1	Heterogeneous Interactions between SO ₂ and
	Organic Peroxides in Submicron Aerosol
2	
3	
4	Shunyao Wang ¹ , Tengyu Liu ² , Jinmyung Jang ¹ ,
5	Jonathan P.D. Abbatt ² and Arthur W.H. Chan ^{1*}
6	
7	
8	
9	
10	¹ Department of Chemical Engineering and Applied Chemistry, University of Toronto,
11	Toronto, Ontario, M5S 3E5, Canada
12	² Department of Chemistry, University of Toronto, Toronto, Ontario, M5S 3H6, Canada
13	
14	
15	
16	
17	
18	
19	
20	
21	*Correspondence to: Arthur W.H. Chan (arthurwh.chan@utoronto.ca)

22 Abstract

Atmospheric models often underestimate particulate sulfate, a major component in ambient 23 24 aerosol, suggesting missing sulfate formation mechanisms. Heterogeneous reactions between SO₂ and aerosol play an important role in particulate sulfate formation and its physicochemical 25 evolution. Here we study the reactive uptake kinetics of SO_2 onto aerosol containing organic 26 27 peroxides. We present chamber studies of SO₂ reactive uptake performed under different relative 28 humidities (RH), particulate peroxide contents, peroxide types, and aerosol acidities. Using 29 different model organic peroxides mixed with ammonium sulfate particles, SO₂ uptake coefficient (γ_{SO2}) was found to be exponentially dependent on RH. γ_{SO2} increases from 10⁻³ at RH 30 25% to 10⁻² at RH 71% as measured for an organic peroxide with multiple O-O groups. Under 31 32 similar conditions, the kinetics in this study were found to be structurally dependent: organic peroxides with multiple peroxide groups have a higher γ_{SO2} than those with only one peroxide 33 34 group, consistent with the reactivity trend observed previously in the aqueous phase. In addition, 35 γ_{SO2} is linearly related to particle-phase peroxide content, which in turn depends on gas-particle partitioning of organic peroxides. Aerosol acidity plays a complex role in determining SO₂ 36 uptake rate, influenced by the effective Henry's Law constant of SO₂ and the condensed phase 37 38 kinetics of the peroxide-SO₂ reaction in the highly concentrated aerosol phase. These uptake 39 coefficients are consistently higher than those calculated from the reaction kinetics in the bulk 40 aqueous phase, and we show experimental evidence suggesting that other factors, such as 41 particle-phase ionic strength, can play an essential role in determining the uptake kinetics. γ_{SO2} for different types of secondary organic aerosol (SOA) were measured to be on the order of 10^{-4} . 42 43 Overall, this study provides quantitative evidence of the multiphase reactions between SO₂ and 44 organic peroxides, highlighting the important factors that govern the uptake kinetics.

45 Introduction

46 Sulfate and organic compounds are ubiquitous particulate components in both polluted and

47 pristine environments (Chen et al., 2009;Andreae et al., 2018;He et al., 2011;Sun et al.,

48 2013;Huang et al., 2014), with important implications for public health and global climate

49 (Hallquist et al., 2009). Particulate sulfate can form via S(IV) oxidation by OH radicals in the gas

50 phase and via oxidation in cloud water, fog droplets or the aerosol aqueous phase, including by

51 H_2O_2 , O_2 (catalyzed by transition metals), O_3 , NO_2 and small organic peroxides (methyl

52 hydroperoxide and peroxyacetic acid) (Seinfeld and Pandis, 2012). However, atmospheric

53 models tend to underestimate particulate sulfate production on both global (Tie et al., 2001; Yang

et al., 2017;Fairlie et al., 2010) and regional scales, especially during heavy haze episodes (Wang

55 et al., 2014;Zheng et al., 2015;Sha et al., 2019;Gao et al., 2016;Li et al., 2017;Huang et al.,

2019), suggesting that the overall kinetics may be underestimated and/or important mechanisms
may be missing in models.

58 To reconcile these differences, studies have investigated novel reaction mechanisms of sulfate formation. Stabilized Criegee intermediates (sCIs) were hypotheiszed to oxidize SO₂ rapidly and 59 potentially serve as an important source of ambient sulfate (Mauldin et al., 2012). In the work by 60 61 Newland et al. (2015) and Nguyen et al. (2016), this sCIs pathway was shown to play a minor role in sulfate formation. More recently, when Liu et al. (2019) applied this mechanism and 62 63 kinetics to a source-oriented WRF-Chem model, the sCIs pathway was found to only account for 64 at most 9% of the total particulate sulfate. Reactive nitrogen species (such as NO₂) have also 65 been put forward to account for the missing sulfate at relatively high aerosol pH (close to 7) (Wang et al., 2016; Cheng et al., 2016). However, such high aerosol pH is not substantiated by 66 67 thermodynamic models, which conclude that pH ranges between 4 and 5 even in polluted regions

(Song et al., 2018;Guo et al., 2017). A recent modeling study incorporating this heterogeneous 68 NO_x mechanism still exhibited a discrepancy of 20% between the predicted and observed sulfate, 69 70 indicating the possibility of unknown mechanisms (Huang et al., 2019). Other factors may play a role in enhancing the particle-phase sulfate formation rates. Chen et al. (2019) investigated the 71 72 synergistic effects of NO₂ and NH₃ on sulfate formation, and found that the rate of this reaction 73 can be enhanced by the high ionic strength in the particle phase. This enhancement effect by 74 solute strength on sulfate formation was also investigated for the H₂O₂ pathway in aerosol liquid 75 water. Liu et al. (2020) found ionic strength and general acid-catalyzed mechanisms can cause 76 the S(VI) formation rate to be nearly 50 times faster in aerosol phase than in dilute solutions. On the other hand, during the severe haze episodes in China (Li et al., 2020; Guo et al., 2017), 77 transition metal ion (TMI) catalysis of SO₂ oxidation by O₂ can be significantly suppressed in the 78 79 aerosol phase due to high ionic strength (Liu et al., 2020; Cheng et al., 2016; Su et al., 2020). 80 In addition to high solute strength, submicron aerosol is also rich in organic compounds (Jimenez 81 et al., 2009;Hallquist et al., 2009). In recent years, many studies have investigated the potential role of heterogeneous interactions between SO₂ and organic aerosol on particulate sulfate 82 formation. Song et al. (2019) found heterogeneous oxidation of hydroxymethanesulfonate 83 84 (HMS) by OH can trigger rapid sulfate formation. Wang et al. (2020) studied photosensitizers in ambient particles and found this pathway could be essential under specific light conditions. 85 86 Recent studies found reactive intermediates from isoprene oxidation (Huang et al., 2019) and 87 benzoic acid (Huang et al., 2020), can yield a variety of organosulfur species upon catalysis by 88 TMI. Other studies have also investigated the interactions between secondary organic aerosol 89 (SOA) and SO₂. Field observations found that ambient sulfate abundance is highly correlated 90 with SOA formation (Yee et al., 2020;Xu et al., 2015). Liu et al. (2019) found that SO₂ enhances

91 SOA formation and average carbon oxidation state during methoxyphenol photooxidation. By performing chamber experiments with limonene SOA formation in the presence of SO₂, Ye et al. 92 (2018) also observed significant SO_2 decay along with increased SOA yields and carbon 93 94 oxidation state, proposing that organic peroxides in SOA may be the key reactive intermediates for SO₂ oxidation. 95 96 Organic peroxides are key intermediates for aerosol formation and ubiquitously exist in many 97 SOA systems (Hallquist et al., 2009; Bianchi et al., 2019). Numerous studies have reported 98 peroxide content of 20-60% for isoprene and monoterpene derived SOA (Surratt et al., 2006;Ng 99 et al., 2008; Ye et al., 2018; Epstein et al., 2014). A significant fraction of organic peroxide (30%-50%) has also been found in naphthalene-derived SOA under low/high NO_x conditions 100 101 (Kautzman et al., 2009). Using model simulations, Bonn et al. (2004) found organic hydroperoxides can account for up to 60% of global SOA. The aqueous phase reaction kinetics 102 103 between organic peroxides and dissolved SO_2 have been explored in previous studies (Lind et al., 104 1987;Gunz and Hoffmann, 1990;Wang et al., 2019;Dovrou et al., 2019;Yao et al., 2019). The 105 second order reaction rate constants for organic peroxides in SOA (Dovrou et al., 2019; Yao et al., 2019) and S(IV) were measured to be on the order of 10^2 - 10^3 M⁻¹ s⁻¹, which are within the 106 107 range of those measured for commercially available organic peroxides (Wang et al., 2019) and 108 small organic peroxides (Lind et al., 1987). Yao et al. (2019) quantified the reactive uptake coefficient of SO₂ (γ_{SO2}) onto α -pinene SOA to be on the order of 10⁻⁴-10⁻³, which is positively 109 110 dependent on RH and inferred particle-phase peroxide content. These reactions are also linked to 111 the formation of organosulfates (Wang et al., 2019). Both inorganic sulfate (85-90%) and 112 organosulfates (10-15%) were observed as products of SO₂ reactive uptake onto SOA (Yao et al., 113 2019).

114 Given the potential significance of SO₂ reactive uptake in particulate sulfate formation, a more in-depth study is needed to determine the important factors that govern the heterogeneous 115 kinetics of SO₂ onto organic peroxide containing aerosol. In this study, we measured γ_{SO2} for two 116 categories of aerosol: 1. Model organic peroxides mixed with ammonium sulfate or malonic acid 117 and 2. SOA from a few representative biogenic and anthropogenic precursors. The impacts of 118 119 RH, peroxide type, peroxide content, and condensed phase pH on SO_2 reactive uptake were 120 evaluated systematically with the goal of better understanding atmospheric multiphase sulfate 121 formation.

122

123 **2. Methods**

The reactive uptake of SO₂ onto peroxide-containing particles was studied in a 1 m³ Teflon chamber under ambient temperature and pressure. In brief, generated particles and SO₂ were introduced into the chamber separately. The consumption of SO₂, changes in particle size distribution and chemical composition were monitored to estimate the reactive uptake coefficients. Particles were also collected on filters for offline chemical characterization.

130 2.1 Seed aerosol generation

In this work, two types of aerosol were used to investigate the uptake of SO₂. The first is ammonium sulfate or malonic acid mixed with model organic peroxides (Fig. S1). In this first set of experiments, an aerosol atomizer (Model 3076, TSI Inc., USA) was used to generate aqueous particles from dilute solution. Each solution consists of ammonium sulfate (\geq 99%, Sigma-Aldrich) or malonic acid (99%, Sigma-Aldrich) and a model organic peroxide in ultrapure water (HPLC grade, Fisher Chemical). For the experiments investigating the relationship between γ_{SO2}

137	and peroxide type (Expt. 2-14, Table S1), different commercially available organic peroxides
138	were used, including tert-butyl hydroperoxide (70 wt. % in water, Sigma-Aldrich), cumene
139	hydroperoxide (80 wt. % in water, Sigma-Aldrich), and 2-butanone peroxide (40% wt. % in
140	water, Sigma-Aldrich). The molar ratio of organic peroxide to ammonium sulfate in the
141	atomizing solution was 2:1 with the aim of being atmospherically relevant (corresponding to
142	maximum particulate peroxide molar fraction of 66% and mass fraction of approximately 50-
143	70% if all the organic peroxides were assumed to remain in the particle phase). This ratio was
144	used as a proxy for total peroxide content in both gas and particle phase relative to that of
145	ammonium sulfate upon atomization. For the experiments studying the relationship between γ_{SO2}
146	and particle-phase peroxide content, the molar ratio of organic peroxide to ammonium sulfate
147	(Expt. 10-12, 15-18, Table S1) in the solution was adjusted to be 0.02, 0.2, 1, 2, and 4,
148	respectively. In experiments where malonic acid was used (Expt. 19-22, Table S1), molar ratios
149	of 0.2, 1, 2, and 4 were adopted. For measuring γ_{SO2} with different aerosol pH (Expt. 17, 23-25,
150	Table S1), different amounts of HCl (37%, Sigma-Aldrich) were added into the solution (0,
151	0.00002 M, 0.0001 M, 0.001 M HCl) prior to atomization. The initial pH of aerosol (2.5, 2.2,
152	1.6, 1, respectively) were modeled using E-AIM III model (Clegg et al., 1998) based on the
153	initial molar ratios of inorganic species (H ⁺ , NH ₄ ⁺ , SO ₄ ²⁻ , Cl ⁻) in the atomizing solution and
154	measured RH (around 50%). The atomized particles were flowed into the chamber without
155	drying, and therefore assumed to remain deliquesced under the range of RH we studied. Expt. 2-
156	14 (Table S1) also represent those where the relationship between γ_{SO2} and RH conditions were
157	studied.
158	In the second set of experiments, the uptake of SO ₂ onto SOA was investigated (Fig. S2, Expt.

159 26-28, Table S1). A custom-built 10 L quartz oxidation flow reactor was used to produce SOA

160	(Ye et al., 2016) from different hydrocarbon precursors. In this work, we studied SOA formed
161	from toluene photooxidation, limonene ozonolysis and α -pinene ozonolysis, 3 of the most
162	commonly studied SOA systems (Ng et al., 2007;Hildebrandt et al., 2009; Hartz et al.,
163	2005;Varutbangkul et al., 2006). Toluene (analytical standard, Sigma Aldrich) was injected
164	continuously into zero air flow by a syringe (1000 mL, Hamilton) installed on a syringe pump
165	(KDS Legato100) to achieve an initial concentration of 0.5 ppm. Limonene (Sigma-Aldrich,
166	97 %) and α -pinene (Sigma-Aldrich, 98 %) were pre-dissolved in cyclohexane (Sigma-Aldrich,
167	99.5 %) with a volumetric ratio of 1: 1500 and 1: 500 to ensure that OH formed from limonene
168	or α -pinene ozonolysis is scavenged by cyclohexane, estimated based on the rate constants
169	(Atkinson and Arey, 2003). The initial steady-state concentrations of limonene and α -pinene
170	were controlled to be around 2 ppm and 1 ppm entering the flow tube. O ₃ , used as the oxidant
171	(for limonene and α -pinene) or the OH precursor (for toluene), was generated by passing 0.5 L
172	min^{-1} pure oxygen (99.6 %, Linde, Mississauga, Canada) through an O ₃ generator (no.
173	97006601, UVP, Cambridge, UK). Humidified air was produced by bubbling zero air through a
174	custom-made humidifier at a flow rate of 1 L min ^{-1} . The photolysis of O ₃ produces O (¹ D),
175	which reacts with water vapour to produce \cdot OH with illumination from the 254 nm UV lamps
176	(UVP, Cambridge, UK) to initiate the photooxidation of toluene. The average residence time
177	inside the flow tube was controlled to be around 5 minutes. A gas chromatography-flame
178	ionization detector (GC-FID, model 8610C, SRI Instruments Inc., LV, USA) equipped with a
179	Tenax® TA trap was used to monitor the concentration of hydrocarbon precursors at the
180	inlet/outlet of the flow reactor. In all cases, the O ₃ concentration was maintained to be at least 10
181	times higher than that of the hydrocarbon. Temperature and relative humidity were monitored by
182	an Omega HX94C RH/T transmitter. Particle size distribution and volume concentration were

monitored using a custom-built scanning mobility particle sizer (SMPS), which is a combination
of a differential mobility analyzer column (DMA, model 3081, TSI, Shoreview, MN, USA) with
flow controls and a condensation particle counter (CPC, model 3772, TSI, Shoreview, MN,
USA).

187

188 **2.2 Quantification of** γso₂

Prior to each experiment, the chamber was flushed by purified air overnight with a flow rate of 189 25 Lmin^{-1} until particle number concentration was less than 5 cm⁻³ and SO₂ was less than 1 ppb. 190 191 To adjust RH, the chamber was humidified by passing purified air through a custom-built humidifier filled with ultra-pure water. For experiments with atomized ammonium sulfate or 192 193 malonic acid, SO₂ was injected into the chamber prior to the introduction of particles. For experiments studying γ_{SO2} onto SOA, aerosol generated from the flow tube was injected into the 194 195 Teflon chamber continuously after passing through an O_3 denuder (Ozone Solutions, Iowa, USA) 196 to achieve specific aerosol concentration inside the chamber prior to SO₂ addition. SO₂ mixing 197 ratio in the chamber during each experiment was continuously monitored using an SO₂ analyzer (Model 43i, Thermo Scientific). The initial mixing ratio of SO₂ in each experiment was 198 199 controlled to be around 200 ppb. Aerosol size distribution was monitored by SMPS. The reactive 200 uptake coefficient of SO_2 was calculated by integrating the following equation:

201 202

$$-\frac{d[SO_2]}{dt} = \frac{1}{4}\gamma_{SO_2}A\bar{c}[SO_2]$$
(1)

Where $[SO_2]$ is the SO₂ mixing ratio (ppb) monitored by the SO₂ analyzer; A is the average surface area concentration (μ m² cm⁻³) derived from the particle size distribution measured by SMPS; \bar{c} represents the mean molecular velocity (cm s⁻¹) of SO₂. d[SO₂]/dt is solved over the initial SO₂ decay, such that the peroxide concentration in the aerosol liquid phase is assumed to

be constant and pseudo-first order kinetics can be applied (Abbatt et al., 2012;Thornton et al., 207 2003). A summary of all the measured γ_{SO2} can be found in Table S1. Typical evolution of 208 209 monitored species can be seen in Fig.1. Control experiments were performed in order to rule out other potential factors (e.g. SO₂ loss in the in-line filter in front of the SO₂ analyzer, interferences 210 211 inside the SO_2 analyzer, chamber wall losses, SO_2 uptake onto wet ammonium sulfate, gas-phase 212 reaction of SO₂ with peroxide vapour) that may contribute to the SO₂ decay observed during the 213 γ_{SO2} measurement inside the chamber (Fig. S3-S6). Measurement uncertainty and precision of 214 γ_{SO2} in this study can be found in Table S1. Also, we observed there was SO₂ repartitioning from 215 the humid chamber wall in the presence of organic peroxide under high RH (Fig. S6b, RH 74%). The observed SO₂ repartitioning rate was then applied to correct the γ_{SO2} measured under high 216 217 RH conditions (above 70%, Expt.14), and this correction amounts to a 40% increase in 218 calculated γ_{SO2} .

219

220 **2.3 Offline peroxide quantification**

Aerosol was collected onto 47 mm PTFE (polytetrafluoroethylene) filters with 0.2 µm pore size 221 (Whatman[®], GE Healthcare) from the chamber by a diaphragm pump (KNF Neuberger Inc., USA) 222 223 for offline chemical analysis. The total particulate peroxide content (H₂O₂, ROOH and ROOR) in 224 these samples prior to SO_2 uptake was quantified using the iodometric-spectrophotometric assay 225 (Docherty et al., 2005). I₂ produced from the reaction between I⁻ and peroxides can further quickly 226 combine with the excess amount of I^{-} to form I_{3}^{-} , which has brown color and absorbs UV-vis at 227 470nm. The SOA extraction was then aliquoted into a 96-well UV plate (Greiner Bio-One, 228 Kremsmünster, AT) with 160 μ L well⁻¹. 20 μ L of formic acid (\geq 95 %, Sigma-Aldrich) was added into each well, following by 20 μ L potassium iodide (BioUltra, \geq 99.5%, Sigma-Aldrich) solution 229

(dissolved in DI water). The plate was then covered by an adhesive plate sealer (EdgeBio, 230 Gaithersburg, USA) immediately in order to avoid reagent evaporation and O₂ oxidation. After 231 incubation for an hour in the dark, the UV-vis absorption at 470nm was measured using a UV-vis 232 spectrophotometer (Spectramax 190, Molecular Devices Corporation, Sunnyvale, CA) and then 233 converted to peroxide concentration using the calibration curve made by tert-butyl hydroperoxide 234 235 (70 wt. % in H_2O , Sigma-Aldrich) with a series of concentrations (0-10mM). An average molecular mass for seed particles (SOA + ammonium sulfate) was assumed based on the chemical 236 237 composition in order to calculate the molar fraction of total peroxides using the following equation:

238

240

239 Molar fraction of peroxide =
$$\frac{N_{peroxide}}{N_{aerosol}} = N_{peroxide} \frac{M_{(NH_4)_2}SO_4 + M_{peroxide}f_{peroxide}}{m_{aerosol}}$$

where $m_{aerosol}$ is the weighed aerosol mass on the filter; $M_{(NH_4)_2SO_4}$ and $M_{peroxide}$ are the molecular mass of ammonium sulfate and peroxide, respectively; $f_{(NH_4)_2SO_4}$ and $f_{peroxide}$ are the initial molar fraction of ammonium sulfate and peroxide; $N_{peroxide}$ and $N_{aerosol}$ are the measured peroxide molar and calculated aerosol molar, respectively. More details about the iodometric-spectrophotometric procedures were described in previous work (Wang et al., 2018).

247 **3 Results and discussion**

248 **3.1 SO₂ uptake and RH**

A positive relationship between γ_{SO2} and RH (between 25 and 71%) was observed for all types of organic peroxides studied (Fig. 2). The positive dependence of the reactive uptake coefficient of water-soluble gaseous species on RH has also been observed in other studies (Thornton et al.,

252 2003;Griffiths et al., 2009;Zhao et al., 2017;Zhang et al., 2019). Recently, the uptake behavior of

SO₂ onto soot, mineral dust and SOA were also shown to positively depend on RH (Zhang et al.,
2019;Zhao et al., 2017;Yao et al., 2019).

255 It is also noteworthy that an exponential dependence of SO_2 reactive uptake coefficient on RH was observed in our study. γ_{SO2} increases with increased relative humidity, which could even be 256 257 more significant under high RH regime. This is consistent with previous laboratory studies that 258 measured the reactive uptake coefficient of SO_2 onto aerosol to be exponentially dependent on 259 RH (Zhang et al., 2019; Yao et al., 2019). Additionally, multiple field campaigns have observed 260 significant correlation between particulate sulfate formation and ambient RH (Song et al., 261 2019;Sun et al., 2013;Huang et al., 2020). Sun et al. (2013) observed faster sulfate formation rate under humid conditions, proposing a significant impact of aerosol liquid water on sulfate 262 production during wintertime in Beijing. Zheng et al. (2015) reported a notably higher SOR 263 264 (molar ratio of sulfate to the sum of sulfate and SO_2) during wet period (RH>50%), indicating the importance of heterogeneous reactions to the secondary sulfur transformation with abundant 265 266 aerosol water content under humid conditions. In a recent study by Song et al. (2019), the rapid sulfate formation rate observed under high RH conditions was found to be significantly higher 267 268 than atmospheric modeling results implemented with homogeneous SO_2 oxidation pathways, 269 which was later attributed to heterogeneous sulfate formation mechanisms. Multiple mechanisms 270 can potentially explain this observed γ_{SO2} -RH dependence. An enhanced relative humidity would 271 result in a nonlinear increase of aerosol water content, which can lead to more SO₂ dissolved in 272 the aerosol aqueous phase (Seinfeld and Pandis, 2012). It should be noted that while the relative 273 humidity is varied systematically in these experiments, the relationship is more complex since RH also affects other aerosol properties which can affect the uptake kinetics in turn. For 274 275 example, a higher aerosol liquid water content could dilute protons and thus lower the aerosol

acidity. In a study by Laskin et al. (2003), an enhanced uptake of SO_2 onto sea-salt particles was observed with an increased aerosol alkalinity at high pH range. 277

278

280

3.2 Dependence of SO₂ uptake on peroxide content and type 279

281 the current study. Fig. 3 shows that γ_{SO2} is linearly proportional to the amount of particulate 282 peroxide for aerosol with similar volume-to-surface ratios and containing the same type of 283 organic peroxides. This positive relationship between γ_{SO2} and condensed phase peroxide content 284 has also been inferred from experiments of SO₂ uptake onto α -pinene SOA (Yao et al., 2019),

As expected, the measured uptake rate of SO_2 is dependent on the particulate peroxide content in

285 where the peroxide content in α -pinene SOA was varied indirectly by introducing NO and

286 adjusting the branching ratio of the peroxide-yielding RO_2+HO_2/RO_2 pathway.

287 In addition to the amount of peroxide injected, the particulate fraction of organic peroxide available for heterogeneous reaction is also influenced by gas-particle partitioning. As indicated 288 289 in Fig. 2, the reactive uptake coefficients of different organic peroxides vary amongst each other 290 by about an order of magnitude in the range of RH studied, despite the same amounts of peroxide 291 relative to ammonium sulfate initially in the atomizing solution. Based on our previous work 292 (Wang et al., 2019), the aqueous-phase rate constants for these organic peroxides with dissolved 293 S(IV) only vary by a factor of 2-3 and therefore cannot fully explain the observed difference in 294 uptake rates. Since vapour pressure vary considerably among the different peroxides in the 295 present study, gas-particle partitioning is likely to influence the amount of peroxide in the 296 particle phase that react with dissolved SO₂. The relative particulate peroxide content on filters 297 of the three peroxides collected from chamber experiments under RH 50% without SO₂ uptake 298 were measured by the offline KI method (Fig. S7). Although the initial ratio of organic peroxide

299 to ammonium sulfate in the atomizing solution was nominally the same, we measured the highest amount of particulate peroxide with 2-butanone peroxide (16.7%), followed by cumene 300 301 hydroperoxide (12.7%) and then tert-butyl hydroperoxide (3.8%) using the offline iodometric method. This trend in particulate peroxide content is consistent with the vapour pressures 302 303 calculated using the SIMPOL group contribution method (Pankow et al., 2008), with 2-butanone 304 peroxide being the least volatile, and tert-butyl hydroperoxide being the most volatile. Also, the order of particle-phase peroxide content is consistent with the order of γ_{SO2} observed, as shown in 305 306 Fig. 2. A simple visualization of these relationships between different peroxide characteristics 307 (number of peroxide groups, vapour pressure and aqueous-phase rate constants) and measured γ_{SO2} (at RH = 50%) is illustrated in Fig. S7, which indicates higher γ_{SO2} can be expected for 308 309 organic peroxides with multiple O-O groups, lower vapour pressures and higher aqueous phase 310 reactivities. It should be noted that the order of magnitude difference in experimentally measured 311 γ_{SO2} among various organic peroxides (Fig.2) is still not fully explained when both volatility and 312 reaction kinetics are taken into account (Fig.S7), suggesting that the reactive uptake may be influenced by other factors. In summary, for our current experiments where we nominally 313 maintained total injected amount of organic peroxide constant, measured γ_{SO2} depends both on 314 315 reactivity and gas-particle partitioning of the organic peroxides.

316

317 **3.3 SO₂ uptake and aqueous phase kinetics**

Since the aqueous phase reaction rate constants between S(IV) and these model organic peroxides have been measured previously (Wang et al., 2019), we can test our understanding of the measured γ_{SO2} using a simple model. By assuming the amount of SO₂ dissolved in the aerosol

is in equilibrium with the gas phase, the overall γ_{SO2} can be expressed using the simplified resistor model (Hanson et al., 1994):

323

324
$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{\overline{c}}{4HRT\sqrt{k^{l}D_{l}}} \frac{1}{\left[\operatorname{coth}(q) - \frac{1}{q}\right]}$$
(2)

where α is the mass accommodation coefficient, \bar{c} is the mean molecular speed of SO₂ (cm s⁻¹), H is the effective Henry's law constant that includes both the dissolution of SO₂ and the dissociation of H₂SO₃ (M atm⁻¹), R is the ideal gas constant (atm L mol⁻¹ K⁻¹), T is the temperature (K), and the parameter q is used to describe the competition between the reaction and diffusion of the dissolved gaseous species within a particle, which is further calculated as:

$$q = r \sqrt{\frac{k^{l}}{D_{l}}}$$
(3)

where r is the radius (cm) of a given particle, D_1 is the aqueous-phase diffusion coefficient (cm² s⁻¹), k^I is the first order rate constant (s⁻¹) for the reaction. For experiments in the current study, the calculated q values were consistently found to be far less than 1, which indicates a volumelimited reaction regime. Combining with the assumption of a relatively fast mass

accommodation process compared with the bulk phase reaction, equation (2) can be further

336 simplified as to describes reactive uptake in the volume-limited regime:

337
$$\gamma = \frac{4HRT[peroxide]k^{II}}{\bar{c}} \frac{V}{s}$$
(4)

Here, we assume all the peroxides remain in the condensed phase upon atomizing and reaction inside the chamber for the upper-bound prediction of γ_{SO2} . [peroxide] represents the particle phase concentration of total organic peroxide (M) based on the initial ratio between organic peroxide and ammonium sulfate in the atomizing solution, and the aerosol water content output by E-AIM III (Clegg et al., 1998), k^{II} is the second order reaction rate constant (M⁻¹ s⁻¹), which we have measured in the bulk phase at dilute concentrations previously (Wang et al., 2019), V/S is the ratio

between particle volume concentration (μm^3 cm⁻³) and particle surface area concentration (μm^2 344 cm⁻³) derived from SMPS measurements. As a result, the observed reactive uptake coefficient of 345 346 SO_2 can be compared to that predicted from the bulk phase reaction rate constant, and the results are shown in Fig. 4 and Fig. S8. Overall, we noticed that this model captures the dependence of 347 γ_{SO2} on peroxide content, but the modeled results were found to be generally 15-50 times lower 348 349 than the experimentally measured values (Fig. S8). The current γ_{SO2} predictions are likely upper-350 bound estimates since all the peroxides were assumed to stay in the condensed phase without 351 partitioning. As a result, this observed 15-50 times of discrepancy could even be larger if the 352 particulate peroxide content during the chamber experiments were lower due to partitioning.

It should be noted that the calculated γ_{SO2} was based on reaction kinetics measured in dilute 353 354 solutions while the experimental γ_{SO2} were measured directly from suspended particles. This large difference in kinetics between those in aerosol and in dilute bulk solution suggests that this 355 356 multiphase interaction is strongly favored in the highly concentrated aerosol environment. One of 357 the potential explanations for this discrepancy could be liquid-liquid phase separation (LLPS) in aerosol between organic peroxide and ammonium sulfate (Ciobanu et al., 2009;O'Brien et al., 358 2015) such that SO₂ can directly interact with the acidic organic phase, where the concentration of 359 360 peroxides can be higher and the kinetics can be different from what we have measured in dilute solution (Wang et al., 2019). However, LLPS is generally governed by the chemical composition 361 362 of the hydrophobic phase (Freedman, 2017). A higher level of oxygenation in organic aerosol is 363 related with higher hydrophilicity, which would favor a homogeneous particle instead of phase 364 separation. Previous studies showed that LLPS did not occur for organic coating with O:C above 365 0.8 (You et al., 2013;You et al., 2014). The LLPS phenomenon in simple organic-inorganic 366 mixtures can also be affected by the functional groups. The maximum O:C for LLPS could be 0.71

for organics with multiple carboxylic and hydroxyl groups but low aromatic content (Song et al., 2012) while the 2-butanone peroxide we used for both γ_{SO2} measurement and prediction in the present study has multiple peroxide groups with an O:C value of 0.75. Particle size could also have impacts on phase separation (Cheng et al., 2015). Particle diameters in the current study are mainly under 200 nm while a previous study showed particles smaller than this size are less likely to experience LLPS (Veghte et al., 2013). We therefore believe that LLPS is not likely to be responsible for the enhanced uptake rate observed under these experimental conditions.

374 Another explanation is the high solute strength in the concentrated aerosol phase. Although the 375 aerosol water content for ammonium sulfate aerosol was found to be higher than that of malonic acid aerosol under RH 50%. As indicated in Fig. 4 and Fig. S8, the difference between the 376 measured and predicted γ_{SO2} is larger for ammonium sulfate aerosol than for malonic acid. 377 Meanwhile, the calculated ionic strength in aerosol liquid phase under RH 50% for ammonium 378 sulfate (40 mol kg⁻¹) is significantly larger than that of malonic acid (0.45 mol kg⁻¹). It has been 379 380 previously reported that the reaction rate between sulfite and hydrogen peroxide in aqueous phase 381 increases with ionic strength (Maaß et al., 1999). Based on the reaction mechanisms proposed for dissolved SO₂ and hydrogen peroxide (Halperin and Taube, 1952), we speculate the reaction 382 383 between aqueous phase S(IV) and organic peroxides to follow a similar mechanism:

HO
$$\stackrel{K}{\longrightarrow}$$
 O $\stackrel{K}{\longrightarrow}$ ROOH $\stackrel{K}{\longrightarrow}$ $\stackrel{K}{\longrightarrow}$ $\stackrel{K}{\longrightarrow}$ S-O-O-R + (1- β) SO₄²⁻ + (1- β) ROH + β H₂O + (1- β) H $^+$ (5)

$$\underbrace{\overset{\bullet}{\overset{\bullet}}_{B}}_{B} \underbrace{\overset{\bullet}{\overset{\bullet}}_{B}}_{C} - C - R + H^{+} \underbrace{\overset{K_{a}^{-1}}{\overset{\bullet}}_{B}}_{C} HO - \overset{H}{\overset{\bullet}}_{B} - C - R$$

$$\underbrace{\overset{\bullet}{\overset{\bullet}}_{B}}_{C} O - R$$

$$HO - S - O - R \xrightarrow{k} O - S - O - R + H^{+}$$

$$HO - S - O - R \xrightarrow{k} O - S - O - R + H^{+}$$

$$HO - S - O - R \xrightarrow{k} O - S - O - R + H^{+}$$

$$HO - S - O - R \xrightarrow{k} O - S - O - R + H^{+}$$

$$HO - S - O - R \xrightarrow{k} O - S - O - R + H^{+}$$

$$HO - S - O - R \xrightarrow{k} O - S - O - R + H^{+}$$

$$HO - S - O - R \xrightarrow{k} O - S - O - R + H^{+}$$

$$HO - S - O - R \xrightarrow{k} O - S - O - R + H^{+}$$

$$HO - S - O - R \xrightarrow{k} O - S - O - R + H^{+}$$

$$HO - S - O - R \xrightarrow{k} O - S - O - R + H^{+}$$

$$HO - S - O - R \xrightarrow{k} O - S - O - R + H^{+}$$

$$HO - S - O - S - O - R + H^{+}$$

$$HO - S - O - R - S - O - R + H^{+}$$

$$HO - S - O - R - S - O - R + H^{+}$$

$$HO - S - O - R - S - O - R - S - O - R + H^{+}$$

$$HO - S - O - R - S -$$

384

 \mathbf{O}

where the overall rate constant is equal to $k \frac{\kappa}{\kappa_{r}}$, assuming fast equilibrium steps for reactions 5 and 385 6. Dissociated solutes are surrounded by an extended solvation shell which could affect the 386 387 reaction rates (Herrmann, 2003). Fewer available free water molecules would therefore shift the equilibrium to the right in equation (5). Additionally, higher ionic strength also corresponds to an 388 increased concentration of electrolytes in the aqueous phase, which could hinder the dissociation 389 390 of the peroxymonosulfurous acid and shift the equilibrium in equation (6) to the right. In recent 391 work by Liu et al. (2020), the rate of S(IV) oxidation by H_2O_2 can be enhanced by up to a factor of 50 in aerosol aqueous phase compared to that of dilute solution. The highest ionic strength at 392 which such enhancement was measured for the H_2O_2 oxidation pathway was 15 mol kg⁻¹ (Liu et 393 394 al., 2020).

395 Whereas the above analysis is based on the assumption that all the chemistry occurs in the bulk 396 component of the particle, it is also possible that some component of the reaction occurs at the gasparticle interface and the overall kinetics can be affected by interfacial characteristics. For example, 397 398 an enhanced ionic strength in the aerosol phase can also impact the interfacial reaction mechanisms. 399 Previous study has shown evidence that interfacial chemistry is important for SO₂ oxidation in the aerosol phase (Laskin et al., 2003). With higher ionic strength, anions partitioning to the air-liquid 400 401 interface can promote the overall reaction kinetics via proton transfer and thus accelerate the 402 interfacial chemistry (Knipping et al., 2000; Mishra et al., 2012; Mekic et al., 2018; Mekic et al., 2020; Wei et al., 2018; Ruiz-Lopez et al., 2020). In addition to the catalytic effects of protons 403 indicated in Eqn.5-7, Hung et al. (2015, 2018) observed significant SO₃⁻⁻ signal at the acidic 404

405 microdroplet surface, which can promote sulfate formation via radical propagation chain initiated
406 by surrounding radicals and molecular oxygen (Eqn. 8-11):

$$HSO_3^- + OH \longrightarrow SO_3^- + H_2O$$
⁽⁸⁾

 $\langle 0 \rangle$

$$SO_3^{-} + O_2 \longrightarrow SO_5^{-}$$
 (9)

$$\operatorname{SO}_5^{\cdot \cdot} + \operatorname{SO}_3^{2 \cdot} \longrightarrow \operatorname{SO}_4^{2 \cdot} + \operatorname{SO}_4^{\cdot \cdot}$$
 (10)

$$SO_4^{-} + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_3^{--}$$
 (11)

407

where the hydroxy radical can potentially be produced from decomposition of the labile organic 408 peroxide in our system (Tong et al., 2016). However, we cannot distinguish whether the interfacial 409 410 protons promote sulfate formation by catalyze the peroxide S(IV) oxidation pathway or the sulfur 411 radical pathway at the current stage. In the recent study by Wei et al. (2018), a pH gradient was observed for phosphate-buffered aerosol droplets with the proton accumulated at the interface. 412 413 Base on the pH-dependent aqueous phase kinetics measured in our previous work (Wang et al., 414 2019), such interfacial proton accumulation could potentially explain the enhanced kinetics we observed for aerosol in the current study. However, the chemical compositions are quite different. 415 416 While phosphate-buffered particles were studied in Wei et al. (2018), acidic ammonium sulfate aerosol was used in our study. Also, the particle size in Wei et al. (2018) is significantly larger (20 417 μ m) than what was studied in the current study (200 nm). Thus, it should be noted that there is no 418 419 direct evidence from the current study showing the relationship between the interfacial properties 420 and γ_{SO2} , and future studies are warranted.

Therefore, while more studies are needed to clearly delineate the roles of ionic strength, interfacial
 activity, bulk reactivity, and particle phase state quantitatively, the enhancement of SO₂ oxidation

kinetics by highly concentrated aerosol particles compared to dilute aqueous solutions areconcluded to be large (factor of 15-50) for the experimental conditions in the current study.

425

426 **3.4 SO₂ uptake and aerosol pH**

427 As indicated by the proposed reaction mechanisms (Eqn. 5-7), protons are important reaction 428 intermediates for this SO₂ oxidation pathway. Previously, the aqueous phase reaction rate 429 constants between organic peroxides and dissolved SO_2 were measured to be pH dependent 430 (Wang et al., 2019). Moreover, the dissolution equilibrium of SO_2 into aqueous phase is also pH 431 sensitive (Seinfeld and Pandis, 2012). Besides, many studies have shown that the uptake kinetics for gaseous species can be affected by the condensed phase pH (Shi et al., 1999;Gaston et al., 432 2014;Drozd et al., 2013;Jang and Kamens, 2001;Liu et al., 2015). Reactive uptake of ammonia 433 was observed to depend on condensed phase acidity (Shi et al., 1999). Heterogeneous 434 435 condensation of isoprene-derived epoxydiol onto seed aerosol was found to increase with proton 436 concentration (Gaston et al., 2014). In the current study, the potential impact from particle phase pH on γ_{SO2} was explored by adding HCl into the atomizing solution. To estimate the particle 437 phase pH, two different methods associated with two different assumptions were used. In the 438 439 first scenario, the aerosol pH in each experiment was estimated using the E-AIM III model (Clegg et al., 1998) based on the initial molar ratios of inorganic species (H^+ , NH_4^+ , SO_4^{2-} , Cl^-) in 440 441 the atomizing solution and measured RH (around 50%). In the second scenario, the additional 442 sulfate formed from reactive uptake of SO_2 was taken into consideration. The partitioning of HCl 443 was allowed in the model simulation for both scenarios. The formation of sulfate would enhance 444 the proton concentration in the aerosol liquid phase thus lower the aerosol pH. The average pH 445 during the SO₂ uptake process is likely in between these two extremes.

Fig. 5 shows the measured reactive uptake coefficients of SO_2 as a function of the calculated pH. 446 The reactive uptake coefficient was found to weakly increase with decreasing pH, which is 447 448 consistent with acid-catalyzed reactions between peroxides and dissolved SO₂ as measured in the bulk phase (Lind et al., 1987; Wang et al., 2019). γ_{SO2} was also predicted for the same range of 449 450 pH based on Eqn. 4 and the pH-dependent bulk-phase reaction rate constants measured 451 previously (Wang et al., 2019). Indicated by Fig. 5, the measured γ_{SO2} again exceeds the 452 predicted γ_{SO2} by about a factor of 50, which is consistent with what we reported earlier and is 453 likely due to the effects of aerosol ionic strength.

454 Unlike the observed γ_{SO2} , however, the predicted γ_{SO2} does not exhibit a monotonic trend. γ_{SO2} is expected to decrease with decreasing pH at high pH (>2) as the effective Henry's law constant of 455 SO_2 decreases with higher acidity (Seinfeld and Pandis, 2012). γ_{SO2} is not expected to increase 456 with decreasing pH until pH is below 2 where the acidity enhancement in reaction rate constant 457 458 exceeds the decrease in SO₂ solubility. As illustrated earlier, extrapolating dilute aqueous-phase 459 kinetics to the highly concentrated aerosol requires considering effects from high solute strength. Solute strength may change the pH dependence of γ_{SO2} in two ways. First, the solubility of SO₂ 460 may decrease and become less dependent on pH as ionic strength increases (Rodríguez-Sevilla et 461 462 al., 2002). A former study (Leng et al., 2015) has shown that the effective Henry's law of triethylamine decreases with increased ionic strength. Another potential explanation is that the 463 464 aqueous phase reaction rate constant can be more pH-dependent at high ionic strengths than what 465 we measured previously in dilute solutions. In either case, the inflection of the predicted γ_{SO2} 466 would change and γ_{SO2} could become more negatively dependent on pH (d[γ_{SO2}]/d[pH] becomes 467 less positive in the high pH range and/or more negative in the low pH range), which would 468 match more closely with the observed dependence. It should also be noted that there are

substantial uncertainties in estimating pH values, originating from the partitioning of organics, 469 organic-inorganic phase separations, mixing state of specific ions, uncertain activity coefficients 470 and the propagation of RH uncertainties (Clegg et al., 2008; Fountoukis et al., 2009; Guo et al., 471 2016). Also, the reactive uptake is a dynamic process and will influence aerosol pH in turn upon 472 473 sulfate formation. In summary, while the magnitude of predicted γ_{SO2} is consistent with our 474 expected values (after accounting for the enhancement by high aerosol solute strength), we cannot fully explain the dependence of γ_{SO2} on aerosol pH at the current stage. Future studies 475 476 should investigate how the effective Henry's law of SO₂ and pH dependence of reaction rate 477 constants vary in aerosol liquid phase with high solute strength in order to have a more comprehensive understanding of the relationship between γ_{SO2} and aerosol pH. 478

479

480 **3.4 SO₂ uptake onto SOA**

481 γ_{SO2} was measured for a few model SOA systems, as organic peroxides are abundant in SOA 482 (Surratt et al., 2006;Kautzman et al., 2009;Krapf et al., 2016;Bonn et al., 2004). Here we studied SOA formed from monoterpene ozonolysis and toluene photooxidation. It should be noted that 483 for the γ_{SO2} measurements of toluene SOA, a strong hydrocarbon interference was observed with 484 485 the SO_2 analyzer, likely stemming from the high concentrations of gas-phase aromatic compounds. A rough estimate of the uptake rate for toluene SOA from aerosol mass 486 487 spectrometer sulfate measurements is provided in the SI (Section 1). The reactive uptake coefficient of SO₂ onto Saharan mineral dust was reported on the order of 10⁻⁵ (Adams et al., 488 2005). y_{SO2} onto dust with the coexistence of NO₂ and NH₃ under various RH conditions were 489 measured to be 10^{-7} to 10^{-5} (Zhang et al., 2019). For a variety of metal oxides, SO₂ reactive 490 uptake coefficients were quantified to be between 10^{-6} and 10^{-4} (Usher et al., 2002; Fu et al., 491

492 2007; Shang et al., 2010). More recently, γ_{SO2} studied for heterogeneous sulfate formation by 493 photolysis of particulate nitrate were reported in the range of 10⁻⁶ to 10⁻⁵ (Gen et al., 2019). As 494 shown in Fig. 6, γ_{SO2} for all SOA systems were measured to be on the order of 10⁻⁴. Similar γ_{SO2} 495 values on the order of 10⁻⁴ were measured for α -pinene SOA by Yao et al. (2019), and 10⁻⁵ for 496 limonene SOA estimated from the chamber study by Ye et al. (2018). The reaction products 497 from this SOA and SO₂ interaction will be reported in a separate study.

498

499 **4. Atmospheric Implications**

500 Oxidation of atmospheric hydrocarbons produces reactive intermediates that can potentially 501 interact with SO₂ and form particulate sulfate, contributing to PM formation and growth (Berndt 502 et al., 2015; Mauldin et al., 2012; Yao et al., 2019). Organic peroxides generated from both 503 biogenic and anthropogenic hydrocarbon emissions are abundant in submicron aerosol. Given 504 that they are highly reactive with relatively short lifetimes (Bonn et al., 2004;Krapf et al., 505 2016; Qiu et al., 2020), these species could serve as important condensed phase oxidants for gas phase SO₂. Combining laboratory measurements and model predictions, the current study 506 investigated heterogeneous reactions between SO_2 and particulate organic peroxide. The 507 measured γ_{SO2} for organic peroxide containing aerosol ranges from 10⁻⁵ to 10⁻² in this study. 508 Based on the modeling work by Wang et al. (2014), adding an SO₂ uptake pathway to GEOS-509 Chem with a reactive uptake coefficient of 10^{-4} could improve the surface sulfate prediction by 510 511 more than 50% during a severe haze episode over North China (RH 50%), suggesting the potential importance of this multiphase reaction pathway, especially when SOA is the dominant 512 513 component in particulate matter.

514 The dependence of the heterogeneous kinetics on RH, aerosol pH, peroxide type, and peroxide content were also evaluated. The experimentally measured γ_{SO2} was found to be consistently 515 516 higher than that predicted from reaction kinetics with organic peroxides in the dilute aqueous phase. This discrepancy can be potentially explained by the effects of high ionic strength 517 presented in the aerosol, suggesting that the impact from highly concentrated solutes needs to be 518 519 taken into consideration when applying aqueous phase kinetics to aerosol multiphase chemistry, 520 especially for particles containing strong electrolytes. We also observed that the kinetics of this 521 multiphase reaction exhibit a weak dependence on pH. Increasing the condensed-phase acidity 522 may enhance the heterogeneous rate constant at low pH, and while this pH dependence is consistent with that of the aqueous phase reaction rate constant measured previously, it is not 523 consistent with the decrease of effective Henry's law constant of SO₂ along with enhanced 524 acidity. Also, it is likely that within the uncertainties, there may not be an observable γ_{SO2} -pH 525 526 trend. Currently, we are not able to fully explain the pH dependence, and further studies are 527 warranted. Particle phase peroxide content was observed to be linearly correlated with γ_{SO2} . Moreover, γ_{SO2} measured for 2-butanone peroxide was found to be orders of magnitude higher 528 than that of cumene hydroperoxide and tert-butyl hydroperoxide. The difference in γ_{SO2} among 529 530 various types of organic peroxides can be partially explained by their condensed-phase reactivity and gas-particle partitioning. 531

532 In general, we found the observed γ_{SO2} in this study can be summarized using the following 533 semiempirical multilinear relationship:

534
$$\log \gamma = -1.7 + 0.0024 \times k^{ll} + 0.46 \times PAS + 0.024 \times RH - 1.9 \times Vp$$
(8)

535 where γ is the reactive uptake coefficient, $k^{"}$ is the aqueous phase S(IV) oxidation rate constant 536 (M⁻¹ s⁻¹), *PAS* is the molar ratio between particulate peroxide and ammonium sulfate in the

537 atomizing solution, which is a proxy for the amount of peroxide in both gas and particle phases applied in the current study, RH is the relative humidity (%), Vp is the vapour pressure (kPa) of 538 539 the peroxide. Fig. 7 illustrates the degree to which this semi-empirical expression describes the 540 experimental data for ammonium sulfate aerosol mixed with the three types of organic peroxides. Residual evaluations of this multilinear regression can be found Fig. S9. We caution that this 541 542 equation is not directly applicable to atmospheric models in its current form, especially since the 543 particle phase peroxide content (PAS) value we applied as input is a calculated value, rather than 544 a measurement. However, it illustrates the internal consistency of our experimental results across a range of RH, peroxide content, and aqueous phase reactivities, which are the key variables for 545 uptake rates. Better understanding of ionic strengths and pH in aerosol, either through modeling 546 or direct measurements of these variables, is needed to establish the coefficient dependence. 547 548 Future studies should be focused on exploring γ_{SO2} and the reaction products for various types of SOA as well as ambient particles under atmospherically relevant conditions, evaluating the 549 550 underlying impacts from photochemical condition, chemical composition, particle morphology, 551 ionic strength and interfacial properties on this multiphase physicochemical process. Overall, 552 γ_{SO2} presented in our study and its relationship with ambient RH, aerosol pH, ionic strength, 553 particulate peroxide content and type could provide a framework for the implementation of this 554 heterogeneous mechanism in atmospheric models to have a better understanding of ambient 555 sulfate formation and particle growth.

- 556
- 557
- 558
- 559

560 Author contributions	Aut	nor con	tributions
--------------------------	-----	---------	------------

- A.W.H. C. and S.W. designed the study. S.W., T. L., and J. J. performed the experiments. S.W.,
- A.W.H. C., T. L., and J. J. analyzed data. S.W. and A.W.H. C. wrote the manuscript with the
- 563 input from all co-authors.
- 564
- 565 *Data availability*
- 566 All data presented in this study are available in the supplemental material and have been
- 567 deposited in figshare.
- 568
- 569 Associated content
- 570 Supporting Information.
- 571
- 572 *Competing interests*
- 573 The authors declare no competing financial interest.
- 574
- 575 Acknowledgements
- 576 This work was supported by Natural Sciences and Engineering Research Council Discovery Grant.
- 577 The authors would like to thank Dr. Greg Evans, Dr. Yue Zhao and Dr. Christopher Lim for helpful
- 578 comments and discussions. Special thanks to SOCAAR for providing the SO₂ analyzer.

- 580
- 581
- 582
- 583

584 **Reference**

- Abbatt, J. P. D., Lee, A. K. Y., and Thornton, J. A.: Quantifying trace gas uptake to tropospheric
- aerosol: recent advances and remaining challenges, Chem. Soc. Rev., 41, 6555–6581,
- 587 https://doi.org/10.1039/c2cs35052a, 2012.
- Adams, J. W., Rodriguez, D., and Cox, R. A.: The uptake of SO_2 on Saharan dust: a flow tube study, Atmos. Chem. Phys., 5, 2643–2676, doi:10.5194/acp-5-2643-2005, 2005.
- 590 Andreae, M.O., Afchine, A., Albrecht, R., Holanda, B.A., Artaxo, P., Barbosa, H.M., Borrmann,
- 591 S., Cecchini, M.A., Costa, A., Dollner, M. and Fütterer, D.: Aerosol characteristics and particle
- production in the upper troposphere over the Amazon Basin, Atmos. Chem. Phys., 18, 921–961,2018.
- Atkinson, R., and Arey, J.: Atmospheric degradation of volatile organic compounds, Chem.
 Rev., 103, 4605-4638, 2003.
- 596 Berndt, T., Richters, S., Kaethner, R., Voigtländer, J., Stratmann, F., Sipilä, M., Kulmala, M.,
- and Herrmann, H.: Gas-phase ozonolysis of cycloalkenes: Formation of highly oxidized RO₂
- radicals and their reactions with NO, NO₂, SO₂, and other RO₂ radicals, J. Phys. Chem. A, 119,
- 599 10336-10348, 10.1021/acs.jpca.5b07295, 2015.
- Bianchi, F., Kurtén, T., Riva, M., Mohr, C., Rissanen, M. P., Roldin, P., Berndt, T., Crounse, J.
- D., Wennberg, P. O., Mentel, T. F., Wildt, J., Junninen, H., Jokinen, T., Kulmala, M., Worsnop,
- D. R., Thornton, J. A., Donahue, N., Kjaergaard, H. G., and Ehn, M.: Highly oxygenated organic
- molecules (HOM) from gas-phase autoxidation involving peroxy radicals: A key contributor to atmospheric aerosol, Chem. Rev., 119, 3472-3509, 10.1021/acs.chemrev.8b00395, 2019.
- Bonn, B., von Kuhlmann, R., and Lawrence, M. G.: High contribution of biogenic
- hydroperoxides to secondary organic aerosol formation, Geophys. Res. Lett., 31, L10108,
 https://doi.org/10.1029/2003GL019172, 2004.
- 608 Chen, Q., Farmer, D. K., Schneider, J., Zorn, S. R., Heald, C. L., Karl, T. G., Guenther, A.,
- Allan, J. D., Robinson, N., Coe, H., Kimmel, J. R., Pauliquevis, T., Borrmann, S., Pöschl, U.,
- 610 Andreae, M. O., Artaxo, P., Jimenez, J. L., and Martin, S. T.: Mass spectral characterization of
- submicron biogenic organic particles in the Amazon Basin, Geophys. Res. Lett., 36, L20806,
- 612 https://doi.org/10.1029/2009GL039880, 2009.
- 613 Chen, T., Chu, B., Ge, Y., Zhang, S., Ma, Q., He, H., and Li, S.-M.: Enhancement of aqueous
- 614 sulfate formation by the coexistence of NO₂/NH₃ under high ionic strengths in aerosol water,
- 615 Environ. Pollut., 252, 236-244, https://doi.org/10.1016/j.envpol.2019.05.119, 2019.
- Cheng, Y., Su, H., Koop, T., Mikhailov, E., and Pöschl, U.: Size dependence of phase transitions
 in aerosol nanoparticles, Nat. Commun., 6, 5923, 10.1038/ncomms6923, 2015.
- 618 Cheng, Y. F., Zheng, G. J., Wei, C., Mu, Q., Zheng, B., Wang, Z. B., Gao, M., Zhang, Q., He, K.
- B., Carmichael, G., Pöschl, U., and Su, H.: Reactive nitrogen chemistry in aerosol water as a
- source of sulfate during haze events in China, Sci. Adv., 2, e1601530, https://doi.org/10.1126/
- 621 sciadv.1601530, 2016.

- 622 Ciobanu, V. G., Marcolli, C., Krieger, U. K., Weers, U., and Peter, T.: Liquid-liquid phase
- separation in mixed organic/inorganic aerosol particles, J. Phys. Chem. A, 113, 10966–10978,
 2009.
- 625 Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic model of the system
- 626 $H^+-NH_4^+ Na^+ SO_4^{2-} NO_3^- C1^- H_2O$ at 298.15 K, J. Phys. Chem. A, 102, 2155–2171,
- 627 https://doi.org/10.1021/jp973043j, 1998.
- 628 Clegg, S. L., Kleeman, M. J., Griffin, R. J., and Seinfeld, J. H.: Effects of uncertainties in the
- 629 thermodynamic properties of aerosol components in an air quality model Part 1: Treatment of
- 630 inorganic electrolytes and organic compounds in the condensed phase, Atmos. Chem. Phys., 8,
- $631 \qquad 1057-1085, {\tt http://www.atmos-chem-phys.net/8/1057/2008/, 2008.}$
- Docherty, K. S., Wu, W., Lim, Y. B., and Ziemann, P. J.: Contributions of organic peroxides to
 secondary aerosol formed from reactions of monoterpenes with O₃, Environ. Sci. Technol., 39,
 4049-4059, 2005.
- 635 Dovrou, E., Rivera-Rios, J. C., Bates, K. H., and Keutsch, F. N.: Sulfate formation via cloud
- processing from isoprene hydroxyl hydroperoxides (ISOPOOH), Environ. Sci. Technol., 53,
 12476-12484, 10.1021/acs.est.9b04645, 2019.
- 638 Drozd, G. T., Woo, J. L., and McNeill, V. F.: Self-limited uptake of α-pinene oxide to acidic
- aerosol: the effects of liquid-liquid phase separation and implications for the formation of
- 640 secondary organic aerosol and organosulfates from epoxides, Atmos. Chem. Phys., 13, 8255–
- 641 8263, doi:10.5194/acp-13-8255-2013, 2013.
- 642 Epstein, S. A., Blair, S. L., and Nizkorodov, S. A.: Direct photolysis of α-pinene ozonolysis
- secondary organic aerosol: effect on particle mass and peroxide content, Environ. Sci. Technol.,
 48, 11251-11258, 2014.
- Fairlie, T. D., Jacob, D. J., Dibb, J. E., Alexander, B., Avery, M. A., van Donkelaar, A., and
- Zhang, L.: Impact of mineral dust on nitrate, sulfate, and ozone in transpacific Asian pollution
 plumes, Atmos. Chem. Phys., 10, 3999–4012, doi:10.5194/acp-10-3999-2010, 2010.
- 648 Fountoukis, C., Nenes, A., Sullivan, A., Weber, R., Van Reken, T., Fischer, M., Matas, E.,
- Moya, M., Farmer, D., and Cohen, R. C.: Thermodynamic characterization of Mexico City
- aerosol during MILAGRO 2006, Atmos. Chem. Phys., 9, 2141–2156, http://www.atmos-chem-
- 651 phys.net/9/2141/2009/, 2009.
- Freedman, M. A.: Phase separation in organic aerosol, Chem. Soc. Rev., 46, 7694–7705,
 https://doi.org/10.1039/C6CS00783J, 2017.
- Fu, H. B., Wang, X., Wu, H. B., Yin, Y., and Chen, J. M.: Heterogeneous uptake and oxidation
 of SO₂ on iron oxides, J. Phys. Chem. C, 111, 6077–6085, 2007.
- Gao, M., Carmichael, G. R., Wang, Y., Saide, P. E., Yu, M., Xin, J., Liu, Z., and Wang, Z.:
- 657 Modeling study of the 2010 regional haze event in the North China Plain, Atmos. Chem. Phys.,
- 658 16, 1673–1691, https://doi.org/10.5194/acp-16-1673-2016, 2016.
- 659 Gaston, C. J., Riedel, T. P., Zhang, Z., Gold, A., Surratt, J. D., and Thornton, J. A.: Reactive
- 660 uptake of an isoprene-derived epoxydiol to submicron aerosol particles, Environ. Sci. Technol., 661 48 11178 11186 10 1021/es5034266 2014
- 661 48, 11178-11186, 10.1021/es5034266, 2014.

- 662 Gen, M., Zhang, R., Huang, D. D., Li, Y., and Chan, C. K.: Heterogeneous SO₂ oxidation in
- sulfate formation by photolysis of particulate nitrate, Environ. Sci. Tech. Let., 6, 86–91,
- 664 https://doi.org/10.1021/acs.estlett.8b00681, 2019.
- 665 Griffiths, P. T., Badger, C. L., Cox, R. A., Folkers, M., Henk, H. H., and Mentel, T. F.: Reactive
- 666 uptake of N₂O₅ by aerosols containing dicarboxylic acids. Effect of particle phase, composition,
- and nitrate content, J. Phys. Chem. A, 113, 5082-5090, 10.1021/jp8096814, 2009.
- Gunz, D. W. and Hoffmann, M. R.: Atmospheric chemistry of peroxides: A review, Atmos.
 Environ., 24A, 1601–1633, https://doi.org/10.1016/0960-1686(90)90496-A, 1990.
- Guo, H., Sullivan, A. P., Campuzano-Jost, P., Schroder, J. C., LopezHilfiker, F. D., Dibb, J. E.,
- Jimenez, J. L., Thornton, J. A., Brown, S. S., Nenes, A., and Weber, R. J.: Fine particle pH
- and the partitioning of nitric acid during winter in the northeastern United States, J. Geophys.
- 673 Res. Atmos., 121, 10355–10376, https://doi.org/10.1002/2016JD025311, 2016.
- Guo, H., Weber, R. J., and Nenes, A.: High levels of ammonia do not raise fine particle pH
- sufficiently to yield nitrogen oxide-dominated sulfate production, Sci. Rep., 7, 12109, 2017.
- Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen,
- J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T.,
- Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W.,
- 679 McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D.,
- 680 Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic
- aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155–5236, https://doi.org/10.51
 94/acp9-5155-2009, 2009.
- Halperin, J., and Taube, H.: The transfer of oxygen atoms in oxidation—reduction reactions. IV.
- The reaction of hydrogen peroxide with sulfite and thiosulfate, and of oxygen, manganese
- dioxide and of permanganate with sulfite, J. Am. Chem. Soc., 74, 380-382, 1952.
- Hanson, D. R., Ravishankara, A. R., and Solomon, S.: Heterogeneous reactions in sulfuric acid
 aerosols: A framework for model calculations, J. Geophys. Res., 99, 3615, https://doi.org/
 10.1029/93JD02932, 1994.
- 689 Hartz, K. E. H., Rosenorn, T., Ferchak, S. R., Raymond, T. M., Bilde, M., Donahue, N. M., and
- 690 Pandis, S. N.: Cloud condensation nuclei activation of monoterpene and sesquiterpene
- 691 secondary organic aerosol, J. Geophys. Res.-Atmos., 110(D14), D14208, doi:10.1029/2004J
- 692 D005754, 2005.
- He, L.-Y., Huang, X.-F., Xue, L., Hu, M., Lin, Y., Zheng, J., Zhang, R., and Zhang, Y.-H.:
- 694 Submicron aerosol analysis and organic source apportionment in an urban atmosphere
- 695 in Pearl River Delta of China using high-resolution aerosol mass spectrometry, J. Geophys. Res.
- 696 Atmos., 116, D12304, https://doi.org/10.1029/2010JD014566, 2011.
- 697 Herrmann, H.: Kinetics of aqueous phase reactions relevant for atmospheric chemistry, Chem.
- 698 Rev., 103, 4691–4716, 2003.
- 699 Hildebrandt, L., Donahue, N. M., Pandis, S. N.: High formation of secondary organic aerosol
- from the photo-oxidation of toluene, Atmos. Chem. Phys., 9, 2973–2986, https://doi.org
- 701 /10.5194/acp-9-2973-2009, 2009.

- Huang, L., An, J., Koo, B., Yarwood, G., Yan, R., Wang, Y., Huang, C., and Li, L.: Sulfate
- 703 formation during heavy winter haze events and the potential contribution from heterogeneous
- $SO_2 + NO_2$ reactions in the Yangtze River Delta region, China, Atmos. Chem. Phys., 19, 14311-
- 705 14328, 10.5194/acp-19-14311-2019, 2019.
- Huang, L., Coddens, E. M., and Grassian, V. H.: Formation of organosulfur compounds from
- aqueous phase reactions of S (IV) with methacrolein and methyl vinyl ketone in the presence of transition metal ions, ACS Earth Space Chem., 3, 1749-1755, 2019.
- 709 Huang, L., Liu, T. and Grassian, V. H.: Radical-initiated formation of aromatic organosulfates
- and sulfonates in the aqueous phase. Environ. Sci. Technol., 54, 11857–11864,
- 711 https://doi.org/10.1021/acs.est.0c05644, 2020.
- Huang, R. J., Zhang, Y. L., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y. M., Daellenbach, K. R.,
- Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa,
- M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J.,
- 715 Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., Haddad, I. E., and Prevot, A. S. H.: High
- secondary aerosol contribution to particulate pollution during haze events in China, Nature, 514,
- 717 218–222, 2014.
- 718 Huang, R. J., He, Y., Duan, J., Li, Y., Chen, Q., Zheng, Y., Chen, Y., Hu, W., Lin, C., Ni, H.,
- 719 Dai, W., Cao, J., Wu, Y., Zhang, R., Xu, W., Ovadnevaite, J., Ceburnis, D., Hoffmann, T., and
- 720 O'Dowd, C. D.: Contrasting sources and processes of particulate species in haze days with low
- and high relative humidity in wintertime Beijing, Atmos. Chem. Phys., 20, 9101-9114,
- 722 10.5194/acp-20-9101-2020, 2020.
- Hung, H. M. and Hoffmann, M. R.: Oxidation of gas-phase SO₂ on the surfaces of acidic
- microdroplets: Implications for sulfate and sulfate radical anion formation in the atmospheric
- liquid phase, Environ. Sci. Technol., 49, 13768–13776, https://doi.org/10.1021/acs.est.5b01658,
 2015
- 726 2015.
- Hung, H. M., Hsu, M. N., and Hoffmann, M. R.: Quantification of SO₂ oxidation on interfacial
- surfaces of acidic micro-droplets: Implication for ambient sulfate formation, Environ. Sci.
- 729 Technol., 52, 9079–9086, https://doi.org/10.1021/acs.est.8b01391, 2018.
- Jang, M., and Kamens, R. M.: Atmospheric secondary aerosol formation by heterogeneous
- reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst, Environ. Sci. Technol.,
 35, 4758-4766, 10.1021/es010790s, 2001.
- Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H.,
- 734 DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M.,
- 735 Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin,
- 736 C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M.,
- Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, J., Huffman, J. A.,
- 738 Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick,
- 739 F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A.,
- 740 Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel,
- J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C.,
- 742 Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of organic
- ⁷⁴³ aerosols in the atmosphere, Science, 326, 1525–1529, https://doi.org/10.1126/science.1180353,
- 744 2009.

- 745 Kautzman, K., Surratt, J., Chan, M., Chan, A., Hersey, S., Chhabra, P., Dalleska, N., Wennberg,
- P., Flagan, R., and Seinfeld, J.: Chemical composition of gas-and aerosol-phase products from
- the photooxidation of naphthalene, J. Phys. Chem. A, 114, 913-934, 2009.
- 748 Knipping, E. M., Lakin, M. J., Foster, K. L., Jungwirth, P., Tobias, D. J., Gerber, R. B., Dabdub,
- 749 D., and Finlayson-Pitts, B. J.: Experiments and simulations of ion-enhanced interfacial chemistry
- 750 on aqueous NaCl aerosols, Science, 288, 301, 10.1126/science.288.5464.301, 2000.
- 751 Krapf, M., El Haddad, I., Bruns, E. A., Molteni, U., Daellenbach, K. R., Prévôt, A. S.,
- Baltensperger, U., and Dommen, J.: Labile peroxides in secondary organic aerosol, Chem, 1,603-616, 2016.
- Laskin, A., Gaspar, D. J., Wang, W., Hunt, S. W., Cowin, J. P., Colson, S. D., and Finlayson-
- Pitts, B. J.: Reactions at interfaces as a source of sulfate formation in sea-salt particles, Science,
 301, 340, 10.1126/science.1085374, 2003.
- Leng, C. B., Roberts, J. E., Zeng, G., Zhang, Y. H., and Liu, Y.: Effects of temperature, pH, and ionic strength on the Henry's law constant of triethylamine, Geophys. Res. Lett., 42, 3569-3575,
- 759 10.1002/2015gl063840, 2015.
- Li, G., Bei, N., Cao, J., Huang, R., Wu, J., Feng, T., Wang, Y., Liu, S., Zhang, Q., Tie, X., and
- Molina, L. T.: A possible pathway for rapid growth of sulfate during haze days in China, Atmos.
 Chem. Phys., 17, 3301–3316, https://doi.org/10.5194/acp17-3301-2017, 2017.
- Li, J., Zhang, Y., Cao, F., Zhang, W., Fan, M., Lee, X., Michalski, G.: Stable sulfur isotopes
 revealed a major role of transition-metal-ion catalyzed SO₂ oxidation in haze episodes,
 doi:10.1021/acs.est.9b07150, 2020.
- Lind, J. A., Lazrus, A. L., and Kok, G. L.: Aqueous phase oxidation of sulfur (IV) by hydrogen peroxide, methylhydroperoxide, and peroxyacetic acid, J. Geophys. Res. Atmos., 92, 4171-4177,
- 767 peroxide, 768 1987.
- Liu, C., Chen, T., Liu, Y., Liu, J., He, H., Zhang, P.: Enhancement of secondary organic aerosol
- formation and its oxidation state by SO₂ during photooxidation of 2-methoxyphenol, Atmos.
 Chem. Phys., 19, 2687-2700, 2019.
- 772 Liu, L., Bei, N., Wu, J., Liu, S., Zhou, J., Li, X., Yang, Q., Feng, T., Cao, J., Tie, X. and Li, G.:
- 773Effects of stabilized Criegee intermediates (sCIs) on sulfate formation: a sensitivity analysis
- during summertime in Beijing–Tianjin–Hebei (BTH), China, Atmos. Chem. Phys., 19, 1334113354, 2019.
- Liu, T., Clegg, S. L. and Abbatt, J. P. D.: Fast oxidation of sulfur dioxide by hydrogen peroxide
 in deliquesced aerosol particles, Proc. Natl. Acad. Sci. U. S. A., 117, 1354–1359, 2020.
- Liu, Y., Liggio, J., Staebler, R., and Li, S. M.: Reactive uptake of ammonia to secondary organic
- aerosols: kinetics of organonitrogen formation, Atmos. Chem. Phys., 15, 13569–13584,
 doi:10.5194/acp-15-13569-2015, 2015.
- 781 Maaß, F., Elias, H., and Wannowius, K. J.: Kinetics of the oxidation of hydrogen sulfite by
- 782 hydrogen peroxide in aqueous solution: ionic strength effects and temperature dependence,
- 783 Atmos. Environ., 33, 4413-4419, https://doi.org/10.1016/S1352-2310(99)00212-5, 1999.

- 784 Mauldin, R. L., Berndt, T., Sipilä, M., Paasonen, P., Petäjä, T., Kim, S., Kurtén, T., Stratmann,
- F., Kerminen, V. M., and Kulmala, M.: A new atmospherically relevant oxidant of sulphur
- 786 dioxide, Nature, 488, 193–196, https://doi.org/10.1038/nature11278, 2012.
- 787 Mekic, M., Loisel, G., Zhou, W., Jiang, B., Vione, D., and Gligorovski, S.: Ionic-strength effects
- on the reactive uptake of ozone on aqueous pyruvic acid: Implications for air-sea ozone
- 789 deposition, Environ. Sci. Technol., 52, 12306-12315, 10.1021/acs.est.8b03196, 2018.
- 790 Mekic, M., Zeng, J., Zhou, W., Loisel, G., Jin, B., Li, X., Vione, D., and Gligorovski, S.: Ionic
- strength effect on photochemistry of fluorene and dimethylsulfoxide at the air–sea interface:
- Alternative formation pathway of organic sulfur compounds in a marine atmosphere, ACS Earth
- 793 Space Chem., 4, 1029-1038, 10.1021/acsearthspacechem.0c00059, 2020.
- Mishra, H., Enami, S., Nielsen, R. J., Hoffmann, M. R., Goddard, W. A., and Colussi, A. J.:
- Anions dramatically enhance proton transfer through aqueous interfaces, Proc. Natl. Acad. Sci.
 U. S. A., 109, 10228-10232, 2012.
- Newland, M. J., Rickard, A. R., Vereecken, L., Muñoz, A., Ródenas, M., and Bloss, W. J.:
- 798 Atmospheric isoprene ozonolysis: impacts of stabilised Criegee intermediate reactions with SO₂,
- H₂O and dimethyl sulfide, Atmos. Chem. Phys., 15, 9521–9536, https://doi.org/10.5194/acp-159521-2015, 2015.
- Ng, N., Kroll, J., Chan, A., Chhabra, P., Flagan, R., and Seinfeld, J.: Secondary organic aerosol
 formation from m-xylene, toluene, and benzene, Atmos. Chem. Phys., 7, 3909–3922,
- 803 http://www.atmos-chem-phys.net/7/3909/2007, 2007.
- Ng, N. L., Kwan, A. J., Surratt, J. D., Chan, A. W. H., Chhabra, P. S., Sorooshian, A., Pye, H. O.
- 805 T., Crounse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic
- aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO₃), Atmos. Chem.
- 807 Phys., 8, 4117–4140, http://www.atmos-chem-phys.net/8/4117/2008/, 2008.
- Nguyen, T. B., Tyndall, G. S., Crounse, J. D., Teng, A. P., Bates, K. H., Schwantes, R. H.,
- 809 Coggon, M. M., Zhang, L., Feiner, P., Miller, D. O., Skog, K. M., Rivera-Rios, J. C., Dorris, M.,
- 810 Olson, K. F., Koss, A., Wild, R. J., Brown, S. S., Goldstein, A. H., de Gouw, J. A., Brune,
- 811 W. H., Keutsch, F. N., Seinfeld, J. H., and Wennberg, P. O.: Atmospheric fates of Criegee
- intermediates in the ozonolysis of isoprene, Phys. Chem. Chem. Phys., 18, 10 241–10 254,
- 813 https://doi.org/10.1039/C6CP00053C, http://dx.doi.org/10.1039/C6CP00053C, 2016.
- O'Brien, R. E., Wang, B., Kelly, S. T., Lundt, N., You, Y., Bertram, A. K., Leone, S. R., Laskin,
- A., and Gilles, M. K.: Liquid–liquid phase separation in aerosol particles: Imaging at the
- 816 nanometer scale, Environ. Sci. Technol., 49, 4995-5002, 10.1021/acs.est.5b00062, 2015.
- 817 Pankow, J. F. and Asher, W. E.: SIMPOL.1: a simple group contribution method for predicting
- 818 vapor pressures and enthalpies of vaporization of multifunctional organic compounds, Atmos.
- 819 Chem. Phys., 8, 2773–2796, http://www.atmos-chem-phys.net/8/2773/2008/, 2008.
- 820 Qiu, J., Liang, Z., Tonokura, K., Colussi, A. J., and Enami, S.: Stability of monoterpene-derived
- 821 α-hydroxyalkyl-hydroperoxides in aqueous qrganic media relevance to the fate of
- hydroperoxides in aerosol particle phases, Environ. Sci. Technol., 10.1021/acs.est.9b07497,
- 823 2020.

- Rodríguez-Sevilla, J., Álvarez, M., Limiñana, G., Díaz, M. C.: Dilute SO₂ absorption equilibria
 in aqueous HCl and NaCl solutions at 298.15 K, J. Chem. Eng. Data, 47, 1339-1345, 2002.
- Ruiz-Lopez, M.F., Francisco, J.S., Martins-Costa, M.T. and Anglada, J.M.: Molecular reactions at aqueous interfaces. Nat. Rev. Chem., 1-17, 2020.
- 828 Seinfeld, J. H., and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to 829 climate change, John Wiley & Sons, 2012.
- 830 Sha, T., Ma, X., Jia, H., Tian, R., Chang, Y., Cao, F., and Zhang, Y.: Aerosol chemical
- 831 component: Simulations with WRF-Chem and comparison with observations in Nanjing, Atmos.
- 832 Environ., 218, 116982, https://doi.org/10.1016/j.atmosenv.2019.116982, 2019.
- Shang, J., Li, J., Zhu, T.: Heterogeneous reaction of SO₂ on TiO₂ particles. Sci. China Chem., 53,
 2637–2643, 2010.
- 835 Shi, Q., Davidovits, P., Jayne, J. T., Worsnop, D. R., and Kolb, C. E.: Uptake of gas-phase
- ammonia. 1. Uptake by aqueous surfaces as a function of pH, J. Phys. Chem. A, 103, 8812-8823,
 10.1021/jp991696p, 1999.
- 838 Song, M., Marcolli, C., Krieger, U. K., Zuend, A., and Peter, T.: Liquid–liquid phase separation
- in aerosol particles: dependence on O:C, organic functionalities, and compositional complexity,
- 840 Geophys. Res. Lett., 39, L19801, doi:10.1029/2012GL052807, 2012.
- Song, S., Gao, M., Xu, W., Shao, J., Shi, G., Wang, S., Wang, Y., Sun, Y., and McElroy, M. B.:
- 842 Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium
- models, Atmos. Chem. Phys., 18, 7423–7438, https://doi.org/10.5194/acp-18-7423-2018, 2018.
- Song, S., Gao, M., Xu, W., Sun, Y., Worsnop, D. R., Jayne, J. T., Zhang, Y., Zhu, L., Li, M.,
- Zhou, Z., Cheng, C., Lv, Y., Wang, Y., Peng, W., Xu, X., Lin, N., Wang, Y., Wang, S., Munger,
- J. W., Jacob, D. J., and McElroy, M. B.: Possible heterogeneous chemistry of hydroxy
- methanesulfonate (HMS) in northern China winter haze, Atmos. Chem. Phys., 19, 1357–1371,
- 848 https://doi.org/10.5194/acp-19-1357-2019, 2019.
- 849 Su, H., Cheng, Y., and Poschl, U.: New multiphase chemical processes influencing atmospheric
- aerosols, air quality, and climate in the anthropocene, Acc. Chem. Res., e1601530-2983,
 https://doi.org/10.1021/acs.accounts.0c00246, 2020.
- 852 Sun, Y., Wang, Z., Fu, P., Jiang, Q., Yang, T., Li, J., and Ge, X.: The impact of relative humidity
- on aerosol composition and evolution processes during wintertime in Beijing, China, Atmos.
 Environ., 77, 927-934, 2013.
- 855 Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A.,
- 856 Szmigielski, R., Vermeylen, R., Maenhaut, W., and Claeys, M.: Chemical composition of
- secondary organic aerosol formed from the photooxidation of isoprene, J. Phys. Chem. A, 110,
 9665-9690, 2006.
- 859 Thornton, J. A., Braban, C. F., and Abbatt, J. P. D.: N₂O₅ hydrolysis on sub-micron organic
- aerosols: the effect of relative humidity, particle phase, and particle size, Phys. Chem. Chem
- 861 Phys., 5, 4593–4603, https://doi.org/10.1039/B307498F, 2003.
- Tie, X., Brasseur, G., Emmons, L., Horowitz, I., and Kinnison, D.: Effects of aerosols on
- tropospheric oxidants: a global model study, J. Geophys. Res. Atmos., 106, 22931–22964, 2001.

- Tong, H., Arangio, A. M., Lakey, P. S. J., Berkemeier, T., Liu, F., Kampf, C. J., Brune, W. H., 864
- Pöschl, U., and Shiraiwa, M.: Hydroxyl radicals from secondary organic aerosol decomposition 865 in water, Atmos. Chem. Phys., 16, 1761–1771, doi:10.5194/acp-16-1761-2016, 2016.
- 866
- Usher, C. R., Al-Hosney, H., Carlos-Cuellar, S., and Grassian, V. H.: A laboratory study of the 867
- heterogeneous uptake and oxidation of sulfur dioxide on mineral dust particles, J. Geophys. Res., 868 869 107, 4713, doi:10.1029/2002JD002051, 2002.
- Varutbangkul, V., Brechtel, F. J., Bahreini, R., Ng, N. L., Keywood, M. D., Kroll, J. H., Flagan, 870
- 871 R. C., Seinfeld, J. H., Lee, A., and Goldstein, A. H.: Hygroscopicity of secondary organic
- aerosols formed by oxidation of cycloalkenes, monoterpenes, sesquiterpenes, and related 872
- compounds, Atmos. Chem. Phys., 6, 2367–2388, http://www.atmos-chem-phys.net/6/23 873 874 67/2006/, 2006.
- Veghte, D. P., Altaf, M. B., and Freedman, M. A.: Size dependence of the structure of organic 875 876 aerosol, J. Am. Chem. Soc., 135, 16046-16049, 2013.
- 877 Wang, G., Zhang, R., Gomez, M. E., Yang, L., Zamora, M. L., Hu, M., Lin, Y., Peng, J., Guo, S.,
- 878 and Meng, J.: Persistent sulfate formation from London Fog to Chinese haze, Proc. Natl. Acad.
- Sci. U. S. A., 113, 13630-13635, 2016. 879
- 880 Wang, S., Ye, J., Soong, R., Wu, B., Yu, L., Simpson, A. J., and Chan, A. W. H.: Relationship
- between chemical composition and oxidative potential of secondary organic aerosol from 881 polycyclic aromatic hydrocarbons, Atmos. Chem. Phys., 18, 3987-4003, 2018.
- 882
- 883 Wang, S., Zhou, S., Tao, Y., Tsui, W. G., Ye, J., Yu, J. Z., Murphy, J. G., McNeill, V. F.,
- Abbatt, J. P. D., and Chan, A. W. H.: Organic peroxides and sulfur dioxide in aerosol: Source of 884
- 885 particulate sulfate, Environ. Sci. Technol., 53, 10695-10704, 10.1021/acs.est.9b02591, 2019.
- Wang, X.; Gemayel, R.; Hayeck, N.; Perrier, S.; Charbonnel, N.; Xu, C.; Chen, H.; Zhu, C.; 886
- 887 Zhang, L.; Wang, L.; Nizkorodov, S. A.; Wang, X.; Wang, Z.; Wang, T.; Mellouki, A.; Riva, M.;
- Chen, J.; George, C. Atmospheric photosensitization: A new pathway for sulfate formation, 888
- Environ. Sci. Technol., 54, 3114-3120, 2020. 889
- Wang, Y., Zhang, Q., Jiang, J., Zhou, W., Wang, B., He, K., Duan, F., Zhang, Q., Philip, S., and 890
- 891 Xie, Y.: Enhanced sulfate formation during China's severe winter haze episode in January 2013
- missing from current models, J. Geophys. Res. Atmos., 119, 10425-10440, 892
- 893 https://doi.org/10.1002/2013JD021426, 2014.
- 894 Wei, H., Vejerano, E. P., Leng, W., Huang, Q., Willner, M. R., Marr, L. C., and Vikesland, P. J.: 895 Aerosol microdroplets exhibit a stable pH gradient, Proc. Natl. Acad. Sci. U. S. A., 115, 7272, 10.1073/pnas.1720488115, 2018. 896
- 897 Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-
- VanWertz, G., Kreisberg, N. M., and Knote, C.: Effects of anthropogenic emissions on aerosol 898
- 899 formation from isoprene and monoterpenes in the southeastern United States, Proc. Natl. Acad.
- Sci. U. S. A., 112, 37-42, 2015. 900
- Yang, Y., Wang, H., Smith, S. J., Easter, R., Ma, P.-L., Qian, Y., Yu, H., Li, C., and Rasch, P. J.: 901
- 902 Global source attribution of sulfate concentration and direct and indirect radiative forcing,
- Atmos. Chem. Phys., 17, 8903–8922, https://doi.org/10.5194/acp17-8903-2017, 2017. 903

- Yao, M., Zhao, Y., Hu, M., Huang, D., Wang, Y.C., Yu, J. Z., and Yan, N.: Multiphase reactions
- between secondary organic aerosol and sulfur dioxide: kinetics and contributions to sulfate
- formation and aerosol aging, Environ. Sci. Tech. Let. 6, 768-774, 10.1021/acs.estlett.9b00657,
 2019.
- Ye, J., Gordon, C. A., and Chan, A. W. H: Enhancement in secondary organic aerosol formation in the presence of preexisting organic particle, Environ. Sci. Technol., 50, 3572-3579, 2016.
- 910 Ye, J., Abbatt, J. P. D., and Chan, A. W. H.: Novel pathway of SO₂ oxidation in the atmosphere:
- 911 reactions with monoterpene ozonolysis intermediates and secondary organic aerosol, Atmos.
- 912 Chem. Phys., 18, 5549–5565, https://doi.org/10.5194/acp18-5549-2018, 2018.
- 913 Yee, L. D., Isaacman-VanWertz, G., Wernis, R. A., Kreisberg, N. M., Glasius, M., Riva, M.,
- 914 Surratt, J. D., de Sá, S. S., Martin, S. T., Alexander, M. L., Palm, B. B., Hu, W., Campuzano-
- Jost, P., Day, D. A., Jimenez, J. L., Liu, Y., Misztal, P. K., Artaxo, P., Viegas, J., Manzi, A., de
- 916 Souza, R. A. F., Edgerton, E. S., Baumann, K., and Goldstein, A. H.: Natural and
- 917 anthropogenically influenced isoprene oxidation in southeastern United States and central
- 918 Amazon, Environ. Sci. Technol., 54, 5980-5991, 10.1021/acs.est.0c00805, 2020.
- 919 You, Y., Renbaum-Wolff, L., Bertram, A. K: Liquid-liquid phase separation in particles
- 920 containing organics mixed with ammonium sulfate, ammonium bisulfate, ammonium nitrate or
- sodium chloride, Atmos. Chem. Phys., 13, 11723–11734, https://doi.org/10.5194/acp-13-117232013, 2013.
- 923 You, Y., Smith, M. L., Song, M., Martin, S. T., and Bertram, A. K.: Liquid–liquid phase
- separation in atmospherically relevant particles consisting of organic species and inorganic salts,
 Int. Rev. Phys. Chem., 33, 43–77, doi:10.1080/0144235X.2014.890786, 2014.
- 26 Zhang, S., Xing, J., Sarwar, G., Ge, Y., He, H., Duan, F., Zhao, Y., He, K., Zhu, L. and Chu, B.:
- Parameterization of heterogeneous reaction of SO₂ to sulfate on dust with coexistence of NH₃
- and NO₂ under different humidity conditions, Atmos. Environ., 208, 133-140, 2019.
- 2929 Zhao, Y., Liu, Y., Ma, J., Ma, Q., and He, H.: Heterogeneous reaction of SO₂ with soot: The
- roles of relative humidity and surface composition of soot in surface sulfate formation, Atmos.
 Environ., 152, 465-476, 2017.
- 232 Zheng, B., Zhang, Q., Zhang, Y., He, K. B., Wang, K., Zheng, G. J., Duan, F. K., Ma, Y. L., and
- 933 Kimoto, T.: Heterogeneous chemistry: a mechanism missing in current models to explain
- secondary inorganic aerosol formation during the January 2013 haze episode in North China,
- Atmos. Chem. Phys., 15, 2031–2049, doi:10.5194/acp-15-2031-2015, 2015.
- 236 Zheng, G. J., Duan, F. K., Su, H., Ma, Y. L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T.,
- 937 Kimoto, T., Chang, D., Pöschl, U., Cheng, Y. F., and He, K. B.: Exploring the severe winter haze
- 938 in Beijing: the impact of synoptic weather, regional transport and heterogeneous reactions,
- Atmos. Chem. Phys., 15, 2969–2983, doi:10.5194/acp-15-2969-2015, 2015.
- 940
- 941





Figure 1. Typical evolution of the species monitored during γ_{SO2} measurement for (a) ammonium sulfate mixed with 2-butanone organic peroxide (2B/AS, Expt. 16) and (b) limonene

SOA (LSOA, Expt. 27). Particle volume concentrations measured by SMPS have been corrected for wall loss assuming a pseudo first-order loss rate (Ye et al., 2016). γ_{SO2} was calculated for the





Figure 2. Exponential relationship between γ_{SO2} and RH for ammonium sulfate aerosol
containing 2-butanone peroxide (2B), cumene hydroperoxide (CP), tert-butyl hydroperoxide
(TB).
965
966
967
968
969
970
971
972





Figure 3. Relationship between γ_{SO2} and particulate peroxide content. γ_{SO2} for ammonium sulfate
(a) and malonic acid aerosol (b) containing different amount of 2-butanone peroxide are shown
here. The observed dependence of γ_{SO2} on the amount of peroxide injected are linear since the
slopes of the relationship are both nearly 1 in (a) and (b).



Figure 4. Relationship between measured γ_{SO2} and γ_{SO2} predicted by Eqn. 4. The large deviation from the 1:1 line, which represents the difference between the measured uptake coefficient and predicted values based on kinetics in the dilute aqueous phase, indicates that aerosol reactive uptake is significantly faster than reactions in dilute aqueous phase. This enhancement is likely driven in part by high ionic strengths, as the difference between measured γ_{SO2} and predicted γ_{SO2} are consistently higher for organic peroxide containing ammonium sulfate (high ionic strength) than for that mixed with malonic acid (lower ionic strength).

993

994

995



Figure 5. Relationship between γ_{SO2} and aerosol phase pH for ammonium sulfate aerosol
containing 2-butanone peroxide.
containing
<l



Figure 6. γ_{SO2} measured for different types of organic aerosol. The reactive uptake coefficient of
SO₂ onto SOA are on the order of 10⁻⁴.
1011
1012
1013
1014
1015
1016
1017
1018



Figure 7. Predicted γ_{SO2} using Equation (8) versus measured γ_{SO2} for ammonium sulfate or
malonic acid aerosol containing 2-butanone peroxide (2B), cumene hydroperoxide (CP), tertbutyl hydroperoxide (TB) under different experimental conditions.