

# The Absolute Value of the Rate Constant of the Liquid-Phase Reaction $\text{SO}_5^{\cdot-} + \text{Fe(II)}$

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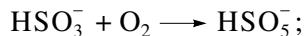
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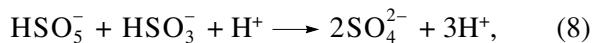
**Abstract**—An analytical method for monitoring the  $\text{Fe}^{2+}$  concentration during liquid-phase sulfite oxidation catalyzed by iron ions is described. The concentration conditions under which the  $\text{Fe(III)}/\text{Fe(II)}$  ratio is uniquely related to the rate constant of the reaction  $\text{SO}_5^{\cdot-} + \text{Fe}^{2+}$  are found by computer analysis. The experimental and calculated  $\text{Fe(III)}/\text{Fe(II)}$  ratio data are in agreement at  $k_{(\text{SO}_5^{\cdot-} + \text{Fe}^{2+})} = 3.2 \times 10^6 \text{ mol}^{-1} \text{ s}^{-1}$ . This is one of the three rate constant values known from the literature, which differ by a factor greater than 70.

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Millions of tons of sulfite are annually oxidized in flue gas scrubbers at the heat power plants of the United States, Western Europe, and Japan [1]. The amount of sulfate that results from sulfite and concentrates in the droplets of the cloud layer is greater by a factor of several tens [2]. Catalysis by iron ions is important in both processes [3–5]. The rate constant data reported for the reactions involving iron ions and S(IV) and S(VI) anionic species are summarized in Table 1 [6]. The observed equilibrium constants of reactions involving  $\text{Fe(III)}$  bisulfite ions are presented in Table 2 [7]. The complicated mechanism of sulfite oxidation includes two conjugated reaction cycles, namely, a catalytic one (reactions (1), (2), and (9)) and a chain one (reactions (2)–(6)). Both cycles come to the same result:



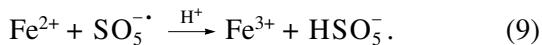
that is, they yield Caro's acid anion as an intermediate. This anion is consumed via two channels [8] (see Table 1):



Our analysis of all available kinetic data concerning sulfite oxidation catalyzed by iron ions [9] suggests that this reaction is a degenerate branched-chain process. This conclusion will be obvious if reactions (1) and (9) are summed:



The main  $\text{Fe(III)}$  regeneration reaction in the catalytic cycle is at the same time a waste of the active intermediate  $\text{SO}_5^{\cdot-}$ :



The kinetic effects caused by the conjugation of the catalytic and chain reaction cycles were considered in detail in an earlier publication [9].

Even an analysis of simpler conjugated reactions often leads to a set of nonlinear differential equations that have no solution in analytical form. In the analysis of the conjugated system of chain and catalytic cycles involved in sulfite oxidation, we used the Kinetika 90 computer program. Different authors report similar values for most of the rate constants presented in Table 1. Only for reaction (9), three authoritative research groups obtained rate constants differing by a factor larger than 70:  $6 \times 10^5$  [10],  $3.2 \times 10^6$  [11], and  $4.3 \times 10^7 \text{ mol}^{-1} \text{ s}^{-1}$  [12]. The purpose of our study is to choose the value that is best consistent with experimental  $[\text{Fe(III)}]/[\text{Fe(II)}]$  data. To obtain these data under steady-state conditions, we had to stop the reaction in some way and measure the concentration of  $\text{Fe(III)}$  or  $\text{Fe(II)}$  ions.

## Verification of the Rate Constant of the Reaction $\text{SO}_5^{\cdot-} + \text{Fe(II)}$

There have already been attempts to measure the ratio of these valent forms of iron ions during catalytic sulfite oxidation. We will not discuss the reliability of the earlier analytical methods. We will only present the experimental values of  $\zeta = [\text{Fe(III)}]/[\text{Fe(II)}]$ . For acidic solutions (pH 3) with rather high sulfite concentrations ( $\sim 2 \times 10^{-3} \text{ mol/l}$ ;  $\alpha = [\text{Fe}]_0/[\text{S(IV)}] \approx 5 \times 10^{-3}$ , where  $[\text{Fe}]_0 = [\text{Fe(II)}] + [\text{Fe(III)}]$ ),  $\zeta \leq 0.2$  [10]. This indicates that the dynamics of the iron ion interconversion cycle is controlled by the  $\text{Fe(III)}$  regeneration reactions (9)–

**Table 1.** Mechanism of the catalytic oxidation of sulfite with iron ions\*

Reaction no.	Reaction	$k_i, 1 \text{ mol}^{-1} \text{ s}^{-1}$
(1)	$\text{Fe}(\text{OH})\text{SO}_3\text{H}^+ \longrightarrow \text{Fe}^{2+} + \text{SO}_3^{\cdot-} + \text{H}_2\text{O}$	0.2**
(2)	$\text{SO}_3^{\cdot-} + \text{O}_2 \longrightarrow \text{SO}_5^{\cdot-}$	$2.5 \times 10^9$
(3a)	$\text{SO}_5^{\cdot-} + \text{HSO}_3^- \longrightarrow \text{HSO}_5^- + \text{SO}_3^{\cdot-}$	$3.4 \times 10^3$
(3b)	$\text{SO}_5^{\cdot-} + \text{HSO}_3^- \longrightarrow \text{SO}_4^{2-} + \text{SO}_4^{\cdot-} + \text{H}^+$	$\leq 2 \times 10^2$
(4a)	$\text{SO}_5^{\cdot-} + \text{SO}_3^{2-} \longrightarrow \text{SO}_5^{2-} + \text{SO}_3^{\cdot-}$	$2.1 \times 10^5$
(4b)	$\text{SO}_5^{\cdot-} + \text{SO}_3^{2-} \longrightarrow \text{SO}_4^{2-} + \text{SO}_4^{\cdot-}$	$5.5 \times 10^5$
(5)	$\text{SO}_4^{\cdot-} + \text{HSO}_3^- \longrightarrow \text{SO}_4^{2-} + \text{SO}_3^{\cdot-} + \text{H}^+$	$7.5 \times 10^8$
(6)	$\text{SO}_4^{\cdot-} + \text{SO}_3^{2-} \longrightarrow \text{SO}_4^{2-} + \text{SO}_3^{\cdot-} + \text{H}^+$	$3.1 \times 10^8$
(7a)	$\text{SO}_5^{\cdot-} + \text{SO}_5^{\cdot-} \longrightarrow \text{SO}_4^{\cdot-} + \text{SO}_4^{\cdot-} + \text{O}_2$	$8.7 \times 10^7$
(7b)	$\text{SO}_5^{\cdot-} + \text{SO}_5^{\cdot-} \longrightarrow \text{S}_2\text{O}_8^{2-} + \text{O}_2$	$1.3 \times 10^7$
(8)	$\text{HSO}_3^- + \text{HSO}_3^- + \text{H}^+ \longrightarrow 2\text{SO}_4^{2-} + 3\text{H}^+$	$\sim 10^7$ ***
(9)	$\text{Fe}^{2+} + \text{SO}_5^{\cdot-} \xrightarrow{\text{H}^+} \text{Fe}^{3+} + \text{HSO}_5^-$	$6 \times 10^5, 3.2 \times 10^6, 4.3 \times 10^7$
(10)	$\text{Fe}^{2+} + \text{SO}_4^{\cdot-} \longrightarrow \text{Fe}^{3+} + \text{SO}_4^{2-}$	$3.0 \times 10^8$
(11)	$\text{Fe}^{2+} + \text{HSO}_5^- \longrightarrow \text{Fe}^{3+} + \text{SO}_4^{\cdot-} + \text{OH}^-$	$3 \times 10^4$

\* The rate constants are taken from earlier reports [6, 9].

\*\* First-order rate constant ( $\text{s}^{-1}$ ).

\*\*\* Third-order rate constant ( $\text{l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ ).

(11). In less acidic solutions (pH 5) and at a lower sulfite concentration ( $[\text{HSO}_3^-] = 2 \times 10^{-5} \text{ mol/l}$ ;  $\alpha \approx 5 \times 10^{-2}$ ), the  $[\text{Fe(III)}]/[\text{Fe(II)}]$  ratio is quite different:  $\zeta \approx 6$  [13]. Under these conditions, the dynamics of the cycle is obviously controlled by the reduction of Fe(III) with sulfite (reaction (1)). These results show that certain concentration conditions should be established in order to verify  $k_9$ . The optimum conditions are an excess of sulfite over iron ( $\alpha \ll k_{3a}/k_9$ ) and a low pH. Under these conditions, the  $[\text{Fe(III)}]/[\text{Fe(II)}]$  ratio is described by the following expression [9]:<sup>1</sup>

$$\zeta \approx k_{3a}k_9k_{11}[\text{Fe}]_0/k_1\chi k_{7b}k_8.$$

<sup>1</sup> Here  $\chi = \frac{K_{\text{IV}}[\text{HSO}_3^-]}{\left(1 + \frac{[\text{H}^+]}{K_{\text{III}}} + K_{\text{IV}}[\text{HSO}_3^-] + \frac{K_{\text{V}}}{[\text{H}^+]} + \frac{K_{\text{VI}}[\text{H}^+][\text{HSO}_3^-]}{K_{\text{III}}}\right) + \frac{K_{\text{II}}K_{\text{VII}}[\text{HSO}_3^-]}{K_{\text{III}}} + \frac{K_{\text{II}}K_{\text{VIII}}[\text{HSO}_3^-]}{[\text{H}^+]}}$

(see Table 2).

The ratio of the concentrations of oxidized and reduced iron ions is proportional to the absolute value of the rate constant of reaction (9).<sup>2</sup>

## EXPERIMENTAL

All experiments were carried out using an earlier described technique [14] at a fixed acidity of pH 3.5. This pH was chosen in order to rule out the formation of insoluble  $\text{Fe}(\text{OH})_3$  (to carry out sulfite oxidation in the homogeneous region), to reduce the emission of  $\text{SO}_2$  from the solution ( $\text{SO}_{2(\text{H}_2\text{O})} \longrightarrow \text{SO}_{2(\text{gas})}$ ) to the maximum possible extent, and, most importantly, to

<sup>2</sup> Note that an attempt to verify the  $k_9$  value by measuring the sulfite oxidation rate would not be successful under the conditions considered. The rate of this process,  $w \approx k_{3a}^2 k_{11}[\text{Fe}]_0/k_{7b}k_8$ , is independent of  $k_9$ . The apparent contradiction between  $\zeta \sim k_9$  and  $w \neq f(k_9)$  is explained by the fact that sulfite oxidation occurs in the reaction cycle involving chain-propagating intermediates rather than in the cycle involving metal ions; that is,  $w_{3a}/w_9 \approx k_{3a}/k_9 \alpha \gg 1$ .

**Table 2.** Equilibrium constants of the dissociation and formation of complexes involving iron ions

Reaction	$K_i$
$\text{SO}_{2(\text{aq})} \rightleftharpoons \text{HSO}_3^- + \text{H}^+$	$\sim 1.4 \times 10^{-2} \text{ mol/l}$
$\text{HSO}_3^- \rightleftharpoons \text{SO}_3^{2-} + \text{H}^+$	$\sim 6.2 \times 10^{-8} \text{ mol/l}$
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+} + \text{H}^+$	$6 \times 10^{-3} \text{ mol/l}$
$[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+} + \text{HSO}_3^- \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_4(\text{HSO}_3)(\text{OH})]^+$	$600 \text{ l/mol}$
$[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+} \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+ + \text{H}^+$	$7 \times 10^{-5} \text{ mol/l}$ [20]
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{HSO}_3^- \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_5(\text{HSO}_3)]^{2+} + \text{H}_2\text{O}$	$72 \text{ l/mol}$
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{SO}_3^{2-} \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_5(\text{SO}_3)]^+ + \text{H}_2\text{O}$	$7.3 \times 10^6 \text{ l/mol}$
$[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+} + \text{SO}_3^{2-} \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_4(\text{SO}_3)] + \text{H}_2\text{O}$	$2.0 \times 10^7 \text{ l/mol}$

Note:  $T = 298 \text{ K}$ ; ionic strength,  $\sim 0$  [7].

establish, if possible, concentration conditions under which  $\zeta < 1$  [9].

The concentration of  $\text{Fe}^{2+}$  during catalytic sulfite oxidation was measured earlier. For this purpose,  $\text{Fe}(\text{II})$  and  $\text{Fe}(\text{III})$  were separated by ion chromatography [5, 15] before determining the concentration of divalent iron. Since the removal of one of the ionic species during the analytical procedure was compensated by new ions resulting from the continuing reaction, the observed iron ion concentrations could differ from the true concentrations. The color reactions of  $\text{Fe}^{2+}$  with 4-pyridyl-2-azoresorcinate [13] and ferrosine [16] were used to measure  $[\text{Fe}^{2+}]$ . The  $\text{Fe}^{2+}$  concentrations thus measured are correct only if  $[\text{Fe}^{2+}] \gg [\text{Fe}^{3+}]$ . Otherwise, adding complexon L will result in both  $\text{Fe}(\text{II})\text{L}$  and  $\text{Fe}(\text{III})\text{L}$ . Since the stability constant of the  $\text{Fe}(\text{II})\text{L}$  complex is higher than that of  $\text{Fe}(\text{III})\text{L}$ , the redox potential of the  $\text{Fe}(\text{III})\text{L}/\text{Fe}(\text{II})\text{L}$  couple is higher than that of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple. Because of the linear relationship between  $\log k$  and  $\Delta G_{298}^\circ$  for one-electron transfer reactions [17], the addition of L considerably increases the rate constant of the reaction between  $\text{Fe}(\text{III})$  and  $\text{HSO}_3^-$ . Therefore, when  $[\text{Fe}^{2+}] \leq [\text{Fe}^{3+}]$ , the results of these measurements will be distorted toward higher  $[\text{Fe}^{2+}]$  values.

The possibility of these distortions taking place is indicated by the results of our preliminary experiments on the spectrophotometric determination of  $[\text{Fe}^{2+}]$  using the color reaction between  $\text{Fe}^{2+}$  and  $\alpha, \alpha'$ -dipyridyl (D). The redox potential of the  $\text{Fe}(\text{III})\text{D}_3/\text{Fe}(\text{II})\text{D}_2$  couple is 1.1 V, which is 0.33 V higher than that of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple. Therefore, the rate constant of the reaction between  $\text{HSO}_3^-$  and  $\text{Fe}(\text{III})\text{L}_3$  must far exceed the rate constant of the reaction between  $\text{HSO}_3^-$  and

$\text{Fe}(\text{III})$ . Therefore, as D is added to a solution containing  $\text{HSO}_3^-$ ,  $\text{O}_2$ , and iron ions, light absorption due to  $\text{Fe}(\text{II})\text{D}_3$  formation is observed first and then the color intensity increases due to the conversion of  $\text{Fe}(\text{III})$  to  $\text{Fe}(\text{II})\text{D}_3$  until all of the  $\text{Fe}^{3+}$  ions turn into  $\text{Fe}^{2+}$ . This procedure can be used in the determination of the total iron content of a sulfite solution. For a correct measurement of  $[\text{Fe}^{2+}]$  in the course of sulfite oxidation, one should prevent the conversion of  $\text{Fe}(\text{III})$  to  $\text{Fe}(\text{II})$  when performing the analysis. The  $\text{Fe}(\text{III})$  valent state is stabilized by the complexation of iron with ethylenediaminetetraacetate (EDTA). According to our data, the rate constant of the reaction of  $\text{Fe}(\text{III})\text{EDTA}^-$  with  $\text{HSO}_3^-$  is only  $\sim 10^{-2} \text{ mol}^{-1} \text{ mol}^{-1} \text{ s}^{-1}$ ; that is,  $\text{Fe}(\text{III})$  has no time to turn into  $\text{Fe}(\text{II})$  during sampling and absorbance measurements ( $\sim 5 \text{ min}$ ). The formation and decomposition of the sulfite complex  $\text{Fe}(\text{EDTA})\text{SO}_3^{3-}$  at higher pH values were studied by the stopped-flow method [18, 19]. However, in the absence of D, the  $\text{Fe}(\text{II})\text{EDTA}$  complex is rapidly converted to an  $\text{Fe}(\text{III})$  complex by reacting with  $\text{O}_2$ . Therefore, to measure the true concentrations of iron ions in different valent states,  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  should simultaneously be bound with EDTA and  $\alpha, \alpha'$ -dipyridyl, respectively (the  $\text{Fe}^{2+}\text{D}_3$  complex is not oxidized with oxygen). Since both EDTA and D form stable complexes with  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ , the question arises of whether  $\text{Fe}^{3+}$  is completely bound by EDTA and whether  $\text{Fe}^{2+}$  is completely bound by  $\alpha, \alpha'$ -dipyridyl under given experimental conditions.

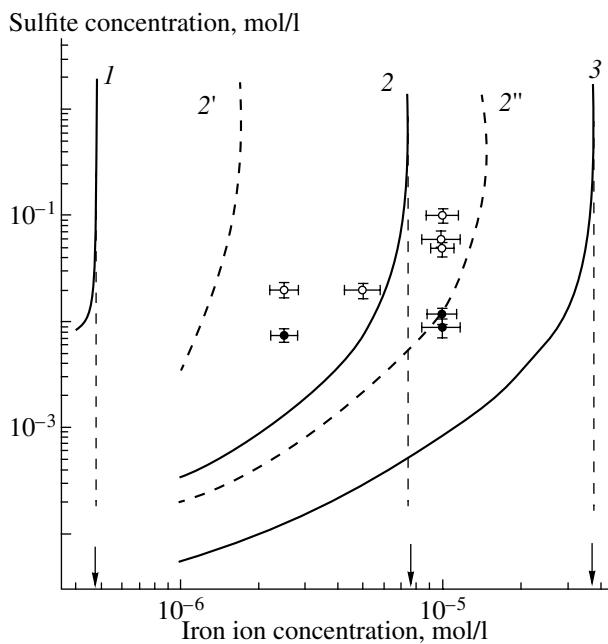
Using the known formation constants of the complexes between  $\text{Fe}^{2+}$  and D and between  $\text{Fe}^{3+}$  and EDTA, the protonation constant of D, and the consecutive acid dissociation constants of EDTA, we found that, in a thermodynamically equilibrated solution with

**Table 3.** Fe(III)-to-Fe(II) concentration ratios measured during sulfite oxidation catalyzed by iron ions

[Fe] <sub>0</sub> , mol/l	[S(IV)] <sub>0</sub> , mol/l	$\alpha = [Fe]_0/[S(IV)]_0$	$\zeta = [Fe(III)]/[Fe(II)]$
$2.5 \times 10^{-6}$	$7.5 \times 10^{-3}$	$\sim 3.33 \times 10^{-4}$	0.25
$2.5 \times 10^{-6}$	$2.0 \times 10^{-2}$	$1.25 \times 10^{-4}$	0.14
$5.0 \times 10^{-6}$	$1.0 \times 10^{-2}$	$5.0 \times 10^{-4}$	0.8
$5.0 \times 10^{-6}$	$2.0 \times 10^{-2}$	$2.5 \times 10^{-4}$	$\sim 1.0$
$1.0 \times 10^{-5}$	$1.0 \times 10^{-2}$	$1.0 \times 10^{-3}$	1.0
$1.0 \times 10^{-5}$	$1.0 \times 10^{-2}$	$1.0 \times 10^{-3}$	1.5
$1.0 \times 10^{-5}$	$5.0 \times 10^{-2}$	$2.0 \times 10^{-4}$	0.67
$1.0 \times 10^{-5}$	$5.0 \times 10^{-2}$	$2.0 \times 10^{-4}$	1.25
$1.2 \times 10^{-5}$	$1.0 \times 10^{-1}$	$1.2 \times 10^{-4}$	0.2

Note:  $T = 293$  K; pH 3.5.

pH 4.5,  $[D]_0/[EDTA]_0 \geq 5$ , and  $[EDTA]_0 \geq [Fe]_0$ ,  $Fe^{2+}$  is almost completely bound into the  $Fe^{2+}D_3$  complex and  $Fe^{3+}$  into the EDTA complex. Thus, the reaction solution will contain only iron ion complexes that are neither reduced by sulfite nor oxidized by oxygen. It is



Calculated [S(IV)]-to-[Fe]<sub>0</sub> ratios at which the concentrations of divalent and trivalent iron ions in the sulfite solution are equal ( $\zeta = 1$ ):  $k_9 = (1) 4.3 \times 10^7$ , (2, 2', 2'')  $3.2 \times 10^6$ , and (3)  $6 \times 10^5$  l mol<sup>-1</sup> s<sup>-1</sup>.  $\zeta = 0.3$  for curve 2' and 1.5 for curve 2''. For comments, see text.

likely that the presence of sulfite in the solution does not change the situation.

Obviously, the characteristic time of the complexation reactions involving the iron ions should be substantially shorter than the characteristic time of the changes in the  $Fe^{3+}$  and  $Fe^{2+}$  concentrations during the reaction. This is likely to be the case. The complexes of  $Fe^{3+}$  with EDTA and of  $Fe^{2+}$  with D at pH 3.5,  $[Fe]_0 = 10^{-5}$  mol/l, and  $D \approx 10^{-4}$  mol/l are formed at a rate equal to the rate of reactant mixing; that is, the characteristic time of complexation does not exceed a fraction of a second. Depending on initial conditions, the characteristic time within which a steady-state rate of sulfite oxidation is established varies from a few minutes (if an  $Fe(III)$  salt is introduced into the solution) to hundreds of minutes (if an  $Fe(II)$  salt is initially added) [3, 15].

These views were experimentally confirmed. A mixture of EDTA and D with the above ratio of the components was added to an aerated solution with known concentrations of  $Fe^{2+}$  and  $FeOH^{2+}$  ions. The observed light absorption by  $Fe^{2+}D_3$  ( $\epsilon_{\lambda} = 8.75 \times 10^3$  l mol<sup>-1</sup> cm<sup>-1</sup> at  $\lambda = 525$  nm) was consistent with the  $Fe^{2+}$  concentration in the solution and did not change with time. The same result was obtained when a mixture of  $Fe^{2+}$  and  $FeOH^{2+}$  with a certain composition was initially introduced into the aerated solution and a mixture of EDTA and D in an acetate buffer with pH 4.5 was added after  $t \leq 10$  s. If  $t$  was several minutes, the observed  $Fe^{2+}$  concentration differed from the initial concentration. Therefore, the  $Fe^{2+}$  concentration detected by this method is equal to the true concentration of  $Fe^{2+}$  during sulfite oxidation at the instant the reaction is stopped.

The measurement of the  $Fe^{2+}$  ion concentration during sulfite oxidation for different initial ratios of  $Fe^{2+}$  to  $FeOH^{2+}$  (but at a fixed total concentration of these ions) showed that, under steady-state sulfite oxidation conditions, the observed  $Fe^{2+}$  concentration is always the same, regardless of the initial ratio of the ion concentrations. The above results indicate that the  $Fe^{2+}$  concentration measured in our experiments is stationary.

## RESULTS AND DISCUSSION

The  $[Fe^{2+}]$  data obtained at pH 3.5 by the above procedure are listed in Table 3.  $Fe^{2+}$  concentrations were determined from the absorbances of solutions in a 5-cm cell on a Specord UV-vis spectrophotometer after an aliquot of a "quencher" (a solution of D and EDTA with pH 4.5) was added to the sample (5 ml). The trivalent-to-divalent iron concentration ratios thus determined lie in the range  $0.14 \leq \zeta \leq 1.3$ . The changes in this ratio as a function of  $[Fe]_0$  and  $[S(IV)]$  are in accord with previous conclusions [9]. An increase in  $[Fe]_0$  at a constant  $[S(IV)]$  leads to an increase in  $\zeta$ . On the contrary, an increase in the sulfite concentration at a fixed iron ion concentration results in a decrease in  $\zeta$ . Computer simulation (see the figure) has provided a more rigorous description for the influence of the metal ion and sub-

strate concentrations on  $\zeta$  and for the dependence of the valent state distribution of iron ions on the absolute value of the rate constant of reaction (9). The curves referring to three different values of the rate constant of reaction (9) indicate that there is a correlation between the  $[S(IV)]$  and  $[Fe]_0$  values at which the concentrations of divalent and trivalent iron ions are equal ( $\zeta = 1$ ). The calculations were carried out for the following rate constants of the  $SO_5^{\cdot-} + Fe^{2+}$  reaction:  $6 \times 10^5$ ,  $3.2 \times 10^6$ , and  $4.3 \times 10^7$   $1 \text{ mol}^{-1} \text{ s}^{-1}$ . In essence, the figure is a kinetic diagram of the chain catalytic sulfite oxidation. The curves presented in the figure represent the boundaries of the catalyst/substrate concentration regions in which the dynamics of the iron ion interconversion cycle is limited by the dynamics of the trivalent iron regeneration reaction (9) (above the curves) or by the dynamics of trivalent iron reduction with sulfite (reaction (1)). A common feature of these curves is the existence of a critical value ( $[Fe]_{0(cr)}$ ) above which the  $Fe(III)$  and  $Fe(II)$  concentrations cannot be equal at any  $[S(IV)]$ . For  $k_9 = 6 \times 10^5$   $1 \text{ mol}^{-1} \text{ s}^{-1}$ , the regeneration of catalytically active  $Fe^{3+}$  ions remains to be the rate-determining step of the iron ion interconversion cycle up to an iron ion concentration of  $\sim 3.5 \times 10^{-5}$   $\text{mol/l}$ . For  $k_9 = 4.3 \times 10^7$   $1 \text{ mol}^{-1} \text{ s}^{-1}$ , this step is rate-determining up to a concentration no higher than  $\sim 5 \times 10^{-7}$   $\text{mol/l}$  (figure). The existence of an  $[Fe]_{0(cr)}$  value is explained by a crossover between the chain and catalytic regimes of sulfite oxidation. This crossover dramatically changes the way in which the  $HSO_5^{\cdot-}$  intermediates are formed and consumed. The chain  $HSO_5^{\cdot-}$  formation process degenerates at  $[Fe]_0 > [Fe]_{0(cr)}$ . An appropriate amount of  $HSO_5^{\cdot-}$  should be produced in the metal ion interconversion cycle for sulfite oxidation to proceed steadily in the catalytic regime [9]. This is possible only if the chain branching rate and, hence, the concentration of  $HSO_5^{\cdot-}$  intermediates increase greatly. This is also clear from the data presented in the figure: as the rate constant of reaction (9) increases, the crossover between the chain and catalytic regimes of sulfite oxidation occurs at a progressively lower  $[Fe]_{0(cr)}$ . If the rate constant  $k_9$  is given the largest of the known values, namely,  $4.3 \times 10^7$   $1 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $[Fe]_{0(cr)}$  will be so small ( $\approx 5 \times 10^{-7}$   $\text{mol/l}$ ) that the chain and catalytic regimes of sulfite oxidation will be experimentally indistinguishable. Therefore, the rate constant value of  $k_9 = 4.3 \times 10^7$   $1 \text{ mol}^{-1} \text{ s}^{-1}$  [12] seems to be improbable.

The points in the figure indicate the concentrations at which  $[Fe(II)]$  was measured. The results of the experiments in which the sulfite concentrations are similar are represented by black points. These data confirm that the value of  $k_9 = 4.3 \times 10^7$   $1 \text{ mol}^{-1} \text{ s}^{-1}$  is overestimated. The value of  $k_9 = 6 \times 10^5$   $1 \text{ mol}^{-1} \text{ s}^{-1}$  seems to be

too low. For the runs in which the measured  $[Fe(II)]$  value corresponds to  $\zeta \approx 1$  (Table 3), the concentration data points are best fitted by the curve calculated for the experimental value of  $k_9 = 3.2 \times 10^6$   $1 \text{ mol}^{-1} \text{ s}^{-1}$  [11]. Data falling rather close to this calculated curve are also obtained at somewhat lower or higher  $\zeta$  values (Table 3). The corresponding curves are shown by dashed lines 2' and 2" in the figure. A comparison between the experimental and calculated sulfite consumption data [9] provides further evidence in favor of  $k_9 = 3.2 \times 10^6$   $1 \text{ mol}^{-1} \text{ s}^{-1}$ .

Why were different rate constants observed for the reaction in earlier studies [10–12]? The fact that the  $k_9$  value measured by Herrmann et al. [12] exceeds  $k_9 = 3.2 \times 10^6$   $1 \text{ mol}^{-1} \text{ s}^{-1}$  by a factor larger than 10 is possibly explained by dithionite being used as the source of  $SO_5^{\cdot-}$  radicals ( $S_2O_6^{2-} \xrightarrow{h\nu} 2SO_3^{\cdot-} \xrightarrow{2O_2} 2SO_5^{\cdot-}$ ). The complexes of this  $\sigma$ -donor with  $Fe^{3+}$  are expected to be more stable than the same complexes with  $Fe^{2+}$ . In other words, the  $\Delta G_{298}^{\circ}$  value must be more favorable for the conversion of  $Fe^{2+}(S_2O_6^{2-})_n$  into  $Fe^{3+}(S_2O_6^{2-})_n$  than for the  $Fe^{2+}/Fe^{3+}$  couple. Correspondingly, the rate constant of the reaction between the  $Fe(II)$  dithionato complex and  $SO_5^{\cdot-}$  must be higher than the rate constant of the similar reaction involving  $Fe(II)$ . The value of  $k_9 = 6 \times 10^5$   $1 \text{ mol}^{-1} \text{ s}^{-1}$  [10] was obtained by an indirect method under the erroneous assumption that  $\zeta$  remains constant as  $[Fe]_0$  changes by a factor of 6. However, we have shown that a change in  $[Fe]_0$  exerts a significant effect on the  $[Fe(III)]/[Fe(II)]$  ratio [9]. Thus, the experiments have demonstrated that the rate constant of the reaction  $SO_5^{\cdot-} + Fe^{2+} \xrightarrow{H_2O} FeOH^{2+} + HSO_5^{\cdot-}$  should be taken to be  $k_9 = 3.2 \times 10^6$   $1 \text{ mol}^{-1} \text{ s}^{-1}$  in the calculation of the dynamics of catalytic sulfite oxidation.

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