The Early Phase of the Iron(III)−Sulfite Ion Reaction. Formation of a Novel Iron(III)−Sulfito Complex

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The kinetics and mechanism of the iron(III)−sulfite ion reaction were studied by using the stopped-flow method at 10.0 °C in 1.0 M $NaClO_4$. The formation of a 1:1 and a 2:1 complex was confirmed in the initial phase of the reaction when the metal ion was in excess over the ligand. In this system the formation of the dimer complex, Fe_2S^{IV}, was not reported before. The following composition is proposed for the new species: $(H_2O)_4Fe(SO_3)(OH)Fe(H_2O)_4{}^{3+}$. The stability constant of the complex formation reaction, $Fe_2(OH)_2{}^{4+} + HSO_3{}^- \rightleftharpoons Fe_2S^{IV}$, was determined from absorbance data at 430 nm: $\log K_{21} = 3.37 \pm 0.16$. According to detailed kinetic studies the complex formation is first order in both $Fe_2(OH)_2{}^{4+}$ and sulfite ion. The pH dependence of the measured rate constants indicates two kinetically significant pathways with the $SO_3{}^{2-}$ and $HSO_3{}^-$ forms of the ligand, respectively. The corresponding rate constants are the following: $k_{HSO_3{}^-} = (4.5 \pm 0.3) \times 10^4\ M^{-1}\ s^{-1}$ and $k_{SO_3{}^{2-}} = (2.1 \pm 0.2) \times 10^9\ M^{-1}\ s^{-1}$. Mechanistic aspects of the complex formation are discussed in detail.

Introduction

Autoxidation of sulfite ion has been the subject of extensive studies for decades.[1] The interest has been generated mainly by the fact that this reaction is the primary source of acid rain formation. The reaction is catalyzed by trace amounts of the most common metal ions. Complex formation reactions between the metal ions and sulfite ion are in the core of the catalytic cycle.

In a recent study involving one of us, a detailed mechanism was proposed for the iron(III)-catalyzed autoxidation of sulfite ion.[2] The catalytic effect was interpreted in terms of fast formation and subsequent decomposition of sulfito complex(es). However, the validity of the model is limited to pH 2.5 and large sulfite ion excess. The mechanism postulates the formation of a "generalized" iron(III)−sulfito complex for which the exact composition is not defined.

Further improvement of the mechanism requires better understanding of the complex equilibria in the iron(III)−sulfite ion system. Although this topic has been studied in great detail, the number and exact composition of the iron(III)−sulfito complexes formed under various conditions are still subject to controversy. Earlier, van Eldik and co-workers reported a series of $Fe(SO_3)_n{}^{3-2n}$ ($n = 1-3$)[3] and the *cis*-$Fe(SO_3)OH$ complexes.[4−7] These results were challenged by Betterton, who interpreted his data by assuming the formation of the $Fe(SO_3)^+$ complex only.[8] Conklin and Hoffmann reached essentially the same conclusion on the basis of experiments in 1.0 M formic acid/formate buffer.[9] Under the conditions applied Fe(III) predominantly existed as formato complexes. However, the formation of such complexes were not considered in their model and the results need to be termed inconclusive, at best.

In all of the previous studies complex formation reactions were investigated either in sulfite ion excess or at comparable metal and ligand concentrations.[4−9] Because of strong kinetic coupling between the formation and redox decomposition of the complex(es) formed, the identification and characterization of various species are expected to be extremely difficult. To avoid complications arising from the coexistence of several complexes, we designed a detailed kinetic study at large excess of iron(III) over sulfur(IV) by anticipating only the formation of the monosulfito complex. Quite surprisingly, the experimental data showed a very complex kinetic pattern. In the present report we discuss the unexpected observations and their implications with respect to results reported earlier.

Experimental Section

Reagents. Sodium sulfite (Merck) and low chloride iron(III) perchlorate (Aldrich) of reagent grade quality were used without further purification. All stock solutions were prepared in doubly deionized and ultrafiltered water obtained from a MILLI-Q RG (Millipore) water purification system and purged with oxygen-free argon. The iron(III) and free acid concentrations of the stock solutions were determined as described earlier.[10,11] Experiments were carried out at 10.0 ± 0.1 °C and ionic strength adjusted to 1.0 M with $NaClO_4$. Sodium perchlorate was prepared from perchloric acid (Carlo Erba) and Na_2CO_3 (Reanal, Hungary).[12] Sulfite ion samples were freshly prepared before use.

Instrumentation. Spectra were recorded on a HP-8543 diode array spectrophotometer and pH measurements were made with a GK2401C

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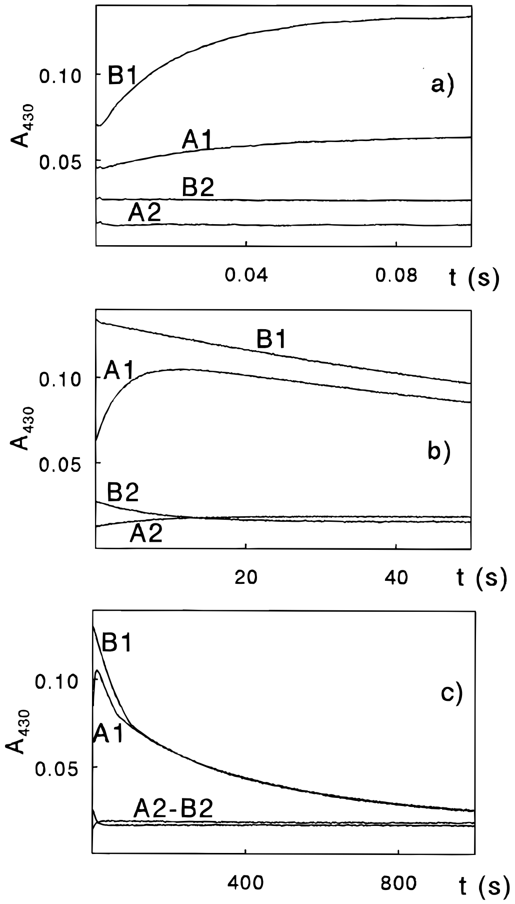

Figure 1. Typical stopped-flow absorbance traces at 430 nm: (curve A1) reaction with sufite ion, pH jump; (curve A2) hydrolysis, pH jump; (curve B1) reaction with sulfite ion, constant pH; (curve B2) hydrolysis, constant pH [pH = 1.68; [Fe(III)] = 0.020 M; [S(IV)] = 5.0×10^{-4} M (curves A1 and B1) and [S(IV)] = 0 (curves A2 and B2); $T = 10.0$ °C; $\mu = 1.0$ M ($NaClO_4$)].

combination glass electrode attached to a PHM85 pH-meter (Radiometer). The pH-meter reading was converted into −log [H^+].[13] In the kinetic runs the pH never exceeded 2.0 and p[H^+] was calculated from the composition of the samples. Kinetic measurements were made with an Applied Photophysics DX-17 MV sequential stopped-flow apparatus at 2 and 10 mm optical path lengths. A standard calibration procedure gave 0.89 ± 0.04 ms for the dead time of the instrument.[14] Each trace was obtained as the average of at least 5 individual runs which were reproducible within 5%.

Results

Preliminary Studies. In a typical set of kinetic experiments at large excess of iron(III) over sulfur(IV) the most significant spectral changes were observed around 340 and 430 nm. Detailed studies were done at these two wavelengths.

At 25.0 °C the stopped-flow traces were consistent with 4−5 different reaction steps in the several milliseconds to 20−30 min time domain. To separate the overlapping effects and also to decelerate the initial phase of the overall reaction, further experiments were made at 10.0 °C. Characteristic kinetic curves at 430 nm are shown in Figure 1 at three different time scales.[15] For comparison, the traces obtained in the absence of sulfite ion are also shown. The initial jump and subsequent increase in the absorbance in the early phase of the reaction (Figure 1a) are consistent with complex formation reaction(s) between iron(III) and sulfur(IV). As an alternative, some sort of fast redox reaction between the reactants can also be considered for the interpretation of the spectral effects. However, this possibility can be rejected since neither iron(III) nor higher oxidation state sulfur species have measurable absorbance in this wavelength region. According to Figure 1, at the same initial reactant concentrations and pH very different absorbance vs time profiles were obtained depending on the initiation method of the reaction. In the first set of experiments (set A, curves A1 and A2) the total amount of perchloric acid required to set the final pH was added to the iron(III) solution. This solution was mixed with a neutral solution of Na_2SO_3 in 1:1 ratio. It follows that at the very beginning of the reaction the reactants were suddenly diluted by a factor of 2 and simultaneously a pH-jump of about 0.3 unit occurred compared to the pH of the iron(III) solution.

In the other set of experiments (set B, curves B1 and B2) reagents of equal pH were mixed; i.e., the pH-jump did not occur. In this case experimental complications may arise due to the depletion of sulfur dioxide from the acidic sulfite ion solutions. To test the interference from this process, conventional stopped-flow experiments were repeated by using the sequential stopped-flow method. In these experiments the acidic sulfite ion solution was prepared by mixing perchloric acid and a neutral sulfite ion solution. After ~100 ms incubation period this reactant was mixed with the iron(III) solution. Since sulfite ion was acidified in the closed flow circuit of the instrument, any loss of sulfur dioxide could be excluded. The excellent reproducibility of the kinetic traces from the different types of experiments confirmed the reliability of the conventional stopped-flow measurements.

The differences between the kinetic profiles of sets A and B reflect the variation of the initial speciation in the reaction mixtures. Acid−base equilibria involving sulfur(IV) and iron(III) species are diffusion controlled and completed well within the dead time of the stopped-flow instrument. Thus, the initial differences in the speciation are most likely due to the relatively slow dimerization reaction of the $Fe(OH)^{2+}$ species:

$$2Fe(OH)^{2+} \rightleftharpoons Fe_2(OH)_2^{4+} \tag{1}$$

Dilution of the reactants leads to the dissociation of the dimer, while an increase in the pH increases the amount of $Fe(OH)^{2+}$ and pushes the reaction to the forward direction. In set A, the net effect was the formation of more dimer species as indicated by the increasing absorbance in the absence of S(IV) (Figure 1, curve A2). The relatively slow dimerization (reaction 1) is completed within 50 s. In the absence of pH-jump (set B) dilution leads to the dissociation of the dimer hydroxo species and the kinetic effect corresponds to this process.[16−18]

A relatively fast increase of the absorbance was observed in the presence of sulfite ion which was completed within 100−200 ms (set B). The kinetic curves showed approximate first-order behavior over a wide range of iron(III) and sulfur(IV) concentrations as long as the metal ion was in excess. As indicated before, the only reasonable explanation for this spectral change is the formation of a complex between iron(III) and sulfur(IV) species. However, the stopped-flow traces show a

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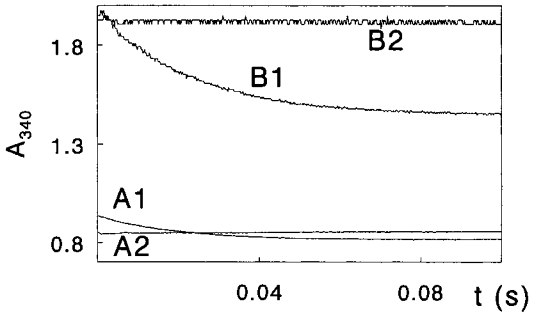

Figure 2. Typical stopped flow absorbance traces at 340 nm: (curve A1) reaction with sufite ion, pH jump; (curve A2) hydrolysis, pH jump; (curve B1) reaction with sulfite ion, constant pH; (curve B2) hydrolysis, constant pH [pH = 1.68; [Fe(III)] = 0.020 M; [S(IV)] = 5.0 × 10^{-4} M (curves A1 and B1) and [S(IV)] = 0 (curves A2 and B2); T = 10.0 °C; μ = 1.0 M ($NaClO_4$)].

composite feature. When the absorbance is extrapolated to the start point of the reaction, the estimated initial absorbance is much higher than the absorbance of the corresponding iron(III) solution in the absence of sulfite ion. This is a clear indication of the fast formation of another species; i.e., the observations are consistent with the formation of at least two different iron(III)−sulfur(IV) complexes in the first 200 ms of the reaction. Kinetic traces at 340 nm correlate reasonably well with those at 430 nm (Figure 2). In the absence of sulfite ion the main absorbing species is $Fe_2(OH)_2^{4+}$ at 340 nm. The absorbance decay at this wavelength can be interpreted by assuming that the hydroxo dimer is involved in the kinetic process. The new species formed in the initial phase of the reaction has smaller molar absorptivity than the hydroxo dimer.

At longer reaction times the kinetic traces are consistent with several concurrent reaction steps, which may include redox decomposition of the complexes and a relatively slow shift in the complex equilibria. It should also be kept in mind that reaction 1 is coupled with the iron(III)−sulfite ion reaction. The dimerization of the iron(III) hydroxo complex may control the overall kinetic process up to 50 s reaction time, and later it can be treated as a fast preequilibrium. The significance of this reaction can also be deduced from the comparison of the kinetic curves in Figure 1. The main difference between sets A and B is that in set A the absorbance maximum occurs at longer times and its value is somewhat lower than in the other experiment. The initial concentration of $Fe_2(OH)_2^{4+}$ is much higher in set B than in set A. In set B the dimer hydroxo species rapidly generates a reaction product which slowly decays at longer reaction times. When an increase in pH is allowed (set A), the reaction between $Fe_2(OH)_2^{4+}$ and sulfite ion is controlled by the relatively slow dimerization reaction. This reaction sequence simultaneously occurs with the decomposition of the new species. After about 40 s the dimerization process is not the rate-determining step any more and the curves from sets A and B run parallel.

In the rest of this paper we attempt to give a quantitative interpretation of the first two steps, i.e., the initial absorbance jump (first step) and the subsequent 100−200 ms process (second step). The two steps are well separated from later phase of the reaction in set B; thus, only kinetic traces from experiments at constant pH were used for the evaluation of the system.

Protolytic Equilibria. At 10.0 °C and μ = 1.0 M, the equilibrium constants are not available for all acid−base reactions of the reactants from the literature[19,20] and were determined in the present study by using standard pH-potentiometric and spectrophotometric methods. The results are listed Table 1.

Table 1. Stability Constants for the Protolytic Reactions of Iron(III) and the Sulfite Ion

reaction	log *K*	ref
$Fe(H_2O)_6^{3+} \rightleftharpoons Fe(H_2O)_5OH^{2+} + H^+$	-3.03 ± 0.05^d	*e*
	-2.73^a	23
$2Fe(H_2O)_6^{3+} \rightleftharpoons Fe_2(OH)_2(H_2O)_8^{4+} + 2H^+ + 2H_2O$	-2.98 ± 0.02^d	*e*
	-3.20^a	23
$Fe(H_2O)_6^{3+} \rightleftharpoons Fe(H_2O)_4(OH)_2^+ + 2H^+$	-6.29^a	23
$H_2O{\cdot}SO_2 \rightleftharpoons HSO_3^- + H^+$	-1.49 ± 0.02^d	*e*
	-1.76^b	19
$HSO_3^- \rightleftharpoons SO_3^{2-} + H^+$	-6.44 ± 0.01^d	*e*
	-7.20^b	19
$HSO_3^- \rightleftharpoons SO_3H^-$	0.80^f	21
$2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$	-1.15^c	22

[a] 25 °C; μ = 1 M ($NaClO_4$). [b] 25.0 °C, corrected to μ = 0 M. [c] 20 °C, varying HCl medium. [d] 10.0 °C; μ = 1.0 M ($NaClO_4$). [e] This work. [f] 10 °C; μ = 1 M (NaCl).

According to earlier literature, the proton may bind to either the sulfur atom or one of the oxygen atoms in HSO_3^-.[21] The two isomers are in fast equilibrium and for all practical purposes HSO_3^- can be treated as a uniform species. Hydrogen sulfite ion is also involved in a dimerization reaction:[22] $2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$ ($K = 7 \times 10^{-2}$ M^{-1}). In our experiments the dimer was always present in negligible concentration.

In acidic iron(III) solutions the formation of the following hydroxo species were reported before:[23,24] $Fe(OH)^{2+}$, $Fe_2(OH)_2^{4+}$, $Fe(OH)_2^+$, and $Fe_3(OH)_4^{5+}$. In agreement with previous results,[23] our experimental data at pH < 2.0 could be fitted by assuming the formation of the first two complexes only. The stability constants agree well with the literature data (Table 1). According to the results, the dominant absorbing species is $Fe_2(OH)_2^{4+}$ in the near-UV region. The molar absorptivities of $Fe(OH)^{2+}$ and $Fe_2(OH)_2^{4+}$ (in cm^{-1} M^{-1}) are 620 ± 50, 2890 ± 120 (340 nm) and ~0, 45 ± 5 (430 nm), respectively. The absorbance of the hexaaqua complex is negligible in the whole spectral region studied.

The protolytic equilibria involving the three sulfur(IV) species and also the hydrolysis of Fe^{3+} are extremely fast and should be treated as fast preequilibria.[25,26] In the discussion of the results at constant pH we refer to the total concentration of free sulfur(IV) species as [S(IV)] and the sum of [Fe^{3+}] and [$Fe(OH)^{2+}$] as $[Fe^{3+}]_{mon}$, respectively.

Acidification of iron(III) samples produced excellent first-order kinetic traces. In agreement with previous literature results,[16−18] the dissociation of the dimer hydroxo complex into the monomer was found to be relatively slow and did not influence the initial phase of the reaction.

First Step. The initial absorbance was extrapolated from the absorbance change in the second step of the reaction by using an exponential fit of the kinetic curves and correcting

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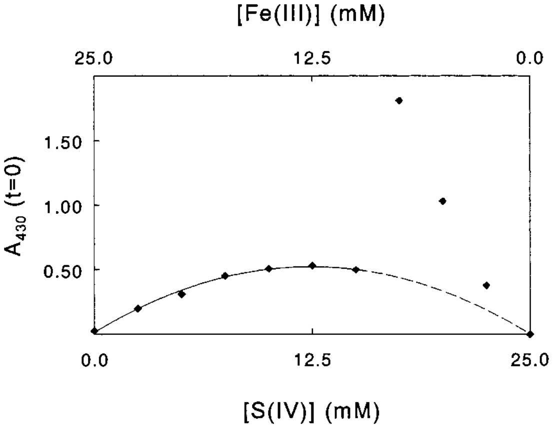

Figure 3. Job plot for the iron(III)−sulfur(IV) system [$\lambda = 430$ nm; pH = 1.40; [Fe(III)] + [S(IV)] = 0.025 M; $T = 10.0$ °C; $\mu = 1.0$ M ($NaClO_4$)].

the time scale for the dead time of the stopped-flow instrument. Calculations on the basis of our detailed model (see later) confirmed that the estimate for the initial absorbance was valid within ±5%. The absorbance jump, $\Delta A_{430}(t = 0)$, was obtained by subtracting the absorbance of the corresponding iron(III) solution from the initial absorbance. The absorbance jump was an excellent linear function of both the monomer iron(III) and the total sulfite ion concentration, provided that the pH and the concentration of the other component were kept constant. On the basis of these observations, we propose that the initial absorbance jump is due to the formation of a 1:1 complex, which we refer to as FeS^{IV}. This interpretation is valid only if we assume very weak complex formation, i.e the concentration of the complex is negligible compared to $[Fe^{3+}]_{mon}$ and [S(IV)]. In this case $[FeS^{IV}] = K_{11}[Fe^{3+}]_{mon}[S(IV)]$ and the absorbance jump is expressed by

$$\Delta A_{430}(t = 0) = K_{11}\epsilon_{11}[Fe^{3+}]_{mon}[S(IV)] \qquad (2)$$

where K_{11} and ϵ_{11} are the apparent stability constant and the molar absorptivity of the complex, respectively.

The composition of the complex was also confirmed by using the Job method.[27] In Figure 3 the absorbance jump is shown as a function of the reactant concentrations while $[Fe^{3+}]_{mon}$ + [S(IV)] = constant. In a regular case a maximum is expected in this curve at which the concentration ratio of the reactants corresponds to the stoichiometry of the complex. As long as iron(III) is in excess or comparable concentration with sulfite ion, the curve shows the expected features. In large sulfite ion excess an abrupt deviation is observed. Under these conditions the second step became very fast and the extrapolation to the initial absorbance value was unreliable. Additional complex formation or/and redox reactions could also contribute to the observed absorbance jump. Despite the limitations, the local maximum of the Job curve at 1:1 metal to ligand concentration ratio confirms the formation of the monosulfito complex.

Because of the small conversion, the stability constant and molar absorptivity of the complex could not be determined separately. By inclusion of all experimental data at various sulfite and iron(III) concentrations, the product of the two parameters (in M^{-2} cm^{-1}) was calculated: $K_{11}\epsilon_{11} = 3160 \pm 71$ (pH = 1.40) and 7772 ± 140 (pH = 1.70). The difference in these values reflects that K_{11} is an apparent stability constant and the $K_{11}\epsilon_{11}$ product is a pH-dependent quantity.

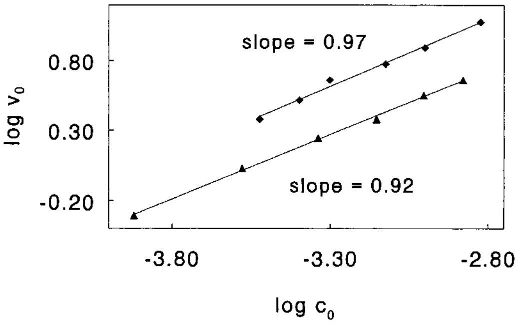

Figure 4. Determination of the order of reaction with respect to sulfur(IV) (◆) and $Fe_2(OH)_2^{4+}$ (▲). v_0 is defined as ABS(dA/dt)($t = 0$), where A is the absorbance measured at 430 nm [pH = 1.40; [Fe(III)] = 0.020 M and [S(IV)] = 5.0×10^{-4} M for the two lines, respectively; $T = 10.0$ °C; $\mu = 1.0$ M ($NaClO_4$)].

Second Step. To evaluate the rate law, the initial rate method was used. The initial rate was calculated for each kinetic curve as the first derivative of a fitted exponential function at $t = 0$. The plots of log v_0 as the function of log $[Fe_2(OH)_2^{4+}]_0$ or log $[S(IV)]_0$ are shown in Figure 4. In all cases the slope is reasonably close to 1.0, which indicates that the reaction is first order in both reactants.

The observed spectral changes and the kinetic results strongly suggest that the second step is due to the formation of a complex between the dimer hydroxo complex and sulfur(IV). Most likely the dimer structure is retained in the new species. If the product were a monomer, it could quickly equilibrate with the uncomplexed Fe^{3+} and the reaction would not explain the observed absorbance changes. For simplicity, we will refer to the new complex as Fe_2S^{IV}:

$$Fe_2(OH)_2^{4+} + HSO_3^{-} = Fe_2S^{IV} \qquad (3)$$

$$K_{21} = \frac{[Fe_2S^{IV}]}{[Fe_2(OH)_2^{4+}][HSO_3^{-}]}$$

When the second step is completed at ~200 ms, the system is in steady state and can be approximated by assuming that the acid−base and complex formation reactions are in equilibrium. The measured absorbance can be expressed by the concentrations of the colored species as follows:

$$A = \epsilon_{11}[FeS^{IV}] + \epsilon_{21}[Fe_2S^{IV}] + \epsilon_d[Fe_2(OH)_2^{4+}] + \epsilon_m[Fe(OH)^{2+}] \qquad (4)$$

Parameters K_{21} and ϵ_{21} were estimated on the basis of eq 4 by using the program PSEQUAD.[28] Other stability constants and molar absorptivities were included with predetermined fixed values in the fitting procedure. According to preliminary calculations, K_{21} and ϵ_{21} did not depend on the pH, and all data points were simultaneously fitted. The relatively large uncertainty of the results (Table 2) is due to the fact that the experimental data were obtained from a limited concentration range. Any attempt to use larger sulfur(IV) concentration or higher pH led to complications. Most importantly, the second step could not be treated separately from the later phase of the reaction.

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Table 2. Equilibrium and Kinetic Parameters for the Complexes Formed in the Iron(III)−Sulfite Ion System at $\mu = 1.0$ M ($NaClO_4$) and 10.0 °C

pH	parameter	value
1.40	$K_{11}\epsilon_{11}$ (M^{-2} cm^{-1})	3160 ± 71
1.70	$K_{11}\epsilon_{11}$ (M^{-2} cm^{-1})	7772 ± 140
1.40	log K_{21}	3.32 ± 0.20
	ϵ_{21} (M^{-1} cm^{-1})	505 ± 87
1.70	log K_{21}	3.55 ± 0.10
	ϵ_{2} (M^{-1} cm^{-1})	468 ± 29
1.10−1.90[a]	log K_{21}	3.37 ± 0.16
	ϵ_{21} (M^{-1} cm^{-1})	499 ± 65
1.40	k_+ (M^{-1} s^{-1})	(7.1 ± 0.8) × 10^5
1.70	k_+ (M^{-1} s^{-1})	(9.6 ± 1.2) × 10^5

[a] All data obtained from the pH-region 1.10−1.90 were simultaneously fitted.

Various sulfur(IV) species can be reactive in the formation of the 2:1 complex. Under the conditions applied the major forms were HSO_3^- and $H_2O{\cdot}SO_2$. Deprotonation of the ligand is expected to significantly enhance the reactivity, and we tentatively assume that the 2:1 complex is predominantly formed via reaction 3:

$$\frac{d[Fe_2S^{IV}]}{dt} = k_+[Fe_2(OH)_2^{4+}][HSO_3^-] - k_-[Fe_2S^{IV}] \quad (5)$$

The rate-determining step is coupled with the following fast preequilibria:

$$Fe^{3+} + S(IV) \rightleftharpoons FeS^{IV} \quad (6)$$

$$Fe^{3+} \rightleftharpoons Fe(OH)^{2+} + H^+ \quad (7)$$

$$HSO_3^- + H^+ \rightleftharpoons H_2O{\cdot}SO_2 \quad (8)$$

Reaction 1 is not part of the kinetic model because it is much slower than the formation of the 2:1 complex.

In the final evaluation only kinetic runs at $[Fe_2(OH)_2]_0 \geq [S(IV)]_0$ were fitted by using the differential equation solver routine of the software package SCIENTIST.[29] It was assumed that the absorbance can be expressed by eq 4 at any reaction time. In these calculations the equilibrium constants of reactions 3 and 6−8 were included with fixed values (Tables 1 and 2) and k_- was replaced with k_+/K_{21}. Two parameters, k_+ and ϵ_{21}, were estimated by individually fitting the kinetic curves at various reactant concentrations (Table 2). The molar absorptivities of the 2:1 complex obtained from the equilibrium and kinetic calculations are in reasonable agreement. At 340 nm the initial absorbance jump could not be quantified and the traces at this wavelength were not used to estimate k_+.

When the pH was increased from 1.10 to 1.90, k_+ increased by almost a factor of 2. Such a pH dependence seems to be consistent with an additional complex formation path with sulfite ion:

$$Fe_2(OH)_2^{4+} + SO_3^{2-} = Fe_2S^{IV} \quad (9)$$

In this case k_+ is given by

$$k_+ = k_{HSO_3^-} + k_{SO_3^{2-}}\frac{K_{s2}}{[H^+]} \quad (10)$$

where $k_{HSO_3^-}$ and $k_{SO_3^{2-}}$ are the formation rate constants with the two corresponding forms of sulfur(IV) and K_{s2} is the acid dissociation constant of hydrogen sulfite ion. The data show excellent correlation with eq 10 (Figure 5). From the intercept and slope of the straight line $k_{HSO_3^-} = (4.5 \pm 0.3) \times 10^4$ M^{-1} s^{-1} and $k_{SO_3^{2-}} = (2.1 \pm 0.2) \times 10^9$ M^{-1} s^{-1}.

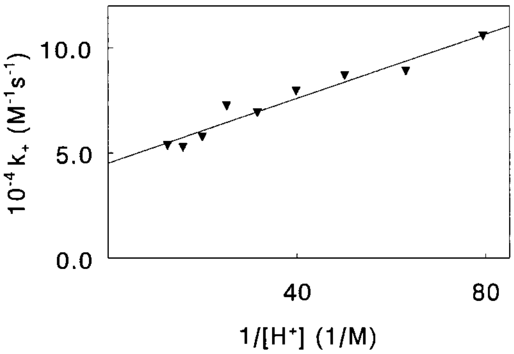

Figure 5. pH dependence of the formation rate constants according to eq 10. $T = 10.0$ °C; $\mu = 1.0$ M ($NaClO_4$).

Discussion

The data presented here unequivocally confirm the formation of two sulfito complexes in the iron(III)−sulfur(IV) system when the metal ion is in excess. The initial absorbance jump is consistent with the formation of the relatively weak 1:1 complex. It was shown that at constant pH the absorbance change is proportional to the concentration product of iron(III) and sulfur(IV). The observed linear concentration dependence of the absorbance can be reproduced as long as we assume that K_{11} is less than ~100 M^{-1} at pH ≤ 1.70. This sets the upper limit for the apparent stability constant which seems to be consistent with data reported earlier.[7,8]

The fast absorbance change completed in the first 100−200 ms of the reaction can be interpreted with the formation of the 2:1 complex. In aqueous solution similar complexes were reported with only a few ligands before (Table 3).[30−32] While the exact composition and structure of these complexes could not be determined, some conclusions can be drawn regarding the general nature of these species.

First of all, it is very unlikely that the ligand is coordinated to only one of the metal ions in Fe_2L. In this case, because of the trans-labilization effect, L would probably coordinate in the trans position to the hydroxide bridges of the $Fe_2(OH)_2^{4+}$ unit. In turn, it would induce fast dissociation of the dimer structure. As a result, the dimer complex could not stabilize. An asymmetric structure would also suggest that the formation of Fe_2L type complexes should be quite common in iron(III) chemistry. However, the existence of 2:1 complexes has not been reported with simple ligands and our attempts to prove the formation of such species with acetate ion and derivatives, SCN^-, N_3^-, etc., also failed. This leads to the conclusion that the ligand needs to possess certain features to form the Fe_2L complex. The most plausible explanation is that the metal ions are kept in position by the OH bridge(s) and L also forms a bridge in the 2:1 complex. With the ligands in Table 3 the formation of a seven-membered ring can be envisioned which includes two adjacent donor groups of the ligand, the two metal ions, and the oxygen atom of the bridging OH group. Sulfite ion is specific in that the suggested dimer structure is consistent with the formation of a six-membered ring.

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Table 3. Composition and Formation Equilibrium Constants of Fe_2L Type Iron(III) Complexes

ligand	reaction	log *K*	ref
squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione)	$Fe_2(OH)_2^{4+} + L^{2-} \rightleftharpoons Fe_2(OH)_2L^{2+}$	5.18[a]	30
tiron (1,2-dihydroxy-3,5-benzenedisulfonate)	$Fe_2(OH)_2^{4+} + H_2L \rightleftharpoons Fe_2(OH)_xLH_x^{4+}$	3.80[b]	31
cysteine	$Fe_2(OH)_2^{4+} + H_3L^+ \rightleftharpoons Fe_2(OH)_2LH^{3+} + 2H^+$	−1.15[a]	32
penicillamine	$Fe_2(OH)_2^{4+} + H_3L^+ \rightleftharpoons Fe_2(OH)_2LH^{3+} + 2H^+$	−0.42[a]	32
sulfite ion	$Fe_2(OH)_2^{4+} + HSO_3^- \rightleftharpoons Fe_2(OH)SO_3^{3+}$	3.37 ± 0.16[c]	*d*

[a] 25 °C, $\mu = 1.0$ M ($LiClO_4$). [b] 25 °C, $\mu = 1.0$ M ($NaClO_4$). [c] 10.0 °C, $\mu = 1.0$ M ($NaClO_4$). [d] This work.

There is some controversy regarding the number of hydroxide groups in Fe_2L. In a few cases it was suggested that the two OH bridges remained intact in the dimer complex.[30,32] However, the fact that the stability constant of Fe_2S^{IV}, as defined in reaction 3, does not show any pH dependence strongly suggests that one of the OH bridges is removed in the reaction. In a regular complex formation reaction the proton of the hydrogen sulfite ion would be liberated and K_{21} should be a pH-dependent quantity. In fact this pH effect is offset most likely by simultaneous loss of an OH group. Thus, we propose the following composition for the dimer sulfito complex: $(H_2O)_4Fe(SO_3)(OH)Fe(H_2O)_4^{3+}$. The very same composition was concluded for the analogous chromium(III) complex earlier with log $K_{21}^{Cr(III)} = 3.96$ (25 °C, $\mu = 1$ M $NaClO_4$).[33]

The kinetic data indicate two dominant pathways in the formation of the Fe_2S^{IV} complex. In the reaction with HSO_3^- the rate-determining step is most likely the coordination of the ligand to one of the metal ions. In accordance with the previous considerations, the complex formation is completed via a series of fast proton transfer steps from the coordinated ligand and to one of the OH groups. These steps are probably diffusion controlled.

For interpreting $k_{SO_3^{2-}}$, the rate constant obtained for the reaction of sulfite ion, the following simplified reaction sequence can be considered:

$$Fe_2(OH)_2(H_2O)_8^{4+} + SO_3^{2-} \rightleftharpoons \{Fe_2(OH)_2(H_2O)_8^{4+}\cdot SO_3^{2-}\} \quad K_{ip}$$

$$\{Fe_2(OH)_2(H_2O)_8^{4+}\cdot SO_3^{2-}\} \rightleftharpoons \{Fe_2(OH)_2(SO_3)(H_2O)_8^{2+}\} \quad k_{in}$$

$$\{Fe_2(OH)_2(SO_3)(H_2O)_8^{2+}\} + H^+ \rightleftharpoons Fe_2(OH)(SO_3)(H_2O)_8^{3+} \quad \text{fast}$$

According to this model $k_{SO_3^{2-}} = K_{ip}k_{in}$. On the basis of the Fuoss equation,[34] K_{ip} is in the order of 10 M^{-1} and $k_{in} \sim 10^8$ s^{-1}. It is not quite clear why inner-sphere coordination of the ligand is so fast. One possible explanation is that the ligand attacks a trans position to the OH groups and trans-labilization accelerate the ligand substitution process. It should be noted that because of the proton ambiguity a reaction between HSO_3^- and the so far hypothetical $Fe_2(OH)_3^{3+}$ complex may also explain the experimentally observed rate law.

The results presented here may explain some of the controversies in the literature data. The formation of the 2:1 iron(III)−sulfito complex was not considered in any of the earlier studies. It should be added that typical experimental conditions were different from ours, i.e., higher pH, lower metal ion concentration, and sulfite ion excess were used and the experiments typically were carried out at 25 °C. Nevertheless, calculations confirm that the initial speciation in those studies[7,8] and in our experiments were similar in that the dimer hydroxo complex was present in about the same relative concentrations.

At the ligand excess used in earlier studies, reaction 3 is shifted to the right and the formation of the 2:1 complex is expected to go to completion. It follows that the formation of the Fe_2S^{IV} complex could cause a very sizable initial spectral change in those studies.

An extrapolation from our results reveals that in some cases[4−8] perhaps as much as 50% of the initial absorbance measured could be caused by the formation of the dimer complex. In light of our findings, earlier data most likely need to be reinterpreted, and the exact kinetic role of the dimer sulfito complex should be explored in the iron(III)-catalyzed autoxidation of sulfite ion.

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Supporting Information Available: Figures showing typical spectral changes in the wavelength region 330−460 nm, typical kinetic curves at 340 nm at three different time scales, a plot of the initial absorbance jump as a function of initial concentrations, and application of the initial rate method at 340 nm (4 pages). Ordering information is given on any current masthead page.

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