$, which has a formal potential (0.051 V)[28] near that for Fe(III) in EDTA but which must be reduced by an outer-sphere route, is catalytically inactive toward the Cr(IV)–ascorbate reaction.

(28) Lim, H. S.; Barclay, D. J.; Anson, F. C. *Inorg. Chem.* **1972**, *11*, 1460.

(29) See, for example: Wuthrich, K.; Connick, R. E. *Inorg. Chem.* **1968**, *7*, 1377.

(30) (a) Symons, M. C. R. *J. Chem. Soc. A* **1970**, 1889. (b) Su, C.-C.; Reed, J. W.; Gould, E. S. *Inorg. Chem.* **1973**, *12*, 337.

(31) See, for example: Tyeklar, A.; Paul, P. P.; Jacobson, R. R.; Farooq, A.; Karlin, K. D.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 388.