

## Substitution and oxidation kinetics in substituted catechol–iron(III) systems

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**Abstract** - The equilibrium constants and kinetics for the complexing of aqueous iron(III) by 2,3-dihydroxybenzoic acid (DHB) and 1,2-dihydroxy-3,5-benzenedisulfonate (Tiron) have been studied with iron(III) in excess over ligand. Formation constant comparisons indicate that DHB complexes in a mode analogous to salicylate. The reaction rate has the hydrogen ion dependence typical for iron(III) complexation, but there is an unusual contribution from a term second order in iron(III). The DHB-iron(III) complex shows a subsequent redox reaction with the rate first order in iron(III) and inverse second order in iron(II). The mechanistic implications for the redox mechanism are described.

### INTRODUCTION

This study is concerned with the equilibrium constants and kinetics for the complexing of iron(III) by 2,3-dihydroxybenzoic acid (DHB) and 1,2-dihydroxy-3,5-benzenedisulfonate (Tiron). The kinetics of the oxidation of DHB by iron(III) also has been studied. There have been several equilibrium studies of the Tiron system<sup>1,2,3</sup> but several features remain uncertain. With DHB, the previous observations<sup>4,5</sup> seem not to fully account for the added complexity of the ligand oxidation reaction.

### RESULTS

The complexation of Tiron has been studied mainly as a point of comparison with DHB. For example the formation constants are used to assess whether DHB is complexed through the carboxylate and phenoxide groups as in salicylate or through two phenoxides as in catechol.

When a solution of DHB is mixed with iron(III) in dilute aqueous acid the solution rapidly turns blue and then fades to yellow in 5 to 10 minutes, and finally changes to brown after several hours. Qualitative tests show that iron(II) is not present at the blue stage but is formed at the yellow stage. These observations indicate that the blue species is an iron(III)-DHB complex, and that the blue to yellow change involves oxidation of DHB by iron(III). When the same experiment is done with Tiron, there is immediate formation of a green color. This color appears to be stable, but spectrophotometric observations show that the absorbance actually decreases slowly on the tens of minutes time scale.

Spectrophotometric methods were used to determine the formation constants of the initial blue and green complexes with DHB and Tiron, respectively. These studies were done with [iron(III)] >> [ligand] at various acidities in 1 M NaClO<sub>4</sub>-HClO<sub>4</sub> at 25°. The results are plotted in Figure 1.

The linearity of the plots in Figure 1 is consistent with the following reactions.



The equilibrium constants are  $3.2 \pm 0.2$  and  $7.0 \pm 0.6$  M for Tiron and DHB respectively.

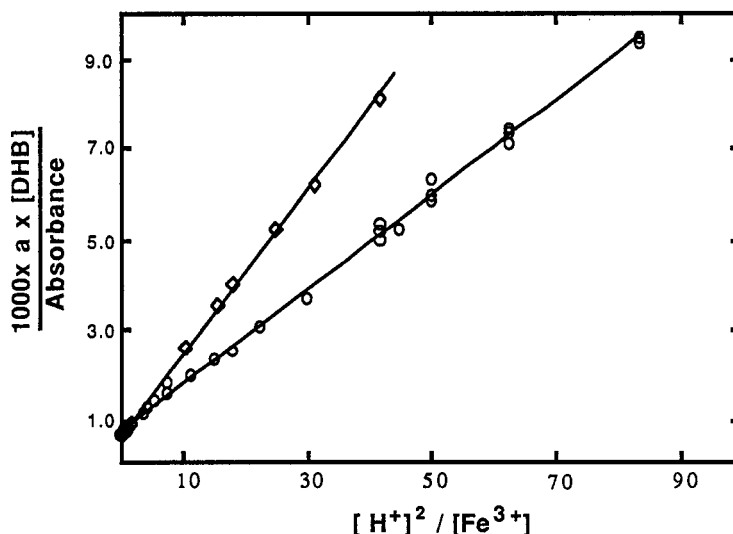
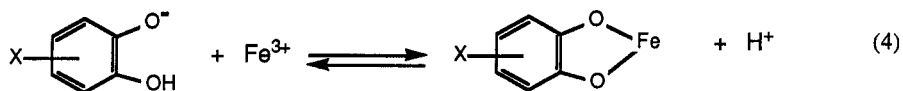
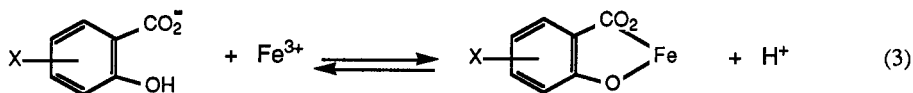


Figure 1. Equilibrium constant results for DHB at 600 nm (O) and Tiron at 662 nm:  $a$  is the path length.

The mode of complexing of DHB can be determined by comparison of the formation constants of substituted systems which must complex by salicylate or catecholate modes as shown in eq 3 and 4 respectively.

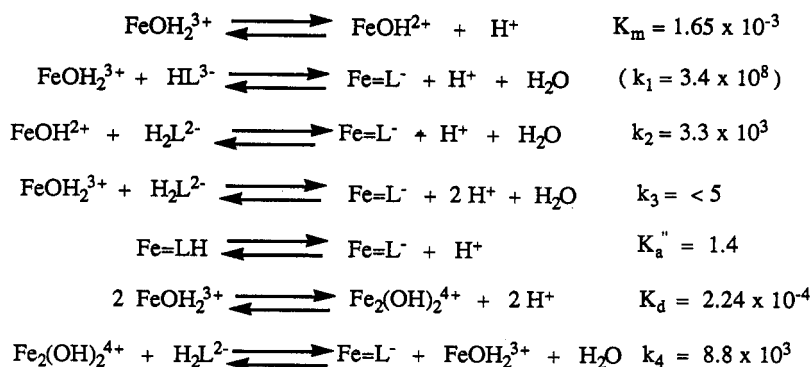


For the salicylate systems the logarithm of the equilibrium constants for eq 3 are in the range of 2.9 to 3.2 for salicylate and its 5-sulfonate and 4-hydroxy derivatives. For the catechol systems, the values for eq 4 are between 6.3 and 7.7 for catechol and its 4-nitro, 4-carboxy, and 3,5-disulfonate (Tiron) derivatives. The equilibrium constant determined here for eq 2 and the  $\text{pK}_a$  values of DHB (2.7 and 10.2) can be used to calculate the logarithm of the equilibrium constant for eq 4 of  $>10.3$  for DHB. This is far outside the range for the normal catechol complexing (6.3 to 7.7). A similar calculation for eq 3 gives 3.5 which is quite close to the range for the other salicylate ligands. It is concluded that DHB is complexing in the salicylate mode under our experimental conditions.

The kinetics of formation of the DHB and Tiron complexes has been studied by stopped-flow methods, under conditions of  $[\text{iron(III)}] \gg [\text{ligand}]$  between 0.01 and 0.7 M  $\text{H}^+$  in 1 M  $\text{NaClO}_4\text{-HClO}_4$  at 25°. The  $[\text{iron(III)}]$  and  $[\text{H}^+]$  dependence of the rate with Tiron can be accounted for by the reactions in Scheme I.

The species  $\text{Fe=L}^-$  represents the fully deprotonated catecholate type chelate. Because of the hydrogen ion ambiguity, the rate law cannot separate the  $k_1$  and  $k_2$  contributions. However the calculated value of  $k_1$  is so much larger than those previously observed<sup>6</sup>, that there is little doubt that  $k_2$  is actually the reaction pathway that is operative. The  $\text{K}_a$  is assumed to involve proton dissociation from an  $\text{-OH}$  coordinated to iron(III) in the chelate<sup>7,8</sup>.

## Scheme 1



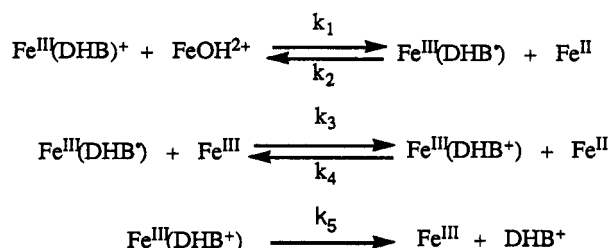
A similar scheme explains the kinetic results with DHB. The rate constants are  $k_1 = 4 \times 10^3$  or  $k_2 = 4.8 \times 10^3$ ,  $k_3 < 5$ ,  $k_4 = 1.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , and  $K_a'' = 2.1 \text{ M}$ . The latter refers to proton dissociation from coordinated -OH in the salicylate type chelate. The values of  $k_1$  and  $k_2$  are both reasonable so that it is not possible to determine which pathway makes the dominant contribution. The only unusual feature of the kinetics is a term second order in [iron(III)] which is explained by reaction of the  $\mu$ -hydroxy dimer of iron(III) as shown in Scheme I. Birus *et al.*<sup>9</sup> have reported a similar effect for the acetohydroxamate system. This contribution is only significant if  $[\text{H}^+] < 0.03 \text{ M}$  for DHB and Tiron, and could not be observed in parallel experiments with salicylate and catechol. It may be that the dimer appears more reactive with the 1,2,3-substituted ligands because of more favorable precursor complex (ion pair) formation.

The kinetics of oxidation of DHB by iron(III) has been studied also at 25° in 1 M NaClO<sub>4</sub>-HClO<sub>4</sub> with  $[\text{iron(III)}] \gg [\text{DHB}]$ . The following concentration ranges were studied:  $[\text{iron(III)}] 2 \times 10^{-3}$  to  $6 \times 10^{-3}$ ;  $[\text{iron(II)}] 0$  to  $5 \times 10^{-3}$ ;  $[\text{H}^+] 7.8 \times 10^{-3}$  to  $8 \times 10^{-2}$ . The observed pseudo-first-order rate constant is given empirically by eq 5.

$$k_{\text{obsd}} = \frac{0.36 \times [\text{Fe}^{3+}]}{([\text{H}^+] + 1.1 \times 10^{-3}) \times (2.9 \times 10^5 \times [\text{Fe}^{2+}]^2 + 1)} \quad (5)$$

Relatively small concentrations of iron(II) strongly inhibit the reaction as shown by the inverse squared dependence of the rate on  $[\text{iron(II)}]$ . There does not seem to be a mechanism which leads directly to eq 5 as the expression for the observed rate constant. It is noteworthy that the empirical constant of  $1.1 \times 10^{-3} \text{ M}$  in the denominator of eq 5 is close to the hydrolysis constant of  $\text{Fe}(\text{OH})_2^{3+}$ ,  $K_m = 1.65 \times 10^{-3} \text{ M}$ . With certain reasonable conditions the mechanism shown in Scheme II will lead to eq 5.

## Scheme 2



For this scheme the observed rate constant is given by eq 6 if a steady state is assumed for the radical and quinone complex products of the first and second reactions, respectively.

$$k_{\text{obsd}} = \frac{k_1 [\text{Fe}^{3+}]^2}{(K_m + [\text{H}^+]) (k_2 k_4 / k_3 k_5 [\text{Fe}^{2+}]^2 + k_2 / k_3 [\text{Fe}^{2+}] + [\text{Fe}^{3+}])} \quad (6)$$

The experimental data are consistent with eq 6, and a least-squares fit gives  $k_1 = 206 \pm 8 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_2 k_4 / k_3 k_5 = (1.4 \pm 0.2) \times 10^3$  and  $k_2 / k_3 < 1$ , so that  $k_4 / k_5 > 1.4 \times 10^3$ . These parameters make eq 6 almost the mathematical equivalent of eq 5 because the  $[\text{Fe}^{2+}]$  term in the denominator is negligible and the  $[\text{Fe}^{3+}]$  term attenuates the  $[\text{Fe}^{3+}]^2$  factor in the numerator.

Perhaps the most surprising feature of the reaction is that the iron(III)-DHB complex does not simply undergo intramolecular electron transfer. The fact that the more labile  $\text{FeOH}^{2+}$  is involved in the first step, rather than the stronger oxidizing  $\text{FeOH}_2^{3+}$ , can be rationalized if the initial step is substitution to give a di-iron(III) species. The coordinated DHB is then made more oxidizable and electron transfer and release of labile iron(II) follows.

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