Modeling the Kinetics of Fe(II) Oxidation in the Presence of Citrate and Salicylate in Aqueous Solutions at pH 6.0−8.0 and 25 °C

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The kinetics of Fe(II) oxidation in the presence of low concentrations of citrate and salicylate have been investigated in aqueous solutions over the pH range 6.0−8.0 using colorimetry. A kinetic model has been developed to describe the oxidation of Fe(II) with specific attention given to the oxidation of inorganic Fe(II), formation and dissociation of Fe(II) complexes and the oxidation of these complexes. At low concentrations of salicylate, both experimental data and model show that the common approach to modeling Fe(II) oxidation that assumes pre-equilibrium between metal and ligand prior to their oxidation is not valid. Complexation of Fe(II) by salicylate is found to be relatively slow, and oxidation of the complex formed occurs rapidly. Citrate, on the other hand was found to be in rapid equilibrium with Fe(II) but the complex formed was oxidized slowly. Both citrate and salicylate complexes are found to dissociate at a rate much faster than previously thought. A model of the oxidation kinetics of Fe(II) species that incorporates the formation and dissociation kinetics of Fe(II) and Fe(III) complexes of citrate and salicylate as well as the reactions of these species with oxygen and reduced oxygen species including superoxide and hydrogen peroxide provides an excellent description of data obtained over a wide range of concentration and pH conditions.

1. Introduction

Iron is essential for virtually all life forms and plays a central role in many biological and chemical processes. [1] Despite being a ubiquitous element in the Earth's crust, iron is present at an extremely low concentration (less than nanomolar) in many natural waters due to the rapid precipitation of its thermodynamically stable oxidation state, Fe(III), resulting in the formation of iron oxides and hydroxides. These particulate forms of iron are highly insoluble at circumneutral pH[2] and are not available for direct biological uptake.[3]

The reduced form of iron, Fe(II), however, is quite soluble with the result that up to millimolar concentrations of Fe(II) may be found in anoxic ground-waters, interstitial pore-waters and hypolimnetic regions of lakes.[4] This more soluble form of iron is thought to be commonly involved in a number of iron uptake strategies by micro-organisms.[5] Thus, the rate of interconversion from Fe(II) to Fe(III) is critical in determining the fate of iron and its bioavailability in many natural waters.

The presence of organic ligands may significantly influence the rate of oxidation of Fe(II) as a result of their capability of complexing both Fe(II) and Fe(III) species. If oxidation of the complexed form of Fe(II) is rapid, it may enhance the removal of Fe(II) and vice versa. The rates of Fe(II) complexation by organic ligands and dissociation of the complexes are also important to the oxidation of Fe(II) if they all occur at similar time scales. In this event, the net removal of Fe(II) should be interpreted as a function of inorganic Fe(II) oxidation, Fe(II) complexation/dissociation and oxidation of the complexed form of Fe(II). Early studies by Theis and Singer[6] reported that the presence of organic ligands may enhance, retard or have no effect on the rate of Fe(II) oxidation.

In recent years, two general approaches have been adopted in modeling the kinetics of Fe(II) oxidation in the absence and presence of organic ligands: the "speciation" approach and the "FeL" approach. In the "speciation" approach, oxidation of Fe(II) is described in terms of oxidation of iron species initially present with equilibrium assumed to exist prior to oxidation occurring. Given the ability of describing the kinetics of Fe(II) oxidation over a range of conditions, the "speciation" approach has been adopted in a number of recent studies.[7–13] The major disadvantage of the speciation approach is that the accuracy of the estimated rate constants of the many individual species in the model depends largely on the accuracy and/or validity of the thermodynamic equilibrium constants of the presumed species present. The pre-equilibrium assumption, which assumes that iron species equilibrate rapidly prior to their oxidation, may be reasonable for inorganic species where exchange kinetics between species are extremely fast but may not always be valid in the presence of organic ligands. This is particularly problematic in the case of ligands of low effective binding concentration (as in the case of salicylate presented here) and/or when higher order or polymeric complexes (with relatively slow dissociation kinetics) are formed.

In contrast to the speciation approach, the so-called "FeL" approach assumes the involvement of a single entity in the oxidation process (e.g., $Fe^{II}L$ where this entity is representative of all organically complexed Fe(II) species). This approach, with far fewer fitting parameters, no pre-equilibrium assumption and no need for detailed knowledge of iron speciation, has been used as the basis for a number of recent studies on the transformation of iron in natural waters.[14–24] The major disadvantage of the "FeL" approach is that it does not provide insight into the oxidation mechanism, which may be necessary to explain the variation in rate of Fe(II) oxidation at different experimental conditions, particularly over a range of pH. The

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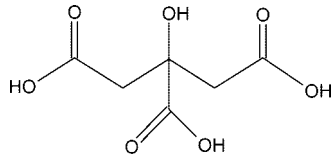
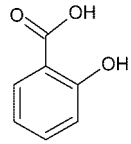


citric acid



salicylic acid

Figure 1. Structures of citric acid (H_3cit) and salicylic acid (H_2sal).

developed model may also not be applicable in a system where different binding entities coexist and/or different complexes are formed.

In this study, the kinetics of Fe(II) oxidation in the presence of citrate and salicylate have been investigated in aqueous solutions over the pH range 6.0−8.0 using colorimetric methods. Both citrate and salicylate (Figure 1) are selected because they are well defined organic compounds and have two functional groups (carboxylic/hydroxyl groups in citrate molecule and carboxylic/phenolic group in salicylate molecule) that are similar to two of the most abundant binding sites found in natural organic matter. In contrast to our previous investigation[13] where the oxidation of Fe(II) was interpreted in terms of contribution of various Fe(II)−citrate species, the oxidation of Fe(II) in the presence of much lower ligand concentrations more typical of the conditions expected in natural waters is considered in this study. Under such conditions, consideration must be given to the oxidation of inorganic Fe(II) as well as formation and dissociation of Fe(II) complexes and oxidation of the complexed Fe(II). Two key issues being addressed in this study are (i) whether the pre-equilibrium assumption (and thus the "speciation" approach) is valid under the conditions used here and (ii) whether the "FeL" approach is capable of describing Fe(II) oxidation kinetics in such complex systems.

2. Experimental Section

2.1. Reagents. All solutions were prepared using 18 MΩ cm Milli-Q water. All chemicals were analytical grade and purchased from Sigma-Aldrich (or as otherwise stated). All glassware was acid washed (using 5% w/v HNO_3) one week before use. Stock solutions were refrigerated (at 4 °C) in the dark when not in use.

Solutions at pH (p^{a}H) 6.0, 6.5, 7.0, 7.5 and 8.0 were prepared by adding appropriate concentrations of NaOH or HCl to solutions containing 10 mM buffer, 2 mM $NaHCO_3$ and 0.1 M NaCl. MES hydrate (2-(*N*-morpholino)ethanesulfonic acid hydrate, SigmaUltra) buffer was used for pH 6.0 and 6.5. HEPES (4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid, SigmaUltra) buffer was used for pH 7.0, 7.5 and 8.0. Both MES and HEPES are noncomplexing agents[25] and do not participate in the various chemical reactions of iron species.[8]

All pH measurements were made using a Hanna HI9025 pH meter combined with a glass electrode and Ag/AgCl reference. The pH electrode was calibrated using NIST buffer solutions (pH 4.01, 7.01 and 10.01). During the course of experiments, no shift in pH was detectable to within ±0.02 pH units.

Temperature was maintained at 25 ± 0.6 °C at all times using a Thermoline recirculator and experiments were conducted in ambient light conditions at a room temperature setting of 25 °C.

Fe(II) stock solutions were prepared by dissolving ferrous ammonium sulfate hexahydrate ($Fe(NH_4SO_4)_2 \cdot 6H_2O$) in 2 mM HCl. This level of acidity prevented Fe(II) oxidation over time scales of interest yet did not induce significant pH change when aliquots of the Fe(II) stock were added to sample solutions. Stock solutions of salicylate and citrate were prepared in buffer solutions (with the above constituents) and pH was adjusted accordingly.

A ferrozine working solution of 1 mM was prepared by dissolving 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-*p,p′*-disulfonic acid, monosodium salt hydrate in buffer solutions and pH was adjusted accordingly. Ferrozine (FZ) was used as a color forming agent for determination of Fe(II) because it reacts extremely rapidly with Fe(II)[26,27] to form a stable purple complex at neutral pH with maximum absorbance at 562 nm and molar absorptivity of $\epsilon_{562} = 30\ 000\ M^{-1}\ cm^{-1}$.[28,29] In addition, FZ does not bind Fe(III) to any significant extent[30] and is commercially available.

2.2. Oxidation of Fe(II) in the Presence of Model Organic Compounds. To examine the kinetics of Fe(II) oxidation in the presence of organic ligands, two different concentrations of Fe(II) were added to solutions containing known concentrations of ligands and the absorbance at 562 nm was recorded over time.

A peristaltic pump was used to draw the sample and ferrozine solutions into a tee junction where they were mixed before being driven through a 1.0 m path length cell (LWCC type II, World Precision Instruments). The resulting $Fe^{II}FZ_3$ complex was measured colorimetrically at 562 nm using an Ocean Optics spectrophotometry system (a combination of a broadband Tungsten Halogen lamp and a S2000 spectrophotometer). The absorbance was baseline corrected at a reference wavelength of 690 nm. The spectrophotometer was zeroed for each run using a control solution (containing no added iron) to account for the absorbance of concentrated ferrozine and background of the sample solutions (containing ligands) at 562 nm. It is important to note that the absorbance of $Fe^{II}FZ_3$ measured in this study has been demonstrated to be equivalent to total Fe(II) (i.e., sum of the concentration of both inorganic Fe(II) and organically complexed Fe(II)) (see Supporting Information). Because the experiments were conducted over the circumneutral pH range 6.0−8.0, reduction of Fe(III) and its complexes by FZ is insignificant.[31]

The molar ratios of Fe(II) to both citrate and salicylate (denoted as L) used were 50 nM Fe(II):5 μM L, 50 nM Fe(II):50 μM L, 0.2 μM Fe(II):0.2 mM L and 0.2 μM Fe(II):1 mM L. Similar metal to ligand molar ratios but different initial Fe(II) concentrations (i.e., 50 nM Fe(II):50 μM L vs 0.2 μM Fe(II):0.2 mM L) were chosen to assess the dependence of rate of Fe(II) oxidation on initial Fe(II) concentration.

Calibration curves were developed at all pH and ligand concentrations examined by recording the absorbance measured (at 562 nm) when different concentrations of Fe(II) were added directly to the buffer solutions containing 0.5 mM FZ and a half of the respective ligand concentration used in the actual kinetic runs (to take into account a dilution factor of 2 that occurs on mixing the sample and reagents).

TABLE 1: Modeled Reactions for the Oxidation of Fe(II) in the Presence of Organic Ligands

no.	reactions	note[a]
1	$Fe(II) + O_2 \rightarrow Fe(III) + O_2^-$	1
2	$Fe(II) + O_2^- + 2H^+ \rightarrow Fe(III) + H_2O_2$	1
3	$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^{\cdot} + OH^-$	1
4	$Fe(III) + O_2^- \rightarrow Fe(II) + O_2$	1
5	$Fe(III) + Fe_I \rightarrow AFO + nH^+$	1
6	$O_2^- + O_2^- + 2H^+ \rightarrow H_2O_2 + O_2$	1
7	$Fe(II) + L \rightarrow Fe^{II}L$	2
8	$Fe^{II}L \rightarrow Fe(II) + L$	2
9	$Fe^{II}L + O_2 \rightarrow Fe^{III}L + O_2^-$	2
10	$Fe^{II}L + O_2^- + 2H^+ \rightarrow Fe^{III}L + H_2O_2$	3
11	$Fe^{II}L + H_2O_2 \rightarrow Fe^{III}L + OH^- + OH^{\cdot}$	3
12	$Fe(III) + L \rightarrow Fe^{III}L$	4
13	$Fe^{III}L \rightarrow Fe(III) + L$	5
14	$Fe^{III}L + O_2^- \rightarrow Fe^{II}L + O_2$	2

[a] Notes: (1) Pham,[32] see Supporting Information; (2) constrained/model fitting parameter, see text; (3) constrained/unimportant fitting parameter, see text; (4) Pham;[40] (5) slow,[18] unimportant fitting parameter.[20]

3. Modeling Overview

3.1. Modeling Approaches and Modeled Reactions for Fe(II) Oxidation in the Presence of Organic Ligands. In this study, the oxidation of Fe(II) in the presence of low concentrations of organic ligand is investigated with the oxidation of Fe(II) described as a function of inorganic oxidation of Fe(II), organic complexation of Fe(II), dissociation of the organic complex and oxidation of the complex. At the low ligand concentrations of interest here, it is possible that these processes occur on a similar time scale. It therefore may not be appropriate to investigate the system using the "speciation" approach in which pre-equilibrium between iron species prior to their oxidation is assumed.

On the other hand, speciation models (see Supporting Information) indicated that at the concentrations of Fe(II) and ligands investigated in this study, most organically bound Fe(II) is present in the form of monomeric complexes (i.e., $Fe^{II}cit^-$ in the case of citrate and $Fe^{II}sal^0$ in the case of salicylate). It is therefore possible to use the "FeL" approach to describe the oxidation of Fe(II). A list of modeled reactions that was developed in a manner similar to that described in the case of inorganic Fe(II) oxidation[32] is given in Table 1.

In Table 1, L represents the organic ligand with total concentration denoted as $[L]_T$. $Fe^{II}L$ and $Fe^{III}L$ are symbols for any complex formed between Fe(II) and Fe(III) and organic ligand L respectively. Rate constants for reactions 7−14 are thereafter defined accordingly. For simplicity, the term Fe(II)−salicylate refers to any complex formed between Fe(II) and salicylate ions whereas the term $Fe^{II}sal^0$ refers to a specific complex involving one ferrous ion (of 2+ charge) and one salicylate ion (of 2− charge). Similar notations are adopted in the case of citrate.

3.2. Estimation of Modeled Reaction Rate Constants. Although the reaction rate constants for the inorganic oxidation of Fe(II) (reactions 1−6) have been reported previously,[32] there are still a number of unknown rate constants in the reaction scheme presented in Table 1. As such, the values produced from the model fitting may not be unique. It is therefore desirable to constrain the values of rate constants for as many of the more important reactions as possible. Several approaches have been adopted for estimating the rate constants of various reactions including: (i) assumption of pseudo-first-order kinetics, (ii) use of the outer-sphere complexation model, and (iii) use of the linear free energy relationship model.

3.2.1. Pseudo-First-Order Kinetics Approach. Estimates of k_9 (in the case of citrate) and k_7 and k_9 (in the case of salicylate) (details are given in the Discussion) can be readily achieved by assuming that pseudo-first-order kinetics hold in the early stages of the oxidation reaction (i.e., ligand concentrations were relatively high and constant compared to Fe(II) concentrations). Because the concentrations of superoxide (O_2^-) and hydrogen peroxide (H_2O_2) will be low initially, reactions 1, 7, 8 and 9 would be expected to control the oxidation of Fe(II) at early times.

3.2.2. Outer-Sphere Complexation Model Approach. Crude estimates of several rate constants (k_7, k_8, k_{10} and k_{14}) were also deduced by assuming that the kinetics of certain reactions involving iron species (specifically those involving interaction with ligands and superoxide) were controlled purely by the water loss kinetics at the metal coordination sphere (i.e., an outer-sphere complexation model was assumed). The rate constant k_f of the reaction between Fe(II) and ligand L, according to the model,[33] is estimated as follows:

$$k_f = \sum K_{OS}(Fe(II)_i, L) \times k_{-w}(Fe(II)_i) \times \alpha_{Fe(II)_i} \quad (1)$$

where $K_{OS}(Fe(II)_i,L)$ is the stability constant of the outer-sphere complex formed between species $Fe(II)_i$ and ligand L, $k_{-w}(Fe(II)_i)$ is the water loss rate of species $Fe(II)_i$ and $\alpha_{Fe(II)_i}$ is the proportion of species $Fe(II)_i$ in the total Fe(II) pool.

Due to the critical importance of reactions 7 and 8 to the oxidation of Fe(II) in the presence of organic ligand, the approach taken to estimating these kinetic constants (defined accordingly in Table 1) deserves particular attention with details given below.

The rate law expression for the disappearance of Fe(II) according to reaction 7 alone gives

$$\frac{d[Fe(II)]}{dt} = -k_7[L][Fe(II)] \quad (2)$$

If L is used in excess of Fe(II), then $[L] \sim [L]_T$ and thus

$$\frac{d[Fe(II)]}{dt} \sim -k_7[L]_T[Fe(II)] \quad (3)$$

If the organic ligand L over the pH range considered is partially protonated, it is possible that only a proportion of L that is present effectively reacts with Fe(II). For simplicity, it is assumed that the effective proportion is dominated by L_{eff} and the complex formed between Fe(II) and L_{eff} is of 1:1 stoichiometry ($Fe^{II}L_{eff}$). The complexation of Fe(II) by L_{eff} is described by:

$$Fe(II) + L_{eff} \xrightarrow{k_7^{eff}} Fe^{II}L_{eff} \quad (4)$$

with k_7^{eff} being estimated from the outer-sphere complexation model (eq 1).

The rate of Fe(II) removal according to eq 4 is given by

$$\frac{d[Fe(II)]}{dt} = -k_7^{eff}[L_{eff}][Fe(II)] \quad (5)$$

Given that $[Fe^{II}L_{eff}] \sim [Fe^{II}L]$, combining eqs 3 and 5 gives

$$k_7 = k_7^{eff}\frac{[L_{eff}]}{[L]_T} \quad (6)$$

It should therefore not be surprising that the estimated value of k_7 (defined accordingly in the model) is much smaller than previously thought if the concentration of L_{eff} constitutes a very

TABLE 2: Estimated Reaction Rate Constants (in M^{-1} s^{-1} Except for k_8 in s^{-1}) at pH 6.0 and $I = 0.1$ Based on the Outer-Sphere Complexation Model and Linear Free Energy Model[a]

	salicylate	citrate
Outer-Sphere Complexation Model		
k_7	0.53	4.46×10^7
k_8	4.17	4.26×10^3
k_{10}	1.55×10^6	6.03×10^5
k_{14}	5.97×10^7	
Linear Free Energy Model		
k_9	1.92×10^3	18.9
k_{11}	1.24×10^8	6.67×10^6

[a] Details of the calculations are given in the Supporting Information.

small fraction of the total ligand concentration, $[L]_T$ (as we will see is the case for salicylate).

It is also worth noting that because different ferrous species are present at different pH, k_7^{eff} and thus k_7 may vary with varying pH. However, both k_7^{eff} and k_7 will not vary with different L concentrations at any given pH because the ratio $[L_{eff}]/[L]_T$ would remain the same (provided the 1:1 stoichiometry is maintained). This may only be correct for simple model organic compounds but may not be true for large organic molecules (e.g., natural organic matter) because factors such as steric hindrance may become significant.

Reaction 8 represents the dissociation of Fe(II) complexes and the general rate law for this reaction is given by

$$\frac{d[Fe^{II}L]}{dt} = -k_8[Fe^{II}L] \quad (7)$$

However, if a 1:1 complex $Fe^{II}L_{eff}$ is assumed to dominate $Fe^{II}L$ at any pH considered, then the dissociation constant of $Fe^{II}L$ (k_8) may be considered similar to that of $Fe^{II}L_{eff}$ (k_8^{eff}), thus

$$k_8 = k_8^{eff} = \frac{k_7^{eff}}{{}^cK} \quad (8)$$

where ${}^cK$ is the conditional stability constant of the 1:1 complex $Fe^{II}L_{eff}$ which may be obtained from the literature[2,34] after correction for the ionic strength of the given experimental conditions.

Estimates of k_7 and k_8 at pH 6.0 and $I = 0.1$ for both cases are given in Table 2. Details of the estimation are given in the Supporting Information.

Rush and Bielski,[35] while examining the reaction of inorganic iron species with superoxide, also suggested that the rate of reaction of Fe^{2+} and $Fe(OH)^{2+}$ with O_2^- may be purely governed by the kinetics of water loss from the metal coordination sphere. If the reactions of organically complexed iron species including both $Fe^{II}L$ and $Fe^{III}L$ with O_2^- follow in the same manner and if the substitution of organic molecules does not significantly alter the rate of water loss from the metal coordination sphere (as has been observed with $Febpy^{2+}$ [36]), then the rate constant of these reactions can be approximated. Estimates of k_{10} and k_{14} at pH 6.0 and $I = 0.1$ for both cases are given in Table 2 (details of the estimation are given in the Supporting Information). It should be noted that, under our specific experimental conditions, the major organically complexed iron species at pH 6.0 are $Fe^{II}cit^-$ (for Fe(II)−citrate complexes), $Fe^{II}sal^0$ (for Fe(II)−salicylate complexes) and $Fe^{III}sal^+$ (for Fe(III)−salicylate complexes). Both monomeric and polymeric Fe(III)−citrate complexes, however, may coexist at this pH.

3.2.3. Linear Free Energy Relationship Approach. Use is made of a linear free energy relationship in obtaining initial estimates of the rate constants for the reaction between organically complexed Fe(II) and H_2O_2. [37,38] Estimates of k_9 and k_{11} are given in Table 2. Details of the estimation are given in the Supporting Information.

3.3. Modeling Procedure. Speciation of Fe(II) and Fe(III) in the presence of organic ligands was computed using the speciation package MINEQL$^+$.[39] Lists of all equilibrium reactions considered in the speciation models in the presence of salicylate and citrate are given in the Supporting Information.

The general model for Fe(II) oxidation in the presence of either citrate or salicylate consists of 14 reactions (Table 1) with reaction rate constants k_1-k_6 predetermined in the inorganic Fe(II) system[32] (a summary is given in the Supporting Informationd), k_{12} is taken from Pham[40] and k_{13} is assumed to be slow[18] and insignificant in the model (in both cases). Rate constants for other reactions of which the values are constrained to the values given in Table 2 are considered to be fitting parameters. The kinetic modeling package PRESTO[41] was used to refine these estimates by fitting the kinetic model to the Fe(II) oxidation kinetics data.

4. Results

For the purpose of comparison, the kinetics of Fe(II) oxidation in the presence of both citrate and salicylate are assumed to be pseudo-first-order in the first half-time of the oxidation. That is,

$$\frac{d[Fe(II)]_T}{dt} = -k'[Fe(II)]_T \quad (9)$$

where k' (in s^{-1}) is the pseudo-first-order rate constant of Fe(II) oxidation.

Solution to this ODE is

$$[Fe(II)]_{T,t} = [Fe(II)]_{T,0} \exp(-k't) \quad (10)$$

Thus k' can be estimated from a plot of $-\ln([Fe(II)]_{T,t}/[Fe(II)]_{T,0})$ versus time t. Summaries of the pseudo-first-order rate constants of Fe(II) oxidation in the absence and presence of various ligand concentrations are given in Table 3 (for the case of salicylate) and Table 4 (for the case of citrate).

4.1. Oxidation of Fe(II) in the Presence of Salicylate. In the presence of low salicylate concentrations (5 and 50 μM), the rate constant for oxidation of 50 nM Fe(II) at pH 6.0−7.5 is slightly higher than observed in the absence of organic ligand. The effect of the presence of organic ligand on rate of Fe(II) oxidation at pH 8.0, however, appeared slight (Table 3).

In the presence of high salicylate concentrations (0.2 and 1 mM), the rate of oxidation of 0.2 μM Fe(II) increases significantly over the organic-free case with this effect observable at all pHs examined (Table 3).

4.2. Oxidation of Fe(II) in the Presence of Citrate. As shown in Table 4, the kinetics of Fe(II) oxidation varied significantly in the presence of 5 μM, 50 μM, 0.2 mM and 1 mM citrate and over the pH range 6.0−8.0. Addition of 5 μM citrate has a minimal effect on the overall oxidation rate. However, in the presence of 50 μM, 0.2 mM and 1 mM citrate, the oxidation of Fe(II) increases remarkably at pH 6.0, 6.5 and 7.0 where the oxidation of inorganic Fe(II) is slow (Table 4).

At pH 7.5 and 8.0, two different effects of citrate addition on the oxidation of Fe(II) are observed. Addition of 50 μM

TABLE 3: Pseudo-First-Order Rate Constant for Fe(II) Oxidation (k', in s^{-1}) in the Presence of Different Initial Fe(II) and Salicylate Concentrations Over the pH Range 6.0−8.0[a]

$[Fe(II)]_0$	$[sal]_T$	pH 6.0	pH 6.5	pH 7.0	pH 7.5	pH 8.0
50 nM	0	4.00×10^{-5}	7.70×10^{-5}	2.31×10^{-4}	6.63×10^{-4}	4.00×10^{-3}
	5 μM	5.93×10^{-5}	1.57×10^{-4}	1.97×10^{-4}	7.34×10^{-4}	4.21×10^{-3}
	50 μM	8.01×10^{-5}	1.61×10^{-4}	2.90×10^{-4}	1.17×10^{-3}	4.66×10^{-3}
0.2 μM	0.2 mM	8.24×10^{-5}	2.61×10^{-4}	4.87×10^{-4}	2.45×10^{-3}	7.05×10^{-3}
	1 mM	2.94×10^{-4}	5.33×10^{-4}	1.31×10^{-3}	5.79×10^{-3}	n.d.[b]

[a] Values of k' are estimated according to eq 10. [b] No measurement was made because Fe(II) oxidized rapidly.

TABLE 4: Pseudo-First-Order Rate Constant for Fe(II) Oxidation (k', in s^{-1}) in the Presence of Different Initial Fe(II) and Citrate Concentrations Over the pH Range 6.0−8.0[a]

$[Fe(II)]_0$	$[cit]_T$	pH 6.0	pH 6.5	pH 7.0	pH 7.5	pH 8.0
50 nM	0	4.00×10^{-5}	7.70×10^{-5}	2.31×10^{-4}	6.63×10^{-4}	4.00×10^{-3}
	5 μM	9.44×10^{-5}		2.30×10^{-4}	6.57×10^{-4}	4.64×10^{-3}[b]
	50 μM	2.15×10^{-4}	4.01×10^{-4}	5.88×10^{-4}	9.13×10^{-4}	3.99×10^{-3}
0.2 μM	0.2 mM	4.28×10^{-4}	3.82×10^{-4}	6.23×10^{-4}	1.23×10^{-3}	3.16×10^{-3}
	1 mM	1.15×10^{-3}	8.86×10^{-4}	1.02×10^{-3}	1.26×10^{-3}	3.26×10^{-3}

[a] Values of k' are estimated according to eq 10. [b] Unexpectedly high oxidation rate constant.

citrate at pH 7.5 results in an increase in the oxidation rate but similar kinetics are observed in the presence of 0.2 mM and 1 mM citrate (Table 4). At pH 8.0, addition of citrate results in a slight reduction in the rate of oxidation of Fe(II) compared to the inorganic case.

Oxidation rate constants of Fe(II) in the presence of 1 mM citrate are similar at all pHs examined except at pH 8.0 where the rate constant is significantly higher (Table 4).

These unpredicted but exciting observations on the kinetics of Fe(II) oxidation in the presence of different citrate and Fe(II) concentrations and over a range of pH will be explained subsequently using a relatively simple Fe(II)/citrate oxidation model.

5. Discussion

5.1. Fe(II) Oxidation in the Presence of Salicylate. ***5.1.1. Validity of the Pre-equilibrium Assumption and the Speciation Approach.*** In the "speciation" approach, iron species (both inorganic and organically complexed species) were assumed to equilibrate rapidly prior to their oxidation. This assumption, as stated above, could be problematic when the ligand present has extremely low effective binding concentration. As an illustrative example, the case of salicylate is described below.

Given $k_7 = 0.53\ M^{-1}\ s^{-1}$ (Table 2), the rate of Fe(II) removal due to complexation by 5 μM salicylate (reaction 7) at pH 6.0 is given by

$$-\frac{d[Fe(II)]}{dt} = k_7[Fe(II)][L] \sim 2.65 \times 10^{-6}[Fe(II)] \quad (11)$$

On the other hand, given ambient oxygen concentration $[O_2]_T = 2.61 \times 10^{-4}\ M^{-1}\ s^{-1}$, the rate of Fe(II) removal due to inorganic oxidation (reaction 1) at pH 6.0 ($k_1 = 0.11$) is given by

$$-\frac{d[Fe(II)]}{dt} = k_1[Fe(II)][O_2] \sim 2.87 \times 10^{-5}[Fe(II)] \quad (12)$$

Equations 11 and 12 clearly indicate that the rate of Fe(II) removal due to complexation by 5 μM salicylate is much slower than the rate of Fe(II) removal due to inorganic oxidation at pH 6.0. In this instance, the pre-equilibrium assumption between Fe(II) and salicylate ion prior to Fe(II) oxidation (i.e., $k_7[L] \gg k_1[O_2]$) is not valid.

The pseudo-first-order rate constant data for Fe(II) oxidation in the presence of salicylate presented in Table 3 also indicates that an assumption of pre-equilibrium between Fe(II) and salicylate prior to Fe(II) oxidation under the experimental conditions used in this study is not appropriate. If pre-equilibrium between Fe(II) and salicylate were established, the proportion of both Fe(II) (unbound) and Fe(II)−salicylate in the total Fe(II) should remain the same if the same Fe(II):salicylate ratio is maintained. The overall oxidation rate constants (calculated as a weighted sum of the oxidation rate constant of individual ferrous species[7,8]) therefore should equally be the same in both systems of 50 nM Fe(II):50 μM salicylate and of 0.2 μM Fe(II):0.2 mM salicylate. The k' values, however, are found to be significantly different between the two systems (Table 3).

Thus, although ferrous ion may react rapidly with deprotonated organic ligand (as predicted from the Eigen and Wilkins complexation model[33]), it is the apparent (conditional) complexation rate constant (k_7) that determines whether or not the pre-equilibrium assumption between Fe(II) and organic ligand is appropriate. The apparent rate constant k_7 and thus the removal of Fe(II) due to complexation (reaction 7) may depend not only on the characteristic of the organic ligand (pK_a) and pH (degree of the ligand protonation) but also on the total concentration of the organic ligand that is present in the system.

5.1.2. Validation of the Estimated Values of k_7 and k_9 Based on the Pseudo-First-Order Rate Constant Data. Because the approach taken in estimating the reaction rate constants provided in Table 2 is crude, it is necessary to validate these values based on the experimental data.

Estimation of k_7 and k_9 can be made by assuming that the oxidation of Fe(II) in the presence of salicylate is predominantly governed by reactions 1, 7, 8 and 9. The rate constants for reactions 1 and 9 in this case should be treated as apparent rate constants and denoted as k_1^{app} and k_9^{app}, respectively. The assumption, however, may only be appropriate at the early stage of the oxidation when reactions 2−6 and 10−14 are not important. At high pH and particularly at high ligand concentrations, pseudo-first-order behavior of Fe(II) oxidation kinetics may not be followed.

Because $Fe^{II}L$ ($Fe^{II}sal^0$ in this instance) is present at an extremely low concentration (see Supporting Information) and the rate of consumption of $Fe^{II}L$ (through reactions 8 and 9) is much faster than the rate of formation (Table 2), it is reasonable to assume that $[Fe^{II}L]$ reaches a steady state concentration almost instantly. The rate law expressions for reactions 7, 8 and 9 give

$$0 = \frac{d[Fe^{II}L]}{dt} = k_7[L][Fe(II)] - k_8[Fe^{II}L] - k_9^{app}[O_2][Fe^{II}L] \quad (13)$$

$$[Fe^{II}L] = \frac{k_7[L]}{k_8 + k_9^{app}[O_2]}[Fe(II)] \quad (14)$$

On the other hand, because $[Fe^{II}L]$ is very small, $-d[Fe(II)]/dt \sim -d[Fe(II)]_T/dt$ and thus,

$$-\frac{d[Fe(II)]}{dt} = \frac{d[Fe(III)]}{dt} + \frac{d[Fe^{III}L]}{dt} = k_1^{app}[O_2][Fe(II)] + k_9^{app}[O_2][Fe^{II}L] \quad (15)$$

Substituting eq 14 to eq 15 gives

$$-\frac{d[Fe(II)]}{dt} = \left(k_1^{app}[O_2] + \frac{k_7[L]k_9^{app}[O_2]}{k_8 + k_9^{app}[O_2]}\right)[Fe(II)] \quad (16)$$

Given $[L]_T$ and $[O_2]_T \gg [Fe(II)]$, the solution to this differential equation is

$$[Fe(II)] = [Fe(II)]_0 \exp\left(-\left(k_1^{app}[O_2]_T + \frac{k_7[L]_T k_9^{app}[O_2]_T}{k_8 + k_9^{app}[O_2]_T}\right)t\right) \quad (17)$$

Hence, a plot of $-\ln([Fe(II)]/[Fe(II)]_0)$ versus t will have a slope of $[k_7k_9^{app}[L]_T[O_2]_T/(k_8 + k_9^{app}[O_2]_T)] + k_1^{app}[O_2]_T$ which is essentially equal to the pseudo-first-order oxidation rate constant of Fe(II) in the presence of salicylate (k', Table 3). A plot of k' at a given pH versus $[L]_T$ then gives a slope s of $k_7k_9^{app}[O_2]_T/(k_8 + k_9^{app}[O_2]_T)$ and y-intercept of $k_1^{app}[O_2]_T$, as shown in Figure 2.

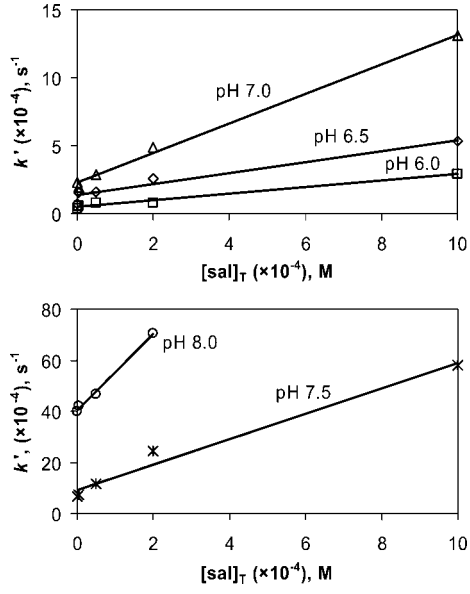


Figure 2. Linearization for the estimation of $k_7k_9^{app}[O_2]_T/(k_8 + k_9^{app}[O_2]_T)$ (see text for further details).

If we write $s = k_7k_9^{app}[O_2]_T/(k_8 + k_9^{app}[O_2]_T)$, then

$$\frac{1}{s} = \frac{k_8}{k_7} \times \frac{1}{k_9^{app}[O_2]_T} + \frac{1}{k_7} \quad (18)$$

Substituting $k_7 = k_7^{eff}([L_{eff}]/[L]_T)$ (eq 6) and $k_8 = (k_7^{eff}/{}^cK)$ (eq 8) to eq 18 gives

$$\frac{1}{s} = \frac{[L]_T}{{}^cK[L_{eff}][O_2]_T} \times \frac{1}{k_9^{app}} + \frac{1}{k_7} \quad (19)$$

Thus a plot of $1/s$ versus $[L]_T/({}^cK[L_{eff}][O_2]_T)$ would give a slope of $1/k_9^{app}$ and y-intercept of $1/k_7$, from which the values of k_7 and k_9^{app} can be roughly estimated.

Because k_7 varies with pH, the plot may not produce a straight line as expected. However, at pH 6.0, 6.5 and 7.0, it is reasonable to assume that k_7 does not vary significantly because the major Fe(II) species is Fe^{2+}. The slope and y-intercept of the plot at these pHs therefore should provide a reasonable estimate of k_9^{app} and k_7.

Linearization of $1/s$ versus $[L]_T/({}^cK[L_{eff}][O_2]_T)$ at pH 6.0, 6.5 and 7.0 (Figure 3) gives an estimated value for k_9^{app} of 7.09×10^3 M^{-1} s^{-1} and that for k_7 of 1.06 M^{-1} s^{-1}. The value of k_7 is quite close to the value estimated earlier from the outer-sphere complexation model of 0.53 M^{-1} s^{-1} at pH 6.0. The values of k_9^{app} (which should be treated as an upper limit of k_9) is in reasonable agreement with the value estimated from the linear free energy model, $k_9 = 1.92 \times 10^3$ M^{-1} s^{-1} (Table 2).

5.2. Modeling the Kinetics of Fe(II) Oxidation in the Presence of Salicylate. ***5.2.1. Fitting Procedure.*** At pH 6.0 and 6.5, because both O_2^- and H_2O_2 accumulate slowly, rate constants for reactions 10−14 are assigned the values given in Table 2 and the values of k_7, k_8 and k_9 are optimized but constrained to be close to the estimated values. At pH 7.0 and particularly 7.5 and 8.0 and in the presence of 0.2 and 1.0 mM salicylate, the non-pseudo-first-order behavior of Fe(II) oxidation kinetics (described by an initial rapid oxidation step followed by a much slower removal process) suggests that the reduction of salicylate bound Fe(III) by O_2^- may become significant at the later stage of the oxidation process. Thus, the two fitting parameters at these pH are k_7 and k_{14} (k_8 and k_9 are estimated from pH 6.0 results and do not vary with varying pH). It should be noted that, under the experimental conditions used in this study and with the estimated values of k_{10} and k_{11} given in Table 2, oxidation of $Fe^{II}sal^0$ by both O_2^- and H_2O_2 (reactions 10 and 11) would be expected to play a minor role in the overall Fe(II) oxidation. This is because $Fe^{II}sal^0$ is oxidized rapidly by O_2 (i.e., $k_9[O_2] \gg k_{10}[O_2^-]$ and $k_{11}[H_2O_2]$).

5.2.2. Model Results. Results of model fitting and experimental data for the oxidation of 50 nM and 0.2 μM Fe(II) at different salicylate concentrations are shown in Figure 4.

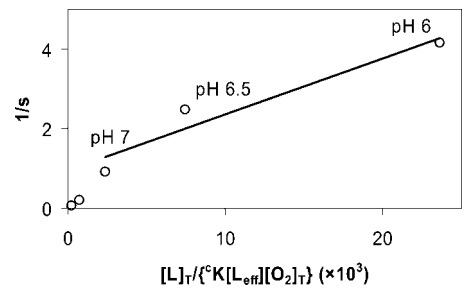


Figure 3. Linearization for the estimation of k_7 and k_9^{app} (see text for further details).

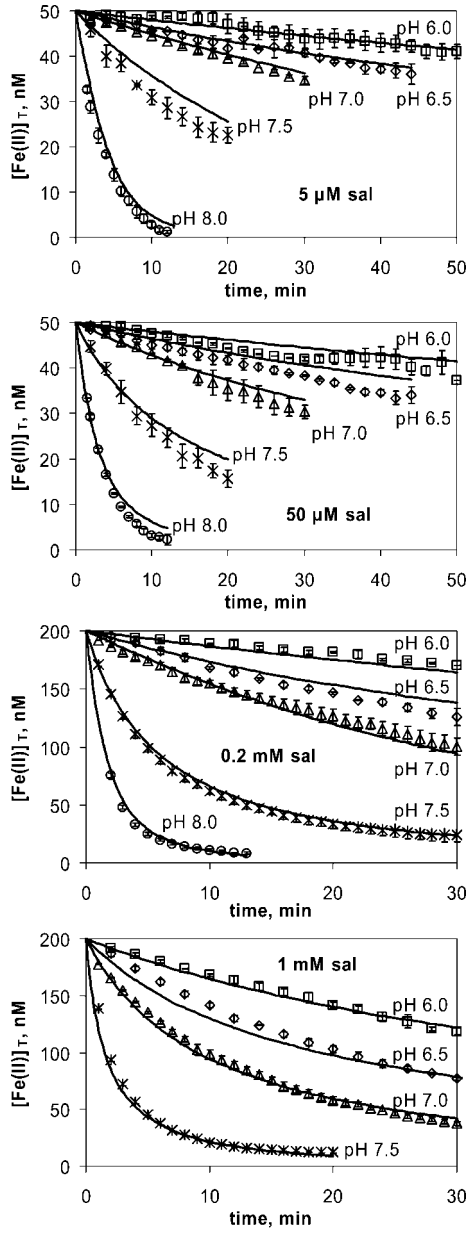


Figure 4. Modeled and experimental data for the oxidation of Fe(II) in the presence of different $[Fe(II)]_0$ and $[sal]_0$ over the pH range 6.0−8.0. Error bars are standard errors for duplicate measurements.

TABLE 5: Additional Modeled Rate Constants[a] for the Oxidation of Fe(II) in the Presence of Salicylate

rate constant k_i[b]	pH 6.0	pH 6.5	pH 7.0	pH 7.5	pH 8.0
k_7	0.34	0.97	1.2	11.4	20
k_8	2.1	2.1	2.1	2.1	2.1
k_9 ($\times 10^3$)	6.53	6.53	6.53	6.53	6.53
k_{10}($\times 10^6$)	1.55	1.55	1.55	1.55	1.55
k_{11}($\times 10^8$)	1.24	1.24	1.24	1.24	1.24
k_{12}($\times 10^3$)	0.6	3.5	5	6.7	12.4
k_{13}	n.d.	n.d.	n.d.	n.d.	n.d.
k_{14}($\times 10^7$)	5.97	1.68	0.91	1.91	0.54

[a] Rate constants for inorganic oxidation of Fe(II) (reactions 1−6) are given in the Supporting Information. [b] Rate constants are in M^{-1} s^{-1} except for k_8 and k_{13} in s^{-1}.

Predicted rate constants for the various reactions in the general model are given in Table 5.

In general, the model provides reasonable fits to the experimental data over a range of pH, particularly at high initial Fe(II) and salicylate concentrations. The agreement between modeled and experimental data at various conditions clearly supports our assumptions and methodology despite a number of uncertainties surrounding the estimated values of $k_{10} - k_{14}$. It is quite possible that the net effect of reactions 10−14 on the overall oxidation of Fe(II) is not significant, particularly at low salicylate concentrations and at low pH because under such conditions only a small concentration of $Fe^{II}sal^0$ would be present.

Among the predicted rate constants given in Table 5, two rate constants deserve additional rationalization. First, the rate of complexation of Fe(II) with salicylate (k_7) was found to increase by almost 2 orders of magnitude with increasing pH from pH 6.0 to pH 8.0. This is likely due to the increase in the proportion of effective binding concentration, $[sal^{2-}]$ (eq 6) in the total salicylate pool as pH increases (the proportion of $[sal^{2-}]$ increases by 2 orders of magnitude from pH 6.0 to pH 8.0). Thus, the effective rate constant ($k_7^{eff} = k_7[L]_T/[L_{eff}]$) of Fe(II) with sal^{2-} does not vary significantly with varying pH despite changes in the composition of Fe(II) species. It is quite possible that the water loss rate of $FeCO_3^0$, another dominant Fe(II) species at high pH, is similar to that of Fe^{2+} [2] and thus the weighted sum k_f (eq 1) would remain the same.

Second, the rate constant of Fe(III)−salicylate reduction by superoxide (k_{14}) was found to decrease slightly with increasing pH. Because higher order Fe(III)−salicylate complexes may be present at high pH (for example, $[Fe^{III}sal_2^-]$ is almost 10 times that of $[Fe^{III}sal^+]$ at pH 8.0 and in the presence of 50 μM salicylate), the observed decrease in the reduction rate constant k_{14} may be due to the effect of charge on the interaction between Fe(III)−salicylate species and O_2^- (i.e., smaller K_{OS} with higher order complexes).

Rose and Waite[20] have reported the rate constant for superoxide-mediated reduction of Fe(III)−salicylate (represented in the general form $Fe^{III}L$) of $(2.3 \pm 0.1) \times 10^5$ M^{-1} s^{-1} at pH 8.1 in seawater. However, this estimate appears to be too low and provides a poor description of our experimental data obtained at pH 7.5 and 8.0.

5.3. Fe(II) Oxidation in the Presence of Citrate. ***5.3.1. Explanation of the Experimental Observations Using the Developed Model.*** Because complexation between Fe(II) and citrate and dissociation of the resulting complex occur very rapidly (Table 2) and, as reported in Pham and Waite,[13] the oxidation of Fe(II)−citrate complexes is rather slow (i.e., $k_7[L][Fe(II)]$, $k_8[Fe^{II}L] \gg k_9[Fe^{II}L][O_2]$), it is reasonable to assume that equilibrium between Fe(II) and citrate exists at all times during the Fe(II) oxidation. In addition, if the overall oxidation of Fe(II) is primarily governed by reactions 1, 7, 8 and 9, particularly in the early stage of the process, then

$$-\frac{d[Fe(II)]_T}{dt} = -\left(\frac{d[Fe(II)]}{dt} + \frac{d[Fe^{II}L]}{dt}\right) = k_1^{app}[O_2][Fe(II)] + k_9^{app}[O_2][Fe^{II}L] \quad (20)$$

where the superscript "app" denotes an apparent rate constant.

Given that $[Fe^{II}L] = {}^cK[Fe(II)][L]$ (where ${}^cK = k_7^{eff}/k_8 \sim k_7/k_8$, equilibrium assumption), $[Fe(II)]_T = [Fe(II)] + [Fe^{II}L]$ and considering that both $[O_2]_T$ and $[L]_T \gg [Fe(II)]$, the solution to the above ODE is

$$[Fe(II)]_T = [Fe(II)]_0 \exp\left(-\frac{k_1^{app}[O_2]_T + k_9^{app}[O_2]_T{}^cK[L]_T}{{}^cK[L]_T + 1}t\right) \quad (21)$$

Therefore, a plot of $-\ln([Fe(II)]_T/[Fe(II)]_0)$ versus t gives the slope of $(k_1^{app}[O_2]_T + k_9^{app}[O_2]_T{}^cK[L]_T)/({}^cK[L]_T + 1)$, which is

also the pseudo-first-order rate constant, k' (with unit s^{-1}), for the oxidation of Fe(II) in the presence of citrate (eq 10 and Table 4).

Let us consider

$$k' = \frac{k_1^{app}[O_2]_T + k_9^{app}[O_2]_T {}^cK[L]_T}{{}^cK[L]_T + 1} \quad (22)$$

Rearranging eq 22 gives

$$\frac{k'}{[O_2]_T} = \frac{k_1^{app} - k_9^{app}}{{}^cK[L]_T + 1} + k_9^{app} \quad (23)$$

Thus, the unusual effect of citrate on the oxidation of Fe(II) can be explained from eq 23 as follows.

From eq 23, given our knowledge of k_1^{app} and k_9^{app} values over a range of pH,[13,32] it is apparent that, at low pH (pH 6.0, 6.5, 7.0 and 7.5), where $k_1^{app} < k_9^{app}$, an increase in concentration of ligand ($[L]_T$) would increase $(k_1^{app} - k_9^{app})/({}^cK[L]_T + 1)$ (because $(k_1^{app} - k_9^{app})$ is negative) and thus increases the total $[(k_1^{app} - k_9^{app})/({}^cK[L]_T + 1)] + k_9^{app}$ (i.e., the pseudo-first-order rate constant of Fe(II) oxidation in the presence of citrate would increase). This illustrates the situation where addition of citrate would enhance the oxidation of Fe(II) at low pH.

At pH 8.0, however, because $k_1^{app} > k_9^{app}$, an increase of $[L]_T$ would decrease $(k_1^{app} - k_9^{app})/({}^cK[L]_T + 1)$ (because $(k_1^{app} - k_9^{app})$ is positive) and thus reduce the rate of oxidation of Fe(II).

When the concentration of citrate is high enough to ensure ${}^cK[L]_T \gg k_1^{app} - k_9^{app}$, then $(k_1^{app} - k_9^{app})/({}^cK[L]_T + 1) \sim 0$ or $(k_1^{app} - k_9^{app})/({}^cK[L]_T + 1) \ll k_9^{app}$, and oxidation of Fe(II) is entirely controlled by the oxidation of the citrate complex i.e., $(k'/[O_2]_T \sim k_9^{app})$. This corresponds to the situation where addition of either 0.2 or 1 mM citrate does not alter the rate of Fe(II) oxidation, as observed in this study at pH 7.5 or 8.0 (Table 4). It also helps to explain the observation that the rate of oxidation of Fe(II) in the presence of 1 mM citrate is similar over the pH range 6.0−7.5.

On the other hand, given ${}^cK = 2.1 \times 10^4$,[42] at 5 μM citrate, ${}^cK[L]_T \ll 1$, $k'/[O_2]_T = [(k_1^{app} - k_9^{app})/({}^cK[L]_T + 1)] + k_9^{app} \sim k_1^{app} - k_9^{app} + k_9^{app} = k_1^{app}$. This corresponds to the situation where addition of 5 μM citrate does not show any observable effect (i.e., the rate of oxidation of Fe(II) in the presence of citrate is similar to the inorganic oxidation rate of Fe(II)).

The fact that the oxidation of Fe(II) in the presence of citrate was observed to follow pseudo-first-order kinetics at all pHs examined (except at pH 8.0) supports the conclusion that equilibrium between Fe(II) and citrate is likely and that reactions 1, 7, 8 and 9 principally control the oxidation of Fe(II) at pH < 8.0 (where eq 21 applies).

5.3.2. Verification of the Reported Value k_9^{app}. The apparent oxidation rate constant of $Fe^{II}cit^-$ species, k_9^{app}, has been reported previously in Pham and Waite,[13] where the oxidation of Fe(II) was investigated in the presence of excess citrate (where Fe(II) is present exclusively in complexed forms). In the current study k_9^{app} can be independently estimated from eq 22 alone as follows.

At pH 6.0 and in the presence of 1.0 mM citrate, ${}^cK[L]_T \sim (2.1 \times 10^4)(1.0 \times 10^{-3}) = 21$.[42] Because ${}^cK$ increases with increasing pH, it is reasonable to approximate ${}^cK[L]_T + 1 \sim {}^cK[L]_T$ and, from eq 22,

$$\frac{k'}{[O_2]_T} \sim \frac{k_1^{app}}{{}^cK[L]_T} + k_9^{app} \sim k_9^{app} \quad (24)$$

at pH 6.0, 6.5, 7.0 and 7.5 (where k_1^{app} is small compared to ${}^cK[L]_T$) . Averaging the ratio of $k'/[O_2]_T$ at these pH values (Table 4) gives the approximation of k_9^{app} of 4.5 M^{-1} s^{-1}, which is close to the estimated value of 5.0 M^{-1} s^{-1} given in Pham and Waite.[13]

5.4. Modeling the Kinetics of Fe(II) Oxidation in the Presence of Citrate. ***5.4.1. Fitting Procedures.*** In contrast to the case of salicylate, the Fe(II)−citrate complex is present at significant concentration in this scenario. As such, the concentrations of both O_2^- and H_2O_2 may accumulate considerably, even at low pH. It is therefore not appropriate to assign the rate constants for reactions 10−14 to the constrained values given in Table 2 at low pH as was done in the case of salicylate. In addition, it is also not possible to estimate the value of k_{14} using the outer-sphere complexation model due to the uncertainty of both the Fe(III)/citrate model[42,43] and the nature of the oxidation products (e.g., competition for $Fe^{III}cit^0$ between O_2^- and citrate ion to form higher order complexes). As a result, the local optimized parameters produced from the model at each pH could be considerably different and may not be unique. To resolve this problem, the local optimized values were modified and the model fitting was inspected manually until it gave the best fit to the experimental data at all pHs. Another important constrain to the model is that, because $Fe^{II}cit^-$ is the predominant ferrous complex in all cases, the rate constants of reactions 8−11 should not vary with varying pH.

5.4.2. Model Results. Results of model fitting and experimental data for the oxidation of 50 nM and 0.2 μM Fe(II) at different citrate concentrations are shown in Figure 5. The predicted rate constants for the various reactions in the kinetic model are given in Table 6.

In general, the model provides a reasonable description for the oxidation of Fe(II) in the presence of different initial Fe(II) and citrate concentrations over a range of pH despite the fact that the values of many of the rate constants are still uncertain. The general agreement between model fitting and experimental data again supports our assumptions and modeling approach. It also suggests that the oxidation of Fe(II) in the presence of citrate may be governed primarily by reactions 1, 7, 8 and 9.

As shown in Table 6, complexation of Fe(II) by citrate (k_7) does not vary significantly with varying pH. This is likely due to the fact that the proportion of effective binding species in the total citrate pool only increases slightly over this pH range ($[L_{eff}]/[L]$ varies from ∼0.5 at pH 6.0 to ∼0.8 at pH 8.0). In addition, the effective complexation constants (k_7^{eff}) between cit^{3-} and Fe(II) which is controlled by the water loss rate of Fe(II) species, do not vary considerably (as observed in the case of salicylate).

The predicted rate constant for the reduction of the Fe(III) complex by superoxide (k_{14}) is approximately 3 orders of magnitude less than that of inorganic Fe(III). If the dominant Fe(III) complex in the system is $Fe(OH)_2cit_2^{5-}$ (as predicted using the Konigsberger et al.[42] model), then the electrostatic repulsion between O_2^- and this highly charged complex may significantly reduce the rate of reduction of Fe(III) complexes by O_2^-. The estimated rate constant for the reaction of $Fe(OH)_2cit_2^{5-}$ with O_2^- according to the Eigen-Wilkins model (eq 1) is $k_{14} = 2.1 \times 10^5$ M^{-1} s^{-1}, which is close to our estimated value. Model simulations of experimental data, however, suggested that the predicted k_{14} should be treated as an upper value for the reduction of Fe(III)−citrate complex by superoxide.

Despite the fact that the predicted values for k_7 and k_8 are much higher than those reported by Rose and Waite,[18] the rate constant for oxidation of $Fe^{II}cit^-$ by O_2 (k_9) that is estimated in this study (2.91 M^{-1} s^{-1}) is very similar to that of 2.6 M^{-1} s^{-1}

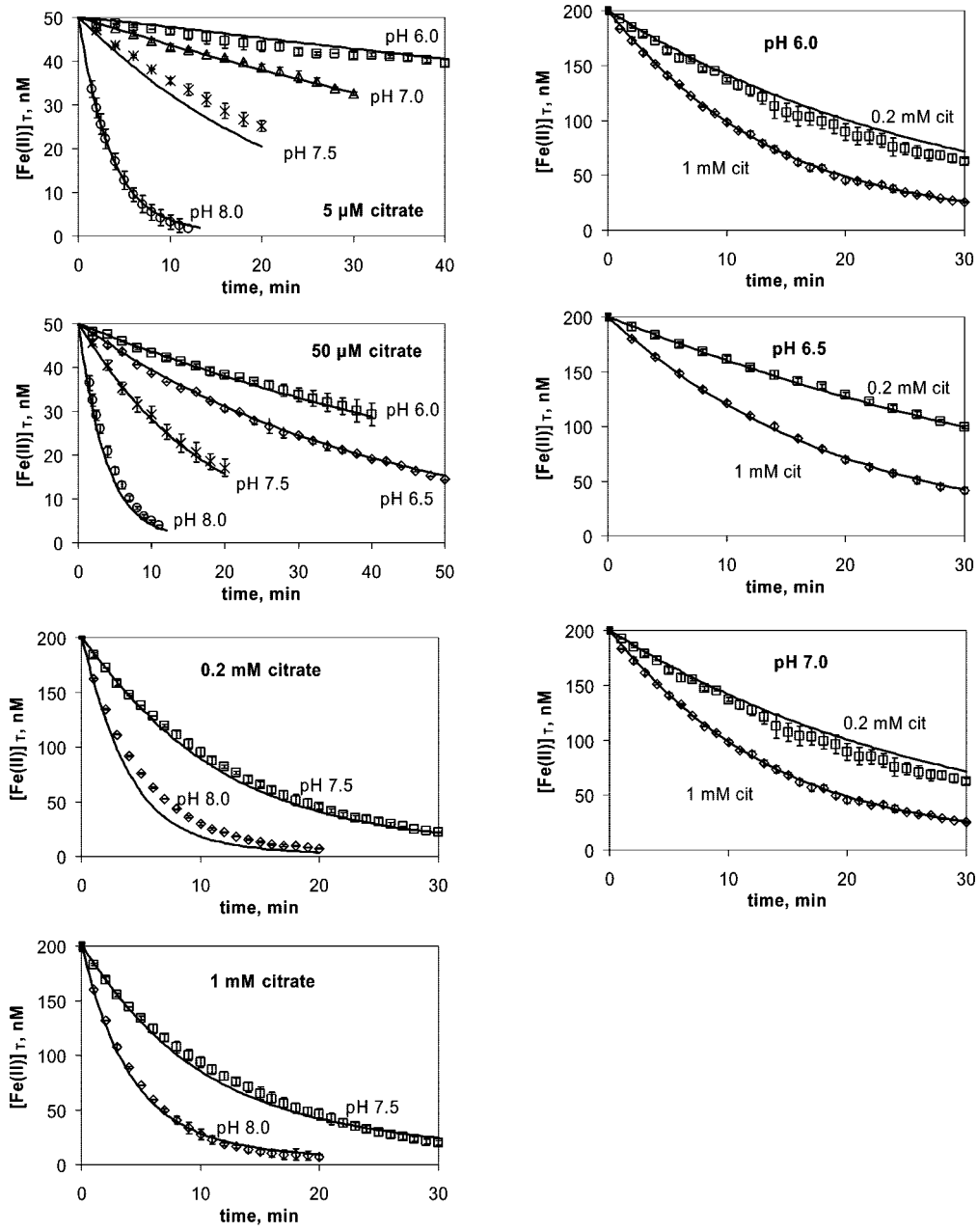


Figure 5. Modeled and experimental data for the oxidation of Fe(II) in the presence of different $[Fe(II)]_0$ and $[cit]_0$ over the pH range 6.0−8.0. Error bars are standard errors for duplicate measurements. Different plots were given for clarity.

TABLE 6: Additional Modeled Rate Constants for the Oxidation of Fe(II) in the Presence of Citrate[a]

rate constant k_i[b]	pH 6.0	pH 6.5	pH 7.0	pH 7.5	pH 8.0
k_7 ($\times 10^6$)	2.2	1.2	1.8	2.7	4.1
k_8 ($\times 10^3$)	2.13	2.13	2.13	2.13	2.13
k_9	2.91	2.91	2.91	2.91	2.91
k_{10} ($\times 10^5$)	6.03	6.03	6.03	6.03	6.03
k_{11} ($\times 10^6$)	6.67	6.67	6.67	6.67	6.67
k_{12} ($\times 10^3$)	0.6	3.5	5.0	6.7	12.4
k_{13}	n.d.	n.d.	n.d.	n.d.	n.d.
k_{14} ($\times 10^5$)	1.2	2.0	2.3	4.2	3.4

[a] Rate constants for inorganic oxidation of Fe(II) (reactions 1−6) are given in the Supporting Information. [b] Rate constants are in M^{-1} s^{-1} except for k_8 and k_{13} in s^{-1}.

reported by Rose and Waite.[18] This similarity suggests that oxidation of the ferrous citrate complex (by oxygen) is more important than any other reaction in the oxidation model. It also implies that pre-equilibrium between Fe(II) and citrate is likely to be the case. Therefore, in contrast to literature reports,[18] dissociation of the ferrous complex should be rapid.

5.5. Uncertainty of the Model. Despite the ability of providing a relatively good description of the oxidation of Fe(II) in the presence of different organic ligands over a range of pH, the model is still limited by a number of uncertainties.

In the presence of organic ligands, estimation of many reaction rate constants and their range was based on the assumption that the rate of complexation (between metal and ligands) and the rate of oxidation/reduction of metal and its complexes with superoxide are controlled by the water exchange kinetics of the metal's coordination sphere (i.e., it is assumed that the first bond formation is the rate limiting step). Although this assumption seems to be valid in many cases, particularly for the complexation between bivalent metals and organic ligands[33] and the reaction between inorganic iron species with superoxide,[35] it may not always be correct. For example, Margerum and co-workers[36] have shown that it is not the water

exchange kinetics of the reacting metal but the later chelating step in the reaction between La^{3+} and H_2CyDTA (cyclohexylenediaminetetraacetic acid) that is rate limiting.

Though the rate constants for reactions 7−9 in the model (in the presence of both salicylate and citrate) are firmly determined through both modeling and numerical approaches, values of other rate constants (particularly those for reactions 10, 11, 13 and 14) are rather speculative. In the presence of salicylate, it is reasonable to assume that oxidation of the salicylate complexes by O_2^- or H_2O_2 is not important because most $Fe^{II}sal^0$ is rapidly oxidized by oxygen. However, this may not be the case in the presence of citrate where the oxidation of ferrous citrate complexes is relatively slow and thus a competition for Fe(II)−citrate between O_2, O_2^- and H_2O_2 is likely, particularly at the later stages of the oxidation process when H_2O_2 has accumulated to significant concentrations. Determination of the rate constant for $Fe^{III}L$ reduction by O_2^- may depend to some extent on the kinetics of dissociation of this complex in both cases.

A major liability of the oxidation model, and particularly in the presence of organic ligands, is the strong dependence on the accuracy of iron speciation models. Significant discrepancies in the suggested species present, their stoichiometry and stability constants are disappointingly evident in the literature, despite the importance of iron complexation by citrate and salicylate in both natural and synthetic systems.

6. Conclusions and Implications

In this study, we have developed a model that is capable of satisfactorily describing the kinetics of Fe(II) oxidation in the presence of low concentrations of the organic ligands citrate and salicylate over a range of circumneutral pH.

Despite the fact that Fe(II) reacts rapidly with the fully deprotonated salicylate ions (sal^{2-}), we have shown that it is not valid to assume that pre-equilibrium between Fe(II) and salicylate exists in the oxidation of Fe(II) at neutral pH. This assumption, however, was shown to be valid in the case of citrate. These results indicate that it is the "effective" binding concentration that determines the kinetics of Fe(II) complexation by organic ligands.

The results of this study also confirm that an outer-sphere complexation model is appropriate to description of both the formation of Fe(II)−organic complexes and the reaction of iron species with O_2^-. Based on this mechanism, it appears that the effective rate constants for the complexation of Fe(II) with organic ligands and the reaction of iron species with O_2^- does not vary significantly with varying pH.

The developed model successfully describes the unexpected kinetic behavior of Fe(II) oxidation in the presence of different salicylate and citrate concentrations at different pH. Rates of complexation of Fe(II) by salicylate and citrate (to form monomeric complexes), dissociation and oxidation of these monomeric complexes are reliably estimated in the model. It was found that complexation of Fe(II) by salicylate was rather slow but that the complex formed was oxidized much faster than the equivalent citrate complex. Citrate, on the other hand, was found to be in rapid equilibrium with Fe(II). Both citrate and salicylate complexes were found to dissociate much more rapidly than previously thought.

It is worth noting that, despite the ability to describe the oxidation of Fe(II) over a range of pH and ligand concentrations, results of the kinetic model are only valid under the specific experimental conditions for which the oxidation of Fe(II) is examined. If higher order complexes are formed in the system, prediction of the kinetic constants based on the kinetics of water exchange and the assumption of a single iron entity (as in the model) may no longer be appropriate.

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Supporting Information Available: Text, calculations, figures, and tables for the following: S-1, testing of the validity of the kinetic analysis methodology; S-2, speciation of Fe(II) in the presence of low concentrations of citrate and salicylate; S-3, estimation of reaction rate constants using the outer-sphere complexation model and the linear free energy relation model; S-4, summary of the kinetic modeling of inorganic Fe(II) oxidation in aqueous solutions over the pH range 6.0−8.0. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Birus, M.; Kujundzic, N.; Pribanic, M. *Prog. React. Kinet.* **1993**, *18*, 171–271.
(2) Morel, F. M. M.; Hering, J. G. *Principles and Applications of Aquatic Chemistry*; Wiley: New York, 1993.
(3) Sunda, W. G. In *The Biogeochemistry of Iron in Seawater*; Turner, D. R., Hunter, K. A., Eds.; John Wiley & Sons Ltd.: West Sussex, England, 2001; Vol. 7.
(4) Waite, T. D. In *Environmental Photochemistry*; Boule, P., Bahnemann, D., Robertson, P., Eds.; Springer-Verlag 2005.
(5) Anderson, M. A.; Morel, F. M. M. *Limnol. Oceanogr.* **1982**, *27*, 789–813.
(6) Theis, T. L.; Singer, P. C. *Environ. Sci. Technol.* **1974**, *8*, 569–573.
(7) Millero, F. J.; Sotolongo, S.; Izaguirre, M. *Geochim. Cosmochim. Acta* **1987**, *51*, 793–801.
(8) King, D. W. *Environ. Sci. Technol.* **1998**, *32*, 2997–3003.
(9) Santana-Casiano, J. M.; Gonzalez-Davila, M.; Rodriguez, M. J.; Millero, F. J. *Marine Chem.* **2000**, *70*, 211–222.
(10) Santana-Casiano, J. M.; Gonzalez-Davila, M.; Millero, F. J. *Marine Chem.* **2004**, *85*, 27–40.
(11) Santana-Casiano, J. M.; Gonzaalez-Davila, M.; Millero, F. J. *Environ. Sci. Technol.* **2005**, *39*, 2073–2079.
(12) Emmenegger, L.; King, D. W.; Sigg, L.; Sulzberger, B. *Environ. Sci. Technol.* **1998**, *32*, 2990–2996.
(13) Pham, A. N.; Waite, T. D. *J. Phys. Chem. A* **2008**, *112*, 643–651.
(14) Rose, A. L.; Waite, T. D. *Anal. Chem.* **2001**, *73*, 5909–5920.
(15) Rose, A. L.; Waite, T. D. *Environ. Sci. Technol.* **2002**, *36*, 433–444.
(16) Rose, A. L.; Waite, T. D. *Environ. Sci. Technol.* **2003**, *37*, 4877–4886.
(17) Rose, A. L.; Waite, T. D. *Environ. Sci. Technol.* **2003**, *37*, 3897–3903.
(18) Rose, A. L.; Waite, T. D. *Marine Chem.* **2003**, *84*, 85–103.
(19) Rose, A. L.; Waite, T. D. *Aquatic Sci.* **2003**, *65*, 375–383.
(20) Rose, A. L.; Waite, T. D. *Environ. Sci. Technol.* **2005**, *39*, 2645–2650.
(21) Fujii, M.; Rose, A. L.; Waite, T. D.; Omura, T. *Environ. Sci. Technol.* **2006**, *40*, 880–887.
(22) Pham, A. N.; Rose, A. L.; Feitz, A. J.; Waite, T. D. *Geochim. Cosmochim. Acta* **2006**, *70*, 640–650.
(23) Rose, A. L.; Waite, D. *Geochim. Cosmochim. Acta* **2006**, *70*, 3869–3882.
(24) Salmon, T. P.; Rose, A. L.; Neilan, B. A.; Waite, T. D. *Limnol. Oceanogr.* **2006**, *51*, 1744–1754.
(25) Kandegedara, A.; Rorabacher, D. B. *Anal. Chem.* **1999**, *71*, 3140–3144.
(26) Thompsen, J. C.; Mottola, H. A. *Anal. Chem.* **1984**, *56*, 755–757.
(27) Lin, J.; Kester, D. R. *Marine Chem.* **1992**, *38*, 283–301.
(28) Stookey, L. L. *Anal. Chem.* **1970**, *42*, 779–781.
(29) Viollier, E.; Inglett, P. W.; Hunter, K.; Roychoudhury, A. N.; Van Cappellen, P. *Appl. Geochem.* **2000**, *15*, 785–790.

(30) Pullin, M. J.; Cabaniss, S. E. *Geochim. Cosmochim. Acta* **2003**, *67*, 4067–4077.
(31) Pullin, M. J.; Cabaniss, S. E. *Geochim. Cosmochim. Acta* **2003**, *67*, 4079–4089.
(32) Pham, A. N.; Waite, T. D. *Geochim. Cosmochim. Acta***2008**, in press.
(33) Eigen, M.; Wilkins, R. G. In *Mechanisms of Inorganic Reactions*; Gould, R. F., Ed.; Advances in Chemistry Series; American Chemical Society: Washington, DC, 1965; Vol. 49, pp 55−80.
(34) Smith, R. M.; Martell, A. E. *Critical Stability Constants. Second Supplements*; Plenum Press: New York, 1989; Vol. 6.
(35) Rush, J. D.; Bielski, B. H. J. *J. Phys. Chem.* **1985**, *89*, 5062–5066.
(36) Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. In *Coordination Chemistry*; Martell, A. E., Ed.; American Chemical Society: Washington, DC, 1978; Vol. 2, pp 1−219.
(37) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.
(38) Tratnyek, P. G.; Hoigne, J. *Water Res.* **1994**, *28*, 57–66.
(39) Schecher, W. D.; McAvoy, D. C. *Comput. Environ. Urban Syst.* **1992**, *16*, 65–76.
(40) Pham, A. N. Ph.D. Thesis, UNSW, 2007.
(41) Wulkow, M. *Presto-Simulation of kinetic models*; CiT GmbH: Rastede, Germany, 2004.
(42) Konigsberger, L. C.; Konigsberger, E.; May, P. M.; Hefter, G. T. *J. Inorg. Biochem.* **2000**, *78*, 175–184.
(43) Gautier-Luneau, I.; Merle, C.; Phanon, D.; Lebrun, C.; Biaso, F.; Serratrice, G.; Pierre, J. L. *Chem.—Eur. J.* **2005**, *11*, 2207–2219.

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