Supporting Information

for

Kinetics and Mechanism of the Photoinitiated Autoxidation of Sulfur(IV) in the Presence of Iodide Ion

Ildikó Kerezsi, Gábor Lente and István Fábián*

University of Debrecen, Department of Inorganic and Analytical Chemistry, Debrecen 10,

P.O.B. 21, Hungary, H-4010; e-mail: ifabian@delfin.unideb.hu



Figure S01. $[\Gamma$ -catalyzed autoxidation of sulfite ion during the disproportionation of dithionate ion. $[S_2O_6^{2^-}] = 0.0689 \text{ M}, [H_2SO_4] = 0.575 \text{ M}, [I^-] = 0.10 \text{ mM}, [O_2]_0 = 0.23 \text{ mM}, T = 75 \text{ °C}.$ The existence of the region where $H_2O \cdot SO_2$ and O_2 are present simultaneously implies that light absorption of $H_2O \cdot SO_2$ is important for initiating the reaction.



Figure S02. Effect of light on the dissolved oxygen concentration in the presence of $H_2O \cdot SO_2$ and I^- . *a*: low-intensity UV-light turned on; *b*: high intensity UV-light turned on; *c*: curve without illumination; *d*: addition of iodide ion. $[I^-] = 0.20$ mM; [S(IV)] = 2.0 mM; $[HCIO_4] = 0.10$ M; T = 25 °C.



Figure S03. Spectra of $H_2O \cdot SO_2$ and I⁻ (left axis). Spectral properties of the chloroform filter (right axis). T = 25.0 °C.



Figure S04. Kinetic traces measured during the photoinitiated and iodide catalyzed autoxidation of sulfur(IV). $[I^-] = 0.20 \text{ mM}$; [S(IV)] = 2.00 mM; $[O_2] = 0.20 \text{ mM}$; $[H_2SO_4] = 0.575 \text{ M}$; path length 1.000 cm; $V = 3.00 \text{ cm}^3$; T = 25.0 °C; $t_i = 1 \text{ s}$; $t_d = 0 \text{ s}$ (*a*), 2 s (*b*), 20 s (*c*).



Figure S05. Initial rates as a function of illumination ratio during the photoinitiated and iodide-catalyzed autoxidation of sulfur(IV). $[I^-] = 0.20 \text{ mM}$; [S(IV)] = 2.00 mM; $[O_2] = 0.20 \text{ mM}$; $[H_2SO_4] = 0.575 \text{ M}$; path length 1.000 cm; $V = 3.00 \text{ cm}^3$; T = 25.0 °C. The straight line drawn would be the expected place of all points if the progress of the reaction were strictly proportional to the time of illumination. In the experiments, an illuminated period is followed by a dark period. t_i is the length of the illumination period.



Figure S06. Spectral properties of nitrate solution filters used in the light intensity studies. Concentrations: 0.5 M (highest transmissions), 1.0 M, 1.5 M, 2.6 M (lowest transmissions). T = 25.0 °C.



Figure S07. Initial rate with chloroform filter (diamonds) and without the filter (circles) as a function of iodide ion concentration during the photoinitiated and iodide-catalyzed autoxidation of sulfur(IV). [S(IV)] = 1.00 mM (squares); [H₂SO₄] = 0.575 M; V = 3.00 cm³; T = 25.0 °C.



Figure S08. Dissolved oxygen concentration and the effect of light in the reaction of peroxomonosulfate ion and sulfur(IV). *a*: addition of sulfur(IV); *b*: UV light turned on; *c*: UV light turned off. $[S(IV)] = 2.0 \text{ mM}; [HSO_5^-] = 0.60 \text{ mM}; [H_2SO_4] = 1.00 \text{ M}; T = 25.0 \text{ °C}.$



Figure S09. Dissolved oxygen concentration and in the reaction between peroxomonosulfate ion and sulfur(IV) in the presence of iodide ion. *a*: addition of peroxomonosulfate ion; $[S(IV)] = 2.0 \text{ mM}; [HSO_5^-] = 0.10 \text{ mM}; [I^-] = 1.00 \text{ mM}; [H_2SO_4] = 0.10 \text{ M}; T = 25.0 \text{ °C}.$



Figure S10. Fitted initial rates as a function of measured initial rates during the photoinitiated and iodide-catalyzed autoxidation of sulfur(IV). The straight line corresponds to the hypothetical 'perfect fit', when all fitted values are exactly equal to the measured one. $[H_2SO_4] = 0.575 \text{ M}; V = 3.00 \text{ cm}^3; T = 25.0 \text{ °C}.$

Derivation of equation 8

Eq 8 can be derived starting from eqs 4 and 7:

$$2a_{I}N_{I} + 2a_{2}N_{s} = 2k_{I0}[SO_{4}^{-}]^{2} + 2k_{II}[SO_{4}^{-}][I_{2}^{-}] + 2k_{I2}[I_{2}^{-}]^{2}$$
(4)

$$v = k_4 [SO_4^{-1}][I^{-1}]$$

$$\tag{7}$$

Let A denote the sum of the concentrations of I_2^{-1} and I

$$A = \begin{bmatrix} \mathbf{I}_2^{-1} \end{bmatrix} + \begin{bmatrix} \mathbf{I}_2 \end{bmatrix}$$
(S1)

From the equilibrium of reaction R8:

$$[I^{-}] = \frac{[I_{2}^{-}]}{K_{g}[I^{-}]}$$
(S2)

Applying the long chain approximation and steady-state assumption simultaneously for $I_2^{-\cdot}$ and I gives (reactions R4, R5, and R9 are involved)

$$0 = \frac{dA}{dt} = k_4 [SO_4^{-1}][I^-] - k_{5a}[I^-][H_2O \cdot SO_2] - k_{5b}[I^-][HSO_3^-] - k_{9a}[I_2^{-1}][H_2O \cdot SO_2] - k_{9b}[I_2^{-1}][HSO_3^-]$$
(S3)

Combining eqs. S3 and S2 gives the steady-state concentration of I_2^{--} :

$$[I_{2}^{-}] = \frac{k_{4}K[SO_{4}^{-}][I^{-}]^{2}}{k_{5a}[H_{2}O \cdot SO_{2}] + k_{5b}[HSO_{3}^{-}] + k_{9a}K[I^{-}][H_{2}O \cdot SO_{2}] + k_{9b}K[I^{-}][HSO_{3}^{-}]}$$
(S4)

From the pre-equilibrium treatment, the concentrations of $H_2O \cdot SO_2$ and HSO_3^- can be obtained from the analytical concentration of sulfur(IV):

$$[H_{2}O \cdot SO_{2}] = \frac{[H^{+}]}{[H^{+}] + K_{a}}[S(IV)]$$
(S5)

$$[\mathrm{HSO}_{3}^{-}] = \frac{K_{a}}{[\mathrm{H}^{+}] + K_{a}} [\mathrm{S}(\mathrm{IV})]$$
(S6)

Simplifying eq. S4 by the introduction of p_1 and p_2 (eqs. 9 and 10 in the manuscript) and using eq. 7 gives:

$$[I_2^-] = \frac{v[I^-]}{p_1[S(IV)] + p_2[I^-][S(IV)]}$$
(S7)

Substituting this steady-state concentration value into eq 4. gives:

$$a_{1}N_{I} + a_{2}N_{S} = \frac{k_{10}v^{2}}{(k_{4}[I_{2}^{-}])^{2}} + \frac{k_{11}v^{2}}{k_{4}(p_{1}[S(IV)] + p_{2}[I^{-}][S(IV)])} + \frac{k_{12}v^{2}[I^{-}]^{2}}{(p_{1}[S(IV)] + p_{2}[I^{-}][S(IV)])^{2}}$$
(S8)

Upon rearrangement, eq. 8 is obtained:

$$v = \sqrt{\frac{(a_1 N_1 + a_2 N_S) k_4^2 [I^-]^2 (p_1 [S(IV)] + p_2 [I^-] [S(IV)])^2}{k_{10} (p_1 [S(IV)] + p_2 [I^-] [S(IV)])^2 + k_{11} k_4 [I^-]^2 (p_1 [S(IV)] + p_2 [I^-] [S(IV)]) + k_{12} k_4^2 [I^-]^4}}$$
(8)