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Evidence for Multistep Reactions in the Iron(III) Catalysed Autoxidation of Sulphur(IV) Oxides: Possible Steps during Acid Rain Formation

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Kinetic and spectroscopic evidence is presented for the formation and decomposition of iron(m)-sulphur(iv) transients during the iron(m) catalysed autoxidation of sulphur(iv) oxides in aqueous solution, for which four different reaction steps could be identified.

The oxidation of sulphur(IV) oxides, viz. SO₂ (aq), HSO₃⁻, and SO₃²⁻, by dissolved oxygen in aqueous solution, has been studied by numerous investigators for almost a century.¹⁻⁴ The mechanism of the process remains uncertain since the reported rate laws and rate constants are inconsistent, most probably because the reaction is very sensitive to the presence of metal impurities which can act as effective catalysts for the oxidation process. In fact, the uncatalysed reaction proceeds very slowly and cannot contribute significantly toward acid rain formation.¹ The role of metal ions in such processes is not at all well understood.

It has been shown that aquated Fe^{III} ions are promising candidates for the metal-catalysed reaction path. A recent compilation of the available kinetic data predicts that the Fe^{III}-catalysed autoxidation of S^{IV} oxides can contribute up to 80% of the overall aqueous phase oxidation rate at pH 4—7.¹ Although the intimate nature of this process remains very uncertain, a few investigators have suggested the formation of Fe^{III}-S^{IV} transients as precursors in the electron-transfer process to initiate the formation of sulphite radicals.⁵ We have now completed a detailed spectroscopic and kinetic study of the Fe^{III}-catalysed autoxidation reactions of S^{IV} oxides in aqueous solution.⁶ Our results reveal direct evidence for the participation of various Fe^{III}-S^{IV} transients in the oxidation



Figure 1. Schematic representation of absorbance at 390 mm versus time for the reaction of Fe^{III} with S^{IV} oxides [Fe^{III}] = 5×10^{-4} mol dm⁻³; [S^{IV}] = 1×10^{-2} mol dm⁻³; pH = 2.5; temp. = 25 °C; ionic strength = 0.1 M.

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process. The overall reaction occurs in four distinguishable reaction steps which are reported here, together with further details, including experimental, given elsewhere.^{6,7} While our work was in progress, Conklin and Hoffmann³ also reported evidence for the formation of Fe^{III}–S^{IV} transients during the autoxidation process.

Aqueous solutions of $Fe^{III}(CIO_4)_3$ and S^{IV} oxide exhibit equilibria (1) to (6) with the corresponding equilibrium constants under the following conditions selected for our investigations:^{6,7} $5 \times 10^{-4} \leq [Fe^{III}] \leq 6 \times 10^{-3} \text{ mol dm}^{-3}$; $5 \times 10^{-4} \leq [\text{total } S^{IV}] \leq 5 \times 10^{-2} \text{ mol dm}^{-3}$; $1.2 \leq \text{pH} \leq 3.0$; $13 \leq \text{temp.} \leq 40 \text{ °C}$, and 0.1 M ionic strength. Of these species, $Fe(H_2O)_5OH^{2+}$ and HSO₃⁻ are the most reactive under the quoted conditions.

$$Fe(H_2O)_6^{3+} \rightleftharpoons Fe(H_2O)_5OH^{2+} + H^+ K_1 = 6.4 \times 10^{-3} \text{ mol } dm^{-3}$$
(1)

$$Fe(H_2O)_5OH^{2+} \rightleftharpoons Fe(H_2O)_4(OH)_2^+ + H^+ K_2 = 3.2 \times 10^{-4} \text{ mol } dm^{-3}$$
(2)

$$2Fe(H_2O)_5OH^{2+} \rightleftharpoons Fe_2(OH)_2(H_2O)_8^{4+} + 2H_2O K_3 = 1.7 \times 10^2 \text{ mol}^{-1} \text{ dm}^3$$
(3)

$$H_2O + SO_2 \rightleftharpoons HSO_3^- + H^+$$

 $K_4 = 1.3 \times 10^{-2} \text{ mol dm}^{-3}$ (4)

 $HSO_3^- \rightleftharpoons SO_3^{2-} + H^+ \qquad K_5 = 5.0 \times 10^{-7} \text{ mol dm}^{-3}$ (5)

 $2\text{HSO}_3^- \rightleftharpoons \text{S}_2\text{O}_5^{2-} + \text{H}_2\text{O}$ $K_6 = 8.8 \times 10^{-2} \,\text{mol}^{-1} \,\text{dm}^3$ (6)

The reaction of aquated Fe^{III} with $SO_2(aq)/HSO_3^-$ is characterised by the rapid formation of yellow/red Fe^{III_SIV} species. The formation and decomposition of these transients can be followed using stopped-flow and rapid-scan techniques with u.v.-visible detection. A schematic representation of the change in absorbance at 390 mm as a function of reaction time is given in Figure 1, from which it follows that the reaction

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$$Fe(H_{2}O)_{6}^{3} + H^{*} = Fe(H_{2}O)_{5}OH^{2*} + H^{*} + HSO_{3}^{-1} = 600\pm 30 \text{ M}^{-1}$$

$$Fe(H_{2}O)_{5}SO_{3}^{*} = cis-Fe(H_{2}O)_{4}(SO_{3})OH + H^{*} + HSO_{3}^{-1} + HSO_{3}^{-1} = HSO_{3}^{-1} + HSO_{3}^{-1} = K_{1D} = 205\pm 20 \text{ M}^{-1} = K_{1D} = 40\pm 20 \text{ M}^{-1}$$

$$frans-Fe(H_{2}O)_{4}(SO_{3})_{2}^{-1} = cis-Fe(H_{2}O)_{4}(SO_{3})_{2}^{-1} + HSO_{3}^{-1} = HSO_{3}^{-1} + HSO_{3}^{-1} = HSO_{3}^{-1} + HSO_{3}^{-1} = K_{1I} = 3270\pm 80 \text{ M}^{-1}\text{s}^{-1}$$

$$k_{-II} = 6.8\pm 1.0 \text{ s} = K_{1I} = 53\pm 8 \text{ M}^{-1} = K_{-II} \leq 5\text{s}^{-1} = K_{1I} \geq 650 \text{ M}^{-1}$$

$$Fe(H_{2}O)_{3}(SO_{3})_{3}^{3-1} = Scheme 1$$

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occurs in at least four distinguishable, consecutive reaction steps. The first two are ascribed to complex formation, whereas the following two are due to redox decomposition during which Fe^{II} , SO_4^{2-} , and $S_2O_6^{2-}$ are produced. Step I occurs within a couple of milliseconds and only qualitative spectral data could be recorded. A detailed spectroscopic and kinetic study of steps I and II as a function of pH, [Fe^{III}], and [total SIV] revealed that different FeIII-SIV complexes (in the ratio 1:1, 1:2, and 1:3) are produced, for which an overall reaction is given in Scheme 1. Important aspects of the complex formation reactions are: Fe(H₂O)₅OH²⁺ and HSO₃⁻ are the main reactive species;⁸ the 1:2 complex can exist as a cis- or trans-isomer; both bis-sulphito complexes produce the tris-sulphito species; product distribution strongly depends on pH; rate and equilibrium constants were determined at 25 °C (subscripts refer to the steps indicated in Figure 1); the selected species are the simplest possibilities; conjugate acid and base species (i.e. bi-sulphito and hydroxo complexes, respectively) are suggested to participate as well; trans labilisation effects of co-ordinated sulphite account for the significantly faster reaction of the *cis*-bis-sulphito complex, which is also accompanied by a remarkably more positive ΔS^* value than for the trans species;6,7 small spectroscopic and kinetic differences are observed in the presence of oxygen, which could point toward the partial formation of oxosulphito species of the type $(O_2)Fe^{III}(SO_3)_x(H_2O)_y$.

Immediately following the complex formation reactions, at least two decomposition reactions occur (Figure 1) within the time frame of a few minutes. Spectroscopic and ion chromatographic analyses demonstrated that Fe^{II}, S₂O₆²⁻, and SO₄²⁻ are the reaction products. Up to 90% of the FeIII is reduced to Fe^{II} during step III, and the rest during step IV in the absence of O₂. The concentration ratio of $S_4 O_6^{2-}$ to SO_4^{2-} strongly depends on [total S^{IV}], pH, [Fe^{III}], and [O₂]. The ratedetermining step involves intramolecular electron-transfer on the bis- and tris-sulphito complexes to produce Fe^{II} and SO₃-, where the sulphite radical can either undergo a subsequent redox reaction or produce $S_2O_6^{2-}$ through radical recombination. The difference in reactivity of steps III and IV is ascribed to the participation of dimeric iron sulphito complexes, which can be sulphite or hydroxy bridged species expected to be produced by the bis- and tris-sulphito complexes. Such species are expected to be more redox resistant and presumably account for the slower redox step IV. Typical rate constants for the redox decomposition in the absence of O2 vary between 0.05 and 0.14 s⁻¹ at 25 °C for step III, with typical values of around 0.01 s^{-1} under similar conditions for step IV.

The redox decomposition exhibits a remarkable dependence on the oxygen concentration. In the presence of O_2 , an additional reaction step IIIa is observed which is approximately six times faster than step III. This step is ascribed to a catalytic cycle involving oxo-sulphito complexes that can undergo the type of reaction sequence shown in Scheme 2. The peroxo complex can decompose in acidic medium to produce H₂O₂, Fe^{III}(aq), S₂O₆²⁻, and/or SO₄²⁻. The produced Fe^{III} can once again rapidly react with free sulphite to produce sulphito complexes that can start the redox cycle again. In this way Fe^{III} can catalyse the autoxidation process as long as there is O₂ available to reoxidise the bridging iron centre.

Scheme 2



The overall decomposition process can be presented schematically as shown in Scheme 3, which includes both reaction paths in the absence and presence of O_2 , as shown in the lower part of the scheme. The exact composition of the participating species cannot be specified at present, and the subscripts *x*, *y*, and *z* are employed to indicate this uncertainty. The catalytic role of Fe^{III} can therefore be visualised in two ways: in the absence of O_2 , intramolecular electron-transfer initiates the redox process and produces Fe^{II} and SO₃⁻ in a free radical chain mechanism;³ in the presence of O_2 , oxo-sulphito complexes are suggested to account for the enhanced reactivity and Fe^{II} can be reoxidised to Fe^{III} to complete the cycle. In this respect it is important to note that the oxidation of Fe^{III} to Fe^{III} by O₂ is significantly faster in the presence of sulphite, *i.e.* in the case of Fe^{II} sulphito complexes.⁹

An important result of our investigations is the identification of the different reaction steps and the characterisation of their kinetic behaviour. Our findings are generally in good agreement with those reported by Conklin and Hoffmann,³

although there are a number of important differences concerning the nature of the participating species.7 Naturally, a comparison of our data with those reported in the literature for a 'one-step' process, is complicated. Nevertheless, our kinetic data for step IIIa suggests a second-order rate constant of 30 mol⁻¹ dm³ s⁻¹ at 25 °C for the reaction of Fe^{III} with SO_3^{2-} at pH 2.5, compared to a value of $24 \pm 6 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ extrapolated from the recommended literature value under such conditions.1 An important fundamental difference is the fact that the inverse hydrogen ion concentration dependence of the observed rate constant is usually ascribed to sulphite being more reactive than bisulphite. We, however, argue that bisulphite is also highly reactive, but that the inverse acid dependence is due to the higher reactivity of $Fe(H_2O)_5OH^{2+}$ compared to $Fe(H_2O)_6^{3+.8}$ The importance of this difference is especially true for the extrapolation of the available kinetic data to higher pH, where model predictions are usually made, and the importance of the metal catalysed path has been stressed.1 We, therefore, conclude that it is extremely important to measure kinetic data at pH > 3, which is presently underway in our laboratories.10

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