1   **Heterogeneous Interactions between SO₂ and**

           Organic Peroxides in Submicron Aerosol

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Abstract

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

44   reactions between SO_2 and organic peroxides, highlighting the important factors that govern the

45   uptake kinetics.

46   **Introduction**

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

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

49   2013;Huang et al., 2014), with important implications for public health and global climate

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

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

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

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

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

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

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

57   2019), suggesting that the overall kinetics may be underestimated and/or important mechanisms

58   may be missing in models.

59   To reconcile these differences, studies have investigated novel reaction mechanisms of sulfate

60   formation. Stabilized Criegee intermediates (sCIs) were hypothesized to oxidize SO_2 rapidly and

61   potentially serve as an important source of ambient sulfate (Mauldin et al., 2012). In the work by

62   Newland et al. (2015) and Nguyen et al. (2016), this sCI pathway was shown to play a minor role

63   in sulfate formation. More recently, when Liu et al. (2019) applied this mechanism and kinetics

64   to a source-oriented WRF-Chem model, the sCIs pathway was found to only account for at most

65   9% of the total particulate sulfate. Reactive nitrogen species (such as NO_2) have also been

66   proposed as a dominant sulfate formation pathway when aerosol pH was estimated to be 5-6 in

67   Cheng et al. (2016) and close to 7 in Wang et al. (2016) under severe haze scenarios. While such

68   high aerosol pH is not substantiated by some thermodynamic modeling results, which concluded

69   that pH ranges between 4 and 5 in polluted regions (Song et al., 2018;Guo et al., 2017), other

70   studies that highlighted the roles of ammonia and dust found aerosol pH could be higher than 6

71   (Shi et al., 2017; Ding et al., 2019). Furthermore, higher aerosol water content and PM mass

72   concentration in polluted areas have been shown to enhance aerosol pH via a multiphase

73   buffering process (Zheng et al., 2020). Meanwhile, a recent modeling study incorporating this

74   heterogeneous NO_x mechanism still exhibited a discrepancy of 20% between the predicted and

75   observed sulfate, indicating the possibility of unknown mechanisms (Huang et al., 2019). Other

76   factors may play a role in enhancing the particle-phase sulfate formation rates. Chen et al. (2019)

77   investigated the synergistic effects of NO_2 and NH_3 on sulfate formation, and found that the rate

78   of this reaction can be enhanced by the high ionic strength in the particle phase. This

79   enhancement effect by solute strength on sulfate formation was also investigated for the H_2O_2

80   pathway in aerosol liquid water. Liu et al. (2020) found ionic strength and general acid-catalyzed

81   mechanisms can cause the S(VI) formation rate to be nearly 50 times faster in aerosol phase than

82   in dilute solutions. On the other hand, during the severe haze episodes in China (Li et al., 2020;

83   Guo et al., 2017), transition metal ion (TMI) catalysis of SO_2 oxidation by O_2 can be

84   significantly suppressed in the aerosol phase due to high ionic strength (Liu et al., 2020;Cheng et

85   al., 2016; Su et al., 2020).

86   In addition to high solute strength, submicron aerosol is also rich in organic compounds (Jimenez

87   et al., 2009;Hallquist et al., 2009). In recent years, many studies have investigated the potential

88   role of heterogeneous interactions between SO_2 and organic aerosol on particulate sulfate

89   formation. Song et al. (2019) found heterogeneous oxidation of hydroxymethanesulfonate

90   (HMS) by OH can trigger rapid sulfate formation. Wang et al. (2020) studied photosensitizers in

91   ambient particles and found this pathway could be essential under specific light conditions.

92   Recent studies found reactive intermediates from isoprene oxidation (Huang et al., 2019) and

93   benzoic acid (Huang et al., 2020), can yield a variety of organosulfur species upon catalysis by

94   TMI. Other studies have also investigated the interactions between secondary organic aerosol

95   (SOA) and SO_2. Field observations found that ambient sulfate abundance is highly correlated

96   with SOA formation (Yee et al., 2020;Xu et al., 2015). Liu et al. (2019) found that SO_2 enhances

97   SOA formation and average carbon oxidation state during methoxyphenol photooxidation. By

98   performing chamber experiments with limonene SOA formation in the presence of SO_2, Ye et al.

99   (2018) also observed significant SO_2 decay along with increased SOA yields and carbon

100   oxidation state, proposing that organic peroxides in SOA may be the key reactive intermediates

101   for SO_2 oxidation.

102   Organic peroxides are key intermediates for aerosol formation and ubiquitously exist in many

103   SOA systems (Hallquist et al., 2009;Bianchi et al., 2019). Numerous studies have reported

104   peroxide content of 20-60% for isoprene and monoterpene derived SOA (Surratt et al., 2006;Ng

105   et al., 2008;Ye et al., 2018;Epstein et al., 2014). A significant fraction of organic peroxide (30%-

106   50%) has also been found in naphthalene-derived SOA under low/high NO_x conditions

107   (Kautzman et al., 2009). Using model simulations, Bonn et al. (2004) found organic

108   hydroperoxides can account for up to 60% of global SOA. The aqueous phase reaction kinetics

109   between organic peroxides and dissolved SO_2 have been explored in previous studies (Lind et al.,

110   1987;Gunz and Hoffmann, 1990;Wang et al., 2019;Dovrou et al., 2019;Yao et al., 2019). The

111   second order reaction rate constants for organic peroxides in SOA (Dovrou et al., 2019;Yao et

112   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

113   range of those measured for commercially available organic peroxides (Wang et al., 2019) and

114   small organic peroxides (Lind et al., 1987). Yao et al. (2019) quantified the reactive uptake

115   coefficient of SO_2 (γ_{SO2}) onto α-pinene SOA to be on the order of 10^{-4}-10^{-3}, which is positively

116   dependent on RH and inferred particle-phase peroxide content. These reactions are also linked to

117   the formation of organosulfates (Wang et al., 2019). Both inorganic sulfate (85-90%) and

118   organosulfates (10-15%) were observed as products of SO_2 reactive uptake onto SOA (Yao et al.,

119   2019).

120   Given the potential significance of SO_2 reactive uptake in particulate sulfate formation, a more

121   in-depth study is needed to determine the important factors that govern the heterogeneous

122   kinetics of SO_2 onto organic peroxide containing aerosol. In this study, we measured γ_{SO2} for two

123   categories of aerosol: 1. Model organic peroxides mixed with ammonium sulfate or malonic acid

124   and 2. SOA from a few representative biogenic and anthropogenic precursors. The impacts of

125   RH, peroxide type, peroxide content, and condensed phase pH on SO_2 reactive uptake were

126   evaluated systematically with the goal of better understanding atmospheric multiphase sulfate

127   formation.

128

129   **2. Methods**

130   The reactive uptake of SO_2 onto peroxide-containing particles was studied in a 1 m^3 Teflon

131   chamber under ambient temperature and pressure. In brief, generated particles and SO_2 were

132   introduced into the chamber separately. The consumption of SO_2, changes in particle size

133   distribution and chemical composition were monitored to estimate the reactive uptake

134   coefficients. Particles were also collected on filters for offline chemical characterization.

135

2.1 Seed aerosol generation

In this work, two types of aerosol were used to investigate the uptake of SO_2. 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_{SO_2}

and peroxide type (Expt. 2-14, Table S1), different commercially available organic peroxides

were used, including tert-butyl hydroperoxide (70 wt. % in water, Sigma-Aldrich), cumene

hydroperoxide (80 wt. % in water, Sigma-Aldrich), and 2-butanone peroxide (40% wt. % in

water, Sigma-Aldrich). The molar ratio of organic peroxide to ammonium sulfate in the

atomizing solution was 2:1 with the aim of being atmospherically relevant (corresponding to

maximum particulate peroxide molar fraction of 66% and mass fraction of approximately 50-

70% if all the organic peroxides were assumed to remain in the particle phase). This ratio was

used as a proxy for total peroxide content in both gas and particle phase relative to that of

ammonium sulfate upon atomization. For the experiments studying the relationship between γ_{SO_2}

and particle-phase peroxide content, the molar ratio of organic peroxide to ammonium sulfate

(Expt. 10-12, 15-18, Table S1) in the solution was adjusted to be 0.02, 0.2, 1, 2, and 4,

respectively. In experiments where malonic acid was used (Expt. 19-22, Table S1), molar ratios

of 0.2, 1, 2, and 4 were adopted. For measuring γ_{SO_2} with different aerosol pH (Expt. 17, 23-25,

Table S1), different amounts of HCl (37%, Sigma-Aldrich) were added into the solution (0,

0.00002 M, 0.0001 M, 0.001 M HCl) prior to atomization. The initial pH of aerosol (2.5, 2.2,

1.6, 1, respectively) were modeled using E-AIM III model (Clegg et al., 1998) based on the

159   initial molar ratios of inorganic species (H^+, NH_4^+, SO_4^{2-}, Cl^-) in the atomizing solution and

160   measured RH (around 50%). The atomized particles were flowed into the chamber without

161   drying, and therefore assumed to remain deliquesced under the range of RH we studied. Expt. 2-

162   14 (Table S1) also represent those where the relationship between γ_{SO2} and RH conditions were

163   studied.

164   In the second set of experiments, the uptake of SO_2 onto SOA was investigated (Fig. S2, Expt.

165   26-28, Table S1). A custom-built 10 L quartz oxidation flow reactor was used to produce SOA

166   (Ye et al., 2016) from different hydrocarbon precursors. In this work, we studied SOA formed

167   from toluene photooxidation, limonene ozonolysis and α-pinene ozonolysis, 3 of the most

168   commonly studied SOA systems (Ng et al., 2007;Hildebrandt et al., 2009; Hartz et al.,

169   2005;Varutbangkul et al., 2006). Toluene (analytical standard, Sigma Aldrich) was injected

170   continuously into zero air flow by a syringe (1000 mL, Hamilton) installed on a syringe pump

171   (KDS Legato100) to achieve an initial concentration of 0.5 ppm. Limonene (Sigma-Aldrich,

172   97 %) and α-pinene (Sigma-Aldrich, 98 %) were pre-dissolved in cyclohexane (Sigma-Aldrich,

173   99.5 %) with a volumetric ratio of 1: 1500 and 1: 500 to ensure that OH formed from limonene

174   or α-pinene ozonolysis is scavenged by cyclohexane, estimated based on the rate constants

175   (Atkinson and Arey, 2003). The initial steady-state concentrations of limonene and α-pinene

176   were controlled to be around 2 ppm and 1 ppm entering the flow tube. O_3, used as the oxidant

177   (for limonene and α-pinene) or the OH precursor (for toluene), was generated by passing 0.5 L

178   min^{-1} pure oxygen (99.6 %, Linde, Mississauga, Canada) through an O_3 generator (no.

179   97006601, UVP, Cambridge, UK). Humidified air was produced by bubbling zero air through a

180   custom-made humidifier at a flow rate of 1 L min^{-1}. The photolysis of O_3 produces O (^{1}D),

181   which reacts with water vapour to produce ·OH with illumination from the 254 nm UV lamps

182   (UVP, Cambridge, UK) to initiate the photooxidation of toluene. The average residence time

183   inside the flow tube was controlled to be around 5 minutes. A gas chromatography–flame

184   ionization detector (GC-FID, model 8610C, SRI Instruments Inc., LV, USA) equipped with a

185   Tenax® TA trap was used to monitor the concentration of hydrocarbon precursors at the

186   inlet/outlet of the flow reactor. In all cases, the O_3 concentration was maintained to be at least 10

187   times higher than that of the hydrocarbon. Temperature and relative humidity were monitored by

188   an Omega HX94C RH/T transmitter. Particle size distribution and volume concentration were

189   monitored using a custom-built scanning mobility particle sizer (SMPS), which is a combination

190   of a differential mobility analyzer column (DMA, model 3081, TSI, Shoreview, MN, USA) with

191   flow controls and a condensation particle counter (CPC, model 3772, TSI, Shoreview, MN,

192   USA).

193

194   **2.2 Quantification of γ_{SO_2}**

195   Prior to each experiment, the chamber was flushed by purified air overnight with a flow rate of

196   25 L min^{-1} until particle number concentration was less than 5 cm^{-3} and SO_2 was less than 1 ppb.

197   To adjust RH, the chamber was humidified by passing purified air through a custom-built

198   humidifier filled with ultra-pure water. For experiments with atomized ammonium sulfate or

199   malonic acid, SO_2 was injected into the chamber prior to the introduction of particles. For

200   experiments studying γ_{SO_2} onto SOA, aerosol generated from the flow tube was injected into the

201   Teflon chamber continuously after passing through an O_3 denuder (Ozone Solutions, Iowa, USA)

202   to achieve specific aerosol concentration inside the chamber prior to SO_2 addition. SO_2 mixing

203   ratio in the chamber during each experiment was continuously monitored using an SO_2 analyzer

204   (Model 43i, Thermo Scientific). The initial mixing ratio of SO_2 in each experiment was

205 controlled to be around 200 ppb. Aerosol size distribution was monitored by SMPS. The reactive

206 uptake coefficient of SO_2 was calculated by integrating the following equation:

207 $$-\frac{d[SO_2]}{dt} = \frac{1}{4}\gamma_{SO_2}A\bar{c}[SO_2] \tag{1}$$

208

209 Where [SO_2] is the SO_2 mixing ratio (ppb) monitored by the SO_2 analyzer; A is the average

210 surface area concentration (μm^2 cm^{-3}) derived from the particle size distribution measured by

211 SMPS; $\bar{c}$ represents the mean molecular velocity (cm s^{-1}) of SO_2. d[SO_2]/dt is solved over the

212 initial SO_2 decay, such that the peroxide concentration in the aerosol liquid phase is assumed to

213 be constant and pseudo-first order kinetics can be applied (Abbatt et al., 2012;Thornton et al.,

214 2003). A summary of all the measured γ_{SO2} can be found in Table S1. Typical evolution of

215 monitored species can be seen in Fig.1. Control experiments were performed in order to rule out

216 other potential factors (e.g. SO_2 loss in the in-line filter in front of the SO_2 analyzer, interferences

217 inside the SO_2 analyzer, chamber wall losses, SO_2 uptake onto wet ammonium sulfate, gas-phase

218 reaction of SO_2 with peroxide vapour) that may contribute to the SO_2 decay observed during the

219 γ_{SO2} measurement inside the chamber (Fig. S3-S6). Measurement uncertainty and precision of

220 γ_{SO2} in this study can be found in Table S1. Also, we observed there was SO_2 repartitioning from

221 the humid chamber wall in the presence of organic peroxide under high RH (Fig. S6b, RH 74%).

222 The observed SO_2 repartitioning rate was then applied to correct the γ_{SO2} measured under high

223 RH conditions (above 70%, Expt.14), and this correction amounts to a 40% increase in

224 calculated γ_{SO2}.

225

226 **2.3 Offline peroxide quantification**

227 Aerosol was collected onto 47 mm PTFE (polytetrafluoroethylene) filters with 0.2 μm pore size

228 (Whatman®, GE Healthcare) from the chamber by a diaphragm pump (KNF Neuberger Inc., USA)

229 for offline chemical analysis. The total particulate peroxide content (H_2O_2, ROOH and ROOR) in

230 these samples prior to SO_2 uptake was quantified using the iodometric–spectrophotometric assay

231 (Docherty et al., 2005). I_2 produced from the reaction between I^- and peroxides can further quickly

232 combine with the excess amount of I^- to form I_3^-, which has brown color and absorbs UV-vis at

233 470nm. The SOA extraction was then aliquoted into a 96-well UV plate (Greiner Bio-One,

234 Kremsmünster, AT) with 160 µL well^{-1}. 20 µL of formic acid ($\geqslant$ 95 %, Sigma-Aldrich) was added

235 into each well, following by 20 µL potassium iodide (BioUltra, $\geqslant$99.5%, Sigma-Aldrich) solution

236 (dissolved in DI water). The plate was then covered by an adhesive plate sealer (EdgeBio,

237 Gaithersburg, USA) immediately in order to avoid reagent evaporation and O_2 oxidation. After

238 incubation for an hour in the dark, the UV-vis absorption at 470nm was measured using a UV-vis

239 spectrophotometer (Spectramax 190, Molecular Devices Corporation, Sunnyvale, CA) and then

240 converted to peroxide concentration using the calibration curve made by tert-butyl hydroperoxide

241 (70 wt. % in H_2O, Sigma-Aldrich) with a series of concentrations (0-10mM). An average

242 molecular mass for seed particles (organics + ammonium sulfate) was assumed based on the

243 chemical composition in order to calculate the molar fraction of total peroxides using the following

244 equation:

245

246 $$\text{Molar fraction of peroxide} = \frac{N_{peroxide}}{N_{aerosol}} = N_{peroxide} \frac{M_{(NH_4)_2SO_4} f_{(NH_4)_2SO_4} + M_{peroxide} f_{peroxide}}{m_{aerosol}} \quad (2)$$

247

248 where $m_{aerosol}$ is the weighed aerosol mass on the filter; $M_{(NH_4)_2SO_4}$ and $M_{peroxide}$ are the

249 molecular mass of ammonium sulfate and peroxide, respectively; $f_{(NH_4)_2SO_4}$ and $f_{peroxide}$ are the

250 initial molar fraction of ammonium sulfate and peroxide; $N_{peroxide}$ and $N_{aerosol}$ are the

251 measured peroxide molar and calculated aerosol molar, respectively. More details about the

252 iodometric-spectrophotometric procedures were described in previous work (Wang et al., 2018).

253

3 Results and discussion

3.1 SO$_2$ 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.,

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

SO$_2$ 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).

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

more significant under high RH regime. This is consistent with previous laboratory studies that

measured the reactive uptake coefficient of SO$_2$ onto aerosol to be exponentially dependent on

RH (Zhang et al., 2019;Yao et al., 2019). Additionally, multiple field campaigns have observed

significant correlation between particulate sulfate formation and ambient RH (Song et al.,

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

production during wintertime in Beijing. Zheng et al. (2015) reported a notably higher SOR

(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

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

than atmospheric modeling results implemented with homogeneous SO$_2$ oxidation pathways,

276   which was later attributed to heterogeneous sulfate formation mechanisms. Multiple mechanisms

277   can potentially explain this observed γ_{SO_2}-RH dependence. An enhanced relative humidity would

278   result in a nonlinear increase of aerosol water content, which can lead to more SO_2 dissolved in

279   the aerosol aqueous phase (Seinfeld and Pandis, 2012). It should be noted that while the relative

280   humidity is varied systematically in these experiments, the relationship is more complex since

281   RH also affects other aerosol properties which can affect the uptake kinetics in turn. For

282   example, a higher aerosol liquid water content could dilute protons and thus lower the aerosol

283   acidity. In a study by Laskin et al. (2003), an enhanced uptake of SO_2 onto sea-salt particles was

284   observed with an increased aerosol alkalinity at high pH range.

285
286   **3.2 Dependence of SO_2 uptake on peroxide content and type**

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

288   the current study. Fig. 3 shows that γ_{SO_2} is linearly proportional to the amount of particulate

289   peroxide for aerosol with similar volume-to-surface ratios and containing the same type of

290   organic peroxides. This positive relationship between γ_{SO_2} and condensed phase peroxide content

291   has also been inferred from experiments of SO_2 uptake onto α-pinene SOA (Yao et al., 2019),

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

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

294   In addition to the amount of peroxide injected, the particulate fraction of organic peroxide

295   available for heterogeneous reaction is also influenced by gas-particle partitioning. As indicated

296   in Fig. 2, the reactive uptake coefficients of different organic peroxides vary amongst each other

297   by about an order of magnitude in the range of RH studied, despite the same amounts of peroxide

298   relative to ammonium sulfate initially in the atomizing solution. Based on our previous work

299 (Wang et al., 2019), the aqueous-phase rate constants for these organic peroxides with dissolved

300 S(IV) only vary by a factor of 2-3 and therefore cannot fully explain the observed difference in

301 uptake rates. Since vapour pressure vary considerably among the different peroxides in the

302 present study, gas-particle partitioning is likely to influence the amount of peroxide in the

303 particle phase that react with dissolved SO_2. The relative particulate peroxide content on filters

304 of the three peroxides collected from chamber experiments under RH 50% without SO_2 uptake

305 were measured by the offline KI method (Fig. S7). Although the initial ratio of organic peroxide

306 to ammonium sulfate in the atomizing solution was nominally the same, we measured the highest

307 amount of particulate peroxide with 2-butanone peroxide (16.7%), followed by cumene

308 hydroperoxide (12.7%) and then tert-butyl hydroperoxide (3.8%) using the offline iodometric

309 method. This trend in particulate peroxide content is consistent with the vapour pressures

310 calculated using the SIMPOL group contribution method (Pankow et al., 2008), with 2-butanone

311 peroxide being the least volatile, and tert-butyl hydroperoxide being the most volatile. Also, the

312 order of particle-phase peroxide content is consistent with the order of γ_{SO2} observed, as shown in

313 Fig. 2. A simple visualization of these relationships between different peroxide characteristics

314 (number of peroxide groups, vapour pressure and aqueous-phase rate constants) and measured

315 γ_{SO2} (at RH = 50%) is illustrated in Fig. S7, which indicates higher γ_{SO2} can be expected for

316 organic peroxides with multiple O-O groups, lower vapour pressures and higher aqueous phase

317 reactivities. It should be noted that the order of magnitude difference in experimentally measured

318 γ_{SO2} among various organic peroxides (Fig.2) is still not fully explained when both volatility and

319 reaction kinetics are taken into account (Fig.S7), suggesting that the reactive uptake may be

320 influenced by other factors. In summary, for our current experiments where we nominally

321   maintained total injected amount of organic peroxide constant, measured γ_{SO2} depends both on

322   reactivity and gas-particle partitioning of the organic peroxides.

323

324   **3.3 SO₂ uptake and aqueous phase kinetics**

325   Since the aqueous phase reaction rate constants between S(IV) and these model organic

326   peroxides have been measured previously (Wang et al., 2019), we can test our understanding of

327   the measured γ_{SO2} using a simple model. By assuming the amount of SO₂ dissolved in the aerosol

328   is in equilibrium with the gas phase, the overall γ_{SO2} can be expressed using the simplified

329   resistor model (Hanson et al., 1994):

330

331    $$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{\bar{c}}{4HRT\sqrt{k^I D_l}} \frac{1}{\left[\coth(q) - \frac{1}{q}\right]}$$ (3)

332   where α is the mass accommodation coefficient, $\bar{c}$ is the mean molecular speed of SO₂ (cm s⁻¹),

333   H is the effective Henry's law constant that includes both the dissolution of SO₂ and the

334   dissociation of H₂SO₃ (M atm⁻¹), R is the ideal gas constant (atm L mol⁻¹ K⁻¹), T is the

335   temperature (K), and the parameter q is used to describe the competition between the reaction

336   and diffusion of the dissolved gaseous species within a particle, which is further calculated as:

337    $$q = r\sqrt{\frac{k^I}{D_l}}$$ (4)

338   where r is the radius (cm) of a given particle, D_l is the aqueous-phase diffusion coefficient (cm²

339   s⁻¹), k^I is the first order rate constant (s⁻¹) for the reaction. For experiments in the current study,

340   the calculated q values were consistently found to be far less than 1, which indicates a volume-

341   limited reaction regime. Combining with the assumption of a relatively fast mass

342   accommodation process compared with the bulk phase reaction, equation (3) can be further

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

$$\gamma = \frac{4HRT[peroxide]k^{\mathrm{II}}}{\bar{c}}\frac{V}{S} \tag{5}$$

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

cm^{-3}) derived from SMPS measurements. As a result, the observed reactive uptake coefficient of

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

γ_{SO2} on peroxide content, but the modeled results were found to be generally 15-50 times lower

than the experimentally measured values (Fig. S8). The current γ_{SO2} predictions are likely upper-

bound estimates since all the peroxides were assumed to stay in the condensed phase without

partitioning. As a result, this observed 15-50 times of discrepancy could even be larger if the

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

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

multiphase interaction is strongly favored in the highly concentrated aerosol environment. One of

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.,

2015) such that SO$_2$ can directly interact with the acidic organic phase, where the concentration of

367 peroxides can be higher and the kinetics can be different from what we have measured in dilute

368 solution (Wang et al., 2019). However, LLPS is generally governed by the chemical composition

369 of the hydrophobic phase (Freedman, 2017). A higher level of oxygenation in organic aerosol is

370 related with higher hydrophilicity, which would favor a homogeneous particle instead of phase

371 separation. Previous studies showed that LLPS did not occur for organic coating with O:C above

372 0.8 (You et al., 2013;You et al., 2014). The LLPS phenomenon in simple organic–inorganic

373 mixtures can also be affected by the functional groups. The maximum O:C for LLPS could be 0.71

374 for organics with multiple carboxylic and hydroxyl groups but low aromatic content (Song et al.,

375 2012) while the 2-butanone peroxide we used for both γ_{SO2} measurement and prediction in the

376 present study has multiple peroxide groups with an O:C value of 0.75. Particle size could also have

377 impacts on phase separation (Cheng et al., 2015). Particle diameters in the current study are mainly

378 under 200 nm while a previous study showed particles smaller than this size are less likely to

379 experience LLPS (Veghte et al., 2013). We therefore believe that LLPS is not likely to be

380 responsible for the enhanced uptake rate observed under these experimental conditions.

381 Another explanation is the high solute strength in the concentrated aerosol phase. Although the

382 aerosol water content for ammonium sulfate aerosol was found to be higher than that of malonic

383 acid aerosol under RH 50%. As indicated in Fig. 4 and Fig. S8, the difference between the

384 measured and predicted γ_{SO2} is larger for ammonium sulfate aerosol than for malonic acid.

385 Meanwhile, the calculated ionic strength in aerosol liquid phase under RH 50% for ammonium

386 sulfate (40 mol kg^{-1}) is significantly larger than that of malonic acid (0.45 mol kg^{-1}). It has been

387 previously reported that the reaction rate between sulfite and hydrogen peroxide in aqueous phase

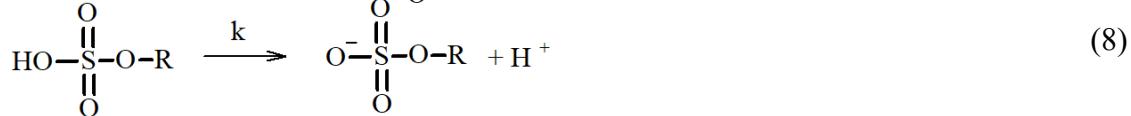
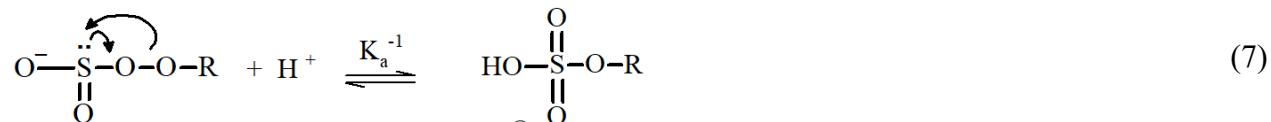
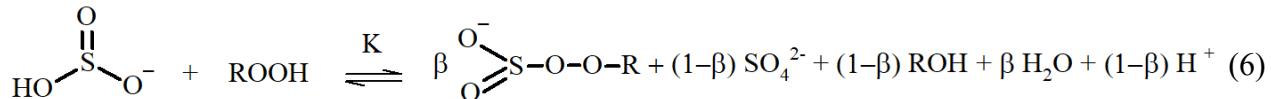
388 increases with ionic strength (Maaß et al., 1999). Based on the reaction mechanisms proposed for

389   dissolved SO_2 and hydrogen peroxide (Halperin and Taube, 1952), we speculate the reaction

390   between aqueous phase S(IV) and organic peroxides to follow a similar mechanism:

$$HO-\overset{\overset{O}{\|}}{\underset{}{S}}-O^- + ROOH \overset{K}{\rightleftharpoons} \beta\ \overset{O^-}{\underset{O}{\diagup}}\!\!\!\!S-O-O-R + (1-\beta)\ SO_4^{2-} + (1-\beta)\ ROH + \beta\ H_2O + (1-\beta)\ H^+ \quad (6)$$

$$O^-\!\!-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-O-R + H^+ \overset{K_a^{-1}}{\rightleftharpoons} HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-R \quad (7)$$

$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-R \overset{k}{\longrightarrow} O^-\!\!-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-R\ + H^+ \quad (8)$$

391

392   where the overall rate constant is equal to $k\dfrac{K}{K_a}$, assuming fast equilibrium steps for reactions 6 and

393   7. Dissociated solutes are surrounded by an extended solvation shell which could affect the

394   reaction rates (Herrmann, 2003). Fewer available free water molecules would therefore shift the

395   equilibrium to the right in equation (6). Additionally, higher ionic strength also corresponds to an

396   increased concentration of electrolytes in the aqueous phase, which could hinder the dissociation

397   of the peroxymonosulfurous acid and shift the equilibrium in equation (7) to the right. In recent

398   work by Liu et al. (2020), the rate of S(IV) oxidation by H_2O_2 can be enhanced by up to a factor

399   of 50 in aerosol aqueous phase compared to that of dilute solution. The highest ionic strength at

400   which such enhancement was measured for the H_2O_2 oxidation pathway was 15 mol kg^{-1} (Liu et

401   al., 2020).

402   Whereas the above analysis is based on the assumption that all the chemistry occurs in the bulk

403   component of the particle, it is also possible that some component of the reaction occurs at the gas-

404   particle interface and the overall kinetics can be affected by interfacial characteristics. For example,

405   an enhanced ionic strength in the aerosol phase can also impact the interfacial reaction mechanisms.

406   Previous study has shown evidence that interfacial chemistry is important for SO_2 oxidation in the

407   aerosol phase (Laskin et al., 2003). With higher ionic strength, anions partitioning to the air-liquid

408   interface can promote the overall reaction kinetics via proton transfer and thus accelerate the

409   interfacial chemistry (Knipping et al., 2000;Mishra et al., 2012;Mekic et al., 2018;Mekic et al.,

410   2020; Wei et al., 2018; Ruiz-Lopez et al., 2020). In addition to the catalytic effects of protons

411   indicated in Eqn.6-8, Hung et al. (2015, 2018) observed significant $SO_3^{\cdot-}$ signal at the acidic

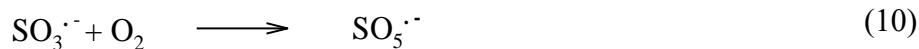
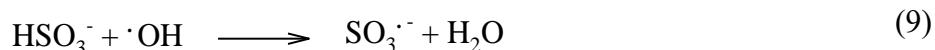
412   microdroplet surface, which can promote sulfate formation via radical propagation chain initiated

413   by surrounding radicals and molecular oxygen (Eqn. 9-12):

$$HSO_3^- + {}^{\cdot}OH \longrightarrow SO_3^{\cdot-} + H_2O \tag{9}$$

$$SO_3^{\cdot-} + O_2 \longrightarrow SO_5^{\cdot-} \tag{10}$$

$$SO_5^{\cdot-} + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_4^{\cdot-} \tag{11}$$

$$SO_4^{\cdot-} + SO_3^{2-} \longrightarrow SO_4^{2-} + SO_3^{\cdot-} \tag{12}$$

414

415   where the hydroxy radical can potentially be produced from decomposition of the labile organic

416   peroxide in our system (Tong et al., 2016). However, we cannot distinguish whether the interfacial

417   protons promote sulfate formation by catalyze the peroxide S(IV) oxidation pathway or the sulfur

418   radical pathway at the current stage. In the recent study by Wei et al. (2018), a pH gradient was

419   observed for phosphate-buffered aerosol droplets with the proton accumulated at the interface.

420   Base on the pH-dependent aqueous phase kinetics measured in our previous work (Wang et al.,

421   2019), such interfacial proton accumulation could potentially explain the enhanced kinetics we

422   observed for aerosol in the current study. However, the chemical compositions are quite different.

423   While phosphate-buffered particles were studied in Wei et al. (2018), acidic ammonium sulfate

424   aerosol was used in our study. Also, the particle size in Wei et al. (2018) is significantly larger (20

425   μm) than what was studied in the current study (200 nm). Thus, it should be noted that there is no

426   direct evidence from the current study showing the relationship between the interfacial properties

427   and γ_{SO2}, and future studies are warranted.

428   Therefore, while more studies are needed to clearly delineate the roles of ionic strength, interfacial

429   activity, bulk reactivity, and particle phase state quantitatively, the enhancement of SO_2 oxidation

430   kinetics by highly concentrated aerosol particles compared to dilute aqueous solutions are

431   concluded to be large (factor of 15-50) for the experimental conditions in the current study.

432

433   **3.4 SO$_2$ uptake and aerosol pH**

434   As indicated by the proposed reaction mechanisms (Eqn. 6-8), protons are important reaction

435   intermediates for this SO_2 oxidation pathway. Previously, the aqueous phase reaction rate

436   constants between organic peroxides and dissolved SO_2 were measured to be pH dependent

437   (Wang et al., 2019). Moreover, the dissolution equilibrium of SO_2 into aqueous phase is also pH

438   sensitive (Seinfeld and Pandis, 2012). Besides, many studies have shown that the uptake kinetics

439   for gaseous species can be affected by the condensed phase pH (Shi et al., 1999;Gaston et al.,

440   2014;Drozd et al., 2013;Jang and Kamens, 2001;Liu et al., 2015). Reactive uptake of ammonia

441   was observed to depend on condensed phase acidity (Shi et al., 1999). Heterogeneous

442   condensation of isoprene-derived epoxydiol onto seed aerosol was found to increase with proton

443   concentration (Gaston et al., 2014). In the current study, the potential impact from particle phase

444   pH on γ_{SO2} was explored by adding HCl into the atomizing solution. To estimate the particle

445   phase pH, two different methods associated with two different assumptions were used. In the

446   first scenario, the aerosol pH in each experiment was estimated using the E-AIM III model

447   (Clegg et al., 1998) based on the initial molar ratios of inorganic species (H^+, NH_4^+, SO_4^{2-}, Cl^-) in

448   the atomizing solution and measured RH (around 50%). In the second scenario, the additional

449 sulfate formed from reactive uptake of SO_2 was taken into consideration. The partitioning of HCl

450 was allowed in the model simulation for both scenarios. The formation of sulfate would enhance

451 the proton concentration in the aerosol liquid phase thus lower the aerosol pH. The average pH

452 during the SO_2 uptake process is likely in between these two extremes.

453 Fig. 5 shows the measured reactive uptake coefficients of SO_2 as a function of the calculated pH.

454 The reactive uptake coefficient was found to weakly increase with decreasing pH, which is

455 consistent with acid-catalyzed reactions between peroxides and dissolved SO_2 as measured in the

456 bulk phase (Lind et al., 1987; Wang et al., 2019). γ_{SO2} was also predicted for the same range of

457 pH based on Eqn. 5 and the pH-dependent bulk-phase reaction rate constants measured

458 previously (Wang et al., 2019). Indicated by Fig. 5, the measured γ_{SO2} again exceeds the

459 predicted γ_{SO2} by about a factor of 50, which is consistent with what we reported earlier and is

460 likely due to the effects of aerosol ionic strength.

461 Unlike the observed γ_{SO2}, however, the predicted γ_{SO2} does not exhibit a monotonic trend. γ_{SO2} is

462 expected to decrease with decreasing pH at high pH (>2) as the effective Henry's law constant of

463 SO_2 decreases with higher acidity (Seinfeld and Pandis, 2012). γ_{SO2} is not expected to increase

464 with decreasing pH until pH is below 2 where the acidity enhancement in reaction rate constant

465 exceeds the decrease in SO_2 solubility. As illustrated earlier, extrapolating dilute aqueous-phase

466 kinetics to the highly concentrated aerosol requires considering effects from high solute strength.

467 Solute strength may change the pH dependence of γ_{SO2} in two ways. First, the solubility of SO_2

468 may decrease and become less dependent on pH as ionic strength increases (Rodríguez-Sevilla et

469 al., 2002). A former study (Leng et al., 2015) has shown that the effective Henry's law of

470 triethylamine decreases with increased ionic strength. Another potential explanation is that the

471 aqueous phase reaction rate constant can be more pH-dependent at high ionic strengths than what

472 we measured previously in dilute solutions. In either case, the inflection of the predicted γ_{SO2}

473 would change and γ_{SO2} could become more negatively dependent on pH ($d[\gamma_{SO2}]/d[pH]$ becomes

474 less positive in the high pH range and/or more negative in the low pH range), which would

475 match more closely with the observed dependence. It should also be noted that there are

476 substantial uncertainties in estimating pH values, originating from the partitioning of organics,

477 organic-inorganic phase separations, mixing state of specific ions, uncertain activity coefficients

478 and the propagation of RH uncertainties (Clegg et al., 2008; Fountoukis et al., 2009; Guo et al.,

479 2016). Also, the reactive uptake is a dynamic process and will influence aerosol pH in turn upon

480 sulfate formation. In summary, while the magnitude of predicted γ_{SO2} is consistent with our

481 expected values (after accounting for the enhancement by high aerosol solute strength), we

482 cannot fully explain the dependence of γ_{SO2} on aerosol pH at the current stage. Future studies

483 should investigate how the effective Henry's law of SO_2 and pH dependence of reaction rate

484 constants vary in aerosol liquid phase with high solute strength in order to have a more

485 comprehensive understanding of the relationship between γ_{SO2} and aerosol pH.

486 **3.4 SO_2 uptake onto SOA**

487 γ_{SO2} was measured for a few model SOA systems, as organic peroxides are abundant in SOA

488 (Surratt et al., 2006;Kautzman et al., 2009;Krapf et al., 2016;Bonn et al., 2004). Here we studied

489 SOA formed from monoterpene ozonolysis and toluene photooxidation. It should be noted that

490 for the γ_{SO2} measurements of toluene SOA, a strong hydrocarbon interference was observed with

491 the SO_2 analyzer, likely stemming from the high concentrations of gas-phase aromatic

492 compounds. A rough estimate of the uptake rate for toluene SOA from aerosol mass

493 spectrometer sulfate measurements is provided in the SI (Section 1). The reactive uptake

494 coefficient of SO_2 onto Saharan mineral dust was reported on the order of 10^{-5} (Adams et al.,

495   2005). γ_{SO2} onto dust with the coexistence of NO_2 and NH_3 under various RH conditions were

496   measured to be 10^{-7} to 10^{-5} (Zhang et al., 2019). For a variety of metal oxides, SO_2 reactive

497   uptake coefficients were quantified to be between 10^{-6} and 10^{-4} (Usher et al., 2002; Fu et al.,

498   2007; Shang et al., 2010). More recently, γ_{SO2} studied for heterogeneous sulfate formation by

499   photolysis of particulate nitrate were reported in the range of 10^{-6} to 10^{-5} (Gen et al., 2019). As

500   shown in Fig. 6, γ_{SO2} for all SOA systems were measured to be on the order of 10^{-4}. Similar γ_{SO2}

501   values on the order of 10^{-4} were measured for α-pinene SOA by Yao et al. (2019), and 10^{-5} for

502   limonene SOA estimated from the chamber study by Ye et al. (2018). The reaction products

503   from this SOA and SO_2 interaction will be reported in a separate study.

504

505   **4. Atmospheric Implications**

506   Oxidation of atmospheric hydrocarbons produces reactive intermediates that can potentially

507   interact with SO_2 and form particulate sulfate, contributing to PM formation and growth (Berndt

508   et al., 2015;Mauldin et al., 2012;Yao et al., 2019). Organic peroxides generated from both

509   biogenic and anthropogenic hydrocarbon emissions are abundant in submicron aerosol. Given

510   that they are highly reactive with relatively short lifetimes (Bonn et al., 2004;Krapf et al.,

511   2016;Qiu et al., 2020), these species could serve as important condensed phase oxidants for gas

512   phase SO_2. Combining laboratory measurements and model predictions, the current study

513   investigated heterogeneous reactions between SO_2 and particulate organic peroxide. The

514   measured γ_{SO2} for organic peroxide containing aerosol ranges from 10^{-5} to 10^{-2} in this study.

515   Based on the modeling work by Wang et al. (2014), adding an SO_2 uptake pathway to GEOS-

516   Chem with a reactive uptake coefficient of 10^{-4} could improve the surface sulfate prediction by

517   more than 50% during a severe haze episode over North China (RH 50%), suggesting the

518   potential importance of this multiphase reaction pathway, especially when SOA is the dominant

519   component in particulate matter.

520   The dependence of the heterogeneous kinetics on RH, aerosol pH, peroxide type, and peroxide

521   content were also evaluated. The experimentally measured γ_{SO2} was found to be consistently

522   higher than that predicted from reaction kinetics with organic peroxides in the dilute aqueous

523   phase. This discrepancy can be potentially explained by the effects of high ionic strength

524   presented in the aerosol, suggesting that the impact from highly concentrated solutes needs to be

525   taken into consideration when applying aqueous phase kinetics to aerosol multiphase chemistry,

526   especially for particles containing strong electrolytes. We also observed that the kinetics of this

527   multiphase reaction exhibit a weak dependence on pH. Increasing the condensed-phase acidity

528   may enhance the heterogeneous rate constant at low pH, and while this pH dependence is

529   consistent with that of the aqueous phase reaction rate constant measured previously, it is not

530   consistent with the decrease of effective Henry's law constant of SO_2 along with enhanced

531   acidity. Also, it is likely that within the uncertainties, there may not be an observable γ_{SO2}-pH

532   trend. Currently, we are not able to fully explain the pH dependence, and further studies are

533   warranted. Particle phase peroxide content was observed to be linearly correlated with γ_{SO2}.

534   Moreover, γ_{SO2} measured for 2-butanone peroxide was found to be orders of magnitude higher

535   than that of cumene hydroperoxide and tert-butyl hydroperoxide. The difference in γ_{SO2} among

536   various types of organic peroxides can be partially explained by their condensed-phase reactivity

537   and gas-particle partitioning.

538   In general, we found the observed γ_{SO2} in this study can be summarized using the following

539   semiempirical multilinear relationship:

540
$$\log \gamma = -1.7 + 0.0024 \times k^{II} + 0.46 \times PAS + 0.024 \times RH - 1.9 \times Vp \qquad (13)$$

541   where γ is the reactive uptake coefficient, $k^{//}$ is the aqueous phase S(IV) oxidation rate constant

542   (M^{-1} s^{-1}) , PAS is the molar ratio between particulate peroxide and ammonium sulfate in the

543   atomizing solution, which is a proxy for the amount of peroxide in both gas and particle phases

544   applied in the current study, RH is the relative humidity (%),Vp is the vapour pressure (kPa) of

545   the peroxide. Fig. 7 illustrates the degree to which this semi-empirical expression describes the

546   experimental data for ammonium sulfate aerosol mixed with the three types of organic peroxides.

547   Residual evaluations of this multilinear regression can be found Fig. S9. We caution that this

548   equation is not directly applicable to atmospheric models in its current form, especially since the

549   particle phase peroxide content (PAS) value we applied as input is a calculated value, rather than

550   a measurement. However, it illustrates the internal consistency of our experimental results across

551   a range of RH, peroxide content, and aqueous phase reactivities, which are the key variables for

552   uptake rates. Better understanding of ionic strengths and pH in aerosol, either through modeling

553   or direct measurements of these variables, is needed to establish the coefficient dependence.

554   Future studies should be focused on exploring γ_{SO2} and the reaction products for various types of

555   SOA as well as ambient particles under atmospherically relevant conditions, evaluating the

556   underlying impacts from photochemical condition, chemical composition, particle morphology,

557   ionic strength and interfacial properties on this multiphase physicochemical process. Overall,

558   γ_{SO2} presented in our study and its relationship with ambient RH, aerosol pH, ionic strength,

559   particulate peroxide content and type could provide a framework for the implementation of this

560   heterogeneous mechanism in atmospheric models to have a better understanding of ambient

561   sulfate formation and particle growth.

562

563

564 *Author contributions*

565 A.W.H. C. and S.W. designed the study. S.W., T. L., and J. J. performed the experiments. S.W.,

566 A.W.H. C., T. L., and J. J. analyzed data. S.W. and A.W.H. C. wrote the manuscript with the

567 input from all co-authors.

568

569 *Data availability*

570 All data presented in this study are available in the supplemental material and have been

571 deposited in figshare.

572

573 *Associated content*

574 Supporting Information.

575

576 *Competing interests*

577 The authors declare no competing financial interest.

578

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588 **Reference**

589 Abbatt, J. P. D., Lee, A. K. Y., and Thornton, J. A.: Quantifying trace gas uptake to tropospheric
590 aerosol: recent advances and remaining challenges, Chem. Soc. Rev., 41, 6555–6581,
591 https://doi.org/10.1039/c2cs35052a, 2012.

592 Adams, J. W., Rodriguez, D., and Cox, R. A.: The uptake of SO_2 on Saharan dust: a flow tube
593 study, Atmos. Chem. Phys., 5, 2643–2676, doi:10.5194/acp-5-2643-2005, 2005.

594 Andreae, M.O., Afchine, A., Albrecht, R., Holanda, B.A., Artaxo, P., Barbosa, H.M., Borrmann,
595 S., Cecchini, M.A., Costa, A., Dollner, M. and Fütterer, D.: Aerosol characteristics and particle
596 production in the upper troposphere over the Amazon Basin, Atmos. Chem. Phys., 18, 921–961,
597 2018.

598 Atkinson, R., and Arey, J.: Atmospheric degradation of volatile organic compounds, Chem.
599 Rev., 103, 4605-4638, 2003.

600 Berndt, T., Richters, S., Kaethner, R., Voigtländer, J., Stratmann, F., Sipilä, M., Kulmala, M.,
601 and Herrmann, H.: Gas-phase ozonolysis of cycloalkenes: Formation of highly oxidized RO_2
602 radicals and their reactions with NO, NO_2, SO_2, and other RO_2 radicals, J. Phys. Chem. A, 119,
603 10336-10348, 10.1021/acs.jpca.5b07295, 2015.

604 Bianchi, F., Kurtén, T., Riva, M., Mohr, C., Rissanen, M. P., Roldin, P., Berndt, T., Crounse, J.
605 D., Wennberg, P. O., Mentel, T. F., Wildt, J., Junninen, H., Jokinen, T., Kulmala, M., Worsnop,
606 D. R., Thornton, J. A., Donahue, N., Kjaergaard, H. G., and Ehn, M.: Highly oxygenated organic
607 molecules (HOM) from gas-phase autoxidation involving peroxy radicals: A key contributor to
608 atmospheric aerosol, Chem. Rev., 119, 3472-3509, 10.1021/acs.chemrev.8b00395, 2019.

609 Bonn, B., von Kuhlmann, R., and Lawrence, M. G.: High contribution of biogenic
610 hydroperoxides to secondary organic aerosol formation, Geophys. Res. Lett., 31, L10108,
611 https://doi.org/10.1029/2003GL019172, 2004.

612 Chen, Q., Farmer, D. K., Schneider, J., Zorn, S. R., Heald, C. L., Karl, T. G., Guenther, A.,
613 Allan, J. D., Robinson, N., Coe, H., Kimmel, J. R., Pauliquevis, T., Borrmann, S., Pöschl, U.,
614 Andreae, M. O., Artaxo, P., Jimenez, J. L., and Martin, S. T.: Mass spectral characterization of
615 submicron biogenic organic particles in the Amazon Basin, Geophys. Res. Lett., 36, L20806,
616 https://doi.org/10.1029/2009GL039880, 2009.

617 Chen, T., Chu, B., Ge, Y., Zhang, S., Ma, Q., He, H., and Li, S.-M.: Enhancement of aqueous
618 sulfate formation by the coexistence of NO_2/NH_3 under high ionic strengths in aerosol water,
619 Environ. Pollut., 252, 236-244, https://doi.org/10.1016/j.envpol.2019.05.119, 2019.

620 Cheng, Y., Su, H., Koop, T., Mikhailov, E., and Pöschl, U.: Size dependence of phase transitions
621 in aerosol nanoparticles, Nat. Commun., 6, 5923, 10.1038/ncomms6923, 2015.

622 Cheng, Y. F., Zheng, G. J., Wei, C., Mu, Q., Zheng, B., Wang, Z. B., Gao, M., Zhang, Q., He, K.
623 B., Carmichael, G., Pöschl, U., and Su, H.: Reactive nitrogen chemistry in aerosol water as a
624 source of sulfate during haze events in China, Sci. Adv., 2, e1601530, 2016.

625 Ciobanu, V. G., Marcolli, C., Krieger, U. K., Weers, U., and Peter, T.: Liquid-liquid phase
626 separation in mixed organic/inorganic aerosol particles, J. Phys. Chem. A, 113, 10966–10978,
627 2009.

Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic model of the system $H^+-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O$ at 298.15 K, J. Phys. Chem. A, 102, 2155–2171, https://doi.org/10.1021/jp973043j, 1998.

Clegg, S. L., Kleeman, M. J., Griffin, R. J., and Seinfeld, J. H.: Effects of uncertainties in the thermodynamic properties of aerosol components in an air quality model – Part 1: Treatment of inorganic electrolytes and organic compounds in the condensed phase, Atmos. Chem. Phys., 8, 1057–1085, http://www.atmos-chem-phys.net/8/1057/2008/, 2008.

Ding, J., Zhao, P., Su, J., Dong, Q., Du, X., and Zhang, Y.: Aerosol pH and its driving factors in Beijing, Atmos. Chem. Phys., 19, 7939-7954, 10.5194/acp-19-7939-2019, 2019.

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 O_3, Environ. Sci. Technol., 39, 4049-4059, 2005.

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.

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 secondary organic aerosol and organosulfates from epoxides, Atmos. Chem. Phys., 13, 8255–8263, doi:10.5194/acp-13-8255-2013, 2013.

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.

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, 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 SO_2 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.: Modeling study of the 2010 regional haze event in the North China Plain, Atmos. Chem. Phys., 16, 1673–1691, https://doi.org/10.5194/acp-16-1673-2016, 2016.

Gaston, C. J., Riedel, T. P., Zhang, Z., Gold, A., Surratt, J. D., and Thornton, J. A.: Reactive uptake of an isoprene-derived epoxydiol to submicron aerosol particles, Environ. Sci. Technol., 48, 11178-11186, 10.1021/es5034266, 2014.

Gen, M., Zhang, R., Huang, D. D., Li, Y., and Chan, C. K.: Heterogeneous SO_2 oxidation in sulfate formation by photolysis of particulate nitrate, Environ. Sci. Tech. Let., 6, 86–91, https://doi.org/10.1021/acs.estlett.8b00681, 2019.

Griffiths, P. T., Badger, C. L., Cox, R. A., Folkers, M., Henk, H. H., and Mentel, T. F.: Reactive uptake of N_2O_5 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. 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., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155–5236, 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.

Hartz, K. E. H., Rosenorn, T., Ferchak, S. R., Raymond, T. M., Bilde, M., Donahue, N. M., and Pandis, S. N.: Cloud condensation nuclei activation of monoterpene and sesquiterpene secondary organic aerosol, J. Geophys. Res.-Atmos., 110(D14), D14208, 2005.

He, L.-Y., Huang, X.-F., Xue, L., Hu, M., Lin, Y., Zheng, J., Zhang, R., and Zhang, Y.-H.: Submicron aerosol analysis and organic source apportionment in an urban atmosphere in Pearl River Delta of China using high-resolution aerosol mass spectrometry, J. Geophys. Res. Atmos., 116, D12304, https://doi.org/10.1029/2010JD014566, 2011.

Herrmann, H.: Kinetics of aqueous phase reactions relevant for atmospheric chemistry, Chem. Rev., 103, 4691–4716, 2003.

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, 2009.

Huang, L., An, J., Koo, B., Yarwood, G., Yan, R., Wang, Y., Huang, C., and Li, L.: Sulfate 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, 14311-14328, 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.

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, 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., 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, 218–222, 2014.

Huang, R. J., He, Y., Duan, J., Li, Y., Chen, Q., Zheng, Y., Chen, Y., Hu, W., Lin, C., Ni, H., Dai, W., Cao, J., Wu, Y., Zhang, R., Xu, W., Ovadnevaite, J., Ceburnis, D., Hoffmann, T., and 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, 10.5194/acp-20-9101-2020, 2020.

Hung, H. M. and Hoffmann, M. R.: Oxidation of gas-phase SO_2 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, 2015.

Hung, H. M., Hsu, M. N., and Hoffmann, M. R.: Quantification of SO_2 oxidation on interfacial surfaces of acidic micro-droplets: Implication for ambient sulfate formation, Environ. Sci. 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., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, 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., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., 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., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of organic aerosols in the atmosphere, Science, 326, 1525–1529, https://doi.org/10.1126/science.1180353, 2009.

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.

Knipping, E. M., Lakin, M. J., Foster, K. L., Jungwirth, P., Tobias, D. J., Gerber, R. B., Dabdub, D., and Finlayson-Pitts, B. J.: Experiments and simulations of ion-enhanced interfacial chemistry on aqueous NaCl aerosols, Science, 288, 301, 10.1126/science.288.5464.301, 2000.

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, 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.L., Cao, F., Zhang, W., Fan, M., Lee, X., and Michalski, G.: Stable sulfur isotopes revealed a major role of transition-metal ion-catalyzed SO_2 oxidation in haze episodes, Environ. Sci. Technol., 54, 2626–2634, https://doi.org/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, 1987.

Liu, C., Chen, T., Liu, Y., Liu, J., He, H., Zhang, P.: Enhancement of secondary organic aerosol formation and its oxidation state by SO_2 during photooxidation of 2-methoxyphenol, Atmos. Chem. Phys., 19, 2687-2700, 2019.

Liu, L., Bei, N., Wu, J., Liu, S., Zhou, J., Li, X., Yang, Q., Feng, T., Cao, J., Tie, X. and Li, G.: Effects of stabilized Criegee intermediates (sCIs) on sulfate formation: a sensitivity analysis during summertime in Beijing–Tianjin–Hebei (BTH), China, Atmos. Chem. Phys., 19, 13341-13354, 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, 2015.

Maaß, F., Elias, H., and Wannowius, K. J.: Kinetics of the oxidation of hydrogen sulfite by hydrogen peroxide in aqueous solution: ionic strength effects and temperature dependence, Atmos. Environ., 33, 4413-4419, https://doi.org/10.1016/S1352-2310(99)00212-5, 1999.

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 dioxide, Nature, 488, 193–196, https://doi.org/10.1038/nature11278, 2012.

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 deposition, Environ. Sci. Technol., 52, 12306-12315, 10.1021/acs.est.8b03196, 2018.

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 Space Chem., 4, 1029-1038, 10.1021/acsearthspacechem.0c00059, 2020.

792 Mishra, H., Enami, S., Nielsen, R. J., Hoffmann, M. R., Goddard, W. A., and Colussi, A. J.:
793 Anions dramatically enhance proton transfer through aqueous interfaces, Proc. Natl. Acad. Sci.
794 U. S. A., 109, 10228-10232, 2012.

795 Newland, M. J., Rickard, A. R., Vereecken, L., Muñoz, A., Ródenas, M., and Bloss, W. J.:
796 Atmospheric isoprene ozonolysis: impacts of stabilised Criegee intermediate reactions with SO_2,
797 H_2O and dimethyl sulfide, Atmos. Chem. Phys., 15, 9521–9536, https://doi.org/10.5194/acp-15-
798 9521-2015, 2015.

799 Ng, N., Kroll, J., Chan, A., Chhabra, P., Flagan, R., and Seinfeld, J.: Secondary organic aerosol
800 formation from m-xylene, toluene, and benzene, Atmos. Chem. Phys., 7, 3909–3922,
801 http://www.atmos-chem-phys.net/7/3909/2007, 2007.

802 Ng, N. L., Kwan, A. J., Surratt, J. D., Chan, A. W. H., Chhabra, P. S., Sorooshian, A., Pye, H. O.
803 T., Crounse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic
804 aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO_3), Atmos. Chem.
805 Phys., 8, 4117–4140, http://www.atmos-chem-phys.net/8/4117/2008/, 2008.

806 Nguyen, T. B., Tyndall, G. S., Crounse, J. D., Teng, A. P., Bates, K. H., Schwantes, R. H.,
807 Coggon, M. M., Zhang, L., Feiner, P., Milller, D. O., Skog, K. M., Rivera-Rios, J. C., Dorris, M.,
808 Olson, K. F., Koss, A., Wild, R. J., Brown, S. S., Goldstein, A. H., de Gouw, J. A., Brune,
809 W. H., Keutsch, F. N., Seinfeld, J. H., and Wennberg, P. O.: Atmospheric fates of Criegee
810 intermediates in the ozonolysis of isoprene, Phys. Chem. Chem. Phys., 18, 10 241–10 254,
811 https://doi.org/10.1039/C6CP00053C, http://dx.doi.org/10.1039/C6CP00053C, 2016.

812 O'Brien, R. E., Wang, B., Kelly, S. T., Lundt, N., You, Y., Bertram, A. K., Leone, S. R., Laskin,
813 A., and Gilles, M. K.: Liquid–liquid phase separation in aerosol particles: Imaging at the
814 nanometer scale, Environ. Sci. Technol., 49, 4995-5002, 10.1021/acs.est.5b00062, 2015.

815 Pankow, J. F. and Asher, W. E.: SIMPOL.1: a simple group contribution method for predicting
816 vapor pressures and enthalpies of vaporization of multifunctional organic compounds, Atmos.
817 Chem. Phys., 8, 2773–2796, http://www.atmos-chem-phys.net/8/2773/2008/, 2008.

818 Qiu, J., Liang, Z., Tonokura, K., Colussi, A. J., and Enami, S.: Stability of monoterpene-derived
819 α-hydroxyalkyl-hydroperoxides in aqueous qrganic media – relevance to the fate of
820 hydroperoxides in aerosol particle phases, Environ. Sci. Technol., 10.1021/acs.est.9b07497,
821 2020.

822 Rodríguez-Sevilla, J., Álvarez, M., Limiñana, G., Díaz, M. C.: Dilute SO_2 absorption equilibria
823 in aqueous HCl and NaCl solutions at 298.15 K, J. Chem. Eng. Data, 47, 1339-1345, 2002.

824 Ruiz-Lopez, M.F., Francisco, J.S., Martins-Costa, M.T. and Anglada, J.M.: Molecular reactions
825 at aqueous interfaces. Nat. Rev. Chem., 1-17, 2020.

826 Seinfeld, J. H., and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to
827 climate change, John Wiley & Sons, 2012.

828 Sha, T., Ma, X., Jia, H., Tian, R., Chang, Y., Cao, F., and Zhang, Y.: Aerosol chemical
829 component: Simulations with WRF-Chem and comparison with observations in Nanjing, Atmos.
830 Environ., 218, 116982, https://doi.org/10.1016/j.atmosenv.2019.116982, 2019.

831 Shang, J., Li, J., Zhu, T.: Heterogeneous reaction of SO_2 on TiO_2 particles. Sci. China Chem., 53,
832 2637–2643, 2010.

833 Shi, G., Xu, J., Peng, X., Xiao, Z., Chen, K., Tian, Y., Guan, X., Feng, Y., Yu, H., Nenes, A.,
834 and Russell, A. G.: pH of aerosols in a polluted atmosphere: Source contributions to highly
835 acidic aerosol, Environ. Sci. Technol., 51, 4289-4296, 10.1021/acs.est.6b05736, 2017.

836 Shi, Q., Davidovits, P., Jayne, J. T., Worsnop, D. R., and Kolb, C. E.: Uptake of gas-phase
837 ammonia. 1. Uptake by aqueous surfaces as a function of pH, J. Phys. Chem. A, 103, 8812-8823,
838 10.1021/jp991696p, 1999.

839 Song, M., Marcolli, C., Krieger, U. K., Zuend, A., and Peter, T.: Liquid–liquid phase separation
840 in aerosol particles: dependence on O:C, organic functionalities, and compositional complexity,
841 Geophys. Res. Lett., 39, L19801, doi:10.1029/2012GL052807, 2012.

842 Song, S., Gao, M., Xu, W., Shao, J., Shi, G., Wang, S., Wang, Y., Sun, Y., and McElroy, M. B.:
843 Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium
844 models, Atmos. Chem. Phys., 18, 7423–7438, https://doi.org/10.5194/acp-18-7423-2018, 2018.

845 Song, S., Gao, M., Xu, W., Sun, Y., Worsnop, D. R., Jayne, J. T., Zhang, Y., Zhu, L., Li, M.,
846 Zhou, Z., Cheng, C., Lv, Y., Wang, Y., Peng, W., Xu, X., Lin, N., Wang, Y., Wang, S., Munger,
847 J. W., Jacob, D. J., and McElroy, M. B.: Possible heterogeneous chemistry of hydroxy
848 methanesulfonate (HMS) in northern China winter haze, Atmos. Chem. Phys., 19, 1357–1371,
849 https://doi.org/10.5194/acp-19-1357-2019, 2019.

850 Su, H., Cheng, Y., and Pöschl, U.: New multiphase chemical processes influencing atmospheric
851 aerosols, air quality, and climate in the anthropocene, Accounts Chem. Res., 53, 2034–2043,
852 https://doi.org/10.1021/acs.accounts.0c00246, 2020.

853 Sun, Y., Wang, Z., Fu, P., Jiang, Q., Yang, T., Li, J., and Ge, X.: The impact of relative humidity
854 on aerosol composition and evolution processes during wintertime in Beijing, China, Atmos.
855 Environ., 77, 927-934, 2013.

856 Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A.,
857 Szmigielski, R., Vermeylen, R., Maenhaut, W., and Claeys, M.: Chemical composition of
858 secondary organic aerosol formed from the photooxidation of isoprene, J. Phys. Chem. A, 110,
859 9665-9690, 2006.

860 Thornton, J. A., Braban, C. F., and Abbatt, J. P. D.: N$_2$O$_5$ hydrolysis on sub-micron organic
861 aerosols: the effect of relative humidity, particle phase, and particle size, Phys. Chem. Chem
862 Phys., 5, 4593–4603, https://doi.org/10.1039/B307498F, 2003.

863 Tie, X., Brasseur, G., Emmons, L., Horowitz, I., and Kinnison, D.: Effects of aerosols on
864 tropospheric oxidants: a global model study, J. Geophys. Res. Atmos., 106, 22931–22964, 2001.

865 Tong, H., Arangio, A. M., Lakey, P. S. J., Berkemeier, T., Liu, F.,Kampf, C. J., Brune, W. H.,
866 Pöschl, U., and Shiraiwa, M.: Hydroxyl radicals from secondary organic aerosol decomposition
867 in water, Atmos. Chem. Phys., 16, 1761–1771, doi:10.5194/acp-16-1761-2016, 2016.

868 Usher, C. R., Al-Hosney, H., Carlos-Cuellar, S., and Grassian,V. H.: A laboratory study of the
869 heterogeneous uptake and oxidation of sulfur dioxide on mineral dust particles, J. Geophys. Res.,
870 107, 4713, doi:10.1029/2002JD002051, 2002.

871 Varutbangkul, V., Brechtel, F. J., Bahreini, R., Ng, N. L., Keywood, M. D., Kroll, J. H., Flagan,
872 R. C., Seinfeld, J. H., Lee, A., and Goldstein, A. H.: Hygroscopicity of secondary organic
873 aerosols formed by oxidation of cycloalkenes, monoterpenes, sesquiterpenes, and related

874 compounds, Atmos. Chem. Phys., 6, 2367–2388, http://www.atmos-chem-phys.net/6/23
875 67/2006/, 2006.

876 Veghte, D. P., Altaf, M. B., and Freedman, M. A.: Size dependence of the structure of organic
877 aerosol, J. Am. Chem. Soc.,135, 16046–16049, 2013.

878 Wang, G., Zhang, R., Gomez, M. E., Yang, L., Zamora, M. L., Hu, M., Lin, Y., Peng, J., Guo, S.,
879 and Meng, J.: Persistent sulfate formation from London Fog to Chinese haze, Proc. Natl. Acad.
880 Sci. U. S. A., 113, 13630-13635, 2016.

881 Wang, S., Ye, J., Soong, R., Wu, B., Yu, L., Simpson, A. J., and Chan, A. W. H.: Relationship
882 between chemical composition and oxidative potential of secondary organic aerosol from
883 polycyclic aromatic hydrocarbons, Atmos. Chem. Phys., 18, 3987-4003, 2018.

884 Wang, S., Zhou, S., Tao, Y., Tsui, W. G., Ye, J., Yu, J. Z., Murphy, J. G., McNeill, V. F.,
885 Abbatt, J. P. D., and Chan, A. W. H.: Organic peroxides and sulfur dioxide in aerosol: Source of
886 particulate sulfate, Environ. Sci. Technol., 53, 10695-10704, 10.1021/acs.est.9b02591, 2019.

887 Wang, X.; Gemayel, R.; Hayeck, N.; Perrier, S.; Charbonnel, N.; Xu, C.; Chen, H.; Zhu, C.;
888 Zhang, L.; Wang, L.; Nizkorodov, S. A.; Wang, X.; Wang, Z.; Wang, T.; Mellouki, A.; Riva, M.;
889 Chen, J.; George, C. Atmospheric photosensitization: A new pathway for sulfate formation,
890 Environ. Sci. Technol., 54, 3114-3120, 2020.

891 Wang, Y., Zhang, Q., Jiang, J., Zhou, W., Wang, B., He, K., Duan, F., Zhang, Q., Philip, S., and
892 Xie, Y.: Enhanced sulfate formation during China's severe winter haze episode in January 2013
893 missing from current models, J. Geophys. Res. Atmos., 119, 10425–10440, 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,
896 10.1073/pnas.1720488115, 2018.

897 Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-
898 VanWertz, G., Kreisberg, N. M., and Knote, C.: Effects of anthropogenic emissions on aerosol
899 formation from isoprene and monoterpenes in the southeastern United States, Proc. Natl. Acad.
900 Sci. U. S. A., 112, 37-42, 2015.

901 Yang, Y., Wang, H., Smith, S. J., Easter, R., Ma, P.-L., Qian, Y., Yu, H., Li, C., and Rasch, P. J.:
902 Global source attribution of sulfate concentration and direct and indirect radiative forcing,
903 Atmos. Chem. Phys., 17, 8903–8922, https://doi.org/10.5194/acp17-8903-2017, 2017.

904 Yao, M., Zhao, Y., Hu, M., Huang, D., Wang, Y.C., Yu, J. Z., and Yan, N.: Multiphase reactions
905 between secondary organic aerosol and sulfur dioxide: kinetics and contributions to sulfate
906 formation and aerosol aging, Environ. Sci. Tech. Let. 6, 768-774, 2019.

907 Ye, J., Gordon, C. A., and Chan, A. W. H: Enhancement in secondary organic aerosol formation
908 in the presence of preexisting organic particle, Environ. Sci. Technol., 50, 3572-3579, 2016.

909 Ye, J., Abbatt, J. P. D., and Chan, A. W. H.: Novel pathway of SO_2 oxidation in the atmosphere:
910 reactions with monoterpene ozonolysis intermediates and secondary organic aerosol, Atmos.
911 Chem. Phys., 18, 5549–5565, https://doi.org/10.5194/acp18-5549-2018, 2018.

912 Yee, L. D., Isaacman-VanWertz, G., Wernis, R. A., Kreisberg, N. M., Glasius, M., Riva, M.,
913 Surratt, J. D., de Sá, S. S., Martin, S. T., Alexander, M. L., Palm, B. B., Hu, W., Campuzano-
914 Jost, P., Day, D. A., Jimenez, J. L., Liu, Y., Misztal, P. K., Artaxo, P., Viegas, J., Manzi, A., de

915 Souza, R. A. F., Edgerton, E. S., Baumann, K., and Goldstein, A. H.: Natural and
916 anthropogenically influenced isoprene oxidation in southeastern United States and central
917 Amazon, Environ. Sci. Technol., 54, 5980-5991, 10.1021/acs.est.0c00805, 2020.

918 You, Y., Renbaum-Wolff, L., Bertram, A. K: Liquid-liquid phase separation in particles
919 containing organics mixed with ammonium sulfate, ammonium bisulfate, ammonium nitrate or
920 sodium chloride, Atmos. Chem. Phys., 13, 11723–11734, https://doi.org/10.5194/acp-13-11723-
921 2013, 2013.

922 You, Y., Smith, M. L., Song, M., Martin, S. T., and Bertram, A. K.: Liquid–liquid phase
923 separation in atmospherically relevant particles consisting of organic species and inorganic salts,
924 Int. Rev. Phys. Chem., 33, 43–77, doi:10.1080/0144235X.2014.890786, 2014.

925 Zhang, S., Xing, J., Sarwar, G., Ge, Y., He, H., Duan, F., Zhao, Y., He, K., Zhu, L. and Chu, B.:
926 Parameterization of heterogeneous reaction of SO_2 to sulfate on dust with coexistence of NH_3
927 and NO_2 under different humidity conditions, Atmos. Environ., 208, 133-140, 2019.

928 Zhao, Y., Liu, Y., Ma, J., Ma, Q., and He, H.: Heterogeneous reaction of SO_2 with soot: The
929 roles of relative humidity and surface composition of soot in surface sulfate formation, Atmos.
930 Environ., 152, 465-476, 2017.

931 Zheng, B., Zhang, Q., Zhang, Y., He, K. B., Wang, K., Zheng, G. J., Duan, F. K., Ma, Y. L., and
932 Kimoto, T.: Heterogeneous chemistry: a mechanism missing in current models to explain
933 secondary inorganic aerosol formation during the January 2013 haze episode in North China,
934 Atmos. Chem. Phys., 15, 2031–2049, doi:10.5194/acp-15-2031-2015, 2015.

935 Zheng, G. J., Duan, F. K., Su, H., Ma, Y. L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T.,
936 Kimoto, T., Chang, D., Pöschl, U., Cheng, Y. F., and He, K. B.: Exploring the severe winter haze
937 in Beijing: the impact of synoptic weather, regional transport and heterogeneous reactions,
938 Atmos. Chem. Phys., 15, 2969–2983, doi:10.5194/acp-15-2969-2015, 2015.

939 Zheng, G., Su, H., Wang, S., Andreae, M. O., Pöschl, U., and Cheng, Y.: Multiphase buffer
940 theory explains contrasts in atmospheric aerosol acidity, Science, 369, 1374-1377,
941 10.1126/science.aba3719, 2020.

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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

initial portion of the decay (first 7 minutes).

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963 **Figure 2.** Exponential relationship between γ_{SO_2} and RH for ammonium sulfate aerosol

964 containing 2-butanone peroxide (2B), cumene hydroperoxide (CP), tert-butyl hydroperoxide

965 (TB).

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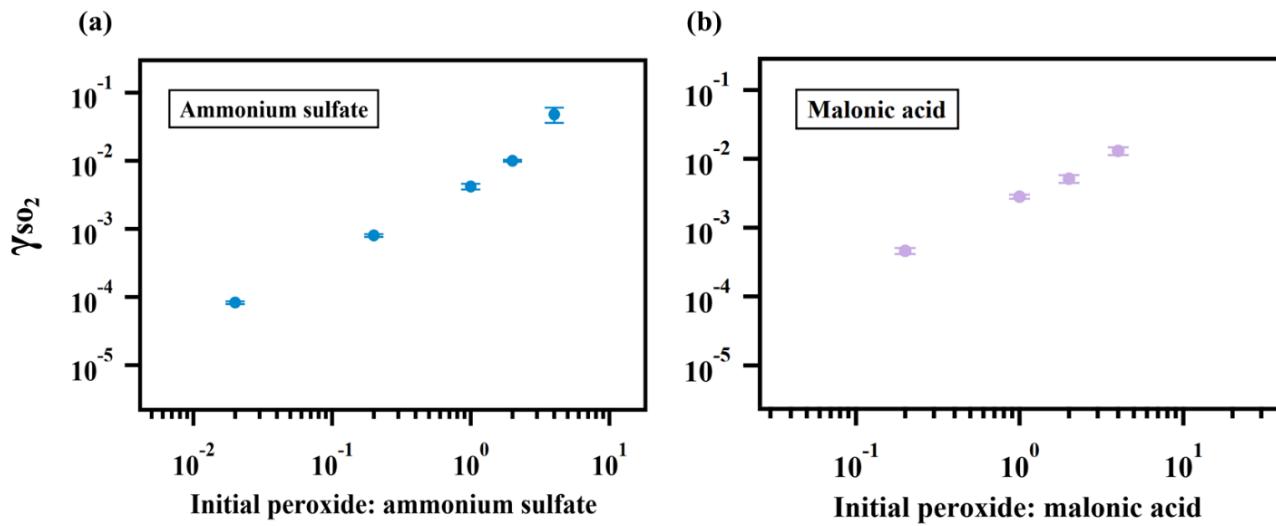
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975 **Figure 3.** Relationship between γ_{SO2} and particulate peroxide content. γ_{SO2} for ammonium sulfate

976 (a) and malonic acid aerosol (b) containing different amount of 2-butanone peroxide are shown

977 here. The observed dependence of γ_{SO2} on the amount of peroxide injected are linear since the

978 slopes of the relationship are both nearly 1 in (a) and (b).

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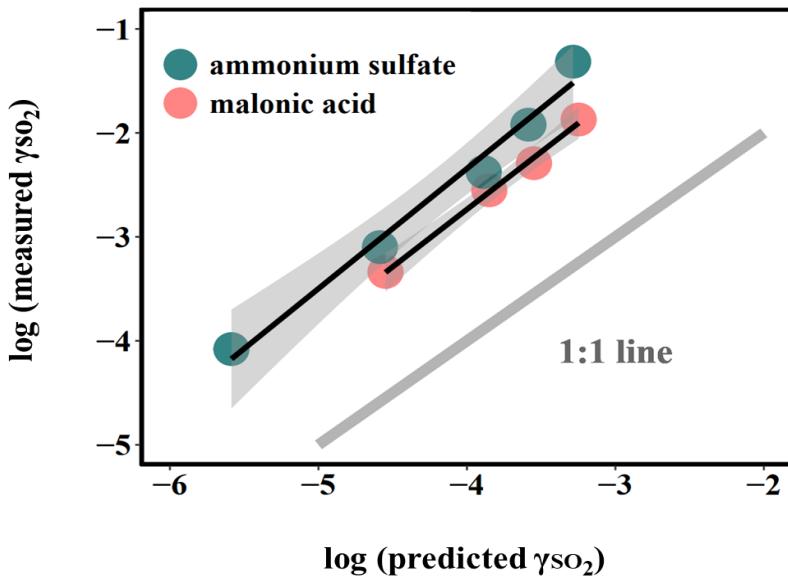
Figure 4. Relationship between measured γ_{SO2} and γ_{SO2} predicted by Eqn. 5. The large deviation

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).

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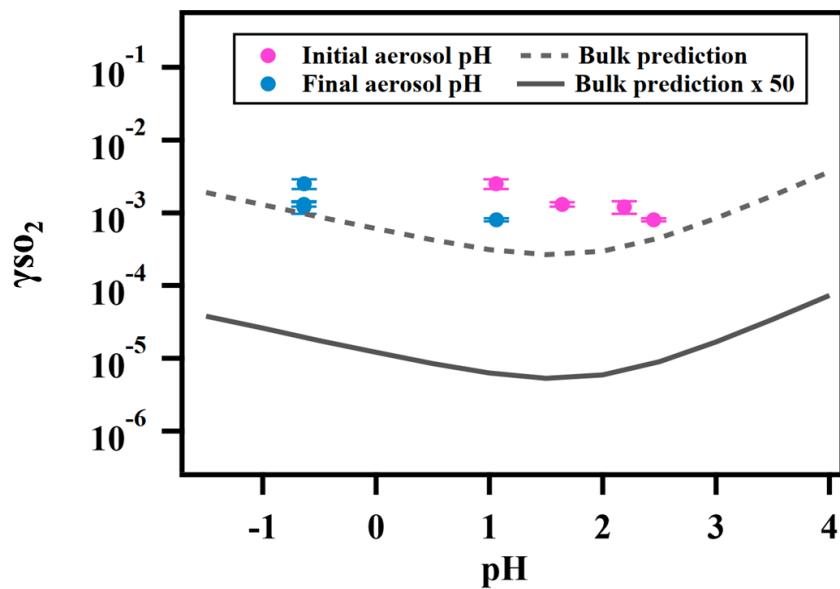
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999 **Figure 5.** Relationship between γ_{SO2} and aerosol phase pH for ammonium sulfate aerosol

1000 containing 2-butanone peroxide.

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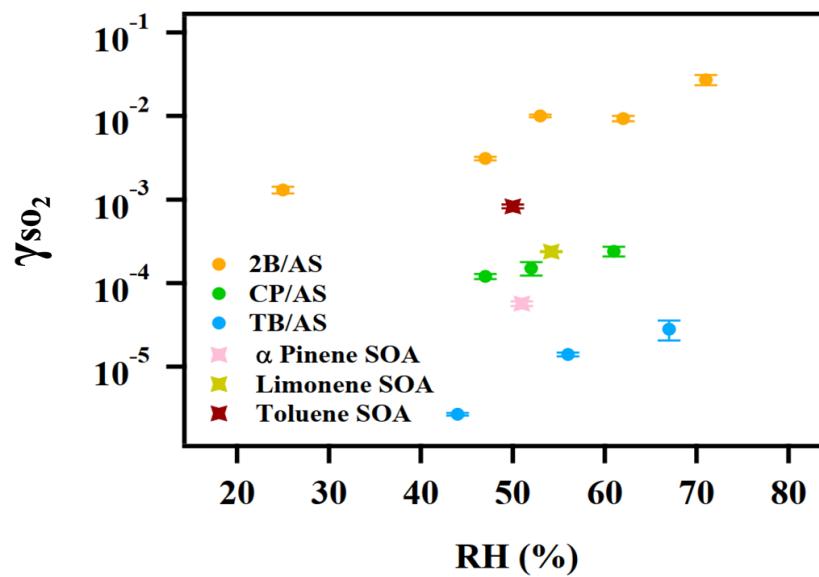
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1010 **Figure 6.** γ_{SO2} measured for different types of organic aerosol. The reactive uptake coefficient of

1011 SO_2 onto SOA are on the order of 10^{-4}.

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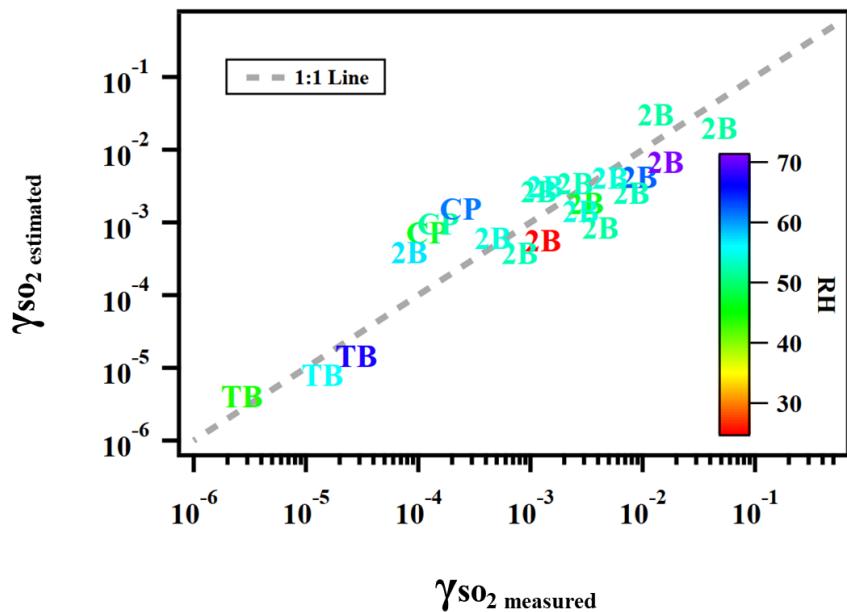
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Figure 7. Predicted γ_{SO2} using Equation (13) versus measured γ_{SO2} for ammonium sulfate or

malonic acid aerosol containing 2-butanone peroxide (2B), cumene hydroperoxide (CP), tert-

butyl hydroperoxide (TB) under different experimental conditions.

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