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Oxidation of Nanomolar Levels of Fe(II) with Oxygen in Natural Waters

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The oxidation of Fe(II) by molecular oxygen at nanomolar levels has been studied using a UV−Vis spectrophotometric system equipped with a long liquid waveguide capillary flow cell. The effect of pH (6.5−8.2), $NaHCO_3$ (0.1−9 mM), temperature (3−35 °C), and salinity (0−36) on the oxidation of Fe(II) are presented. The first-order oxidation rates at nanomolar Fe(II) are higher than the values at micromolar levels at a pH below 7.5 and lower than the values at a higher pH. A kinetic model has been developed to consider the mechanism of the Fe(II) oxidation and the speciation of Fe(II) in seawater, the interactions between the major ions, and the oxidation rates of the different Fe(II) species. The concentration of Fe(II) is largely controlled by oxidation with O_2 and $O_2^{•-}$ but is also affected by hydrogen peroxide that may be both initially present and formed from the oxidation of Fe(II) by superoxide. The model has been applied to describe the effect of pH, concentration of $NaHCO_3$, temperature, and salinity on the kinetics of Fe(II) oxidation. At a pH over 7.2, $Fe(OH)_2$ is the most important contributing species to the apparent oxidation rate. At high levels of CO_3^{2-} and pH, the $Fe(CO_3)_2^{2-}$ species become important. At pH values below 7, the oxidation rate is controlled by Fe^{2+}. Using the model, log k_i values for the most kinetically active species (Fe^{2+}, $Fe(OH)^+$, $Fe(OH)_2$, $Fe(CO_3)$, and $Fe(CO_3)_2^{2-}$) are given that are valid over a wide range of temperature, salinity, and pH in natural waters. Model results show that when H_2O_2 concentrations approach the Fe(II) concentrations used in this study, the oxidation of Fe(II) with H_2O_2 also needs to be considered.

Introduction

The concentration of total dissolved iron (Fe(II) and Fe(III)) that can be present in seawater is influenced by redox conditions of the marine environment (*1*). Over the years a number of authors have studied the rates of oxidation of Fe(II) in different aqueous solutions to elucidate the behavior of Fe(II) in natural waters (*2−16*).

The rates of oxidation of Fe(II) with O_2 have been expressed as an apparent oxidation rate, independent of the mechanism describing the process, given by
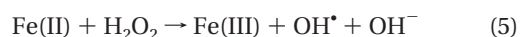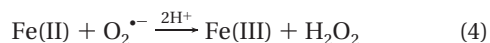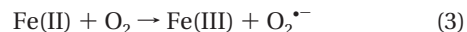
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$$\mathrm{d}[\mathrm{Fe(II)}]/\mathrm{d}t = -k_{\mathrm{app}}[\mathrm{Fe(II)}][\mathrm{O_2}] \tag{1}$$

The brackets denote the total molar concentration. When the reactions are studied with an excess of O_2, the reaction becomes pseudo-first-order (*8*):

$$\mathrm{d}[\mathrm{Fe(II)}]/\mathrm{d}t = -k'[\mathrm{Fe(II)}] \tag{2}$$

where $k' = k_{\mathrm{app}}[\mathrm{O_2}]$.

The most accepted mechanism to describe the Fe(II) oxidation with O_2 in natural waters is the Haber−Weiss mechanism:

$$\mathrm{Fe(II)} + \mathrm{O_2} \rightarrow \mathrm{Fe(III)} + \mathrm{O_2^{•-}} \tag{3}$$

$$\mathrm{Fe(II)} + \mathrm{O_2^{•-}} \xrightarrow{2\mathrm{H^+}} \mathrm{Fe(III)} + \mathrm{H_2O_2} \tag{4}$$

$$\mathrm{Fe(II)} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe(III)} + \mathrm{OH^•} + \mathrm{OH^-} \tag{5}$$

$$\mathrm{Fe(II)} + \mathrm{OH^•} \rightarrow \mathrm{Fe(III)} + \mathrm{OH^-} \tag{6}$$

At micromolar Fe(II) solutions, a 4:1 stoichiometry of Fe(II) oxidation by oxygen (*8*, *17*) and a 2:1 stoichiometry for the oxidation by hydrogen peroxide (*18*) have been measured. At nanomolar Fe(II) concentrations, the rates for reactions 3−6 need to be considered. The superoxide ($O_2^{•-}$) and $OH^•$ intermediates produced in the Fe(II) oxidation can be effective as oxidants to other reduced compounds (Br^-, Cl^-, HCO_3^-, and dissolved organic matter) (*11*, *19*, *20*). The newly generated radicals can perform the role of $OH^•$ intermediates in reaction 6, as the radical derivatives are likely to also be extremely reactive (*10*, *11*). Moreover, the back-reaction of Fe(III) with $O_2^{•-}$ (*10*, *13*), the scavenging of $O_2^{•-}$ by nanomolar concentrations of inorganic Cu(II) present in solution (*13*), and the hydrolysis of Fe(III) to form insoluble $Fe(OH)_3$ have been included in the latest models (*13*, *21*). Rose and Waite (*13*) studied the Fe(II) oxidation in seawater at nanomolar concentrations at a fixed pH (8.09) and salinity (42.7) considering the above-mentioned processes.

The oxidation rate constants are a strong function of pH and the speciation of Fe(II) (*15*, *18*). The overall rate constants for reactions 3−6 are a function of the composition and physical−chemical properties of the solution. To define the oxidation of Fe(II) in seawater, it is necessary to know the effect these properties have on the oxidation rates before one can account for the effect of other competing components, in particular organic material.

In this paper, we examine the oxidation of Fe(II) in seawater at nanomolar levels as a function of pH, HCO_3^- concentration, temperature, and salinity by defining a kinetic model that include speciation changes valid over a wide range of experimental conditions. Measurements are also carried out in pure water and NaCl solutions with different bicarbonate concentrations in order to define the role played by various Fe(II) species present in the solutions. A model was used to describe the rates of the reactions in terms of the species of Fe(II) in the solutions (Fe^{2+}, $Fe(OH)^+$, $Fe(OH)_2$, $FeCO_3$, and $Fe(CO_3)_2^{2-}$).

Experimental Section

Stock solutions of Fe(II) (2×10^{-3} and 4×10^{-4} M) were prepared using ferrous ammonium sulfate hexahydrate (Fisher), acidified at a pH 2 with Suprapur HCl. The initial concentrations of Fe(II) were kept at 250 nM in the reaction vessel in most of the studies. To validate the model results,

studies were also carried out at 20–50 nM initial concentrations of Fe(II). All the chemicals used for the Fe(II) determination were trace analysis grade. The seawater used in this study was collected in the Gulf Stream off the coast of Miami, FL. The practical salinity determined by using an Autosal was 36.056. Dilutions were made with Milli-Q ion exchanged water (18 MΩ).

Oxidation Experiments. The reactions in NaCl solutions and in seawater were studied in a 250 mL glass thermostated vessel (*15*). The temperature was controlled to $\pm 0.02\ °C$ with a NesLab circulating bath in the range of 3–35 °C. After the solution was bubbled with pure air for 1 h, the pH was adjusted to the desired value with additions of small amounts of 1 M HCl. The addition of the Fe(II) stock solution (25 μL of 2 mM Fe(II) in HCl 0.01 M) to the seawater corresponds to the zero time of reaction. The pH for the study was recorded during the reaction to account for any change after the addition of the Fe(II). The change in pH was always less than 0.02 units, with the highest effects occurring at low pH where the buffer capacity of the carbonate is lowest. In all cases, the gas stream was passed through a MnO_4^- solution to eliminate any H_2O_2 and through a trap with Milli-Q water. A small stream of air was passed over the solutions during the experiments. Fe(II) oxidation experiments at different bicarbonate concentrations were carried out under the same conditions after increasing the concentration of $NaHCO_3$ from the initial value (2.05 mM) to the desired level.

The pH measurements were made on the free scale (*22, 23*). Tris buffers were used to calibrate the electrodes. The effect of temperature on the pK* of the Tris buffers was considered in each study (*22*).

The Fe(II) concentrations were determined spectrophotometrically using a modified version of the ferrozine method (*24*). The details of the methods we used are given elsewhere (*15, 25, 26*).

A 5 m long waveguide capillary flow cell (LWCFC) from World Precision Instruments was used in order to carry out measurements at nanomolar levels of Fe(II) (*27*). The response of the system was linear over 2 orders of magnitude Fe(II) ([Fe(II)] = 0.408 + 82.92 Abs), with a standard error for the Fe(II) determination of σ =1.0 nM in [Fe(II)].

Hydrogen peroxide was determined using an enzyme-mediated fluorescent decay method (*28*) utilizing horseradish peroxidase and scopoletin (*29*). Dissolved oxygen concentration in seawater was determined using a modified Winkler method described by Hansen (*30*).

Numerical Model. The Gepasi Version 3.21 (*31*) software system was used to simulate the chemical kinetics and to compute the time-dependent concentrations of all the reactants. The overall and the individual rate constants k_i are obtained by adjusting the observed Fe(II) concentration/time pair of data for the different experimental conditions with the kinetic model output. A response surface methodology (*32*) together with initial conditions and k_i values were used in the Gepasi program to generate theoretical Fe(II) concentrations as a function of time. The Statistica Program for Windows (1995) was used in the minimization procedure.

Results and Discussion

pH Dependence. In our first series of measurements, we determined the pseudo-first-order rate constant (k' in units of min^{-1}) in 0.7 M NaCl solutions with 2 mM NaHCO$_3$ and in seawater (S = 36.056) with a similar total carbonate concentration as a function of pH. A pseudo-first-order behavior was not always observed, in particular in the latter stages of the reaction as with previous studies (*10, 13*). The back-reaction of Fe(III) with $O_2^{\bullet-}$, the hydrolysis of Fe(III), and the scavenging of $O_2^{\bullet-}$ by reactive species such as copper (*33*) have the effect of slowing the apparent oxidation rates. The reactions below the half-time ($t_{1/2}$) always showed a linear

TABLE 1. Pseudo-First-Order Rate Constants for Oxidation of Fe(II) in 0.7 M NaCl and 2 mM NaHCO$_3$ Solutions and in Gulf Stream Seawater Collected off the Coast of Miami, FL (DOM = 87 μM, S = 36.056) at Micromolar and Nanomolar Fe(II)

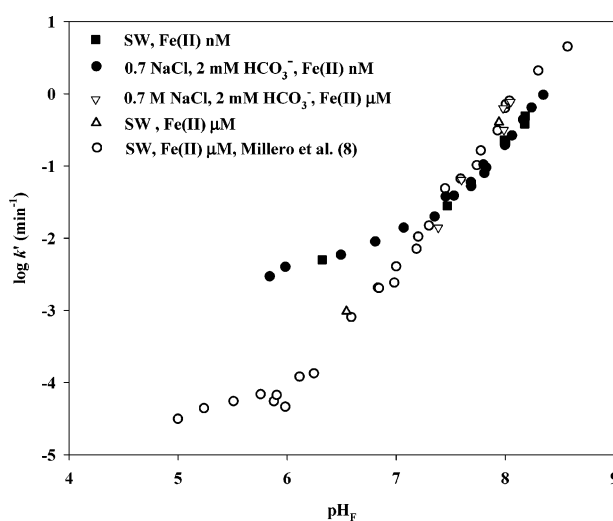| media	pH	log k' (min^{-1})
0.7 M NaCl, 2 mM NaHCO$_3$, [Fe(II)]$_0$ = 250 nM	8.35	−0.014
	8.24	−0.190
	8.16	−0.356
	8.06	−0.577
	8.00	−0.710
	7.69	−1.279
	7.53	−1.411
	7.35	−1.699
	7.07	−1.854
	6.81	−2.046
	6.49	−2.229
	5.98	−2.398
	5.84	−2.529
SW, [Fe(II)]$_0$ = 250 nM	8.18	−0.308
	8.00	−0.660
	7.99	−0.638
	7.80	−0.979
	7.69	−1.252
	7.47	−1.553
	6.32	−2.301
0.7 M NaCl, 2 mM NaHCO$_3$, [Fe(II)]$_0$ = 20 μM	7.98	−0.201
	8.05	−0.114
	7.39	−1.854
	7.60	−1.194
SW, [Fe(II)]$_0$ = 20 μM	7.94	−0.395
	6.54	−3.015

FIGURE 1. Effect of pH$_F$ in the values of the log k' (min^{-1}) for the oxidation of Fe(II) at nanomolar levels in 0.7 M NaCl and 2 mM NaHCO$_3$ solutions and in seawater (closed symbols). Data at micromolar Fe(II) levels by Millero et al. (*8*) and some new measurements in 0.7 M NaCl and 2 mM NaHCO$_3$ are included (open symbols).

behavior with a correlation coefficient over 0.98. The rate constants, k', assuming a pseudo-first-order behavior valid at times below $t_{1/2}$ at 25°C (Table 1) are shown in Figure 1, together with data at micromolar Fe(II) levels by Millero et al. (*8*) and some new measurements in 0.7 M NaCl and seawater. Previous studies in NaCl solutions (*8*) were made in 9 mM NaHCO$_3$ and showed higher oxidation rates than in seawater. Figure 1 also shows the Fe(II) oxidation rates at nanomolar levels in seawater and 0.7 M NaCl. The rates are similar when the HCO$_3^-$ concentration is equal to the value in seawater. The pseudo-first-order rate constants at nanomolar levels of Fe(II) are higher than the values at micromolar levels at pH below 7.5 and lower than the values at micromolar

TABLE 2. Apparent Oxidation Rate Constants[a] in Seawater of Different Salinities and Temperatures and in Pure Water[b]

salinity	pH_F	T	log k (M^{-3} min^{-1})	salinity	pH_F	T	log k (M^{-3} min^{-1})
36.056	8.00	35	14.357	28.80	8.00	25	14.327
36.056	8.00	25	14.257	19.80	8.00	25	14.436
36.056	8.00	20	14.253	9.90	7.99	25	14.575
36.056	7.99	10	14.310	4.90	7.99	25	14.766
36.056	7.99	6	14.402	0.0	8.24	25	15.193
36.056	8.14	10	14.396	0.0	8.02	25	15.187
36.056	7.54	10	14.897	0.0	7.68	25	15.511
36.056	7.07	10	15.653	0.0	7.50	25	15.681
36.056	6.62	10	16.230	0.0	6.95	25	16.089
36.056	7.74	10[c]	15.251				

[a] k in units of M^{-3} min^{-1} assuming a pseudo-first order dependence valid at times lower than $t_{1/2}$. [b] $[HCO_3^-] = 2$ mM, $[Fe(II)]_0 = 250$ nM. [c] $[HCO_3^-]_T = 9.0$ mM.

levels at high pH (Table 1). As will be discussed later, these differences are related to relative contributions of the various reactions that comprise the overall mechanism of the oxidation.

To study the effect of carbonate on the rates (*8, 15, 17*), in our second series of studies we determined the pseudo-first-order rate constants in 0.7 M NaCl as a function of HCO_3^- concentration. When the concentration is increased from 2 mM HCO_3^- to 9 mM, as used in most early studies (*8, 10, 12*), the oxidation rate at nanomolar Fe(II) increases from $k' = 0.19$ min^{-1} to $k' = 0.7$ min^{-1}.

The effect of salinity on the oxidation of Fe(II) in seawater was determined by diluting the seawater with Milli-Q water, at a constant concentration of HCO_3^-. The effect of salinity on the pH and oxygen solubility was considered for each experimental condition. The values of the total rate constant over a limited pH range (*8*) (k in units of M^{-3} min^{-1} assuming a 4:1 Fe(II):O_2 stoichiometry):

$$\text{d}[Fe(II)]/\text{d}t = -k[Fe(II)][O_2][OH^-]^2 \qquad (7)$$

for the oxidation as a function of ionic strength [$I = 0.0199S/(1 - 10^{-3}S)$] at 25 °C are given in Table 2. These results have been fitted to an equation of the form

$$\log k = \log k_0^* - 1.58I^{1/2} + 0.59I \qquad (8)$$

with $\sigma = 0.02$ and $\log k_0^*$ is the value of $\log k_o$ in pure water with 2 mM NaHCO$_3$. Millero et al. (*8*) studied the salinity effect at micromolar Fe(II), and found that within experimental error the salinity dependence of k is independent of temperature. Their results were fitted to

$$\log k = \log k_0^* - 3.29I^{1/2} + 1.52I \qquad (9)$$

where the seawater samples were corrected for the bicarbonate effect (9 mM) at a salinity below 7.5. The larger ionic strength dependence observed in eq 9 is due in part to the bicarbonate effect on the oxidation rate constants.

To determine the k_o value for pure water and compare it with previous studies by King (*17*), measurements were made in pure water at different pH and concentrations of HCO_3^-. Our experimental results (Table 2) agree with the results of King (*17*). At pH_F 8.02, the rate constant in pure water including 2 mM NaHCO$_3$ is $\log k_0^* = 15.19$ (Table 2). The oxidation value in pure water without HCO_3^- obtained, using eq 8 is $\log k_0 = 15.07$, which is in reasonable agreement with the value of $\log k_0 = 15.4$ (valid in the pH range of 7.5 ± 0.5) of Millero et al. (*8, 9*) at micromolar levels of Fe(II).

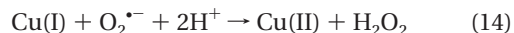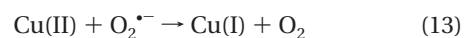In our next series of measurements, we determined the effect of pH at a temperature of 10 °C in seawater and with

increased amounts of NaHCO$_3$ (Table 2). When the $[HCO_3^-]$ in seawater is increased to 9 mM, the $\log k'$ value increases at pH 7.74 from 0.02 to 0.07 min^{-1} at 10 °C. The effect of temperature on the oxidation of nanomolar Fe(II) has been determined in seawater at a pH 8.00 from 3 to 35 °C. The effect of temperature on the pseudo-first-order rate constant (Table 2) has been fitted to the equation

$$\log k' = 17.36 - 5362/T \qquad (10)$$

with an energy of activation of 45 kJ mol^{-1}. The effect of temperature on k' is related to the effect of temperature on the solubility of oxygen, on the K_w^* for the ionization of water, and on the apparent rate constant.

Values of $\log k$ for the total rate equation at various temperatures in seawater are given in Table 2. The values of k are independent of temperature within the experimental error of the measurements as found for the oxidation of Fe(II) with H$_2$O$_2$ (*18*) and indicates that the temperature dependence of k at a given pH is largely related to the effect of temperature on K_w^*.

Kinetic Model. We have applied a kinetic model to our results that includes the contributions of others (*10, 13, 15, 17, 36*) making it valid and appropriate for the results of this study. This extends the model of Rose and Waite (*13*) to include speciation of Fe(II) (*10, 15, 17, 36*). Total inorganic copper was assumed to be constant to about 4 nM in the seawater used in our study, according to previous determinations (*34*). The full reaction scheme includes reactions 3–6 and reactions 11–14 as previously mentioned:

$$Fe(III) + O_2^{\bullet-} \rightarrow Fe(II) + O_2 \qquad (11)$$

$$Fe(III) + 3OH^- \rightarrow Fe(OH)_3(s) \qquad (12)$$

$$Cu(II) + O_2^{\bullet-} \rightarrow Cu(I) + O_2 \qquad (13)$$

$$Cu(I) + O_2^{\bullet-} + 2H^+ \rightarrow Cu(II) + H_2O_2 \qquad (14)$$

The oxidation reaction of Fe(II) (eqs 3–6) is composed of several parallel reactions in which the individual Fe(II) species react at different rates with oxygen. The Fe(II) oxidation rate for each equation can be determined as a function of the weighted sum of the oxidation rates of the individual Fe(II) species:

$$\begin{aligned} k_{app} = {}&k_{Fe^{2+}}\alpha_{Fe^{2+}} + k_{FeOH^+}\alpha_{FeOH^+} + k_{Fe(OH)_2}\alpha_{Fe(OH)_2} + \\ &k_{FeHCO_3^+}\alpha_{FeHCO_3^+} + k_{Fe(CO_3)}\alpha_{Fe(CO_3)} + k_{Fe(CO_3)_2^{2-}}\alpha_{Fe(CO_3)_2^{2-}} + \\ &k_{Fe(CO_3)OH^-}\alpha_{Fe(CO_3)OH^-} + k_{FeCl^+}\alpha_{FeCl^+} + k_{FeSO_4}\alpha_{FeSO_4} \end{aligned} \qquad (15)$$

where $\alpha_i = [FeX_i]/[Fe(II)]$ is the molar fraction of each Fe(II) species in the solution and is a function of the ionic media. The values of k_{app} and k_i are the second-order rate constants for the oxidation by oxygen and [Fe(II)] is the total Fe(II) concentration in the solution. To verify this model and to determine the rate constants, we have defined a kinetic model with all pertinent dissociation, complex formation, ion-pair formation (*35*), and oxidation reactions for the different Fe(II) species involved in the solution (*15*). Due to the role played by H$_2$O$_2$ in the Fe(II) oxidation chemistry (*10, 18, 36, 37*), the Fe(II) oxidation by H$_2$O$_2$ initially present in the solution ((3–4) × 10^{-8} M) and that generated over the reaction time were considered.

Values for the rate constants are based on values from the literature for reactions 3–6 and 11–14 and are given in Table 3. The rate constant k_4 for soluble iron and k_{11} for the back-reaction of Fe(III) at pH > 6, were 1.0×10^7 and 1.5×10^8 M^{-1} s^{-1}, respectively (*38*). Values for the individual oxidation rates contributing to k_4 were adjusted to account for the

no.	exptl conditions	log k (M^{-1} s^{-1})
3	$I = 0.7$, 25°C	$22.14 - 6.54$ pH $+ 0.49$ pH^2
4	$I = 0.7$, 25°C	$-14.80 + 3.69$ pH $- 0.12$ pH^2
5	$I = 0.7$, 25°C	$-25.75 + 0.63$ pH $+ 0.03$ pH^2
6	$I = 0.7$, 25°C	$13.89 - 1.53$ pH $+ 0.11$ pH^2
11	25°C	1.5×10^8
12	25°C	1.4×10^4
13	25°C	6.6×10^8
14	25°C	2.0×10^9
3	25 °C, pH 8.0	$1.58 - 1.09 I^{1/2} + 0.74 \cdot I$
4	25 °C, pH 8.0	$7.08 - 3.62 I^{1/2} - 0.07 \cdot I$
5	25 °C, pH 8.0	$5.39 - 1.75 I^{1/2} - 0.94 \cdot I$
6	25 °C, pH 8.0	$8.81 - 0.29 I^{1/2} + 0.18 \cdot I$
3	$I = 0.7$, 10 °C	$25.85 - 7.49$ pH $+ 0.54$ pH^2
4	$I = 0.7$, 10 °C	$27.56 - 6.26$ pH $+ 0.46$ pH^2
5	$I = 0.7$, 10 °C	$20.51 - 4.90$ pH $+ 0.35$ pH^2
6	$I = 0.7$, 10 °C	$-11.82 - 1.00$ pH $+ 0.08$ pH^2

assumed value. The reaction of Fe(II) with the hydroxyl radical (eq 6, Table 3) was assumed to be constant in the pH range of our studies while the reactions between Fe(II) and any radical derivative for OH$^•$ in seawater is assumed to be extremely fast (*11*). The value of k_{12} is expected to be a function of pH (*13*). Since no data is presently available for the pH dependence, we have used the values at pH 8 (8×10^3 M^{-1} s^{-1}) from the results of Rose and Waite (*13*). This is the best we can do at the present time and limits the reliability of the model at values of pH greater or less than 8. The scavenging rates of superoxide by copper are those given by Zafiriou et al. (*33*). The k_{14} value is not strongly pH dependent while k_{13} will be affected by changes in the concentration of carbonate, hydroxo, and chloro complexes as pH changes. However, the increase in Cu(I) concentration as pH decreases from 8 to 6 is only 10% (*33*), and a negligible increase in k_{13} was assumed. Considering the individual rate constants and speciation calculations of González-Dávila et al. (*37*) for the Fe(II) oxidation with H$_2$O$_2$ in the pH range 6—8.5 (Table 3), a value of $k_5 = 3.9 \times 10^4$ M^{-1} s^{-1} is obtained at pH 8.05. This value is comparable to that obtained by Millero et al. (*8*) and that assumed by Rose and Waite of 3.1×10^4 M^{-1} s^{-1} (*13*).

To get values for the overall and individual rate constants for the oxidation of Fe(II) with O$_2$ and O$_2^{•-}$, the kinetic model was applied to the experimental results at the different pH and [HCO$_3^-$] in both NaCl solutions and seawater. In both cases, an initial H$_2$O$_2$ concentration around 30 nM was considered to be present in fitting the model to the measurements. Using the method described earlier, the computed rate constants that best fitted the experimental data are given in Tables 3 (overall rate constants) and 4 (individual rate constants). The accuracy of these rate constants in describing the experimental data is shown in Figure 2 in 0.7 M NaCl (2 mM HCO$_3^-$), where the lines represent the output from the kinetic model using the individual oxidation rates in Table 4. The studies carried out at different pH and [HCO$_3^-$] allow us to obtain reasonable values for the oxidation rate of carbonate and hydroxo iron(II) complexes. Chloro and sulfate complexes were considered inactive to the observed oxidation rate (*15, 17*). The rate constant for reaction 3, when the back-reaction and hydrolysis of Fe(III) are considered (eqs 11 and 12), was first estimated from the computed individual oxidation rates and speciation. Its value is shown as a function of pH in Table 3. These results are valid for water solutions with an ionic strength of 0.7—0.74 M and with 2 mM total inorganic carbon. The rate presents a value of 15.4 M^{-1} s^{-1} as the best fit of data at pH 8 ($I = 0.7$, [HCO$_3^-$] = 2 mM). Rose and Waite (*13*) obtained a value of 13 M^{-1} s^{-1} for a seawater of higher salinity
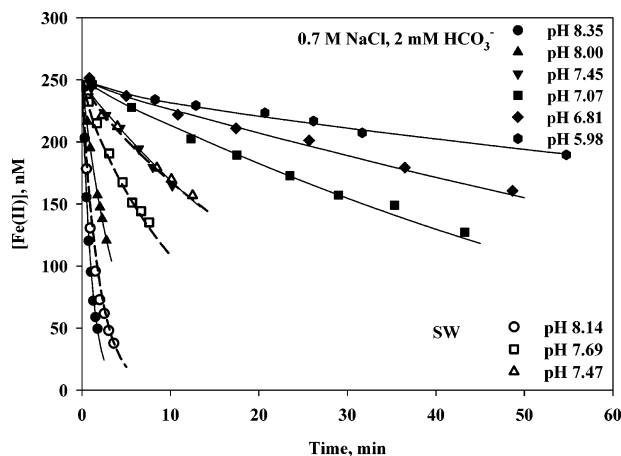
FIGURE 2. Experimental and predicted Fe(II) concentration as a function of pH in 0.7 M NaCl and 2 mM NaHCO$_3$ (closed symbols) and in seawater (sw; open symbols) at 25 °C, using the kinetic model and constants presented in Tables 3 and 4.

TABLE 4. Fe(II) Oxidation Rates (log k) with Oxygen and Superoxide in Seawater (M^{-1} min^{-1}) at Different Salinities Valid for the pH Range 6—8.2 and 25 °C Calculated from the Kinetic Model[a]

species	$I = 0.7$, 25 °C			$I = 0$, 25 °C		
	O$_2$	O$_2^{•-}$	H$_2$O$_2$	O$_2$	O$_2^{•-}$	H$_2$O$_2$
Fe^{2+}	0.544	3.84	2.68	0.72	4.08	3.25
FeHCO$_3^+$	-1.0	0.31	1.48	-0.6	0.35	2.05
FeCO$_3$	0.60	2.94	4.57	0.55	3.10	5.15
Fe(CO$_3$)$_2^{2-}$	3.69	9.60	7.49	4.19	9.78	7.06
Fe(CO$_3$)OH$^-$	1.87	2.54	4.18	2.02	2.75	2.27
FeOH$^+$	2.38	4.96	6.50	3.16	5.59	7.07
Fe(OH)$_2$	6.06	12.18	9.60	6.69	12.34	10.17

^{a} Oxidation rates with hydrogen peroxide are from Gonzalez-Davila et al. (*37*). The FeCl$^+$ and FeSO$_4$ species are inactive in all cases.

($I = 0.89$). Considering the experimental conditions of our study, values for the individual oxidation rates of Fe(II) with O$_2^{•-}$ were also determined (Table 4), which give a rate k_4 of 1.01×10^7 M^{-1} s^{-1} at pH 8 (Table 3) in accordance with the well-established value in the literature (*38*).

Figure 3 shows the contributions of the different Fe(II) species to the Fe(II) oxidation rate with O$_2$ (k_3) and O$_2^{•-}$ (k_4). At a pH over 7.7, Fe(OH)$_2$ is the most important contributing species to k_3, reaching 50% at pH 8.2, while Fe(CO$_3$)$_2^{2-}$ contributes 20%. Both species show second-order dependence to pH, which is consistent with the previously reported second-order dependence with pH for the oxidation rate. At a pH lower than 7.7, Fe^{2+} is the most important contributing species with more than 80% at a pH below 7. The k_4 values are dominated (over 80%) by the Fe(OH)$_2$ species at a pH over 6.5. Fe(CO$_3$)$_2^{2-}$ reaches a value of 20% around pH 7.5. Results from Gonzalez-Dávila et al. (*37*) have shown FeOH$^+$ is the dominant species to the oxidation rate with H$_2$O$_2$, while FeCO$_3$ contributes half of the FeOH$^+$ value. Both species show a first-order dependence to pH that is consistent with the previously reported first-order dependence with pH for the oxidation rate of Fe(II) with H$_2$O$_2$. At values of a pH higher than 8.1, the Fe(OH)$_2$ is the most dominant species.

The results presented in Tables 3 and 4 determined with initial Fe(II) concentrations of 250 nM were also applied to studies carried out at concentrations between 20 and 50 nM. At these concentrations (pH 8.00 and 25 °C), the pseudo-first-order oxidation rate was $k' = 0.215$ min^{-1}, a value similar to that obtained at 250 nM (Table 1). In both cases, the initial concentration of H$_2$O$_2$ in seawater was 30 nM, enough to
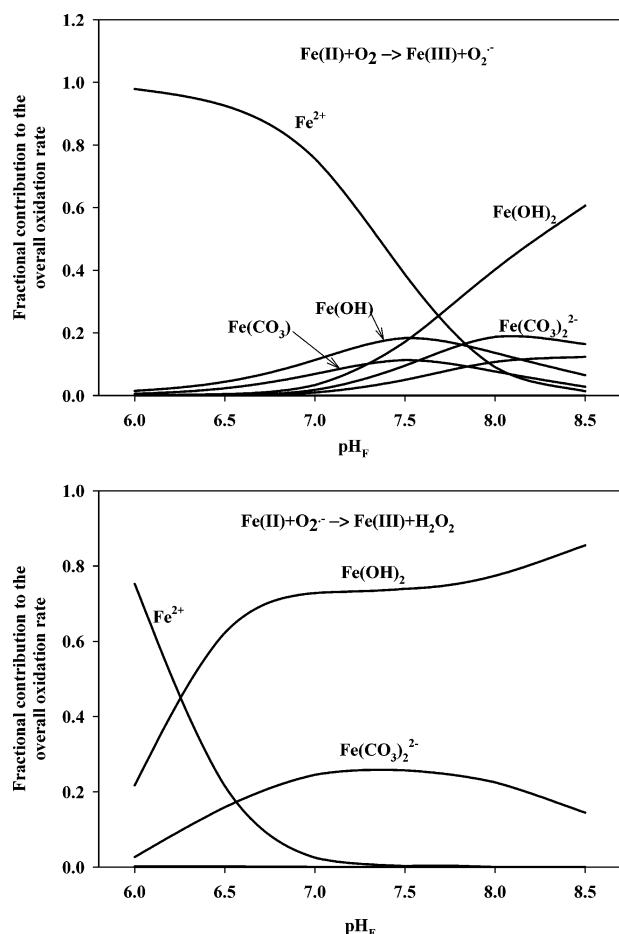
FIGURE 3. Contribution of specific Fe(II) species in total Fe(II) oxidation rate by oxygen and superoxide in seawater ($S = 36.056$) and 25 °C.
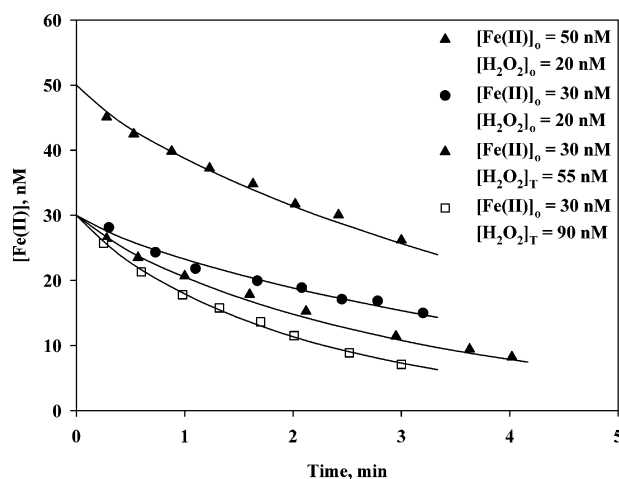

FIGURE 4. Experimental and predicted Fe(II) concentrations at lower Fe(II) initial levels with different concentrations of H_2O_2 in natural seawater ($[NaHCO_3]_T = 2.05$ mM), using the kinetic model and constants presented in Tables 3 and 4.

reach a steady-state concentration after a few seconds. The agreement between modeled and observed Fe(II) concentration is shown in Figure 4. Some studies were made with different concentrations of H_2O_2 added to the original seawater. Figure 4 shows the increased oxidation rates even with very low additions of hydrogen peroxide and the agreement between experimental and model concentration. The kinetic model allows us to study the relative importance of the individual reactions at micro- and nanomolar levels.

The inclusion of copper reactions with superoxide even at high initial Fe(II) concentration makes it possible to apply the model at low Fe(II) where Cu(II) competes with Fe(II). Fe(III) competes more efficiently than Fe(II) with copper for superoxide, making copper an important superoxide scavenger at low iron concentrations (13, 33). The oxidation of Fe(II) with H_2O_2 (k_5 and k_6) has been considered to slightly affect the oxidation process at low concentration of H_2O_2 and Fe(II) (13). At initial Fe(II) concentration of 250 nM, the steady-state concentration of H_2O_2 is 25 nM. This H_2O_2 level is approached only toward the end of the Fe(II) oxidation process (after 300 s at pH 8) with a monomolecular rate constant of 9.9×10^{-4} s^{-1} for reaction 5 as compared with 3.2×10^{-3} s^{-1} for reaction 3. In the presence of natural dissolved H_2O_2 levels in seawater (20−50 nM), relatively constant values for $[H_2O_2]$ are obtained after the first 60 s, approaching the monomolecular rate constant for the reaction 5 to reaction 3 (1.1×10^{-3} s^{-1} with $[H_2O_2]_0 = 50$ nM). In surface seawater, the $[H_2O_2]$ reaches 100−150 nM (39) and monomolecular oxidation rate for k_5 becomes 3.6−5.4 $\times 10^{-3}$ s^{-1}, with an initial Fe(II) concentration of 25 nM and pH 8.0. The levels of hydroxyl radicals are very low at low Fe(II) concentrations (7×10^{-13} M with initial Fe(II) of 25 nM). King et al. (10) found that less than 1% of the OH$^{\bullet-}$ radical is reduced directly by Fe(II) in the presence of Cl$^-$, carbonate oxidation, and organic matter. All of these generated radicals can oxidize Fe(II) in place of OH$^{\bullet-}$. Consequently, Fe(II) in surface seawater is oxidized by O_2 and $O_2^{\bullet-}$ but can also be oxidized by the hydrogen peroxide accumulated in the surface waters and by that coming from the oxidation of Fe(II) by superoxide in the latter stages of the oxidation. When the pH decreases, the oxidation rates decrease as shown in Table 3. At a pH 7 and with 250 nM Fe(II), the steady-state concentrations of H_2O_2 and $O_2^{\bullet-}$ are 1.4×10^{-8} and 1×10^{-12} M, respectively. The monomolecular rate constants for reactions 4 and 5 are over an order of magnitude less than that for reaction 3 during most of the oxidation, and most of the Fe(II) is oxidized by O_2.

At micromolar levels of Fe(II), a 4:1 stoichiometry has been confirmed (10), and reaction 3 is rate limiting ($k_3 = k_{app}/4$). The Fe(II) oxidation is faster at micromolar levels of Fe(II) at pH over 7.7 (Figure 1) due to the rapid formation of significant levels of hydrogen peroxide within a few seconds. Reaction of Fe(II) with superoxide will occur at a very fast rate while the back-reaction of Fe(III) with $O_2^{\bullet-}$ and the formation of insoluble Fe(OH)$_3$ becomes irrelevant, as the fate of Fe(III) in the system does not affect the oxidation of remaining Fe(II) (10). Moreover, autocatalysis of Fe(II) oxidation can occur in the presence of the high concentrations of Fe(OH)$_3$ at higher pH, thereby substantially increasing the net rate of Fe(II) oxidation. At lower pH, the oxidation of Fe(II) is slower than values obtained at nanomolar levels (Figure 1). Fe(III) becomes more soluble at lower pH and efficiently competes with Fe(II) for superoxide, decreasing the observed oxidation rate.

The studies carried out at different salinity and pH allow us to determine the individual oxidation rate constants as a function of the ionic strength. The oxidation rate constants are given in Table 3. The values that fit our results and those of King's (17) data in pure water (Table 4) indicate that the Fe(OH)$_2$ species is the major contributor to the oxidation at pH 8.0 and different ionic strengths.

Using the studies made at 10 °C at different pH and $[HCO_3^-]$, values for the rate constants k_3-k_6 were determined (Table 3). The rate constants $k_{11}-k_{14}$ were assumed to be constant in the range of pH studied and were computed considering the effect of temperature on the equilibrium constant for the hydrolysis reaction, k_{12} (40), and using the dependence with temperature given in eq 10. Assuming a linear dependence between log k and $1/T$, the overall

oxidation rate constants over the entire temperature and salinity range have been fitted to the equations

$$\log k_3 = 21.24 - 5861/T - 1.09I^{1/2} + 0.74I \quad \sigma = 0.03 \quad (16)$$

$$\log k_4 = 8.02 - 282/T - 3.62I^{1/2} + 0.71I \quad \sigma = 0.02 \quad (17)$$

$$\log k_5 = 19.47 - 4198/T - 1.75I^{1/2} + 0.94I \quad \sigma = 0.05 \quad (18)$$

$$\log k_6 = 10.64 - 545/T - 0.29I^{1/2} + 0.18I \quad \sigma = 0.03 \quad (19)$$

where the energy of activation for each constant has been considered independent of ionic strength (18). Further measurements are planned to investigate the effect of dissolved organic matter on these oxidation rate constants since they are important in natural waters (15, 21).

Environmental Significance. These studies made at nanomolar Fe(II) show that the oxidation of Fe(II) in natural seawater takes place at a much slower apparent rate than the previous results made at micromolar Fe(II). The results using Gulf Stream seawater characterized by low nutrients, trace metals, and organics (total dissolved organic carbon, DOC = 87 μM) support a longer lifetime for Fe(II) in oxic waters and cold waters making iron available to phytoplankton species. One might expect the presence of higher concentrations of natural organic compounds, released by organisms to form complexes with iron to affect the oxidation rates resulting in different half times for the Fe(II) in seawater. The results of this study can be used to study the oxidation of Fe(II) in pure water, estuaries, and seawater over a wide range of conditions.

Acknowledgments

Literature Cited

(1) Pankow, J. F. Kinetics for the aquatic environment. *Aquatic Chemistry Concepts*; Lewis Publishers: Chelsea, MI, 1991; pp 1155−1164.

(2) Stumm, W.; Lee, G. F. Kinetic product of ferrous iron. *Ind. Eng. Chem.* **1961**, *53*, 143−146.

(3) Ghost, M. M. Oxygenation of ferrous iron(II) in highly buffered waters. In *Aqueous Environmental of Metals*; Rubin, A. J., Ed.; Ann Arbor Science: Ann Arbor, MI, 1974; pp 193−217.

(4) Kester, D. R.; Byrne, R. H., Jr.; Liang, Y. Redox reactions and solution complexes of iron in marine systems. In *Marine Chemistry of the Coastal Environment*; Chuch, I. M., Ed.; ACS Symposium Series 18; American Chemical Society: Washington, DC, 1975; pp 56−79.

(5) Tamura, H.; Goto, K.; Nagayama, M. Effects of anions of the oxygenation of ferrous iron in neutral solutions. *J. Inorg. Nucl. Chem.* **1976**, *38*, 113−117.

(6) Sung, W.; Morgan, J. J. Kinetics and product of ferrous iron oxygenation in aqueous solutions. *Environ. Sci. Technol.* **1980**, *14*, 561−568.

(7) Davison, W.; Seed G. The kinetics of the oxidation of ferrous iron in synthetic and natural waters. *Geochim. Cosmochim. Acta* **1983**, *47*, 67−79.

(8) Millero, F. J.; Sotolongo, S.; Izaguirre, M. The oxidation kinetics of Fe(II) in seawater. *Geochim. Cosmochim. Acta* **1987**, *51*, 793−801.

(9) Millero, F. J.; Izaguirre, M. Effect of ionic strength and ionic interactions on the oxidation of Fe(II). *J. Solution Chem.* **1989**, *18*, 585−599.

(10) King, D. W.; Lounsbury, H. A.; Millero, F. J. Rates and mechanism of Fe(II) oxidation at nanomolar total iron concentration. *Environ. Sci. Technol.* **1995**, *29*, 818−824.

(11) Emennegger, L.; King, D. W.; Sigg, L.; Sulzberger, B. Oxidation kinetics of Fe(II) in a eutrophic Swiss lake. *Environ. Sci. Technol.* **1998**, *32*, 2990−2996.

(12) Santana-Casiano, J. M.; González-Dávila, M.; Rodríguez, M. J.; Millero, F. J. The effect of organic compounds in the oxidation kinetics of Fe(II). *Mar. Chem.* **2000**, *70*, 211−222.

(13) Rose, A. L.; Waite, T. D. Kinetic model for Fe(II) oxidation in seawater in the absence and presence of natural organic matter. *Environ. Sci. Technol.* 2002, *36*, 433−444.

(14) Pullin, M. J.; Cabaniss, S. E. The effects of pH, ionic strength and iron-fulvic acid interactions on the kinetics of non-photochemical iron transformations. I. Iron(II) oxidation and iron(III) colloid formation. *Geochim. Cosmochim. Acta* **2003**, *67*, 4067−4077.

(15) Santana-Casiano, J. M.; González-Dávila, M.; Millero, F. J. The oxidation of Fe(II) in NaCl−HCO$_3^-$ and seawater solutions in the presence of phthalate and salicylate ions: a kinetic model. *Mar. Chem.* **2004**, *85*, 27−40.

(16) Gunnars, A.; Blomqvist, S.; Johansson, P.; Andersson, C. Formation of Fe(III) oxyhydroxide colloids in freshwater and brackish seawater, with incorporation of phosphate and calcium. *Geochim. Cosmochi. Acta* **2002**, *66*, 746−758.

(17) King, D. W. Role of carbonate speciation on the oxidation rate of Fe(II) in aquatic systems. *Environ. Sci. Technol.* **1998**, *32*, 2997−3003.

(18) Millero, F. J.; Sotolongo, S. The oxidation of Fe(II) with H$_2$O$_2$ in seawater. *Mar. Chem.* **1989**, *53*, 1867−1873.

(19) Hoigné, J. The chemistry of ozone in water. In *Process Technologies for Water Treatment*; Stucki, S., Ed.; Plenum Press: New York, 1998; pp 121−143.

(20) McElroy, W. J. A laser photolysis study of the reaction of SO$_4^-$ with Cl$^-$ and the subsequent decay of Cl$_2^-$ in aqueous solution. *Phys. Chem.* **1990**, *94*, 2435−2441.

(21) Rose, A. L.; Waite, T. D. Effect of dissolved natural organic matter on the kinetics of ferrous iron oxygenation in seawater. *Environ. Sci. Technol.* **2003**, *37*, 4877−4886.

(22) Millero, F. J. The pH of estuarine waters. *Limnol. Oceanogr.* **1986**, *31*, 839−847.

(23) Millero, F. J.; Hersey, J. P.; Fernandez, M. The pK* of TRISH$^+$ in Na−K−Mg−Ca−Cl−SO$_4$ brines-pH scales. *Geochim. Cosmochim. Acta* **1987**, *51*, 707−711.

(24) King, D. W.; Lin, J.; Kester, D. R. Determination of Fe(II) in seawater at nanomolar concentrations. *Anal. Chim. Acta* **1991**, *247*, 176−179.

(25) Violler, E.; Inglett, P. W.; Hunter, K., Roychuodhury, A. N.; Cappellen, P. The ferrozine method revisited: Fe(II)/Fe(III) determination in natural waters. *Appl. Geochem.* **2000**, *15*, 785−790.

(26) Millero, F. J.; Gonzalez-Davila, M.; Santana-Casiano, J. M. Reduction of Fe(III) with sulfite in natural waters. *J. Geophys. Res.* **1995**, *100*, 7235−7244.

(27) Zhang, J. Z.; Kelble, C.; Millero, F. J. Gas-segmented continuous flow analysis of iron in water with a long liquid waveguide capillary flow cell. *Anal. Chim. Acta* **2001**, *438*, 49−57.

(28) Zika, R. G.; Saltzmann, E. S. Interaction of ozone and hydrogen peroxide in water: Implication for analysis of H$_2$O$_2$ in air. *Geophys. Res. Lett.* **1982**, *9*, 231−234.

(29) Moore, C. A.; Farmer, C. T.; Zika, R. G. Influence of the Orinoco River on hydrogen peroxide distribution and production in the eastern Caribbean. *J. Geophys. Res.* **1993**, *98*, 2289−2298.

(30) Hansen, H. P. In *Methods of Seawater Analysis*; Grasshoff, K., Kremling, K., Ehrhardt, M., Eds.; Wiley-VCH: Berlin, 1999.

(31) Mendes, P. Biochemistry by numbers: simulation of biochemical pathways with Gepasi 3. *Trends Biochem. Sci.* **1997**, *22*, 361−363.

(32) Box, G. E. P.; Draper, N. R. *Empirical Model-Building and Response Surfaces*; Wiley: New York, 1987.

(33) Zafiriou, O. C.; Voelker, B. M.; Sedlak, D. L. Chemistry of the superoxide radical (O$_2^-$) in seawater: reactions with inorganic copper complexes. *J. Phys. Chem. A* **1998**, *102*, 5693−5700.

(34) González-Dávila, M.; Millero. F. J. The adsorption of copper to chitin in seawater. *Geochim. Cosmochim. Acta* **1990**, *54*, 761−768.

(35) Millero, F. J., Schreiber, D. R. Use of the ion pairing model to estimate activity coefficients of the ionic components of natural waters. *Am. J. Sci.* **1982**, *282*, 1508−1540.

(36) King, D. W.; Farlow, R. Role of carbonate speciation on the oxidation of Fe(II) by H$_2$O$_2$. *Mar. Chem.* **2000**, *70*, 201−209.

(37) González-Dávila, M.; Santana-Casiano, J. M.; Millero, F. J. Oxidation of Fe(II) nanomolar with H$_2$O$_2$ in seawater. *Geochim. Cosmochim. Acta* **2005**, *69*, 83−93.

(38) Rush, J. D.; Bielski, B. H. J. Pulse radiolytic studies of the reaction of HO_2/O_2^- with Fe(II)/Fe(III) ions. The reactivity of HO_2/O_2^- with ferric ions and its implications on the occurrence of the Haber-Weiss reaction. *J. Phys. Chem.* **1985**, *89*, 5062−5066.

(39) Zika, R. G.; Moffett, J. W.; Pestane, R. G.; Cooper, W. J.; Saltzmann, E. S. Spatial and temporal variations of hydrogen peroxide in Gulf of Mexico waters. *Geochim. Cosmochim. Acta* **1985**, *49*, 1173−1184.

(40) Liu, X, Millero, F. J. The solubility of iron in seawater. *Mar. Chem.* **2002**, *77*, 43−54.