

117229-22-8;  $C_6H_4CO(CO)NCH_2COCH_3$ , 3416-57-7; *p*-[Co(tren)- $[NH_2CH_2CH(OH)]_2Cl$ ](ClO<sub>4</sub>), 52675-78-2;  $H_2NCH_2CH(OC_2H_5)_2$ , 645-36-3; [Co(tren)Cl<sub>2</sub>](ClO<sub>4</sub>), 33393-50-9; *p*-[Co(tren)(NH<sub>2</sub>CH<sub>2</sub>-(CH<sub>3</sub>)COCH<sub>2</sub>CH<sub>2</sub>O)Cl](ClO<sub>4</sub>)<sub>2</sub>, 117229-04-6; *p*-[Co(tren)-(NH<sub>2</sub>CH<sub>2</sub>COCH<sub>2</sub>)Cl](ClO<sub>4</sub>)<sub>2</sub>, 117229-06-8; *i*-[Co(trenpnim)Cl](ClO<sub>4</sub>)<sub>2</sub>, 117229-08-0; NH<sub>2</sub>CH<sub>2</sub>COCH<sub>3</sub>, 298-08-8; *s*-(SR,RS)-[Co(trenpn)Cl](ClO<sub>4</sub>)<sub>2</sub>, 117229-10-4; *p*-[Co(tren)(NH<sub>2</sub>CH<sub>2</sub>CH(C<sub>6</sub>H<sub>5</sub>)OH)Cl](ClO<sub>4</sub>)<sub>2</sub>, 117229-12-6; *p*-[Co(tren)(H<sub>2</sub>NCH<sub>2</sub>COC<sub>6</sub>H<sub>5</sub>)Cl](ClO<sub>4</sub>)<sub>2</sub>, 117229-14-8; H<sub>2</sub>NCH<sub>2</sub>COC<sub>6</sub>H<sub>5</sub>, 613-89-8; *s*-[Co(trenphenol)Cl](ClO<sub>4</sub>)<sub>2</sub>, 117229-16-0; *i*-[Co(trenphenim)Cl](ClO<sub>4</sub>)<sub>2</sub>, 117229-18-2; *s*-[Co(trenphen)Cl](ClO<sub>4</sub>)<sub>2</sub>, 117229-20-6; *β-p-Δ(R,Δ(S))*-[Co(tren)(H<sub>2</sub>NCH<sub>2</sub>CH(OCH<sub>2</sub>CH<sub>3</sub>))<sub>2</sub>Cl]Br<sub>2</sub>, 117229-21-7; *β-p-(RR(SS))*-[Co(tren)(H<sub>2</sub>NCH<sub>2</sub>CH(OH))<sub>2</sub>Cl]Cl<sub>2</sub>, 117229-23-9; *αβ-i*-[Co(tetraenim)Cl](ClO<sub>4</sub>)<sub>2</sub>, 117229-25-1; H<sub>2</sub>NCH<sub>2</sub>CH(OH)<sub>2</sub>, 117229-01-3; *αβ-Δ(S,Δ(R))*-[Co(tetraen)Cl]<sup>2+</sup>, 16961-56-1; *αβ-Δ(R,Δ(S))*-[Co(tetraen)Cl]<sup>2+</sup>, 117306-66-8; *αβ-i*-[Co(tetraenim)NO<sub>2</sub>]ZnCl<sub>4</sub>, 117229-27-3; *αβ-p*-[Co(tetraenim)Cl](ClO<sub>4</sub>)<sub>2</sub>, 117306-68-0; *αβ-Δ(S,Δ(R))*-[Co(tetraen)NO<sub>2</sub>]<sup>2+</sup>, 117306-69-1; *αβ-Δ(R,Δ(S))*-[Co(tetraen)NO<sub>2</sub>]<sup>2+</sup>, 117306-70-4; *α*-[Co(tren){H<sub>2</sub>NCH<sub>2</sub>-

(CH<sub>3</sub>)C(OCH<sub>2</sub>CH<sub>2</sub>O)}Cl]Br<sub>2</sub>, 117229-28-4; *α*-[Co(tren)(H<sub>2</sub>NCH<sub>2</sub>COCH<sub>3</sub>)Cl](ClO<sub>4</sub>)<sub>2</sub>, 117229-30-8; *αβ-s*-[Co(Metetraenim)Cl](ClO<sub>4</sub>)<sub>2</sub>, 117229-32-0; [Co(Metetraen)Cl](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (isomer T), 117229-35-3; [Co(Metetraen)Cl](ClO<sub>4</sub>)<sub>2</sub> (isomer N), 117306-72-6; *αβ-s*-[Co(Metetraenim)NO<sub>2</sub>]ZnCl<sub>4</sub>, 117229-37-5; *αα*-[Co(tetraen)Cl]<sup>2+</sup>, 16961-55-0; potassium phthalimide, 1074-82-4; chloroacetone, 78-95-5; 2-(phthalimidomethyl)-2-methyl-1,3-dioxolane, 1775-18-4; ethane-1,2-diol, 107-21-1; 2-methyl-2-(aminomethyl)-1,3-dioxolane, 3289-19-8.

**Supplementary Material Available:** Listings of anisotropic thermal parameters (Tables SUP-1 and SUP-2), hydrogen atom parameters (Tables SUP-3 and SUP-4), ligand and anion geometries (Tables SUP-5-SUP-7), ligand string torsion angles (Table SUP-8), and cyclization (Table SUP-9) and carbinolamine dehydration rate constants (Table SUP-10) (13 pages); listings of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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University of Alberta, Edmonton, Alberta, Canada T6G 2G2

## Kinetics and Mechanism of the Oxidation of 2,3-Dihydroxybenzoic Acid by Iron(III)

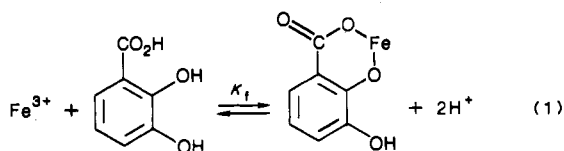
Jinhuang Xu and R. B. Jordan\*

Received November 23, 1987

The kinetics of the oxidation of 2,3-dihydroxybenzoic acid (DHB) by aqueous iron(III) have been studied in aqueous acid with [Fe(III)] ≫ [DHB]. The initial complexation reaction of Fe(OH<sub>2</sub>)<sub>6</sub><sup>3+</sup> and DHB was studied previously. The iron(III)-DHB complex is oxidized by iron(III) with a rate law that is first order in iron(III) and has terms that are inverse first order in [H<sup>+</sup>] and inverse second order in [Fe(OH<sub>2</sub>)<sub>6</sub><sup>2+</sup>]. It is shown that the oxidation does not proceed by simple intramolecular electron transfer within the iron(III)-DHB complex. A mechanism is proposed in which the latter complex reacts first by substitution on free iron(III) followed by two reversible electron-transfer steps to give the quinone product.

### Introduction

In a previous paper<sup>1</sup> it was reported that, in acidic aqueous solution, 2,3-dihydroxybenzoic acid (DHB) reacts with hexaaquairon(III) in three stages. The initially colorless solution turns blue and then yellow within a few minutes and finally brown after several hours. The colorless to blue stage was identified with the formation of an iron(III)-DHB complex as shown in eq 1. The



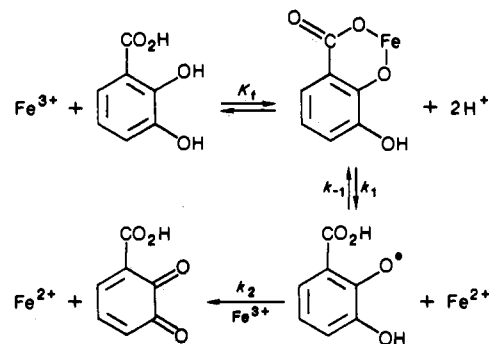
equilibrium constant for eq 1 was found to be 7.0 M (25 °C, 1 M NaClO<sub>4</sub>, HClO<sub>4</sub>). The magnitude of the equilibrium constant was found to be most consistent with the salicylate mode of complexation shown in eq 1. The kinetics of the complexation reaction were reported previously.<sup>1</sup>

A kinetic study of the second stage of the reaction (blue to yellow) is reported here. It is shown that iron(II) is produced during this stage so that it is an oxidation-reduction process. This is expected from other studies which have shown that 1,2-dihydroxybenzene systems are oxidized to the corresponding quinone by hexaaquairon(III)<sup>2,3</sup> and other oxidizing agents.<sup>4</sup>

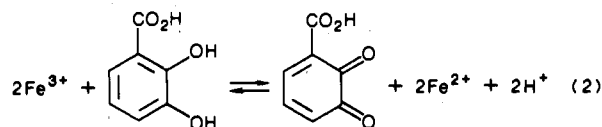
### Results and Discussion

A study of the reaction stoichiometry under conditions of [Fe(III)] ≫ [DHB] shows that 2 mol of iron(II) are produced/mol

### Scheme I



of DHB initially present. These observations are consistent with the overall oxidation of DHB to the quinone as shown in eq 2.



The blue to yellow color change that accompanies the reaction is observed spectrophotometrically as a decrease in absorbance in the region of the initial 600-nm maximum, with a corresponding increase in absorbance at 400 nm and an isosbestic point at 506 nm. The reaction kinetics have been studied as a function of the concentration of iron(III), iron(II) and H<sup>+</sup>, always with [Fe(III)] ≫ [DHB]. The results are summarized in Table I.

Under the concentration conditions of this study, the complexation reaction (eq 1) is known<sup>1</sup> to be at least 25 times faster than the redox reaction. Therefore the complexation can be viewed as a rapid preequilibrium. It should be noted also that the DHB is more than 95% complexed for all but 6 of the 28 different concentration conditions listed in Table I.

The first 11 runs in Table I show that the apparent pseudo-first-order rate constant (*k*<sub>obs</sub>) decreases as the [H<sup>+</sup>] increases.

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- (a) Pelizzetti, E.; Mentasti, E. *Z. Phys. Chem. (Munich)* **1977**, *105*, 21.  
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**Table I.** Kinetic Data for the Oxidation of 2,3-Dihydroxybenzoic Acid by Iron(III) at 25 °C in 1.0 M NaClO<sub>4</sub>-HClO<sub>4</sub>

10 <sup>2</sup> [H <sup>+</sup> ], M	10 <sup>3</sup> [Fe(III)], M	10 <sup>3</sup> [Fe(II)], M	10 <sup>2</sup> k, s <sup>-1</sup>	
			obsd <sup>a</sup>	calcd <sup>c</sup>
0.736	2.53	0.00	7.74	8.34
1.00	2.53	0.00	6.74	6.90
1.25	2.53	0.00	6.07	5.88
1.54	2.53	0.00	5.02	5.00
2.00	2.53	0.00	3.96	4.04
3.00	2.53	0.00	2.74	2.85
4.00	2.53	0.00	2.15	2.19
5.00	2.53	0.00	1.70	1.77
6.00	2.53	0.00	1.45	1.47
8.00	2.53	0.00	1.06	1.06
10.00	2.53	0.00	0.84	0.80
1.00	2.00	0.00	5.03	5.49
1.00	2.00	0.00	5.09 <sup>b</sup>	5.49
1.00	3.00	0.00	8.14	8.14
1.00	3.00	0.00	8.08 <sup>b</sup>	8.14
1.00	4.00	0.00	11.2	10.71
1.00	4.00	0.00	11.2 <sup>b</sup>	10.71
1.00	5.00	0.00	14.1	13.20
1.00	5.00	0.00	14.1 <sup>b</sup>	13.20
1.00	6.00	0.00	17.3	15.63
2.00	2.00	0.00	3.07	3.18
2.00	3.00	0.00	4.89	4.80
2.00	4.00	0.00	6.66	6.41
2.00	5.00	0.00	8.50	8.01
2.00	6.00	0.00	10.4	9.60
2.00	5.00	4.87	0.87 <sup>b</sup>	0.96
2.00	5.00	3.89	1.39 <sup>b</sup>	1.41
2.00	5.00	2.92	2.43 <sup>b</sup>	2.20
2.00	5.00	1.95	3.86 <sup>b</sup>	3.68
3.00	5.00	2.92	1.70 <sup>b</sup>	1.56
3.00	5.00	1.95	2.65 <sup>b</sup>	2.62
3.00	5.00	0.97	3.89 <sup>b</sup>	4.43

<sup>a</sup>Three figures are carried to avoid round-off errors in the fitting.

<sup>b</sup>Solutions were deoxygenated by bubbling argon and handled with syringes under an argon atmosphere. <sup>c</sup>Calculated from a least-squares best fit to eq 4.

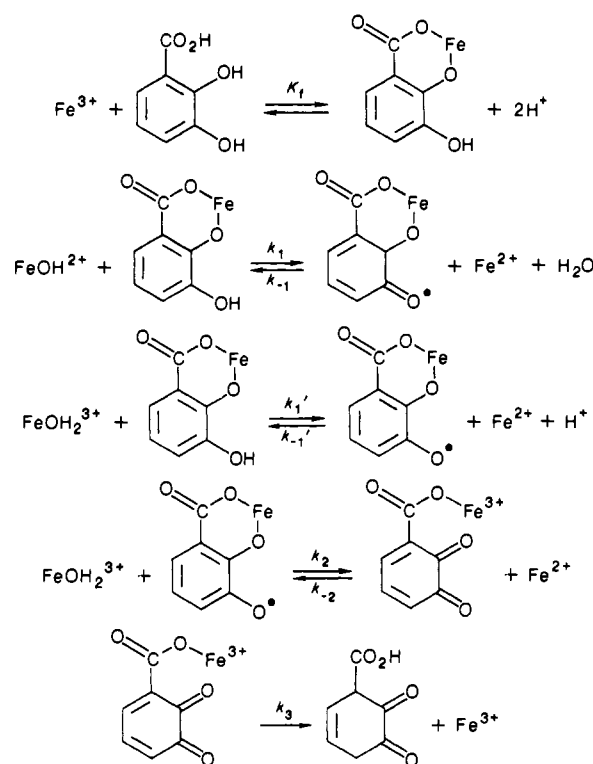
This might be due to decreased complex formation at higher [H<sup>+</sup>] (eq 1) and/or reactivity of (H<sub>2</sub>O)<sub>5</sub>FeOH<sup>2+</sup>. The following 10 runs show that *k*<sub>obsd</sub> increases with increasing [Fe(III)] at two different acidities. In the remaining runs, iron(II) was added to the initial iron(III) solution, and this caused a decrease in *k*<sub>obsd</sub> with increasing [Fe(II)]. At higher [Fe(III)] values the *k*<sub>obsd</sub> seems to have an inverse second-order dependence on [Fe(II)].

The simplest mechanism that one might expect for this system is shown in Scheme I. This involves intramolecular electron transfer within the iron(III)-DHB complex to give iron(II) and the DHB radical. The latter would be oxidized by the excess iron(III) to the quinone product. If a steady state is assumed for the organic radical, then the predicted pseudo-first-order rate constant is given by eq 3. Then *k*<sub>calcd</sub> is predicted to be inde-

$$k_{\text{calcd}} = \left( \frac{K_f[\text{Fe}(\text{OH})_2]_6^{3+}}{K_f[\text{Fe}(\text{OH})_2]_6^{3+} + [\text{H}^+]^2} \right) \left( \frac{k_1 k_2 [\text{Fe}(\text{OH})_2]_6^{3+}}{k_1 [\text{Fe}^{2+}] + k_2 [\text{Fe}(\text{OH})_2]_6^{3+}} \right) \quad (3)$$

pendent of [Fe(OH)<sub>2</sub>]<sub>6</sub><sup>3+</sup> when *K*<sub>f</sub>[Fe(OH)<sub>2</sub>]<sub>6</sub><sup>3+</sup> ≫ [H<sup>+</sup>]<sup>2</sup> and *k*<sub>2</sub>[Fe(OH)<sub>2</sub>]<sub>6</sub><sup>3+</sup> ≫ *k*<sub>-1</sub>[Fe<sup>2+</sup>]. The latter condition is obeyed for [Fe<sup>2+</sup>] = 0, and the former is true for many of the runs in Table I, yet the reaction is first order in [Fe(OH)<sub>2</sub>]<sub>6</sub><sup>3+</sup>. In addition to this major inconsistency, Scheme I does not explain the higher than inverse first-order dependence on [Fe<sup>2+</sup>] or the [H<sup>+</sup>] dependence. The observed hydrogen ion dependence could be predicted by Scheme I if the Fe(III) in the *k*<sub>2</sub> step was (H<sub>2</sub>O)<sub>5</sub>FeOH<sup>2+</sup>. However, that seems unreasonable because Fe(OH)<sub>2</sub><sub>6</sub><sup>3+</sup> is by far the dominant form and the stronger oxidizing agent.

The above observation concerning (H<sub>2</sub>O)<sub>5</sub>FeOH<sup>2+</sup> as a means to explain the [H<sup>+</sup>] dependence is a clue toward a reaction scheme

**Scheme II**

that will explain the results. It was also helpful to know that a major difference between Fe(OH)<sub>2</sub><sub>6</sub><sup>3+</sup> and (H<sub>2</sub>O)<sub>5</sub>FeOH<sup>2+</sup> is that the latter is much more labile to substitution.<sup>5,6</sup> Finally, the inverse second-order term in [Fe(II)] requires two reversible reactions that produce iron(II) in the reaction sequence. A reaction scheme that incorporates these features is shown in Scheme II.

For Scheme II, the predicted pseudo-first-order rate constant is given by eq 4. In eq 4 substitution has been made for *k*<sub>-1</sub>' = *k*<sub>1</sub>'*k*<sub>-1</sub>/*k*<sub>1</sub>*K*<sub>m</sub>.

$$k_{\text{calcd}} = \{K_f[\text{Fe}(\text{OH})_2]_6^{3+} / (K_f[\text{Fe}(\text{OH})_2]_6^{3+} + [\text{H}^+]^2)\} \times \{k_1[\text{FeOH}^{2+}] + k_1'[\text{FeOH}_2^{3+}]\} k_2 k_3 [\text{FeOH}_2^{3+}] / \{(k_{-1} + (k_1' k_{-1} / k_1 K_m)[\text{H}^+]) (k_{-2}[\text{Fe}^{2+}]^2 + k_3[\text{Fe}^{2+}]) + k_2 k_3 [\text{FeOH}_2^{3+}]\} \quad (4)$$

The *k*<sub>1</sub>'[FeOH<sub>2</sub><sup>3+</sup>] term is not dominant, but its significance can be seen from a consideration of the data with [Fe<sup>2+</sup>] = 0. Then eq 4 can be rearranged after substitution for [FeOH<sub>2</sub><sup>3+</sup>] = [H<sup>+</sup>][Fe(III)]<sub>tot</sub> / (*K*<sub>m</sub> + [H<sup>+</sup>]) to give

$$\frac{k_{\text{calcd}}(K_f[\text{FeOH}_2^{3+}] + [\text{H}^+]^2)(K_m + [\text{H}^+])}{K_f[\text{FeOH}_2^{3+}][\text{Fe(III)}]_{\text{tot}}} = k_1 K_m + k_1'[\text{H}^+] \quad (5)$$

The left-hand side of eq 5 is plotted versus [H<sup>+</sup>] in Figure 1. The horizontal line corresponds to the best fit with *k*<sub>1</sub>' = 0 (*K*<sub>f</sub>*K*<sub>m</sub> = 0.37). However inclusion of *k*<sub>1</sub>' clearly gives a better representation of the data (sloped line) and improves the standard error of the fit by a factor of 1.7.

A nonlinear least-squares fit of the data to eq 4 gives the following parameters with *K*<sub>m</sub> = 1.65 × 10<sup>-3</sup> M and *K*<sub>f</sub> = 7 M: *k*<sub>1</sub> = (1.96 ± 0.14) × 10<sup>2</sup> M<sup>-1</sup> s<sup>-1</sup>; *k*<sub>1</sub>' = 1.82 ± 0.76 M<sup>-1</sup> s<sup>-1</sup>; *k*<sub>-1</sub>*k*<sub>-2</sub>/*k*<sub>2</sub>*k*<sub>3</sub> = (1.27 ± 0.17) × 10<sup>3</sup>. The term first order in [Fe<sup>2+</sup>] in the denominator of eq 4 gave too small a contribution to define *k*<sub>-1</sub>/*k*<sub>2</sub>. The latter appears to have an upper limit of ≲2 since this value causes the standard error of the fit to increase by 10% over

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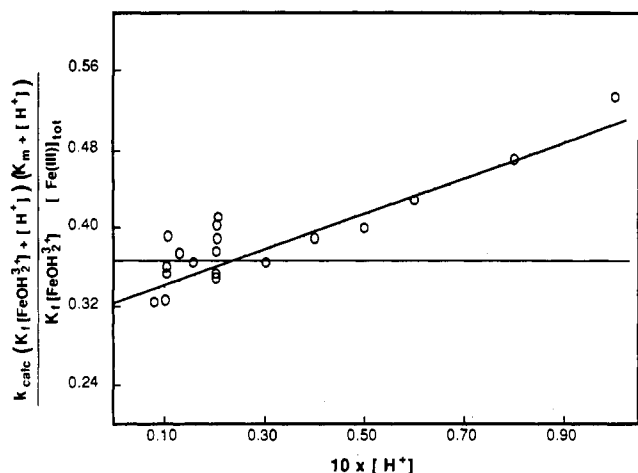


Figure 1. Variation of the rate constant for oxidation of DHB by  $\text{Fe}(\text{OH}_2)_6^{3+}$  with  $[\text{H}^+]$  in the absence of added iron(II) according to eq 5. Horizontal line assumes  $k_1 = 0$ .

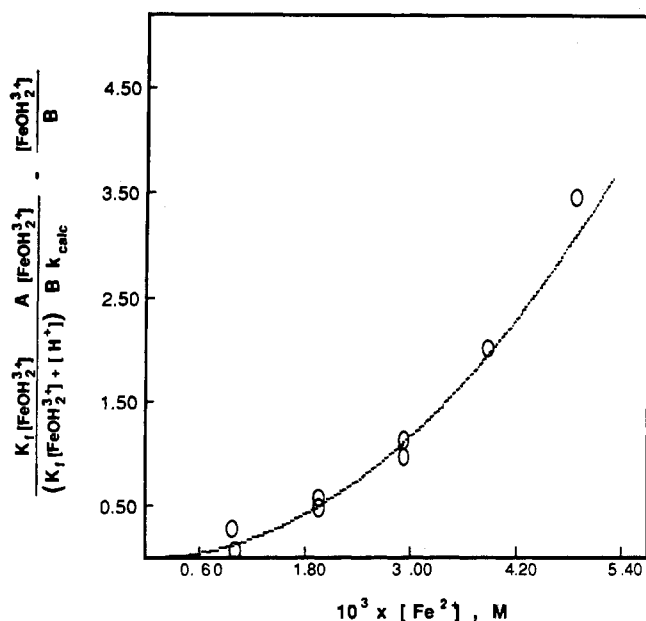


Figure 2. Variation of the rate constant for the oxidation of DHB by  $\text{Fe}(\text{OH}_2)_6^{3+}$  with  $[\text{Fe}^{2+}]$  plotted according to eq 6. The curve represents the best fit to an  $[\text{Fe}^{2+}]^2$  dependence.  $A$  and  $B$  are defined by eq 6.

the best standard error. The experimental and calculated values are compared in Table I.

The relationship between  $k_{\text{obsd}}$  and  $[\text{Fe}^{2+}]$  can be represented most simply by a rearranged version of eq 4, given by eq 6, where

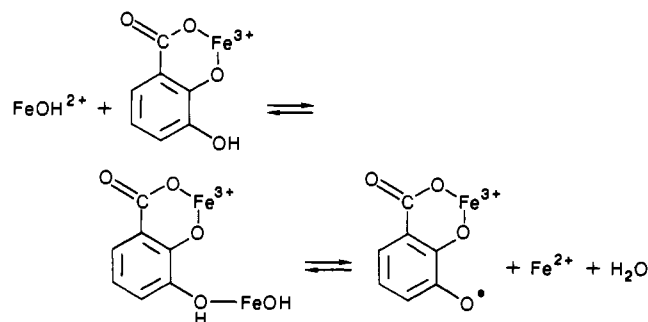
$$\left( \frac{K_1[\text{FeOH}_2^{3+}]}{K_1[\text{FeOH}_2^{3+}] + [\text{H}^+]} \right) \left( \frac{A[\text{FeOH}_2^{3+}]}{Bk_{\text{calcd}}} \right) - \frac{[\text{FeOH}_2^{3+}]}{B} = \frac{k_{-1}k_{-2}}{k_2k_3}[\text{Fe}^{2+}]^2 \quad (6)$$

$A \equiv k_1[\text{FeOH}^{2+}] + k_1'[\text{FeOH}_2^{3+}]$  and  $B = 1 + (k_1'[\text{H}^+]/k_1K_m)$ . In Figure 2, the left-hand side of eq 6 is plotted versus  $[\text{Fe}^{2+}]$ , and the plot is clearly nonlinear and shows that the dependence is greater than first order on  $[\text{Fe}^{2+}]$ . The curve in Figure 2 represents the best fit for an  $[\text{Fe}^{2+}]^2$  dependence.

The reaction sequence in Scheme II is consistent with the observed rate law. However the proposed reactions and numerical values should lead to a rational mechanism if the proposal is correct.

Perhaps the most unexpected feature of Scheme II is that the iron(III)-DHB complex does not undergo intramolecular electron transfer. This may be because the oxidizing power of the complexed iron(III) has been decreased sufficiently so that the initial

## Scheme III



one-electron transfer has too high a thermodynamic barrier to make this path observable. It should be noted that the reduction potentials of the fully protonated<sup>4a</sup> and fully deprotonated<sup>7</sup> semiquinone radicals are 1.38 and 1.18 V respectively. Therefore the first step is unfavorable by at least 10 kcal mol<sup>-1</sup> even with  $\text{Fe}(\text{OH}_2)_6^{3+}$  as the oxidizing agent.

Another unusual feature of Scheme II is that  $\text{FeOH}^{2+}$  is much more reactive than  $\text{FeOH}_2^{3+}$  in the first step ( $k_1 \gg k_1'$ ), although  $\text{FeOH}_2^{3+}$  is the stronger oxidizing agent and the dominant stoichiometric species. This can be understood if the first step requires ligand substitution on the oxidizing species when it is recognized that  $\text{FeOH}^{2+}$  is much more substitution labile than  $\text{Fe}(\text{OH}_2)_6^{3+}$ . It is interesting to note that the water-exchange rates<sup>5,6</sup> on these two species differ by a factor of  $\sim 10^3$  and  $k_1/k_1' = 1.1 \times 10^2$ . The quantitative aspects of this argument cannot be exploited, because it is believed that activation for the substitution is dissociative for  $\text{FeOH}^{2+}$  and associative for  $\text{FeOH}_2^{3+}$ .<sup>5,6</sup>

The type of substitution that might precede electron transfer is shown in Scheme III, which gives a more detailed proposal of the  $k_1$  path in Scheme II. A similar path ( $k_1'$ ) can be envisaged for  $\text{FeOH}_2^{3+}$ , but the substitution step would be slower for reasons of general lability discussed above, as well as ionic charge.

The third step ( $k_2$ ) in Scheme II involves reversible oxidation of the coordinated ligand radical by  $\text{FeOH}_2^{3+}$ . This appears to be an outer-sphere redox process since  $\text{FeOH}_2^{3+}$  rather than  $\text{FeOH}^{2+}$  is the oxidizing agent. The last step ( $k_3$ ) is dissociation of the iron(III) carboxylato-quinone complex, also shown in Scheme II.

It is difficult to dissect and analyze the values of the ratios  $(k_{-1}k_{-2}/k_2k_3) = 1.3 \times 10^3$  and  $k_{-1}/k_2 < 2$ . The latter value indicates that the high-energy semiquinone complex is relatively indiscriminant with respect to being reduced ( $k_{-1}$ ) or oxidized ( $k_2$ ).

Mentasti et al.<sup>3</sup> have observed that catecholate-iron(III) complexes are oxidized by  $\text{Fe}(\text{OH}_2)_6^{3+}$  rather than  $(\text{H}_2\text{O})_5\text{FeOH}^{2+}$ . This difference with the present system is consistent with Scheme II because the catecholates do not have a third function available for complexation of  $(\text{H}_2\text{O})_5\text{FeOH}^{2+}$ . The small contribution of  $\text{Fe}(\text{OH}_2)_6^{3+}$  oxidation ( $k_1'$ ) observed here has a rate constant that fits the correlation of  $E^\circ$ <sup>4a</sup> and  $\log k$  for this path noted by Mentasti et al.<sup>3</sup> This suggests that the  $\text{Fe}(\text{OH}_2)_6^{3+}$  oxidation may proceed by an outer-sphere mechanism.

There is one anomaly in the earlier work<sup>3</sup> in that it has been interpreted to indicate that free catechol is oxidized by  $(\text{H}_2\text{O})_5\text{FeOH}^{2+}$  rather than the dominant and stronger oxidizing agent  $\text{Fe}(\text{OH}_2)_6^{3+}$ . This interpretation is based on a term in the rate law that is first order in iron(III) and inverse first order in  $[\text{H}^+]$ . An alternative suggestion for this pathway is shown in Scheme IV and involves monodendate phenolate type complexes ( $K_p$  in Scheme IV).

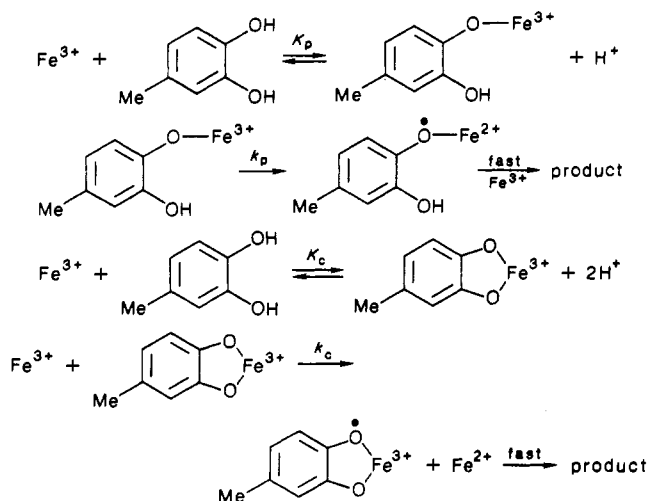
The results of Cavasino and Di Dio<sup>8</sup> on phenolate-iron(III) complexes can be used to estimate that  $K_p \sim 1 \times 10^{-2}$ . If 4-methylbenzene-1,2-diol is taken as an example, the formation constant for the chelate ( $K_c$  in Scheme IV) is  $2.84 \times 10^{-2} \text{ M}^{-1}$ .<sup>9</sup>

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Scheme IV



Under the acidity conditions of the study of Mentasti et al.<sup>3</sup> the amount of complexation is small, but there would be similar amounts of monodentate and chelate.

The net reaction sequence shown in Scheme IV predicts the observed pseudo-first order rate constant given by eq 7. Since

$$k_{\text{calcd}} = \frac{k_p K_p [\text{H}^+][\text{FeOH}_2^{3+}] + k_c K_c [\text{FeOH}_2^{3+}]^2}{[\text{H}^+]^2 + K_p [\text{H}^+][\text{FeOH}_2^{3+}] + K_c [\text{FeOH}_2^{3+}]^2} \quad (7)$$

$[\text{H}^+]^2 \gg (K_p [\text{H}^+] + K_c)[\text{FeOH}_2^{3+}]$ , the analysis of the data is insensitive to the values of  $K_p$  and  $K_c$ . The plot given in Figure 3 shows that the results for 4-methylbenzene-1,2-diol are consistent with eq 7. A least-squares analysis gives  $k_p K_p = 1.1 \pm 0.05 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_c K_c = 4 \pm 0.5 \text{ M}^2 \text{ s}^{-1}$ . The mathematical form of eq 7 is equivalent to that used in the original work and  $k_p K_p$  and  $k_c K_c$  are equivalent to  $k'$  and  $k''$  given in Table III of ref 3 by Mentasti et al.<sup>3</sup>

As a final comment it must be noted that Scheme IV proposes that oxidation of the monodentate species proceeds by initial intramolecular electron transfer, while the chelate requires a second iron(III). The latter behavior was also proposed for the DHB chelate (Scheme III). The simplest explanation for this difference between the monodentate and bidentate systems would seem to be an extension of the argument above that chelation reduces the oxidizing power of iron(III) too much to make intramolecular transfer favorable. Monodentate formation does not have as much of an effect, and intramolecular transfer is observed.

### Experimental Section

**Materials.** The preparation and standardization of iron(III) perchlorate solutions have been described.<sup>1</sup> The iron(II) solutions ( $\leq 0.01$

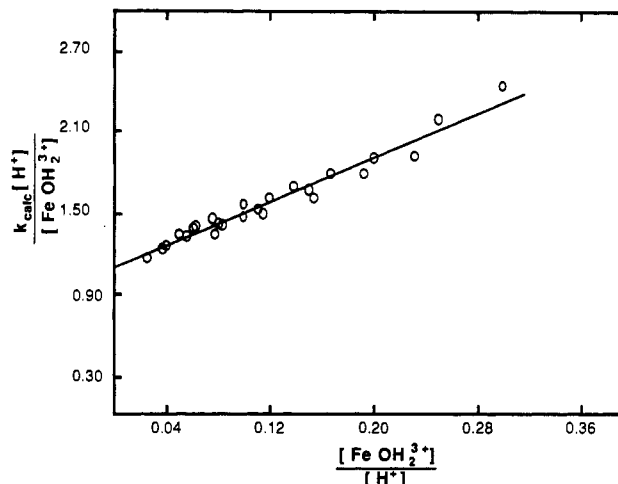


Figure 3. Variation of the rate constant for oxidation of 4-methylbenzene-1,2-diol by  $\text{Fe}(\text{OH}_2)_6^{3+}$  with  $[\text{Fe}(\text{OH}_2)_6^{3+}]$  and  $[\text{H}^+]$  for the data of Mentasti et al.<sup>3</sup>

M iron(II) were made by dissolving weighed amounts of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  in dilute perchloric acid of the required concentration. The solutions were deoxygenated by bubbling argon before adding the iron(II) and were stored under an argon atmosphere.

The reaction stoichiometry was determined by mixing a solution containing a known amount of 2,3-dihydroxybenzoic acid (DHB) with a solution of  $\text{Fe}(\text{OH}_2)_6^{3+}$  in perchloric acid, with the iron in excess, under an argon atmosphere. The amount of iron(II) produced was determined by adding phenanthroline and comparing the absorbance of the reactant solution to standards containing known amounts of iron(II). For initial  $10^3[\text{iron(III)}]$  and  $10^3[\text{DHB}]$  of 2.0 and 0.82, 2.0 and 0.50, 3.0 and 1.0, 3.0 and 0.82, 3.0 and 0.50 M, the moles of iron(II) produced per mole of DHB were 2.06, 2.03, 1.96, 1.95 and 2.07 mol, respectively, to give an average of  $2.0 \pm 0.06$  mol.

**Kinetic Measurements.** The equipment and general procedures are described elsewhere.<sup>1,10</sup> The increase in absorbance at 415 nm was used to monitor the reaction rate. All kinetic runs involving iron(II) were done anaerobically. Some runs with just iron(III) and DHB were done in deoxygenated solutions, and there was no measurable difference with solutions containing dissolved dioxygen. The two solutions mixed on the stopped-flow system contained the iron(III) (and iron(II) when added) in one solution and DHB in the other both at the same acidity and adjusted to 1.0 M ionic strength with  $\text{NaClO}_4$ .

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Registry No. DHB, 303-38-8;  $\text{Fe}^{3+}$ , 20074-52-6.

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