Kinetics and Mechanism of the Redox Behaviour of the Ethylenediaminetetraacetatoferrate(III)–Sulfite System in Aqueous Solution

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The decomposition reaction of $[Fe^{III}(edta)(SO_3)]^{3-}$ has been studied as a function of total sulfite, $[Fe^{III}(edta)^-]$, oxygen concentration, pH and temperature using spectrophotometric, potentiometric and ion-chromatographic techniques. The catalysed autoxidation of sulfite is significantly slower for $[Fe^{III}(edta)]^-$ than for aquated iron(III) ions. The reaction exhibits a strong oxygen dependence, and the participation of oxygenated complexes is suggested to account for this effect. The major redox products are sulfate and $[Fe^{II}(edta)]^{2-}$, which is rapidly reoxidized to $[Fe^{III}(edta)]^-$ in the presence of oxygen. Various possible redox mechanisms are discussed, and the results are compared to corresponding data for the non-chelated iron(III) system.

We are interested in the mechanisms of metal-ion catalysed autoxidation reactions of sulfur(IV) oxides in order to elucidate the important role of metal ions and complexes in atmospheric oxidation processes. These reactions can largely account for the oxidation of SO_2 in cloud or fog water droplets during night-time reactions.[1–8] We have performed detailed studies on the effect of aquated metal ions on such processes, which revealed rather complicated mechanisms partly due to the high reactivity and large number of labile co-ordination sites on such metal ions.[9–15] These factors complicated the identification of intermediate species produced prior to the redox reactions. We have therefore started to introduce certain ligands on the metal centre in order to reduce its reactivity and the number of labile sites, and to be able to work in a higher pH range.

In the present study ethylenediaminetetraacetate (edta) was employed as a chelate ligand to block the majority of the co-ordination sites on the iron(III) centre. We have described a detailed study of the complex formation kinetics of $[Fe^{III}(edta)]^-$ with sulfite,[16] and report here on the redox behaviour of the system. The results reveal important reaction paths that are relevant to the aquated iron(III)-catalysed autoxidation of sulfate.[9,10,13,15]

Experimental

The $[Fe^{III}(edta)(SO_3)]^{3-}$ complex was prepared in solution by mixing $[Fe(edta)]^-$ with sulfite as described before.[16] Chemicals of analytical reagent grade and deionized water were used throughout this study. The salt $NaClO_4{\cdot}H_2O$ (Merck) was used to adjust the ionic strength of the test solutions, whereas NaOH and $HClO_4$ were used to adjust the pH. The latter was measured on a Metrohm instrument equipped with a glass electrode, the reference compartment of which was filled with 3 mol dm^{-3} NaCl to prevent precipitation of $KClO_4$ when KCl was used as electrolyte instead of NaCl.

The decomposition of $[Fe(edta)(SO_3)]^{3-}$ was followed spectrophotometrically on Hitachi U 3200 and Shimadzu UV250 spectrophotometers. The reactions were either followed in the thermostatted (±0.1 °C) cell compartment of the spectrophotometer, or by a sampling technique using a thermostatted batch reactor. In the latter case the reaction mixture was placed in a glass flask, heated and treated in different ways as indicated in the following section. A number of blank experiments were performed in which no $[Fe(edta)]^-$ was employed in order to determine the rate of oxidation of sulfite under the selected experimental conditions. In this work $[Fe(edta)]^-$ was used as an indicator solution to determine the sulfite concentration following the oxidation reaction. The dioxygen concentration was varied in a series of experiments by using different procedures to saturate the bulk solution after samples were taken. Glass inlet tubes were used to introduce O_2, in order to exclude contamination by metal ions. More details are given in the following section.

Ion chromatography was employed to analyse the sulfur oxide reaction products. In these experiments the ionic strength of the test solutions was not adjusted with $NaClO_4$ since the latter damages the chromatography column and prevents its effective regeneration. The pH of the solution was adjusted by using a combination of sulfur(IV) oxides and a minimum of other acids and bases. The analyses were performed on a Sykam instrument, with a conductivity detector and a C-R3A integrator. For the detection of SO_3^{2-} and SO_4^{2-} an anion-exchange column (Sykam AO3) and a 3 mmol dm^{-3} Na_2CO_3 eluent were used. The ions $S_2O_4^{2-}$ and $S_2O_6^{2-}$ were analysed on an ion-pair column (Sykam LCANOI) with an eluent consisting of 1 mmol dm^{-3} $Na_2CO_3{\cdot}1OH_2O$ (Merck), 2.5 mmol dm^{-3} NBu_4OH (Merck) and 15% MeCN (Chromasolv, Riedel-de-Häen). The concentrations of the test solutions were significantly lower than for the spectrophotometric work, or were diluted prior to injection into the ion chromatograph.

Results

The redox decomposition of $[Fe^{III}(edta)(SO_3)]^{3-}$ was investigated using various experimental techniques as indicated in the previous section. The experimental parameters $[Fe(edta)^-]$, $[S^{IV}]_T$, pH, $[O_2]$ and temperature were varied systematically in order to optimize the conditions for the redox process, depending on the method selected to follow the reaction.

The decomposition of $[Fe(edta)(SO_3)]^{3-}$ can be followed spectrophotometrically when a concentration of 5×10^{-3} mol dm^{-3} is employed. This complex is characterized by a strong absorbance between 400 and 550 nm[16] (see Fig. 1), which strongly depends on $[S^{IV}]_T$ and the pH of the solution, since these factors control the formation of $[Fe(edta)(SO_3)]^{3-}$ as indicated by the overall Scheme 1. The bell-shaped pH dependence of the absorbance (see Fig. 3 of ref. 16) indicated that the maximum concentration of $[Fe(edta)(SO_3)]^{3-}$ is

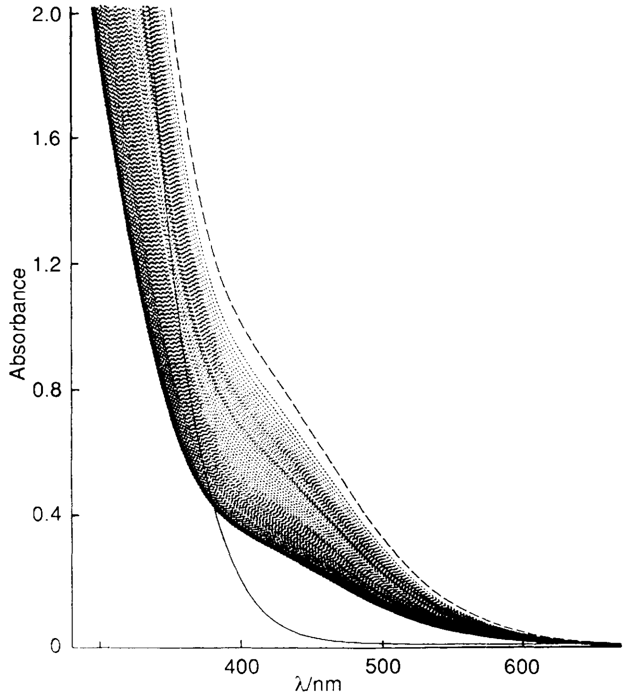


Fig. 1 UV/VIS spectra observed during the reaction of $[Fe^{III}(edta)]^-$ with sulfite. Experimental conditions: $[Fe^{III}(edta)^-] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[S^{IV}]_T = 0.20$ mol dm^{-3}, pH 6.5, 40 °C, $I = 0.82$ mol dm^{-3}. ——, Before mixing; ——, after mixing; ···, slow decomposition, Δt = 1 h

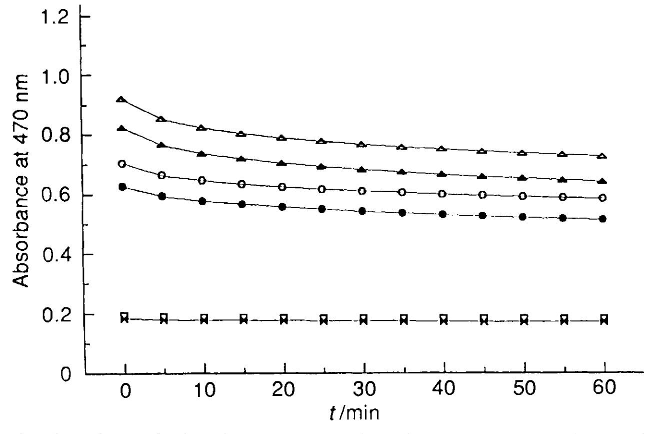
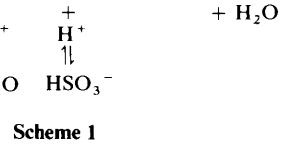


Fig. 2 Plots of absorbance *versus* time for the decomposition of $[Fe^{III}(edta)(SO_3)]^{3-}$ in the absence of oxygen saturation. Experimental conditions: $[Fe^{III}(edta)^-] = 5.0 \times 10^{-3}$ mol dm^{-3}, 60 °C, $I = 0.5$ mol dm^{-3} ($NaClO_4$). Curves: X, $[S^{IV}]_T$ 0.025, pH 7.3; □, 0.050, 8.06; ●, 0.10, 7.30; ○, 0.15, 7.53; ▲, 0.20, 7.54; △, 0.25 mol dm^{-3}, 7.62

produced at pH ≈ 7. The decrease in absorbance at lower pH was ascribed to the protonation of SO_3^{2-} to HSO_3^-, which has a lower nucleophilicity, whereas the decrease at higher pH was



$$\begin{array}{lcl}
[Fe(edta)(H_2O)]^- & + SO_3^{2-} \rightleftharpoons & [Fe(edta)(SO_3)]^{3-} \\
\upharpoonleft\downharpoonright & + & + H_2O \\
[Fe(edta)(OH)]^{2-} + H^+ & H^+ & \\
\upharpoonleft\downharpoonright & \upharpoonleft\downharpoonright & \\
[\{Fe(edta)\}_2O]^{4-} + H_2O & HSO_3^- &
\end{array}$$

Scheme 1

ascribed to the deprotonation of $[Fe(edta)(H_2O)]^-$ to produce $[Fe(edta)(OH)]^{2-}$ and $[\{Fe(edta)\}_2O]^{4-}$, which are substitution-inert species.[16] Such plots can serve as calibration curves when the redox decomposition of $[Fe(edta)(SO_3)]^{3-}$ is studied spectrophotometrically, especially under conditions where the decomposition reaction is accompanied by a significant decrease in pH due to the oxidation of sulfite to sulfate.

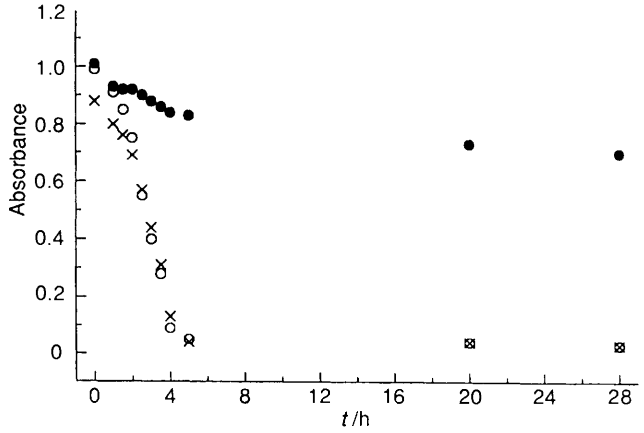


Fig. 3 Absorbance *vs.* time plots to illustrate the effect of oxygen on the oxidation of sulfite in the presence of $[Fe^{III}(edta)]^-$. Experimental conditions: $[S^{IV}]_T = 0.15$ mol dm^{-3}, $I = 0.5$ mol dm^{-3}, 40 °C. ●, Without dioxygen saturation, $[Fe^{III}(edta)^-] = 1.0 \times 10^{-2}$ mol dm^{-3}, pH 7.28; λ = 510 nm; ○, with dioxygen saturation, $[Fe^{III}(edta)^-] = 1.0 \times 10^{-2}$ mol dm^{-3}, pH 7.28, λ = 510 nm; X, with dioxygen saturation, $[Fe^{III}(edta)^-] = 5.0 \times 10^{-3}$ mol dm^{-3}, pH 7.32, λ = 480 nm

A typical repetitive-scan spectrum for the redox decomposition of $[Fe(edta)(SO_3)]^{3-}$ in the presence of 0.2 mol dm^{-3} sulfite is shown in Fig. 1. The decomposition consists of two consecutive reaction steps, the first of which occurs within 1 h of mixing. Some typical absorbance (at 470 nm) *vs.* time plots under various experimental conditions are given in Fig. 2. The absorbances at $t = 0$ are in good agreement with those predicted on the basis of the spectral data reported before[16] and the initial pH of the test solution. In these experiments air-saturated solutions were employed ($[O_2] \approx 2 \times 10^{-4}$ mol dm^{-3}) and the reactions were performed in sealed quartz cuvettes. A significant absorbance decrease occurs within the first hour of the reaction, especially at the higher sulfur(IV) concentrations, followed by a subsequent slower decrease as shown in Fig. 1. This observation is ascribed to dissolved O_2 that is used up during the initial part of the redox process.

The influence of oxygen on the redox behaviour of $[Fe(edta)(SO_3)]^{3-}$ was studied in more detail for long reaction times. For this purpose the reaction mixtures saturated with O_2, were thermostatted in sealed flasks in a water-bath, and samples were withdrawn as a function of time and analysed spectrophotometrically. Typical results are shown in Fig. 3, from which the drastic influence of O_2 is clear. Once again these results are in good agreement with the observations reported above. An increase in the sulfite concentration leads to an apparent stabilization of the $[Fe(edta)(SO_3)]^{3-}$ species, *i.e.* a slower redox decomposition according to the data in Fig. 4. This trend is accompanied by a steady increase in the half-life of the reaction from *ca.* 1 to 6 h. An increase in the $[Fe(edta)]^-$ concentration did not seem to have a significant effect on the stability of $[Fe(edta)(SO_3)]^{3-}$. However, in the presence of a stabilizer, *i.e.* where the spontaneous autoxidation of sulfite was suppressed, an increase in the $[Fe(edta)]^-$ concentration caused a substantial increase in the redox rate as demonstrated by a steady decrease in the half-life of the reaction. The absorbance *vs.* time data in Figs. 3 and 4 can only be interpreted in a qualitative way since the redox reaction is accompanied by a significant decrease in pH due to the formation of sulfate.

The redox process was also followed using ion chromatography, typical results being shown in Fig. 5. Mainly sulfate

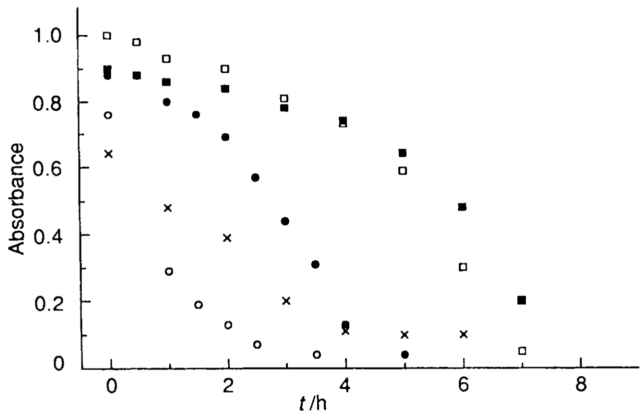


Fig. 4 Absorbance *vs.* time plots for the decomposition of $[Fe^{III}(edta)(SO_3)]^{3-}$ under oxygen-saturated conditions. Experimental conditions: $[Fe^{III}(edta)^-] = 5.0 \times 10^{-3}$ mol dm^{-3}, 40 °C, $I = 0.5$ mol dm^{-3}. X, $[S^{IV}]_T$ 0.50, $\lambda = 450$, pH 7.34; ○, 0.10, 480, 7.13; ●, 0.15, 480, 7.32; □, 0.20, 480, 7.31; ■, 0.25 mol dm^{-3}, 490 nm, 7.31

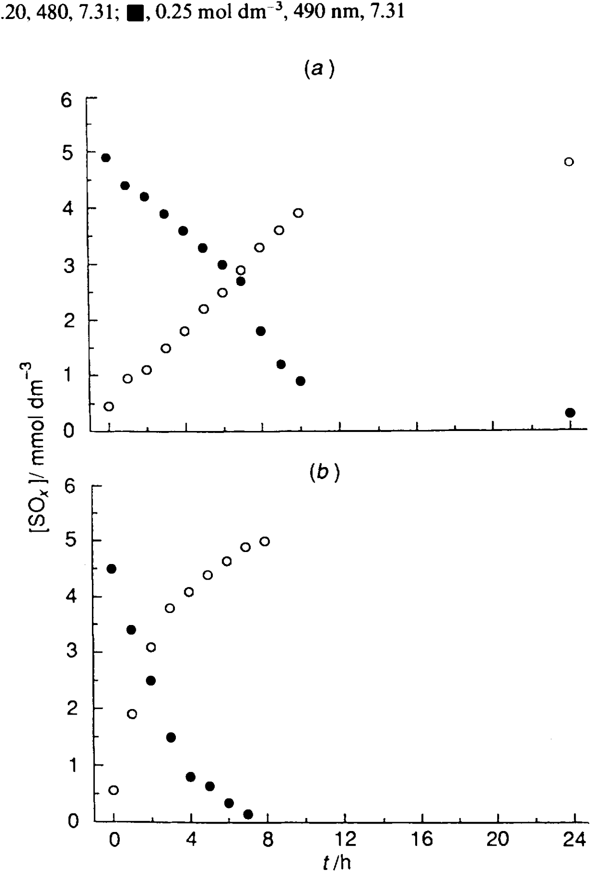


Fig. 5 Ion-chromatographic analysis of the oxidation of sulfite in the presence of $[Fe^{III}(edta)]^-$. Experimental conditions: $[Fe^{III}(edta)^-] = 5.0 \times 10^{-4}$ mol dm^{-3}, $[S^{IV}]_T = 5.0 \times 10^{-3}$ mol dm^{-3}, pH ≈ 7.8, 40 °C. (*a*) Without dioxygen saturation; (*b*) with dioxygen saturation; ●, concentration of SO_3^{2-}; ○, concentration SO_4^{2-}

is produced during the oxidation of sulfite at a rate that strongly depends on the oxygen concentration. Extremely low concentrations (less than 1% of the total sulfur oxide content) of $S_2O_6^{2-}$ were detected under conditions where no oxygen was employed. In the presence of oxygen no $S_2O_6^{2-}$ could be detected, whereas no $S_2O_3^{2-}$ and $S_2O_4^{2-}$ could be detected under any experimental conditions. It follows that the $[Fe(edta)]^-$-induced autoxidation of sulfite leads to the formation of some dithionate, however at considerably lower concentration levels than found for the aquated iron(III) autoxidation process.[9,10]

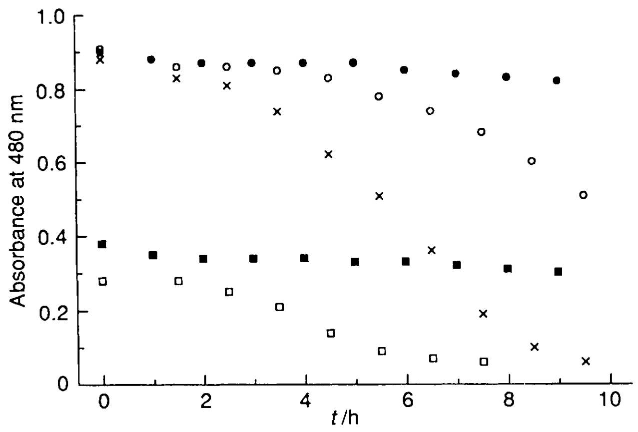


Fig. 6 Absorbance *vs.* time plots for the decomposition of oxygen-saturated solutions of sulfite at 40 °C. Experimental conditions: $[Fe^{III}]_T = 5 \times 10^{-3}$ mol dm^{-3} in all final solutions used for analysis; O_2 was bubbled for 1 min through all the test solutions each hour to ensure saturated conditions throughout the reaction. ○, $[S^{IV}]_T = 0.15$ mol dm^{-3}, pH 7.36; ●, $[S^{IV}]_T = 0.15$ mol dm^{-3}, $[Na_2(H_2edta)] = 0.010$ mol dm^{-3}, pH 7.31; □, $[S^{IV}]_T = 0.075$ mol dm^{-3}, pH 6.8; ■, $[S^{IV}]_T = 0.075$ mol dm^{-3}, $[Na_2(H_2edta)] = 5.0 \times 10^{-3}$ mol dm^{-3}, pH 7.43; X, $[S^{IV}]_T = 0.15$ mol dm^{-3}, pH 7.36, $[Fe^{III}(edta)]^-$ was added to the solution at the start of the reaction

The above results can arise partly from the spontaneous autoxidation of sulfite. Therefore, a series of experiments were performed in which the autoxidation of sulfite was studied in the absence of $[Fe(edta)]^-$, and where the latter was employed as an indicator to follow the oxidation of sulfite. In these experiments the sulfite solutions were heated in a thermostat, samples withdrawn as a function of time and analysed by ion chromatography and *via* the complexation with $[Fe(edta)]^-$ to produce $[Fe(edta)(SO_3)]^{3-}$, which was analysed spectrophotometrically. The oxidation rate strongly depends on the $[S^{IV}]_T$, $[O_2]$ and metal-ion impurities, where the latter play an important role especially at lower $[S^{IV}]_T$. The catalytic effect of metal impurities can be suppressed when $Na_2(H_2edta)$ is added as a stabilizer, *i.e.* it chelates the metal ions and prevents their catalytic activity when an excess is employed.

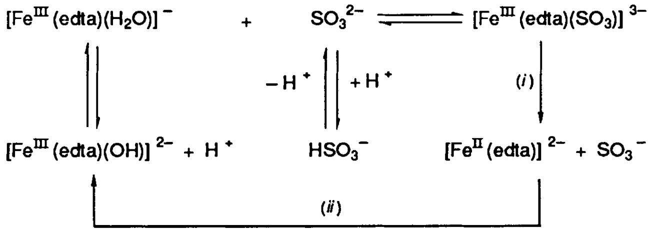
Some typical spectrophotometric results are summarized in Fig. 5. Oxygen-saturated solutions exhibit a rapid oxidation of sulfite, as seen from the decrease in the absorbance of $[Fe(edta)(SO_3)]^{3-}$, especially at lower sulfite concentrations. Addition of a stabilizer such as $Na_2(H_2edta)$ slows down the oxidation process considerably. Addition of 5×10^{-3} mol dm^{-3} $[Fe(edta)]^-$ to 0.15 mol dm^{-3} sulfite at the start of the oxidation reaction caused a significant increase in the decomposition rate (compare the experimental curves denoted by O and X in Fig. 6). Once again these redox reactions are accompanied by a significant decrease in pH which prevents a quantitative analysis of the data. This is ascribed to the oxidation of HSO_3^- to HSO_4^- followed by deprotonation of the latter since it is a considerably stronger acid (pK_a: HSO_4^-, *ca.* 1.9; HSO_3^-, 6.3).[9,16] Similar conclusions regarding the effect of a stabilizer, O_2 and $[Fe(edta)]^-$ were drawn from ion-chromatographic analyses. The only oxidation product that could be detected was SO_4^{2-}, although the samples were also analysed for $S_2O_3^{2-}$, $S_2O_4^{2-}$ and $S_2O_6^{2-}$.

Discussion

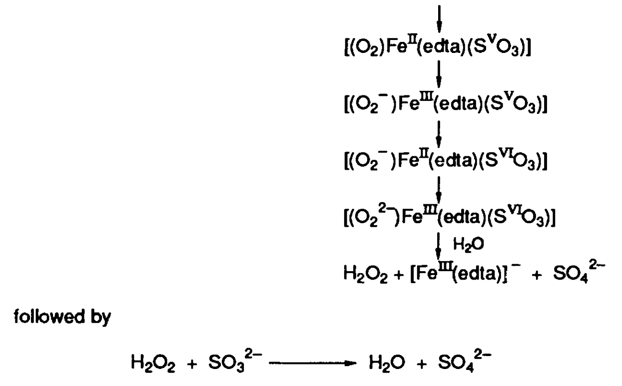
Mechanistic Interpretation.—The results of this investigation once again demonstrate the extreme sensitivity of the spontaneous autoxidation of sulfur(IV) oxides towards catalytic effects of trace metal impurities. The stabilization of such solutions by the addition of edta results in a drastic decrease in the oxidation rate, in agreement with earlier reports.[9,17] This process is generally accepted to follow the Bäckström

$$\begin{aligned}
SO_3^{2-} + M^{n+} &\longrightarrow SO_3^- + M^{(n-1)+}\\
SO_3^- + O_2 &\longrightarrow SO_5^-\\
SO_5^- + SO_3^{2-} &\longrightarrow SO_5^{2-} + SO_3^-\\
SO_5^{2-} + SO_3^{2-} &\longrightarrow 2SO_4^{2-}\\
SO_5^- + SO_5^- &\longrightarrow S_2O_6^{2-} + 2O_2\\
SO_5^- + SO_3^- &\longrightarrow S_2O_6^{2-} + O_2
\end{aligned}$$

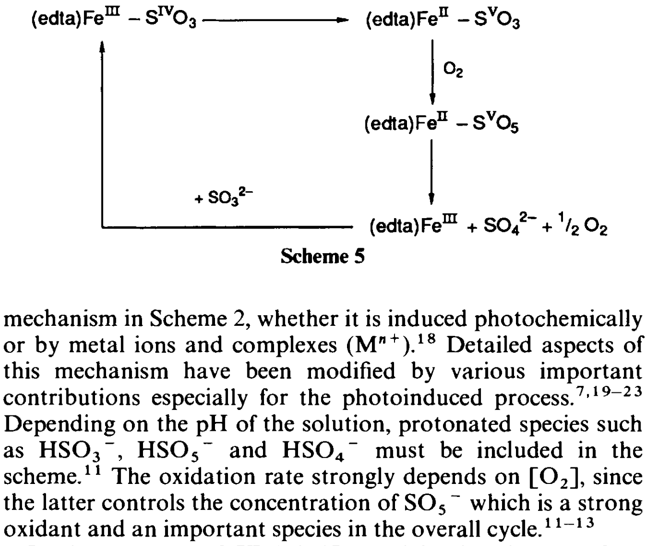
Scheme 2



Scheme 3 (*i*) Electron transfer; (*ii*) $+O_2$, induced by sulfite



Scheme 4



Scheme 5

mechanism in Scheme 2, whether it is induced photochemically or by metal ions and complexes (M^{n+}).[18] Detailed aspects of this mechanism have been modified by various important contributions especially for the photoinduced process.[7,19–23] Depending on the pH of the solution, protonated species such as HSO_3^-, HSO_5^- and HSO_4^- must be included in the scheme.[11] The oxidation rate strongly depends on $[O_2]$, since the latter controls the concentration of SO_5^- which is a strong oxidant and an important species in the overall cycle.[11–13]

In the presence of $[Fe(edta)]^-$ and in the absence of an oxygen-saturated solution, the autoxidation of sulfite is slowed presumably due to the formation of the rather stable $[Fe(edta)(SO_3)]^{3-}$ complex. This complex undergoes intramolecular electron transfer during which Fe^{III} is reduced to Fe^{II} and SO_3^{2-} is oxidized to SO_3^-, the sulfite radical which can undergo the subsequent reactions outlined in Scheme 2. The concentration of $[Fe(edta)(SO_3)]^{3-}$ is controlled by the sulfite concentration and the pH of the solution.[16] The $[Fe^{II}(edta)]^{2-}$ produced is extremely oxygen sensitive and is rapidly oxidized, to $[Fe(edta)]^-$ [24] to complete the cycle shown in Scheme 3. At low oxygen concentrations it is quite likely that sulfite can induce the autoxidation of $[Fe^{II}(edta)]^{2-}$, as found for aquated Fe^{II} and azide complexes of Co^{II} and Mn^{II}.[11–13] The redox reaction is accelerated significantly by the presence of dissolved oxygen, which would account for the initial faster reactions observed in Figs. 1 and 2. The effect of oxygen (Figs. 3–5) must partly be due to a direct interaction with the $[Fe(edta)(SO_3)]^{3-}$ complex, which is also seen in the effect of $[SO_3^{2-}]$ and $[Fe^{III}(edta)^-]$ on the redox process under these conditions (Fig. 4).

To account for these observations it is suggested that O_2 can react with $[Fe^{III}(edta)(SO_3)]^{3-}$ in two possible ways. In the first O_2 binds directly to the iron(III) centre *via* dechelation of the edta ligand induced by the *trans* labilization effect of the co-ordinated sulfite ligand. The $[(O_2)Fe^{III}(edta)(SO_3)]^{3-}$ complex can then undergo a series of intramolecular electron-transfer reactions similar to those suggested before[10] (see Scheme 4). In the second possibility oxygen can attack the co-ordinated sulfite radical to produce co-ordinated SO_5^-, which can simultaneously oxidize Fe^{II} and sulfite as reported elsewhere.[11–13] This mechanism is to some extent related to one suggested for the autoxidation of SO_2 catalysed by metal phthalocyanine complexes[25] and is presented in Scheme 5. It follows from the suggested mechanisms that SO_4^{2-} is the main oxidation product, in agreement with the experimental findings. The cyclic nature of the overall process in Scheme 3 will depend on $[S^{IV}]_T$ and $[O_2]$. This accounts for the apparent stabilization of $[Fe^{III}(edta)(SO_3)]^{3-}$ in the presence of an excess of sulfite as shown in Fig. 4.

Comparison with the Iron(III)-*catalysed Reaction*.—This study was undertaken in an effort to throw more light on the aquated iron(III)-catalysed autoxidation of sulfur(IV) oxides. The redox reactions of the iron(III) system are orders of magnitude faster than those found in this study, from which it follows that the introduction of the edta ligand has helped us to slow down the overall process. The formation of the $[Fe^{III}(edta)(SO_3)]^{3-}$ complex is significantly faster than for the aquated iron(III) species, most probably due to the labilization effect of the multidentate chelate.[16] Our investigation of the iron(III) system was restricted to $pH < 3.0$,[8,10] which could now be increased to $pH \leqslant 9$. The present study revealed clear evidence for the formation and participation of an oxygenated complex, something that could only be suggested on the basis of indirect evidence in the case of the aquated iron(III) system.[9] The latter difficulty was mainly due to the high reactivity of the system. In both systems the complex formation reactions are not influenced by the presence of O_2, although the subsequent redox reactions are very O_2 sensitive. Significant concentrations of $S_2O_6^{2-}$ were detected as oxidation product during the iron(III)-catalysed reaction, whereas almost no $S_2O_6^{2-}$ could be found for the $[Fe^{III}(edta)]^-$ system. This may be related to the acidity range in which these measurements were performed, or to the difference in the co-ordination stoichiometry of the intermediate sulfito complexes. The available evidence points toward 1:2 and 1:3 iron(III)–sulfito complexes under the conditions that only a 1:1 complex is produced with $[Fe^{III}(edta)]$. The presence of more than one sulfite ion or radical on the iron(III) centre may facilitate the direct recombination of two SO_3^- radicals to produce $S_2O_6^{2-}$, as suggested before.[9,10] In terms of the suggested mechanism in Scheme 3, followed by the reactions in Scheme 2, it is understandable that in the presence of O_2 the SO_3^- radical will be scavenged to produce SO_5^- and so prevent the possible formation of $S_2O_6^{2-}$ *via* the recombination of SO_3^-. Similar results were reported elsewhere.[26]

We conclude that the results of this investigation nicely supplement observations and arguments presented for the aquated iron(III) system.[9,10] The redox reaction has become too slow to be of environmental interest, and it is therefore our intention to decrease the number of blocked co-ordinated sites on the iron(III) centre, to move gradually closer to the aquated iron(III) system. We are presently investigating the $[Fe^{III}(hedtra)]$–SO_3^{2-} system, where hedtra = *N*-2-hydroxyethylethylenediaminetriacetate.

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