# Supporting information

## Aqueous phase oxidation of bisulfite influenced by nitrate photolysis

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**Contents:**

**References**

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

$$\text{Sulfate production} = C_t - C_0$$

$$\text{The average rate of sulfate formation} = \frac{\text{Sulfate production}}{\text{Reaction time}}$$
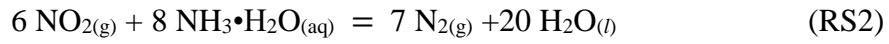
$C_t$: sulfate content after reaction;

$C_0$: initial sulfate content;

Reaction time: 120 min.

Table S1. Sulfate production and average formation rate

| Line | Sulfate production ($\mu M$) | Average rate of sulfate formation ($\mu M \cdot min^{-1}$) |
|---|---|---|
| S1: $NH_4NO_3$+Light (Xe lamp) +Air | 1629.69 | 13.58 |
| S'1: $NH_4NO_3$+Light (UV) +Air | 7656.56 | 63.80 |
| S2: $NH_4NO_3$+Dark+Air | 1560.16 | 13.00 |
| S3: Dark + Air | 1048.44 | 8.74 |
| S4: $NH_4NO_3$+Light (Xe lamp) +$N_2$ | 837.76 | 6.98 |
| S'4: $NH_4NO_3$ + 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

$NH_4^+ + H_2O \rightleftharpoons NH_3 \cdot H_2O_{(aq)} + H^+ \rightleftharpoons NH_{3(aq)} + H_3O^+_{(aq)}$      (RS1)

$6\ NO_{2(g)} + 8\ NH_3 \cdot H_2O_{(aq)} = 7\ N_{2(g)} + 20\ H_2O_{(l)}$      (RS2)

$\Delta G_{S1} = -2942.56\ kJ \cdot mol^{-1}$

$5\ NO_{2(g)} + 2\ NH_3 \cdot H_2O_{(aq)} = 7\ NO_{(g)} + 5\ H_2O_{(l)}$      (RS3)

$\Delta G_{S2} = -301.99\ kJ \cdot mol^{-1}$

$6\ NO_{2(g)} + 8\ NH_{3(aq)} = 7\ N_{2(g)} + 12\ H_2O_{(l)}$      (RS4)

$\Delta G_{S3} = -2942.08\ kJ \cdot mol^{-1}$

$5\ NO_{2(g)} + 2\ NH_{3(aq)} = 7\ NO_{(g)} + 3\ H_2O_{(l)}$      (RS5)
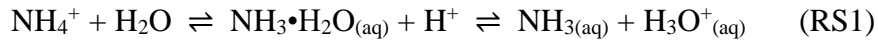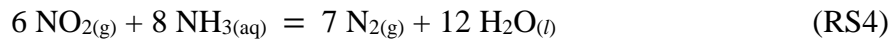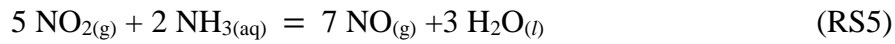
$\Delta G_{S4} = -301.87\ kJ \cdot mol^{-1}$

## 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 $NH_4NO_3$ 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)

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

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

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

where $\varepsilon_{2NB,\lambda}\Phi_{2NB,\lambda}$ 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% $H_2O$, run at a flow rate of 0.8 mL·$min^{-1}$.

As shown in Figure S2, the average value of $j_{2NB,313}$ 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)

$$SA + \cdot OH \rightarrow 2,3\text{-DHBA} + 2,5\text{-DHBA} + other \qquad (RS8)$$
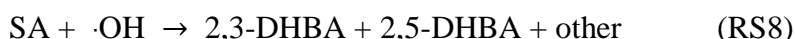
SA, 2,3-DHBA and 2,5-DHBA were determined using high performance liquid chromatography (HPLC, Ultimate 3000, Thermo Fisher Scientific) with a diode array detector ($\lambda = 220$ nm); C-18 Beta Basic reverse-phase column (4.6 mm × 250 mm, 5 μm bead); Column temperature 25 °C. The eluent was methanol/0.1% TFA/$H_2O$, 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 $NH_4NO_3$ solutions in our experiments. Under these low light-absorbing conditions the rate of •OH formation can be expressed as (Chu and Anastasio, 2003)

$$R_{OH,\lambda} = 2.303 I_\lambda \varepsilon_{NO3^-,\lambda} \Phi_{OH,\lambda} l [NO_3^-] \qquad (RS9)$$

where $\varepsilon_{NO3^-,\lambda}$ is the molar absorptivity of nitrate (5.3 M$^{-1}$ cm$^{-1}$ at 313nm), $\Phi_{OH,\lambda}$ is the quantum yield of •OH from nitrate photolysis, and $[NO_3^-]$ is the molar concentration

of nitrate. Rearranging eq S7 to solve for $I_\lambda$ and substituting that into eq S9 produces an expression for the quantum yield of •OH.

$$\Phi_{OH,\lambda} = \frac{\varepsilon_{2NB,\lambda}\Phi_{2NB,\lambda}R_{OH,\lambda}}{j_{2NB,\lambda}\varepsilon_{NO3^-,\lambda}[NO_3^-]} \qquad \text{(RS10)}$$

**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 $H_2O_2$ is directly proportional to absorbance.

Through the pre-experiment, experimental conditions were established as follows: tsulfuric 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$^{-1}$ $H_2O_2$ bulk solution was prepared. Take 0.2, 0.6, 0.8, and 1 mL $H_2O_2$ 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 $H_2O_2$ 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.
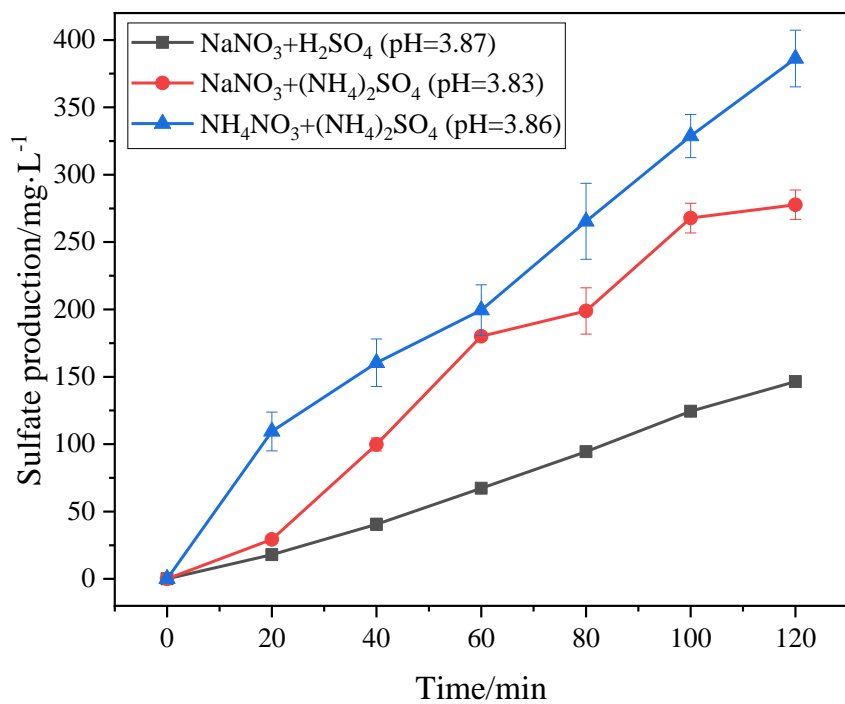
Figure S1. Effect of $NH_4^+$ on nitrate photolysis and sulfate formation.
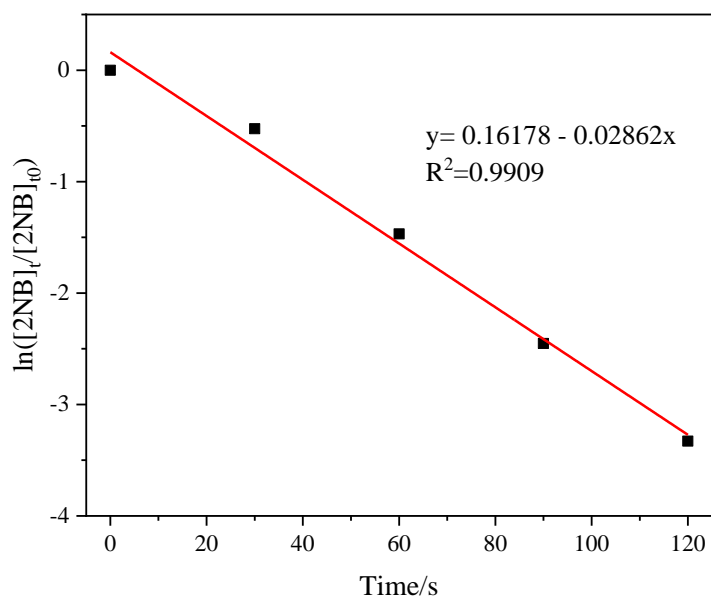
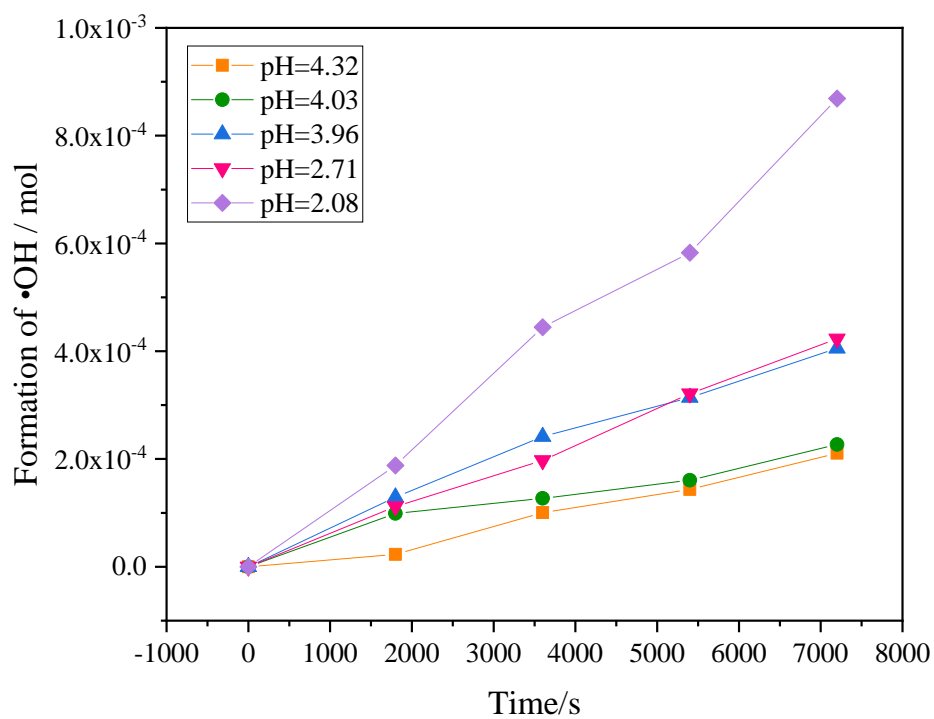Figure S2. First-order photodegradation of 2-nitrobenzaldehyde (2NB) under 313 nm
UV irradiation.

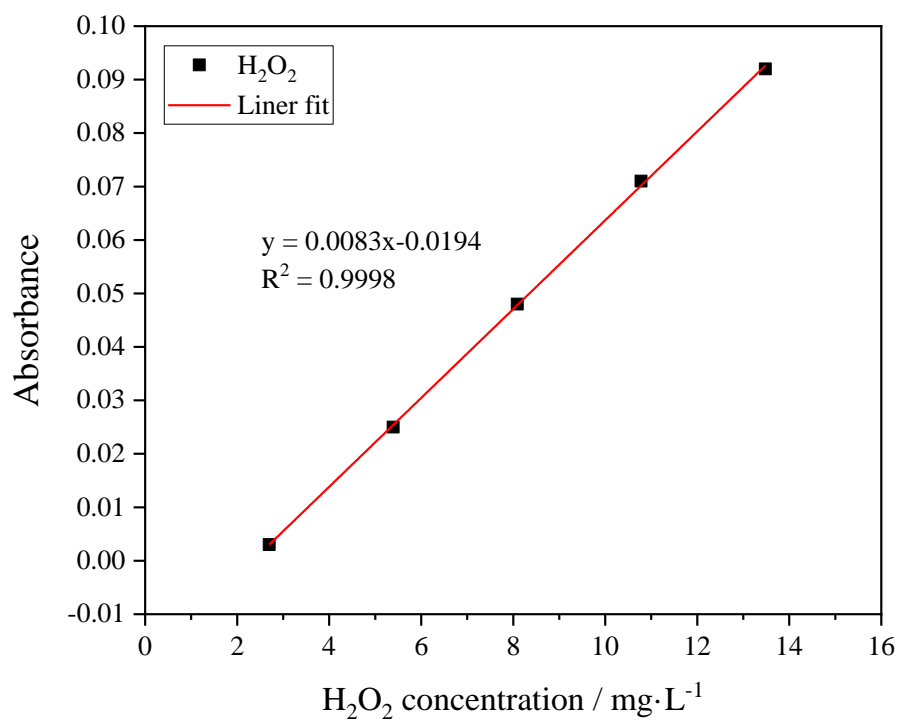Figure S3. Formation of •OH during nitrate photolysis at different pH.
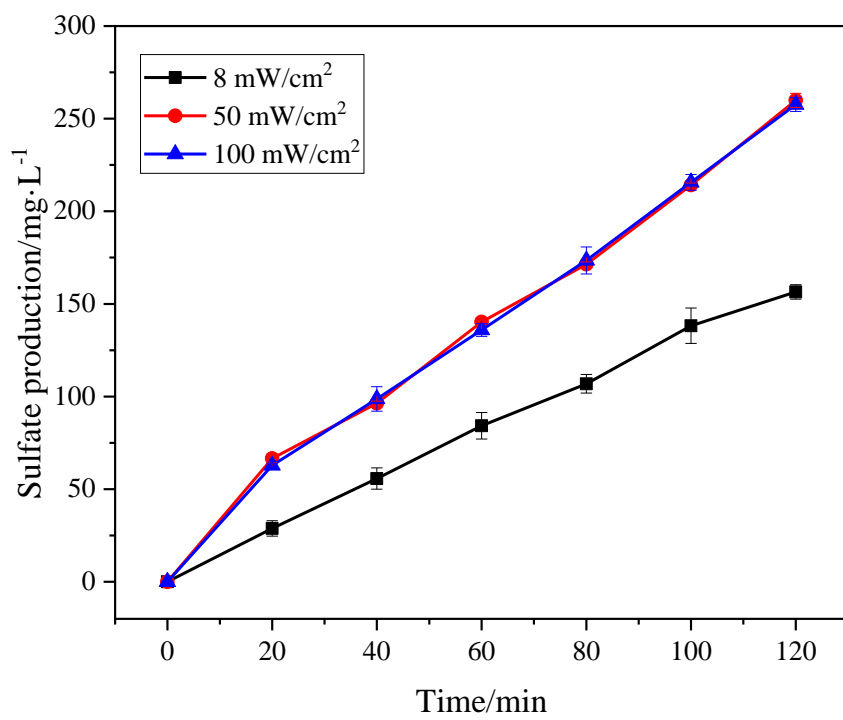
Figure S4. Standard curve of hydrogen peroxide.

Figure S5. Effect of light intensity on aqueous-phase formation of sulfate.

# References

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