

## Kinetics and Mechanism of the Reaction of Aqueous Iron(III) with Ascorbic Acid

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The kinetics of the reaction of iron(III) perchlorate with ascorbic acid in dilute aqueous acid have been studied by stopped-flow spectrophotometry at 16.1 °C, under conditions of [iron(III)]  $((2-7) \times 10^{-3} \text{ M})$  greater than [ascorbic acid]  $(2 \times 10^{-4} \text{ M})$  and  $[\text{H}^+]$  between 0.01 and 0.15 M. The reaction is biphasic with a rapid increase in absorbance at 560 nm followed by a decrease. The faster reaction is assigned to formation of an iron(III)-ascorbate complex consistent with previous observations. However, the reaction is much faster than normally observed substitutions on aquairon(III). The dependence of the rate constant on  $[\text{H}^+]$  indicates the formation of two protonated iron(III) complexes,  $\text{Fe}(\text{AH})^{2+}$  and  $\text{Fe}(\text{AH}_2)^{3+}$ . The slower reaction involves reduction of iron(III) and is inhibited by iron(II). The rate law is consistent with the iron(III)-ascorbate complex undergoing reversible electron transfer with  $\text{Fe}(\text{OH}_2)_6^{3+}$  followed by oxidation of the ascorbate radical by  $\text{Fe}(\text{OH}_2)_6^{3+}$ .

## Introduction

Although there have been a number of studies of the aqueous iron(III)-ascorbic acid ( $\text{H}_2\text{A}$ ) system, there is limited agreement on the qualitative behavior of the system and even less quantitative information. It has been observed generally that a colored intermediate forms very rapidly and there is a slower redox step to form iron(II). An interpretation of the available results is difficult in some cases because  $[\text{H}_2\text{A}] \geq 2[\text{Fe}(\text{III})]$  so that bis complex formation is possible. In other cases, the pH is  $>3$  so that hydrolysis and oligomerization of aqueous iron(III) are important complicating factors. The present study attempts to quantify the kinetic behavior of the system under conditions of  $[\text{iron(III)}] \gg [\text{ascorbic acid}]$ , to ensure mono complex formation at most, and in 0.01–0.1 M  $\text{H}^+$ , where the state of the hydrated iron(III) ion is known. The potential to obtain mechanistic information under such conditions has been demonstrated recently in studies on 2,3-dihydroxybenzoic acid.<sup>1,2</sup>

Laurence and Ellis<sup>3</sup> seem to have been the first to obtain quantitative information on the aqueous iron(III)-ascorbate system. They used a stopped-flow system to mix  $\text{Fe}(\text{ClO}_4)_3$  and ascorbic acid in the range of  $5 \times 10^{-2} \text{ M}$  and  $[\text{H}^+] = 0.2 \text{ M}$  and detected a small absorbance increase at  $\sim 550 \text{ nm}$ , which was complete in  $\leq 5 \text{ ms}$ . This was followed by another increase due to a blue transient with an absorbance maximum at  $\sim 560 \text{ nm}$ , which persisted for several hundred milliseconds. They assigned the more persistent transient to an iron(III) complex  $\text{Fe}(\text{AH})^{2+}$  with a formation constant  $([\text{Fe}(\text{AH})][\text{H}^+]/[\text{Fe}][\text{H}_2\text{A}])$  of  $\sim 0.6$  and molar absorptivity ( $\epsilon$ ) of  $\sim 11 \text{ M}^{-1} \text{ cm}^{-1}$ . Keypour et al.<sup>4</sup> studied solutions of aqueous  $\text{FeCl}_3$  (0.025 M) at pH 2 with excess ascorbic acid and claimed to observe two different transients. One is assigned to  $\text{Fe}(\text{AH})^{2+}$  ( $\lambda_{\text{max}} = \sim 550 \text{ nm}$ ), and the other, to an iron(II) complex of the ascorbate radical ( $\lambda_{\text{max}} = 630 \text{ nm}$ ). By pH jump studies in 80% methanol, Keypour et al. found evidence for transients, which they assigned to  $\text{Fe}(\text{AH})^{2+}$  and  $\text{Fe}(\text{AH}_2)^{3+}$ . Martinez et al.<sup>5</sup> observed a blue transient formed in  $<30 \text{ ms}$  at pH 5 in solutions containing  $5 \times 10^{-4} \text{ M}$  iron(III) and  $1 \times 10^{-3} \text{ M HA}^-$ . The blue species was assigned to  $\text{Fe}(\text{AH})_2^+$  with  $\epsilon = 325 \text{ M}^{-1} \text{ cm}^{-1}$  at  $\lambda_{\text{max}} = 545 \text{ nm}$ , with a formation constant of  $2.3 \times 10^6 \text{ M}^{-2}$  at 25 °C, on the basis of the temperature dependence of the limiting absorbance after  $\sim 30 \text{ ms}$ . It is difficult to assess these quantitative results because of the extensive hydrolysis and oligomerization of aqueous iron(III) at pH 5. Martinez and co-workers<sup>6</sup> have reported the rapid formation of a transient red species with  $\lambda_{\text{max}}$  at 490 nm when excess ascorbic acid is mixed with tris(oxalato)ferrate(III) at pH 3–5. This is assigned to a mixed ascorbate/oxalate complex although its rapid

formation appears unusual. Quite recently Ghosh and Gould<sup>7</sup> have reported kinetic results on the formation of a blue species in the reaction of iron(III) and ascorbic acid at pH 4.4 in acetate buffer with  $[\text{ascorbate}] \gg [\text{iron(III)}]$ . The rate constants indicate a much slower reaction than that observed by Laurence and Ellis<sup>3</sup> in 0.2 M  $\text{H}^+$ . This implies an unexpected pH dependence for a substitution reaction on aqueous iron(III), but the results of Ghosh and Gould may be complicated by acetate complexing and iron(III) polymerization.

The slower reaction stage, which generally has been assigned to the redox process, initially was studied at 330 nm by Martinez and Uribe.<sup>8</sup> These results have been reinterpreted recently by Hynes and Kelly,<sup>9</sup> who ascribe the original observations to decomposition of  $\text{FeCl}_2^+$ . With excess ascorbic acid, Hynes and Kelly find that the rate is first order in  $[\text{H}_2\text{A}]$  and the  $[\text{H}^+]$  dependence indicates that both  $\text{H}_2\text{A}$  and  $\text{HA}^-$  are reduced. Hynes and Kelly suggest what seems to be an outer-sphere electron-transfer mechanism, since no inner-sphere precursor complex is proposed. Apparently, there are no saturation effects that might be due to complex formation although these might not be apparent at their acidities, which are unspecified but seem to be  $\geq 0.1 \text{ M}$ .

There have been a number of studies of the oxidation of ascorbate species by well-characterized outer-sphere oxidizing agents. The difficulties in interpreting these results have been discussed by Creutz.<sup>10</sup> Macartney and Sutin<sup>11</sup> found that the rates of these reactions can be rationalized in terms of the Marcus theory<sup>12</sup> and calculated a self-exchange rate constant of  $1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  and  $E^\circ = 0.71 \text{ V}$  for the  $\text{HA}^-/\text{HA}^\bullet$  couple. More recently, a self-exchange constant of  $1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  has been suggested by Akhtar and Haim<sup>13</sup> to give a more consistent analysis, but we have been unable to confirm their calculations.

## Results and Discussion

The reaction of  $\text{Fe}(\text{OH}_2)_6^{3+}$  (3–7 mM) with ascorbic acid (0.2 mM) in aqueous acid (9–15 mM) occurs in two stages when observed at 560 nm and 16 °C. These stages correspond to an increase in absorbance with half-times in the range 10–20 ms and a slower decrease in absorbance with half-times  $\sim 20$  times longer. The rates of both reactions increase with increasing iron(III) concentration and decrease with increasing hydrogen ion concentration. The rate of the slower stage also decreases with increasing iron(II) concentration (10–50 mM), but the faster stage is unaffected by iron(II). The kinetic results are given in Tables I and II, and the details of the rate laws and mechanistic assignments are discussed below.

**Kinetics of the Faster Stage.** The observed pseudo-first-order rate constants are given in Table I. First of all, it should be noted that this reaction is generally much faster than expected for a

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**Table I.** Kinetic Results for the Faster Reaction of Iron(III) with Ascorbic Acid, 16.1 °C, at  $\mu = 1.0$  M (HClO<sub>4</sub>/NaClO<sub>4</sub>)

10 <sup>3</sup> [Fe <sup>3+</sup> ] <sub>i</sub> <sup>a</sup> M	10 <sup>2</sup> [H <sup>+</sup> ] <sub>i</sub> <sup>b</sup> M	10 <sup>2</sup> [H <sup>+</sup> ] <sub>f</sub> <sup>c</sup> M	k, s <sup>-1</sup>		
			obsd	calcd <sup>d</sup>	calcd <sup>e</sup>
3.00	0.900	0.943	40.5	40.8	44.5
4.00	0.900	0.961	53.1	52.9	54.1
5.00	0.900	0.981	60.9	64.6	63.3
6.00	0.900	1.02	69.5	75.9	72.3
7.00	0.900	1.04	82.0	86.8	80.9
3.00	1.80	1.82	38.8	33.9	38.2
4.00	1.80	1.83	46.0	44.7	46.6
4.00	1.80	1.83	45.9 <sup>f</sup>	44.7	46.6
5.00	1.80	1.84	56.0	55.3	54.7
5.00	1.80	1.84	55.5 <sup>f</sup>	55.3	54.7
6.00	1.80	1.85	66.5	65.6	62.8
6.00	1.80	1.85	65.4 <sup>f</sup>	65.6	62.8
7.00	1.80	1.88	77.1	75.9	70.6
3.00	4.00	4.01	36.0	28.6	33.5
4.00	4.00	4.01	41.8	38.0	40.6
5.00	4.00	4.02	48.4	47.3	47.5
6.00	4.00	4.02	56.9	56.6	54.5
7.00	4.00	4.03	67.9	65.8	61.4
3.00	8.00	8.00	31.9	26.5	31.4
4.00	8.00	8.01	37.8	35.1	37.7
5.00	8.00	8.01	42.9	43.7	44.0
6.00	8.00	8.01	47.9	52.2	50.2
7.00	8.00	8.01	53.2	60.8	56.5
3.00	15.0	15.0	30.9	26.7	30.3
4.00	15.0	15.0	35.5	34.9	36.2
5.00	15.0	15.0	40.9	43.1	42.2
6.00	15.0	15.0	47.1	51.3	48.1
7.00	15.0	15.0	51.2	59.4	54.0

<sup>a</sup>Total iron(III) concentration; total ascorbic acid concentration is  $2 \times 10^{-4}$  M. <sup>b</sup>Initial H<sup>+</sup> added. <sup>c</sup>Calculated final H<sup>+</sup> including that from hydrolysis and dimerization of Fe(OH<sub>2</sub>)<sub>6</sub><sup>3+</sup> as described in the Experimental Section. <sup>d</sup>Calculated from a least-squares fit to eq 1. <sup>e</sup>Calculated from a least-squares fit to eq 4. <sup>f</sup>These runs were done with all reagents in an argon atmosphere.

substitution reaction on aquairon(III) species on the basis of our own experience<sup>1</sup> and that of others.<sup>14-18</sup> This is why the system has been studied at 16 °C rather than the more usual 25 °C and probably explains why there have been no reports on the kinetics of this stage.

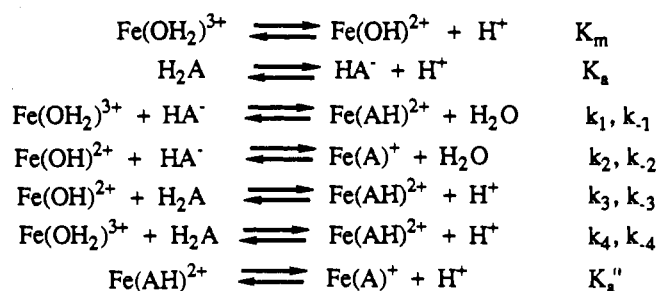
It has been assumed that this is a complexation reaction primarily because the magnitude of the absorbance change shows the expected change with pH and iron(III) and ascorbic acid concentrations.<sup>3</sup> In addition, it is noteworthy that the absorbance maximum at ~550 nm is consistent with an iron(III)-ascorbate complex, since the complex with the closely analogous squaric acid has a maximum at 545 nm.<sup>19</sup> The kinetics of the slower stage discussed below also are consistent with a redox process after initial formation of an iron(III)-ascorbate complex. It seems that something unusual is happening with regard to the substitution stage in the iron(III)-ascorbic acid system.

In order to assess the possibility that this stage might be an outer-sphere redox reaction, we have calculated the outer-sphere rate constants at 25 °C on the basis of a Marcus theory model, which has been found<sup>11</sup> to be successful for ascorbic acid oxidations. We have used an Fe(OH<sub>2</sub>)<sub>6</sub><sup>2+/3+</sup> self-exchange rate of 4 M<sup>-1</sup> s<sup>-1</sup> and the parameters of Macartney and Sutin<sup>11</sup> for calculations at 25 °C: for Fe(OH<sub>2</sub>)<sub>6</sub><sup>3+</sup> + H<sub>2</sub>A,  $k_{os} \approx 0.02$  M<sup>-1</sup> s<sup>-1</sup>; for Fe(OH<sub>2</sub>)<sub>6</sub><sup>3+</sup> + HA<sup>-</sup>,  $k_{os} \approx 1 \times 10^3$  M<sup>-1</sup> s<sup>-1</sup>; for Fe(OH<sub>2</sub>)<sub>6</sub><sup>3+</sup> + A<sup>2-</sup>,  $k_{os} \approx 8 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>. For typical conditions of this study ([Fe(OH<sub>2</sub>)<sub>6</sub><sup>3+</sup>] =  $4 \times 10^{-3}$  M, [H<sup>+</sup>] = 0.04 M), it is possible to calculate half-times for these outer-sphere paths of 9000, 80, and  $2 \times 10^7$  s, respectively, since  $K_{a1}$  and  $K_{a2}$  for ascorbic acid are

**Table II.** Kinetic Results for the Slower Reaction of Iron(III) with Ascorbic Acid, 16.1 °C, 1 M NaClO<sub>4</sub>/HClO<sub>4</sub>

10 <sup>3</sup> [Fe <sup>3+</sup> ] M	10 <sup>2</sup> [H <sup>+</sup> ] <sub>i</sub> <sup>a</sup> M	10 <sup>2</sup> [Fe <sup>2+</sup> ] M	k, s <sup>-1</sup>	
			obsd	calcd <sup>b</sup>
4.00	0.900	0	3.91	3.97
5.00	0.900	0	4.88	4.94
6.00	0.900	0	5.74	5.85
7.00	0.900	0	6.59	6.71
4.00	1.80	0	2.02	1.88
4.00	1.80	0	2.17 <sup>c</sup>	1.88
5.00	1.80	0	2.42	2.42
5.00	1.80	0	2.41 <sup>c</sup>	2.42
6.00	1.80	0	2.94	2.94
6.00	1.80	0	3.00 <sup>c</sup>	2.94
7.00	1.80	0	3.27	3.46
20.00	5.31	0	2.87	2.97
30.00	5.31	0	4.48	4.44
40.00	5.31	0	5.55	5.83
20.00	10.62	0	1.49	1.34
30.00	10.62	0	2.28	2.05
40.00	10.62	0	2.93	2.75
7.00	0.900	1.00	6.03	6.07
7.00	0.900	2.00	5.60	5.54
7.00	0.900	3.00	5.20	5.09
7.00	0.900	4.00	4.94	4.72
7.00	0.900	5.00	4.75	4.39
7.00	1.80	1.00	2.97	3.11
7.00	1.80	2.00	2.76	2.83
7.00	1.80	3.00	2.59	2.60
7.00	1.80	3.00	2.62 <sup>c</sup>	2.60
7.00	1.80	4.00	2.47	2.40
7.00	1.80	4.00	2.48 <sup>c</sup>	2.40
7.00	1.80	5.00	2.36	2.23
7.00	1.80	5.00	2.39 <sup>c</sup>	2.23
40.00	10.62	1.95	2.49	2.52
40.00	10.62	3.89	2.30	2.33
40.00	10.62	5.84	2.06	2.17
40.00	10.62	7.78	1.89	2.02
40.00	10.62	9.73	1.76	1.90

<sup>a</sup>These initial values have been corrected for H<sup>+</sup> formed by hydrolysis and dimerization in the data analysis as described in Table I. <sup>b</sup>Calculated from a least-squares fit to eq 5. <sup>c</sup>These runs were done with all reagents in an argon atmosphere.

**Scheme I**

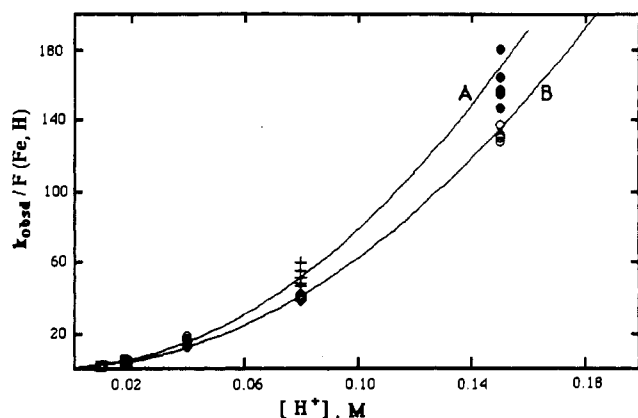
approximately  $9 \times 10^{-5}$  and  $5 \times 10^{-12}$  M, respectively. These outer-sphere reactions are predicted to be  $\sim 5 \times 10^3$  times slower than the first stage. These observations plus those described in the previous paragraph leave one with little alternative but to assume that this is a substitution reaction.

The hydrogen ion dependence of the kinetics of complexation by Fe(OH<sub>2</sub>)<sub>6</sub><sup>3+</sup> are generally described by some combination of the reactions in Scheme I. The rate law for this scheme with [Fe(OH<sub>2</sub>)<sub>6</sub><sup>3+</sup>]  $\gg$  [H<sub>2</sub>A]<sub>tot</sub> is given by eq 1 where  $K_f = [\text{Fe(A)}^+][\text{H}^+]^2 / [\text{Fe(OH}_2\text{)}_6^{3+}][\text{H}_2\text{A}]$  and  $[\text{Fe}^{\text{III}}]_t = [\text{Fe(OH}_2\text{)}_6^{3+}] + [\text{Fe(OH)}_6^{2+}]$ .

$$k_{\text{obsd}} = (k_2 K_m K_a + (k_1 K_a + k_3 K_m)[\text{H}^+] + k_4[\text{H}^+]^2) F(\text{Fe}^{\text{III}}, \text{H}^+) \quad (1)$$

$$F(\text{Fe}^{\text{III}}, \text{H}^+) = \left\{ \frac{[\text{Fe}^{\text{III}}]_t}{(K_m + [\text{H}^+])(K_a + [\text{H}^+])} + \frac{K_a''}{K_f(K_a'' + [\text{H}^+])} \right\}$$

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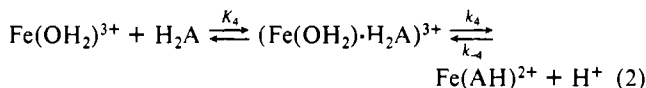
**Figure 1.** Variation of  $k_{\text{obsd}}/F(\text{Fe,H})$  with  $[\text{H}^+]$  for the faster reaction of aqueous iron(III) with ascorbic acid: (A)  $F(\text{Fe,H})$  from eq 1; (B)  $F(\text{Fe,H})$  from eq 4.

The experimental results were fitted by nonlinear least squares to eq 1, initially with the assumption that  $[\text{H}^+] \gg K_a''$ , which would seem most consistent with the observations of Laurence and Ellis.<sup>3</sup> This analysis indicates that the  $k_2K_mK_a$  term is not contributing significantly and gives  $(k_1K_a + k_3K_m) = 93 \pm 23 \text{ s}^{-1}$  and  $k_4 = (6.0 \pm 1.6) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  while only an upper limit is obtained for  $K_a''/K_f \leq 0.015$ . Given the latter result, it is not surprising that the alternative assumption that  $K_a'' \gg [\text{H}^+]$  yields an essentially equivalent fit with  $(k_1K_a + k_3K_m) = 85 \pm 25 \text{ s}^{-1}$ ;  $k_4 = (7.7 \pm 1.3) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , and  $1/K_f \leq 0.01 \text{ M}^{-1}$ . The observed and calculated values are compared in Table I.

It must be noted that the limit on  $K_f/K_a'' \geq 67$  is not consistent with the value of 0.6 determined by Laurence and Ellis.<sup>3</sup> The latter value and  $\epsilon = 11 \text{ M}^{-1} \text{ cm}^{-1}$  would predict that we should not even be able to observe any reaction in the higher acidity range of this study.

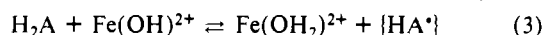
The experimental results are compared to the best-fit curve (A) in Figure 1, where  $k_{\text{obsd}}$  has been divided by the right-hand term in braces in eq 1 to give a function that should be independent of  $[\text{Fe}^{\text{III}}]_t$ . It is apparent from Figure 1 that eq 1 generally describes the trend of  $k_{\text{obsd}}$  with  $[\text{H}^+]$ , but the spread of points at 0.08 and 0.15 M  $\text{H}^+$  indicates that the variation with  $[\text{Fe}^{\text{III}}]_t$  at constant  $[\text{H}^+]$  is not entirely accounted for by eq 1. These deviations reduce the quality of the fit and account for the rather large error limits on the fitting parameters. It is of greater concern that the deviations are systematic with points at low  $[\text{Fe}^{\text{III}}]_t$  consistently above the curve and the range increases as the  $[\text{H}^+]$  increases.

A model involving preassociation complexes will account for the numerical shortcomings mentioned above, but it requires rather unrealistic values for the formation constants for the preassociation complexes. For example, the dominant path at higher acidities, which is shown in eq 2, requires  $K_4 \approx 80 \text{ M}^{-1}$  to fully explain the



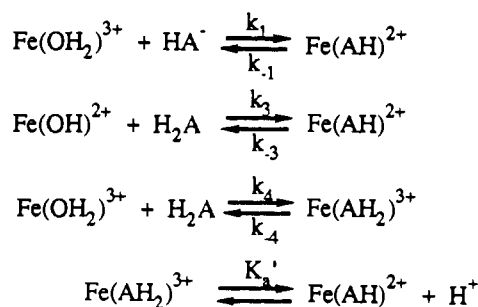
$[\text{Fe}^{\text{III}}]_t$  dependence. Mentastil<sup>17</sup> has estimated that an ion dipole interaction such as that involved in eq 2 would predict  $K_4 \approx 0.2 \text{ M}^{-1}$ . Although these estimates are open to question, they have been found to be reasonably successful in interpreting the substitution kinetics on  $\text{Ni}(\text{OH}_2)_6^{2+}$  and it seems unlikely that they would be off by a factor of 400.

Another model that has been considered involves essentially iron(II)-catalyzed substitution after an initial H atom transfer reaction shown in eq 3. This step would be followed by proton



dissociation to give  $\{\text{A}^*\}^-$ , which must then complex with  $\text{Fe}(\text{OH}_2)_6^{2+}$ . This complex must undergo intramolecular oxidation of iron(II) to give the iron(III) complex  $\text{Fe}^{\text{III}}(\text{A}^{2-})$ . Thermodynamic considerations indicate that such a mechanism is possible if the latter complex has a formation constant similar to that of

## Scheme II



iron(III) catecholates. It requires that  $\{\text{A}^*\}^-$  cannot be free in solution, where it would simply be oxidized by the iron(III) present, and must substitute on iron(II) within the successor complex in eq 3. Recent work<sup>20</sup> indicates that this could be an Fe-C-bonded species, which has been identified in  $\text{Fe}(\text{NTA})$  type systems but not in aquairon systems. However this mechanism is not consistent with the  $[\text{H}^+]$  dependence of our observed rate constants because it requires  $\text{Fe}(\text{OH})^{2+}$  as the sole reactant.

The final model we have considered involves formation of a fully protonated complex of ascorbic acid and aquairon(III) as shown in Scheme II. The  $k_2$  path has been omitted from Scheme II because the previous analysis indicated that it did not contribute. The predicted pseudo-first-order rate constant is given by eq 4

$$k_{\text{obsd}} = ((k_1K_a + k_3K_m)[\text{H}^+] + k_4[\text{H}^+]^2)F(\text{Fe}^{\text{III}},\text{H}^+) \quad (4)$$

$$F(\text{Fe}^{\text{III}},\text{H}^+) = \left\{ \frac{[\text{Fe}^{\text{III}}]_t}{(K_m + [\text{H}^+])(K_a + [\text{H}^+])} + \frac{K_a'}{K_{f1}[\text{H}^+](K_a' + [\text{H}^+])} \right\}$$

where  $K_{f1} = [\text{Fe}(\text{AH})^{2+}][\text{H}^+]/\text{Fe}(\text{OH}_2)^{3+}[\text{H}_2\text{A}]$ . This equation gives an excellent least-squares fit of the data, as can be seen from curve B in Figure 1, and the calculated values in Table I. The best-fit parameters are  $(k_1K_a + k_3K_m) = 74 \pm 9 \text{ s}^{-1}$ ,  $k_4 = (5.48 \pm 0.9) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ,  $K_a'/K_{f1} = (2.3 \pm 1.1) \times 10^{-3} \text{ M}$ , and  $K_a' = 0.015 \pm 0.05 \text{ M}$ . Parameter correlation causes the latter two values to be rather poorly defined, but the standard error of this fit is 20% smaller than when it is assumed that  $[\text{H}^+] \gg K_a'$ .

The unexpected feature of Scheme II is the formation of the fully protonated ascorbic acid complex  $\text{Fe}(\text{AH}_2)^{3+}$  with a formation constant of  $\sim 4 \times 10^2 \text{ M}^{-1}$  ( $K_{f1}/K_a'$ ). It is only possible to estimate  $K_{f1}$  because of the uncertainties in  $K_a'/K_{f1}$  and  $K_a'$ , which give  $K_{f1}$  between 3 and 16 compared to 0.6 obtained by Laurence and Ellis.<sup>3</sup> The agreement is probably not unreasonable considering the difficulties in the determination in both this and the earlier work.

The value of  $k_4 = 5.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  for ascorbic acid is unprecedented, since previous studies on 1,2-dihydroxybenzene ligands,<sup>14</sup> which are formally analogous to ascorbic acid, have always indicated an undetectably small contribution for the reaction of the protonated ligand ( $\text{H}_2\text{L}$ ) with  $\text{Fe}(\text{OH}_2)^{3+}$  ( $k_4$ ). For example, Tiron (1,2-dihydroxy-3,5-benzenesulfonate) has  $k_4 \ll 10 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C, and the contribution could not be detected even though the study<sup>1</sup> extended to 0.7 M  $\text{H}^+$ . For acetic acid derivatives, rate constants of the order of  $10 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C have been reported.<sup>15</sup> However substitution on  $\text{Fe}(\text{OH}_2)^{3+}$  is thought to be by an associative mechanism<sup>18,21</sup> so that comparisons between different ligands are difficult. The implication of the magnitude of  $k_4$  is that ascorbic acid is a much better nucleophile toward  $\text{Fe}(\text{OH}_2)^{3+}$  than might have been expected.

The value of  $(k_1K_a + k_3K_m)$  requires that  $k_1 \approx 2.9 \times 10^5$  and  $k_3 \approx 2.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  if both terms contribute equally or that one of them be twice this value if the other is much smaller.

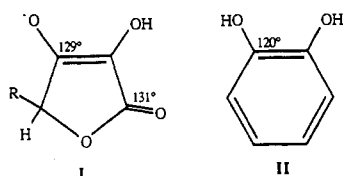
(20) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1988**, *27*, 3429. These authors note that they are unable to reproduce the earlier report of  $(\text{H}_2\text{O})_4\text{Fe}-\text{CH}(\text{CH}_3)_2\text{OH}^{2+}$  (Pribush, A. G.; Brunseneva, S. A.; Shubin, V. N.; Dolin, P. I. *High Energy Chem. (Engl. Transl.)* **1975**, *9*, 206).

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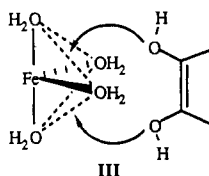
Mentasti and co-workers<sup>14</sup> have found for catechols that  $k_3$  values are in a narrow range around  $2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C. The results of Cavasino and Di Dio<sup>16</sup> on phenolate complexes indicate that the only significant pathway corresponds to  $k_3$  again with values of  $\sim 2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ . Mentasti<sup>17</sup> has come to a similar conclusion for several  $\alpha$ -hydroxy carboxylic acids which have  $k_3 \approx 4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ . On the other hand, Lappin and McAuley<sup>22</sup> found that the reaction of mercaptoacetic acid with  $\text{Fe}(\text{OH})^{2+}$  has a rate constant of  $2.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  at 15 °C and the value drops to  $1.1 \times 10^3$  with two methyl groups on the mercapto carbon in 2-mercapto-2-methylpropanoic acid. Therefore the value of  $k_3$  for the ascorbic acid system is not beyond the realm of previous observations.

The expected magnitude of  $k_1$  is uncertain because of the mechanism probably being associative in nature<sup>18,21</sup> and because of the proton ambiguity in separating  $k_1$  and  $k_3$ .<sup>15</sup> If  $k_1 \approx 3 \times 10^5$ , then it is in the same range as possible values for carboxylate anions, but the latter are more reasonably assigned to the  $k_3$  path.<sup>15</sup>

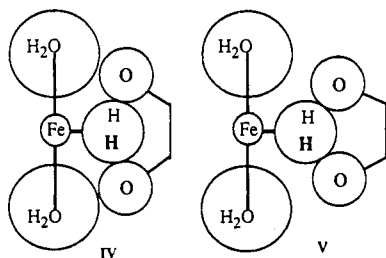
The above analysis of the rate constants gives a quantitative basis for the initial qualitative observation that this stage is unusually fast for substitution on aquairon(III). The most obvious structural difference between ascorbic acid and the 1,2-dihydroxybenzene derivatives is the bite distance of the coordinating oxygens. In ascorbic acid and its sodium salt<sup>23</sup> this is  $\sim 3.0 \text{ \AA}$  for either pair of oxygens, while it is  $\sim 2.65 \text{ \AA}$  in catechol.<sup>24</sup> This difference results mainly from the greater O-C bond angle in ascorbate compared to catechol, as shown in structures I and II, respectively.



The larger distance allows the entering ligand to approach more easily over an octahedral edge with two oxygens simultaneously moving toward the center of separate octahedral faces where they have the most favorable interaction with the iron(III) in a precursor complex or transition state as shown in III.

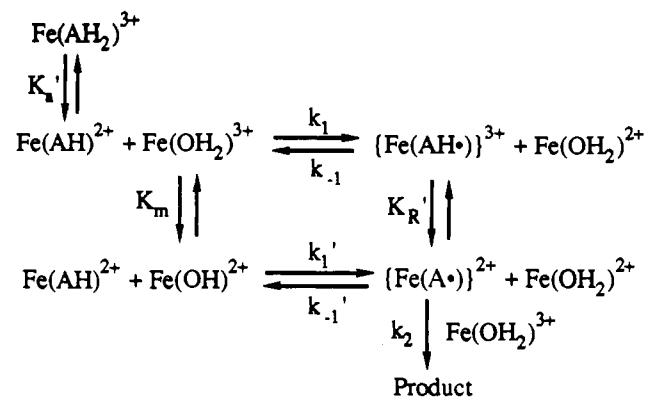


The possible significance of this structural difference is illustrated in the scale diagrams IV and V, which have the O-O separations of ascorbate and catecholate, respectively. The critical



excluded volume at the center of the octahedral edge has been assumed to have a radius equal to the sum of the covalent radii of two hydrogens on the basis of the idea that there could be one H above and another below the line on the octahedral edge joining the two water ligands. The Fe-O and C-O bond lengths of 2.0

## Scheme III



and 1.3 Å, respectively, are representative values from known structures.<sup>23,24</sup> Simple geometry shows that the Fe is 1.4 Å from the center of the octahedral edge. A diameter for a coordinated water molecule of 2.4 Å has been assumed.<sup>25</sup> Structure IV indicates that it is quite possible for ascorbic acid to simultaneously position two oxygen atoms at the centers of two octahedral faces while catechol cannot achieve such a favorable position. Clearly, the extent of the interaction depends on the excluded volume at the center of the octahedral edge, but ascorbic acid will always have an advantage unless this volume is much smaller than we have assumed.

**Kinetics of the Slower Stage.** The kinetics have been studied at 560 nm as a function of the concentration of iron(III) ( $4 \times 10^{-3}$ – $4 \times 10^{-2} \text{ M}$ ), hydrogen ion ( $9 \times 10^{-3}$ – $0.106 \text{ M}$ ), and iron(II) ( $1 \times 10^{-2}$ – $5 \times 10^{-2} \text{ M}$ ) with  $2 \times 10^{-4} \text{ M}$  ascorbic acid. The results are given in Table II. In general, the rate increases with increasing iron(III) and decreases with increasing hydrogen ion and iron(II) concentrations. In addition, it has been found that the rate is the same if the reaction occurs in an atmosphere of air or argon. The latter is not inconsistent with earlier observations<sup>26</sup> because our conditions are such that  $[\text{iron(III)}] \gg [\text{ascorbic acid}]$ . The experimental results in Table II are consistent with the rate law predicted by the reactions in Scheme III.

Scheme III was arrived at from preliminary observation of the dependence of the pseudo-first-order rate constant ( $k_{\text{obsd}}$ ) on  $[\text{Fe}(\text{OH}_2)^{3+}]$  and  $[\text{H}^+]$  in the absence of iron(II) and the essentially inverse first-order dependence of  $k_{\text{obsd}}$  on  $[\text{Fe}^{2+}]$ . It should be noted that the  $k_1'$  path, which involves oxidation by  $\text{Fe}(\text{OH})^{2+}$ , could also be attributed to reaction of  $\text{Fe}(\text{A})^+$  but the latter species was not implicated by the substitution reaction; therefore we prefer the assignment shown in Scheme III. The  $k_1'$  path could proceed by H atom transfer rather than electron transfer.

If the initial complexation and proton dissociation reactions are treated as rapidly established equilibria and a steady state is assumed for the radical species, then the predicted rate law is given by eq 5, which has been simplified by using the relationship

$$k_{\text{obsd}} = \left\{ \frac{(k_1 + k_1'K_m[\text{H}^+]^{-1})[\text{Fe}^{3+}]^2}{k_1'k_2K_m(k_1 + k_1'K_m[\text{H}^+]^{-1})[\text{H}^+][\text{Fe}^{2+}] + [\text{Fe}^{3+}]} \right\} \times \left\{ \frac{K_{f1}[\text{Fe}^{3+}]}{(K_a + [\text{H}^+]) + (K_{f1}/K_a')[\text{Fe}^{3+}](K_a' + [\text{H}^+])} \right\} \quad (5)$$

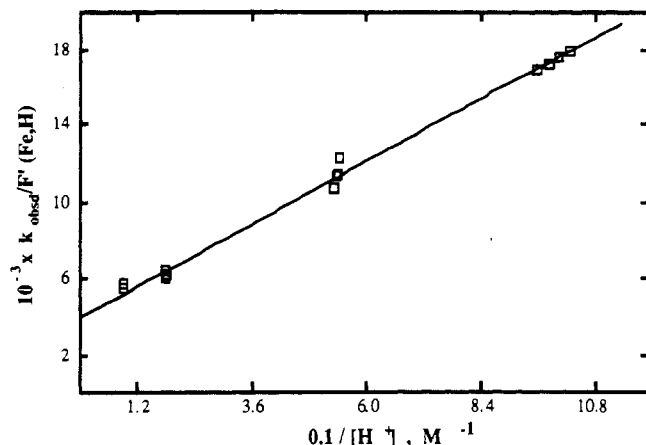
$k_1K_R/k_{-1} = k_1'K_m/k_{-1}'$ . In eq 5,  $K_{f1}$  is as defined for eq 4 and  $[\text{Fe}^{3+}]$  is the concentration of  $\text{Fe}(\text{OH}_2)_6^{3+}$  calculated as described in the Experimental Section.

When  $[\text{Fe}^{2+}] = 0$ , then eq 5 predicts that the plot shown in Figure 2 should be linear with an intercept of  $k_1K_{f1}$  and slope of  $k_1'K_mK_{f1}$ . Clearly, this prediction is verified by the data and

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**Figure 2.** Variation of  $k_{\text{obsd}}/F'(\text{Fe,H})$  with  $[\text{H}^+]^{-1}$  for the slower reaction of aqueous iron(III) with ascorbic acid for runs without added iron(II), where  $F'(\text{Fe,H}) = [\text{Fe}^{3+}]^2 / \{K_a + [\text{H}^+] + (K_{\text{fl}}/K_a')[\text{Fe}^{3+}](K_a' + [\text{H}^+])\}$  derived from eq 5.

the intercept and slope are well defined. A nonlinear least-squares analysis of all the data in Table II by eq 5 gives the following parameters:  $k_1 K_{\text{fl}} = (3.8 \pm 0.3) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_1' K_{\text{m}} K_{\text{fl}} = (1.39 \pm 0.11) \times 10^2$ ;  $k_1'/k_2 = (4.5 \pm 1.0) \times 10^{-2}$ . The calculated and observed values of  $k$  are compared in Table II.

The ratio of the first and second parameters gives  $k_1/k_1' = 2.7 \times 10^{-2}$ , and this ratio and the third parameter can be used to calculate  $k_1/k_2 = 1.2K_{\text{R}}'$ . Since it is known that the radical  $\text{AH}^\cdot$  has a  $\text{p}K_{\text{a}} \approx -0.45$ ,<sup>27</sup> it seems probable that  $K_{\text{R}}'$  is about 1, so that  $k_{-1}/k_2$  is of the order of 1 and  $k_{-1}/k_{-1}' \approx 20$ . This ratio is consistent with the fact that  $\text{AH}^\cdot$  is a stronger oxidizing agent than  $\text{A}^-$ .<sup>10,11</sup>

The value of  $k_1/k_1' = 2.7 \times 10^{-2}$  indicates that  $\text{Fe}(\text{OH})_2^{2+}$  is more reactive than  $\text{Fe}(\text{OH})_2^{3+}$  in the first electron-transfer step. This seems surprising because the latter is a stronger oxidizing agent; however the same effect has been seen in the study of the oxidation of 1,2-dihydroxybenzoic acid<sup>2</sup> where the ratio is  $0.9 \times 10^{-2}$ . The previous explanation, that the greater substitution lability of  $\text{Fe}(\text{OH})_2^{2+}$  facilitates an inner-sphere electron-transfer path, would seem to be equally applicable to the ascorbic acid system.

The mechanism in Scheme III is analogous to that for 1,2-dihydroxybenzoic acid<sup>2</sup> in that the iron(III)-ligand complex is oxidized by a second iron(III) rather than undergoing intramolecular electron transfer. Since both studies were done with excess iron(III), this does not necessarily mean that intramolecular electron transfer cannot occur, but it must be slow enough so that the second-order intermolecular process can compete effectively at iron(III) concentrations in the millimolar range. A consideration of the reduction potentials for  $\text{Fe}^{3+}/\text{Fe}^{2+}$  (0.77 V),  $\text{H}_2\text{A}^{\cdot+}/\text{H}_2\text{A}$  (1.17 V), and  $\text{HA}^\cdot/\text{HA}^-$  (0.71 V)<sup>11</sup> shows that  $\text{H}_2\text{A}$  is not a strong enough reducing agent to reduce  $\text{Fe}(\text{OH})_2^{3+}$  and the situation is marginal with  $\text{HA}^\cdot$ . The reducing power of the ligand would be decreased by complexation, so that the initial intramolecular electron transfer would be thermodynamically unfavorable.

It is of interest to compare the present results to those of Hynes and Kelly<sup>9</sup> on the slower reaction. The latter authors observed the system at 330 nm with  $[\text{ascorbic acid}] \gg [\text{iron(III)}]$  and found

that the  $[\text{H}^+]$  dependence of the rate is consistent with an apparent outer-sphere reduction mechanism for  $\text{H}_2\text{A}$  and  $\text{HA}^-$  with rate constants of  $7.3$  and  $6.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , respectively.<sup>28</sup> These values are larger by 350 and 60 times,<sup>29</sup> respectively, than the outer-sphere constants calculated above, but such deviations are not sufficient grounds to negate the interpretation. However Hynes and Kelly do not indicate that any correction has been made for complex formation, which affects the stoichiometric concentrations and therefore the experimental rate law, even if the complexes are not on the reaction pathway. For the conditions of  $[\text{ascorbic acid}] \gg [\text{iron(III)}]$  used by Hynes and Kelly, the mechanism in Scheme III may not be applicable because radical intermediates may react with free ascorbic acid rather than iron(II). It is interesting to note that, if we disregard complexation, iron(II) hydrolysis, and iron(II) inhibition, the first 14 entries in Table II give  $k_{\text{obsd}} = 7.7[\text{iron(III)}]/[\text{H}^+]$  and one might divide the 7.7 by the  $K_{\text{a}}$  of ascorbic acid to obtain an apparent rate constant of  $8.2 \times 10^4$  for the oxidation of  $\text{HA}^-$ . This value is reasonably close to the  $6.1 \times 10^4$  reported by Hynes and Kelly and implies that the two studies are not in major disagreement as to the reactivity time scale for the oxidation step. We conclude that the  $k$ 's calculated by Hynes and Kelly are complex quotients rather than the specific rate constants implied in their conclusions.

### Experimental Section

**Materials.** Solutions of iron(III) perchlorate in perchloric acid were prepared and standardized as described previously.<sup>1</sup> Solutions of iron(II) were prepared by dissolving ferrous ammonium sulfate in excess perchloric acid and stored under argon as described elsewhere.<sup>2</sup> Solutions of L-ascorbic acid (Eastman Kodak) were prepared by weight immediately before use.

**Kinetic Measurements.** The observations were done on the modified Aminco-Morrow system used previously.<sup>1,2</sup> Reported rate constants are the average of at least eight replicate determinations. The optimum observation wavelength of 560 nm was determined from preliminary experiments on a Hewlett-Packard 8451 diode array spectrophotometer. Experiments in the absence of dioxygen were done by passing argon through solutions protected by serum caps for at least 90 min, and solutions were handled subsequently by standard syringe techniques.

For all of the results reported, the concentrations of  $\text{Fe}(\text{OH})_2^{2+}$ ,  $\text{Fe}(\text{OH})_2^{3+}$ , and  $\text{Fe}_2(\text{OH})_2^{4+}$  have been calculated from the appropriate equilibrium constants<sup>30</sup> at 16 °C and the amount of  $\text{H}^+$  added has been corrected for formation of these iron(III) species. The amount of  $\text{Fe}_2(\text{OH})_2^{4+}$  in the stock solution was calculated before mixing, and this was assumed to be simply diluted by a factor of 2 after mixing because of its relative kinetic stability.<sup>31</sup> These corrections generally are minor and  $\sim 10\%$  for the worst conditions at low acidity and high iron(III) concentration. The initial and corrected  $[\text{H}^+]$  are given for the runs in Table I. The data of Kimura et al.<sup>32</sup> indicate  $K_{\text{a}1} = 0.94 \times 10^{-4} \text{ M}$  for ascorbic acid at 16 °C in 1.0 M  $\text{NaClO}_4$ . Since  $K_{\text{a}1} \ll [\text{H}^+]$ , uncertainty in this value does not affect our rate law analysis.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada for financial support. J.X. thanks the Beijing Medical University for granting a study leave.

**Registry No.**  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ , 15377-81-8; ascorbic acid, 50-81-7.

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