

Supplementary Information

for

Kinetics of the autoxidation of sulfur(IV) catalyzed by peroxodisulfate and silver(I) ions

Éva Dóka, Gábor Lente*, István Fábián

University of Debrecen, Department of Inorganic and Analytical Chemistry, Debrecen 10, P.O.B.
21, Hungary, H-4010

e-mail: lenteg@delfin.unideb.hu Tel: + 36 52 512-900/22373 Fax: + 36 52 489-667

S2

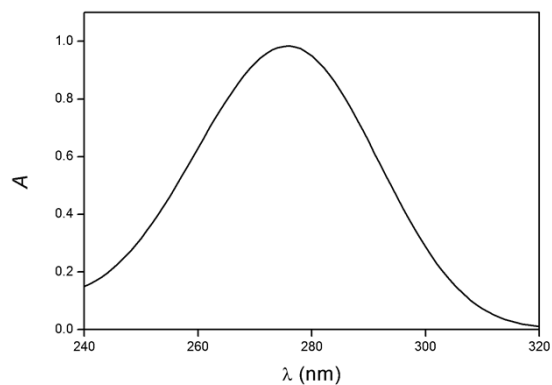


Figure S1. Spectrum of sulfur(IV) in aqueous sulfuric acid solution. $[S(IV)] = 2.7 \text{ mM}$; $[H_2SO_4] = 0.17 \text{ M}$; path length 1.000 cm ; $V = 3.00 \text{ cm}^3$; $T = 25.0 \text{ }^\circ\text{C}$.

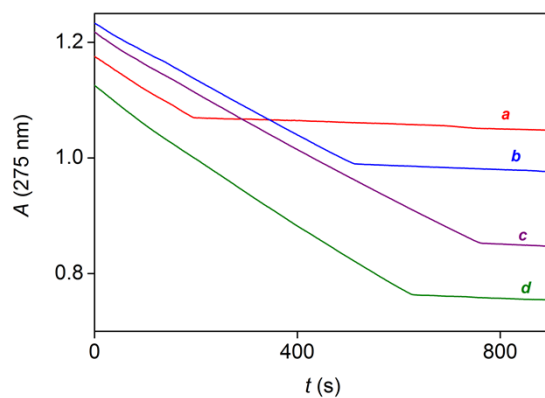


Figure S2. Kinetic curves as a function of the dissolved oxygen concentration in the autoxidation of sulfur(IV). $[S(IV)] = 2.5\text{-}3.0 \text{ mM}$; $[S_2O_8^{2-}] = 3.00 \cdot 10^{-2} \text{ M}$; $[H_2SO_4] = 0.103 \text{ M}$; $[Ag^+] = 0.260 \text{ mM}$; path length 1.000 cm ; $T = 25.0 \text{ }^\circ\text{C}$; $[O_2] = 0.130 \text{ mM}$ (a), 0.209 mM (b), 0.296 mM (c), 0.444 mM (d).

S3

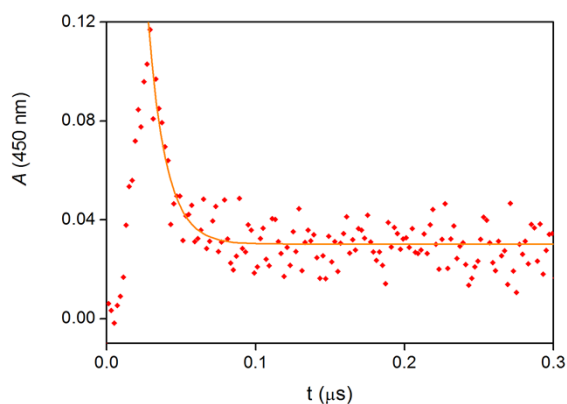


Figure S3. Kinetic trace detected in the reaction between sulfate ion radical and silver(I) ion. $[\text{K}_2\text{S}_2\text{O}_8] = 0.100 \text{ M}$, containing $[\text{AgNO}_3] = 6.12 \text{ mM}$, $\text{pH} = 7$ (unbuffered). The solid line represent the fitted single exponential curve with a pseudo-first order rate constant of $3.76 \times 10^7 \text{ s}^{-1}$.

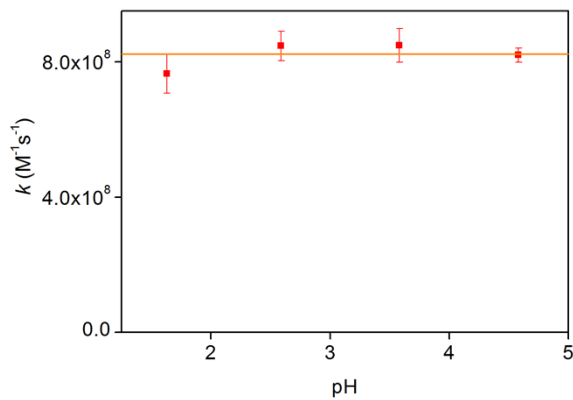


Figure S4. Second order rate constants for the recombination of sulfate ion radical as a function of pH. $[\text{K}_2\text{S}_2\text{O}_8] = 0.100 \text{ M}$, $T = 25 \text{ }^\circ\text{C}$.

Derivation of the rate law

The derivation used the long chain approximation. All the chain carriers (Ag^{2+} , Ag(III) , $\text{SO}_3^{\cdot-}$, $\text{SO}_4^{\cdot-}$, $\text{SO}_5^{\cdot-}$) are assumed to be present at low steady-state concentrations. The rate of initiation or termination steps is assumed to be much lower than the rate of chain propagation steps. These assumptions give two relationships generally used in the derivations of rate laws for chain reactions:

- 1) The rates of all propagation steps are equal to the overall rate of the reaction.
- 2) The rates of the initiation and termination step are equal. If there are more than one initiation and termination steps, the equation hold for the sum of initiation rates and terminations rates.

Based on this background, the rate of oxygen loss, which is identical to the overall rate of reaction, can be given from any of the propagation steps (R2)-(R5). A fortunate choice is selecting step (R3)

$$v = k_3 [\text{Ag}^{2+}]_{\text{ss}} [\text{S(IV)}] \quad (\text{S1})$$

The subscript ss refers to the fact that it is a concentration under steady-state conditions. All reactions in the scheme are second order processes, although reactions (R3), (R5) and (R9) are not elementary steps. In these three steps, the two pH-dependent forms of sulfur(IV) must be taken into account ($\text{H}_2\text{O}\cdot\text{SO}_2$ and HSO_3^-), which are connected through a fast acid-base equilibrium. The rate of reaction (R3) can thus be re-stated

$$v = k_{3A} [\text{Ag}^{2+}]_{\text{ss}} [\text{HSO}_3^{2-}] + k_{3B} [\text{Ag}^{2+}]_{\text{ss}} [\text{H}_2\text{SO}_3] \quad (\text{S2})$$

Taking into account the equilibrium between $\text{H}_2\text{O}\cdot\text{SO}_2$ and HSO_3^- , eqn (S2) can be reformulated as follows:

$$v = \frac{[\text{Ag}^{2+}]_{\text{ss}}[\text{S(IV)}]}{[\text{H}^+] + K_a} (k_{3\text{B}}[\text{H}^+] + k_{3\text{A}}) \quad (\text{S3})$$

Following this example, it is convenient to think of the rate constants of reactions (R3), (R5) and R(9) as quantities with the following pH-dependence:

$$k_3 = \frac{(k_{3\text{B}}[\text{H}^+] + k_{3\text{A}})}{[\text{H}^+] + K_a} \quad (\text{S4})$$

$$k_5 = \frac{(k_{5\text{B}}[\text{H}^+] + k_{5\text{A}})}{[\text{H}^+] + K_a} \quad (\text{S5})$$

$$k_9 = \frac{(k_{9\text{B}}[\text{H}^+] + k_{9\text{A}})}{[\text{H}^+] + K_a} \quad (\text{S6})$$

The rate of initiation and termination must be equal:

$$2k_1[\text{Ag}^+][\text{S}_2\text{O}_8^{2-}] + 2k_8[\text{Ag}^+][\text{Ag(III)}]_{\text{ss}} = 2k_7[\text{Ag}^{2+}]_{\text{ss}}^2 + 2k_6[\text{SO}_4^{\bullet-}]_{\text{ss}}^2 \quad (\text{S7})$$

The steady state concentration of silver(III), which is not a chain carrier but still a minor intermediate, can be given as:

$$[\text{Ag(III)}]_{\text{ss}}[\text{S(IV)}] \frac{k_{9\text{B}}[\text{H}^+] + k_{9\text{A}}}{[\text{H}^+] + K_a} + k_8[\text{Ag(III)}]_{\text{ss}}[\text{Ag}^+] = k_7[\text{Ag}^{2+}]_{\text{ss}}^2 \quad (\text{S8})$$

After rearrangement:

$$[\text{Ag(III)}]_{\text{ss}} = \frac{k_7[\text{Ag}^{2+}]_{\text{ss}}^2}{[\text{S(IV)}] \frac{k_{9\text{B}}[\text{H}^+] + k_{9\text{A}}}{[\text{H}^+] + K_a} + k_8[\text{Ag}^+]} \quad (\text{S9})$$

The steady state concentration of sulfite ion radicals can be given based on the fact that the rates of the chain propagation steps are equal:

$$k_2[\text{SO}_4^{\bullet-}]_{\text{ss}}[\text{Ag}^+] = [\text{Ag}^{2+}]_{\text{ss}}[\text{S(IV)}] \frac{k_{3\text{B}}[\text{H}^+] + k_{3\text{A}}}{[\text{H}^+] + K_a} \quad (\text{S10})$$

S6

The equation giving the concentration of sulfite ion radical is:

$$[\text{SO}_4^{\bullet-}]_{\text{ss}} = \frac{[\text{Ag}^{2+}]_{\text{ss}}[\text{S(IV)}]}{[\text{Ag}^+]} \cdot \frac{k_{3\text{B}}[\text{H}^+] + k_{3\text{A}}}{k_2([\text{H}^+] + K_a)} \quad (\text{S11})$$

Substituting the steady concentration given eqns (S9) and (S11) back into eqn (S7) gives:

$$k_1[\text{Ag}^+][\text{S}_2\text{O}_8^{2-}] + k_8[\text{Ag}^+] \frac{k_7[\text{Ag}^{2+}]_{\text{ss}}^2}{[\text{S(IV)}] \frac{k_{9\text{B}}[\text{H}^+] + k_{9\text{A}}}{k_{\text{p1}}([\text{H}^+] + K_a)} + k_8[\text{Ag}^+]} = \quad (\text{S12})$$

$$= k_7[\text{Ag}^{2+}]_{\text{ss}}^2 + k_6 \frac{[\text{Ag}^{2+}]_{\text{ss}}^2 [\text{S(IV)}]^2}{[\text{Ag}^+]^2} \cdot \left(\frac{k_{3\text{B}}[\text{H}^+] + k_{3\text{A}}}{k_2([\text{H}^+] + K_a)} \right)^2$$

The steady state concentration of the silver(II) ion can be obtained from this equations as:

$$[\text{Ag}^{2+}]_{\text{ss}}^2 = \frac{\frac{k_1}{k_7}[\text{Ag}^+][\text{S}_2\text{O}_8^{2-}]}{1 + \frac{k_6}{k_7} \frac{[\text{S(IV)}]^2}{[\text{Ag}^+]^2} \cdot \left(\frac{k_{3\text{B}}[\text{H}^+] + k_{3\text{A}}}{k_2([\text{H}^+] + K_a)} \right)^2 - \frac{k_8[\text{Ag}^+]}{[\text{S(IV)}] \frac{k_{9\text{B}}[\text{H}^+] + k_{9\text{A}}}{[\text{H}^+] + K_a} + k_8[\text{Ag}^+]}} \quad (\text{S13})$$

Comparing eqns (S3) and (S13) gives the following rate equation:

$$v = \frac{[\text{S(IV)}](k_{3\text{B}}[\text{H}^+] + k_{3\text{A}})}{[\text{H}^+] + K_a} \times \sqrt{\frac{\frac{k_1}{k_7}[\text{Ag}^+][\text{S}_2\text{O}_8^{2-}]}{1 + \frac{k_6}{k_7} \frac{[\text{S(IV)}]^2}{[\text{Ag}^+]^2} \cdot \left(\frac{k_{3\text{B}}[\text{H}^+] + k_{3\text{A}}}{k_2([\text{H}^+] + K_a)} \right)^2 - \frac{k_8[\text{Ag}^+]}{[\text{S(IV)}] \frac{k_{9\text{B}}[\text{H}^+] + k_{9\text{A}}}{[\text{H}^+] + K_a} + k_8[\text{Ag}^+]}}}} \quad (\text{S14})$$