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# Reduction of Fe(III) with sulfite in natural waters

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**Abstract.** The Fe(III) in marine aerosols and rainwaters can be reduced to Fe(II) by photochemical processes and by reactions with sulfite. In this paper, measurements of the rates of reduction of nanomolar levels of Fe(III) with sulfite (without $O_2$) have been determined in NaCl and seawater solutions as a function of temperature (0° to 40°C), $p$H (2 to 6.8), ionic strength ($I = 0.1$ to $6\ M$), and composition ($Na^+$, $Mg^{2+}$, $Ca^{2+}$, $F^-$, $Cl^-$, $Br^-$, $HCO_3^-$, $SO_4^{2-}$). The overall rate constant ($k$, $M^{-1}\ min^{-1}$) for the reaction, $Fe(III) + S(IV) \xrightarrow{k}$ products, is given by $d[Fe(III)]/dt = -k[Fe(III)]\ [S(IV)]$. The reaction was found to be first order with respect to Fe(III) and S(IV). The rate constants as a function of $p$H increased from a $p\mathrm{H} = 2$ to 4 and decreased at higher $p$H. The effect of temperature and ionic strength on the rates could be represented by $\log k = \log k^0 + AI^{0.5}/(1 + I^{0.5})$, where $A = -1.1$ in NaCl and $-2.2$ in seawater and $\log k^0 = 25.39 - 6{,}323/T$. The energy of activation was found by 121 ± 6 kJ $mol^{-1}$. The measured rates in seawater as a function of salinity were lower than the rates in NaCl at the same ionic strength. Measurements in NaCl solutions with added sea-salt ions ($Mg^{2+}$, $Ca^{2+}$, $F^-$, $Br^-$, and $SO_4^{2-}$) at $p\mathrm{H} = 3.5$ indicate that the formation of inert $FeF^{2+}$ may be responsible for the lower rates. The effect of changes in the composition on the rates was interpreted by examining the speciation of Fe(III) and S(IV). This analysis indicates that the rate-determining steps from a $p$H of 2.5 to 4.0 are $FeOH^{2+} + HSO_3^- \longleftrightarrow HOFeSO_3H^+$ and $HOFeSO_3H^+ \xrightarrow{k_1} FeOH^+ + HSO_3\cdot$ and at $p$H of 4 to 6, the reactions $Fe(OH)_2^+ + HSO_3^- \longleftrightarrow (HO)_2FeSO_3H$ and $(HO)_2FeSO_3H \xrightarrow{k_2} Fe(OH)_2 + HSO_3\cdot$ become important. The changes in the concentration of $FeOH^{2+}$ and $HSO_3^-$ as a function of $p$H and composition can account for most of the changes in the rates. These kinetic studies indicate that the rates of reduction of Fe(III) with S(IV) in acidic water droplets at natural levels of S(IV) may be an important source of Fe(II).

## Introduction

Iron is essential for the growth of phytoplankton in the oceans. In several regions of the open ocean the deposition of atmospheric mineral aerosols may be an important source of iron to surface waters where phytoplankton growth may be limited by the availability of iron [*Martin and Fitzwater*, 1988]. The availability of iron from aerosols may be a function of the solubility and oxidation state. The iron in aerosols and water droplets (clouds, fog, or rainwaters) is also involved in a number of chain and redox reactions which influence the chemistry of other important atmospheric species [*Zuo and Hoigné*, 1993; *Faust et al.*, 1993; *Faust and Hoigné*, 1990; *Jacob et al.*, 1985; *Weschler et al.*, 1986; *Graedel et al.*, 1986; *Hoffmann and Jacobs*, 1984]. In most atmospheric studies of the solubility of iron, it has been assumed [*Hardy and Crecelius*, 1981; *Moore et al.*, 1984; *Pandis and Seinfeld*, 1989; *Zhuang et al.*, 1992; *Zhu et al.*, 1992] that the element was present as Fe(III). Fe(III) as an oxide, the most common mineral phase, is not very soluble in aqueous solutions. Fe(II) is thermodynamically and kinetically unstable in aerosols and water droplets with $O_2$ and $H_2O_2$ [*Millero et al.*, 1987; *Millero and Sotolongo*, 1989]. Thus one would expect that any Fe(II) produced in these waters would be rapidly converted to Fe(III). Recent work suggests that Fe(II) could in fact be quite high (20–90% of total iron) in fog water [*Behra and Sigg*, 1990; *Dedik et al.*, 1992; *Erel et al.*, 1993] and marine aerosols [*Zhuang*, 1992; *Zhuang et al.*, 1992; *Zhu et al.*, 1993]. The recent work by *Zhu et al.* [1993], however, indicates that the concentrations of Fe(II) are low (7.5% of total iron) in marine aerosols.

The production of Fe(II) in aerosols and water droplets is thought to be due to the photoreduction of inorganic and organic complexes of Fe(III) [*Faust and Hoffmann*, 1986; *Faust et al.*, 1989; *Warneck*, 1989; *Zhu et al.*, 1992]. This photoreduction is a function of light, $p$H, and the concentration of inorganic and organic ligands in the aqueous solutions [*Erel et al.*, 1993]. Recent workers [*Behra and Sigg*, 1990; *Zhuang et al.*, 1992] have suggested that the reduction of Fe(III) with sulfite, present in most marine aerosols and water droplets, could be important in the production of Fe(II). *Reddy et al.* [1991] also suggested that the sulfite-induced autoxidation of Fe(II) to Fe(III) is an important step in the cycling of iron in water droplets.

A number of studies have been made on the effect of Fe(III) on the autoxidation of S(IV) in natural waters due to the interest in the formation of acid rain [*Hoffmann and Calvert*, 1985; *Weschler et al.*, 1986; *Martin and Hill*, 1987; *Conklin and Hoffmann*, 1988; *Kraft and van Eldik*, 1989a, b,

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c]. The process in acidic solutions is thought to be initiated by the formation of iron sulfite complexes [*Conklin and Hoffmann*, 1988; *Betterton*, 1993; *Kraft and van Eldik*, 1989 a, b, c, d]. Recent work [*Betterton*, 1993] indicates that the complexes formed are

$$Fe^{3+} + HSO_3^- \longleftrightarrow Fe\text{-}SO_3H^{2+} \tag{1}$$

$$FeOH^{2+} + HSO_3^- \longleftrightarrow HOFe\text{-}SO_3H^+ \tag{2}$$

The conditional stability constants for the formation of these iron sulfite complexes ($K_{app}$) have recently been determined by *Betterton* [1993] using spectrophotometric techniques. He found values of $K_{FeSO_3H} = 55\ M^{-1}$ and $K_{FeOHSO_3} = 850\ M^{-1}$ by evaluating the $p$H dependence of the spectra at 400 nm. The reduction of Fe(III) and oxidation of sulfite occurs as an electron transfer reaction that results in the formation of Fe(II) and the sulfite free radical

$$FeOH^{2+} + HSO_3^- \longleftrightarrow HOFe\text{-}SO_3H^+$$

$$HOFe\text{-}SO_3H^+ \xrightarrow{k} Fe(OH)^+ + \cdot SO_3H \tag{3}$$

where $HOFe\text{-}SO_3H^+$ is an inner sphere complex that may undergo a rearrangement to form $HOFe\text{-}OSO_2H$ [*Conklin and Hoffmann*, 1988].

The proposed free radical mechanism for the further oxidation of sulfite to sulfate with and without oxygen has been discussed in detail by many workers [*Brandt et al.*, 1994; *Reddy et al.*, 1991, 1992a; *van Eldik et al.*, 1992; *Grgic et al.*, 1991, 1992; *Kraft and van Eldik*, 1989a, b; *Conklin and Hoffmann*, 1988]. The rates of the reduction of Fe(III) and oxidation of S(IV) without oxygen have been studied by a number of workers [*Karraker*, 1963; *Carlyle*, 1971; *Carlyle and Zeck*, 1973; *Conklin and Hoffmann*, 1988]. Most of these studies have emphasized the oxidation of S(IV) and were made at high concentrations of reactants in a perchlorate media. The back oxidation of Fe(II) by sulfur species to form Fe(III) has also been studied [*Reddy and van Eldik*, 1992; *van Eldik et al.*, 1992]. A limitation of most of these past studies is that the concentrations of Fe(III) were at levels above the solubility of iron at values of $p$H over 3.0.

In the present paper we present results for the reduction of nanomolar levels of Fe(III) with S(IV) without oxygen as a function of ionic strength ($I$ = 0.1 to 6 $M$ in NaCl), temperature (0° to 40°C), $p$H (2 to 6.8), and composition ($Mg^{2+}$, $Ca^{2+}$, $F^-$, $Br^-$, and $SO_4^{2-}$). By making these measurements at concentrations of Fe(III), which are more representative of the levels in natural waters, we have been able to stay below the solubility limits to $p$H 6.0. The results are used to examine how the speciation of Fe(III) affects the rates of reduction with sulfite in natural waters.

## Experiment

### Instrumentation

The reduction studies were performed in a 550 $cm^3$ water-jacketed glass cell. The vessel was cleaned first with concentrated HCl and then with 2 $M$ HCl between runs. The temperature was controlled to ±0.02°C with a Forma temperature bath and monitored with a Guildline Pt thermometer. The solutions were stirred at the same rate during all the experiments. The top of the vessel had five openings: one for a Teflon tube connected to the flow injection analysis (FIA) system, two for the glass and reference electrodes, one to add the iron and sulfite solutions, and one to bubble $N_2$ through the solutions. The $p$H was determined with an Orion glass $p$H electrode and an Ag-AgCl double junction reference electrode using an Orion 720A $p$H meter. The electrode system was calibrated with *tris*(hydroxymethyl)-aminomethane (TRIS) buffers [*Millero*, 1986]. The values of $p$H for seawater and NaCl solutions were calculated according to the free proton scale [*Millero*, 1986; *Millero et al.*, 1987]. Most of the measurements were made at a $p$H = 3.5, where the reaction rate is at a maximum, to speed up the acquisition of data.

The system used for the detection of the chemiluminescent reaction was an improved version of the stopped flow instrument developed by *O'Sullivan et al.* [1995] and adapted to FIA by *King et al.* [1995]. The sample containing the Fe(II) formed in the reaction vessel, the reagent (luminol solution), and carrier solutions entered the instrument separately driven by a Rabbit peristaltic pump through a six-channel electrical Valco two-position valve. The reactants are continuously mixed in a coiled reaction chamber positioned directly in front of a photomultiplier tube (Hamamatsu PMT HC124-02 biased at 1000 V) to measure the chemiluminescent emission. The entire system is computer controlled. In the load position, the sample is pumped to a loop with a 0.7-$\mu$L capacity. In the inject position, the sample is transported by the carrier to the coiled reaction chamber. The intensity of the signals was recorded as a function of time from the moment the sample was injected until the signal intensities were negligible.

The formation of Fe(II) in the reduction kinetics studies was followed directly in the thermostated cell at a given $p$H. After the addition of a known concentration of Fe(III) to the solution the residual amount of Fe(II) present in the solution was determined. The zero time corresponds to when the sulfite was added. As the chemiluminescence signal of iron(II)-luminol complexes has been found to depend on factors such as flow rate, organic complexation, $p$H, and ionic strength [*Seitz and Hercules*, 1972; *Klopf and Nieman*, 1983], a determination of the sensitivity of the instrument was carried out for each experimental condition. After a blank determination of the medium, a known amount of Fe(II) was added and the light emission was determined. To avoid any oxidation of the Fe(II) formed when the $p$H of the solution was greater than 5 [*Millero et al.*, 1987], the solution was bubbled with 99.999% $N_2$ for 20 min before the measurements and an inert atmosphere was kept in the top on the cell during the measurements. At a $p$H lower than 5, no effects were observed in $N_2$ stripped and unstripped solutions.

The standard addition of Fe(II) to seawater and NaCl solutions showed that the detection limit of the technique is in the subnanomolar level (0.2 n$M$) which is consistent with that found by *Klopf and Nieman* [1983]. The concentrations were found to be linear to 75 n$M$ Fe(II) in seawater with a standard error of 0.4 n$M$ (±1.5%) (see Figure 1).

### Chemicals

Luminol (3-aminophthalhydrazide) (sigma) was dissolved by adding the minimal amount of 1 $M$ NaOH in 0.5 $M$ NaCl to prepare 0.5-m$M$ luminol solution. This solution was added to a 0.2 $M$ $H_3BO_3$-NaOH buffer in 0.5 $M$ NaCl. The $p$H was

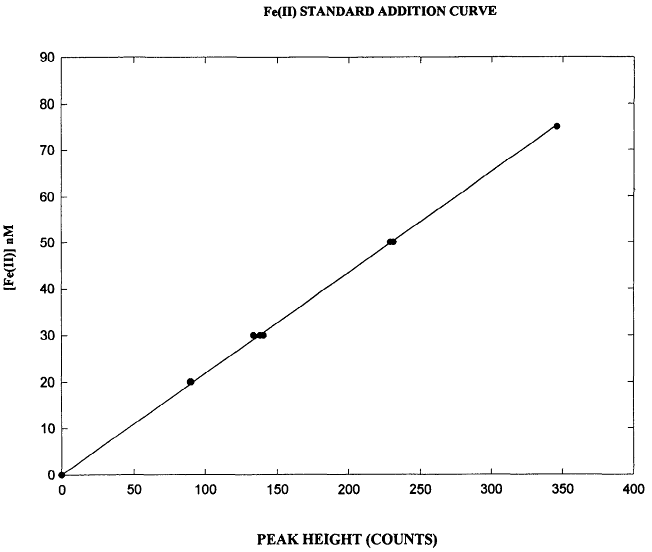

**Figure 1.** Calibration of the flow injection system used to determine the concentration of Fe(II) in seawater.

adjusted with NaOH to $p$H 10.8. The carrier solution was a NaCl (sigma ultra) solution prepared at the same ionic strength as the sample to be analyzed to avoid any signal variation. A 1.0 m$M$ standard Fe(II) solution was prepared by weighing reagent grade $Fe(NH_4)_2(SO_4)_2 \cdot 6\,H_2O$ (Fisher) and dissolving in an acidic solution (0.1 $M$ HCl) (Fisher-trace metal grade). Other standards were freshly prepared by acidic dilution. A 30 $\mu M$ Fe(III) solution was prepared by dilution of a Fe(III) atomic absorption standard solution (sigma). These solutions were kept at $p$H 8 to oxidize any Fe(II) present in the stock solution and then acidified at $p$H 1 with HCl 0.1 $M$. Under these conditions the Fe(II) blank was negligible. A 0.01 $M$ $Na_2SO_3$ solution (Baker) was freshly prepared in NaCl at the same ionic strength as the sample to be analyzed.

The seawater used was Gulf Stream water collected 10 miles off the coast of Miami and filtered prior to the studies through a 0.45-$\mu$m Millipore filter. The salinity was determined with a Guildline Autosal conductance bridge using the practical salinity scale. The NaCl (sigma ultra) solutions were prepared by weight and buffered with $NaHCO_3$ (0.002 $M$). All the other chemicals used were reagent grade.

## Results and Calculations

The rates of reduction of Fe(III) with S(IV) can be represented by

$$\mathrm{Fe(III)} + \mathrm{S(IV)} \xrightarrow{k} \mathrm{products} \qquad (4)$$

with the overall rate equation

$$d[\mathrm{Fe(III)}]/dt = -k[\mathrm{Fe(III)}]^a[\mathrm{S(IV)}]^b \qquad (5)$$

where $a$ and $b$ are the order of the reactions with respect to Fe(III) and S(IV). The rate constant was determined by measuring the appearance of Fe(II) (see Figure 2). The disappearance of total Fe(III) ($[\mathrm{Fe(III)}]_T = [\mathrm{Fe(III)}]_0 - [\mathrm{Fe(II)}]$), where the subscript zero denotes the initial concentration) was determined as a function of time under pseudo-first-order conditions (an excess of S(IV)). The first-order rate constant for the disappearance of Fe(III) under these conditions is given by

$$d[\mathrm{Fe(III)}]/dt = -k'[\mathrm{Fe(III)}] \qquad (6)$$

where $k' = k[\mathrm{S(IV)}]^b$. The validity of this first-order disappearance of Fe(III) in seawater at various initial levels of S(IV) is shown in Figure 3 (S = 34.97, 25°C, and $p$H = 3.5). The values of ln $k'$ as a function of ln $[\mathrm{S(IV)}]_0$ are shown in Figure 4. The least squares line gives a slope of 1.07 ± 0.05 and demonstrates that the reaction is first order with respect to S(IV) in agreement with earlier workers [*Karraker*, 1963; *Grgic et al.*, 1991]. These results yield an overall rate constant ln $k$ = 7.34 ± 0.04 for seawater at $p$H = 3.5 and 25°C.

The effect of ionic strength on the rate of reduction of Fe(III) by S(IV) has been determined in NaCl and seawater

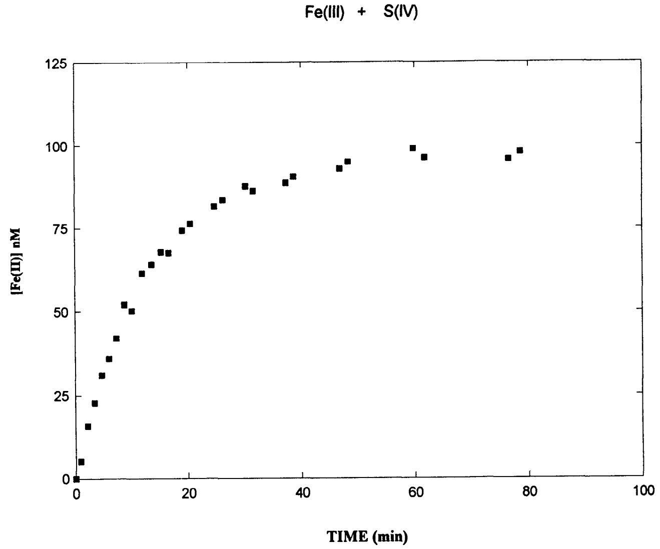

**Figure 2.** Measured values of Fe(II) formed during the reduction of Fe(III) by S(IV) in seawater (S = 35) at 25°C ($[\mathrm{Fe(III)}]_0$ = 100 n$M$ and $[\mathrm{S(IV)}]_0$ = 100 $\mu M$).

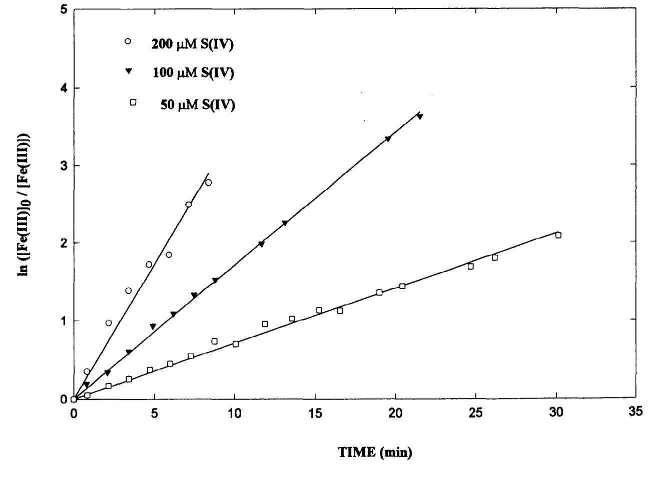

**Figure 3.** Plots of ln ($[\mathrm{Fe(III)}]_0/[\mathrm{Fe(III)}]$) versus time for the reduction of Fe(III) by S(IV) in seawater at 25°C (S = 35, $p$H = 3.5, and $[\mathrm{Fe(III)}]_0$ = 100 n$M$).

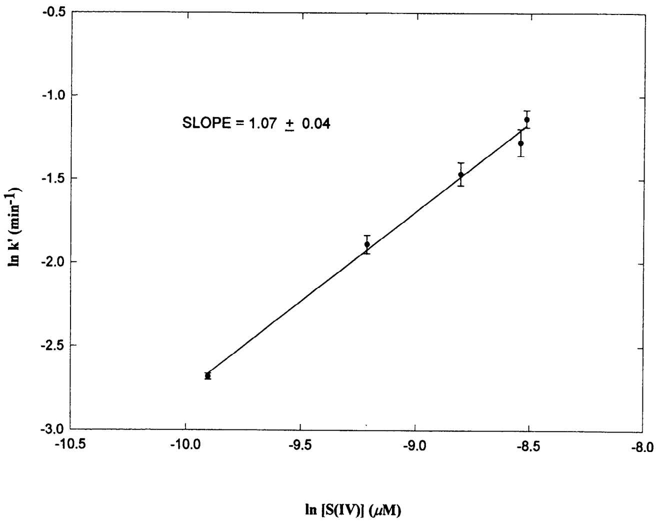

**Figure 4.** Plots of ln $k'$ versus ln [S(IV)] for the reduction of Fe(III) by S(IV) in seawater at 25°C (S = 35, $p$H = 3.5, and $[\mathrm{Fe(III)}]_0 = 100$ n$M$).

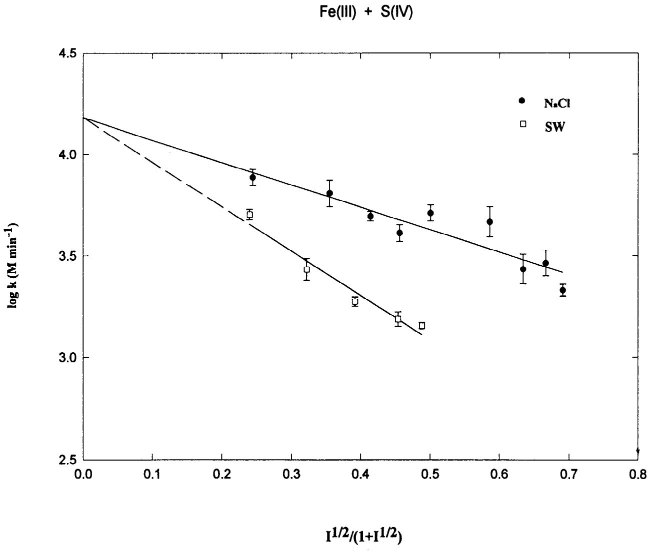

**Figure 5.** The effect of ionic strength (I) on the rates of reduction of Fe(III) by S(IV) in NaCl and seawater at 25°C ($p$H = 3.5, and $[\mathrm{Fe(III)}]_0 = 100$ n$M$).

at 25°C and $p$H = 3.5. The results for the overall rate constant $k = k'/[\mathrm{S(IV)}]$ are given in Table 1 and are shown plotted versus ionic strength in Figure 5. The results in NaCl and seawater have been fitted to the equation

$$\log k = \log k^0 + AI^{1/2}(1 + I^{1/2}) \qquad (7)$$

where the value in pure water is $\log k^0 = 4.18 \pm 0.09$ and where $A = -1.1 \pm 0.2$ and $-2.2 \pm 0.3$, in NaCl and seawater, respectively.

The effect of temperature (1° to 40°C) on the overall rate constant $k$ ($M^{-1}$ min$^{-1}$) for the reduction of Fe(III) by S(IV) in seawater is shown as a function of $1/T$ ($K$) in Figure 6. The energy of activation is 121 ± 6 kJ mol$^{-1}$ and is only relevant to our reaction conditions. This energy of activation is similar to the value (104 kJ mol$^{-1}$) found for the catalytic effect of Fe(III) on the oxidation of S(IV) [*Grbic et al.*, 1991]. If we assume that the energy of activation is independent of ionic strength, all the 25°C data can be represented by (7) where $\log k^0 = 25.39 - 6323/T$.

The lower rates for the reduction of Fe(III) in seawater were examined by measuring the rates in NaCl (with 0.002 $M$ $\mathrm{HCO_3^-}$) solutions with various amounts of sea salts equivalent to their concentrations in seawater ($\mathrm{Na^+} = 0.56$ $M$, $\mathrm{Mg^{2+}} = 0.053$ $M$, $\mathrm{Ca^{2+}} = 0.01$ $M$, $\mathrm{K^+} = 9$ m$M$, $\mathrm{Cl^-} = 0.6$ $M$, $\mathrm{SO_4^{2-}} = 0.028$ $M$, $\mathrm{Br^-} = 800$ $\mu M$, $\mathrm{HCO_3^-} = 2.2$ m$M$, and $\mathrm{F^-} = 70$ $\mu M$). The results of $\Delta\ln k = \ln k(\text{media}) - \ln k(\text{NaCl})$ are shown in Table 2 and in Figure 7. The addition of $\mathrm{F^-}$, $\mathrm{SO_4^{2-}}$, $\mathrm{Mg^{2+}}$, and $\mathrm{Ca^{2+}}$ cause the rate to decrease, while the addition of $\mathrm{K^+}$ and $\mathrm{Br^-}$ cause the rate to increase slightly. The addition of the major sea salts ($\mathrm{Na^+}$, $\mathrm{Mg^{2+}}$, $\mathrm{Cl^-}$, and $\mathrm{SO_4^{2-}}$) yields a relative rate (−0.60) that is higher than the value in seawater (−1.05) or artificial seawater (−1.04) with all the major components ($\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{Mg^{2+}}$, $\mathrm{Ca^{2+}}$, $\mathrm{F^-}$, $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{HCO_3^-}$, and $\mathrm{SO_4^{2-}}$). The addition of boric acid or deletion of $\mathrm{HCO_3^-}$ (not shown) had no effect on the rate. The addition of $\mathrm{F^-}$ to NaCl yielded a relative rate (−1.06) that was in good agreement with the seawater results. These experiments show that $\mathrm{F^-}$ is the most important anion in seawater that causes the rate to be lower than in NaCl at the same ionic strength. The decrease due to

**Table 1.** Overall Rate Constant $k$($M^{-1}$ min$^{-1}$) for the Reduction of Fe(III) by S(IV) at Different Concentrations in Seawater and NaCl ($p$H = 3.5, 25°C, $[\mathrm{Fe(III)}]_0 = 100$ n$M$, and $[\mathrm{S(IV)}]_0 = 100$ $\mu M$)

| Salinity | ln $k$ | NaCl, $M$ | ln $k$ |
|---|---|---|---|
| 5.0 | 8.52 ± 0.02 | 0.98 | 8.95 ± 0.09 |
| 11.4 | 7.90 ± 0.06 | 0.298 | 8.77 ± 0.15 |
| 21.0 | 7.60 ± 0.02 | 0.498 | 8.51 ± 0.05 |
| 35.0 | 7.34 ± 0.04 | 0.698 | 8.37 ± 0.08 |
| 45.9 | 7.25 ± 0.02 | 0.998 | 8.54 ± 0.09 |
| | | 1.998 | 8.44 ± 0.17 |
| | | 2.998 | 7.91 ± 0.17 |
| | | 3.998 | 7.98 ± 0.15 |
| | | 4.998 | 7.66 ± 0.07 |
| | | 5.998 | 7.28 ± 0.10 |

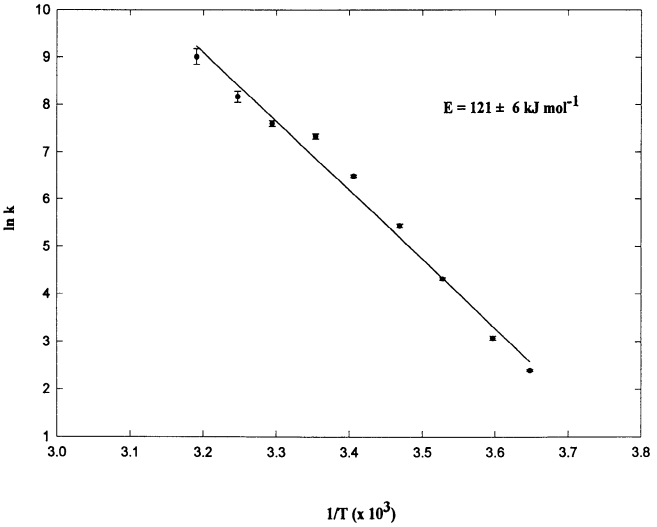

**Figure 6.** The effect of temperature ($T$/K) on the rates of reduction of Fe(III) by S(IV) in seawater ($p$H = 3.5, $[\mathrm{Fe(III)}]_0 = 100$ n$M$ and $[\mathrm{S(IV)}]_0 = 100$ $\mu M$).

**Table 2.** Effect of Composition on the Overall Rate Constant ($k$, $M^{-1}$ min$^{-1}$) for the Reduction of Fe(III) by S(IV) in NaCl (0.6 $M$) Solutions (25°C, $p$H = 3.5, $[\mathrm{Fe(III)}]_0$ = 100 n$M$, and $[\mathrm{S(IV)}]_0$ = 100 $\mu M$)

| Ion | $\Delta \ln k$[a] | Molality | $\ln k/dm$ |
|---|---|---|---|
| $SO_4$ | −0.19 | 0.028 | −6.8 |
| Mg | −0.10 | 0.053 | −1.9 |
| Ca | −0.33 | 0.010 | −3.3 |
| K | 0.24 | 0.009 | 111 |
| Br | 0.32 | 0.0008 | 400 |
| F | −1.06 | 0.00007 | −15142 |
| $B(OH)_3$ | 0.0 | 0.0004 | 0 |
| Major sea salts[b] | −0.60 | | |
| Art. SW[c] | −1.04 | | |
| SW | −1.05 | | |

[a] $\Delta \ln k = \ln k(\text{media}) - \ln k(\text{NaCl})$.
[b] Na, Mg, Ca, $SO_4$.
[c] Na, K, Mg, Ca, $HCO_3$, F, Cl, Br.

**Table 3.** Overall Rate Constants for the Reduction of Fe(III) by S(IV) in Seawater As a Function of $p$H (S = 35, $t$ = 25°C, $[\mathrm{Fe(III)}]_0$ = 100 n$M$, and $[\mathrm{S(IV)}]_0$ = 100 $\mu M$)

| $p$H | $\ln k$, $M^{-1}$ min$^{-1}$ |
|---|---|
| 1.996 | 4.08 ± 0.03 |
| 2.490 | 5.38 ± 0.08 |
| 2.968 | 6.48 ± 0.03 |
| 3.500 | 7.32 ± 0.05 |
| 3.750 | 7.44 ± 0.03 |
| 3.817 | 7.40 ± 0.03 |
| 4.267 | 7.41 ± 0.05 |
| 4.399 | 7.51 ± 0.07 |
| 4.856 | 7.42 ± 0.04 |
| 5.389 | 7.20 ± 0.04 |
| 6.088 | 6.75 ± 0.06 |
| 6.357 | 5.15 ± 0.23 |
| 6.740 | 4.42 ± 0.02 |

the addition of $SO_4^{2-}$, $Mg^{2+}$, and $Ca^{2+}$ (−0.62) is nearly balanced by the increase due to the addition of $K^+$ and $Br^-$ (0.53).

The effects of $p$H on the values of ln $k$ in seawater were also determined and the results are given in Table 3 and shown in Figure 8. The values increase from a $p$H = 2.0 to a maximum near $p$H = 4.0 and decrease at higher $p$H. Our measurements as a function of $p$H are similar to the Mn(II)-Fe(III) catalyzed rate of S(IV) oxidation measurements of *Grgic et al.* [1991, 1992]. It is difficult to compare our results in NaCl and seawater to the earlier work [*Karraker*, 1963; *Conklin and Hoffmann*, 1988] made in perchloric solutions because they were made in different media at much higher concentrations of reactants. These earlier workers found half-times of 3–18 min between $p$H 0 and 2. Our results in seawater at $p$H = 2 give $t_{1/2}$ = 12 min at [S(IV)] = 1 m$M$, which is the same order of magnitude as found by *Karraker* [1963] and *Conklin and Hoffmann* [1988].

## Discussion

Our rate constants for the reduction of Fe(III) by S(IV) are strong functions of $p$H and the solution composition. To analyze the effects of composition on the reaction rate, it is necessary to be able to determine the speciation of the reacting species. Recently, we [*Millero et al.*, 1995] have developed a computer code to determine the speciation of iron in aqueous solutions as a function of composition (Na, K, Mg, Ca, Sr, Cl, $SO_4$, $HCO_3$, Br, $CO_3$, F) and ionic strength (0 to 2 $M$). The model uses the *Pitzer* [1991] equations to determine the activity coefficients of all the major components of the media and the interactions of the minor divalent [*Millero and Hawke*, 1992] and trivalent [*Millero*, 1992] ions with these major components. The stability constants for the formation of the ion pairs are then determined in the ionic media as well as the fraction of the various species. The stability constants used in the model have been extrapolated to infinite dilution in the media in which they were determined ($NaClO_4$). The values in a given ionic media are determined using the estimated activity coefficients. For example, for the formation of $FeOH^{2+}$ the hydrolysis constant $K^*_{FeOH}$ is determined from

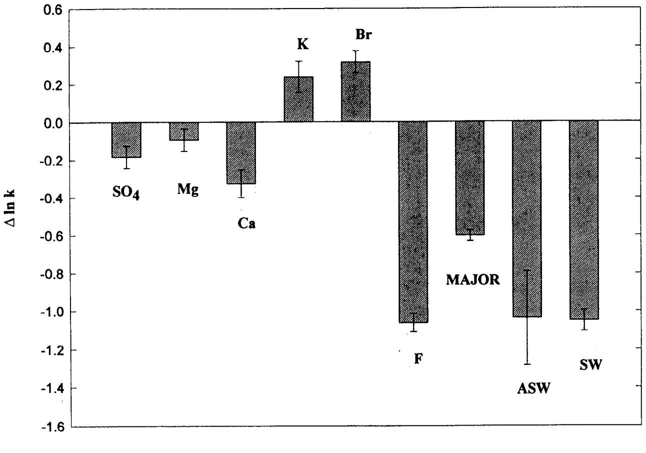

**Figure 7.** The effect of composition ($\Delta \ln k = \ln k(\text{soln}) - \ln k(\text{NaCl})$ on the rates of reduction of Fe(III) by S(IV) in NaCl with various sea salts at 25°C ($p$H = 3.5, $[\mathrm{Fe(III)}]_0$ = 100 n$M$, and $[\mathrm{S(IV)}]_0$ = 100 $\mu M$).

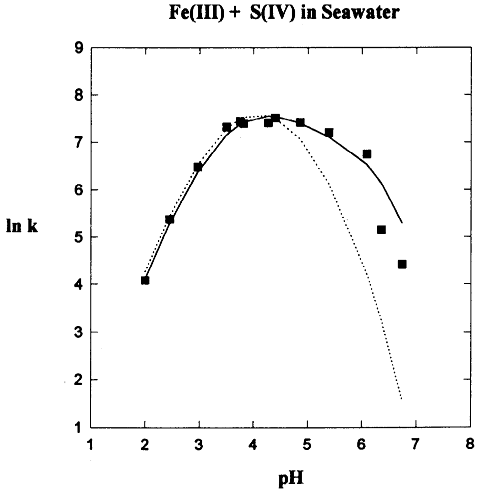

**Figure 8.** The effect of $p$H on the rates of reduction of Fe(III) by S(IV) in seawater at 25°C (S = 35, $[\mathrm{Fe(III)}]_0$ = 100 n$M$, and $[\mathrm{S(IV)}]_0$ = 100 $\mu M$). The dotted curve is calculated from equation (11) using only $k_1$ and the solid curve is calculated using $k_1$ and $k_2$.

**Table 4.** Stability and Hydrolysis Constants for the Formation of Fe(III) Ion Pairs at 25°C

| | log $K$ | | |
|---|---|---|---|
| | Water | $NaClO_4$ (I = 0.4) | Seawater (I = 0.7) |
| $FeCl^{2+}$ | 1.28 | 0.53 | 0.57 |
| $FeCl_2^+$ | 1.16 | −0.65 | −0.13 |
| $FeF^{2+}$ | 6.03 | 5.21 | 5.24 |
| $FeF_2^+$ | 10.66 | 9.38 | 9.45 |
| $FeF_3$ | 13.66 | 11.97 | 11.84 |
| $FeSO_4^+$ | 4.27 | 2.55 | 2.58 |
| $Fe(SO_4)^-$ | 6.11 | 3.59 | 3.40 |
| $FeOH^{2+}$ | −2.20 | −2.68 | −2.62 |
| $Fe(OH)_2^+$ | −6.33 | −7.03 | −6.79 |
| $Fe(OH)_3$ | −12.82 | −13.73 | −13.62 |
| HF | 3.17 | 2.86 | 2.77 |
| $HSO_4^-$ | 1.98 | 1.22 | 1.02 |
| $FeSO_3H^{2+}$ | | 55[a] (0)[b] | |
| $HOFeSO_3H^+$ | | 850[a] (638)[b] | |

From *Millero et al.* [1995].
[a]From *Betterton et al.* [1993].
[b]This study.

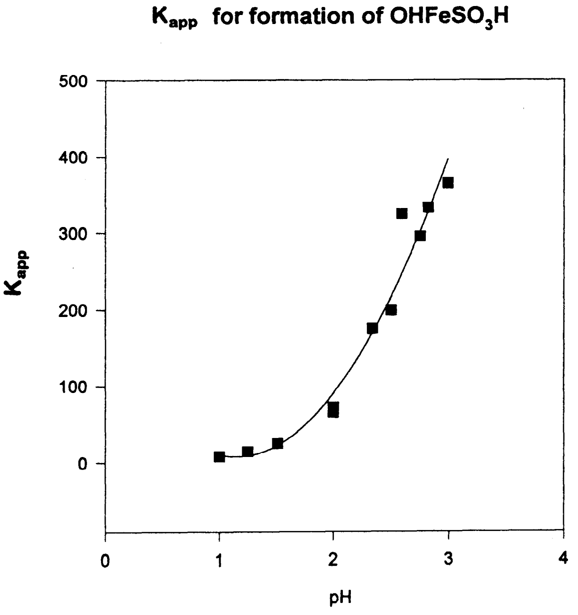

**Figure 9.** Values of the conditional formation constant $K_{app}$ [*Betterton*, 1993] as a function of $p$H. The smooth curve is calculated using $K_{FeSO_3H} = 0$ and $K_{HOFeSO_3H} = 638$ $M^{-1}$ (equation (9)).

$$K^*_{FeOH} = K_{FeOH}\gamma(FeOH^{2+})a(H_2O)/\{(\gamma(H^+)\gamma(FeOH^{2+})\} \tag{8}$$

where $K_{FeOH}$ is the value in water, $\gamma$(i) are the activity coefficients, and $a(H_2O)$ is the activity of water determined with the *Pitzer* [1991] equations. Values of $K_{FeX}$ used to determine the speciation of Fe(III) and S(IV) in water, $NaClO_4$, and seawater solutions are given in Table 4. We also include the values estimated for the formation of $FeSO_3H$ and $HOFeSO_3H$ determined from the work of *Betterton* [1993]. Since the formation of these complexes are important in interpreting the rates, we have reevaluated the effect of $p$H on the experimental values of $K_{app}$ for the formation of Fe(III)-S(IV) [*Betterton*, 1993] using our stability constants [*Millero et al.*, 1995] and the equation

$$K_{app} = K_{FeSO_3H}\alpha_{Fe}\alpha_{HSO_3} + K_{HOFeSO_3H}\alpha_{FeOH}\alpha_{HSO_3} \tag{9}$$

Our stability constants give $K_{FeSO_3H} = 28 \pm 30\ M^{-1}$ and $K_{HOFeSO_3H} = 611 \pm 40\ M^{-1}$ with a standard error of $\pm 26$ $M^{-1}$ in $K_{app}$. If the formation of $FeSO_3H$ is neglected, we obtain $K_{HOFeSO_3H} = 638 \pm 25\ M^{-1}$ with a standard error of $\pm 26\ M^{-1}$. This estimate of $K_{HOFeSO_3H}$ is in good agreement with those tabulated by *Brandt et al.* [1994] near a $p$H of 3.0. These results indicate that the effect of $p$H on the formation of Fe(III)-S(IV) complexes can be attributed to the formation of only the $HOFeSO_3H$ complex (see Figure 9) over the $p$H range of 1 to 3.

The speciations of Fe(III) [*Millero et al.*, 1995] and S(IV) [*Millero et al.*, 1989] in seawater as a function of $p$H determined from the stability constants given in Table 4 are shown in Figures 10 and 11. Both $Fe(OH)_2^+$ and $FeOH^{2+}$ as well as $HSO_3^-$ go through a maximum between a $p$H of 3 to 5, the same region where the ln $k$ goes through a maximum. The addition of S(IV) at the levels used in our experiments (100 $\mu M$) had little effect on the speciation of Fe(III) in seawater which is dominated by the formation of $FeF^{2+}$, $FeF_2^+$ and $FeSO_4^+$ at low $p$H and $FeOH^{2+}$ and $Fe(OH)_2^+$ at high $p$H. The $HSO_3^-$ species is dominant over the $p$H range of our studies (2 to 7). These speciation diagrams indicate that the effect of $p$H on the rate constant for the reduction of Fe(III) can be attributed to

$$k[Fe(III)][S(IV)] = k_0[Fe^{3+}][HSO_3^-] + k_1[FeOH^{2+}][HSO_3^-] + k_2[Fe(OH)_2^+][HSO_3^-] \tag{10}$$

This equation can be simplified to

$$k = k_0\alpha_{Fe}\alpha_{HSO_3} + k_1\alpha_{FeOH}\alpha_{HSO_3} + k_2\alpha_{Fe(OH)_2}\alpha_{HSO_3} \tag{11}$$

where $\alpha_i$ are the molar ratios of species $i$ and the individual rate constants are for

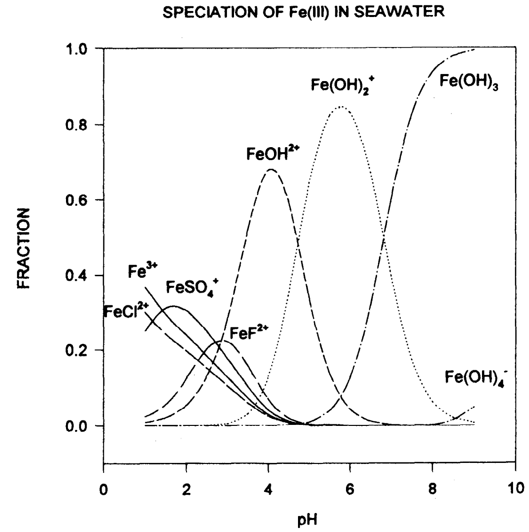

**Figure 10.** Speciation of Fe(III) in seawater as a function of $p$H [*Millero et al.*, 1995].

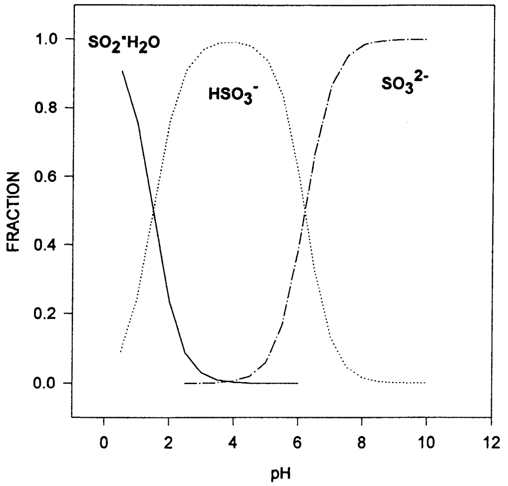

**Figure 11.** Speciation of S(IV) in seawater as a function of $p$H [*Millero et al.*, 1989].

$$Fe^{3+} + HSO_3^- \xrightarrow{k_0} Fe^{2+} + \cdot SO_3H \qquad (12)$$

$$FeOH^{2+} + HSO_3^- \xrightarrow{k_1} FeOH^+ + \cdot SO_3H \qquad (13)$$

$$Fe(OH)_2^+ + HSO_3^- \xrightarrow{k_2} Fe(OH)_2 + \cdot SO_3H \qquad (14)$$

The values of $k_0$, $k_1$, and $k_2$ were determined from the calculated values of $\alpha_i$ determined from our speciation model and experimental values of $k$. The value of $k_0$ was not needed to represent the results. From a $p$H of 2 to 4 the results could be adequately represented by using only $k_1$ = 6160 ± 300 $M$ min$^{-1}$ (see Figure 8). The measurements above a $p$H = 4 required values of $k_1$ = 4650 ± 500 $M$ min$^{-1}$ and $k_2$ = 1213 ± 210 $M$ min$^{-1}$ to represent the results (see Figure 8). These results indicate that the rate constant for $FeOH^{2+}$ with $HSO_3^-$ is 2 times larger than for $Fe(OH)_2^+$. The results between $p$H = 2 to 4 are similar to the earlier results at low $p$H [*Conklin and Hoffmann*, 1988; *Betterton*, 1993] for the formation of the complex $OHFeSO_3H$, as described above. Our finding that the reaction of $Fe(OH)_2^+$ and $HSO_3^-$ is important at a higher $p$H (between 4 and 6) is possible because we have been able to make our measurements below the solubility limits of Fe(III) (≈10 n$M$ at $p$H = 6).

The effect of composition on the rates of reduction of Fe(III) with S(IV) in NaCl media with added cations and anions can qualitatively be attributed to changes in the interaction of Fe(III) with various anions and S(IV) with various cations. A small part of the decrease in the rates due to the addition of $Mg^{2+}$ and $Ca^{2+}$ can be attributed to a decrease in the concentration of free $HSO_3^-$. Both of these cations are known to form complexes with sulfite [*Roy et al.*, 1991]. The increase in the rate with the addition of $K^+$ may be related to it having weaker interactions with $HSO_3^-$ than $Na^+$. The decrease in the rate with the addition of $SO_4^{2-}$ and $F^-$ can be attributed to the formation of $FeSO_4^+$ and $FeF^{2+}$ ion pairs that are nonreactive to reduction with S(IV). The increase in the rate with the addition of $Br^-$ may be related to it having weaker interactions with Fe(III) than $Cl^-$.

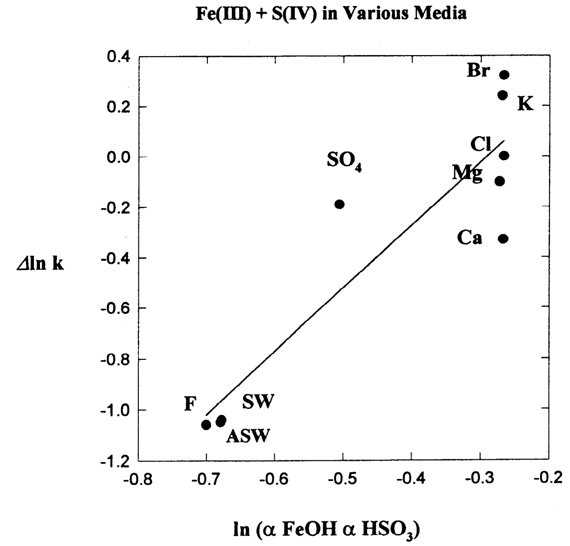

**Figure 12.** Changes in the rate constant upon the addition of sea salts to NaCl (Δln $k$ = ln $k$(soln) − ln $k$(NaCl)) versus the natural log of the molar fraction of $FeOH^{2+}$ and $HSO_3^-$ ($p$H = 3.5 and 25°C).

The effect of $F^-$ is quite large and demonstrates the influence the formation of strong complexes can have on the reaction rates of metals at low concentrations. These effects would not be seen if the rates of reduction of Fe(III) by S(IV) were made at high concentrations of Fe(III). The total effect of the ions in seawater is smaller than the effect of the individual ions due to the interactions of the sea-salt ions with each other. For example, $Mg^{2+}$ and $Ca^{2+}$ can form complexes with $F^-$ and $SO_4^{2-}$ and lower the concentration of free $F^-$ and $SO_4^{2-}$ that can interact with $Fe^{3+}$.

The effect of composition and ionic strength on the rates at $p$H = 3.5 can be examined quantitatively by considering reaction (13) to be dominant. The lower rates in seawater relative to NaCl at the same ionic strength can be related to the changes in the speciation of Fe(III). From a simplistic view, one would expect that the decrease in the rates due to the addition of sea salts would be related to changes in the fraction of $FeOH^{2+}$ in the solutions (the fraction of $HSO_3^-$ is not strongly dependent on the composition). The values of Δln $k$ = ln $k$(soln) − ln $k$(NaCl) versus the ln ($\alpha$FeOH $\alpha$HSO$_3$) are shown in Figure 12. The results show a rough correlation with the fraction of $FeOH^{2+}$ in agreement with the rates being directly related to the levels of $HOFeSO_3H$ in the solutions.

The values of ln $\{k/\alpha_{Fe}\alpha_{HSO_3}\}$ for NaCl and seawater shown in Figure 13 indicate that this simple view has some problems. The values of ln $\{k/\alpha_{Fe}\alpha_{HSO_3}\}$ in NaCl can be attributed to changes in the rate due to ionic strength. The results in seawater, however, are not the same as found for NaCl. The rates in seawater are about 2.8 times lower than the rates in NaCl at the same ionic strength, while the product $\alpha_{FeOH}\alpha_{HSO_3}$ is 1.8 times lower. This discrepancy may be due to interactions of $FeOH^{2+}$ with the ions in seawater ($F^-$, $SO_4^{2-}$) not accounted for in determining the speciation. Measurements in NaCl and sea salts as a function of $p$H are needed to prove this postulation.

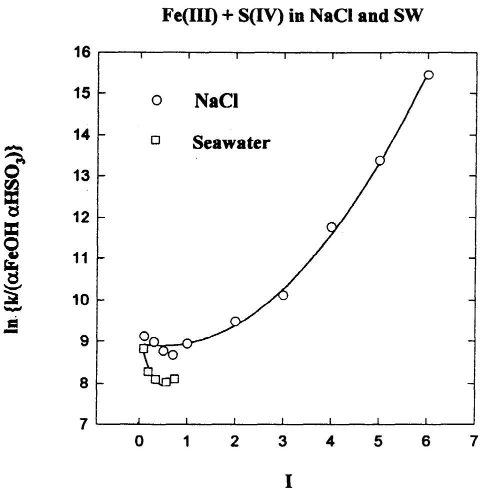

**Figure 13.** Values of $k/\alpha_{\mathrm{FeOH}}\alpha_{\mathrm{HSO_3}}$) for NaCl and seawater solutions as a function of ionic strength ($p$H = 3.5 and 25°C).

Our results support the mechanism suggested by *Conklin and Hoffmann* [1988] for the autoxidation of S(IV) with a few minor modifications due to the work of *Betterton* [1993] and our results at high $p$H. The proposed mechanism is

$$SO_2 + H_2O \overset{K_{1S}}{\Leftrightarrow} H^+ + HSO_3^- \quad (15)$$

$$HSO_3^- \overset{K_{2S}}{\Leftrightarrow} H^+ + SO_3^{2-} \quad (16)$$

$$Fe^{3+} + H_2O \overset{\beta_1}{\Leftrightarrow} FeOH^{2+} + H^+ \quad (17)$$

$$Fe^{3+} + 2H_2O \overset{\beta_2}{\Leftrightarrow} Fe(OH)_2^+ + 2H^+ \quad (18)$$

$$FeOH^{2+} + HSO_3^- \overset{K_A}{\Leftrightarrow} HOFe\text{-}SO_3H^+ \quad (19)$$

$$Fe(OH)_2^+ + HSO_3^- \overset{K_B}{\Leftrightarrow} (HO)_2Fe\text{-}SO_3H \quad (20)$$

$$HOFe\text{-}SO_3H^+ \overset{K_I}{\Leftrightarrow} HOFe\text{-}OSO_2H^+ \quad (21)$$

$$(HO)_2Fe\text{-}SO_3H \overset{K_{II}}{\Leftrightarrow} (HO)_2Fe\text{-}OSO_2H \quad (22)$$

$$HOFeO\text{-}SO_2H \overset{k_a}{\rightarrow} FeOH^+ + \cdot SO_3H \quad (23)$$

$$(HO)_2Fe\text{-}OSO_2H \overset{k_b}{\rightarrow} Fe(OH)_2 + \cdot SO_3H \quad (24)$$

where $K_{1S}$ and $K_{2S}$ are the first and second dissociation constants for the ionization of $SO_2 \cdot H_2O$, $\beta_1$ and $\beta_2$ are the stepwise hydrolysis constants for Fe(III); $K_A$ and $K_B$ are the formation constants of Fe(III)-S(IV) complexes [*Betterton*, 1993]; and $K_I$ and $K_{II}$ are related to changes in the bonding of Fe-S to Fe-O that may occur in the complex [*Conklin and Hoffmann*, 1988]. The overall rate constant is related to reactions (23) and (24) by

**Table 5.** Half-Times (min) for the Reduction of Fe(III) by S(IV) in 0.1 $M$ NaCl Solutions at $p$H = 3.50 and 25°C

| S(IV), $M$ | $t_{1/2}$, min |
|---|---|
| $10^{-7.0}$ | 1081 |
| $10^{-6.5}$ | 342 |
| $10^{-6.0}$ | 108 |
| $10^{-5.5}$ | 34 |
| $10^{-5.0}$ | 10 |
| $10^{-4.5}$ | 3.4 |
| $10^{-4.0}$ | 1.1 |
| $10^{-3.5}$ | 0.34 |
| $10^{-3.0}$ | 0.1 |

$$\begin{aligned} -d[\mathrm{Fe(III)}]/dt &= k[\mathrm{Fe(III)}][\mathrm{S(IV)}] \\ &= k_a[\mathrm{HOFe\text{-}OSO_2H}] \\ &\quad + k_b[\mathrm{(HO)_2Fe\text{-}OSO_2H}] \end{aligned} \quad (25)$$

The substitution of the equilibrium concentrations gives

$$[\mathrm{HOFe\text{-}OSO_2H}] = K_A K_I \alpha_{\mathrm{FeOH}}\alpha_{\mathrm{HSO_3}}[\mathrm{Fe(III)}][\mathrm{S(IV)}] \quad (26)$$

$$[\mathrm{(HO)_2Fe\text{-}OSO_2H}] = K_B K_{II} \alpha_{\mathrm{Fe(OH)_2}}\alpha_{\mathrm{HSO_3}}[\mathrm{Fe(III)}][\mathrm{S(IV)}] \quad (27)$$

where the fractions of $Fe^{3+}$, $FeOH^{2+}$, $Fe(OH)_2^+$, and $HSO_3^-$ are given by

$$\alpha_{\mathrm{Fe}} = 1/\{1 + \beta_1/[H^+] + \beta_2/[H^+]^2 + \beta_3/[H^+]^3 + \Sigma\, K_{\mathrm{FeXn}}[X]^n\} \quad (28)$$

$$\alpha_{\mathrm{FeOH}} = \{\beta_1/[H^+]\}\alpha_{Fe} \quad (29)$$

$$\alpha_{\mathrm{Fe(OH)_2}} = \{\beta_2/[H^+]^2\}\alpha_{Fe} \quad (30)$$

$$\alpha_{\mathrm{HSO_3}} = K_{1S}[H^+]/\{[H^+]^2 + K_{1S}[H^+] + K_{1S}K_{2S}\} \quad (31)$$

where $X$ is a ligand such as $Cl^-$ and $F^-$.

The substitution of (26) and (27) into (25) gives

$$k = k_a K_A K_I \alpha_{\mathrm{FeOH}}\alpha_{\mathrm{HSO_3}} + k_b K_B K_{II}\alpha_{\mathrm{Fe(OH)_2}}\alpha_{\mathrm{HSO_3}} \quad (32)$$

which is consistent with our rate equation (11) where $k_1 = K_a K_A K_I$ and $k_2 = k_b K_B K_{II}$. This reaction mechanism without oxygen is consistent with the mechanism with oxygen [*Brandt et al.*, 1994] with the exception of the possible formation of $(HO)_2Fe\text{-}SO_3H$ at high $p$H. Further measurements of the reduction of Fe(III) with S(IV) in the presence of oxygen at high $p$H are needed to access the importance of this species.

The importance of the reduction of Fe(III) by S(IV) in controlling the state of iron in aerosols and water droplets can be demonstrated by examining the first-order formation of Fe(II) in waters as a function of the concentration of S(IV). The half-times for the reduction of Fe(III) as a function of S(IV) are given in Table 5 ($p$H = 3.5, I = 1 $M$ NaCl, 25°C). As is apparent from this table, the rates can be quite fast for waters with a $p$H 3.5 and [S(IV)] = 10 to 500 $\mu M$. It should be pointed out that although the half-times are not a strong function of ionic strength, the composition of trace anions can be quite important. The levels of S(IV) in acidic fog and cloud waters [*Munger et al.*, 1984; *Warneck*, 1989] have been shown to reach concentrations as high as 3000 $\mu M$, while the values in marine aerosol are normally less than 1 $\mu M$. These calculations indicate that the higher levels of Fe(II) found in water droplets [*Behra and Sigg*, 1990] compared to marine aerosols [*Zhu et al.*, 1992] may be due to the reduction of Fe(III) by S(IV). The rates of reduction given in this paper should prove useful in modeling the changes in the redox state of iron in acidic aerosols and water droplets. Studies on these rates under the presence of $O_2$ are presently under way. Further measurements of Fe(II) as a function of S(IV) are needed in water droplets and marine aerosols to prove that they are kinetically linked in natural waters.

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