Redox Cycling of Iron in Atmospheric Water: the Important Role of Sulphite

K. Bal Reddy, N. Coichev and R. van Eldik*

Institute for Inorganic Chemistry, University of Witten/Herdecke, Stockumer Straße 10, 5810 Witten, Germany

The sulphite-induced autoxidation of Fe^{II} to Fe^{III} is shown to be an important reaction step in the redox cycling of iron under atmospheric conditions.

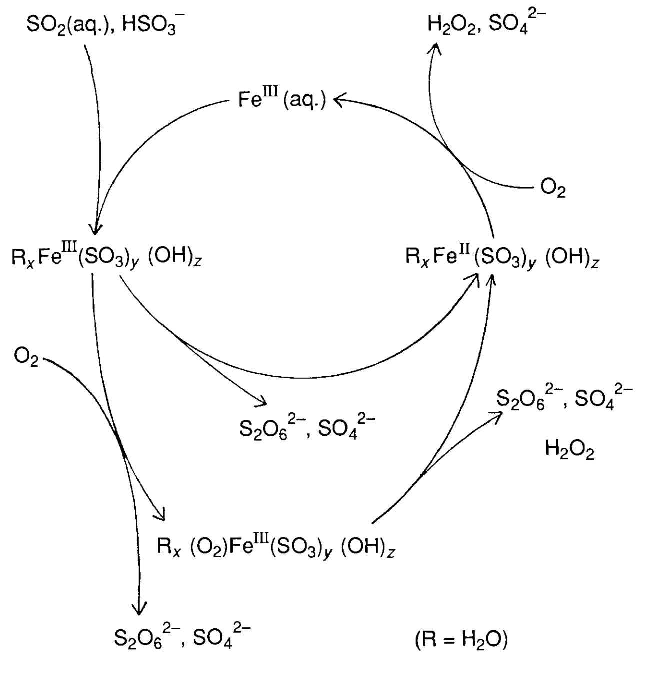
Recently, Behra and Sigg[1] reported evidence for the redox cycling of iron in atmospheric water droplets. They reported that a large fraction of the total iron is present as aquated Fe^{II} with concentrations as high as 200 μmol dm^{-3} in fog water at pH 3.4 to 5.4. A possible mechanism for the Fe^{II}/Fe^{III} cycle includes the reduction of Fe^{III} by sulphite, aldehydes, radicals ($HO_2^{\cdot}/O_2^{-\cdot}$, $RO_2^{\cdot}$), Cu^I, H_2O_2, and photolysis, and the oxidation of Fe^{II} by O_2, O_3, H_2O_2 in the dark and by H_2O_2, $HO_2^{\cdot}/H_2^{-\cdot}$ and $OH^{\cdot}$ in the light.[1–4] The reduction of Fe^{III} by sulphite (or the Fe^{III} catalysed autoxidation of sulphite) has been suggested to play a major role in atmospheric oxidation processes.[5,6] Our own work[6,7] has demonstrated how aquated Fe^{III} can interact with sulphur(IV) oxides to initiate the autoxidation process *via* the formation of $SO_3^{-\cdot}$ radicals (Scheme 1).

A major problem with the suggested redox cycles,[1,6] concerns the reoxidation of Fe^{II} to Fe^{III} to complete the catalytic sequence. The rate of homogeneous oxidation of Fe^{II} by dissolved oxygen is extremely slow at pH < 6[1] and indirect evidence favours a sulphite-induced autoxidation reaction.[8–11] We have recently clearly demonstrated the significance of sulphite-induced autoxidation of Co^{II} in an azide medium[12] and of aquated Fe^{II} species.[13] This process is crucial to the suggested redox cycling of $Fe^{II/III}$ under atmospheric conditions and can account for the catalytic activity of Fe^{II} species.[1,6]

In a typical experiment,[13] Fe^{II} was treated with sulphite in the presence of dissolved oxygen at pH 2–4.† In the presence of an excess of Fe^{II}, *i.e.* at low sulphite concentration, the autocatalytic formation of Fe^{III} is observed spectrophoto-

---

† Experiments were restricted to this pH range due to the precipitation of Fe^{III} hydroxy species at pH > 4.



Scheme 1 The possible catalytic role of $\mathrm{Fe^{III}}$ and its sulphito complexes during the autoxidation of $\mathrm{S^{IV}}$-oxides (ref. 6)

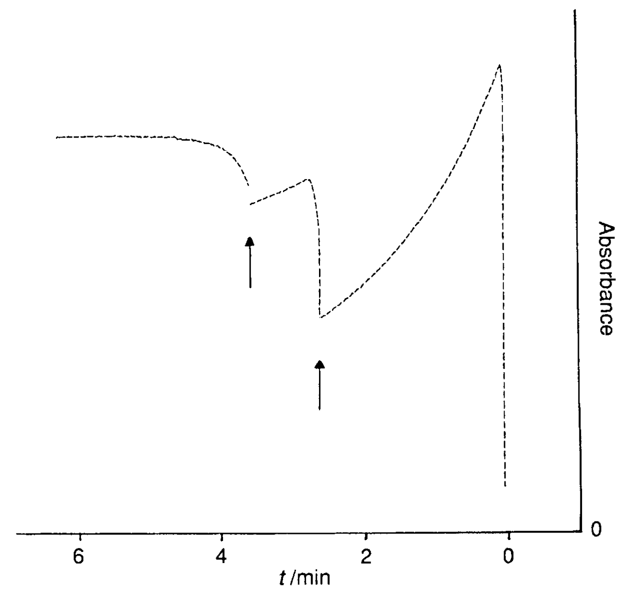


Fig. 1 Absorbance time traces to demonstrate the redox cycling of iron in aqueous solutions. *Conditions*: $[\mathrm{Fe^{II}}] = 1.5 \times 10^{-3}$ mol dm^{-3}; $[\mathrm{Fe^{III}}]_i = 1 \times 10^{-4}$ mol dm^{-3}; pH = 3.0; [total $\mathrm{S^{IV}}$] = 7.5×10^{-4} mol dm^{-3}; arrow indicates introduction of one 10 ml syringe filled with air.

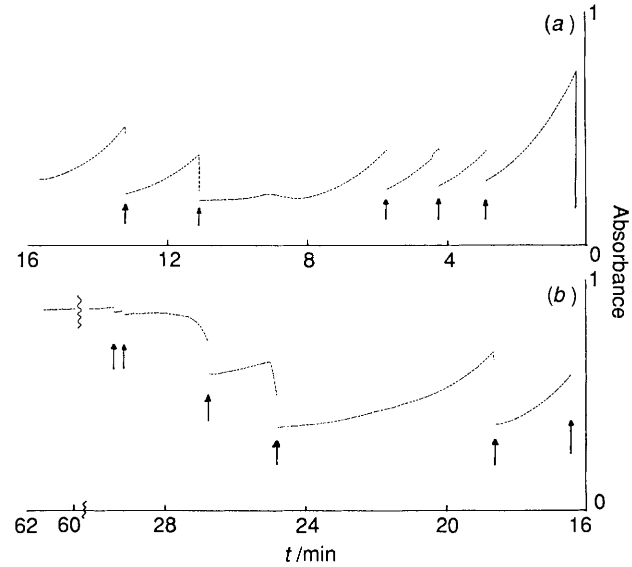


Fig. 2 Absorbance time traces to demonstrate the redox cycling of iron in aqueous solution. *Conditions*: $[\mathrm{Fe^{II}}] = 1.0 \times 10^{-3}$ mol dm^{-3}; $[\mathrm{Fe^{III}}]_i = 1 \times 10^{-4}$ mol dm^{-3}; pH = 3.0; [total $\mathrm{S^{IV}}$] = 3×10^{-3} mol dm^{-3}; arrow indicates introduction of one 10 ml syringe filled with air.

metrically. Addition of $\mathrm{Fe^{III}}$ to the initial solution resolved the autocatalytic behaviour and first-order oxidation of $\mathrm{Fe^{II}}$ to $\mathrm{Fe^{III}}$ was observed. The extent of the oxidation process correlates directly with sulphite concentration. A detailed kinetic study[13] led to the catalytic cycle represented by eqn. (1).[14,15]

$$\mathrm{Fe^{III} + HSO_3^- \xrightarrow{k} Fe^{II} + SO_3^- + H^+}$$
$$\left.\begin{array}{r} \mathrm{SO_3^- + O_2 \rightarrow SO_5^-} \\ \mathrm{SO_5^- + Fe^{II} + H^+ \rightarrow Fe^{III} + HSO_5^-} \\ \mathrm{HSO_5^- + Fe^{II} \rightarrow Fe^{III} + SO_4^- + OH^-} \\ \mathrm{SO_4^- + Fe^{II} \rightarrow Fe^{III} + SO_4^{2-}} \\ \mathrm{SO_5^- + HSO_3^- \rightarrow HSO_5^- + SO_3^-} \\ \mathrm{and \rightarrow SO_4^{2-} + SO_4^- + H^+} \end{array}\right] - \text{fast} \qquad (1)$$

These reactions are followed by a series of product formation and termination reactions[13,16–20] that are irrelevant to the present discussion. This suggested sulphite-induced autoxidation of $\mathrm{Fe^{II}}$ also accounts for all the observations and suggestions reported in the literature.[8–11]

The rate-determining step involves reduction of $\mathrm{Fe^{III}}$ and oxidation of sulphite to produce the sulphite radical $\mathrm{SO_3^{-\bullet}}$, which rapidly reacts with dissolved oxygen to produce $\mathrm{SO_5^-}$ (and $\mathrm{HSO_5^-}$). The latter species are powerful oxidants and oxidize $\mathrm{Fe^{II}}$ to $\mathrm{Fe^{III}}$ in such a way that there is a net increase in the $\mathrm{Fe^{III}}$ concentration. A typical value for k is 318 ± 15 dm^3 mol^{-1} s^{-1} at 25 °C, pH = 3.1 and 0.1 mol dm^{-3} ionic strength.[13] The final reaction products are $\mathrm{Fe^{III}}$ and sulphate, which means that $\mathrm{Fe^{II}}$ and sulphite are oxidized simultaneously (in a ratio 1 : 1.3) by dissolved oxygen under these conditions. The kinetics of the oxidation process are independent of $[\mathrm{Fe^{II}}]$ and $[\mathrm{O_2}]$ provided that these species are present in solution.

In the presence of an excess of sulphite, the rapid formation of $\mathrm{Fe^{III}}$ is followed by a subsequent redox process.[6,7] It follows that the ratio of iron to sulphite concentration will determine whether the final product is $\mathrm{Fe^{II}}$ or $\mathrm{Fe^{III}}$.

The cyclic nature of the redox process is shown schematically in Fig. 1. Under the experimental conditions, the formation of $\mathrm{Fe^{III}}$, as indicated by the absorbance increase at 300 nm,[13] is followed by the reduction of $\mathrm{Fe^{III}}$ by sulphite. If at any stage air is introduced into the solution, an immediate increase in the $\mathrm{Fe^{III}}$ concentration occurs owing to dissolved oxygen. The reduction of $\mathrm{Fe^{III}}$ then ensues provided an excess of sulphite is still available. The final absorbance is due to the partial formation of $\mathrm{Fe^{III}}$ under conditions where all the sulphite has been oxidized to sulphate. When a higher initial sulphite concentration is selected the redox cycle can be repeated many times (see Fig. 2) by introducing air into the solution. It follows that the rapid autoxidation of $\mathrm{Fe^{II}}$ to $\mathrm{Fe^{III}}$ is induced by sulphite and can be repeated in a cyclic way by replacing the dissolved oxygen as long as sulphite is present in the solution. If the final solutions in the experiments described in Figs. 1 and 2 are treated with sulphite, the redox cycle repeats. The results in Fig. 2 demonstrate how, in a cyclic way,

Fe^{III} is reduced by sulphite and reoxidized by oxygen in the presence of sulphite, during which sulphite is oxidized to sulphate in both steps.

The inclusion of the sulphite-induced autoxidation step into the redox cycle of iron under atmospheric conditions is essential to the understanding of the important role played by metal ions in atmospheric oxidation processes. The results of this study demonstrate that Fe^{III} is a stable species in the absence of sulphite, whereas Fe^{II} is rapidly oxidized to Fe^{III} by dissolved oxygen in the presence of sulphite.

The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, Bundesministerium für Forschung und Technologie and Commission of the European Communities. Stipends to K. B. R. (from DAAD) and to N. C. (from FAPESP, Brasilian Foundation) enabled their participation in this work and are kindly acknowledged.

Received, 19th November 1990; Com. 0/05189F

References

1 P. Behra and L. Sigg, *Nature*, 1990, **344**, 419.

2 D. J. Jacob, E. W. Gottlieb and M. J. Prather, *J. Geophys. Res.*, 1989, **94**, 12975.

3 C. J. Weschler, M. L. Mandich and T. E. Graedel, *J. Geophys. Res.*, 1986, **91**, 5189.

4 T. E. Graedel, M. L. Mandich and C. J. Weschler, *J. Geophys. Res.*, 1980, **91**, 5205.

5 M. R. Hoffmann and J. G. Calvert, *Chemical Transformation Modules for Eulerian Acid Deposition Models*, vol. II. *The Aqueous-phase Chemistry*. Interagency agreement DW 930237, 1985.

6 J. Kraft and R. van Eldik, *Atmos. Environ.* 1989, **23**, 2708.

7 J. Kraft and R. van Eldik, *Inorg. Chem.*, 1989, **28**, 2297; 2306.

8 P. Brimblecombe, and D. J. Spedding, *Atmos. Environ.*, 1974, **8**, 937.

9 J. Freiberg, *Atmos. Environ.*, 1975, **9**, 661.

10 A. Huss, P. K. Lim and C. A. Eckert, *J. Phys. Chem.*, 1982, **86**, 4224.

11 T. Sato, T. Gotto, T. Okabe and F. Lawson, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2082.

12 N. Coichev and R. van Eldik, *Inorg. Chem.*, in the press.

13 K. Bal Reddy and R. van Eldik, *Atmos. Environ.*, submitted for publication.

14 B. C. Gilbert and J. K. Stell, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1281.

15 W. J. McElroy and S. J. Waygood, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 2557.

16 E. Hayon, A. Treinin and J. Wilf, *J. Am. Chem. Soc.*, 1972, **94**, 47.

17 A. Hong, D. W. Bahnemann and M. R. Hoffmann, *J. Phys. Chem.*, 1987, **91**, 6245.

18 E. A. Betterton and M. R. Hoffmann, *J. Phys. Chem.*, 1988, **92**, 5962.

19 B. C. Faust, M. R. Hoffmann and D. W. Bahnemann, *J. Phys. Chem.*, 1989, **93**, 6371.

20 U. Deister and P. Warneck, *J. Phys. Chem.*, 1990, **94**, 2191.