

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

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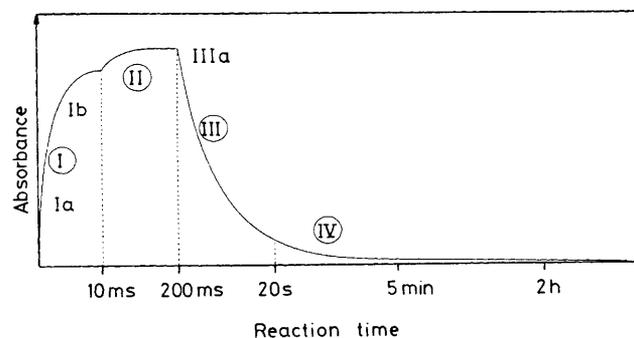
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Kinetic and spectroscopic evidence is presented for the formation and decomposition of iron(III)–sulphur(IV) transients during the iron(III) catalysed autoxidation of sulphur(IV) oxides in aqueous solution, for which four different reaction steps could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

The oxidation of sulphur(IV) oxides, *viz.*  $\text{SO}_2(\text{aq})$ ,  $\text{HSO}_3^-$ , and  $\text{SO}_3^{2-}$ , by dissolved oxygen in aqueous solution, has been studied by numerous investigators for almost a century.<sup>1–4</sup> 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.<sup>1</sup> The role of metal ions in such processes is not at all well understood.

It has been shown that aquated  $\text{Fe}^{\text{III}}$  ions are promising candidates for the metal-catalysed reaction path. A recent compilation of the available kinetic data predicts that the  $\text{Fe}^{\text{III}}$ -catalysed autoxidation of  $\text{S}^{\text{IV}}$  oxides can contribute up to 80% of the overall aqueous phase oxidation rate at pH 4–7.<sup>1</sup> Although the intimate nature of this process remains very uncertain, a few investigators have suggested the formation of  $\text{Fe}^{\text{III}}\text{--S}^{\text{IV}}$  transients as precursors in the electron-transfer process to initiate the formation of sulphite radicals.<sup>5</sup> We have now completed a detailed spectroscopic and kinetic study of

the  $\text{Fe}^{\text{III}}$ -catalysed autoxidation reactions of  $\text{S}^{\text{IV}}$  oxides in aqueous solution.<sup>6</sup> Our results reveal direct evidence for the participation of various  $\text{Fe}^{\text{III}}\text{--S}^{\text{IV}}$  transients in the oxidation



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



