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### Stoichiometry and Kinetics of the Cobalt(III) Oxidation of L-Ascorbic Acid in Acid Perchlorate Solution

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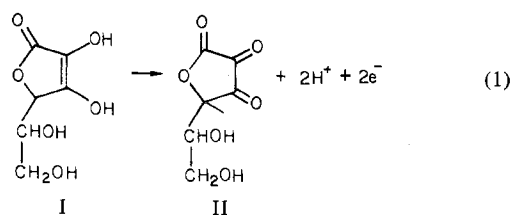
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In recent years a considerable amount of kinetic data has been accumulated for redox reactions of aquocobalt(III) species.<sup>2,3</sup> These results are of interest in view of the strongly oxidizing character of the cobalt(III)/cobalt(II) couple ( $E^\circ = 1.86$  V at  $[\text{HClO}_4] = 3$  M, 23 °C),<sup>4</sup> which evidently gives rise to limiting mechanisms for both inner- and outer-sphere aquocobalt(III) reactions.<sup>5,6</sup>

The rates of reduction of aquocobalt(III) species are characteristically first order in  $[\text{Co}^{\text{III}}]$  and  $[\text{reductant}]$  and the second-order rate constant generally obeys the empirical relationship  $k_{\text{obsd}} = a + b/[\text{H}^+]$ . The parameters  $a$  and  $b$  are associated with reactions of  $\text{Co}^{3+}(\text{aq})$  and  $\text{CoOH}^{2+}(\text{aq})$ , respectively.<sup>3,6</sup> Consideration of the values of kinetic parameters  $a$  and  $b$  for complexation and redox reactions indicates that the rates of reactions of  $\text{CoOH}^{2+}$  with such reductants as  $\text{Br}^-$ ,  $\text{H}_2\text{O}_2$ , and oxalic acid are limited by substitution of the reductant at the metal center with  $a \ll b$ ,<sup>5</sup> while those of both cobalt(III) species with  $\text{Fe}^{2+}$ ,<sup>7</sup> benzenediols,<sup>2,8</sup> and  $\text{I}^-$ <sup>2</sup> are much faster and must therefore proceed through an outer-sphere mechanism. Another interesting feature of this latter class of reactions is the increasing importance of  $a$  relative to  $b$  in the empirical rate law.<sup>5</sup>

L-Ascorbic acid (I) plays an important reductive role in biochemical systems. This molecule has a stable enediol structure<sup>9</sup> and is oxidized by many transition metal centers to dehydroascorbic acid (II) (eq 1), a process which is formally



analogous to the oxidation of benzenediols to the corresponding

Table I. Kinetic Data for Reduction of Aquocobalt(III) Species by Ascorbic Acid (Asc) at Ionic Strength 3.0 M

Temp, °C	$[\text{H}^+]^a$	$10^3[\text{Asc}]^a$	$k_{\text{obsd}}^b$	$k_{\text{calcd}}^{b,c}$	
5.0	3.0	4.12	1.36	1.22	
		7.39	2.20	2.18	
		14.7	3.91	4.34	
	2.0	3.0	4.11	1.65	1.66
			7.38	2.96	2.98
			14.7	5.26	5.94
	1.0	3.0	4.25	3.31	3.10
			7.41	5.71	5.41
			14.15	10.1	10.3
	0.60	3.0	4.14	4.93	4.82
			7.39	8.13	8.61
			14.76	16.7	17.1
15.0	3.0	4.11	2.72	2.85	
		7.34	5.37	5.10	
		14.7	10.6	10.2	
	2.0	3.0	4.50	4.50	4.21
			7.42	7.57	6.94
			14.73	14.7	13.8
	1.0	3.0	7.45	13.0	12.4
			13.34	23.2	22.1
			4.15	10.4	10.9
	0.6	3.0	7.36	20.5	19.3
			14.7	40.1	38.6
			5.14 <sup>d</sup>	8.02	8.00
25.0	3.0	10.2	16.1	15.9	
		10.2 <sup>d</sup>	15.4	15.9	
		15.3	26.0	23.8	
	2.0	3.0	39.4 <sup>d</sup>	58.3	61.3
			4.13	8.46	8.52
			7.20	15.8	14.9
	1.0	3.0	7.42	15.4	15.2
			14.5 <sup>d</sup>	30.0	29.4
			14.7	29.2	30.4
	0.6	3.0	19.3	37.4	39.8
			23.2	44.5	47.9
			29.6	56.0	61.2
0.6	3.0	3.92	18.7	14.1	
		15.3 <sup>d</sup>	59.8	54.9	
		4.42	23.5	24.8	
		5.84	30.9	32.8	

<sup>a</sup> All concentrations are M.  $[\text{Co}^{\text{III}}]_0 = (8.43-23.2) \times 10^{-4}$  M;  $[\text{Co}^{\text{II}}] = (1.36-5.25) \times 10^{-3}$  M. <sup>b</sup> Units are  $\text{s}^{-1}$ . Average error of repeated runs is ca.  $\pm 5\%$ . <sup>c</sup> Calculated from eq 3 using the data in Table II. The data were weighted proportional to  $(1/k_{\text{obsd}})^2$ . <sup>d</sup> Alternate independent source of ascorbic acid.

quinones.<sup>2,8</sup> Since a considerable amount of kinetic data has been accumulated for oxidation by aquocobalt(III) in these latter systems,<sup>2,8</sup> it seemed worthwhile to investigate the kinetic validity of this analogy for L-ascorbic acid oxidation.

In this paper we report a stopped-flow spectrophotometric determination of the rate law for the rapid oxidation of L-ascorbic acid by aquocobalt(III) species in aqueous perchloric acid at ionic strength 3 M.

### Experimental Section

**Materials and Analytical Methods.** All water used in this investigation was either doubly distilled or distilled and then deionized. Stock solutions of approximately 6 M sodium perchlorate were prepared by neutralizing sodium carbonate with perchloric acid and were standardized gravimetrically. Cobalt(II) perchlorate hexahydrate was used to prepare the stock solutions of cobalt(III),<sup>3</sup> which were analyzed spectrophotometrically ( $\epsilon_{605} 35.3 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{509} 4.84 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively<sup>2</sup>). L-Ascorbic acid (different samples from Eastman) was used as supplied to make up stock aqueous solutions which were used within 1 h of preparation. Ascorbic acid concentrations were determined by coulometric titration with iodine.<sup>10</sup>

**Stoichiometry Measurements.** The stoichiometry of the oxidation reaction was determined by adding aliquots of a standardized solution of  $\text{Co}^{\text{III}}$  to excess analyzed ascorbic acid, neutralizing the excess perchloric acid with standard sodium hydroxide, and then determining the amount of unreacted ascorbic acid as described above in a solution

Table II. Rate Law Parameters for Reduction of Aquocobalt(III) Species by Ascorbic Acid at Ionic Strength 3.0 M<sup>a</sup>

Temp, °C	a <sup>b</sup>	b <sup>c</sup>
5.0	58.7 ± 15.5	648 ± 15
15.0	221 ± 28	1496 ± 50
25.0	564 ± 94	2960 ± 180

$$\Delta H_a^\ddagger = 15 \pm 2, \Delta S_a^\ddagger = 6 \pm 8, \Delta H_b^\ddagger = 12.1 \pm 0.6, \Delta S_b^\ddagger = -2 \pm 2^e$$

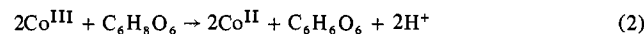
<sup>a</sup> Errors shown are one standard deviation. <sup>b</sup> Units are M<sup>-1</sup> s<sup>-1</sup>. <sup>c</sup> Units are s<sup>-1</sup>. <sup>d</sup> Units are kcal mol<sup>-1</sup>. <sup>e</sup> Units are cal deg<sup>-1</sup> mol<sup>-1</sup> at 25.0 °C.

buffered with sodium bicarbonate, using starch to detect the end point.<sup>10</sup> The concentration ranges employed were [H<sup>+</sup>] = 0.14–2.5 M, [ascorbic acid]<sub>T</sub> = (1.14–8.17) × 10<sup>-3</sup> M, [Co<sup>III</sup>]<sub>0</sub> = (0.681–1.22) × 10<sup>-2</sup> M, and [Co<sup>II</sup>] = (0.17–3.00) × 10<sup>-2</sup> M at 25 °C.

**Kinetics.** A stopped-flow apparatus<sup>11</sup> was used to monitor the disappearance of cobalt(III) at 605 nm, where it has an absorption maximum and is the major absorbing species. Pseudo-first-order conditions were established by employing at least a ninefold equivalent excess of ascorbic acid in all cases. Constant temperature was maintained in the range 5.0–25.0 °C to within ±0.2 °C. In all cases the ionic strength was adjusted to 3 M by addition of sodium perchlorate.

## Results

**Stoichiometry.** The stoichiometry of the title reaction was found to be Δ[Co<sup>III</sup>]/Δ[ascorbic acid]<sub>T</sub> = 2.000 ± 0.003, consistent with the overall reaction



No reaction of ascorbic acid with perchloric acid was detected on the time scale of the stoichiometric measurements.

**Kinetics.** Under pseudo-first-order conditions the disappearance of cobalt(III) was invariably first order for at least 3 half-lives. The pseudo-first-order rate constant, *k*<sub>obsd</sub>, was reproducible, to within ±5%, under fixed experimental conditions and was proportional, to within ±5%, to [ascorbic acid]<sub>T</sub> at fixed acidity. No dependence of the reaction rate on [Co<sup>II</sup>] or the reductant sample lot was detected within experimental error. Studies in the range [H<sup>+</sup>] = 0.60–3.00 M indicated that the empirical rate law for the reaction is given by

$$\frac{-d \ln [\text{Co}^{\text{III}}]}{dt} = (a + b/[\text{H}^+])[\text{ascorbic acid}]_T \quad (3)$$

Values for *a* and *b* obtained from a linear least-squares fit of the data to eq 3 at three experimental temperatures (Table I) are given in Table II. Activation parameters were calculated by nonlinear least-squares fitting of the data to eq 3, where *a* and *b* were replaced by [(*k*/2π)*T*/*h*][exp(-Δ*H*<sub>a</sub><sup>‡</sup>/RT) exp(Δ*S*<sub>a</sub><sup>‡</sup>/R)] and [(*k*/2π)*T*/*h*][exp(-Δ*H*<sub>b</sub><sup>‡</sup>/RT) exp(Δ*S*<sub>b</sub><sup>‡</sup>/R)], respectively, and the symbols in these alternative forms have their usual significance. Calculated values of the first-order rate constants from this latter fit of the data are

Table III. Kinetic Data for Outer-Sphere Reduction of Aquocobalt(III) Species at 25.0 °C

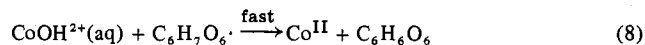
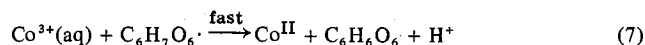
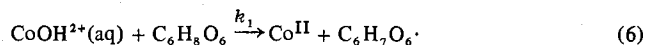
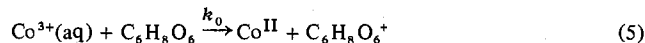
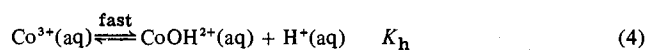
Reductant	10 <sup>-3</sup> <i>k</i> <sub>0</sub> <sup>a</sup>	Δ <i>H</i> <sub>0</sub> <sup>‡b</sup>	Δ <i>S</i> <sub>0</sub> <sup>‡c</sup>	10 <sup>-3</sup> <i>k</i> <sub>1</sub> <i>K</i> <sub>h</sub> <sup>d</sup>	Δ <i>H</i> <sub>b</sub> <sup>‡b,e</sup>	Δ <i>S</i> <sub>b</sub> <sup>‡c,f</sup>	Ref
Benzene-1,4-diol	2.2	18	18	1.28	18.6	19	1 <sup>g</sup>
2-Methylbenzene-1,4-diol	1.5	16	6	1.12	19	19	15 <sup>h</sup>
2,5-Dihydroxybenzenesulfonic acid	0.32	14	-9	0.70	15	2	15 <sup>h</sup>
2,3,5-Trimethylbenzene-1,4-diol	5.7	11	-3	2.60	12	-3	8 <sup>h</sup>
Adrenaline	0.16	15	2	0.40	18	12	8 <sup>h</sup>
2,3-Dihydroxybenzoic acid	~0.040			0.16	17	9	8 <sup>h</sup>
4-Cyanobenzene-1,2-diol	~0.015			0.24	12	-8	8 <sup>h</sup>
Ascorbic acid	0.28	15 ± 2	6 ± 8	1.46	12.1 ± 0.6	-2 ± 2	<i>g, i</i>

<sup>a</sup> Units are M<sup>-1</sup> s<sup>-1</sup>. <sup>b</sup> Units are kcal mol<sup>-1</sup>. <sup>c</sup> Units are cal deg<sup>-1</sup> mol<sup>-1</sup>. <sup>d</sup> Units are s<sup>-1</sup>. <sup>e</sup> Not corrected for enthalpy of acid dissociation of Co<sup>3+</sup>(aq). <sup>f</sup> Not corrected for entropy of acid dissociation of Co<sup>3+</sup>(aq). <sup>g</sup> Data at ionic strength 3 M. <sup>h</sup> Data at ionic strength 2 M. <sup>i</sup> Present work.

included in Table I for comparison with *k*<sub>obsd</sub>.

## Mechanism

The following mechanism, with (5) and (6) as the rate-determining steps, is consistent with the stoichiometric and kinetic results.



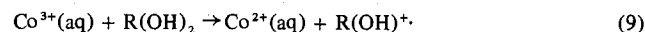
Here C<sub>6</sub>H<sub>7</sub>O<sub>6</sub>· and C<sub>6</sub>H<sub>8</sub>O<sub>6</sub><sup>+</sup> represent differently protonated forms of the radical produced by one-electron oxidation of neutral ascorbic acid.<sup>9,12</sup> Ion-radical reactions such as (7) and (8) are very rapid. Assumption of a steady state in [C<sub>6</sub>H<sub>7</sub>O<sub>6</sub>·] and [C<sub>6</sub>H<sub>8</sub>O<sub>6</sub><sup>+</sup>] with *K*<sub>h</sub>/[H<sup>+</sup>] << 1 over the experimental acidity range<sup>3</sup> leads to *a* = 2*k*<sub>0</sub> and *b* = 2*k*<sub>1</sub>*K*<sub>h</sub> in eq 3.<sup>6</sup> Thus, according to this mechanism, *k*<sub>0</sub> = 280 ± 47 M<sup>-1</sup> s<sup>-1</sup> and *k*<sub>1</sub>*K*<sub>h</sub> = 1480 ± 90 s<sup>-1</sup> at 25.0 °C and ionic strength 3 M.

## Discussion

Ascorbic acid is oxidized to dehydroascorbic acid by aquocobalt(III) species in a reaction with an acid-dependent, second-order rate law, eq 3, which is typical of aquocobalt(III) system.<sup>2,3</sup> The absence of extra acid-dependent rate law terms in eq 3 is consistent with the virtual absence of anionic forms of ascorbic acid over the experimental acidity range.<sup>13</sup>

Comparison of the kinetic parameters *k*<sub>0</sub> and *k*<sub>1</sub>*K*<sub>h</sub> for oxidation of ascorbic acid with the corresponding values for complexation by Cl<sup>-</sup> or oxidation of Br<sup>-</sup>, H<sub>2</sub>O<sub>2</sub>, HNO<sub>2</sub>, and HN<sub>3</sub><sup>3</sup> indicates that ascorbic acid is oxidized in the outer coordination sphere of both Co<sup>3+</sup>(aq) and CoOH<sup>2+</sup>(aq).

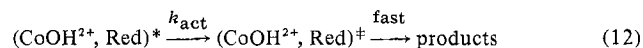
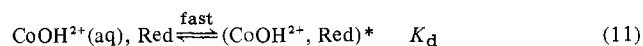
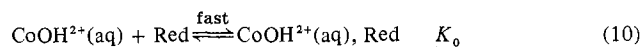
Representative kinetic data for outer-sphere reduction of aquocobalt(III) species by some hydroxy compounds, including ascorbic acid, are shown in Table III. The values of *k*<sub>0</sub> for Co<sup>3+</sup>(aq) reduction by hydroxybenzenes decrease as the overall free energy change of reaction 9 becomes more negative.<sup>14,15</sup>



Interpolation of our results for the corresponding reaction with ascorbic acid leads to *E*<sup>o</sup> ≈ 1.2 V for the reduction potential of the C<sub>6</sub>H<sub>8</sub>O<sub>6</sub><sup>+</sup>/C<sub>6</sub>H<sub>8</sub>O<sub>6</sub> couple at 25 °C.<sup>16</sup> Although the uncertainties in Δ*H*<sub>0</sub><sup>‡</sup> and Δ*S*<sub>0</sub><sup>‡</sup> are generally rather large,<sup>8,15</sup> our data for ascorbic acid are typical of neutral molecules as outer-sphere reductants for Co<sup>3+</sup>(aq).

The data in Table III also demonstrate that a much smaller range of *k*<sub>1</sub>*K*<sub>h</sub> product values is observed for reduction of CoOH<sup>2+</sup>(aq), suggestive of some sort of limiting mechanism.<sup>5,6</sup> Variations in the kinetic data for reduction of CoOH<sup>2+</sup>(aq)

by  $\text{Fe}^{2+}(\text{aq})$ , benzene-1,4-diol, and  $\text{I}^{-}(\text{aq})$  have been analyzed<sup>6</sup> according to the scheme



Here  $\text{CoOH}^{2+}$ , Red is the outer-sphere precursor formed between  $\text{CoOH}^{2+}(\text{aq})$  and the reductant species Red,  $(\text{CoOH}^{2+}, \text{Red})^*$  is a precursor form in which the distribution of  $\text{OH}^{-}$  in the inner coordination sphere is optimal for  $\text{OH}^{-}$ -mediated electron transfer within the precursor and  $(\text{CoOH}^{2+}, \text{Red})^{\ddagger}$  is the transition state for electron transfer. According to this scheme  $k_1 K_h = K_0 K_d K_h k_{\text{act}}$ ; i.e.,  $k_1 = K_0 K_d k_{\text{act}}$ . If  $k_{\text{act}}$  is essentially independent of the nature of Red,<sup>6</sup> then small variations in  $k_1 K_h$  can be ascribed to minor variations in  $K_0$  and/or  $K_d$ .

However, examination of the activation parameters for reduction of  $\text{CoOH}^{2+}(\text{aq})$  in Table III reveals substantial compensating variations of  $\Delta H_b^{\ddagger}$  and  $\Delta S_b^{\ddagger}$ . These variations are presumably a reflection of the different enthalpy and entropy changes associated with equilibria 10 and 11 for different reductant species; unfortunately, current electrostatic models for precursor formation in (10),<sup>5</sup> which neglect any influence of the structure of Red on the stability of  $\text{CoOH}^{2+}$ , Red or the possibility of hydrogen bonding within such a precursor, are too crude for a more detailed and unambiguous analysis of these interesting activation parameter variations.<sup>17</sup>

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**Registry No.** Asc, 50-81-7;  $\text{Co}^{3+}(\text{aq})$ , 15275-05-5.

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- (17) In addition to the uncertainties associated with a structureless model for precursor formation,<sup>5</sup> one would also have to contend with typical standard deviations of  $\pm 1.5$  kcal mol<sup>-1</sup> and  $\pm 7$  cal deg<sup>-1</sup> mol<sup>-1</sup> in the activation enthalpies and entropies for reduction of  $\text{CoOH}^{2+}(\text{aq})$  by benzenediols, which are somewhat higher than are those for ascorbic acid (present work).

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## Magnetic Susceptibility of the Chloro(2-diethylaminoethanolato)copper(II) Tetramer

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In recent years there has been much interest in the magnetic properties of transition metal cluster complexes. The magnetic susceptibilities of copper tetramer complexes have been successfully described by the Heisenberg spin-spin exchange model with appropriate geometrical considerations. The series of  $\text{Cu}_4\text{OX}_6\text{L}_4$  complexes where X = Cl or Br and L = pyridine,<sup>1</sup>  $(\text{C}_6\text{H}_5)_3\text{PO}$ ,<sup>2</sup> or Cl,<sup>3</sup> for example, consist of a tetrahedral arrangement of copper ions bonded to a central oxygen atom, and the magnetic properties of many of these compounds can be described with  $T_d$  symmetry models although there are complications.<sup>2</sup> Other clusters with four copper(II) ions which have been studied include the basic quinoline adduct of copper trifluoroacetate  $[\text{Cu}_2\text{OH}(\text{O}_2\text{CCF}_3)_3(\text{quin})]_2$ , an essentially symmetric linear<sup>4</sup> system, and several Schiff base complexes of copper.<sup>5,6</sup> These latter systems are formed by associated dimers. The magnetic properties of a new four-copper cluster formed from chloro(2-diethylaminoethanolato)copper(II) units,  $[\text{Cu}(\text{deae})\text{Cl}]_4$ , are described here. X-ray structural studies have shown this cluster to consist of an approximately tetrahedral arrangement of copper ions bridged by ethanolate oxygens.<sup>7,8</sup> It has not been possible to explain the magnetic properties of  $[\text{Cu}(\text{deae})\text{Cl}]_4$  with the simple  $T_d$  model; however, we show in this report that it is possible to rationalize the magnetic properties of chloro(2-diethylaminoethanolato)-copper(II) in terms of a low-symmetry model.

## Experimental Section

A sample of the complex chloro(2-diethylaminoethanolato)copper(II),  $[\text{Cu}(\text{deae})\text{Cl}]_4$ , was prepared by mixing 1.34 g of copper(II) chloride in 150 mL of absolute alcohol with 2.34 g of 2-diethylaminoethanol in 50 mL of absolute alcohol. Dark green crystals formed after the solution was allowed to stand at room temperature for several days. Anal. Calcd for  $\text{Cu}(\text{C}_6\text{H}_{14}\text{NO})\text{Cl}$ : C, 33.49; H, 6.55; N, 6.51; Cl, 16.47. Found: C, 33.53; H, 6.36; N, 6.54; Cl, 16.41. Magnetic susceptibilities were obtained using a Foner-type<sup>9</sup> vibrating-sample magnetometer,<sup>10</sup> calibrated with a nickel sphere at room temperature. The computer fits were made with an IBM 360/70 and a Raytheon 706 computer using a Simplex function minimization routine<sup>11</sup> and a standard least-squares procedure. The experimental magnetic susceptibilities were corrected for the diamagnetism of the constituent atoms and for temperature-independent paramagnetism, which was assumed to be  $60 \times 10^{-6}$  cgsu.<sup>12</sup>

## Description of the Structure

The bond distances and bond angles which were reported for  $[\text{Cu}(\text{deae})\text{Cl}]_4$  are shown on the illustration of the structure in Figure 1. The x-ray crystal structure results reveal the presence of a  $C_2$  axis, which passes through the centers of the Cu(1)-Cu(2) and the Cu(3)-Cu(4) faces. It will be seen below that this structural feature provides the unifying theme for the description of the magnetic properties.

## Magnetic Susceptibility Theory

The Heisenberg spin-spin exchange Hamiltonian

$$H = -2 \sum_{i < j} J_{ij} \hat{S}_i \hat{S}_j \quad (1)$$

was adopted for the description of the magnetic properties. In the Hamiltonian (1)  $J_{ij}$  is the exchange constant and the subscripts  $i$  and  $j$  number the pairwise interacting magnetic