

Complexation of the Aqua–Iron(III) Dimer by Tiron: Kinetics of Complex Formation and Dissociation

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The reaction of Tiron (1,2-dihydroxy-3,5-benzenesulfonate) with aqueous iron(III) has been studied at moderate acidities (0.1–0.02 M H⁺) by stopped-flow spectrophotometry at 25 °C in 1.0 M NaClO₄/HClO₄. The concentration of the bis(μ-hydroxo) dimer of iron(III) has been systematically varied by controlling the H⁺ and iron(III) concentrations in the iron(III) solutions before mixing with Tiron solutions at various acidities to give the desired final [H⁺]. The absorbance change at 660 nm is biphasic, and the absorbance–time profiles for the slower absorbance decrease have been modeled by numerical integration. It is found that the faster absorbance increase is due to reaction of (H₂O)₈Fe₂(μ-OH)₂⁴⁺ with Tiron to give a blue complex with $k = 5.1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, but no protons are released during the complexation, and the formation equilibrium constant is $6.3 \times 10^3 \text{ M}^{-1}$. The dimer complex decomposes to the less strongly colored monomeric complex and Fe(OH₂)₆³⁺ with $k = 0.2 \text{ s}^{-1}$. The possible nature of the dimeric complex is considered, and the relevance of these observations to previous studies on catechols, squaric acid, and ascorbic acid is discussed.

Introduction

This study began as an investigation of the reaction of isopropylideneascorbic acid with aqueous iron(III). However, it soon became apparent that even the qualitative observations on that system were sufficiently unusual and complex that they would be difficult to unravel without further background information. For that reason, it was decided to investigate the reaction of 1,2-dihydroxy-3,5-benzenesulfonate (Tiron). This system is simpler because the ligand is quite stable under acidic conditions, the reduction potential of Tiron ($E^\circ = 0.955 \text{ V}$)¹ requires that no oxidation–reduction will occur, and only complexation reactions will be observed. Although this system had been the subject of two previous kinetic studies,^{2,3} there was reason to believe that the complexities we were observing were due to the bis(μ-hydroxo) dimer of iron(III), (H₂O)₈Fe₂(OH)₂⁴⁺, and that these had been avoided as much as possible in the earlier work. This suspicion was reinforced by a recent study⁴ of squaric acid and aqueous iron(III) in which the dimer complexation was found to be an important feature. It may be noted at the outset that some of the observations here have close analogies to those with squaric acid.

In the present work, the amount of bis(μ-hydroxo) dimer was varied systematically by controlling the total iron(III) and acidity of the iron(III)-containing solution before mixing with the neutral or acidic Tiron solution in the stopped-flow system. The conditions were controlled so that the concentration of the dimer was almost always in reasonable pseudo-first-order excess over Tiron. Although the dimer undergoes some dissociation to monomer on the time scale of some of our observations, the kinetics of this process are known^{5,6} and can be taken into account.

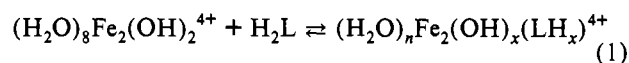
Results and Analysis

Qualitative Observations. The reaction is biphasic with an initial absorbance increase which is complete in ~100 ms or less. This is followed by an absorbance decrease over a time of ~5 s.

Observations on a stopped-flow diode array system show that the increase is associated with formation of a blue species with an absorbance maximum at ~660 nm. The decrease is associated with loss in intensity at all wavelengths, but the final absorbance is often finite and even substantial under some conditions. One would expect the absorbance increase due to complexation, but the source of the decrease in absorbance seems problematic, since Tiron is not oxidized by iron(III).

The absorbance–time curves are fitted well by a standard two-exponential first-order model, and the apparent absorbancies of the intermediate (A_{max}) and rate constants for the faster and slower reactions are summarized in Tables 1 and 2. Since the rate constant for the faster process (k_f) is at least 10 times greater than that for the slower process, the values are well defined.

Kinetics and Equilibrium for the Faster Reaction. An examination of the magnitude of the absorbance of the intermediate (A_{max} in Table 1) reveals that it appears to be independent of the acidity and does not correlate with total iron(III) concentration, but does correlate with the concentrations of Tiron and iron(III) dimer. The values of $A_{\text{max}}/[\text{Tiron}]$ have a limiting value of ~2200 for $[\text{dimer}] > 18 \times 10^{-4} \text{ M}$ and $[\text{Tiron}] > 1 \times 10^{-4} \text{ M}$. These results are qualitatively consistent with the faster reaction being an equilibrium reaction of the general form of eq 1. The site of



protonation of the product is left ambiguous at this stage, but no protons are released by the reaction because A_{max} is independent of [H⁺], and the kinetics described below show no H⁺ dependence for decomposition of the product.

From the limited knowledge of the reactivity of the dimer,^{2,4} it is not surprising that it undergoes more rapid complexation than monomeric aquairon(III) species. However, it is unexpected that the complexation should proceed without the release of protons and that the equilibrium constant is so large that the equilibrium is essentially completely to the right for the low dimer and Tiron concentrations noted above. These imply an equilibrium constant of ~10⁴ M⁻¹ for eq 1.

It is well-known^{2,3} that Fe(OH₂)₆³⁺ forms complexes with a wide range of 1,2-dihydroxybenzene derivatives (H₂L, catechols) as shown by eq 2. The equilibrium constants for these reactions (K_{F1}) depend on the pK_a of the catechol, and the value for Tiron²

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Table 1. Observations on the Increase of Absorbance at 660 nm for the Reaction of Tiron with Aqueous Iron(III) in 1.0 M NaClO₄/HClO₄ at 25 °C

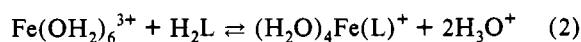
10 ⁴ [Tiron], M	[iron] _{tot} , M	10 ⁴ [(H ₂ O) ₁₀ - Fe ₂ (OH) ₂ ⁴⁺], M	[H ⁺], M	A _{max}	k _i , s ⁻¹	
					obsd	calcd
2.0	0.041	27.4	0.0241	0.455	35.4	34.7
2.0 ^a	0.041	27.4	0.0241	0.447	36.8	34.7
2.0	0.041	27.4	0.1005	0.434	18.9	19.5
2.0 ^a	0.041	27.4	0.1005	0.432	19.0	19.5
0.50	0.041	27.4	0.0241	0.107	33.8	34.7
1.0	0.041	27.4	0.0241	0.211	33.0	34.7
2.0	0.041	27.4	0.0241	0.422	34.5	34.7
3.0	0.041	27.4	0.0241	0.616	35.5	34.7
4.0	0.041	27.4	0.0241	0.832	31.8	34.7
1.0	0.0205	0.413	0.1057	0.117	(1.24) ^b	1.32
1.0	0.041	1.63	0.1062	0.138	(2.91) ^b	2.12
1.0	0.0205	18.4	0.1102	0.213	13.0	13.1
1.0	0.041	39.1	0.115	0.225	27.2	26.4
1.0	0.0205	18.4	0.110	0.220	13.3	13.1
1.0	0.0308	35.6	0.110	0.236	27.5	24.4
1.0	0.0410	43.7	0.114	0.227	32.6	29.5
1.0	0.0512	51.1	0.117	0.225	36.9	34.1
0.50	0.0410	27.4	0.217	0.102	14.5	16.9
0.50	0.0410	27.4	0.120	0.106	18.4	18.7
0.50	0.0410	27.4	0.0908	0.108	20.2	20.0
0.50	0.0410	27.4	0.0618	0.111	23.3	22.5
0.50	0.0410	27.4	0.0427	0.111	28.2	26.0
0.50	0.0410	27.4	0.0241	0.119	34.6	34.7

^a Under anaerobic conditions in an argon atmosphere. ^b Not used in the least-squares fit to eq 4 because of non-first-order conditions. Analyzed by numerical integration: see Figures 2 and 3B.

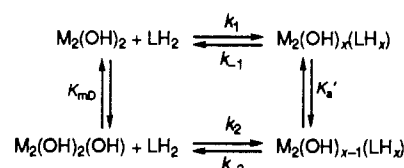
Table 2. Observations on the Decrease of Absorbance at 660 nm for the Reaction of Tiron with Aqueous Iron(III) in 1.0 M NaClO₄/HClO₄ at 25 °C

10 ⁴ [Tiron], M	[iron] _{tot} , M	10 ⁴ [(H ₂ O) ₁₀ - Fe ₂ (OH) ₂ ⁴⁺], M	[H ⁺], M	A _f	k _s , s ⁻¹
2.0	0.041	27.4	0.0241	0.197	0.335
2.0 ^a	0.041	27.4	0.0241	0.206	0.335
2.0	0.041	27.4	0.1005	0.182	0.362
2.0 ^a	0.041	27.4	0.1005	0.185	0.367
0.50	0.041	27.4	0.0241	0.017	0.18
1.0 ^b	0.041	27.4	0.0241	0.058	0.225
2.0 ^b	0.041	27.4	0.0241	0.179	0.324
3.0 ^b	0.041	27.4	0.0241	0.329	0.416
4.0 ^b	0.041	27.4	0.0241	0.470	0.487
1.0 ^c	0.0205	0.413	0.1057	0.050	0.176
1.0	0.0205	18.4	0.1102	0.033	0.175
1.0 ^d	0.0205	18.4	0.110	0.030	0.182
1.0 ^d	0.0308	35.6	0.110	0.060	0.234
1.0 ^c	0.0410	1.63	0.1062	0.085	0.284
1.0 ^c	0.0410	39.1	0.115	0.075	0.259
1.0 ^d	0.0410	43.7	0.114	0.080	0.281
1.0 ^d	0.0512	51.1	0.117	0.095	0.360
0.50	0.0410	27.4	0.217	0.016	0.185
0.50	0.0410	27.4	0.120	0.015	0.184
0.50	0.0410	27.4	0.0908	0.017	0.186
0.50	0.0410	27.4	0.0618	0.016	0.185
0.50	0.0410	27.4	0.0427	0.019	0.185
0.50	0.0410	27.4	0.0241	0.022	0.175

^a Under anaerobic conditions in an argon atmosphere. ^b Calculated and observed results are given in Figures 1 and 3A. ^c Calculated and observed results are given in Figures 2 and 3B. ^d Calculated and observed results are given in Figure 4.



is ~3 M. Clearly, the reaction with the dimer is different because no protons are released and product formation is much more favorable in acidic solution. Nevertheless, under conditions where the dimer concentration is <5 × 10⁻⁴ M, reaction 2 does become a significant contributor and conditions are not pseudo-first-order. This applies for two of the runs in Tables 1 and 2, and these are

Scheme 1

not included in the following analysis but are discussed with the slower reaction.

The rate constants (*k_i*, Table 1) are consistent with the equilibrium arguments above in that the values increase with increasing dimer concentration and do not change with increasing [H⁺]. The values of *k_i* are consistent with the reactions in Scheme 1, where M₂(OH)₂ represents the dimer and M₂(OH)₂(OH) is a hydrolyzed dimer species. An alternative *k₂* path is discussed below. Scheme 1 predicts that the pseudo-first-order rate constant is given by eq 3, where [M₂]_t = [M₂(OH)₂] + [M₂(OH)₂(OH)]

$$k_i = (k_1[\text{H}^+] + k_2K_{\text{mD}}) \left(\frac{[\text{M}_2]_t}{K_{\text{mD}} + [\text{H}^+]} + \frac{1}{K_{\text{f2}}(K_a' + [\text{H}^+])} \right) \quad (3)$$

and *K_{f2}* = *k₁*/*k₋₁*. If [H⁺] ≫ *K_{mD}* and [H⁺] ≫ *K_a'*, then eq 3 simplifies to eq 4. Least-squares analysis gives *k₁* = (5.05 ± 0.25)

$$k_i = (k_1 + k_2K_{\text{mD}}[\text{H}^+]^{-1}) \left([\text{M}_2]_t + \frac{1}{K_{\text{f2}}} \right) \quad (4)$$

× 10³ M⁻¹ s⁻¹, *k₂K_{mD}* = (1.67 ± 0.13) × 10² s⁻¹, and *K_{f2}* = (6.37 ± 0.73) × 10³ M⁻¹. The fit of the data is quite reasonable, as can be seen from a comparison of the experimental and calculated values in Table 1. The value of *K_{f2}* is consistent with the qualitative prediction above from the *A_{max}* values.

It should be noted that, in Scheme 1, the *k₂* path also could involve M₂(OH)₂ + LH, in which case *k₂K_{mD}* would be replaced by *k₂'K_a* (*K_a* = 6.3 × 10⁻⁸ M, the acid dissociation constant of Tiron) in eqs 3 and 4. This alternative has not been considered further because it gives an unreasonably large value for *k₂'* of 2.7 × 10⁹ M⁻¹ s⁻¹. Although *K_{mD}* is unknown, the analogous chromium(III) species, (H₂O)₈Cr₂(OH)₂⁴⁺, has *K_{mD}* = 2.09 × 10⁻⁴ M,⁷ and this would yield a more reasonable value for *k₂* ≈ 8 × 10⁵ M⁻¹ s⁻¹.

Discussion of the nature of the dimer–Tiron complex will be deferred until the slower reaction has been analyzed.

Kinetics of the Slower Reaction. This process shows a decrease in absorbance and appears to involve conversion of the initially formed dimer complex to a less strongly absorbing species. The observations are summarized in Table 2. The first four entries in Table 2 indicate that this reaction is unaffected by the presence of O₂ and is not strongly affected by [H⁺]. The 5th–9th entries show that the rate constant increases with increasing Tiron concentration. This is surprising because Tiron is the deficient reagent. The next nine entries are at constant Tiron concentration and nearly constant [H⁺] with varying total iron(III) and dimer. From the several runs at 0.0205 and 0.0410 M H⁺, it appears that the rate is not affected by the dimer concentration, but throughout this series the rate increases with total iron(III) concentration. The last six entries confirm that the rate constant for the slower reaction is independent of the dimer and H⁺ concentrations.

The *A_f* values in Table 2 increase with increasing Tiron concentration and have a small dependence on the total iron(III) and H⁺ concentrations. The latter observation seems rather disconcerting, since one might expect that the final solution could be described by the equilibrium in eq 2. However, it turns out

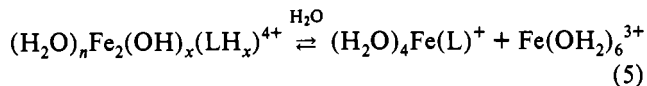
(7) Crimp, S. J.; Spiccia, L.; Krouse, H. R.; Swaddle, T. W. *Inorg. Chem.* 1994, 33, 465.

Table 3. Summary of Equilibrium and Rate Constants for the Reactions of Aqueous Iron(III) with Tiron at 25 °C in 1.0 M NaClO₄/HClO₄

reaction	rate or equilibrium constant
$\text{Fe}_2(\text{OH})_2^{4+} + \text{H}_2\text{L} \rightarrow \text{Fe}_2(\text{OH})_x(\text{LH}_x)^{4+}$	$k_5 = 5.1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$
$\text{Fe}_2(\text{OH})_2^{4+} + \text{H}_2\text{L} \rightleftharpoons \text{Fe}_2(\text{OH})_x(\text{LH}_x)^{4+}$	$K_{f2} = 6.4 \times 10^3 \text{ M}^{-1}$
$\text{Fe}_2(\text{OH})_2(\text{OH})^{3+} + \text{H}_2\text{L} \rightarrow \text{Fe}_2(\text{OH})_{x+1}(\text{LH}_x)^{3+}$	$k_2 = (8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1})^a$
$\text{Fe}_2(\text{OH})_2^{4+} + \text{HL}^- \rightarrow \text{Fe}_2(\text{OH})_{x+1}(\text{LH}_x)^{3+}$	$k_2' = (2.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})^a$
$\text{Fe}_2(\text{OH})_x(\text{LH}_x)^{4+} \rightarrow \text{Fe}(\text{L})^+ + \text{Fe}(\text{OH})_2^{3+}$	$k_5 = 0.2 \text{ M}^{-1} \text{ s}^{-1}$
$\text{Fe}(\text{OH})^{2+} + \text{H}_2\text{L} \rightarrow \text{Fe}(\text{L})^+ + \text{H}_3\text{O}^+$	$k_6 = 2.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$

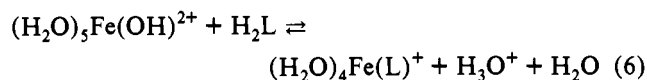
^a These values involve a proton ambiguity and are estimated from $(k_2 K_{\text{MD}} + k_2' K_{\text{a}}) = 1.7 \times 10^2 \text{ s}^{-1}$ with $K_{\text{MD}} = 2.1 \times 10^{-4}$ or $K_{\text{a}} = 6.3 \times 10^{-8} \text{ M}$ as described in the text; assignment to k_2 is preferred on the basis of its magnitude.

that, because of the strong complexation by the dimer discussed above, the system is better represented qualitatively by eq 5,



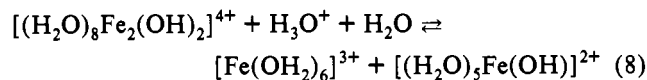
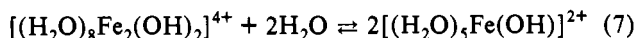
which is independent of $[\text{H}^+]$. A qualitative assessment of the absorbance decrease indicates that the dimeric and monomeric complexes have molar absorptivities of $\sim 2.5 \times 10^3$ and $\sim 1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, respectively, and it is this difference which causes the decrease in absorbance. The A_t values are too uncertain to warrant a quantitative analysis because the value is often small and therefore sensitive to the initial setup parameters. Additionally, there is some drift of the final absorbance due to diffusion into the mixing chamber over times of 5–10 s required to reach completion.

In order to analyze the kinetics of the absorbance decrease, it is necessary to consider the probable reactions involved. It seems reasonable that eq 5 will dominate the absorbance decrease, but one must allow that some $(\text{H}_2\text{O})_4\text{Fe}(\text{L})^{2+}$ may form directly via eq 6. This is the major pathway for complexation of monomeric



aqueous iron(III), and much previous work indicates that the rate constant $k_6 \approx 2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for neutral ligands. The pathway involving $\text{Fe}(\text{OH})_2^{3+} + \text{H}_2\text{L}$ (k_6') typically has rate constants⁸ of $\sim 10 \text{ M}^{-1} \text{ s}^{-1}$ and normally is not important at the acidities of this study but has been included for completeness.

Furthermore, the kinetic analysis must allow for formation and decomposition of the dimer as described by eqs 7 and 8. The



rate constants for this process are known,^{4,5} and the half-time for dimer dissociation is in the range 1–2 s for 0.02–0.1 M H^+ , so that it could have some influence on the observations.

The absorbance–time curves were calculated by numerical integration based on reactions 5–8 by using the known values of K_{m} and K_{D} ($= [(\text{H}_2\text{O})_8\text{Fe}_2(\text{OH})_2^{4+}][\text{H}^+]^2 / [\text{Fe}(\text{OH})_2^{3+}]^2$) and K_{f2} from the above analysis and varying K_{f1} (eq 2) along with k_5 and k_6 . Details are described in the Appendix. The reverse rate constants were determined from the equilibrium constants, and k_7 and k_8 were fixed at published values.^{5,6} The absorbance was assumed to be given by eq 9, so that ϵ_1 and ϵ_2 are also variables

$$A_t = \epsilon_1 [(\text{H}_2\text{O})_4\text{Fe}(\text{L})^+]_t + \epsilon_2 [(\text{H}_2\text{O})_n\text{Fe}_2(\text{OH})_x(\text{LH}_x)^{4+}]_t \quad (9)$$

in the analysis. Although the system appears to have an

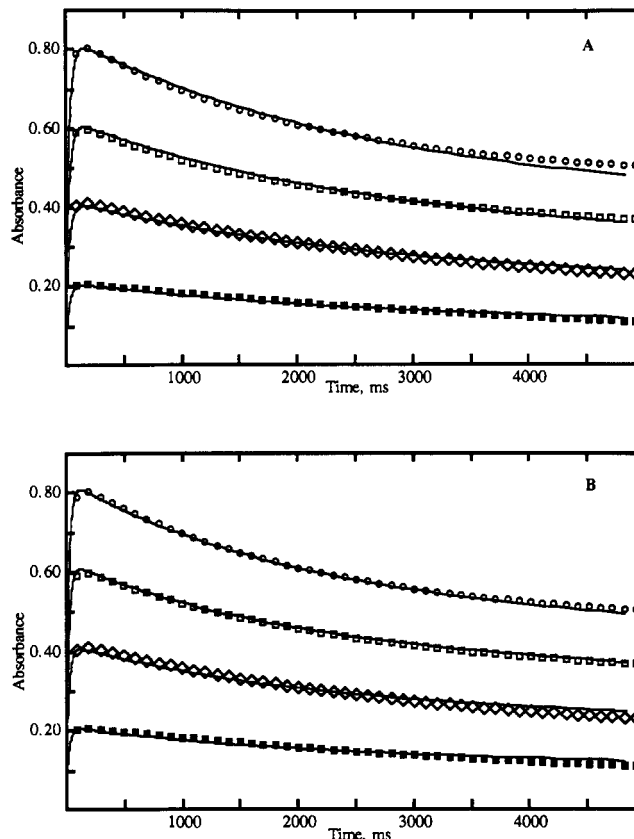


Figure 1. Observed and calculated absorbance–time profiles (660 nm) for the reaction of aqueous iron(III) with Tiron for initial conditions after mixing of 0.0410 M total iron(III), 0.0241 M H^+ , and $2.27 \times 10^{-3} \text{ M}$ iron(III) dimer and varying Tiron concentrations (M) of 4.00×10^{-4} (\circ), 3.00×10^{-4} (\square), 2.00×10^{-4} (\diamond), and 1.00×10^{-4} (\blacksquare). For part A, $k_5 = 0.35 \text{ s}^{-1}$, $k_6 = 0$, $\epsilon_1 = 940 \text{ M}^{-1} \text{ cm}^{-1}$, and $\epsilon_2 = 2210 \text{ M}^{-1} \text{ cm}^{-1}$. For part B, $k_5 = 0$, $k_6 = 4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, $\epsilon_1 = 980$, $\epsilon_2 = 2500 \text{ M}^{-1} \text{ cm}^{-1}$.

unmanageable number of variables, it should be noted that the magnitude of ϵ_2 was established from the faster reaction analysis, and the magnitudes of k_6 and K_{f1} are reasonably established from previous work. In the final analysis, $K_{f1} = 5 \text{ M}$ has been used as most consistent with the observations, but it is not well defined because it is correlated with ϵ_1 . For example, a 2 times smaller K_{f1} can be compensated by a 10% smaller ϵ_1 . The main unknowns are ϵ_1 and k_5 . In fact, it might be questioned as to whether k_5 represents a significant reaction pathway, because the dimer complex might decompose by simple dissociation (k_{-1} in Scheme 1).

With the readers' forbearance and understanding that the authors have already seen the outcome of the analysis of the runs in Table 2, we will proceed first to determine if k_5 is required by the observations and also to see if the reactions proposed mimic the apparent Tiron dependence of the rates of the slower step. The calculated curves for the 6th–9th runs in Table 2 are shown in Figure 1. This simulations show that the model does predict the Tiron dependence of the rate, but these runs do not define k_5 and k_6 . These observations can be fitted reasonably by assuming that $k_5 \approx 0.35 \text{ M}^{-1} \text{ s}^{-1}$ and k_6 is negligible (Figure 1A)

(8) Birus, M.; Kujundzic, N.; Probanic, M. *Prog. React. Kinet.* 1993, 18, 171.

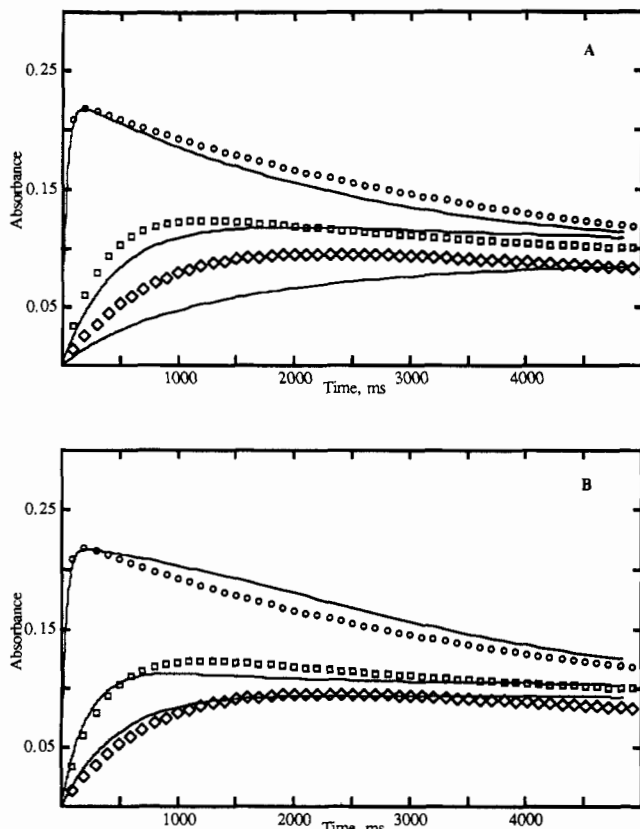


Figure 2. Observed and calculated absorbance–time profiles (660 nm) for the reaction of aqueous iron(III) with Tiron for initial conditions after mixing of total iron(III), H^+ , and iron(III) dimer. Respective concentration: 0.0410, 0.115, 3.91×10^{-3} M (○); 0.0410, 0.1062, 6.22×10^{-4} M (□); 0.0205, 0.1057, 3.13×10^{-4} M (◇). For part A, $k_5 = 0.35$ s $^{-1}$, $k_6 = 0$, $\epsilon_1 = 970$ M $^{-1}$ cm $^{-1}$, and $\epsilon_2 = 2380$ M $^{-1}$ cm $^{-1}$. For part B, $k_5 = 0$, $k_6 = 4 \times 10^3$ M $^{-1}$ s $^{-1}$, $\epsilon_1 = 960$ M $^{-1}$ cm $^{-1}$, and $\epsilon_2 = 2390$ M $^{-1}$ cm $^{-1}$.

or that k_5 is negligible and $k_6 \approx 4 \times 10^3$ M $^{-1}$ s $^{-1}$ (Figure 1B). The magnitude of k_6 is reasonable from previous studies. The main value of these observations is that they place upper limits on the values of k_5 and k_6 .

If one turns to runs in which the Tiron concentration and acidity are constant and the total iron(III) and dimer concentrations are changed, then more revealing patterns emerge. The observed and calculated absorbance for the 10th, 14th, and 15th runs in Table 2 are plotted in Figure 2. The first two of these are for low dimer concentrations which were excluded from the analysis of the faster absorbance increase above. These fits are not very satisfactory, and it can be seen that at the highest dimer concentration (upper curves) the predicted rate is too fast if $k_5 \approx 0.35$ M $^{-1}$ s $^{-1}$ and too slow if $k_6 \approx 4 \times 10^3$ M $^{-1}$ s $^{-1}$. For the two low dimer concentrations, the predicted rates are much too slow for the former condition (Figure 2A) and slightly too fast for the latter condition (Figure 2B). This pattern reveals that the observations might be fitted if both k_5 and k_6 have values which can influence the calculated absorbance. For the low dimer concentrations, reaction 6, giving the monomer complex, is actually the dominant color-producing reaction, and this is why the predicted rate is too small for these conditions if k_6 is not included. It should also be apparent that the evaluation of k_6 in this study relies heavily on the fits at the low dimer concentrations.

The results in Figure 3 confirm that the data are consistent with a common set of extinction coefficients and rate constants. In Figure 3, the runs from Figures 1 and 2 are compared to calculated curves with $\epsilon_1 = 1 \times 10^3$ M $^{-1}$ cm $^{-1}$, $\epsilon_2 = 2.45 \times 10^3$ M $^{-1}$ cm $^{-1}$, $k_5 = 0.2$ s $^{-1}$, and $k_6 = 2.2 \times 10^3$ M $^{-1}$ s $^{-1}$.

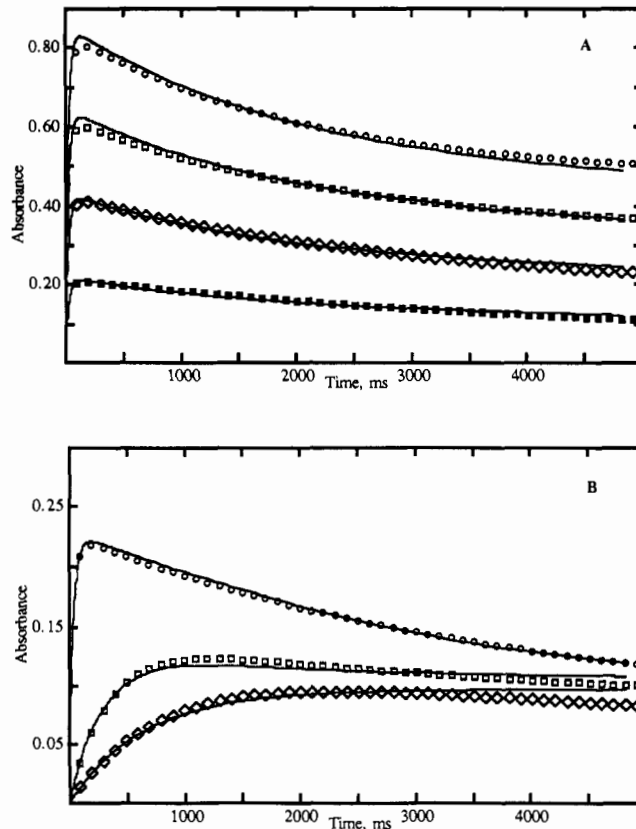


Figure 3. Observed and calculated absorbance–time profiles (660 nm) for the reaction of aqueous iron(III) with Tiron calculated with $k_5 = 0.2$ s $^{-1}$, $k_6 = 2.2 \times 10^3$ M $^{-1}$ s $^{-1}$, $\epsilon_1 = 1000$ M $^{-1}$ cm $^{-1}$, and $\epsilon_2 = 2450$ M $^{-1}$ cm $^{-1}$. For part A, the conditions are the same as for Figure 1. For part B, the concentrations are the same as for Figure 2.

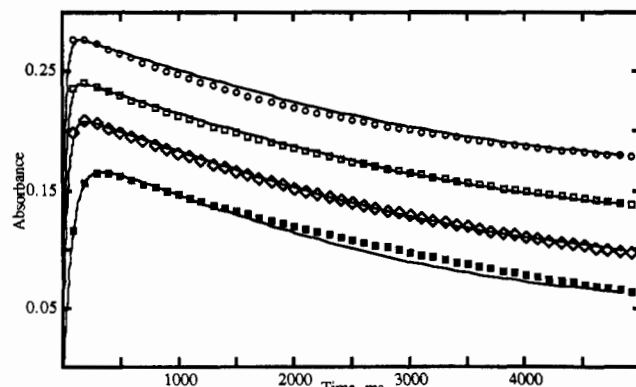


Figure 4. Observed and calculated absorbance–time profiles (660 nm) for the reaction of aqueous iron(III) with Tiron calculated with $k_5 = 0.2$ s $^{-1}$ and $k_6 = 2.2 \times 10^3$ M $^{-1}$ s $^{-1}$. Initial conditions after mixing of total iron(III), H^+ , and iron(III) dimer: 0.0512, 0.117, 5.11×10^{-3} M (○); 0.410, 0.114, 4.37×10^{-3} M (□); 0.0308, 0.110, 3.56×10^{-3} M (◇); 0.0205, 0.110, 1.84×10^{-3} M (■). For clarity of presentation, the curves are displaced vertically, beginning with the upper curve, by 0.06, 0.02, -0.02 , and -0.045 absorbance unit, respectively. The ϵ_1 values are calculated as $0.408 \epsilon_2$, and the ϵ_2 values are 2350, 2400, 2520, and 2510 M $^{-1}$ cm $^{-1}$ from the upper to lower curves.

There is a remaining feature which must be tested. The results of runs 10–17 show that k_5 increases with increasing $[iron]_{tot}$, and the question is whether this is consistent with the model. The results are shown in Figure 4, where it can be seen that the predicted and observed values are in reasonable agreement for different $[iron]_{tot}$ values with $k_5 = 0.2$ M $^{-1}$ s $^{-1}$. For these curves, the value of ϵ_2 has been adjusted to fit the maximum absorbance in each case, but the ϵ_2/ϵ_1 ratio is the same for all runs. This allows for changes in sensitivity of the instrumentation between runs.

Discussion

The most novel result from this work is the kinetic and thermodynamic characterization of the complex formed between Tiron and the bis(μ -hydroxo) dimer of aquairon(III). Work in progress indicates that complexation of the dimer is a general phenomenon with 1,2-dihydroxy ligands, and an analogous species appears to form with ascorbic acid. In fact, earlier reports from our own⁹ and other laboratories¹⁰ on the iron(III)-ascorbate system appear to need reevaluation on the basis of the present observations. One problem with the ascorbate systems is that the disappearance of the blue complex may be a combination of oxidation-reduction and dimer complex decomposition. This would explain why the oxidation rate of ascorbic acid by aqueous iron(III) at higher acidity¹¹ (≥ 0.3 M) seems to be slower than expected from the rate of disappearance of blue color at lower acidity⁹ (≤ 0.1 M). Furthermore, it now seems quite likely that the unusually large rate constant assigned to complexation of $\text{Fe}(\text{OH})_2^{3+}$ by ascorbic acid is really due to a reaction with the iron dimer, analogous to Scheme 1.

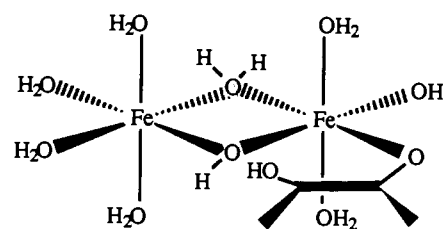
Several of the kinetic parameters from this study can be compared to previous results. The rate constant for complexation of $(\text{H}_2\text{O})_5\text{Fe}(\text{OH})^{2+}$ by Tiron (k_6) has been reported^{2,3} as 3.1×10^3 and $2.1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ in good agreement with the present value of $2.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ (all at 25 °C, in 1.0 M $\text{NaClO}_4/\text{HClO}_4$). We now suspect that the higher value reported by Xu and Jordan² may have been influenced by dimer complex formation because the iron(III) concentrations was ~ 10 times higher than that in the study of Mentasi et al.³

The rate constant for dimer complex formation, $k_1 = 5.1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, is a factor of 2 smaller than that reported by Xu and Jordan.² The latter value was extracted as an $[\text{Fe}(\text{III})]_2$ -dependent term in a complex rate law in which the $[\text{H}^+]^{-1}$ -dependent term (k_2) of this pathway could not be resolved, so that the current smaller value is preferred and is not inconsistent with the earlier observations. The reactivity of Tiron with $(\text{H}_2\text{O})_8\text{Fe}_2(\text{OH})_2^{4+}$ is similar to that of neutral ligands such as acetohydroxamic acid¹² and 2,3-dihydroxybenzoic acid,² which have rate constants of 8.4×10^3 and $\sim 5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, respectively, while ligands with anionic reaction sites (squarate,⁴ 2,3-dihydroxybenzoate²) are about 50 times more reactive. These rather limited data are consistent with an ion pair interchange process.

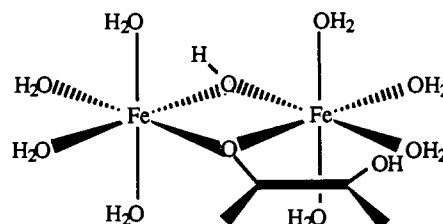
The dissociation of the Tiron dimer complex to the monomeric complex has a rate constant $k_5 = 0.2 \text{ s}^{-1}$, which is similar to that for uncatalyzed dissociation of $(\text{H}_2\text{O})_8\text{Fe}_2(\text{OH})_2^{4+}$ (0.4 s^{-1}).^{5,6} The formally analogous value for the squarate dimer complex,⁴ $(\text{H}_2\text{O})_6\text{Fe}_2(\text{OH})_2(\text{Sq})^{2+}$, is much larger, $3 \times 10^3 \text{ s}^{-1}$. However, the squarate and Tiron dimers are different because the latter contains two more protons, as shown by the present and previous⁴ equilibrium and kinetic measurements. Probably they are structurally different as well. The structure of the squarate dimer has been assigned, on the basis of analogy to the known bis(μ -squarato) dimer of chromium(III),¹³ to have squarate bridging between two irons while the two bridging OH^- groups are retained. Bridging is more favorable for squarate because of the long distance of 3.3 Å between the oxygen donor atoms, compared to ~ 2.6 Å for catechols.¹⁴ This may be compared to the Fe-Fe distance of ~ 3.1 Å in the bis(μ -hydroxo) complex (DiPicFe -

$(\text{OH}_2)(\mu\text{-OH})_2$)¹⁵ (Dipic = 2,6-pyridinedicarboxylate). It should be noted that the structure of the aquairon(III) dimers has not been determined. An EXAFS study¹⁶ has been disputed¹⁷ and retracted.¹⁸ A later EXAFS and Mössbauer study¹⁹ of hydrated iron(III) on Nafion as been interpreted to give a dimer structure with an oxo bridge having with an Fe-O-Fe angle of 155° and an Fe-Fe distance of 3.42 Å. Throughout the present analysis, the bis(μ -hydroxo) formulation has been adopted, justified by the well-known analogous species in the aquachromium(III) system.^{7,13}

This brings us to the final question of the formulation of the Tiron-iron(III) dimer complex. The kinetic analysis indicates that this is a dimeric iron(III) species which is formed from Tiron and $(\text{H}_2\text{O})_8\text{Fe}_2(\text{OH})_2^{4+}$ and decomposes to the monomeric complex and $\text{Fe}(\text{OH})_2^{3+}$. The difficult feature is that no protons are released during complexation. This is shown by the fact that the absorbance after complexation is independent of acidity and that the complexation kinetics do not show an $[\text{H}^+]$ dependence for the reverse reaction. The complex has been formulated generically as $(\text{H}_2\text{O})_n\text{Fe}_2(\text{OH})_x(\text{LH}_x)^{4+x}$, and several possibilities might explain the proton count. If $x = 0$, then the dimer complex could be a normal chelate catechol dianion, with one or two water molecules bridging the irons but no bridging hydroxides. This seems rather unlikely because the complex breaks up at a rate similar to that of the parent bis(μ -hydroxo) dimer, while one would expect water bridges to be more labile than hydroxo bridges. If $x = 1$, the catechol anion could be monodentate with ($\mu\text{-H}_2\text{O}$)-($\mu\text{-OH}$) bridges, as illustrated in 1, for one of several possible



1



2

isomers. Another candidate with $x = 1$ could have a monodentate bridging catechol anion to give a ($\mu\text{-OC}$)($\mu\text{-OH}$) species, as shown in 2. A bridging catecholate has precedence in structurally characterized iron(III)²⁰ and titanium(IV) systems, although the catechol is present as the bidentate dianion in these examples. The titanium(IV) complex also contains a monodentate catecholate anion and provides some precedent for this binding mode.

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Recently, Kitajima et al.²¹ reported hydrotris(3,5-diisopropyl-1-pyrazolyl)borate complexes of iron(III) with monodentate and bidentate 4-nitrocatecholate. Monodentate formation also would be favored by the acidic conditions of the present study. The conformations shown for **1** and **2** have been selected to emphasize the possibilities for hydrogen bonding of the uncoordinated -OH, but other conformations obviously are possible. The kinetic arguments above would suggest that the bridging water in **1** is not consistent with the small value of k_3 , and **2** would be favored on this basis. It is interesting to note that 3-methylascorbic acid,²² in which one -OH is converted to -OCH₃, does not seem to give this dimeric species and undergoes complexation with aqueous iron(III) at normal rates. In 3-methylascorbate, the -OCH₃ cannot participate in hydrogen bonding, and this interaction only needs to contribute 3 kcal mol⁻¹ to make K_{f2} 6×10^{-3} times smaller with 3-methylascorbate than with ascorbate.

Experimental Section

Materials. Solutions of iron(III) perchlorate, from analytical grade iron wire, were prepared and standardized as described previously.² Solutions of Tiron were prepared by weight from the disodium salt of 1,2-dihydroxy-3,5-benzenesulfonate (BDH or Fisher). Perchloric acid and sodium perchlorate were prepared and standardized by standard methods.

Stopped-Flow Studies. Equal volumes of solutions of iron(III) and Tiron were mixed on a Triton Dynamics Model IIA system described previously⁴ and monitored at 660 nm. The iron(III) concentration and acidities were adjusted before mixing to give the desired concentrations of H⁺ and the bis(μ -hydroxo) iron(III) dimer. The required conditions were calculated using the equilibrium constants in the Appendix. The calculations assume that the Fe(OH)₂·3H₂O + (H₂O)₅Fe(OH)²⁺ equilibrium is immediately established, but the monomer-dimer equilibrium is slowly established and modeled by the numerical analysis.

Numerical Analysis. The nonlinear least-squares and numerical integration methods have been described previously.⁴

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Appendix

The absorbance-time profiles for the slower reaction have been modeled by numerical integration using a fourth-order Runge-Kutta algorithm. Each reaction involved is reversible, and the rate can be represented in

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terms of the forward (k_f) and reverse (k_r) rate constants and the equilibrium constant (K_e) by the following equation:

$$\text{rate} = k_f[\text{reactants}] - k_r[\text{products}] = k_f([\text{reactants}] - [\text{products}]/K_e)$$

If the rate is represented by U_i , then one obtains the following expressions for reactions 6-8, Scheme 1, and reaction 5, respectively:

$$U_1 = (k_6'[\text{H}^+] + k_6K_m)([\text{Fe}^{\text{III}}][\text{Tiron}]/(K_m + [\text{H}^+])) - ([\text{H}^+][\text{FeL}]/K_{f1})$$

$$U_2 = (k_7 + k_8[\text{H}^+])([\text{Fe}_2(\text{OH})_2] - (K_D[\text{Fe}^{\text{III}}][\text{Fe}^{\text{III}}]/((K_m + [\text{H}^+])^2)))$$

$$U_3 = (k_1 + k_2K_{mD}[\text{H}^+]^{-1})([\text{Fe}_2(\text{OH})_2][\text{Tiron}] - ([\text{Fe}_2\text{L}]/K_{f2}))$$

$$U_4 = k_5([\text{Fe}_2\text{L}] - (K_{f2}K_D[\text{H}^+][\text{Fe}^{\text{III}}][\text{FeL}]/(K_{f1}(K_m + [\text{H}^+])))$$

where $[\text{Fe}^{\text{III}}] = [\text{Fe}(\text{OH})_2\cdot 6\text{H}_2\text{O}] + [(\text{H}_2\text{O})_5\text{Fe}(\text{OH})^{2+}]$, $[\text{Fe}_2(\text{OH})_2] = [(\text{H}_2\text{O})_{10}\text{Fe}_2(\text{OH})_2^{4+}]$, $[\text{FeL}] = [(\text{H}_2\text{O})_4\text{FeL}^{2+}]$, and $[\text{Fe}_2\text{L}] = [(\text{H}_2\text{O})_8\text{Fe}_2\text{L}^{4+}]$. The following constants were fixed during the analysis: $K_m = 1.62 \times 10^{-3} \text{ M}^{21}$; $K_D = 1.9 \times 10^{-3} \text{ M}^{23}$; $k_6' = 10 \text{ M}^{-1} \text{ s}^{-1}$; $k_7 = 0.4 \text{ s}^{-1}$; $k_8 = 3.1 \text{ M}^{-1} \text{ s}^{-1}$; $K_{f2} = 6.3 \times 10^3 \text{ M}^{-1}$; $k_1 = 5.05 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$; $k_2K_{mD} = 1.67 \times 10^2 \text{ s}^{-1}$. Then the set of differential equations to be solved are the following:

$$d[\text{Fe}^{\text{III}}]/dt = -U_1 + 2U_2 + U_4$$

$$d[\text{Fe}_2(\text{OH})_2]/dt = -U_3 - U_2$$

$$d[\text{Tiron}]/dt = -U_1 - U_3$$

$$d[\text{FeL}]/dt = U_1 + U_4$$

$$d[\text{Fe}_2\text{L}]/dt = U_3 - U_4$$

The concentrations of each species are calculated at successive times, and the absorbance at each time is calculated as $\epsilon_1[\text{FeL}] + \epsilon_2[\text{Fe}_2\text{L}]$ to generate the absorbance-time profiles.