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Supplementary Information

pH affects the aqueous-phase nitrate-mediated photooxidation of phenolic compounds: Implications for brown carbon formation and evolution

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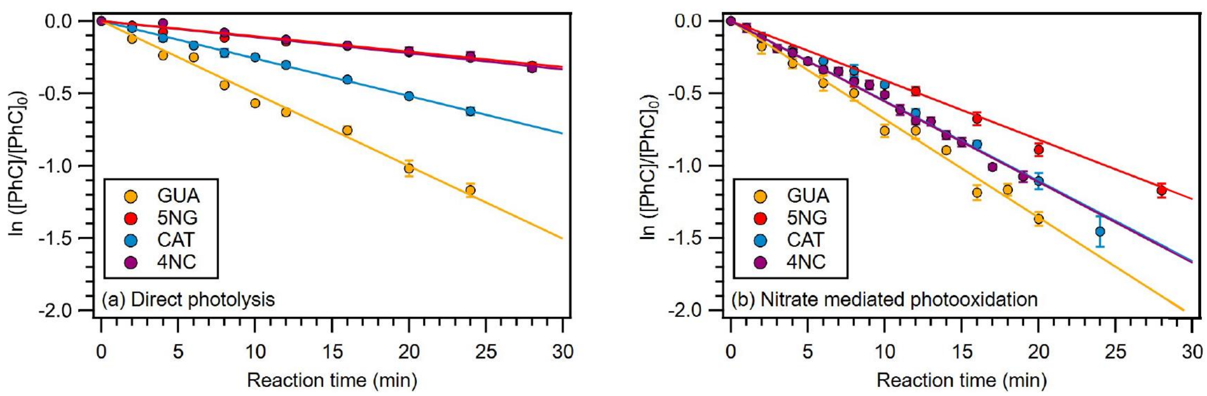


Figure S1: Kinetic decay results of the four phenolic compounds in (a) direct photolysis, and (b) nitrate-mediated photooxidation experiments. Lines show the exponential fit to the kinetic data. Error bars indicate standard deviations between multiple experiments.

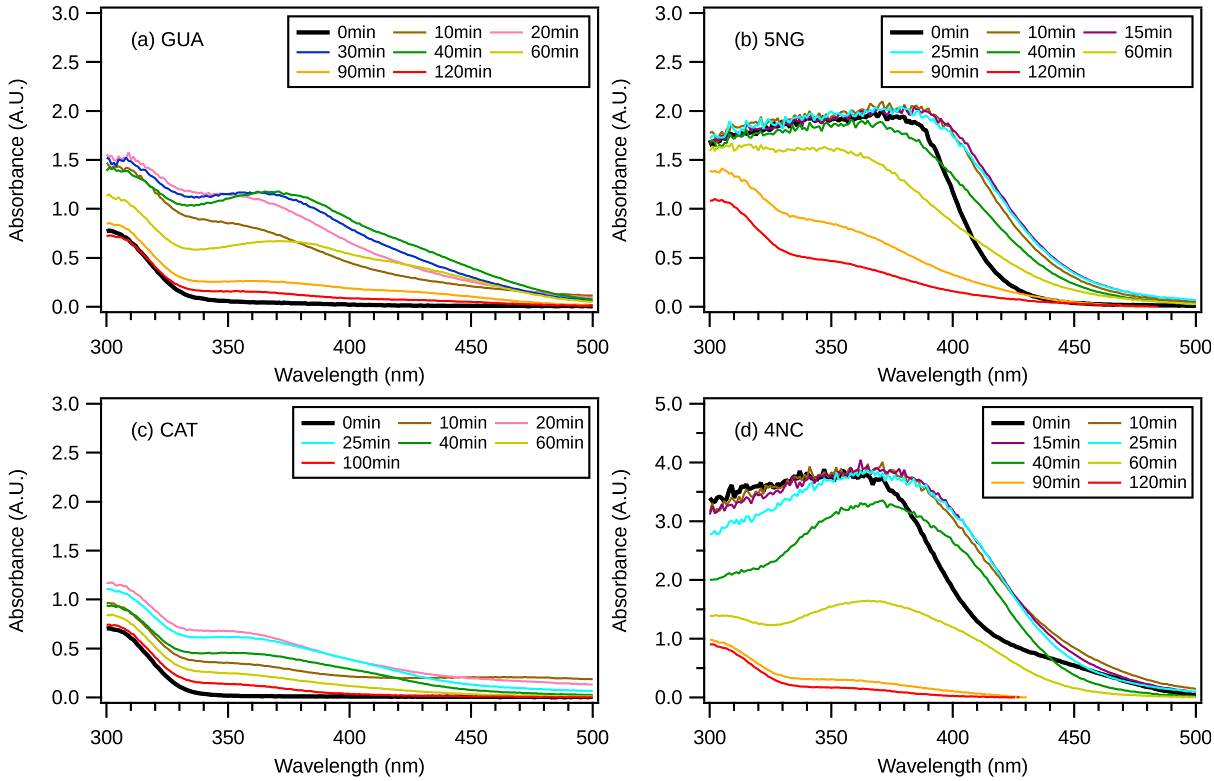


Figure S2: Absorption spectra of (a) guaiacol, (b) 5-nitroguaiacol, (c) catechol, and (d) 4-nitrocatechol during nitrate-mediated photooxidation at solution pH 6. These absorption spectra were taken at sequential time steps during the reaction.

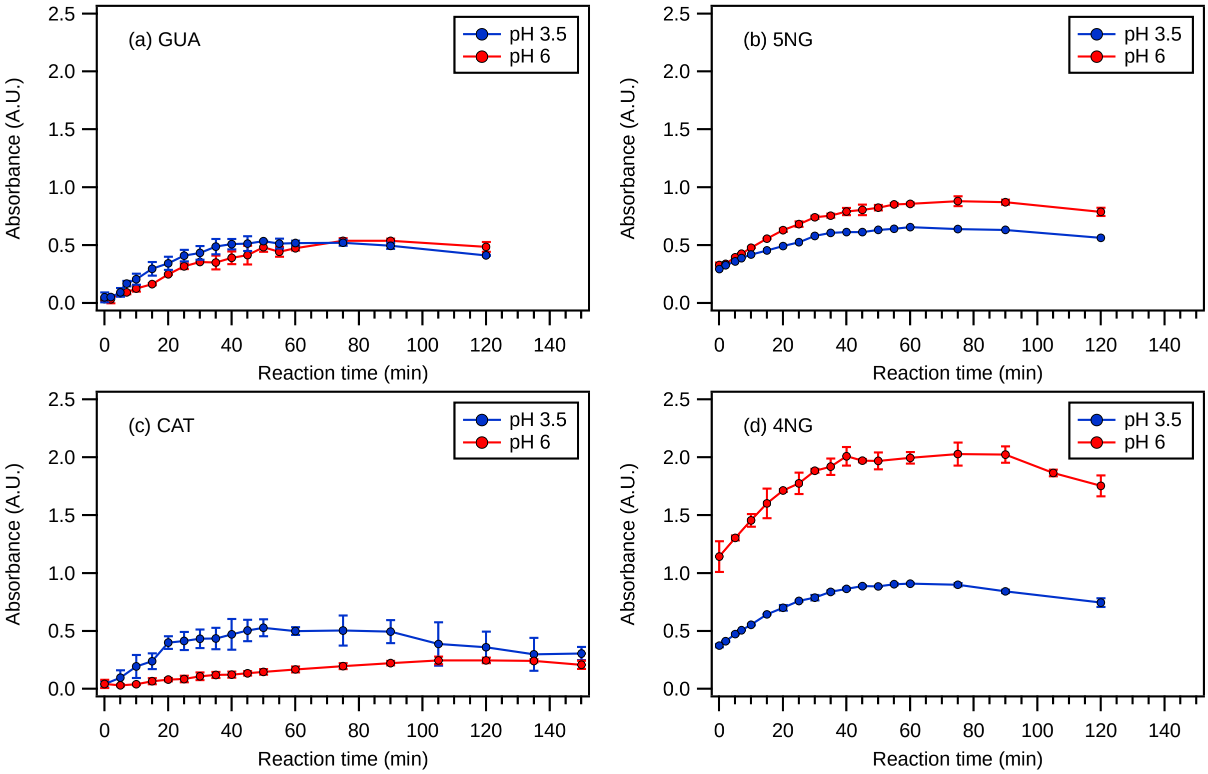


Figure S3: Changes in the absorbance of (a) guaiacol at 365 nm, (b) 5-nitroguaiacol and 420 nm, (c) catechol at 365 nm, and (d) 4-nitrocatechol at 420 nm during direct photolysis. The experiments were performed using solutions that were either unacidified (pH 6, red symbols and lines), or were acidified to pH 3.5 (blue symbols and lines). Error bars indicate standard deviations between multiple experiments.

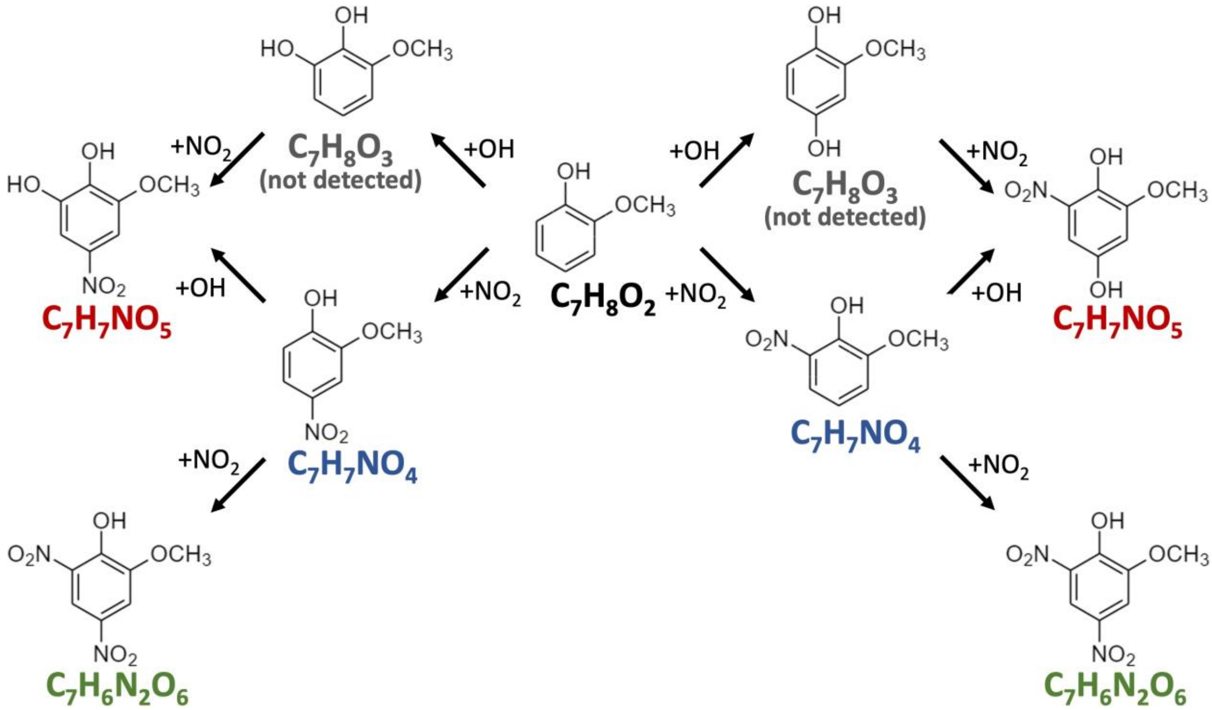


Figure S4: Proposed structures of the prominent products measured by the UPLC-MS during the nitrate-mediated photooxidation of guaiacol. Note that although this figure proposes that several isomers can potentially be formed for some of these products, only one isomer is detected most of the time, and MS/MS analysis is usually unable to conclusively determine the chemical structures of the detected isomer. All the products will undergo further reaction, which will eventually lead to ring-opening and the formation of smaller, highly oxygenated molecules. Note that while $C_7H_8O_3$ can be a potential first-generation product, it was not detected.

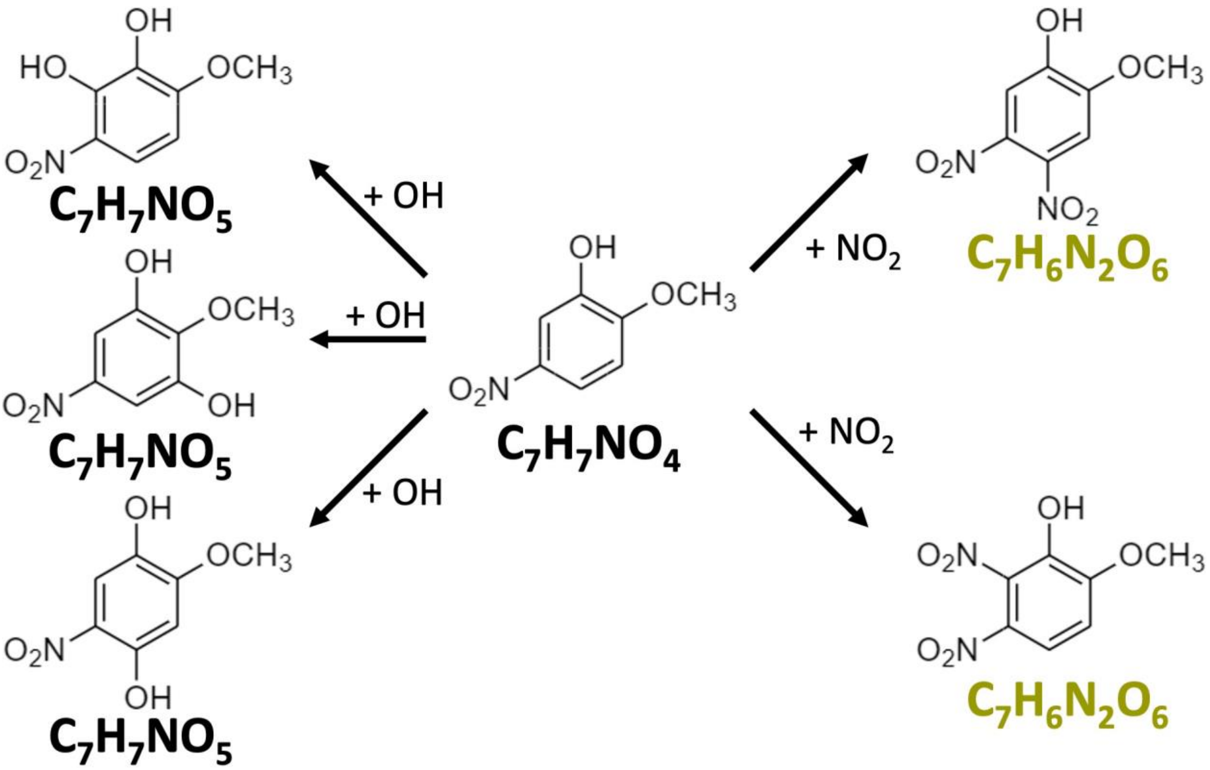


Fig. S5: Proposed structures of the prominent products measured by the UPLC-MS during the nitrate-mediated photooxidation of 5-nitroguaiacol. Note that although this figure proposes that several isomers can potentially be formed for some of these products, only one isomer is detected most of the time, and MS/MS analysis is usually unable to conclusively determine the chemical structures of the detected isomer. All the products will undergo further reaction, which will eventually lead to ring-opening and the formation of smaller, highly oxygenated molecules.

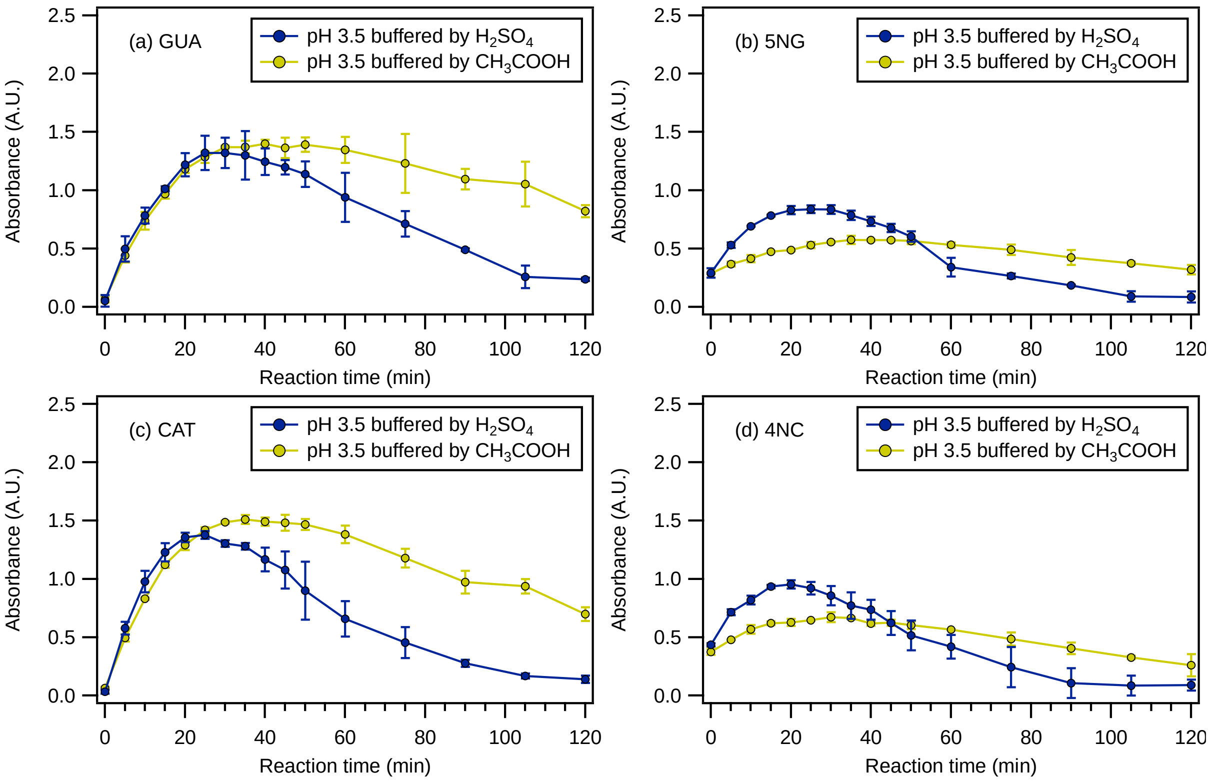


Figure S6: Changes in the absorbance of (a) guaiacol at 365 nm, (b) 5-nitroguaiacol at 420 nm, (c) catechol at 365 nm, and (d) 4-nitrocatechol at 420 nm during nitrate-mediated photooxidation. The experiments were performed using solutions that were either acidified with H_2SO_4 (blue symbols and lines) or with CH_3COOH (green symbols and lines). Error bars indicate standard deviations between multiple experiments.

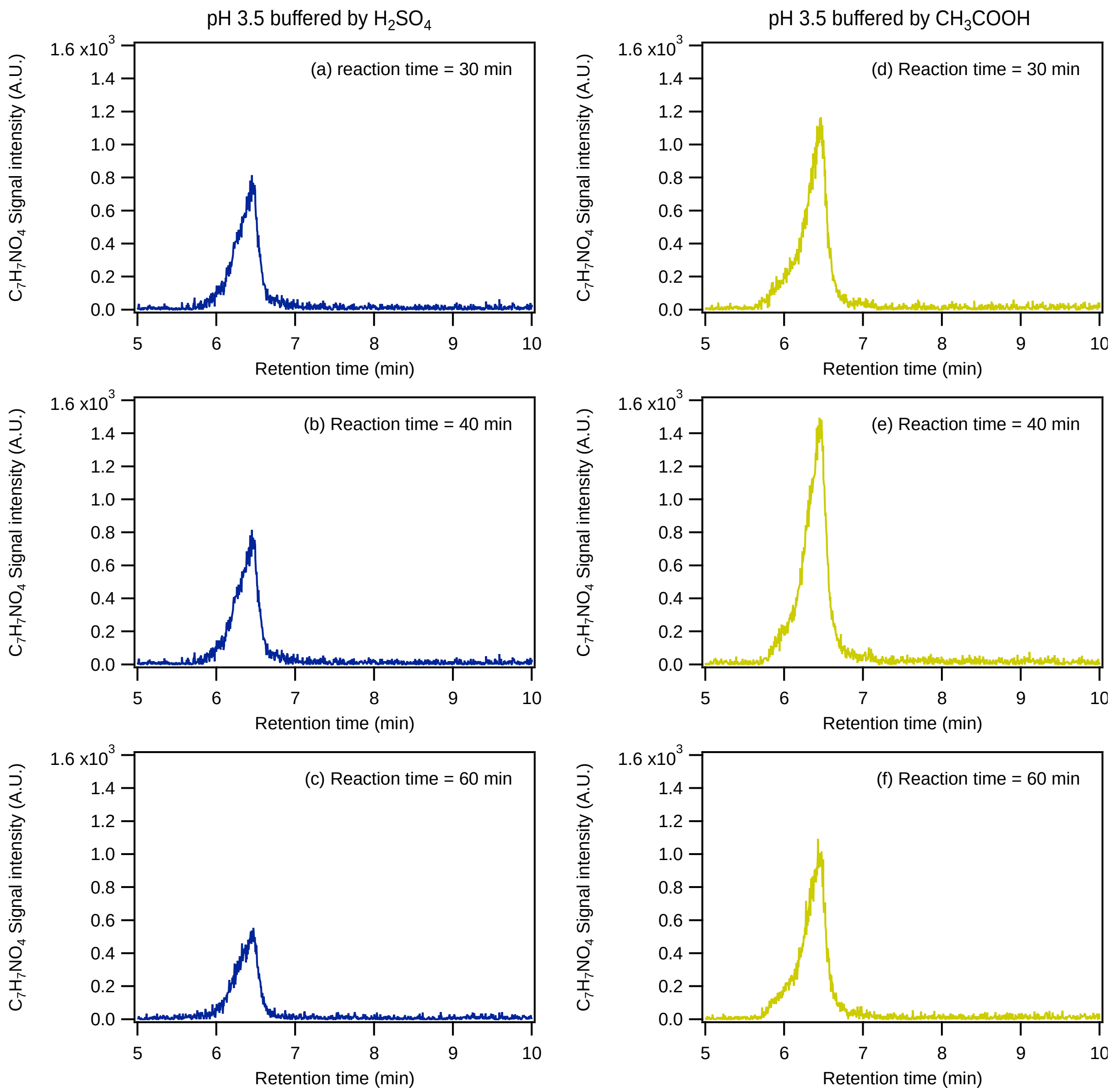


Figure S7: XIC chromatograms of $C_7H_7NO_4$ during the nitrate-mediated photooxidation of guaiacol at pH 3.5 using CH_3COOH-acidified (right side) vs. H_2SO_4-acidified (left side) solutions at reaction times 30 min, 40 min, and 60 min.

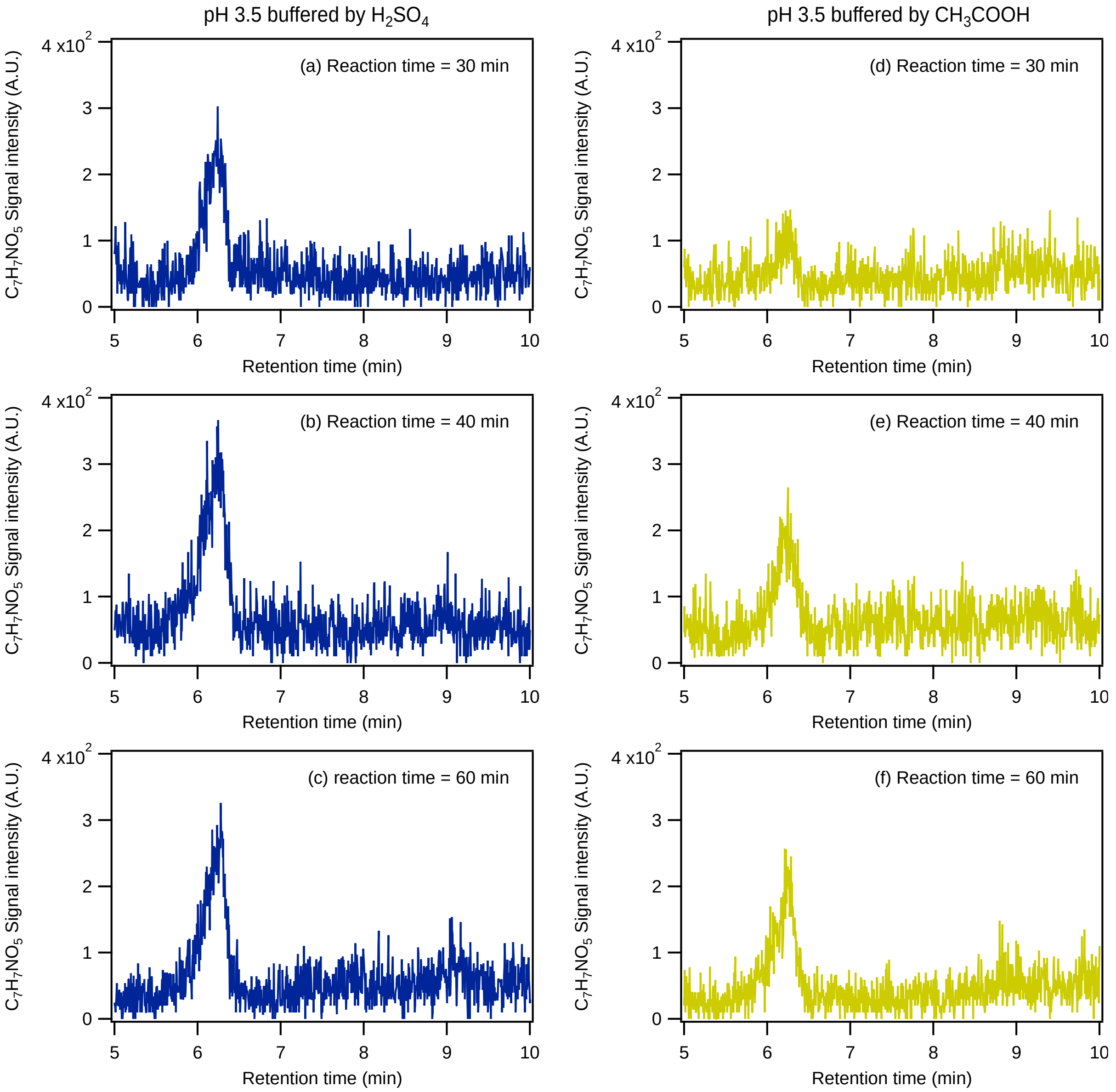


Figure S8: XIC chromatograms of $C_7H_7NO_5$ during the nitrate-mediated photooxidation of guaiacol at pH 3.5 using CH_3COOH-acidified (right side) vs. H_2SO_4-acidified (left side) solutions at reaction times 30 min, 40 min, and 60 min.

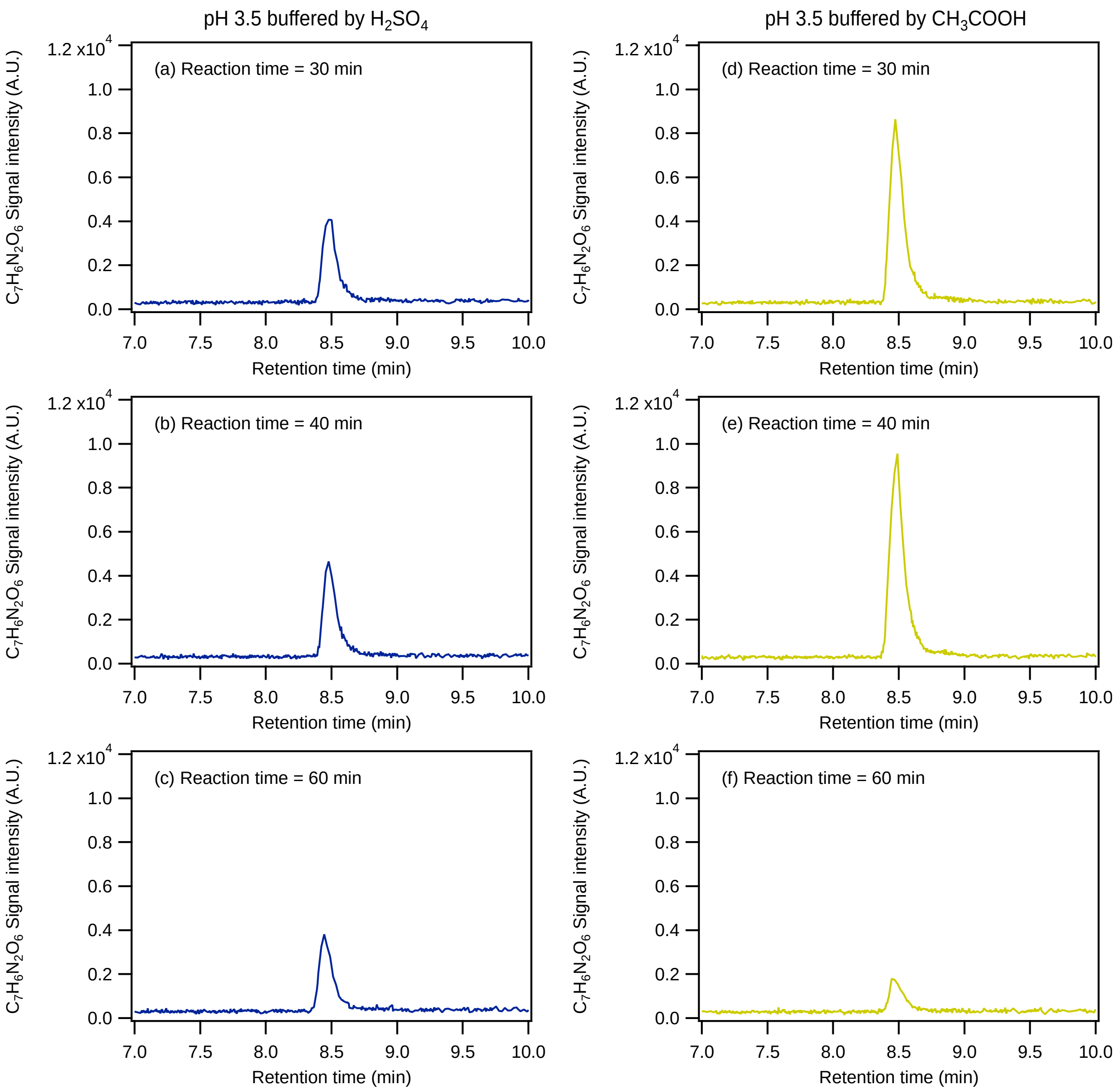


Figure S9: XIC chromatograms of $C_7H_6N_2O_6$ during the nitrate-mediated photooxidation of 5-nitroguaiacol at pH 3.5 using CH_3COOH-acidified (right side) vs. H_2SO_4-acidified (left side) solutions at reaction times 30 min, 40 min, and 60 min.

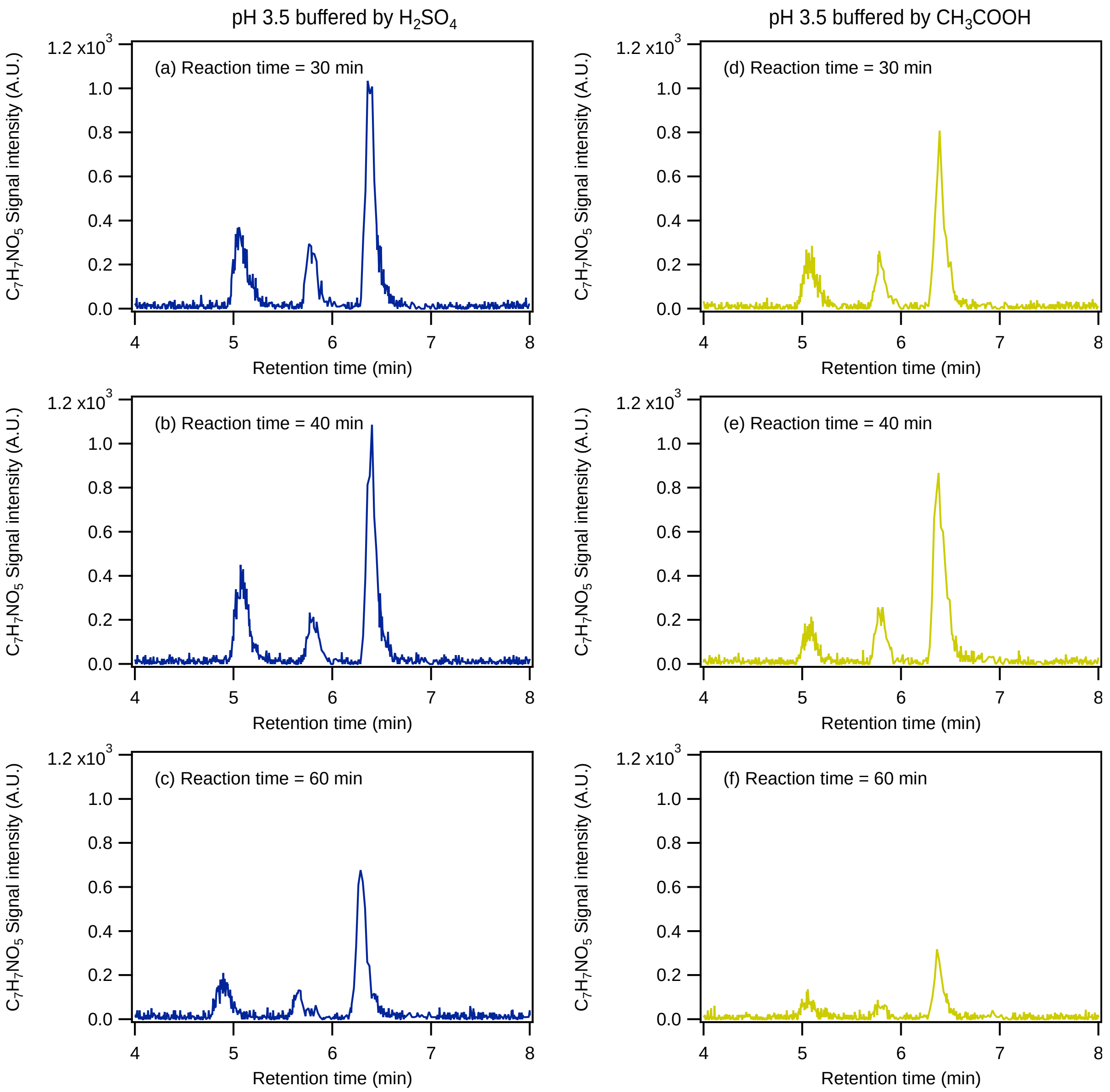


Figure S10: XIC chromatograms of $C_7H_7NO_5$ isomers during the nitrate-mediated photooxidation of 5-nitroguaiacol at pH 3.5 using CH_3COOH-acidified (right side) vs. H_2SO_4-acidified (left side) solutions at reaction times 30 min, 40 min, and 60 min.

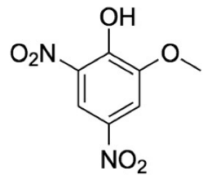
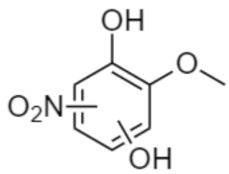
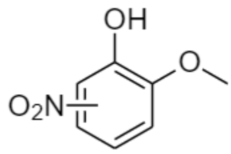
Table S1. The photoreaction pathways initiated by the aqueous-phase photolysis of inorganic nitrate.[1-3]

No.	Reactions	Quantum yield (Φ)/ Acid dissociation constant (pK_a)
1	$NO_3^- + h\nu \rightarrow [\bullet NO_2 + O\bullet^-]_{cage}$	$\Phi = 0.01$
2	$[\bullet NO_2 + O\bullet^-]_{cage} \rightarrow \bullet NO_2 + O\bullet^-$	—
3	$O\bullet^- + H_2O \rightleftharpoons \bullet OH + OH^-$	$pK_a(\bullet OH) = 11.9$
4	$[\bullet NO_2 + O\bullet^-]_{cage} \rightarrow OONO^-$	—
5	$OONO^- + H^+ \rightleftharpoons HOONO$	$pK_a = 7$
6	$HOONO \rightarrow \bullet OH + \bullet NO_2$	—
7	$2\ \bullet NO_2 \rightleftharpoons N_2O_4$	—
8	$N_2O_4 + H_2O \rightarrow HNO_2 + NO_3^- + H^+$	—
9	$HNO_2 \rightleftharpoons H^+ + NO_2^-$	$pK_a = 3 \sim 3.5$
10	$NO_2^- + h\nu \rightarrow \bullet NO + O\bullet^-$	$\Phi = 0.025–0.065$
11	$NO_2^- + h\nu \rightarrow \bullet NO_2 + e^-$	$\Phi = \sim 0.001$
12	$NO_2^- + \bullet OH \rightarrow \bullet NO_2 + OH^-$	—
13	$\bullet NO + \bullet NO_2 \rightleftharpoons N_2O_3$	—
14	$N_2O_3 + H_2O \rightarrow 2\ NO_2^- + 2\ H^+$	—
15	$HNO_2 + h\nu \rightarrow \bullet NO + \bullet OH$	$\Phi = 0.35$
16	$HNO_2 + \bullet OH \rightarrow \bullet NO_2 + H_2O$	—
17	$2\ HNO_2 \rightarrow \bullet NO + \bullet NO_2 + H_2O$	—

Table S2. Experimental conditions for the aqueous-phase nitrate-mediated photooxidation of guaiacol, catechol, 5-nitroguaiacol, and 4-nitrocatechol.

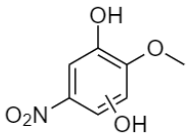
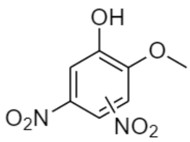
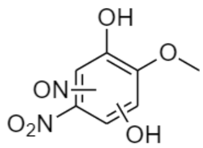
Experiment	Phenolic compounds	pH	NH_4NO_3 (μM)	Acid added
1	2 μM guaiacol	6	200	—
2	2 μM guaiacol	3.5	200	H_2SO_4
3	2 μM guaiacol	3.5	200	CH_3COOH
4	2 μM 5-nitroguaiacol	6	200	—
5	2 μM 5-nitroguaiacol	3.5	200	H_2SO_4
6	2 μM 5-nitroguaiacol	3.5	200	CH_3COOH
7	2 μM catechol	6	200	—
8	2 μM catechol	3.5	200	H_2SO_4
9	2 μM catechol	3.5	200	CH_3COOH
10	2 μM 4-nitrocatechol	6	200	—
11	2 μM 4-nitrocatechol	3.5	200	H_2SO_4
12	2 μM 4-nitrocatechol	3.5	200	CH_3COOH

Table S3: List of products detected during the nitrate-mediated photooxidation of guaiacol at pH 6 and pH 3.5 identified using UPLC-MS.

No.	Retention time (min)	m/z	Proposed product molecular formula and structure	MS/MS fragments
1	2.29	186.1128	$C_{11}H_{13}N_3$	Unknown
2	2.34	172.0973	$C_{10}H_{11}N_3$	Unknown
3	5.95	213.0146	$C_7H_6N_2O_6$ 	$-CH_3$ $-NO_2$
4*	6.23	184.0258	$C_7H_7NO_5$ 	$-OH$ $-CH_3$
5*	6.41	168.0295	$C_7H_7NO_4$ 	$-NO_2$ $-CH_3$
6	7.96	323.2333	Unknown	Unknown
7	11.50	157.1230	$C_9H_{18}O_2$	Unknown

* Only these two products were detected in pH 3.5.

Table S4: List of products detected during the nitrate-mediated photooxidation of 5-nitroguaiacol at pH 6 and pH 3.5 identified using UPLC-MS.

No.	Retention time (min)	m/z	Proposed product molecular formula and structure	MS/MS fragments
1*	5.07	184.0258	$C_7H_7NO_5$	Unknown
2**	5.17	172.0248	$C_6H_7NO_5$	Unknown
3*	5.69	139.0035	Unknown	Unknown
4**	5.80	184.0258	$C_7H_7NO_5$	Unknown
5**	6.40	184.0258	$C_7H_7NO_5$ 	—OH —CH_3
6	7.74	224.0282	Unknown	Unknown
7**	8.47	213.0141	$C_7H_6N_2O_6$  	—CH_3
8	9.23	224.0306	$C_8H_7N_3O_5$	Unknown
9	9.28	223.0285	Unknown	Unknown

* These two products were only detected at pH 3.5.
** These four products were detected at both pH 6 and pH 3.5.

S1. Determination of the steady-state OH radical concentrations in photooxidation experiments initiated by NH_4NO_3 photolysis

The steady-state OH radical concentrations ($[OH]_{ss}$) in nitrate-mediated photooxidation experiments were measured separately using the method described in our previous work.[4] Benzoic acid (99.5%, J&K Scientific) was used as the probe compound to estimate the $[OH]_{ss}$. Similar concentrations (i.e., 2 μM benzoic acid and 200 μM NH_4NO_3) and reaction conditions were used in these separate experiments. Briefly, the time-dependent formation of 4-hydroxybenzoic acid was measured in these experiments. 4-hydroxybenzoic acid was assumed to be produced only from the OH + benzoic acid reaction with a yield of 0.17.[5] The time-dependent concentrations of benzoic acid that reacted with OH radicals was then determined from the time-dependent formation of 4-hydroxybenzoic acid. $[OH]_{ss}$ was calculated using the time-dependent concentrations of benzoic acid which reacted with OH radicals and the second-order reaction rate constant for the OH + benzoic acid reaction (5.9×10^9 M^{-1} s^{-1}).[6] The measured $[OH]_{ss}$ concentrations were within the range of [OH] values in atmospheric cloudwater (10^{-16} to 10^{-12} M).[7]

4-hydroxybenzoic acid in separate $[OH]_{ss}$ quantification experiments was measured using an ultra-high performance liquid chromatography system (1290 Infinity LC, Agilent) coupled to a high-resolution quadrupole-time-of-flight mass spectrometer (Sciex X500R QTOF) equipped with an ESI source that was operated in negative mode. All the samples were desalted using the SPE procedure described above. A reverse phase Kinetex (Phenomenex) PS-C18 column (150 × 2.1 mm, 2.6 μm, 100 Å) equipped with a security guard and a PS-C18 pre-column was used for UPLC-MS analysis. The temperatures for the column oven and the UPLC autosampler were set to 25 °C. A gradient elution program was used. The binary mobile phases consisted of A (10 mM ammonium acetate) and B (acetonitrile) delivered at a flow rate 300 μL min^{-1}. The sample injection volume was set to 10 μL. The following mobile phase gradient was used: 0 to 3 min 1% B, 3 to 5 min linear gradient to 80% B, 5 to 6 min 80% B, 6 to 6.5 min linear gradient to 1% B, 6.5 to 7 min 1% B. The following tandem MS conditions were used: -4500 V ESI ion spray voltage, -80 V declustering potential, -15 V collision energy, 25 PSI curtain gas, and 450 °C source temperature.

S2. Sample pretreatment by solid phase extraction (SPE)

SPE was performed on all the samples using SPE cartridges (HLB, 60 mg, 3 cc, 30 μm, Waters) to desalt the samples before UPLC-MS analysis. The SPE procedure used was as follows: Firstly, the SPE cartridge was activated and conditioned by filling it with 1 mL methanol and 1 mL ultrapure water. After that, 3 mL sample solution was loaded to the SPE cartridge. Then, the cartridge was flushed by adding 10 mL ultrapure water and dried by flushing air through the cartridge using an air pump. Finally, the elution was conducted by the addition of 3 mL acetonitrile and dried with flushing air. The eluted acetonitrile with organic compounds was collected for UPLC-MS analysis.

References

1. J. Mack and J. R. Bolton, Photochemistry of nitrite and nitrate in aqueous solution: A review, *Journal of Photochemistry and Photobiology A: Chemistry*, 1999, **128**, 1-13.
2. G. Marussi and D. Vione, Secondary Formation of Aromatic Nitroderivatives of Environmental Concern: Photonitration Processes Triggered by the Photolysis of Nitrate and Nitrite Ions in Aqueous Solution, *Molecules*, 2021, **26**, 2550.
3. D. Vione, B. Sur, B. K. Dutta, V. Maurino and C. Minero, On the effect of 2-propanol on phenol photonitration upon nitrate photolysis, *Journal of Photochemistry and Photobiology A: Chemistry*, 2011, **224**, 68-70.
4. J. Yang, W. C. Au, H. Law, C. H. Lam and T. Nah, Formation and evolution of brown carbon during aqueous-phase nitrate-mediated photooxidation of guaiacol and 5-nitroguaiacol, *Atmospheric Environment*, 2021, **254**, 118401.
5. C. Anastasio and K. G. McGregor, Chemistry of fog waters in California's Central Valley: 1. In situ photoformation of hydroxyl radical and singlet molecular oxygen, *Atmospheric Environment*, 2001, **35**, 1079-1089.
6. H. Herrmann, D. Hoffmann, T. Schaefer, P. Bräuer and A. Tilgner, Tropospheric aqueous-phase free-radical chemistry: radical sources, spectra, reaction kinetics and prediction tools, *Chemphyschem*, 2010, **11**, 3796-3822.
7. H. Herrmann, T. Schaefer, A. Tilgner, S. A. Styler, C. Weller, M. Teich and T. Otto, Tropospheric Aqueous-Phase Chemistry: Kinetics, Mechanisms, and Its Coupling to a Changing Gas Phase, *Chemical Reviews*, 2015, **115**, 4259-4334.