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## Supplement of

## Roles of pH, ionic strength, and sulfate in the aqueous nitrate-mediated photooxidation of green leaf volatiles

Yuting Lyu et al.

Correspondence to: Theodora Nah (theodora.nah@cityu.edu.hk)

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## S1. Measurement of p-hydroxybenzoic acid

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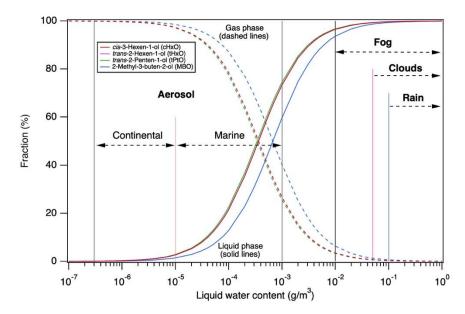
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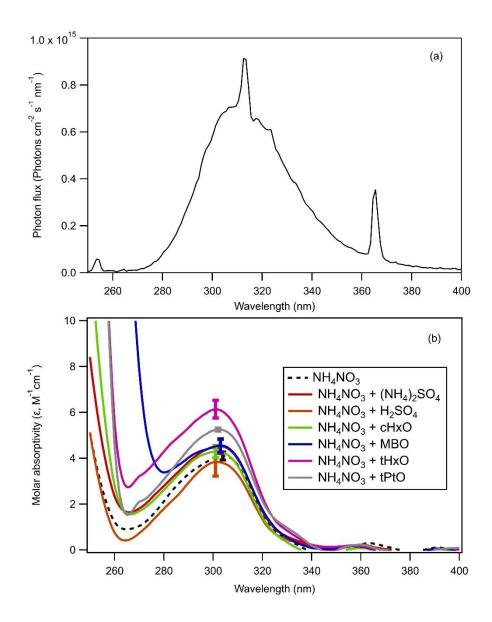
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p-hydroxybenzoic acid, which is formed from the reaction of ·OH with BA  $(k_{BA+OH} =$  $5.9 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> (Herrmann et al., 2010)) at a yield of 0.17 (Anastasio and Mcgregor, 2001), was measured in separate experiments using an ultra-high performance liquid chromatography system (1290 system, Agilent) coupled to a high-resolution quadrupole-time-of-flight mass spectrometer (X500R QTOF MS/MS, Sciex) (UPLC-MS) equipped with an electrospray ionization (ESI) source that was operated in negative mode. A reverse phase Kinetex (Phenomenex) Polar C18 column (2.6 µm, 150 × 2.1 mm) equipped with a Polar C18 guard 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. For the mobile phase, eluent A was 10 mM ammonia acetate in Milli-Q water buffered with 0.03% acetic acid, and eluent B was pure methanol. A gradient elution program was used, and it was delivered at a flow rate of 0.3 mL min<sup>-1</sup>. The following mobile phase gradient was used for the detection of BA and its product PHBA: 0 to 3 min 1% B, 3 to 5 min linear rise to 80% B and hold to 6 min, 6 to 6.5 min linear drop to 1% B and then hold to 10 min for equilibrium. The sample injection volume was set to 10 μL. The following tandem MS conditions were used: -4500 V ESI ion spray voltage, 80 V declustering potential, -20 V collision energy, 50 psi ion source gas, 25 psi curtain gas, and 450 °C source temperature.

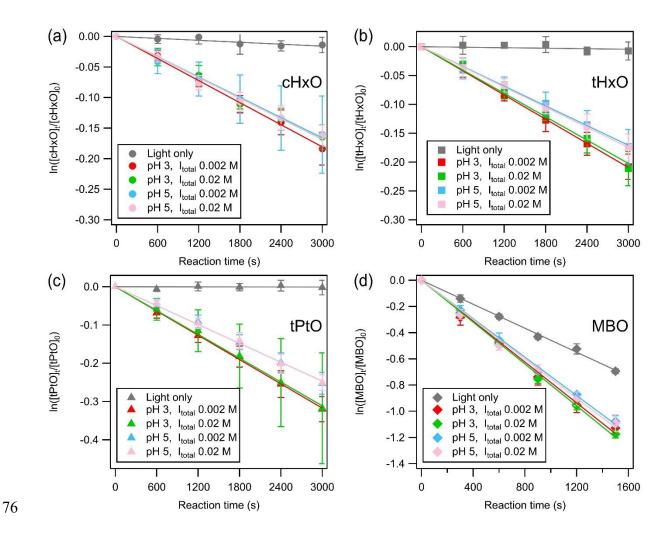
Solid phase extraction (SPE) was performed to desalt the samples using two different types of SPE cartridges: Oasis MAX (60 mg, 3 cc, 60  $\mu$ m, Waters) and Bond PPL Elut (200 mg, 3 mL, 125  $\mu$ m, Agilent). First, the sorbent was conditioned and equilibrated using 3 mL of methanol (LC-MS grade) followed by 3 mL of Milli-Q water. Next, the cartridge was loaded with 3 mL of 1× diluted sample solution and then purged with 6 mL of Milli-Q water. A vacuum pump was used to dry out the sorbent before elution using 3 mL of 2% formic acid in methanol. All the desalted samples were filtered using 0.2  $\mu$ m nylon syringe filters to remove any particulates prior to UPLC-MS analysis.



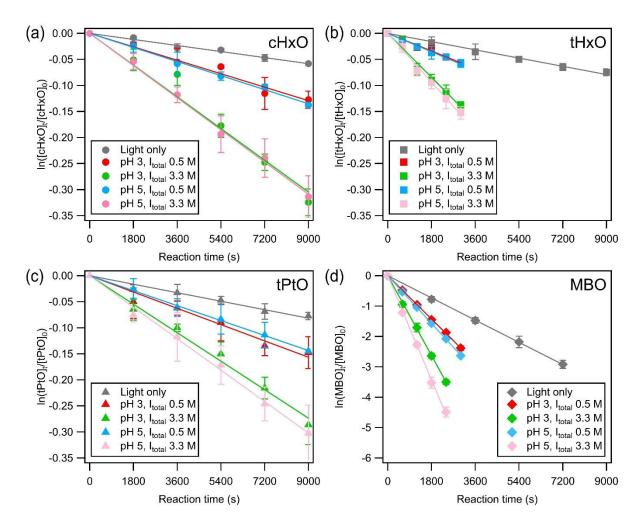
**Figure S1.** Calculated partitioning of the GLVs between the gas and aqueous phases as a function of liquid water content. The Henry's law solubility coefficients used for the calculation of cHxO, tHxO, tPtO, and MBO were 113 M atm<sup>-1</sup>, 94 M atm<sup>-1</sup>, 120 M atm<sup>-1</sup>, and 61 M atm<sup>-1</sup>, respectively (Sarang et al., 2021; Sander, 2023).



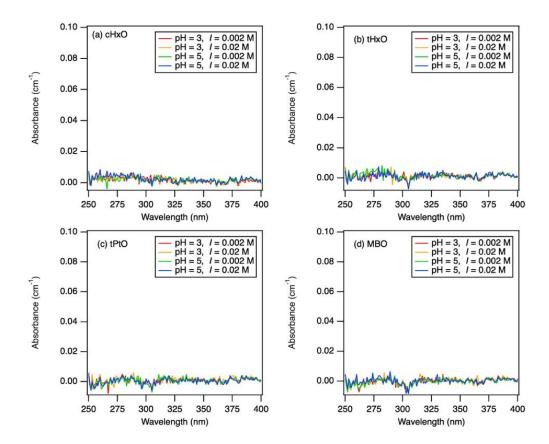
**Figure S2.** (a) Photon flux inside the Rayonet photoreactor under our experimental conditions (black solid line), and (b) molar absorptivities (ε) of the solutions of 25 mM NH<sub>4</sub>NO<sub>3</sub> (black dotted line) and 25 mM NH<sub>4</sub>NO<sub>3</sub> mixed with 1085 mM (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (red solid line), 0.5 mM H<sub>2</sub>SO<sub>4</sub> (orange solid line), 10 mM cHxO (green solid line), 10 mM MB (blue solid line), 10 mM tHxO (pink solid line), and 10 mM tPto (grey solid line). Also shown are the error bars of the peak molar absorptivities of the different solutions. The error bars represent one standard deviation originating from triplicate absorption measurements. Only the addition of tPto and tHxO were found to have significant effects on the peak molar absorptivities of NH<sub>4</sub>NO<sub>3</sub> (p < 0.05).



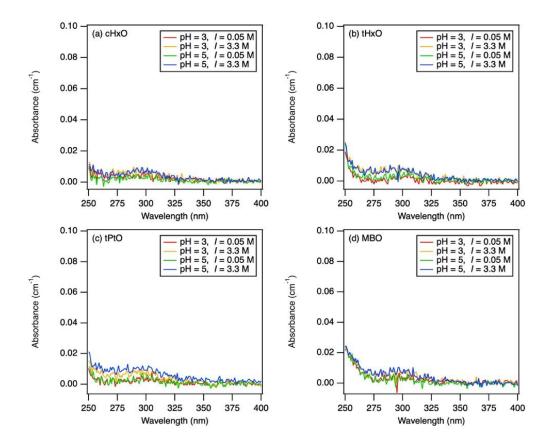
**Figure S3.** Decays of the GLVs in the absence ("Light only") and presence of nitrate and sulfate under cloud/fog-like conditions (Table 1). The error bars represent one standard deviation originating from triplicate experiments and triplicate measurements at each reaction time. The  $k_{obs}$  for MBO at different pH and ionic strengths were corrected by subtracting the loss rates from control experiments conducted in the absence of nitrate and sulfate ("Light only" experiments).



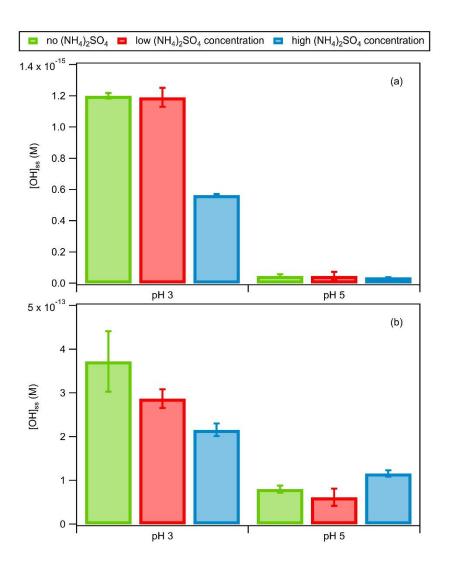
**Figure S4.** Decays of the GLVs in the absence ("Light only") and presence of nitrate and sulfate under aqueous aerosol-like conditions (Table 1). The error bars represent one standard deviation originating from triplicate experiments and triplicate measurements at each reaction time. The  $k_{obs}$  for the four GLVs at different pH and ionic strengths were corrected by subtracting the loss rates from control experiments conducted in the absence of nitrate and sulfate ("Light only" experiments).



**Figure S5.** Light absorption spectra of the four GLVs at different ionic strengths under cloud/fog-like condition. The GLV concentrations were set to 0.1 mM, and the ionic strength of the solutions were adjusted with only H<sub>2</sub>SO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The absorbances of all the solutions were weak in the spectral region of the light output in the Rayonet photoreactor (Figure S2).

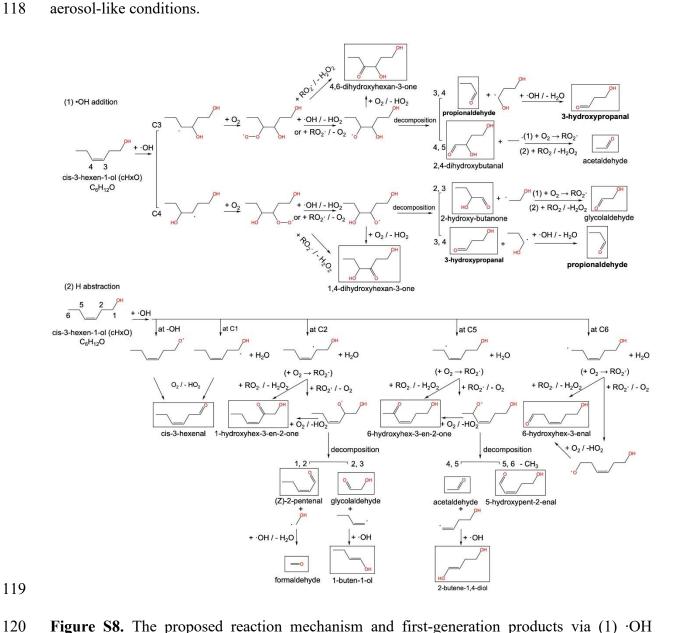


**Figure S6.** Light absorption spectra of the four GLVs at different ionic strengths under cloud/fog-like condition. The GLV concentrations were set to 0.1 mM, and the ionic strength of the solutions were adjusted with only H<sub>2</sub>SO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The slightly increased absorption from 275 to 325 nm could be due to the additions of large amounts of (NH<sub>4</sub>)<sub>4</sub>SO<sub>4</sub> (Cope et al., 2022). In general, the absorbances of all the solutions were weak in the spectral region of the light output in the Rayonet photoreactor (Figure S2).

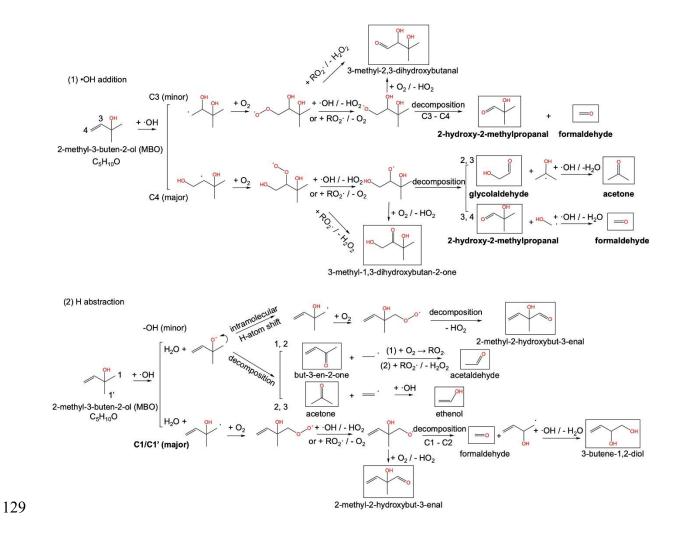


**Figure S7.** Estimated [·OH]<sub>ss</sub> in nitrate-mediated photooxidation experiments under (a) cloud/fog-like, and (b) aqueous aerosol-like conditions. These values were obtained from a separate set of experiments (i.e., GLVs were not present in the solutions) using benzoic acid (10 μM) as the ·OH probe compound and measuring the formation of p-hydroxybenzoic acid from the reaction of ·OH with BA (Lyu et al., 2023; Yang et al., 2021; Yang et al., 2023). The error bars represent one standard deviation originating from triplicate experiments and triplicate measurements. For the low (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> concentration conditions (red bars), 0.135 mM and 0.583 mM of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was added into the solutions for pH 3 and 5, respectively, for cloud/fog-like conditions, whereas 158 mM of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was added into the solutions for both pH 3 and 5 for aqueous aerosol-like conditions (Table 1). For the high (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> concentration conditions (blue bars), 6.135 mM and 6.580 mM of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was added into the solutions for pH 3 and 5, respectively, for cloud/fog-like conditions, whereas 1085 mM was added into the solutions for both pH 3 and 5 for aqueous aerosol-like conditions (Table 1). At present, it

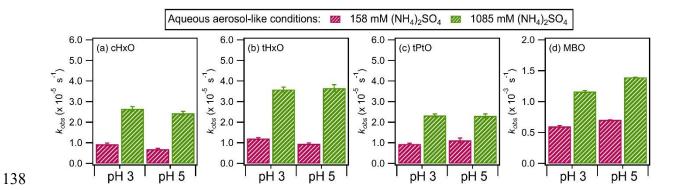
is unclear why the [·OH]<sub>ss</sub> increased with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> concentration at pH 5 under aqueous aerosol-like conditions.



**Figure S8.** The proposed reaction mechanism and first-generation products via (1) ·OH addition, and (2) H abstraction for the oxidation cHxO by ·OH in the aqueous phase based on the existing literature (Reisen et al., 2003; Sarang et al., 2023). Similar reaction mechanisms are expected for the ·OH oxidation of tHxO and tPtO given their similar molecular structures. The expected products are shown in boxes, while expected key products are highlighted in boldface. Note that ·OH can also react with organic compounds through electron transfer pathways, which are not included here due to their expected minor roles in oxidation with GLVs. Bimolecular combination reaction pathways involving  $RO_2$ · and RO· (e.g.,  $RO_2$ · +  $RO_2$ ·) that lead to oligomer formation are also not known here.



**Figure S9.** The proposed reaction mechanism and first generation products via (1) ·OH addition and (2) H abstraction for the oxidation MBO by ·OH in the aqueous phase based on the existing literature (Atkinson and Arey, 2003; Carrasco et al., 2007; Chan et al., 2009; Reisen et al., 2003; Sarang et al., 2023). The expected products are shown in boxes, while expected key products are highlighted in boldface. Note that ·OH can also react with MBO through electron transfer pathways, which are not included here due to their expected minor roles in oxidation with GLVs. Bimolecular combination reaction pathways involving RO<sub>2</sub>· and RO· (e.g.,  $RO_2$ · +  $RO_2$ ·) that lead to oligomer formation are also not known here.



**Figure S10.** The  $k_{obs}$  values for the decays of the four GLVs upon irradiation when only sulfate (in the form of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and (for pH 3) H<sub>2</sub>SO<sub>4</sub>) was present in the solutions. The error bars represent one standard deviation originating from triplicate experiments and measurements.

Table S1. List of reactions pathways initiated by the aqueous photolysis of nitrate compiled from the literature (Gligorovski et al., 2015; Herrmann, 2007; Mack and Bolton, 1999; Marussi and Vione, 2021; Scharko et al., 2014).

No.	Reactions	Quantum yield (Φ)/
		Acid dissociation constant (pKa)
1	$NO_3^- + h\nu \rightarrow [NO_2^{\bullet} + O^{\bullet}]_{cage}$	$\Phi = 0.01$
2	$[NO_2^{\bullet} + O^{\bullet}]_{cage} \rightarrow NO_2^{\bullet} + O^{\bullet}$	_
3	$O^{\bullet^-} + H_2O \leq \bullet OH + OH^-$	$pK_a(\bullet OH) = 11.9$
4	$[NO_2^{\bullet} + O^{\bullet}]_{cage} \rightarrow OONO^-$	_
5	OONO <sup>-</sup> + H <sup>+</sup> \$ HOONO	$pK_a = 7$
6	$\text{HOONO} \rightarrow \bullet \text{OH} + \text{NO}_2 \bullet$	_
7	$2NO_2 \bullet \Rightarrow N_2O_4$	_
8	$N_2O_4 + H_2O \rightarrow HNO_2 + NO_3^- + H^+$	_
9	$HNO_2 \Rightarrow H^+ + NO_2^-$	$pK_a = \sim 3.3$
10	$NO_2^- + hv \rightarrow NO^{\bullet} + O^{\bullet}$	$\Phi = 0.025 - 0.065$
11	$NO_2^- + hv \rightarrow NO_2 \bullet + e^-$	$\Phi = \sim 0.001$
12	$NO_2^- + \bullet OH \rightarrow NO_2 \bullet + OH^-$	_
13	$NO \bullet + NO_2 \bullet \Rightarrow N_2O_3$	_
14	$N_2O_3 + H_2O \rightarrow 2 NO_2^- + 2 H^+$	_
15	$HNO_2 + h\nu \rightarrow NO^{\bullet} + {}^{\bullet}OH$	$\Phi = 0.35$
16	$HNO_2 + \bullet OH \rightarrow NO_2 \bullet + H_2O$	_
17	$2 \text{ HNO}_2 \rightarrow \text{NO} \bullet + \text{NO}_2 \bullet + \text{H}_2\text{O}$	_

**Table S2.** List of  $k_{obs}$  and one lifetime (i.e.,  $\tau = \frac{1}{k_{obs}}$ , when 37 % of the initial concentration of the GLV remained) of GLVs during nitrate-mediated photooxidation under cloud/fog-like conditions (Table 1).

CI V-	сНхО		tHxO		tPtO		MBO	
GLVs	$k_{obs}$ (s <sup>-1</sup> )	τ (min)						
$pH 3$ $I_{total} = 0.002 M$	6.02×10 <sup>-5</sup>	277	6.98×10 <sup>-5</sup>	239	1.06×10 <sup>-4</sup>	158	3.23×10 <sup>-4</sup>	52
$pH 3$ $I_{total} = 0.02 M$	5.61×10 <sup>-5</sup>	297	6.74×10 <sup>-5</sup>	247	1.04×10 <sup>-4</sup>	161	3.41×10 <sup>-4</sup>	49
$pH 5$ $I_{total} = 0.002 M$	5.5×10 <sup>-5</sup>	301	5.69×10 <sup>-5</sup>	293	8.22×10 <sup>-5</sup>	203	2.76×10 <sup>-4</sup>	60
$pH 5$ $I_{total} = 0.02 M$	5.6×10 <sup>-5</sup>	298	5.82×10 <sup>-5</sup>	287	8.23×10 <sup>-5</sup>	203	2.92×10 <sup>-4</sup>	57

**Table S3.** List of  $k_{obs}$  and one lifetime (i.e.,  $\tau = \frac{1}{k_{obs}}$ , when 37 % of the initial concentration of the GLV remained) of GLVs during nitrate-mediated photooxidation under aqueous aerosol-like conditions (Table 1).

CI V-	сНхО		tHxO		tPtO		MBO	
GLVs	$k_{obs}$ (s <sup>-1</sup> )	τ (min)						
pH 3 $I_{total} = 0.5 \text{ M}$	7.91×10 <sup>-6</sup>	2108	1.00×10 <sup>-5</sup>	1663	1.74×10 <sup>-5</sup>	959	3.86×10 <sup>-4</sup>	43
pH 3 $I_{total} = 3.3 \text{ M}$	2.74×10 <sup>-5</sup>	608	3.82×10 <sup>-5</sup>	437	3.04×10 <sup>-5</sup>	548	1.05×10 <sup>-3</sup>	16
$pH 5$ $I_{total} = 0.5 M$	8.55×10 <sup>-6</sup>	1949	1.08×10 <sup>-5</sup>	1538	1.60×10 <sup>-5</sup>	1045	4.65×10 <sup>-4</sup>	36
pH 5 $I_{total} = 3.3 \text{ M}$	2.78×10 <sup>-5</sup>	599	4.32×10 <sup>-5</sup>	386	3.36×10 <sup>-5</sup>	497	1.50×10 <sup>-3</sup>	11

**Table S4.** List of reactions pathways hypothesized to be associated with the aqueous photolysis of sulfate compiled from the literature (Cope et al., 2022; De Semainville et al., 2007; Herrmann et al., 1999). Note that the mechanisms behind the formation of sulfur containing radicals from the aqueous photolysis of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> are still unknown.

No.	Reactions
1	$SO_4^{2-} + H^+ \Rightarrow HSO_4^-$
2	$\bullet OH + HSO_4^- \rightarrow SO_4 \bullet^- + H_2O$
3	$SO_4 \bullet^- + SO_4 \bullet^- \longrightarrow S_2 O_8^{2-}$
4	$SO_4^{\bullet^-} + HO_2^{\bullet} \longrightarrow SO_4^{2^-} + H^+ + O_2$
5	$SO_4 \bullet^- + O_2^- \rightarrow SO_4^{2-} + O_2$
6	$SO_4 \bullet^- + OH^- \rightarrow SO_4^{2-} + \bullet OH$
7	$SO_4 \bullet^- + H_2O \rightarrow SO_4^{2-} + H^+ + \bullet OH$
8	$S_2O_8^{2-} + hv \rightarrow 2SO_4^{\bullet}$
9	$SO_4 \bullet^- + NO_3^- \longrightarrow SO_4^{2-} + NO_3 \bullet$

Table S5. Previously reported second-order reaction rate constants for the GLVs against ·OH,
 SO<sub>4</sub>·-, and NO<sub>3</sub>·.

GLVs	Oxidant	Rate constant (×10 <sup>-9</sup> M <sup>-1</sup> s <sup>-1</sup> )	Temp. (K)	рН	Reference	
		$5.1 \pm 0.8$		3.1	(D: 1, 1, II 1,	
cHxO	·OH	$5.3 \pm 0.3$	298	5.4	(Richards-Henderson	
		$5.3 \pm 0.2$		6.9	et al., 2014)	
		$7.5 \pm 1.4$		3.1	(Richards-Henderson	
MBO	·OH	$8.0 \pm 0.6$	298	5.4		
WIBO	OII	$7.3 \pm 0.7$	276	6.9	et al., 2014)	
	·OH	$6.3 \pm 0.1$				
1-peten-3-ol	SO <sub>4</sub> ·-	$0.94 \pm 0.10$	298	7	(Sarang et al., 2021)	
	NO <sub>3</sub> ·	$0.15 \pm 0.015$				
	·OH	$6.7 \pm 0.3$				
cis-2-hexen-1-ol	SO <sub>4</sub> ·-	$2.5 \pm 0.3$	298	7	(Sarang et al., 2021)	
	NO <sub>3</sub> ·	$0.84 \pm 0.23$				
	·OH	$4.8 \pm 0.3$				
trans-2-hexen-1-al	SO <sub>4</sub> ·-	$0.48 \pm 0.02$	298	7	(Sarang et al., 2021)	
	NO <sub>3</sub> ·	$0.03 \pm 0.07$				

Table S6. Statistical analyses (student's t test) for the differences in  $k_{obs}$  at different pH and ionic strengths under cloud/fog-like conditions for cHxO (Figure 2 in the main text).

ш.о	pH 3	pH 3	pH 5	pH 5	
сНхО	$I_{total} = 0.002 \text{ M}$	$I_{total} = 0.02 \text{ M}$	$I_{total} = 0.002 \text{ M}$	$I_{total} = 0.02 \text{ M}$	
pH 3	/	NCC	< 0.05	NCC	
$I_{total} = 0.002 \text{ M}$	/	N.S.S.	<i>p</i> < 0.05	N.S.S.	
рН 3	N.S.S.	/	N.S.S.	N.S.S.	
$I_{total} = 0.02 \text{ M}$	N.S.S.	,	14.5.5.	1	
pH 5	<i>p</i> < 0.05	N.S.S.	/	N.S.S.	
$I_{total} = 0.002 \text{ M}$	p < 0.03	14.5.5.	,	14.5.5.	
pH 5	N.S.S.	N.S.S.	N.S.S.	/	
$I_{total} = 0.02 \text{ M}$	14.5.5.	14.5.5.	14.5.5.	,	

Table S7. Statistical analyses (student's t test) for the differences in  $k_{obs}$  at different pH and ionic strengths under cloud/fog-like conditions for tHxO (Figure 2 in the main text).

	pH 3	pH 3	pH 5	pH 5	
tHxO	$I_{total} = 0.002 \text{ M}$	$I_{total} = 0.02 \text{ M}$	$I_{total} = 0.002 \text{ M}$	$I_{total} = 0.02 \text{ M}$	
pH 3	/	N.S.S.	p < 0.05	n < 0.05	
$I_{total} = 0.002 \text{ M}$	1	11.5.5.	p < 0.03	<i>p</i> < 0.05	
рН 3	N.S.S.	/	<i>p</i> < 0.05	<i>p</i> < 0.05	
$I_{total} = 0.02 \text{ M}$	N.S.S.	,	p < 0.05	p < 0.03	
pH 5	<i>p</i> < 0.05	<i>p</i> < 0.05	/	N.S.S.	
$I_{total} = 0.002 \text{ M}$	ρ < 0.03	$\rho \sim 0.03$	1	11.5.5.	
pH 5	<i>p</i> < 0.05	<i>p</i> < 0.05	N.S.S.	/	
$I_{total} = 0.02 \text{ M}$	p < 0.03	p < 0.05	14.5.5.	,	

Table S8. Statistical analyses (student's t test) for the differences in  $k_{obs}$  at different pH and ionic strengths under cloud/fog-like conditions for tPtO (Figure 2 in the main text).

	pH 3	рН 3	pH 5	pH 5
tPtO	$I_{total} = 0.002 \text{ M}$	$I_{total} = 0.02 \text{ M}$	$I_{total} = 0.002 \text{ M}$	$I_{total} = 0.02 \text{ M}$
pH 3	,	NGG	.0.05	.0.05
$I_{total} = 0.002 \text{ M}$	/	N.S.S.	<i>p</i> < 0.05	p < 0.05
рН 3	N.S.S.	/	<i>p</i> < 0.05	<i>p</i> < 0.05
$I_{total} = 0.02 \text{ M}$	14.5.5.	,	P	P
pH 5	<i>p</i> < 0.05	<i>p</i> < 0.05	/	N.S.S.
$I_{total} = 0.002 \text{ M}$	p 10.03	p (0.03	,	14.5.5.
pH 5	<i>p</i> < 0.05	<i>p</i> < 0.05	N.S.S.	/
$I_{total} = 0.02 \text{ M}$	p - 0.03	p - 0.03	14.5.5.	,

**Table S9.** Statistical analyses (student's t test) for the differences in  $k_{obs}$  at different pH and ionic strengths under cloud/fog-like conditions for MBO (Figure 2 in the main text).

-	pH 3	pH 3	pH 5	pH 5
МВО	$I_{total} = 0.002 \text{ M}$	$I_{total} = 0.02 \text{ M}$	$I_{total} = 0.002 \text{ M}$	$I_{total} = 0.02 \text{ M}$
pH 3				
$I_{total} = 0.002 \text{ M}$	/	N.S.S.	<i>p</i> < 0.05	<i>p</i> < 0.05
pH 3				
$I_{total} = 0.02 \text{ M}$	N.S.S.	/	<i>p</i> < 0.05	<i>p</i> < 0.05
pH 5				
$I_{total} = 0.002 \text{ M}$	<i>p</i> < 0.05	<i>p</i> < 0.05	/	N.S.S.
pH 5	<i>p</i> < 0.05	<i>p</i> < 0.05	N.S.S.	1
$I_{total} = 0.02 \text{ M}$	$p \sim 0.03$	p < 0.03	11.5.5.	1

**Table S10.** Statistical analyses (student's t test) for the differences in  $Y_{SOA}$  between pH and ionic strength under cloud/fog-like conditions for cHxO (Figure 3 in the main text).

	pH 3	pH 3	pH 5	pH 5
сНхО	$I_{total} = 0.002 \text{ M}$	$I_{total} = 0.02 \text{ M}$	$I_{total} = 0.002 \text{ M}$	$I_{total} = 0.02 \text{ M}$
pH 3 $I_{total} = 0.002 \text{ M}$	/	N.S.S.	p < 0.05	p < 0.05
pH 3 $I_{total} = 0.02 \text{ M}$	N.S.S.	/	p < 0.05	<i>p</i> < 0.05
pH 5 $I_{total} = 0.002 \text{ M}$	p < 0.05	p < 0.05	/	<i>p</i> < 0.05
pH 5 $I_{total} = 0.02 \text{ M}$	p < 0.05	p < 0.05	p < 0.05	/

**Table S11.** Statistical analyses (student's t test) for the differences in  $Y_{SOA}$  between pH and ionic strength under cloud/fog-like conditions for tHxO (Figure 3 in the main text).

	pH 3	pH 3	pH 5	pH 5
tHxO	$I_{total} = 0.002 \text{ M}$	$I_{total} = 0.02 \text{ M}$	$I_{total} = 0.002 \text{ M}$	$I_{total} = 0.02 \text{ M}$
pH 3 $I_{total} = 0.002 \text{ M}$	/	p < 0.05	N.S.S.	p < 0.05
pH 3 $I_{total} = 0.02 \text{ M}$	p < 0.05	/	N.S.S.	N.S.S.
pH 5 $I_{total} = 0.002 \text{ M}$	N.S.S.	N.S.S.	/	N.S.S.
pH 5 $I_{total} = 0.02 \text{ M}$	p < 0.05	N.S.S.	N.S.S.	/

**Table S12.** Statistical analyses (student's t test) for the differences in  $Y_{SOA}$  between pH and ionic strength under cloud/fog-like conditions for tPtO (Figure 3 in the main text).

	pH 3	pH 3	pH 5	pH 5
tPtO	$I_{total} = 0.002 \text{ M}$	$I_{total} = 0.02 \text{ M}$	$I_{total} = 0.002 \text{ M}$	$I_{total} = 0.02 \text{ M}$
pH 3 $I_{total} = 0.002 \text{ M}$	1	N.S.S.	N.S.S.	p < 0.05
pH 3 $I_{total} = 0.02 \text{ M}$	N.S.S.	/	N.S.S.	<i>p</i> < 0.05
pH 5 $I_{total} = 0.002 \text{ M}$	N.S.S.	N.S.S.	/	<i>p</i> < 0.05
pH 5 $I_{total} = 0.02 \text{ M}$	p < 0.05	p < 0.05	p < 0.05	/

Table S13. Statistical analyses (student's t test) for the differences in  $Y_{SOA}$  between pH and ionic strength under cloud/fog-like conditions for MBO (Figure 3 in the main text).

	pH 3	pH 3	pH 5	pH 5
МВО	$I_{total} = 0.002 \text{ M}$	$I_{total} = 0.02 \text{ M}$	$I_{total} = 0.002 \text{ M}$	$I_{total} = 0.02 \text{ M}$
pH 3 $I_{total} = 0.002 \text{ M}$	/	N.S.S.	N.S.S.	N.S.S.
pH 3 $I_{total} = 0.02 \text{ M}$	N.S.S.	/	N.S.S.	N.S.S.
pH 5 $I_{total} = 0.002 \text{ M}$	N.S.S.	N.S.S.	/	N.S.S.
pH 5 $I_{total} = 0.02 \text{ M}$	N.S.S.	N.S.S.	N.S.S.	/

Table S14. Statistical analyses (student's t test) for the differences in  $k_{obs}$  at different pH and ionic strengths under aqueous aerosol-like conditions for cHxO (Figure 4 in the main text).

сНхО	pH 3	pH 3	pH 5	pH 5
спхо	$I_{total} = 0.5 \text{ M}$	$I_{total} = 3.3 \text{ M}$	$I_{total} = 0.5 \text{ M}$	$I_{total} = 3.3 \text{ M}$
pH 3	/	p < 0.05	N.S.S.	p < 0.05
$I_{total} = 0.5 \text{ M}$ pH 3				
$I_{total} = 3.3 \text{ M}$	<i>p</i> < 0.05	/	<i>p</i> < 0.05	N.S.S.
pH 5 $I_{total} = 0.5 \text{ M}$	N.S.S.	P< 0.05	/	<i>p</i> < 0.05
pH 5	<i>p</i> < 0.05	N.S.S.	<i>p</i> < 0.05	/
$I_{total} = 3.3 \text{ M}$	p < 0.05	14.5.5.	p < 0.05	,

Table S15. Statistical analyses (student's t test) for the differences in  $k_{obs}$  at different pH and ionic strengths under aqueous aerosol-like conditions for tHxO (Figure 4 in the main text).

411-0	pH 3	pH 3	pH 5	pH 5
tHxO	$I_{total} = 0.5 \text{ M}$	$I_{total} = 3.3 \text{ M}$	$I_{total} = 0.5 \text{ M}$	$I_{total} = 3.3 \text{ M}$
рН 3	/	p < 0.05	N.S.S.	p < 0.05
$I_{total} = 0.5 \text{ M}$				
pH 3	<i>p</i> < 0.05	/	<i>p</i> < 0.05	<i>p</i> < 0.05
$I_{total} = 3.3 \text{ M}$	P		P	Γ
pH 5	N.S.S.	<i>p</i> < 0.05	/	<i>p</i> < 0.05
$I_{total} = 0.5 \text{ M}$	1.1.5.1.5.1	P	·	p stoc
pH 5	<i>p</i> < 0.05	<i>p</i> < 0.05	<i>p</i> < 0.05	/
$I_{total} = 3.3 \text{ M}$	$p \sim 0.03$	$\rho \sim 0.03$	p < 0.03	,

Table S16. Statistical analyses (student's t test) for the differences in  $k_{obs}$  at different pH and ionic strengths under aqueous aerosol-like conditions for tPtO (Figure 4 in the main text).

tPtO	pH 3	pH 3	pH 5	pH 5
trio	$I_{total} = 0.5 \text{ M}$	$I_{total} = 3.3 \text{ M}$	$I_{total} = 0.5 \text{ M}$	$I_{total} = 3.3 \text{ M}$
pH 3	/	p < 0.05	p < 0.05	p < 0.05
$I_{total} = 0.5 \text{ M}$				
pH 3	<i>p</i> < 0.05	/	<i>p</i> < 0.05	<i>p</i> < 0.05
$I_{total} = 3.3 \text{ M}$	p . 0.03	,	p . 0.05	p - 0.05
pH 5	<i>p</i> < 0.05	<i>p</i> < 0.05	/	<i>p</i> < 0.05
$I_{total} = 0.5 \text{ M}$	p old	P	•	p stoc
pH 5	<i>p</i> < 0.05	<i>p</i> < 0.05	<i>p</i> < 0.05	/
$I_{total} = 3.3 \text{ M}$	p < 0.05	p - 0.03	p < 0.03	,

Table S17. Statistical analyses (student's t test) for the differences in  $k_{obs}$  at different pH and ionic strengths under aqueous aerosol-like conditions for MBO (Figure 4 in the main text).

MPO	pH 3	pH 3	pH 5	pH 5
МВО	$I_{total} = 0.5 \text{ M}$	$I_{total} = 3.3 \text{ M}$	$I_{total} = 0.5 \text{ M}$	$I_{total} = 3.3 \text{ M}$
рН 3	/	p < 0.05	p < 0.05	p < 0.05
$I_{total} = 0.5 \text{ M}$				
pH 3	<i>p</i> < 0.05	/	<i>p</i> < 0.05	<i>p</i> < 0.05
$I_{total} = 3.3 \text{ M}$	P		P	P
pH 5	<i>p</i> < 0.05	<i>p</i> < 0.05	/	<i>p</i> < 0.05
$I_{total} = 0.5 \text{ M}$	p (0.03	p < 0.03	,	p < 0.03
pH 5	<i>p</i> < 0.05	<i>p</i> < 0.05	<i>p</i> < 0.05	/
$I_{total} = 3.3 \text{ M}$	p < 0.03	p < 0.03	p < 0.03	/

Table S18. Statistical analyses (student's t test) for the differences in  $Y_{SOA}$  between pH and ionic strength under aqueous aerosol-like conditions for cHxO (Figure 5 in the main text).

-11-0	pH 3	pH 3	pH 5	pH 5
сНхО	$I_{total} = 0.5 \text{ M}$	$I_{total} = 3.3 \text{ M}$	$I_{total} = 0.5 \text{ M}$	$I_{total} = 3.3 \text{ M}$
рН 3	/	p < 0.05	N.S.S.	p < 0.05
$I_{total} = 0.5 \text{ M}$ pH 3				
$I_{total} = 3.3 \text{ M}$	<i>p</i> < 0.05	/	<i>p</i> < 0.05	<i>p</i> < 0.05
pH 5	N.S.S.	n < 0.05	/	n < 0.05
$I_{total} = 0.5 \text{ M}$	N.S.S.	<i>p</i> < 0.05	1	<i>p</i> < 0.05
pH 5	<i>p</i> < 0.05	<i>p</i> < 0.05	<i>p</i> < 0.05	/
$I_{total} = 3.3 \text{ M}$				

Table S19. Statistical analyses (student's t test) for the differences in  $Y_{SOA}$  between pH and ionic strength under aqueous aerosol-like conditions for tHxO (Figure 5 in the main text).

tHxO	pH 3	pH 3	pH 5	pH 5
thxo	$I_{total} = 0.5 \text{ M}$	$I_{total} = 3.3 \text{ M}$	$I_{total} = 0.5 \text{ M}$	$I_{total} = 3.3 \text{ M}$
рН 3	/	p < 0.05	p < 0.05	p < 0.05
$I_{total} = 0.5 \text{ M}$				
рН 3	<i>p</i> < 0.05	/	<i>p</i> < 0.05	N.S.S.
$I_{total} = 3.3 \text{ M}$	P		P	
pH 5	<i>p</i> < 0.05	P< 0.05	/	<i>p</i> < 0.05
$I_{total} = 0.5 \text{ M}$	1			•
pH 5	<i>p</i> < 0.05	N.S.S.	<i>p</i> < 0.05	/
$I_{total} = 3.3 \text{ M}$	•		1	

Table S20. Statistical analyses (student's t test) for the differences in  $Y_{SOA}$  between pH and ionic strength under aqueous aerosol-like conditions for tPtO (Figure 5 in the main text).

tPtO	pH 3	pH 3	pH 5	pH 5
trio	$I_{total} = 0.5 \text{ M}$	$I_{total} = 3.3 \text{ M}$	$I_{total} = 0.5 \text{ M}$	$I_{total} = 3.3 \text{ M}$
pH 3	/	p < 0.05	p < 0.05	p < 0.05
$I_{total} = 0.5 \text{ M}$				
pH 3	<i>p</i> < 0.05	/	<i>p</i> < 0.05	<i>p</i> < 0.05
$I_{total} = 3.3 \text{ M}$	p . 0.03	,	p . 0.05	p - 0.05
pH 5	<i>p</i> < 0.05	<i>p</i> < 0.05	/	<i>p</i> < 0.05
$I_{total} = 0.5 \text{ M}$	p old	P	•	p stoc
pH 5	<i>p</i> < 0.05	<i>p</i> < 0.05	<i>p</i> < 0.05	/
$I_{total} = 3.3 \text{ M}$	p < 0.05	p - 0.03	p < 0.03	,

Table S21. Statistical analyses (student's t test) for the differences in  $Y_{SOA}$  between pH and ionic strength under aqueous aerosol-like conditions for MBO (Figure 5 in the main text).

MDO	pH 3	pH 3	pH 5	pH 5
MBO	$I_{total} = 0.5 \text{ M}$	$I_{total} = 3.3 \text{ M}$	$I_{total} = 0.5 \text{ M}$	$I_{total} = 3.3 \text{ M}$
pH 3 $I_{total} = 0.5 \text{ M}$	/	p < 0.05	N.S.S.	p < 0.05
pH 3	<i>p</i> < 0.05	/	<i>p</i> < 0.05	N.S.S.
$I_{total} = 3.3 \text{ M}$	r		P	
pH 5	N.S.S.	<i>p</i> < 0.05	/	<i>p</i> < 0.05
$I_{total} = 0.5 \text{ M}$				
pH 5	<i>p</i> < 0.05	N.S.S.	<i>p</i> < 0.05	/
$I_{total} = 3.3 \text{ M}$	-		-	

## 249 References

- Anastasio, C. and McGregor, K. G.: Chemistry of fog waters in California's Central Valley:
- 1. In situ photoformation of hydroxyl radical and singlet molecular oxygen, Atmos Environ,
- 252 35, 1079-1089, 10.1016/S1352-2310(00)00281-8, 2001.
- 253 Atkinson, R. and Arey, J.: Atmospheric degradation of volatile organic compounds, Chem
- 254 Rev, 103, 4605-4638, 10.1021/cr0206420, 2003.
- 255 Carrasco, N., Doussin, J. F., O'Connor, M., Wenger, J. C., Picquet-Varrault, B., Durand-
- Jolibois, R., and Carlier, P.: Simulation chamber studies of the atmospheric oxidation of 2-
- 257 methyl-3-buten-2-ol: Reaction with hydroxyl radicals and ozone under a variety of
- 258 conditions, J Atmos Chem, 56, 33-55, 10.1007/s10874-006-9041-y, 2007.
- Chan, A. W. H., Galloway, M. M., Kwan, A. J., Chhabra, P. S., Keutsch, F. N., Wennberg, P.
- O., Flagan, R. C., and Seinfeld, J. H.: Photooxidation of 2-Methyl-3-Buten-2-ol (MBO) as a
- 261 Potential Source of Secondary Organic Aerosol, Environ Sci Technol, 43, 4647-4652,
- 262 10.1021/es802560w, 2009.
- 263 Cope, J. D., Bates, K. H., Tran, L. N., Abellar, K. A., and Nguyen, T. B.: Sulfur radical
- 264 formation from the tropospheric irradiation of aqueous sulfate aerosols, P Natl Acad Sci
- 265 USA, 119, 10.1073/pnas.2202857119, 2022.
- de Semainville, P. G., Hoffmann, D., George, C., and Herrmann, H.: Study of nitrate radical
- 267 (NO3) reactions with carbonyls and acids in aqueous solution as a function of temperature,
- 268 Phys Chem Chem Phys, 9, 958-968, 10.1039/b613956f, 2007.
- 269 Gligorovski, S., Strekowski, R., Barbati, S., and Vione, D.: Environmental Implications of
- 270 Hydroxyl Radicals (center dot OH), Chemical Reviews, 115, 13051-13092,
- 271 10.1021/cr500310b, 2015.
- Herrmann, H.: On the photolysis of simple anions and neutral molecules as sources of
- 273 O-/OH, SOx- and Cl in aqueous solution, Physical Chemistry Chemical Physics, 9, 3935-
- 274 3964, 10.1039/B618565G, 2007.
- Herrmann, H., Ervens, B., Nowacki, P., Wolke, R., and Zellner, R.: A chemical aqueous
- 276 phase radical mechanism for tropospheric chemistry, Chemosphere, 38, 1223-1232, 1999.
- Herrmann, H., Hoffmann, D., Schaefer, T., Bräuer, P., and Tilgner, A.: Tropospheric
- 278 Aqueous-Phase Free-Radical Chemistry: Radical Sources, Spectra, Reaction Kinetics and
- 279 Prediction Tools, ChemPhysChem, 11, 3796-3822, 10.1002/cphc.201000533, 2010.
- Lyu, Y., Chow, J. T. C., and Nah, T.: Kinetics of the nitrate-mediated photooxidation of
- 281 monocarboxylic acids in the aqueous phase, Environ Sci-Proc Imp, 25, 461-471,
- 282 10.1039/d2em00458e, 2023.

- Mack, J. and Bolton, J. R.: Photochemistry of nitrite and nitrate in aqueous solution: a
- 284 review, J Photoch Photobio A, 128, 1-13, Doi 10.1016/S1010-6030(99)00155-0, 1999.
- 285 Marussi, G. and Vione, D.: Secondary Formation of Aromatic Nitroderivatives of
- 286 Environmental Concern: Photonitration Processes Triggered by the Photolysis of Nitrate and
- Nitrite Ions in Aqueous Solution, Molecules, 26, 2550, 2021.
- Reisen, F., Aschmann, S. M., Atkinson, R., and Arey, J.: Hydroxyaldehyde products from
- 289 hydroxyl radical reactions of
- 290 -3-hexen-1-ol and 2-methyl-3-buten-2-ol quantified hy SPME and API-MS, Environ Sci
- 291 Technol, 37, 4664-4671, 10.1021/es034142f, 2003.
- 292 Richards-Henderson, N. K., Hansel, A. K., Valsaraj, K. T., and Anastasio, C.: Aqueous
- 293 oxidation of green leaf volatiles by hydroxyl radical as a source of SOA: Kinetics and SOA
- 294 yields, Atmos Environ, 95, 105-112, 10.1016/j.atmosenv.2014.06.026, 2014.
- 295 Sander, R.: Compilation of Henry's law constants (version 5.0.0) for water as solvent,
- 296 Atmospheric Chemistry and Physics, 23, 10901-12440, 10.5194/acp-23-10901-2023, 2023.
- Sarang, K., Otto, T., Rudzinski, K., Schaefer, T., Grgic, I., Nestorowicz, K., Herrmann, H.,
- and Szmigielski, R.: Reaction Kinetics of Green Leaf Volatiles with Sulfate, Hydroxyl, and
- Nitrate Radicals in Tropospheric Aqueous Phase, Environ Sci Technol, 55, 13666-13676,
- 300 10.1021/acs.est.1c03276, 2021.
- 301 Sarang, K., Otto, T., Gagan, S., Rudzinski, K., Schaefer, T., Brüggemann, M., Grgic, I.,
- 302 Kubas, A., Herrmann, H., and Szmigielski, R.: Aqueous-phase photo-oxidation of selected
- green leaf volatiles initiated by OH radicals: Products and atmospheric implications, Sci
- 304 Total Environ, 879, 10.1016/j.scitotenv.2023.162622, 2023.
- 305 Scharko, N. K., Berke, A. E., and Raff, J. D.: Release of nitrous acid and nitrogen dioxide
- from nitrate photolysis in acidic aqueous solutions, Environ Sci Technol, 48, 11991-12001,
- 307 10.1021/es503088x, 2014.
- Yang, J., Au, W. C., Law, H., Lam, C. H., and Nah, T.: Formation and evolution of brown
- 309 carbon during aqueous-phase nitrate-mediated photooxidation of guaiacol and 5-
- 310 nitroguaiacol, Atmos Environ, 254, 118401, 10.1016/j.atmosenv.2021.118401, 2021.
- Yang, J., Au, W. C., Law, H., Leung, C. H., Lam, C. H., and Nah, T.: pH affects the aqueous-
- 312 phase nitrate-mediated photooxidation of phenolic compounds: implications for brown
- carbon formation and evolution, Environ Sci Process Impacts, 25, 176-189,
- 314 10.1039/d2em00004k, 2023.