Supplementary information

for

Kinetics and Mechanism of the Oxidation of Sulfur(IV) by Iron(III) at Metal Ion Excess

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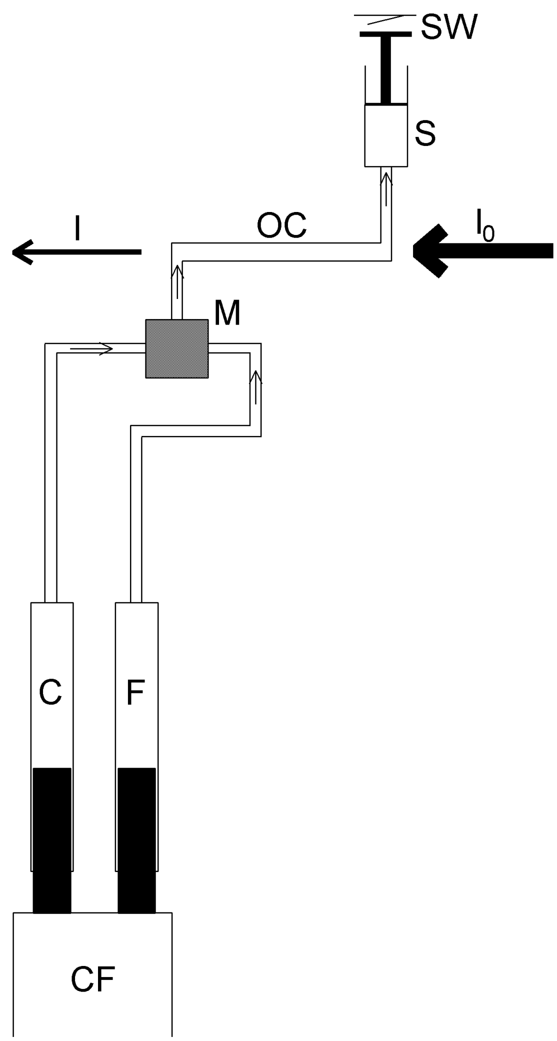

Fig. S1 Flow scheme of the stopped flow instrument. C, F: syringes; CF: ram; M: mixer, OC: optical cell; S: stop syringe; SW microswitch; I_0: incident light beam; I: exiting light beam.

The following method was used to test the possible effects of linear diffusion in stopped-flow instruments at longer time scales:

Syringe F was filled with a suitable solution with a very strongly absorbing component. Syringe C contained a colourless solution (usually the pure solvent). During the test the plunger of syringe C was pushed manually without moving the plunger of syringe F. Thus, the cell (OC) was filled with a colourless solution and the diffusion of the highly absorbing component from syringe C into the cell could be monitored as a function of time. A variation of this method involved the use of a suitable indicator solution in syringe C and some strong acid in syringe F.

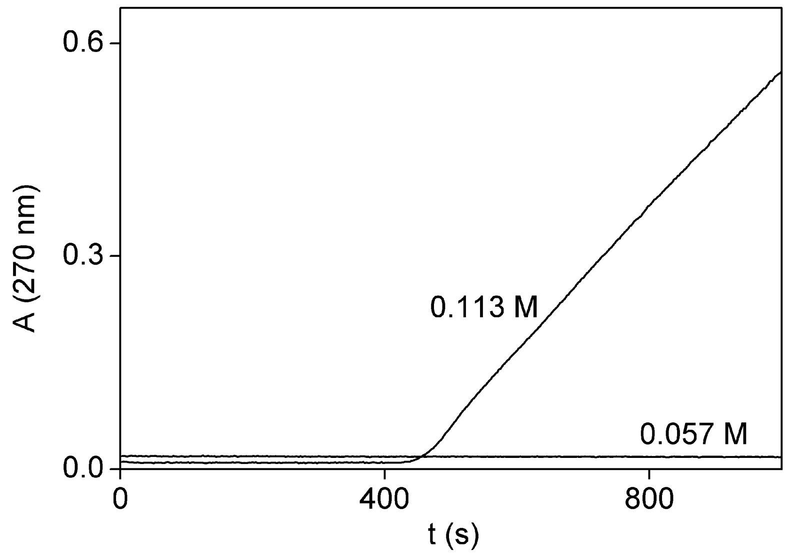

Fig. S2 Diffusion test. Syringe C: distilled water. Syringe F: Acidic solution of $Fe(ClO_4)_3$, concentrations are given inside the graph. T = 10. 0 ° C; optical pathlength 1 cm.

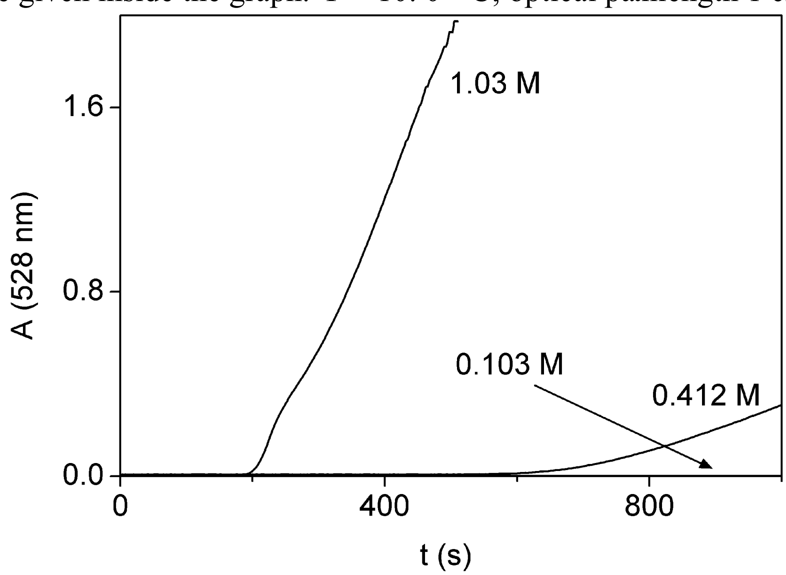

Fig. S3 Diffusion test. Syringe C: distilled water. Syringe F: Mildly acidic solution of $KMnO_4$, concentrations are given inside the graph. T = 25. 0 ° C; optical pathlength 1 cm.

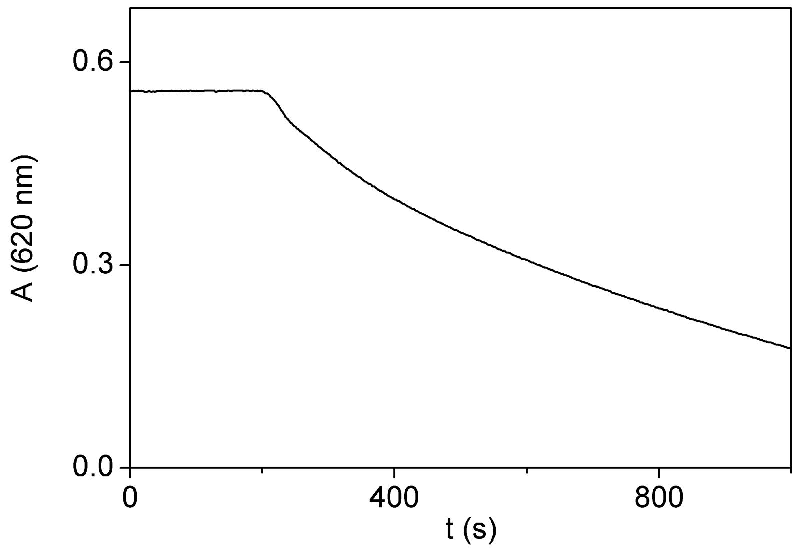

Fig. S4 Diffusion test. Syringe C: 45 mg/l bromocresolgreen solution (neutral). Syringe F: 2 M H_2SO_4. T = 25. 0 °C; optical pathlength 1 cm.

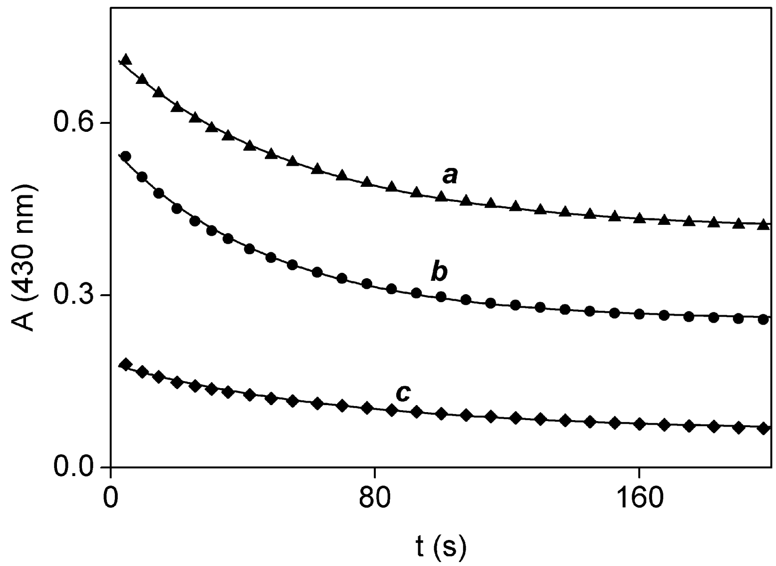

Fig. S5 Measured (markers) and fitted (solid lines) curves in the iron(III) – sulfite ion reaction. [Fe(III)] = 75.0 mM, [S(IV)] = 1.00 mM, pH = 1.44, pH_{Fe} = 1.14 (***a***); [Fe(III)] = 50.0 mM, [S(IV)] = 1.00 mM, pH = 1.51, pH_{Fe} = 1.21 (***b***);[Fe(III)] = 34.8 mM, [S(IV)] = 2.00 mM, pH = 0.95; pH_{Fe} = 0.64 (***c***); T = 25.0 °C; μ = 1.0 M ($NaClO_4$); optical pathlength 1 cm. Only about 7% of the measured points is shown for clarity.

Derivation of equation (3)

Ref. 40 and ref. 41 give an example of the derivation of the full formula for the case of sulfate ion. The same derivation can be used here, i.e. assuming that R1-R6 are fast pre-equilibria, the pseudo first-order rate constant k_{II} can be given by the following formula:

$$k_{II} = k_f + 4k_r[Fe_{mn}] \tag{S1}$$

where k_f and k_r are

$$k_f = \frac{k_{hdr}(1 + [H^+]/K_{a1}) + k_8K_5[S(IV)]}{1 + [H^+]/K_{a1} + K_5[S(IV)]} \tag{S2}$$

$$k_r = k_{-hdr} + \frac{k_{-8}K_FK_H[S(IV)]}{(1 + [H^+]/K_{a1})(K_H + [H^+])^2} \tag{S3}$$

As k_{II} shows no significant dependence on $[Fe_{mn}]$, it can be assumed that $k_f \gg 4k_r[Fe_{mn}]$ in the concentration range of this study. The relationship $1 + [H^+]/K_{a1} \gg K_5[S(IV)]$ also holds. Combining these inequalities with equations (S1)-(S3) gives equation (3).

$$k_{II} \approx k_{hdr} + \frac{k_8K_5[S(IV)]}{1 + [H^+]/K_{a1}} \tag{3}$$