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# Electron Transfer. 85. Reduction of Chromium(V) with Ascorbic Acid[1]

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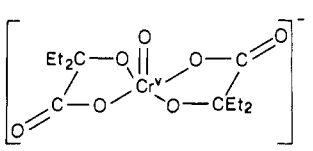
Ascorbic acid ($H_2A$) is very rapidly oxidized by the chromium(V) chelate bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) in solutions buffered by the ligand acid, 2-ethyl-2-hydroxybutanoic acid, and its anion. Equimolar quantities of the two redox reagents are consumed, corresponding to the formation of dehydroascorbic acid and Cr(III). As in the reductions of $I^-$ and $HSO_3^-$ examined previously, the reaction proceeds through Cr(IV), which accumulates gradually but disappears quickly after Cr(V) is gone. The overall reaction is catalyzed by Cr(IV) and passes through the ascorbate radical ($HA^•$), for which Cr(IV) and Cr(V) complete. The proposed reaction sequence (eq 2–5 in the text), in conjunction with rate constants for the component steps obtained by least-squares refinement of the stop-flow kinetic data, reproduces the observed rate profiles. The 1e oxidations of ascorbic acid by both Cr(IV) and Cr(V) are strongly inhibited by $H^+$, indicating that the conjugate base of ascorbic acid, $HA^-$, is a more powerful reductant than its acidic form. The reaction step involving Cr(V) and $HA^-$ is subject to kinetic saturation, pointing to formation of a Cr(V)–$HA^-$ complex having an association constant of 110 $M^{-1}$ and a limiting specific rate of $1.9 \times 10^3$ $s^{-1}$ (24 °C, $\mu$ = 0.4 M) for electron transfer. Properties of the Cr(III) products are those of chelates derived from the ligand anion, $Lig^-$—the first a unipositive bis chelate of $(H_2O)_2Cr^{III}$ and the second an uncharged bis chelate of $(H_2O)(Lig)Cr^{III}$. Preservation of the rings present in the Cr(V) reactant indicates that chelation persists during all steps involving Cr(V) and Cr(IV). Comparison of specific rates with those for known outer-sphere transformation leads to the conclusion that at least three of the four individual steps in the suggested sequence proceed through inner-sphere activated complexes. It is proposed that the observed autocatalysis requires that the radical intermediate, $HA^•$, exist in an uncomplexed state after it is formed but before it is destroyed.

The reductions of carboxyl-bound derivatives of Cr(V)[3] to Cr(III) using 1e reagents must, in principle, pass through Cr(IV). This atypical state reacts with some reductants (e.g., $TiOH^{2+}$ and $IrCl_6^{3-}$)[4,5] much more rapidly than does the Cr(V) complex from which it is formed, and its intervention is consequently not detected. In other instances (reductions with Fe(II) and $VO^{2+}$)[6,7] reactions with Cr(V) and Cr(IV) are more nearly competitive, and it has been possible to estimate rates for both the formation of Cr(IV) and its subsequent reduction.

More complicated kinetic behavior may arise when reductants that undergo both 1e and 2e oxidations are taken, for in such cases four different acts of single electron transfer may occur. Suitable interplay of competing rate processes can then lead to autocatalysis, as has been observed for reductions by $H_3PO_2$ (which passes through a $P^{II}$ intermediate),[8] by $HSO_3^-$ (which passes through $S^{V}$),[9] and by iodide (in which $I^•$ is implicated).[10] Moreover, in the latter two systems the gradual growth and sudden decay of Cr(IV) have been shown to generate a clocklike pattern.

The reductions of Cr(V) by a variety of organic compounds have been described by a number of workers,[11] but no worker appears to have observed a Cr(IV) intermediate or reported substantial autocatalysis. The present extension deals with the reduction of the bischelated $Cr^{V}O$ derivative of 2-ethyl-2-hydroxybutyric acid (I) with ascorbic acid (II). The latter reagent was chosen in view of its recognized capacity to enter into both one- and two-electron transactions,[12] leading us to anticipate that



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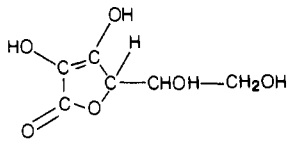

II

it might exhibit kinetic characteristics related to those of the simpler "ambifunctional" inorganic reductants previously examined. This was found to be the case, although differences in detail were noted, reflecting an unusually high activity of this reductant and the occurrence of kinetic saturation in a key reaction step.

## Experimental Section

**Materials.** Sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (the sodium salt of I) was prepared[3a] and purified[7] as described. Lithium perchlorate, used in kinetic experiments, was prepared by the procedure of Dockal[13] and was recrystallized twice before use. 2-Hydroxy-2-ethylbutanoic acid (the "ligand acid") and L-ascorbic acid (Aldrich) were used as received, but all solutions of the latter were prepared in distilled water that had been previously boiled and purged with $N_2$ for at least 4 h (to remove $O_2$). Such solutions were used within 1 h after preparation. Cation-exchange resin (Bio-Rad 50W-X2; 200–400 mesh) was treated before use as described.[14]

**Stoichiometric Studies.** The stoichiometry of the Cr(V)–ascorbic acid reaction was determined by spectrophotometric titration at 510 nm. To measured quantities of Cr(V) (0.003–0.007 mmol), in a solution buffered with equivalent quantities of the ligand acid and its sodium salt, were added small known portions of ascorbic acid solution. Optical densities were recorded immediately after each addition. Plots of absorbance vs. added reductant showed sharp break points as [ascorbic acid]/[$Cr^{V}$] = 1.04 ± 0.04.

**Examination of the Cr(III) Reaction Products.** Reaction mixtures (volume 2.5 mL) were 0.056 M in Cr(V) and were buffered by equal concentrations (0.3 M) of 2-ethyl-2-hydroxybutyric acid and its sodium salt. These were treated with excess ascorbic acid, and the resulting mixture was subjected to cation-exchange chromatography at 3 °C.[15] The major fraction was eluted with distilled water and exhibited absorption maxima at 588 ($\epsilon$ = 55) and 414 nm ($\epsilon$ = 70 $M^{-1}$ $cm^{-1}$); this fraction constituted 70% of the chromium taken when the buffering

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(3) (a) Krumpolc, M.; Roček, *J. Am. Chem. Soc.* **1979**, *101*, 3206. (b) Gould, E. S. *Acc. Chem. Res.* **1986**, *198* 66.
(4) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2645.
(5) Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3357.
(6) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2832.
(7) Fanchiang, Y.-T.; Bose, R. N.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 4679.
(8) Ghosh, S. K.; Bose, R. N.; Laali, K.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 4737.
(9) Bose, R. N.; Rajasekar, N.; Thompson, D. M.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3349.
(10) Ghosh, S. K.; Bose, R. N.; Gould, E. E. *Inorg. Chem.* **1987**, *26*, 899.
(11) (a) Krumpolc, M.; Roček, J. *Inorg. Chem.* **1985**, *24*, 617. (b) Samsel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606. (c) Groves, J. T.; Kruper, W. J., Jr. *Isr. J. Chem.* **1985**, *25*, 148. (d) Haight, G. P.; Jursich, G. M.; Kelso, M. T.; Merrill, P. J. *Inorg. Chem.* **1985**, *24*, 2740.
(12) See, for example: (a) Lannon, A. M.; Lappin, A. G.; Segal, M. G. *J. Chem. Soc., Dalton Trans.* **1986**, 619. (b) Pelizzetti, E.; Mentasti, E.; Pramauro, E. *Inorg. Chem.* **1976**, *15*, 2898; **1978**, *17*, 1181.
(13) Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *93*, 5661.
(14) Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792.
(15) Separations were carried out with use of Bio-Rad 50W-X2 sulfonate resin, $H^+$ form, 200–300 mesh, column length 5 cm, capacity 2.0 meq. For estimates of extinction coefficients of Cr(III) complexes, aliquots 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. Spectra of our Cr(III) products were taken at pH 3.3; these exhibited some variation with acidity, due presumably to partial deprotonation of aquo ligands.

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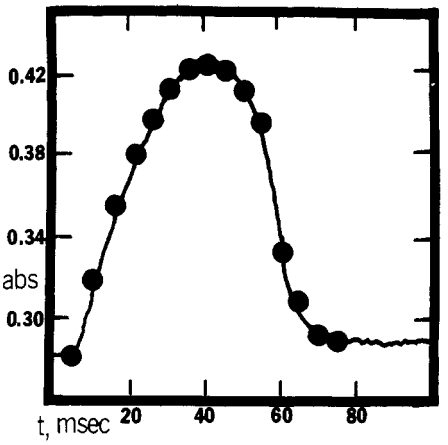



**Figure 1.** Kinetic profile at 600 nm for the reaction of Cr(V) chelate I ($3.7 \times 10^{-3}$ M) with ascorbic acid ($7.5 \times 10^{-3}$ M) at 23.8 °C. The supporting medium was 0.050 M in 2-ethyl-2-hydroxybutyric acid, 0.10 M in its sodium salt, and 0.30 M in $LiClO_4$; the pH was 3.66. The solid line is the experimental curve, whereas the circles represent absorbances calculated form the sequence (2)–(5) in the text, taking $k_1$ and $k_3$ as $2.82 \times 10^2$ and $5.31 \times 10^4$ $M^{-1}$ $s^{-1}$, respectively, and the ratio $k_2/k_4$ as 13.2. Extinction coefficients used ($M^{-1}$ $cm^{-1}$): Cr(III), 39, Cr(IV), 516; Cr(V), 38. Mixing time: 0.005 s. Optical path length: 2.00 cm.

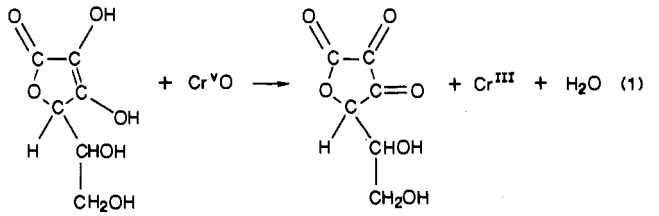
carboxylate anion was 0.3 M but dropped to 50% when [$Lig^-$] was 0.03 M. A smaller fraction, readily eluted with 1.0 M $NaClO_4$, had maxima at 583 ($\epsilon = 47$) and 414 nm ($\epsilon = 62$ $M^{-1}$ $cm^{-1}$). Recovery of chromium generally fell between 88 and 93%.

**Kinetic Measurements and Estimates of Specific Rates.** Reactions were monitored by following absorbance changes at 510 and 600 nm with a Durrum-Gibson stop-flow spectrophotometer. Total ionic strength was maintained near 0.40 M by addition of $LiClO_4$, and pH values were regulated by addition of measured quantities of 2-ethyl-2-hydroxybutyric acid ($pK_A$ 3.32)[16] and its sodium salt. All runs were carried out at 23.7 ± 0.2 °C with ascorbic acid in excess.

Kinetic traces at 510 nm were dominated by the decay of Cr(V). Slopes increased markedly as the reaction proceeded, indicating autocatalysis, and then leveled off near the final 10% of reaction when Cr(V) was almost exhausted. Curves taken at 600 nm, where Cr(V) and the Cr(III) product have nearly equal extinction coefficients, were more complex, showing the growth of a strongly absorbing intermediate and then its more rapid consumption (Figure 1). Depending upon reagent concentrations, maximal absorbance were observed from 0.015 to 0.080 s after mixing. Fits of our profiles to a reaction sequence featuring autocatalysis by Cr(IV) (as described in the Discussion) were accomplished initially by using the program INTEGRAL to generate curves that were compred to those observed.[9,17,18] Individual rate constants giving reasonable agreement between observed and calculated optical densities were subjected to further refinement using an iterative nonlinear least-squares procedure.[19,20] Parameters resulting from the final refinements reproduced the observed curves closely, and agreement between specific rates obtained from replicate runs with different master solutions was within 10% for the slower reactions (featuring peak absorbances at 50 ms or more). As reactions were accelerated by increasing pH or [ascorbate], results became progressively more erratic, and agreement between parameters pertaining to most rapid runs (maximal absorbance near 15 msec) was generally no better than 20%, probably reflecting lower instrumental sensitivity at short time intervals.

## Results and Discussion

Spectrophotometric titration of Cr(V) with ascorbic acid (at 510 nm) indicates that very nearly equimolar quantities of the two redox reagents are used in the transformation at hand. Hence, ascorbic acid, like Cr(V), has entered into a net 2e transaction. In accord with a large number of past reports of such ascorbate oxidations,[12,21] the organic product is taken to be dehydroascorbic acid (III):[22]

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Since the $pK_A$ of ascorbic acid (4.01)[23] lies close to the pH range used in the kinetic experiments, the acid must be partially converted to its conjugate base in our systems.

The relatively high molar absorptivities of the two predominant Cr(III) products indicate that both are bis chelates derived from the parent α-hydroxy acid.[24] The spectrum of that product quickly eluted from our cation-exchange resin with 1 M $NaClO_4$ corresponds closely to that of the species formed by reduction of bis chelate I with Fe(II), $VO^{2+}$, and $TiOH^{2+}$.[4,6,7] This component is taken to be a bischelated dicarboxylato complex of $(H_2O)_2Cr^{III}$ (net charge +1), and its observed elution behavior confirms this. The more rapidly moving fraction, which is eluted with water alone, exhibits still higher extinction coefficients ($\epsilon_{588} = 55$, $\epsilon_{414} = 70$ $M^{-1}$ $cm^{-1}$) and appears to be uncharged. Its properties are consistent with a bischelated structure in which one of the coordinated waters has been replaced by a carboxylato ligand derived from the buffering acid, and its yield is seen to rise as the concentration of buffer in the generating solution is increased.[25]

Reaction profiles taken at 510 nm, where Cr(V) absorbs much more strongly than Cr(III), features slopes that increase steadily during the first 90% reaction before falling off near the end. We are thus dealing with an autocatalytic system in which the growth of a catalytic species (as the reaction progresses) more than compensates for the attendant loss of substrate(s). Kinetic curves recorded at 600 nm (e.g. Figure 1), where Cr(V) and Cr(III) have very nearly equal molar absorptivities, are even more informative, showing the generation and consumption of an intermediate that aborbs strongly in the region characteristic of Cr(IV) complexes.[8,9] Note that the falling portion of the curve is markedly steeper than the rising portion, in contrast to the more usual curves resulting from the straightforward superposition of first-order processes,

(16) Srinivasan, V. S.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 3176.
(17) Kinetic fits, which utilized a fourth-order Runge–Kutta integration technique,[18] were accomplished by a FORTRAN-77 program on an IBM 3081D computer system. The FORTRAN-IV version of the program, for which we thank Professor Gilbert Gordon (Miami University, Oxford, OH), was modified to incorporate the appropriate differential equations and stoichiometric relationships. Copies of the modified program may be obtained from R.N.B.
(18) (a) Margenau, H.; Murphy, G. M. "*The Mathematics of Physics and Chemistry*"; Van Nostrand: New York, 1943; p 469. (b) Wiberg, K. In "Techniques of Chemistry", 3rd ed.; Lewis, E. S., Ed.; Wiley: New York, 1974; Vol. VI, Part I, p 764.
(19) This program, which was developed by R. Moore and T. W. Newton of Los Alamos National Laboratory, was obtained from Professor Gilbert Gordon. The FORTRAN-IV version was changed, with the help of Dr. J. W. Reed, to FORTRAN-77 in order to adapt to the IBM 3100 system. The program, which minimizes the function $(Abs_{calcd} - Abs_{obsd})^2$, uses the Gaussian method described by McWilliams and coworkers.[20] Trial values of the rate constants were those obtained from the "INTEGRAL" procedure. Individual experimental points were unweighted.
(20) McWilliams, P.; Hall, W. S.; Wegner, H. E. *Rev. Sci. Instr.* **1965**, *33*, 76.
(21) See, for example: (a) Kustin, K.; Toppen, D. L. *Inorg. Chem.* **1973**, *12*, 1404. (b) Mushran, S. P.; Agrawal, R. M.; Mehrotra, R. M.; Sanehi, R. *J. Chem. Soc., Dalton Trans.* **1974**, 1460.
(22) For a critical consideration of the usual triketo structure for dehydroascorbic acid and evidence that it exists as a dimer in the solid state, see: Hvoslef, J. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cyrst. Chem.* **1972**, *B28*, 916.
(23) This $pK_A$, determined by partial titration in 0.50 M $NaClO_4$ at 21.5 °C, is in agreement with the value 4.03 (20 °C, $\mu = 1.0$) reported by Pelizzetti.[12b]
(24) Visible spectra of a number of chelated and nonchelated carboxylato complexes of Cr(III) have been compiled by Fanchiang.[7] Note that the 2-hydroxyalkanoic acid enters into chelation with Cr(III) as its uninegative anion but loses both its carboxyl and hydroxyl protons when it coordinates with the more acidic Cr(V) center.[16]
(25) The same strongly absorbant uncharged Cr(III) complex is formed in the reduction of Cr(V) complex I with cysteine (S.K.G., unpublished experiments, 1986). It was not, however, observed when Cr(V) was reduced with Fe(II) or $TiOH^{2+}$.[4,6] Reactions with these metal center reductants were carried out at pH's near 2; hence the concentration of carboxylate anion available for ligation was much lower.

**Table I.** Kinetic Parameters for the Reduction of Carboxylato-Bound Chromium(V) with Ascorbate[a]

| [Red],[b] M | pH | [LigH],[c] M | [Lig$^-$],[d] M | $10^{-2}k_1$,[e] $M^{-1}$ $s^{-1}$ | $10^{-4}k_3$,[e] $M^{-1}$ $s^{-1}$ | $k_2/k_4$[e] | $10^{-2}\epsilon_{Cr(IV)}$,[e,f] $M^{-1}$ $cm^{-1}$ |
|---|---|---|---|---|---|---|---|
| 0.0075 | 3.32 | 0.10 | 0.10 | 2.7 | 4.1 | 15 | 4.8 |
| 0.0148 | 3.32 | 0.10 | 0.10 | 2.8 | 3.0 | 9.8 | 4.0 |
| 0.0220 | 3.32 | 0.10 | 0.10 | 2.6 | 2.5 | 8.7 | 3.8 |
| 0.0296 | 3.32 | 0.10 | 0.10 | 2.2 | 2.2 | 8.4 | 3.6 |
| 0.0370 | 3.32 | 0.10 | 0.10 | 2.2 | 1.9 | 7.7 | 3.4 |
| 0.0555 | 3.32 | 0.10 | 0.10 | 2.0 | 1.8 | 5.7 | 3.5 |
| 0.0740 | 3.32 | 0.10 | 0.10 | 1.8 | 1.5 | 4.9 | 3.3 |
| 0.0075 | 2.46 | 0.30 | 0.050 | 0.47 | 0.7 | 18 | 6.3 |
| 0.0075 | 2.67 | 0.20 | 0.050 | 1.1 | 1.1 | 16 | 5.6 |
| 0.0075 | 3.03 | 0.10 | 0.050 | 1.5 | 1.2 | 19 | 4.9 |
| 0.0075 | 3.66 | 0.050 | 0.10 | 2.8 | 5.3 | 13 | 5.2 |
| 0.0075 | 3.99 | 0.050 | 0.20 | 3.4 | 7.7 | 9.4 | 5.6 |
| 0.0075 | 4.26 | 0.050 | 0.30 | 4.6 | 7.1 | 11 | 4.8 |

[a] Reactions were carried out at 24 °C; $\mu$ = 0.4 M ($LiClO_4$); chromium(V), added as sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I), was 0.0037 M throughout. [b] Total concentration of reductant, ascorbic acid, added. [c] 2-Ethyl-2-hydroxybutyric acid. [d] 2-Ethyl-2-hydroxybutyrate. [e] Parameters obtained from nonlinear least-squares refinement in which absorbances were compared with those obtained by integration of differential equations based on the sequence (2)–(5) (see text and ref 9 and 19). [f] 600 nm.

for which the reverse holds true. The more sudden drops are strongly reminiscent of the profiles for reductions of Cr(V) with $HSO_3^-$ and $I^-$, each of which has been shown to have a prominent autocatalytic component.[9,10]

Both the intervention of Cr(IV) and the observed autocatalysis require that the reducing agent, ascorbic acid (like the oxidant), participate in single-electron transactions in our systems, giving rise to a radical intermediate (abbreviated HA•) en route to the 2e product, dehydroascorbate, III ($A^0$). A number of workers[12,21,26] have presented evidence that this radical intercedes in ascorbate oxidations, and its ESR spectrum has been described in detail.[27]

The reaction sequence (2)–(5), consisting of four single-electron steps, fits the observed kinetic curve for each individual run. The

$$Cr^V + H_2A \xrightarrow{k_1} Cr^{IV} + HA^\bullet + H^+ \quad (2)$$

$$Cr^V + HA^\bullet \xrightarrow{k_2} Cr^{IV} + A^0 + H^+ \quad (3)$$

$$Cr^{IV} + H_2A \xrightarrow{k_3} Cr^{III} + HA^\bullet + H^+ \quad (4)$$

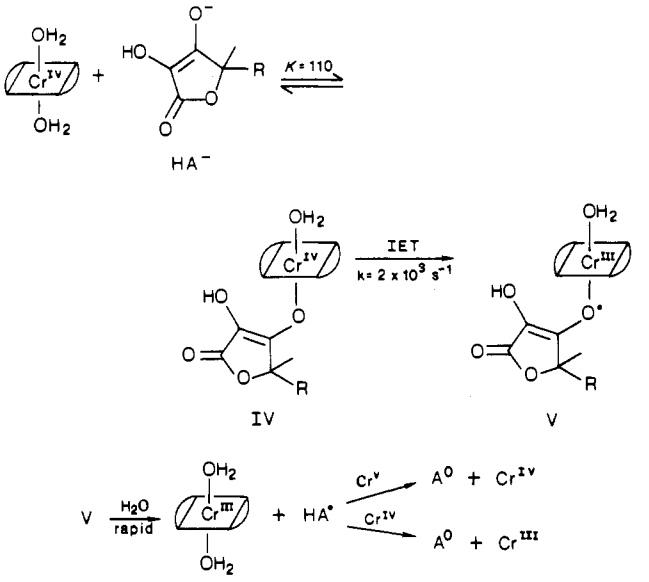
$$Cr^{IV} + HA^\bullet \xrightarrow{k_4} Cr^{III} + A^0 + H^+ \quad (5)$$

early stages of reaction involve only (2) and (3); as $[Cr^{IV}]$ increases, reaction 4 assumes importance, thus increasing $[HA^\bullet]$. The latter radical reacts more rapidly with $Cr^V$ ($k_2$) than with $Cr^{IV}$ ($k_4$), and the $Cr^V$–$HA^\bullet$ reaction regenerates $Cr^{IV}$, leading to the observed autocatalysis. When $Cr^V$ is depleted, (4) and (5) continue until all $Cr^{IV}$ is converted to $Cr^{III}$.

Derivation of differential equations generated by sequence 2–5, application of the steady-state approximation to radical HA•, and employment of the Runge–Kutta integration procedure were carried out as described for the Cr(V)–S(IV) reaction.[9] Values of $k_1$, $k_3$, and the ratio $k_2/k_4$ were allowed to vary independently. Integration then yielded the concentrations of the three chromium oxidation states and ascorbate at 5-ms intervals. Incorporation of molar absorbances of Cr(V), Cr(IV), and Cr(III) gave calculated absorbance values of the mixture at each point.[28] The set of parameters giving the closest fit to the observed profiles were used as trial values for a final iterative nonlinear least-squares refinement.[19]

Table I lists values of the parameters $k_1$, $k_3$, $k_2/k_4$, and $\epsilon_{Cr}$(IV) resulting from these refinements. Calculated absorbances (solid circles) obtained from one set of parameters are compared with the appropriate experimental curve in Figure 1. The quick drop in absorbance at 600 nm, soon after the maximum is attained, reflects the decay of Cr(IV).

**Scheme I**[29]




As emphasized in connection with earlier treatments of this sort,[9,10] these parameters are much less precise than those associated with more straightforward kinetic systems requiring just one specific rate for each kinetic run. It is clear, however, that the sets of rate constants reproducing the experimental curves for individual runs show substantial variation with changes in the reaction medium. Both the Cr(V)–ascorbate component ($k_1$) and the Cr(IV)–ascorbate component ($k_3$) are more rapid at higher pH's. Moreover, the apparent value of $k_3$ decreases at higher ascorbic acid concentrations, pointing to the formation of a Cr(IV)–ascorbate complex. If formation of this complex entails a mobile equilibrium, kinetic evidence alone cannot tell us whether electron transfer takes place within the complex or between the free redox partners in equilibrium with it, although comparisons of individual specific rates leads us to favor the former alternative (see below). In any case, the limiting specific rate, $(k_3)_{lim}$, for this kinetic component and the association constant for the complex ($K$) are related to the various values of $k_3$

$$k_3 = \frac{(k_3)_{lim}}{1 + K[H_2A]} \quad (6)$$

Least-squares refinement of $k_3$ values at pH 3.32 yields $(k_3)_{lim}$ = (3.6 ± 0.4) × $10^4$ $M^{-1}$ $s^{-1}$ and an association constant of 18.6 ± 5.1 $M^{-1}$.[29]

(26) See, for example: (a) Taqui-Khan, M. M.; Martell, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 6011; 1969, *91*, 4668. (b) Laurence, G. S.; Ellis, K. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1667.

(27) (a) Yamazaki, I.; Mason, H. S.; Piette, L. H. *J. Biol. Chem.* **1960**, *235*, 2444. (b) Yamazaki, I.; Piette, L. H. *Biochem. Biophys. Acta* **1961**, *50*, 62.

(28) The value of $\epsilon_{Cr(V)}$ was taken from the initial absorbance of the reaction mixture and that of $\epsilon_{Cr(III)}$ from the final abosrbance. Both of these were kept fixed, but $\epsilon_{Cr(IV)}$ was allowed to vary. Ascorbate and dehydroascorbate absorb negligibly at the wavelengths used.

Values of $k_1$ remain very nearly constant if [ascorbic acid] is kept below 0.05 M, although there is a hint of an approach toward kinetic saturation at higher concentrations. The downward trend, with increasing ascorbate, in the ratio $k_2/k_4$ (which pertains to the competition between $Cr^V$ and $Cr^{IV}$ for the radical $HA^•$) probably reflects again the partial conversion of Cr(IV) to an ascorbate complex, but for this step, (eq 5) in the redox sequence, the adduct appears to be more reactive than the unbound oxidant.

The marked accelerations, with increasing pH, of the one-electron reductions by ascorbic acid of both Cr(V) and Cr(IV) ($k_1$ and $k_3$) undoubltedly relfect, in part, the conversion of the reductant to the more reactive[12b] uninegative form, $HA^-$. In addition, however, both Cr(V) and Cr(IV) are thought to be involved in acid–base equilibria within the acidity range examined.[7,10,30] Hence, at least three components may be undergoing partition between protonation levels, each with a different acidity constant, complicating the relationships between rates and acidity. Values of $k_1$ and $k_3$ resulting from our treatment appear to be of insufficient precision to justify an overall multiparameter refinement dealing with runs at seven acidities.

Neither of the two principal Cr(III) products, both of which are taken to be bischelated derivatives, is thermodynamically favored, for both undergo eventual aquation on standing in our media. Preservation of the rings shows us that chelation persists during all steps involving Cr(V) and Cr(IV). Partial conversion of the diaquo fraction to the unhcarged species having an additional carboxylato group at an axial position almost certainly occurs at the Cr(IV) level, for this state is now recognized to be more substitution labile than either Cr(V) or Cr(III).[8]

The most remarkable aspect of the present study is undoubtedly the very high reactivity of ascorbate in this system, a facet which is particularly striking in view of the weakly reducing formal potential (0.93 V) that has been estimated[12b] for 1e oxidation of $HA^-$ to $HA^•$. It is instructive to compare the specific rate for the initial Cr(V)–$HA^-$ step ($k_1 \sim 7 \times 10^2$ $M^{-1}$ $s^{-1}$) to that for the reaction of the same Cr(V) complex with $IrCl_6^{3-}$ ($3.4 \times 10^{-2}$),[5] a reductant with nearly the same formal reduction potential as $HA^-$.[31] The self-exchange rate for the Ir(III,IV) couple is recorded as $2.3 \times 10^5$ $M^{-1}$ $s^{-1}$,[32] whereas that for $HA^-$,$HA^•$ has been estimated as $3.5 \times 10^5$.[33] The Marcus model[34] stipulates that two reductants having the same formal potentials and very nearly equal self-exchange rates should react with a given oxidant at very nearly the same specific rates, provided that both "cross-reactions" are outer sphere. The observed rate ratio ($k_{HA}/k_{Ir(III)} = 2 \times 10^4$) pertaining to the two reductants then implies strongly that the Cr(V)–ascorbate reaction ($k_1$) is utilizing an additional (i.e., an inner-sphere) path.

Although both $k_3$ and $k_1$ are seen to vary with pH, their ratio in a given medium falls between 100 and 200 throughout the range examined, being substantially above the corresponding $k_{Cr(IV)}/k_{Cr(V)}$ ratios for reductions with U(IV) (10–20)[35] and with $I^-$ (30–60),[10] which are thought, on the basis of other evidence, to proceed by outer-sphere paths. Since a large inner-sphere component appears to contribute to $k_1$, the ratio $k_3/k_1$ would be expected to fall below 20 if $k_3$ were to employ only an outer-sphere route. The reverse is the case, indicating that the Cr(IV)–$HA^-$ reaction is, like $k_1$, predominantly inner sphere. Furthermore, the inversion in relative rates ($k_2/k_4$) for oxidation of $HA^•$, which reacts with Cr(V) 5–20 times as rapidly as with Cr(IV), points to the operation of an inner-sphere path for the Cr(V)–$HA^•$ reaction but leaves open the question with respect to the Cr(IV)–$HA^•$ step.[36] Thus, rate comparisons with known systems suggest that at least three of the four steps in the proposed redox sequence involve bridged activated complexes.

In principle, an inner-sphere Cr(IV)–ascorbate reaction should produce a Cr(III)-bound oxidation product. However, oxidation of ascorbate disrupts its enediol function, leaving the oxidized forms ($HA^•$ and $A^0$) much less effective ligands than ascorbate itself. Thus, Cr(III)-bound products would be expected to suffer rapid aquation in the medium used.

A number of workers have suggested that reductions of the higher oxidation states of chromium by organic hydroxyl compounds proceed through ester-like intermediates having at least one Cr–O–C unit.[11d,37] It is reasonable to suspect that a similar species (e.g., "precursor complex" IV in Scheme I) intervenes in each of the inner-sphere steps in the proposed sequence. Internal electron transfer (IET) within IV may yield a Cr(III)–$HA^•$ intermediate (V), which, upon rapid aquation, releases radical $HA^•$, for which Cr(V) and Cr(IV) compete. Analogous schemes may apply to the Cr(V)–$HA^-$ reaction (2) and the Cr(V)–$HA^•$ reaction (3), the latter yielding the Cr(IV) complex of dehydroascorbate ($Cr^{IV}$–$A^0$), which should also experience rapid aquation. An alternate route for the overall conversion, involving a Cr(V)–$HA^-$ intermediate that can undergo internal electron transfer to Co(IV)–$HA^•$ and thence to Cr(III) + dehydroascorbate, cannot be considered a major contributor, for it does not entail release of free $HA^•$; hence, it does not accomodate the observed autocatalysis.

It is likely that the latter point helps explain why, despite the extensive body of past work pertaining to the oxidations of organic compounds by the higher valence states of chromium,[3a,37,38] autocatlaysis is reported only rarely. The sequence we propose requires not only that the organic substrate exist at three oxidation levels differing by a single unit but also that the middle (radical) state be stable enough to allow two metal oxidation states to compete for it. Since the radical must exist in uncomplexed state after it is formed but before it is destroyed, chelation involving the substrate would be expected to disfavor autocatalysis. Ascorbate yields a stabilized radical, in which the unpaired electron is delocalized over the enediol system, and in the present case, possible chelation with the chromium center is hampered by the ligand environment about the oxidant, which has blocked off four coordination positions. Only two coordination sites remain, and these lie trans to each other. Autocatalysis should become less likely if less effective "blocking ligands" were to occupy the coordination sphere of the oxidant. A final requirement is the inversion in relative rates of the two higher states of the oxidant in attacking the primary reductant (on one hand) and the radical intermediate (on the other). This inversion occurs in the four autocatalytic Cr(V) systems examined thus far, but its source remains a puzzling point.

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**Registry No.** I (anion), 75476-70-9; II, 50-81-7.

(29) At pH 3.32, 17% of the added ascorbic acid exists as $HA^-$.[23] In an alternative treatment, individual values of $k_3$ could be calculated on the basis of $[HA^-]$ in the reacting solution, and values of $[HA^-]$ used in place of total ascorbic acid in (6). Calculations carried out in this manner will result in values of $(k_3)_{lim}$ and $K$, both of which exceed, by a factor of 5.9, the values given. The larger values, $2.1 \times 10^5$ $M^{-1}$ $s^{-1}$ and $1.1 \times 10^2$ $M^{-1}$, apply to higher pH's, which allow virtually complete conversion of ascorbic acid to $HA^-$. If this reaction step is taken to proceed through the Cr(IV)–ascorbate complex, (see Scheme I) its unimolecular specific rate would be calculated as $(k_3)_{lim}/K$, or $1.9 \times 10^3$ $s^{-1}$.

(30) The observed variation of $\epsilon_{Cr(IV)}$ with acidity (Table I) is also in accord with a protonation equilibrium involving this oxidation state. Fanchiang[7] has reported a $pK_A$ value of 3.42 for Cr(IV) in perchlorate media.

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