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Formation of Transient Iron(III)−Sulfur(IV) Complexes Revisited. Application of Rapid-Scan Techniques

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Introduction

The iron(III)-catalyzed autoxidation reaction of sulfur(IV) oxides plays an important role in atmospheric oxidation processes and has been suggested to be partly responsible for the acidification of precipitation.[1] A number of investigations have been undertaken in recent years in an effort to understand the catalytic role of Fe(III), and of transition metal ions and complexes in general, during such autoxidation processes.[2−8] It is in general agreed that the metal ion in the higher oxidation state can initiate the free radical process via an electron-transfer reaction shown in (1), which leads to the formation of the sulfite

$$M^{n+} + HSO_3^{-} \rightarrow M^{(n-1)+} + SO_3^{\bullet-} + H^{+} \tag{1}$$

radical. The mechanistic details of this initiation process have received attention from various groups, but nevertheless a number of aspects remain unresolved. Of these, one concerns the possible participation of various Fe(III)-S(IV) complexes that could produce the sulfite radical in (1) via an intramolecular electron-transfer process.

Complex-formation between aquated Fe(III) and S(IV) oxides can be studied using stopped-flow techniques. These reactions are in general significantly faster than the subsequent redox reaction at a pH of ca. 2.5. Earlier work in our laboratories[2] indicated the possible formation of 1:1, 1:2 and 1:3 iron(III)−sulfito complexes, depending on the concentration ratio employed. The most probable reactions under these conditions[2] are as follows:

$$Fe(H_2O)_5OH^{2+} + HSO_3^{-} \overset{K_1}{\rightleftharpoons} Fe(H_2O)_5SO_3^{+} + H_2O \tag{2}$$

$$Fe(H_2O)_5SO_3^{+} + HSO_3^{-} \overset{K_2}{\rightleftharpoons} Fe(H_2O)_4(SO_3)_2^{-} + H_3O^{+} \tag{3}$$

$$Fe(H_2O)_4(SO_3)_2^{-} + HSO_3^{-} \overset{K_3}{\rightleftharpoons} Fe(H_2O)_3(SO_3)_3^{3-} + H_3O^{+} \tag{4}$$

As mentioned before[2] there is strong evidence in favor of the sulfito complexes being S-bonded although no definite proof is available. In a parallel study by Conklin and Hoffmann,[4] evidence for only the formation of a 1:1 complex was presented. Recently Betterton[9] used continuous and pulse-accelerated-flow techniques and also reported evidence for the formation of only a 1:1 iron(III)−sulfito complex in solution.

In recent years significant progress has been made with the development of rapid-scan spectrophotometric techniques, which coupled to a stopped-flow instrument enable the recording of UV−vis spectra on a millisecond time scale. We have now reinvestigated the complex-formation reactions in the Fe(III)−S(IV) system using different rapid-scan techniques in an effort to resolve the apparent discrepancy outlined above. The reported results clearly underline the validity of our earlier assignments[2] and indicate the participation of at least three different complexes in solution, which depends on the pH and concentration employed.

Experimental Section

Materials. All chemicals used in this study were of analytical reagent grade and were used without further purification: $Fe(ClO_4)_3\cdot 9H_2O$, $NaClO_4$, $HClO_4$, NaOH, and $Na_2S_2O_5$.

Preparation of Solutions. The reactant solutions were prepared with Millipore Milli-Q water (resistivity $> 18\ \mathrm{M\Omega}$ cm) and the pH was adjusted with the aid of $HClO_4$ or NaOH by using a Metrohm pH meter with an Ingold pH electrode. Buffers were not used in order to avoid complexation with the highly labile Fe(III) species. The ionic strength of the final reaction mixtures was adjusted to 0.1 M with $NaClO_4$.

Instrumentation. UV−vis repetitive spectra were recorded on two rapid-scan instruments. In the first instrument a Dionex D110 stopped-flow equipped with a J & M detector connected to a TIDAS 16-416 spectrophotometer was used. The latter has a 2 cm optical path length. It was possible to record 250 spectra during the reaction time of 0.5 s; the first spectrum was recorded 2 ms after mixing the solutions. The spectra were recorded in the wavelength range 250 to 600 nm.

The second instrument was a Bio Sequential SX-17MV stopped flow spectrofluorimeter. In this case time dependent spectra were generated from individual absorbance−time traces at different wavelengths. In a typical experiment, repetitive scan spectra were recorded by measuring absorbance changes over a desired time range and at constant wavelength intervals (typically $\Delta\lambda = 5$ nm). In this way multiple wavelength kinetic data are generated, which are arranged in matrix form with the spectra occupying the rows and the kinetic profiles occupying the columns. Each row vector contains a spectrum and each column vector a kinetic trace. The instrument was run on-line with an Applied Photophysics kinetic spectrometer workstation (RISC OS 3 operating system) on which data acquisition and processing was done. Data fitting was performed with the SX.17MV kinetic package.

Results and Discussion

The various equilibria, associated equilibrium constants and resulting distribution curves when $Fe(ClO_4)_3$ and $Na_2S_2O_5$ are dissolved in aqueous solutions have been discussed in detail elsewhere[1,3,4,8,9] and will not be discussed here again. We investigated the reaction of aquated Fe(III) with HSO_3^- at constant ionic strength (0.1 M) and temperature (25 °C) for the experimental conditions: $0.5 \le [\mathrm{Fe(III)}] \le 1$ mM, $2 < \mathrm{pH} \le 3$, $0.3 \le [\mathrm{S(IV)}] \le 20$ mM, and $300 \le \lambda \le 700$ nm. In this pH range $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5OH^{2+}$, $Fe(H_2O)_4(OH)_2^{+}$, and

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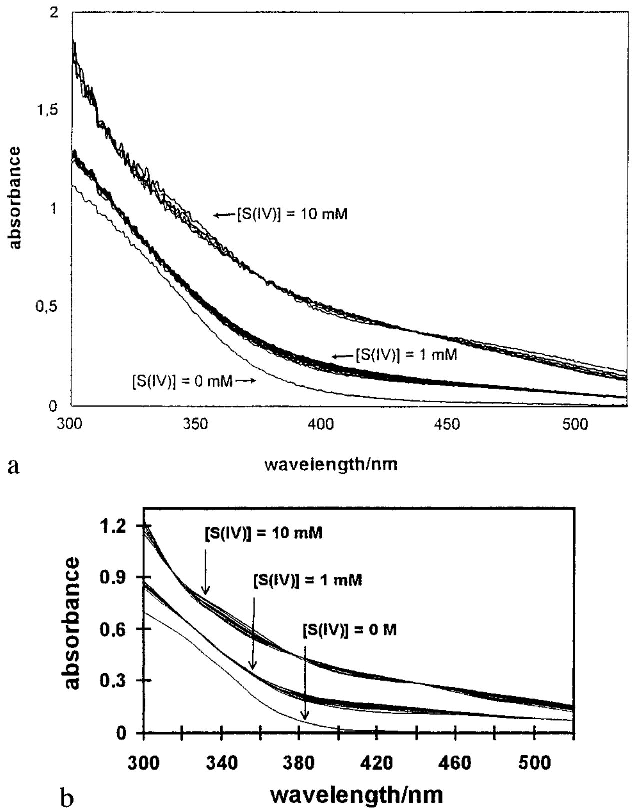

Figure 1. UV−vis spectra recorded on mixing Fe(III) and S(IV) solutions at 25 °C and ionic strength 0.1 M: (a) Spectra recorded with the J & M detector, [Fe(III)] = 0.5 mM, pH = 2.5, $\Delta t = 0.1$ s ([S(IV)] = 1 mM), $\Delta t = 0.05$ s ([S(IV)] = 10 mM); (b) Spectra recorded with the Bio Sequential SX-17MV stopped flow spectrofluorimeter, [Fe(III)] = 1 mM, pH = 2.5, $\Delta t = 0.05$ s ([S(IV)] = 1 mM), $\Delta t = 0.01$ s ([S(IV)] = 10 mM).

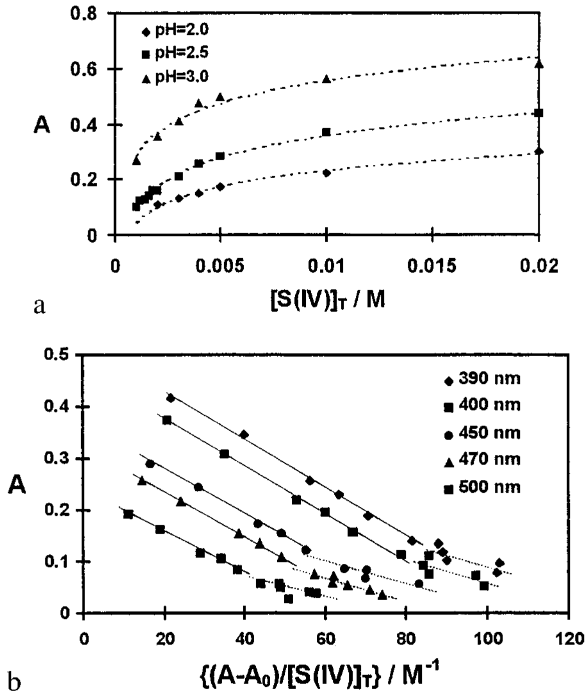

Figure 2. (a) Absorbance increase at 390 nm as a function of [S(IV)] and pH for the fast reaction step (see text). Experimental conditions: [Fe(III)] = 1 mM, ionic strength = 0.1 M, $T = 25$ °C, optical pathlength 1 cm, Ar atmosphere. (b) Determination of complex-formation constants for the fast reaction step at pH 2.5 (based on the data in Figure 2a and data obtained in a similar way).

$(H_2O)_4Fe(\mu\text{-}OH)_2Fe(H_2O)_4{}^{4+}$ species can exist in solution. At pH ≤ 3 and $[Fe(III)]_T \leq 2$ mM the main species present in solution are $Fe(H_2O)_6{}^{3+}$ and $Fe(H_2O)_5OH^{2+}$. In order to decrease the possible interference of dimeric species the total [Fe(III)] was kept at 0.5 or 1 mM. At pH < 4 and $[S(IV)]_T \leq 0.05$ M the main S(IV) oxides in solution are SO_2(aq) and $HSO_3{}^-$.

In agreement with our earlier observations[2] and those of Conklin and Hoffmann,[4] we observed an initial fast reaction on mixing the Fe(III) and S(IV) solutions, which was complete within a few milliseconds and was too fast to be followed with stopped-flow techniques. The spectra, recorded using both rapid-scan techniques in the absence and presence of S(IV), are reported in Figure 1 and clearly confirm the existence of a fast reaction step. The spectra reported in parts a and b of Figure 1 show a remarkably good agreement between the two rapid-scan techniques employed. The spectrum quality is apparently higher in the case of Figure 1b, but it should be kept in mind that these spectra are constructed from individual kinetic traces at different wavelength intervals, which involves considerable data smoothing procedures. In the absence of S(IV) no meaningful spectral changes are observed during dilution of the Fe(III) solution in the stopped-flow instrument and during the subsequent 0.5 s. At low S(IV) concentration the rapid increase in absorbance is followed by the formation of a product with a broad shoulder at ca. 420 nm (see Figure 1b). At higher S(IV) concentration the formation of this shoulder is accompanied by significant decreases in absorbance at 350 and 500 nm with clean isosbestic points at 317, 378, and 438 nm. Similar spectral changes were also observed at pH 3.0. It can be concluded from Figure 1 that the different observed reaction steps and the dependence of the spectral changes on the selected [S(IV)] indicate the formation of several Fe(III)−S(IV) complexes in solution. It is important to note that the complex-formation reactions are almost complete within 50 to 100 ms after mixing, depending on the selected experimental conditions. According to these results it is understandable that Betterton[9] only found evidence for the formation of a single Fe(III)−S(IV) complex since his measurements were performed at a time interval of 160 ms, which did not enable him to distinguish between the different complex formation steps. Furthermore, the spectra reported in Figure 1 are in exact agreement with our earlier observations[2] in which a very primitive data treatment procedure was employed. As the following treatment will show, the observed spectral changes can be interpreted in terms of the formation of 1:1, 1:2, and 1:3 iron(III)-sulfito complexes as outlined in reactions 2−4, respectively.

The change in absorbance associated with the first complex-formation reaction exhibits a nonlinear dependence on the total [S(IV)] as shown in Figure 2a. When these spectral data are analysed in terms of an equilibrium constant for the formation of a Fe(III)−S(IV) complex from an Arcand−Newton plot[10] of A vs $\Delta A/[S(IV)]$ (Figure 2b), clear evidence for the stepwise formation of two complex species as a function of [S(IV)] is observed. The corresponding complex-formation constants for the formation of the 1:1 and 1:2 Fe(III)−S(IV) species can be calculated from the slopes ($=1/K$) of the dotted and solid lines, respectively. The results are summarized as a function of pH and wavelength in Table 1. Due to the large error limits associated with the values of K_1, and by way of comparison, a series of experiments were performed under conditions where Fe(III) was used in excess, i.e. where only the formation of a 1:1 complex is possible. The formation constant for this complex was found to be 980 ± 112 M^{-1} at pH = 3 and $\lambda = 400$ nm under these conditions, which is in excellent agreement with the data reported in Table 1.

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Table 1. Apparent Complex-Formation Constants Determined for the Fe(III)−S(IV) System as a Function of pH, [Fe(III)], and Wavelength[a]

pH	formation const/M^{-1} (molar extinction coeff)/M^{-1} cm^{-1}	[Fe(III)]/ mM	wavelength/nm				
			390	400	450	470	500
2.5	K_1 ($\epsilon_{1:1}$)	0.5	649 ± 75 (420)	572 ± 26 (400)	760 ± 45 (320)	1058 ± 98 (300)	1181 ± 112 (240)
	K_2 ($\epsilon_{1:2}$)		319 ± 19 (540)	307 ± 56 (500)	374 ± 39 (400)	469 ± 42 (360)	589 ± 56 (280)
	K_3 ($\epsilon_{1:3}$)		127 ± 10 (456)	128 ± 11 (440)	136 ± 21 (288)	103 ± 29 (223)	
2.5	K_1 ($\epsilon_{1:1}$)	1.0	416 ± 113 (330)	412 ± 127 (280)	425 ± 105 (240)	416 ± 71 (210)	456 ± 78 (160)
	K_2 ($\epsilon_{1:2}$)		213 ± 8 (520)	220 ± 5 (430)	232 ± 5 (360)	234 ± 5 (320)	254 ± 12 (240)
	K_3 ($\epsilon_{1:3}$)		166 ± 6 (398)	182 ± 6 (366)	149 ± 8 (149)	134 ± 14 (134)	
3.0	K_1 ($\epsilon_{1:1}$)	1.0	984 ± 113 (600)	920 ± 82 (530)	861 ± 81 (320)	877 ± 120 (280)	664 ± 82 (210)
	K_2 ($\epsilon_{1:2}$)		620 ± 46 (710)	592 ± 42 (640)	640 ± 72 (370)	648 ± 72 (310)	520 ± 21 (230)
	K_3 ($\epsilon_{1:3}$)		187 ± 22 (656)	213 ± 5 (569)	209 ± 43 (283)	150 ± 46 (202)	

[a] Experimental conditions: ionic strength = 0.1 M, T = 25 °C, Ar atmosphere.

The complex-formation constants in Table 1 show a fairly consistent trend at the higher [Fe(III)] employed. This is mainly due to the larger absorbance changes and smaller error limits under such conditions. The data obtained for 0.5 mM Fe(III) at pH 2.5 seem to be consistent for the lower wavelength range where significant absorbance changes could be measured. In general K_1 has significantly larger values than K_2, and both values increase on increasing the pH from 2.5 to 3.0. This is ascribed to the influence of a higher concentration of the more labile $Fe(H_2O)_5OH^{2+}$ species at pH 3.0. The average values of K_1 and K_2 at pH 2.5 are rather close to those reported before[2], viz. 600 ± 30 and 205 ± 20 M^{-1}, respectively. The K_1 value furthermore corresponds favorably with those reported by Conklin and Hoffmann[4] (534 M^{-1} at I = 0.4 M and 25 °C) and Betterton[9] (850 M^{-1} at I = 0.2 M and 25 °C). Thus we conclude that the spectral data for the first complex-formation step support the formation of 1:1 and 1:2 Fe(III)−S(IV) complexes for which $K_1 = 425 \pm 18$, $K_2 = 231 \pm 16$ M^{-1} (at pH = 2.5) and $K_1 = 861 \pm 120$ and $K_2 = 604 \pm 52$ M^{-1} (at pH 3.0). The pH dependence of the formation constants can be related to the speciation of the Fe(III)[2] and S(IV) species[11] as function of pH, as well as possible acid−base equilibria of coordinate sulfite.

The spectra reported in Figure 1 clearly indicate that the rapid complex-formation reaction is followed by a slower step during the subsequent 50 to 100 ms. The absorbance changes associated with this reaction are plotted as a function of [S(IV)] and pH in Figure 3a. The observed trends are very similar to those reported before (see Figure 8a in ref 2), where the increase in absorbance at low [S(IV)] and decrease at high [S(IV)] must be related to different concentrations of the 1:1 and 1:2 complexes formed as a function of [S(IV)]. A fit of the data similar to that performed for the first reaction step (see Figure 3b) results in good linear relationships with clear evidence for the occurrence of only a single complex-formation step. This can only be assigned to the formation of the 1:3 complex as outlined in reaction 4. The values of K_3 in Table 1 are almost independent of [Fe(III)], pH, and wavelength and are of the same order as those reported before.[2]

We conclude that the results of the present study, in which sophisticated rapid-scan techniques were employed, underline our earlier findings[2] and support the formation of 1:1, 1:2, and 1:3 Fe(III)−S(IV) complexes in the presence of an excess of S(IV) in the pH range 2.5−3.0. The results are also in agreement with earlier work[12] in which the formation of different $Fe(SO_3)_n^{3-2n}$ complexes (n = 1, 2, and 3) as a function of pH, [Fe(III)] and [S(IV)] was reported. The results reported in this study are important in order to understand the radical initiation process indicated in reaction 1. It is reasonable to expect the sulfur(IV) concentration to be significantly higher than the metal ion concentration under atmospheric conditions, such that the rate of the initiation process will strongly depend on the nature of the iron−sulfito complex formed in solution. The reported complex-formation constants (K_1, K_2, and K_3) can thus be used in chemical transformation models. Our earlier work[3] showed that the reactivity sequence of the different complexes follows the order 1:3 > 1:2 > 1:1.

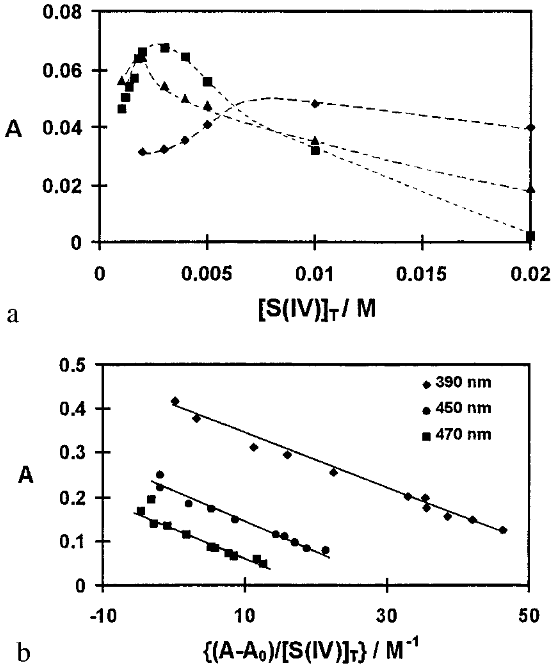

Figure 3. (a) Absorbance change at 390 nm as a function of [S(IV)] for the slow reaction step (see text). Experimental conditions: [Fe(III)] = 1 mM, ionic strength = 0.1 M, T = 25 °C, optical pathlength 1 cm, Ar atmosphere. (b) Determination of complex-formation constants for the slow reaction step at pH 2.5 (based on the data in Figure 3a and data obtained in a similar way).

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