Aqueous Reactions of Sulfate Radical-Anions with Nitrophenols in Atmospheric Context

Supporting Information

Krzysztof J. Rudziński and Rafał Szmigielski

Contents

1. Generation of sulfate-radical-anions
   a. Table S1. Chain mechanism of $S^{IV}$ autoxidation catalyzed by $Fe^{III}$

2. Experimental results for 2-NP, 3-NP, 2,4-DNP and 2,4,6-TNP
   a. Figure S1. Concentration of oxygen recorded during autoxidation of NaHSO$_3$ solution in the presence of nitrophenols
   b. Figure S2. Linear plots of reciprocal quasi-stationary rates for autoxidation of S(IV) in the presence of nitrophenols

3. Correction of the rate constants for diffusional limitations
   a. Table S2. Properties of nitrophenols and sulfate radical anion

4. Atmospheric significance
   a. Figure S3. The ratio of the gas-phase and the aqueous-phase conversions of 2-NP by OH and NO$_3$ radicals

5. References
1. Generation of sulfate radical-anions

Sulfate radical-anions were generation during autoxidation of sulfite anions catalyzed by Fe$^{III}$ cations. The detailed mechanism of autoxidation was presented by Ziajka and Rudzinski [1] and is recalled here, in Table 0.

**Table S1.** Chain mechanism of S$^{IV}$ autoxidation catalyzed by Fe$^{III}$.

<table>
<thead>
<tr>
<th>Nr</th>
<th>Reaction</th>
<th>Rate constant, 25 °C</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>M$^{-1}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Fe$^{III}$ OH + HSO$_3^-$ → Fe$^{II}$ + SO$_4^{2-}$ + H$_2$O</td>
<td>30</td>
<td>[2]</td>
</tr>
<tr>
<td></td>
<td><strong>Chain initiation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>SO$_4^{2-}$ + O$_2$ → SO$_5^{2-}$</td>
<td>1.5×10$^9$</td>
<td>[3]</td>
</tr>
<tr>
<td>3</td>
<td>SO$_4^{2-}$ + HSO$_3^-$ → HSO$_5^{2-}$ + SO$_3^{2-}$</td>
<td>8.6×10$^9$, 2.5×10$^4$</td>
<td>[4,5]</td>
</tr>
<tr>
<td>4</td>
<td>SO$_4^{2-}$ + HSO$_3^-$ → SO$_5^{2-}$ + SO$_3^{2-}$ + H$^+$</td>
<td>3.6×10$^8$, 2.5×10$^4$</td>
<td>[4,5]</td>
</tr>
<tr>
<td>5</td>
<td>SO$_4^{2-}$ + HSO$_3^-$ → SO$_5^{2-}$ + SO$_3^{2-}$ + H$^+$</td>
<td>3.1×10$^9$, 3.4×10$^8$, 2×10$^9$</td>
<td>[4-6]</td>
</tr>
<tr>
<td>6</td>
<td>SO$_4^{2-}$ + SO$_3^{2-}$ → SO$_5^{2-}$ + SO$_4^{2-}$ + O$_2$</td>
<td>5.2×10$^8$, 2.2×10$^8$</td>
<td>[5,7,8]</td>
</tr>
<tr>
<td></td>
<td><strong>Formation of sulfate</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>HSO$_3^-$ + HSO$_3^-$ → SO$_4^{2-}$ + SO$_3^{2-}$ + 2 H$^+$</td>
<td>7.14×10$^6$</td>
<td>[9]</td>
</tr>
<tr>
<td></td>
<td><strong>Regeneration of the initiator</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>SO$_3^{2-}$ + Fe$^{II}$ → SO$_5^{2-}$ + Fe$^{III}$</td>
<td>4.6×10$^6$, 3.2×10$^6$</td>
<td>[10,11]</td>
</tr>
<tr>
<td>9</td>
<td>SO$_3^{2-}$ + Fe$^{II}$ → SO$_5^{2-}$ + Fe$^{III}$ (OH$^-$)</td>
<td>3.6×10$^4$</td>
<td>[11]</td>
</tr>
<tr>
<td>10</td>
<td>SO$_3^{2-}$ + Fe$^{II}$ → SO$_5^{2-}$ + Fe$^{III}$</td>
<td>3.5×10$^7$</td>
<td>[2]</td>
</tr>
<tr>
<td>11</td>
<td>HSO$_3^-$ + Fe$^{II}$ → SO$_4^{2-}$ + Fe$^{III}$ (OH)</td>
<td>3.4×10$^4$</td>
<td>[10]</td>
</tr>
<tr>
<td></td>
<td><strong>Termination</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>SO$_3^{2-}$ + SO$_3^{2-}$ → S$_2$O$_5^{2-}$</td>
<td>1.6×10$^8$</td>
<td>[5]</td>
</tr>
<tr>
<td>13</td>
<td>SO$_3^{2-}$ + SO$_3^{2-}$ → S$_2$O$_5^{2-}$</td>
<td>1.6×10$^8$, 4.6×10$^8$</td>
<td>[7,8,12]</td>
</tr>
<tr>
<td>14</td>
<td>SO$_3^{2-}$ + SO$_3^{2-}$ → S$_2$O$_5^{2-}$ + O$_2$</td>
<td>1.3×10$^8$, 4.8×10$^7$</td>
<td>[3,6,7]</td>
</tr>
</tbody>
</table>

2. Experimental results for 2-NP, 3-NP, 2,4-DNP and 2,4,6-TNP

Experimental runs with autoxidation of S(IV) in the presence of 2-nitrophenol (2-NP), 3-nitrophenol (3-NP), 2,4-dinitrophenol (2,4-DNP) and 2,4,6-trinitrophenol (2,4,6-TNP). Plots in Figure S1 show consumption of oxygen in reacting solutions.
Fig. S1. Concentration of oxygen recorded during autoxidation of NaHSO₃ solution in the presence of: (a) 2-NP; (b) 3-NP; (c) 2,4-DNP and (d) 2,4,6-TNP at various initial concentrations.
Figure S2 shows the dependence of reciprocal rates of autoxidation on the initial concentrations of 2-NP, 3-NP, 2,4-DNP and 2,4,6-TNP. All dependencies are linear. The corresponding slopes of linear relations are given on the plots. The quasi-stationary rates of autoxidation were obtained from plots in Fig. S1.

**Fig. S2.** Linear plots of reciprocal quasi-stationary rates for autoxidation of S(IV) in the presence of: (a) 2-NP; (b) and (d) 2,4,6-TNP at various initial concentrations.

### 3. Correction of the rate constants for diffusional limitations

The observed second order rate constants were corrected for diffusional limitations using a simple resistance-in-series model:

\[
k_{\text{observed}}^{-1} = k_{\text{reaction}}^{-1} + k_{\text{diffusion}}^{-1}
\]

\[k_{\text{diffusion}} = 4\pi(D_A + D_B)(r_A + r_B)N \times 10^3
\]

(S1 a.k.a 4))

(S2 a.k.a 5)
where all \( k \) are second order rate constants (M\(^{-1}\) s\(^{-1}\)), \( D \) are diffusion coefficients of reactants A and B (m\(^2\) s\(^{-1}\)), \( r \) are reaction radii of reactant molecules A and B (m), and \( N \) is the Avogadro number.

Diffusion coefficients of nitrophenols in aqueous solutions were calculated using the method of Wilke and Chang [13]:

\[
D = 7.4 \times 10^{-12} \frac{(XM)^{0.5}}{V_m^3 \eta} \text{ m}^2 \text{ s}^{-1},
\]

(S3)

where: \( X = 2.6 \) for water; \( M \) – molar mass of a diffusing compound, g mol\(^{-1}\); \( T \) – temperature, K; \( V_m \) – molar volume of a diffusing compound, cm\(^3\) mole\(^{-1}\); \( \eta \) – viscosity of the solvent, mPa s or 0.01 g cm\(^{-1}\) s\(^{-1}\) (0.8891 mPa s for water at 298 K).

Molar volumes of nitrophenols were calculated using the method of Tyn and Calus [14,15]:

\[
V_m = 0.285V_c^{1.048} \text{ cm}^3 \text{ mole}^{-1}
\]

(S4)

where: \( V_c \) is a critical volume, cm\(^3\) mole\(^{-1}\), which can be estimated using the method of group contributions by Joback and Reid [16].

Molecular radii of nitrophenols were calculated using Equation (S5). The values of \( V_c, V_m, D \) and \( r \) are collected in Table S1.

\[
r = \sqrt[3]{\frac{3V_m}{4\pi N}}.
\]

(S5)

### Table S2. Properties of nitrophenols and sulfate radical anion

<table>
<thead>
<tr>
<th></th>
<th>2-NP</th>
<th>3-NP</th>
<th>4-NP</th>
<th>2,4-DNP</th>
<th>2,4,6-TNP</th>
<th>SO(_4)(^{2-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_c ) cm(^3) mol(^{-1})</td>
<td>370.5</td>
<td>370.5</td>
<td>370.5</td>
<td>432.5</td>
<td>534.5</td>
<td></td>
</tr>
<tr>
<td>( V_m ) cm(^3) mol(^{-1})</td>
<td>140.3</td>
<td>140.3</td>
<td>140.3</td>
<td>165.0</td>
<td>205.9</td>
<td></td>
</tr>
<tr>
<td>( D ) m(^2) s(^{-1})</td>
<td>2.429\times10^{-9}</td>
<td>2.429\times10^{-9}</td>
<td>2.429\times10^{-9}</td>
<td>2.536\times10^{-9}</td>
<td>2.476\times10^{-9}</td>
<td>1.06\times10^{-9} ( A )</td>
</tr>
<tr>
<td>( r ) m</td>
<td>3.817\times10^{-10}</td>
<td>3.817\times10^{-10}</td>
<td>3.817\times10^{-10}</td>
<td>4.029\times10^{-10}</td>
<td>4.339\times10^{-10}</td>
<td>3.8\times10^{-10} ( B )</td>
</tr>
</tbody>
</table>

\( A \) – the same as for S:O\(_4\)\(^{2-}\) [17]; \( B \) – the same as for hydrated sulfate ion [18].

### 4. Atmospheric significance

Rate of conversion of a NP by a reactant X in the gas phase (\( r_{x,g} \)) was compared to the rate of conversion of this NP by sulfate radical anions in the aqueous phase contained within the gas phase (\( r_{SO_4,aq} \times (\omega) \)):

\[
\frac{r_{x,g}}{r_{SO_4,aq} \times (\omega)} = \frac{k_{x,g}}{k_{SO_4,aq} H_d \Delta H_d \Delta NP} \frac{[X]_{aq}}{[SO_4^{2-}]}.
\]

(S6 a.k.a 10)

where: \( \omega \) m\(^3\) m\(^{-2}\) is the atmospheric liquid water contents; \( k_{x,g} \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) is the rate constant for the reaction of X with NP in the gas phase; \( k_{SO_4,aq} \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) is the rate constant for the reaction of SO\(_4^{2-}\) with NP in the aqueous phase; \( H_d \) is the dimensionless Henry’s constant for X or for NP defined by Equations (S7); \([X]_{aq}\) and \([SO_4^{2-}]_{aq}\) are the aqueous-phase concentrations of X and SO\(_4^{2-}\).

\[
H_d = \frac{HRT}{H} \text{ if } H \text{ is in mol dm}^{-3} \text{atm}^{-1}
\]

(S7a)

\[
H_d = \frac{HRT \rho}{H} \text{ if } H \text{ is in mol kg}^{-1} \text{atm}^{-1},
\]

(S7b)

where \( R \) is the gas constant, atm dm\(^3\) mol\(^{-1}\) K\(^{-1}\); \( \rho \) is the density of the solution, practically equal to the density of solvent.
Fig. S3. The ratio of the gas-phase and the aqueous-phase conversions of 2-NP by OH and NO₃ radicals (the gas-phase and aqueous-phase concentrations are bound by Henry’s equilibria).

References


© 2019 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license ([http://creativecommons.org/licenses/by/4.0/](http://creativecommons.org/licenses/by/4.0/)).