Supporting information

Aqueous phase oxidation of bisulfite influenced by nitrate photolysis

Lu Chen\textsuperscript{a}, Lingdong Kong\textsuperscript{a,b,*}, Songying Tong\textsuperscript{a}, Kejing Yang\textsuperscript{a}, Shengyan Jin\textsuperscript{a}, Chao Wang\textsuperscript{a}, Lin Wang\textsuperscript{a}

\textsuperscript{a} Department of Environmental Science & Engineering, Jiangwan Campus, Fudan University, No. 2205 Songhu Road, Shanghai, 200438, China.
\textsuperscript{b} Institute of Eco-Chongming, East China Normal University, No. 3663 Northern Zhongshan Road, Shanghai 200062, China.

\*Corresponding author: ldkong@fudan.edu.cn (L. Kong).
Contents:

Text S1. Calculation of the average rate of sulfate formation..................................................3

Text S2. Reactions of NH$_4^+$ to promote the formation of sulfate........................................4

Text S3. Calculation of the photon fluxes (I$_\lambda$) under 313 nm UV irradiation.........................5

Text S4. Calculation of ·OH quantum yield...............................................................................6

Text S5. Detection of hydrogen peroxide...................................................................................8

Figure S1. Effect of NH$_4^+$ on nitrate photolysis and sulfate formation.................................9

Figure S2. First-order photodegradation of 2-nitrobenzaldehyde (2NB) under 313 nm UV irradiation......................................................................................................................10

Figure S3. Formation of ·OH during nitrate photolysis at different pH.....................................11

Figure S4. Standard curve of hydrogen peroxide......................................................................12

Figure S5. H$_2$O$_2$ produced during the photochemical reaction of nitrate under 313 nm irradiation.......................................................................................................................................13

Figure S6. Effect of light intensity on aqueous-phase formation of sulfate............................14

References
Text S1. Calculation of the average rate of sulfate formation

\[ \text{Sulfate production} = C_t - C_0 \]

The average rate of sulfate formation = \( \frac{\text{Sulfate production}}{\text{Reaction time}} \)

\( C_t \): sulfate content after reaction;

\( C_0 \): initial sulfate content;

Reaction time: 120 min.

Table S1. Sulfate production and average formation rate

| Line | Sulfate production (μM) | Average rate of sulfate formation (μM·min\(^{-1}\)) |
|------|-------------------------|---------------------------------------------------|
| S1: NH\(_4\)NO\(_3\)+Light (Xe lamp) +Air | 1629.69 | 13.58 |
| S'1: NH\(_4\)NO\(_3\)+Light (UV) +Air | 7656.56 | 63.80 |
| S2: NH\(_4\)NO\(_3\)+Dark+Air | 1560.16 | 13.00 |
| S3: Dark + Air | 1048.44 | 8.74 |
| S4: NH\(_4\)NO\(_3\)+Light (Xe lamp) +N\(_2\) | 837.76 | 6.98 |
| S'4: NH\(_4\)NO\(_3\) + Light (UV)+N\(_2\) | 1430.94 | 11.92 |
| S5: Light (Xe lamp) +N\(_2\) | 250.78 | 2.09 |
Text S2. Reactions of NH$_4^+$ to promote the formation of sulfate

\[
\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3\text{O}^+ + \text{H}^+ \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \quad \text{(RS1)}
\]

\[
6 \text{NO}_2(\text{g}) + 8 \text{NH}_3\text{O}(\text{aq}) = 7 \text{N}_2(\text{g}) + 20 \text{H}_2\text{O}(\text{l}) \quad \text{(RS2)}
\]

\[
\Delta G_{\text{S1}} = -2942.56 \text{ kJ} \cdot \text{mol}^{-1}
\]

\[
5 \text{NO}_2(\text{g}) + 2 \text{NH}_3\text{O}(\text{aq}) = 7 \text{NO}(\text{g}) + 5 \text{H}_2\text{O}(\text{l}) \quad \text{(RS3)}
\]

\[
\Delta G_{\text{S2}} = -301.99 \text{ kJ} \cdot \text{mol}^{-1}
\]

\[
6 \text{NO}_2(\text{g}) + 8 \text{NH}_3(\text{aq}) = 7 \text{N}_2(\text{g}) + 12 \text{H}_2\text{O}(\text{l}) \quad \text{(RS4)}
\]

\[
\Delta G_{\text{S3}} = -2942.08 \text{ kJ} \cdot \text{mol}^{-1}
\]

\[
5 \text{NO}_2(\text{g}) + 2 \text{NH}_3(\text{aq}) = 7 \text{NO}(\text{g}) + 3 \text{H}_2\text{O}(\text{l}) \quad \text{(RS5)}
\]

\[
\Delta G_{\text{S4}} = -301.87 \text{ kJ} \cdot \text{mol}^{-1}
\]
Text S3. Calculation of the photon fluxes ($I_\lambda$) under 313 nm UV irradiation

**Materials.** Aqueous stock solutions of 2-nitrobenzaldehyde (2NB, 99%, Aladdin) was prepared by dissolving 2NB in Milli-Q water.

The photon fluxes ($I_\lambda$) in the sample chamber was measured by using 500 μM 2NB of the same volume as the NH$_4$NO$_3$ samples as a chemical actinometer. For the low light-absorbing conditions of our actinometry, 2-nitrobenzaldehyde undergoes first-order photodegradation such that: (Galbavy et al., 2010)

$$\ln \left( \frac{[2\text{NB}]_t}{[2\text{NB}]_0} \right) = -j_{2\text{NB},\lambda} \times t \quad \text{(RS6)}$$

where $[2\text{NB}]_t$ and $[2\text{NB}]_0$ are the concentration at illumination times $t$ and zero, respectively. The measured rate constant for 2NB loss ($j_{2\text{NB},\lambda}$) is related to photon fluxes through

$$j_{2\text{NB},\lambda} = 2.303 I_\lambda \varepsilon_{2\text{NB},\lambda} \Phi_{2\text{NB},\lambda} l \quad \text{(RS7)}$$

where $\varepsilon_{2\text{NB},\lambda} \Phi_{2\text{NB},\lambda}$ is the product of the molar absorptivity and quantum efficiency of 2NB (640 M$^{-1}$ cm$^{-1}$ at 313nm (Anastasio et al., 1994)) and $l$ is the effective path length of the sample(cm). 2NB was determined using high performance liquid chromatography (HPLC, Ultimate 3000, Thermo Fisher Scientific) with a diode array detector ($\lambda = 355$ nm); C-18 Beta Basic reverse-phase column (4.6 mm × 250 mm, 5 μm bead); Column temperature 25 °C. The eluent was 70% acetonitrile/30% H$_2$O, run at a flow rate of 0.8 mL·min$^{-1}$.

As shown in Figure S2, the average value of $j_{2\text{NB},313}$ in our experiments was $2.86\times10^{-2}$ s$^{-1}$, corresponding to a surface-area normalized actinic flux of $1.078\times10^{-5}$ photons cm$^{-2}$ s$^{-1}$ (8mW cm$^{-2}$).
Text S4. Calculation of ·OH quantum yield

**Materials.** Stock solutions of salicylic acid (ACS, ≥99.0%), 2,3-dihydroxybenzoic (99%), 2,5-dihydroxybenzoic (>99.0%, HPLC) were prepared by dissolving the corresponding reagent in ethanol.

**Determination of ·OH.** Hydroxyl radicals were characterized by using a chemical probe technique where photoformed ·OH reacts with salicylic acid (SA) to form stable, measurable products including 2,3-dihydroxybenzoic acid (2,3-DHBA) and 2,5-dihydroxybenzoic acid (2,5-DHBA). Catechol is also one of the possible products, but it can be ignored due to its low concentration. The total yield of ·OH is the sum content of 2,3-DHBA and 2,5-DHBA. (Diez et al., 2001)

\[
\text{SA} + \cdot \text{OH} \rightarrow 2,3\text{-DHBA} + 2,5\text{-DHBA} + \text{other} \quad (\text{RS8})
\]

SA, 2,3-DHBA and 2,5-DHBA were determined using high performance liquid chromatography (HPLC, Ultimate 3000, Thermo Fisher Scientific) with a diode array detector (\( \lambda = 220 \text{ nm} \)); C-18 Beta Basic reverse-phase column (4.6 mm × 250 mm, 5 \( \mu \text{m bead} \)); Column temperature 25 °C. The eluent was methanol/0.1% TFA/H\(_2\)O, run at a flow rate of 1.0 mL·min\(^{-1}\).

**Calculation of ·OH quantum yield.** As mentioned above, only a small fraction of this incident light was absorbed by the NH\(_4\)NO\(_3\) solutions in our experiments. Under these low light-absorbing conditions the rate of ·OH formation can be expressed as (Chu and Anastasio, 2003)

\[
R_{\text{OH},\lambda} = 2.303I_{\lambda} \varepsilon_{\text{NO3}^{-},\lambda} \Phi_{\text{OH},\lambda} [\text{NO}_3^-] \quad (\text{RS9})
\]

where \( \varepsilon_{\text{NO3}^{-},\lambda} \) is the molar absorptivity of nitrate (5.3 M\(^{-1}\) cm\(^{-1}\) at 313nm), \( \Phi_{\text{OH},\lambda} \) is the quantum yield of ·OH from nitrate photolysis, and [NO\(_3^-\)] is the molar concentration.
of nitrate. Rearranging eq S7 to solve for $I$, and substituting that into eq S9 produces an expression for the quantum yield of $\cdot$OH.

$$\Phi_{\text{OH},\lambda} = \frac{\varepsilon_{2NB,\lambda} \Phi_{2NB,\lambda} \Phi_{\text{OH},\lambda}}{\varepsilon_{2NB,\lambda} \varepsilon_{\text{NO}_3,\lambda} \lambda \text{[NO}_3\text{]} } \quad (\text{RS10})$$
Text S5. Detection of hydrogen peroxide

Materials. Hydrogen peroxide (AR) and sulfuric acid (Tech) were purchased from Sinopharm Chemical Reagent Co., Ltd. Titanium (III) sulfate (20% in 1-4% sulfuric acid) was purchased from Alfa Aesar (China) Chemical Co.Ltd.

Methods. Hydrogen peroxide in products was measured by titanium salt UV spectrophotometry using an UV-6300 double beam spectrophotometer (Shanghai mapada Instrument Co., Ltd). A stable yellow complex with a characteristic absorption wavelength forms when hydrogen peroxide reacts with trivalent titanium ion. At this wavelength, the concentration of H$_2$O$_2$ is directly proportional to absorbance.

Through the pre-experiment, experimental conditions were established as follows: sulfuric acid: 0.3 mol·L$^{-1}$; titanium sulphate: 0.3 mmol·L$^{-1}$; absorption wavelength: 400 nm and chromogenic time: 10 min.

67.4 mg·L$^{-1}$ H$_2$O$_2$ bulk solution was prepared. Take 0.2, 0.6, 0.8, and 1 mL H$_2$O$_2$ solution respectively, add 0.5 mL mixed solution of titanium sulfate and sulfuric acid, dilute to 5 mL with ultrapure water. These standard solutions were measured by spectrophotometer at 400 nm wavelength after 10 min. Standard curve of H$_2$O$_2$ was shown in Fig.S1. There is a linear relationship between the concentration of hydrogen peroxide and the absorbance. The regression equation is $y = 0.0083x - 0.0194$, $R^2$=0.9998.
Figure S1. Effect of $\text{NH}_4^+$ on nitrate photolysis and sulfate formation.
Figure S2. First-order photodegradation of 2-nitrobenzaldehyde (2NB) under 313 nm UV irradiation.
Figure S3. Formation of •OH during nitrate photolysis at different pH.
Figure S4. Standard curve of hydrogen peroxide.

\[ y = 0.0083x - 0.0194 \]

\[ R^2 = 0.9998 \]
Figure S5. Effect of light intensity on aqueous-phase formation of sulfate.
References

Anastasio, C., Faust, B. C., and Allen, J. M.: Aqueous phase photochemical formation of hydrogen peroxide in authentic cloud waters, J. Geophys. Res. A, 99, 8231, https://doi.org/10.1029/94JD00085, 1994.

Chu, L., and Anastasio, C.: Quantum yields of hydroxyl radical and nitrogen dioxide from the photolysis of nitrate on ice, J. Phys. Chem. A, 107, 9594-9602, https://doi.org/10.1021/jp0349132, 2003.

Diez, L., Marie-Helene, L., Avishay-Abraham, S., Maria, W. R., and Leroy, P.: High-performance liquid chromatographic assay of hydroxyl free radical using salicylic acid hydroxylation during in vitro experiments involving thiols, J. Chromatogr. B, 763, 185-193, https://doi.org/10.1016/S0378-4347(01)00396-6, 2001.

Galbavy, E. S., Ram, K., and Anastasio, C.: 2-Nitrobenzaldehyde as a chemical actinometer for solution and ice photochemistry, J. Photochem. Photobio. A, 209, 186-192, https://doi.org/10.1016/j.jphotochem.2009.11.013, 2010.