

Novel Pathway of SO₂ Oxidation in the Atmosphere: Reactions with Monoterpene Ozonolysis Intermediates and Secondary Organic Aerosol

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Abstract. Ozonolysis of monoterpenes is an important source of atmospheric biogenic secondary organic
10 aerosol (BSOA). While enhanced BSOA formation has been associated with sulfate-rich conditions, the
underlying mechanisms remain poorly understood. In this work, the interactions between SO₂ and reactive
intermediates from monoterpene ozonolysis were investigated under different humidity conditions (10%
vs. 50%). Chamber experiments were conducted with ozonolysis of α -pinene or limonene in the presence
of SO₂. Limonene SOA formation was enhanced in the presence of SO₂, while no significant changes in
15 SOA yields were observed during α -pinene ozonolysis. Under dry conditions, SO₂ primarily reacted with
stabilized Criegee Intermediates (sCI) produced from ozonolysis, but at 50% RH, heterogeneous uptake
of SO₂ onto organic aerosol was found to be the dominant sink of SO₂, likely owing to reactions between
SO₂ and organic peroxides. This SO₂ loss mechanism to organic peroxides in SOA has not previously
been identified in experimental chamber study. Organosulfates were detected and identified using
20 electrospray ionization-ion mobility time of flight mass spectrometer (ESI-IMS-TOF) when SO₂ was
present in the experiments. Our results demonstrate the synergistic effects between BSOA formation and
SO₂ oxidation through sCI chemistry and SO₂ uptake onto organic aerosol and illustrate the importance
of considering the chemistry of organic and sulfur-containing compounds holistically to properly account
for their reactive sinks.

25 1. Introduction

Secondary organic aerosol (SOA) is formed from condensation of low-volatility products from atmospheric oxidation of volatile organic compounds (VOCs) and comprises a major fraction of atmospheric organic aerosol (Jimenez et al., 2009). Globally, the dominant fraction of SOA is formed from oxidation of biogenic precursors, as suggested by the high fractions of modern carbon in atmospheric organic aerosol (Goldstein et al., 2009; Weber et al., 2007; Szidat et al., 2006; de Gouw et al., 2005). While emissions of biogenic hydrocarbons are largely uncontrollable, laboratory studies and field observations have shown that biogenic SOA (BSOA) formation is influenced by anthropogenic emissions, such as primary organic aerosol and NO_x (Ye et al., 2016; Xu et al., 2015; Goldstein et al., 2009; Ng et al., 2007, 2008). As a result, it has been suggested that atmospheric BSOA could be significantly reduced by controlling anthropogenic pollutants (Carlton et al., 2010; Heald et al., 2008).

One important pollutant that can affect BSOA formation is SO₂, with up to 94% of its emissions from anthropogenic activities such as fuel combustion in the U.S. (Year 2014; U.S. EPA, 2014) and more than 78% globally (Year 2007-2009; McLinden et al., 2016). Oxidation of SO₂ in the atmosphere leads to formation of sulfuric acid that plays a crucial role in atmospheric new particle formation (Brock et al., 2002) and enhances SOA formation through acid-catalyzed mechanisms (Jang et al., 2002). Long-term ground observations in Southeast U.S. show that the decrease of BSOA is correlated strongly to the decrease in sulfate content in aerosols (Marais et al., 2017), implying co-benefits in controlling SO₂ emission to reduce both sulfate and BSOA. It is further demonstrated by Xu et al. (2015) that anthropogenic NO_x and sulfate correlate strongly with 43-70% of total measured organic aerosol in this area. The mechanisms by which sulfate influences BSOA formation have also been demonstrated through laboratory studies. For example, SOA yields of isoprene, as well as α -pinene and limonene, increased with increasing the acidity of the seed aerosol (Iinuma et al., 2007; Surratt et al., 2007; Gao et al., 2004; Czoschke et al., 2003). The formation of high-molecular-weight (high-MW) oligomers and organosulfates is enhanced in the presence of sulfuric acid (Surratt et al., 2008; Tolocka et al., 2004).

There is also increasing evidence that SO₂ may directly influence BSOA formation by influencing OH reactivity. In the presence of SO₂, enhanced gas-phase products from α-pinene and β-pinene photooxidation were observed with a decreased oxidation state of gas-phase semivolatile species (Friedman et al., 2016). Liu et al. (2017) demonstrated that SOA yields of cyclohexene photooxidation were lower at atmospherically relevant concentrations of SO₂, implying that SO₂ may indirectly decrease SOA formation when the acid-catalyzed SOA enhancement is insufficient to compensate for the loss of OH reactivity towards VOCs. SO₂ can also directly influence VOC oxidation mechanisms through reactions with stabilized Criegee intermediates (sCI) formed from olefin ozonolysis (Huang et al., 2015a; Welz et al., 2012). Field observations suggested that SO₂ + sCIs reactions may contribute up to 50% of the total gaseous sulfuric acid production in the forest atmosphere, which is comparable to that from gas-phase oxidation by OH (Mauldin III et al., 2012). Consistent with this observation, model calculations with CH₂OO, the simplest sCI, suggested that the SO₂ and sCI reaction could be significant in atmospheric sulfuric acid formation under dry conditions, but suggest that this pathway may become less important as humidity increases due to the scavenging effect of water and water dimer towards sCIs (Calvert and Stockwell, 1983). However, the reactivity of sCI towards SO₂ is observed to be strongly dependent on its molecular structure. While CH₂OO may primarily react with water and water dimer, Huang et al. (2015) demonstrated that the di-substituted sCI has a long lifetime under atmospherically relevant humidity conditions and may react with SO₂. Sipilä et al. (2014) also demonstrated that the formation rates of sulfuric acid, the product of the sCI + SO₂ reaction, are nearly independent of humidity for monoterpene ozonolysis. In addition to OH and sCIs, it has been proposed that SO₂ may react with peroxy radicals (RO₂) (Kan et al., 1981). While the gas-phase reaction of SO₂ + RO₂ is usually too slow to compete with other RO₂ sinks (Berndt et al., 2015), Richards-Henderson et al. (2016) proposed that in polluted areas ([SO₂] ≥ 40 ppb), SO₂ may react with RO₂ radicals at the surface of aerosol, and significantly accelerate (10-20 times higher) the heterogeneous oxidation rate of aerosol by OH radicals through chain propagation mechanism of alkoxy radicals. The reaction rate of particle-phase SO₂ + RO₂ (~10⁻¹³ cm³ molecule⁻¹ s⁻¹) was calculated to be 4 orders of magnitude larger than that for the gas phase (10⁻¹⁷ cm³ molecule⁻¹ s⁻¹) (Richards-Henderson et al., 2016), indicating that this mechanism may be important for heterogeneous oxidation of aerosols, but the contribution to SO₂ sink is likely small.

Not only can SO₂ react with reactive species in the gas phase, it can also either partition into aqueous droplets and submicron particles or through heterogeneous reactions with the potential to alter SOA formation mechanisms and products. Reactions with dissolved H₂O₂ and O₃ are usually considered as the dominant sinks of SO₂ in aqueous droplets (Seinfeld and Pandis, 2006), and the reaction rates are a strong function of particle acidity (Hung and Hoffmann, 2015; Seinfeld and Pandis, 2006). However, it was highlighted that in polluted areas, dissolved NO₂ and heterogeneous reactions on the surface of mineral dust could also contribute significantly to atmospheric SO₂ oxidation (He et al., 2014; Xue et al., 2016). More recently, Shang et al. (2016) and Passananti et al. (2016) proposed that without assistance of other oxidants, gaseous SO₂ can also be directly taken up by unsaturated fatty acid or long-chain alkenes through a [2+2] cycloaddition mechanism under atmospheric conditions with observation of organic sulfur compounds as direct formation products.

Despite the importance of SO₂ in modulating BSOA formation, there have been few studies investigating the role of SO₂ in SOA formation from monoterpene ozonolysis, an important source of BSOA. In this work, we study the direct interactions between SO₂ and reactive intermediates formed from ozonolysis of limonene and α -pinene, two important monoterpenes. We hypothesize that the presence of SO₂ changes SOA formation mechanisms and may lead to changes in SOA products and SOA yields. Interactions between SO₂ and reactive intermediates such as sCI and organic peroxides during SOA formation were investigated under different humidity conditions. We report synergistic effects between SOA formation and SO₂ oxidation with observation of organosulfate formation. Results in this study provide a better mechanistic understanding of BSOA formation and atmospheric SO₂ oxidation.

2. Experimental Methods

Experiments were conducted both in a 1-m³ Teflon chamber for examining the time evolution of gaseous species and particles, and in a quartz flow tube for collection of particles onto filters and offline chemical analysis.

2.1 Chamber experiments

Before each experiment, the chamber was flushed with purified air until the total particle number concentration, ozone concentration and SO₂ concentration was less than 10 # cm⁻³, 1 ppb and 1 ppb, respectively. (R)-Limonene (97%, Sigma-Aldrich)/cyclohexane (99%, Caledon Laboratories Ltd.) or α-pinene (99%, Sigma-Aldrich)/cyclohexane solution was injected into a glass vessel and then introduced into the chamber by purified compressed air at a flow rate of ~ 10 L min⁻¹. The injection ratio (v/v) of limonene/cyclohexane and α-pinene/cyclohexane was 1:1500 and 1:500, respectively. At these ratios, the reaction of OH with cyclohexane is calculated to be around 100 times faster than that of OH with monoterpene. SO₂ (5.2 ppm, balanced in N₂, Linde Canada) was injected into the chamber at 10 L min⁻¹ to achieve the desired initial concentrations. Ozone was added at a concentration more than 5 times higher than that of monoterpene to ensure complete consumption. Ammonium sulfate seed particles were introduced by a collision type atomizer (TSI 3076). In dry experiments (10-16% RH), seed particles were dried using a custom-made diffusion dryer before injection into the chamber. In humid experiments, seed particles were not dried when injected into the chamber. Chamber RH was controlled using a custom-made humidifier and maintained at 47-55% which is above the efflorescence point of ammonium sulfate. Therefore, the liquid water content in seed particles in the humid experiments is expected to be higher than that in the dry experiments. However, it is noted that a diffusion dryer was placed before the particle sampling inlet to remove liquid water from the particles in order to eliminate its influence on calculating the change of organic particle volume/mass concentration. In all experiments, monoterpene concentration was measured using a gas chromatograph with flame ionization detector (GC-FID, SRI 8610C) equipped with a Tenax TA trap sampled at a rate of 0.14 L min⁻¹ for 3 min. SO₂ and O₃ were measured by SO₂ analyzer (Model 43i, Thermo Scientific) and O₃ analyzer (Model 49i, Thermo Scientific), respectively. Particle size distribution and volume concentration were monitored using a custom-built scanning mobility particle sizer (SMPS) with a differential mobility analyzer (TSI 3081) and a condensation particle counter (TSI 3772). Relative humidity and temperature were monitored using an RH/T transmitter (HX94C, Omega). The temperature was monitored to be 23 ± 2 °C. To maintain a positive pressure inside the chamber, a 1 L min⁻¹ dilution flow was added to balance the total sampling flow. Each experiment lasted for 4-5 h. Particle loss (including particle wall loss and dilution) in the chamber was corrected in a

size-dependent manner assuming first-order loss within each particle size bin, and the loss rate was measured at the end of each experiment. Initial conditions and results are summarized in Table 1. It is noted that no correction for semivolatile vapor wall loss was made in the chamber experiments in this study. Therefore, the absolute values for SOA yields may be underestimated (Zhang et al., 2014). However, with relatively high seed area concentrations ($1535\text{-}3309\ \mu\text{m}^2\ \text{cm}^{-3}$) and volume concentrations ($45\text{-}122\ \mu\text{m}^3\ \text{cm}^{-3}$) used in this study, effects of vapor wall loss are expected to be similar across different experiments and may not be important for relative SOA yield comparison. For example, similar SOA yields were observed when the injected seed volume concentration ranged from 47 to 82 $\mu\text{m}^3\ \text{cm}^{-3}$ for Exp. #1-3, and 59 to 71 $\mu\text{m}^3\ \text{cm}^{-3}$ for Exp. #11-13.

2.2 Flow tube experiments

To collect sufficient SOA mass for offline chemical analysis, SOA was also produced in a quartz flow tube by reacting limonene or α -pinene with ozone (~ 3 ppm) in the presence or absence of SO_2 under dry (10-13% RH) and humid (55-60% RH) conditions. The flow tube has a diameter of 10.2 cm and length of 120 cm, and the residence time in the flow tube is 4 min. Cyclohexane was used as OH scavenger. Limonene/cyclohexane (1:1500 v/v) and α -pinene/cyclohexane solution (1:500 v/v) was pre-filled in a 1 mL syringe (Hamilton) and injected into the flow tube using a syringe pump (Legato 100, KDS). Two injection ratios of limonene and SO_2 (500 ppb/250 ppb and 500 ppb/100 ppb) were used to investigate the effects of SO_2 on SOA formation. No seed aerosol was used during SOA formation to eliminate the influence of inorganic salt on chemical analysis, particularly that of sulfate. SOA was collected onto pre-baked quartz filters for 24 h. Filters were stored at -20°C prior to analysis and extracted in 5 mL HPLC-grade methanol ($>99.9\%$, Caledon Laboratories Ltd.) by sonication for 10 min. The extract was filtered using a $0.2\ \mu\text{m}$ pore size syringe filter and prepared for composition analysis or peroxide quantification.

2.3 Chemical Characterization of SOA by ESI-IMS-TOF

Prior to chemical analysis, the SOA extract was concentrated to $0.5\text{-}1\ \text{mg}\ \text{mL}^{-1}$ under a gentle N_2 stream in an evaporator (N-EVAP, Organomation). Particle composition was analyzed using electrospray ionization-ion mobility spectrometry-high resolution time-of-flight mass spectrometry (ESI-IMS-ToF,

160 TOFWERK, hereafter referred to as IMS-TOF) with a mass spectral resolution of 3500-4000 FWHM at
m/z 250. Mass calibration was performed before each measurement with a mass accuracy within 5 ppm
of each calibration chemical. Details of the IMS-TOF technique are described in recent publications by
Krechmer et al. (2016) and Zhang et al., (2016). Briefly, SOA solution was introduced into IMS-TOF
using direct infusion with a syringe pump (Legato 100, KDS) at 1-2 $\mu\text{L min}^{-1}$. Organic compounds in the
165 SOA extract were ionized by ESI in the negative mode. Ion droplets were evaporated in a desolvation
tube and then separated in the ion drift tube based on ion mobility. The ion mobility (K) of an organic
compound is a function of its molecular structure and ion-neutral interactions with N_2 buffer gas, and is
calculated by measuring the drift time (t_d) in the IMS drift tube:

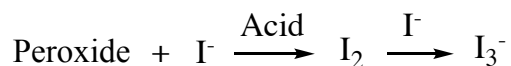
170
$$K = \frac{1}{t_d} \frac{L_d^2}{V_d}$$

where L_d is the length of the drift tube (20.5 cm) and V_d is the drift voltage (-9600 V). In all analyses, the
desolvation tube and the ion drift tube were maintained at 333 ± 2 K and atmospheric pressure (~ 1000
mbar). Generally, small and compact molecules have shorter ion drift times and higher ion mobilities than
175 large and elongated molecules. One key feature of the IMS-TOF is that collision induced dissociation
(CID) with nitrogen gas can be introduced between the ion drift tube and the time of flight region. CID
analysis allows for attributing a fragment ion to its parent ion, as they share the same ion drift time (Zhang
et al., 2016). Post-processing was performed with an Igor-based data analysis package (Tofware V2.5.7,
TOFWERK).

180 **2.4 Quantification of peroxides in SOA**

Peroxide content in SOA was quantified using an iodometric-spectrophotometric method adapted from
Docherty et al. (2005). Briefly, the iodide ion (I^-) can be oxidized by a peroxide moiety (including H_2O_2 ,
 ROOH and ROOR) to form I_2 under acidic conditions. I_2 then complexes with I^- to form I_3^- . I_3^- is an
orange-brown color complex which absorbs strongly at 470 nm.

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Peroxide content was measured for limonene SOA formed under humid conditions. Limonene SOA (LSOA) extract was concentrated to around 2 mg mL⁻¹ and added into a 96 well UV plate (160 μL/well, No. 655801, Greiner Bio-One). 20 μL Formic acid (≥98%, Sigma-Aldrich) and 20 μL 0.1 g mL⁻¹ potassium iodide (KI) solution were added to initiate reaction. KI solution was prepared by dissolving KI (≥99%, Sigma-Aldrich) into MilliQ water (18.2 MΩ·cm). The plate was sealed with a UV transparent film (EdgeBio) to eliminate contact with ambient O₂. After 1 h at room temperature, the absorbance of the solution was measured using an absorbance plate reader (SpectraMax 190, Molecular Devices) at 470 nm. The absorbance signal was calibrated using benzoyl peroxide, and converted to a mass fraction assuming a MW of 242.23 g mol⁻¹ (same as benzoyl peroxide). Background absorbance from a negative control (160 μL methanol + 20 μL formic acid + 20 μL KI) was subtracted from all reported absorbances. Each measurement was repeated at least two times.

2.5 Bulk solution SO₂ bubbling experiments

In addition to chamber and flow tube experiments, the reaction of SO₂ with peroxides was also investigated in bulk solutions. LSOA was collected from flow tube experiments mentioned previously and extracted using a methanol/H₂O (1:1) solution. The solution was divided into two and added into glass bottles. SO₂ (5.2 ppm balanced by N₂) was bubbled through one of the solutions at a flowrate of 0.02 L min⁻¹ for 2.5 h. N₂ was bubbled through the other solution in parallel for 2.5 h at the same flow rate as a negative control. The total peroxide content was measured using the iodometric-spectrophotometric method mentioned in previous section and compared between the two solutions. As a positive control, a solution of 2-Butanone peroxide (technical grade, Sigma-Aldrich) was also bubbled with SO₂ and N₂ in parallel in the same manner.

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2.6 Chamber experiments with SO₃

Experiments were also conducted to investigate the reactivity of SO₃ with organic compounds. The chamber was cleaned and filled with limonene (63 ppb) before experiment. Relative humidity in the chamber was maintained at 10-12%, which is similar to the LSOA experiments under dry conditions in Table 1 (Exp. #4-10). SO₃ was generated by blowing fuming sulfuric acid (20% free SO₃ basis, Sigma-Aldrich) into the chamber. Briefly, 0.2 mL fuming sulfuric acid was injected into a glass vessel and then blown with dry N₂ flow with a flow rate < 5 L min⁻¹. The upper limit of SO₃ injected into the chamber was estimated to be around 24 ppm.

3. Results and Discussion

3.1 SO₂ decay and limonene SOA formation under dry conditions (RH < 16%)

Reactions of SO₂ and SOA formation from limonene ozonolysis were investigated through experiments with and without SO₂. Synergistic effects were observed between LSOA formation and SO₂ oxidation, as SO₂ was consumed at the same time scales as the formation of LSOA. As shown in Fig. 1, as soon as ozone was added into the chamber prefilled with limonene and SO₂ at $t = 0$, concentrations of limonene and SO₂ began to decrease simultaneously, and particle concentration began to increase, suggesting that limonene ozonolysis produces intermediates that react with SO₂. After about 100 min, limonene concentrations were below detection limits, and both SO₂ consumption and particle formation began to slow down. In order to confirm that limonene was needed to produce the intermediates reactive towards SO₂, more limonene was added into the chamber at $t = 175$ min and both SO₂ consumption and particle formation resumed immediately. Tests have also been performed by injecting ozone in two separate batches into the chamber prefilled with limonene, as shown in Fig. S1. Similar to the experiments conducted under ozone-rich conditions (e.g. Fig. 1), synergistic effects have been observed. We therefore infer from the correlation between depletion rate of SO₂ and particle formation that similar species or processes are responsible for SO₂ reaction and LSOA formation.

When comparing SOA formation across different experiments under dry conditions (as shown in Fig. 2), we observed that aerosol formation increased with increasing initial SO₂ concentration when initial [SO₂]

< 140 ppb. At initial $[\text{SO}_2] > 140$ ppb, it appears that SO_2 has no further effect on SOA yields with initial [Limonene] ~ 30 ppb. Here we expect that the observed enhancement in total aerosol formation by SO_2 is the result of formation and condensation of sulfuric acid and/or increased SOA formation owing to increased particle acidity (Gao et al., 2004; Jang et al., 2002). Based on the measured loss of SO_2 , we calculate the maximum contribution of condensed sulfuric acid to the increased aerosol mass by assuming all of the reacted SO_2 formed particle-phase sulfuric acid as a lower limit for SOA enhancement. As shown in Table 1, we compare two experiments (Exp. #1 and #7) in which similar amounts of limonene was consumed in the presence of 139 ppb of SO_2 (Exp. #7) and in the absence of SO_2 (Exp. #1). In Exp. #7, we observed a 5.7 ppb decay in SO_2 concentration, which would add a maximum of $14.7 \mu\text{m}^3 \text{cm}^{-3}$ to the particle volume concentration, assuming a density of 1.58 g cm^{-3} for an aqueous sulfuric acid solution under 10% RH (Heym, 1981). This amount of sulfuric acid can only account for 68% of the difference in particle volume between Exp. #7 and #1. There is still 32% of the enhancement of particle volume concentration that cannot be fully explained by introducing sulfate into the particle phase. Based on previous work demonstrating that acid catalysis by sulfuric acid increases SOA yields, we expect that SOA yields were enhanced as a result of increased particle acidity from condensation of sulfuric acid (Czoschke et al., 2003; Surratt et al., 2007).

3.2 SO_2 decay and limonene SOA formation under humid conditions (RH ~ 47 -55%)

SO_2 reaction and SOA formation were also examined under humid conditions. As shown in Table 1 and Fig. 3A, an increase in particle volume concentration was also observed in the presence of SO_2 under humid conditions. However, the enhancements of particle volume concentration were smaller compared to those experiments conducted under dry conditions with similar initial conditions (e.g. Exp. #8 vs. Exp. #14, and Exp. #10 vs. Exp. #15). One of the possible reasons is that the formation of high-MW organic compounds and organosulfate is favored under high acidity conditions. The liquid water content in the particle phase under humid conditions is suggested to be higher than that under dry conditions as demonstrated in Section 2.1. Increased liquid water content reduces particle acidity through dilution and leads to decreased SOA enhancement. In addition, in all humid experiments, a diffusion dryer was used

265 before the SMPS particle sampling inlet to remove water and eliminate the influence of condensed water
on particle volume concentration measurement. However, this may in turn lead to evaporation of
semivolatile species, resulting in the smaller changes in the particle volume concentration. The loss of
reactive intermediate onto the chamber walls may also play a role. We expect that the wall loss of reactive
intermediates may be higher under humid conditions than under dry conditions (Loza et al., 2010). It
270 should also be noted that in all the experiments, particle volume concentration instead of mass
concentration was measured. Particle density may increase as its composition changes, leading to apparent
changes in SOA yields.

On the other hand, greater SO₂ consumption was observed under humid conditions. For example, with an
275 initial SO₂ concentration of 141 ppb, only 6 ppb of SO₂ was consumed under dry conditions (Exp. #8,
Table 1 and Fig. 3B). Meanwhile, under humid conditions, the decay in SO₂ concentration was 15 ppb
with a similar set of initial conditions (Exp. #14, Table 1 and Fig. 3B). The difference in amounts of SO₂
reacted and SOA yield enhancements between dry and humid conditions suggest that the mechanisms of
the organic-SO₂ interactions are different between the two regimes. To identify these mechanisms, we
280 conducted further experiments in which the experimental conditions were systematically varied to probe
specific mechanisms.

3.3 Mechanisms of SO₂ reaction

3.3.1 Under dry conditions: Interaction between SO₂ and Criegee intermediates

Stabilized Criegee intermediates generated from alkene ozonolysis have been proposed to be important
285 oxidants of SO₂ in the atmosphere (Mauldin III et al., 2012; Vereecken et al., 2012; Huang et al., 2015).
The rates of bimolecular sCI reactions depend strongly on molecular structure. The reaction of CH₂OO
with water and water dimer is rapid, with rate constants of $<1.5 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ and $6.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
(Chao et al., 2015), respectively, and is likely the dominant sink of CH₂OO under almost all humidity
conditions. However, Huang et al. demonstrated that (CH₃)₂COO, a di-substituted Criegee Intermediate
290 has lower reaction rate constants with water and water dimer ($<1.5 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ and $<1.3 \times 10^{-13} \text{ cm}^3$
 s^{-1}), suggesting that the reaction of a di-substituted sCI with SO₂ can be competitive with the water

reactions at atmospherically relevant RH. Since di-substituted sCIs can be produced from O₃ addition to either the endocyclic or exocyclic double bonds of limonene that yield sCI-1 and sCI-2, respectively (Scheme 1), we hypothesize that sCIs from limonene ozonolysis are responsible for the observed SO₂ decay under dry conditions.

To examine the contribution of sCI + SO₂ to the observed SO₂ consumption, formic acid was added as a sCI scavenger for both dry and humid experiments (Exp. #18-20). The initial concentration of formic acid added in these experiments was ~13 ppm. Based on the previously measured rate constant for reaction between sCIs from monoterpenes and formic acid (about 3 times higher than that of sCIs + SO₂) (Sipilä et al., 2014), we expect that at these formic acid concentrations, sCI + SO₂ reactions are minimized. As shown in Table 1 and Fig. S2 (see Supporting Information), much smaller SO₂ consumption was observed in the presence of 13 ppm of formic acid under dry conditions (Exp. #9 vs. Exp. #18, Table 1, Fig. S2A and S2B). This observation indicates without formic acid, the reaction with sCIs from monoterpene ozonolysis is a significant sink of SO₂. Results shown here are consistent with the observations from Sipilä et al. who demonstrated the importance of sCI + SO₂ reactions through measuring the production of sulfuric acid (Sipilä et al., 2014). Therefore, in the presence of SO₂, limonene ozonolysis can produce sCIs that can directly oxidize SO₂ to sulfuric acid, which may then proceed to enhance aerosol acidity and SOA formation, as discussed in Section 3.1.

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3.3.2 Under humid conditions: Interaction between SO₂ and peroxides

On the other hand, under more humid conditions (RH~50%), SO₂ consumption did not decrease even in the presence of a large excess of formic acid (Exp. #18 vs. Exp. #19, Table 1, Fig. S2B and S2C), suggesting that, unlike sCIs from smaller precursors (e.g. dimethyl substituted sCIs (Huang et al., 2015a)), sCIs from monoterpenes is not an important sink for SO₂ under humid conditions. The SO₂ consumption remains significant and is even greater than under dry conditions, pointing to a yet unidentified sink of SO₂ that involves other reactive intermediates from monoterpene ozonolysis.

Here we propose that organic peroxides and/or hydrogen peroxide contribute significantly to the observed
320 consumption of SO₂. To test this hypothesis, the total peroxide content in SOA produced in the presence
or absence of SO₂ was measured using the iodometric-spectrophotometric method mentioned previously
(Section 2.4). Shown in Fig. 4, the mass fraction of total peroxides in LSOA is (48 ± 6) % in the absence
of SO₂. When SO₂ is present during SOA formation (SO₂ : limonene = 250 ppb : 500 ppb), the peroxide
fraction decreases to (13 ± 1) %. To further confirm this interaction, bulk experiments were conducted
325 by bubbling SO₂ into a solution of LSOA extract. Shown in Fig. S3 (left panel), the peroxide fraction
decreased significantly after SO₂ was bubbled through the LSOA solution, when compared to the negative
control experiment using N₂ bubbling to account for potential evaporation and/or decomposition at room
temperature. As a positive control, experiments were conducted by bubbling SO₂ through a solution of 2-
butanone peroxide. Again, a significant decrease in the peroxide content was observed (Fig. S3, right
330 panel), confirming that organic peroxides are reactive towards SO₂.

Since the observed SO₂ decay is greater under humid conditions than dry conditions during the chamber
experiments and higher liquid water content is expected under humid conditions, it is likely that SO₂ first
dissolves into the aqueous particle and the reaction proceeds in the aqueous phase. It is well known that
335 the aqueous phase reaction of hydrogen peroxide is the dominant sink of SO₂ in the atmosphere (Seinfeld
and Pandis, 2006). However, to the best of the authors' knowledge, this work is the first experimental
chamber study to suggest organic peroxides from monoterpene ozonolysis in aqueous particles are
reactive towards SO₂ under atmospherically relevant RH conditions. With the iodometric-
spectrophotometric method used in this study, we cannot distinguish between different types of peroxides,
340 specifically ROOH and ROOR. Previous work has shown that ROOH are important products of
monoterpene ozonolysis and precursors to peroxyhemiacetal formation (Docherty et al., 2005; Tobias et
al., 2000) and a major component of SOA formed from low NO_x photooxidation of many VOCs,
including isoprene (Surratt et al., 2006) and n-alkanes (Schilling Fahnstock et al., 2014). SOA from
reactions between isoprene and nitrate radicals has been shown to contain significant amounts of ROOR-
345 type peroxides (Ng et al., 2008). Further work should focus on the mechanisms and kinetics of reaction
between SO₂ and different types of organic peroxides, which are ubiquitous in the atmosphere.

3.3.3 Other mechanisms of SO₂ reactions: SO₂ + ozone, SO₂ + OH

Experiments were also conducted to rule out other possible explanations for SO₂ decay. Aqueous phase
350 SO₂ has been shown to react with dissolved ozone at appreciable rates at high pH (Seinfeld and Pandis,
2006). To rule out the reaction between SO₂ + ozone, formic acid (13 ppm to minimize sCI reactions),
ammonium sulfate seed (246 μm³ cm⁻³, 4.9 × 10⁴ # cm⁻³), SO₂ (289 ppb) and ozone (485 ppb) were
injected and kept in the chamber under humid conditions (50% RH) for 6 h. Over the course of the
experiment, the change in [SO₂] was less than 1 ppb, which is within experimental uncertainty (Fig. S4A),
355 suggesting that reactions between SO₂ and ozone either in the gas or particle phase have negligible effects
on SO₂ consumption. This is likely because that ammonium sulfate seed is slightly acidic. The pH value
calculated based on the E-AIM Aerosol Thermodynamic Model for ammonium sulfate at 50% RH is ~5
(Clegg et al., 1998; Wexler and Clegg, 2002). Under this pH condition, SO₂ oxidation by ozone is slow
and less favorable in the aqueous phase. It is noted that the pH value was estimated without considering
360 the partitioning of trace gases (i.e. NH₃). Even lower pH (i.e. higher acidity) would be yielded if taking
into account this effect. In addition, unlike SO₂ oxidation in a cloud droplet, the liquid water content in
ammonium sulfate particles is limited. Therefore, little SO₂ depletion was observed. Another potential
sink of SO₂ is the gas-phase reaction with OH radicals, which may be produced from unimolecular
decomposition of the Criegee Intermediate. We conducted experiments with an initial concentration of
365 30 ppb limonene, 68 ppm cyclohexane and 300 ppb SO₂. At these concentrations, reaction rate of
cyclohexane and OH is calculated to be around 130 times higher than that of SO₂ and OH with
 $k_{\text{cyclohexane}+\text{OH}} = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003) and $k_{\text{SO}_2+\text{OH}} = 1.2 \times 10^{-12}$
 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2004). Therefore, under our experimental conditions, the role of OH
reaction is minimized. To confirm that OH reactions are not important, the concentration of cyclohexane,
370 the OH scavenger, was doubled in additional limonene ozonolysis experiments (Exp. #7-8 vs. Exp. #16-

17). No decrease of SO₂ consumption was observed ((14 ± 2) % in Exp. #7-8 vs. (15 ± 1) % in Exp. #16-17), confirming that gas phase OH radicals play a minor role in SO₂ oxidation in this study.

3.4 Organosulfate formation

375 Reactions between organic and sulfur-containing compounds are illustrated by the observed formation of organosulfates in the presence of SO₂. Previous work has shown that the bisulfate ion can react with alcohol or epoxide to form organosulfates, and organosulfate formation may be enhanced by particle acidity (Surratt et al., 2008). In this work, organosulfates present in SOA were identified using ESI-IMS-TOF through elemental formulas that are calculated from high resolution *m/z* ratios, and by matching ion drift times to either of the two most abundant sulfate fragments (HSO₄⁻ and CH₃SO₄⁻) in the mass spectra.

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Shown in Fig. 5A and 5B, eight parent ion peaks were matched to HSO₄⁻ and CH₃SO₄⁻ fragment ion peaks in LSOA. The mass-to-charge ratios of these ions are consistent with sulfate-containing elemental formulas, confirming the organosulfate moiety. In addition, the assigned organosulfate ions were further validated by identifying trends (C, CH₂, O, CH₂O and CO₂) in Kendrick mass defect plots (Walser et al., 2008), as shown in Fig. S5 and Table S1. For example, in Fig. 5C, the ion with *m/z* 297.0835 was observed to have the same IMS drift time as CH₃SO₄⁻ (drift time = 30.14 ms), indicating that *m/z* 297.0835 is an organosulfate ion. The *m/z* ratio is also consistent with the molecular formula of C₁₀H₁₇O₈S⁻, and falls within the trend lines of adding CH₂O and O groups in the Kendrick mass defect plots to other identified organosulfate parent ions (e.g. C₉H₁₅O₇S⁻ and C₁₀H₁₇O₇S⁻). These ions were present only when SO₂ was added during SOA formation.

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It should be noted that the number of organosulfate ions identified increased with increasing SO₂ concentrations. Shown in Fig. S6, we were able to identify 8 organosulfate ions when LSOA was formed in the presence of 100 ppb of SO₂, and 16 organosulfate ions when SO₂ was 250 ppb. We also observed that the total signal fraction of these organosulfate ions increased, but since no authentic standards were available for quantification, no conclusions can be drawn about the difference in organosulfate amounts between the two experiments. By comparing ESI mass spectra, we observe that when SO₂ is present, there

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is a significant decrease in signal fraction from the high-MW species (m/z 320-500) and an increase in the signal fraction from low-MW compounds (m/z 150-320). The change of MW distribution may be due to the formation of organosulfate, and/or the formation and/or the uptake of low-MW compounds. As shown in Fig. S5, all the identified organosulfates are within the mass range of m/z 150-320. Although the hygroscopicity of organosulfate is not known, the sulfuric acid produced in the experiments with SO_2 may take up water and encourage uptake of small water-soluble organics, such as peroxides, epoxides and small aldehydes, also leading to the change of MW distribution in the ESI mass spectrum. Formation of low-MW compounds is also possible in the experiments with SO_2 . For example, peroxide may react with bisulfite in the particle phase instead of forming peroxyhemiacetals, that will affect MW distribution. In all experiments, the average carbon oxidation state ($\text{OSc} = 2 \text{ O/C} - \text{H/C}$) of SOA was observed to increase with SO_2 . It is noted that since the negative mode in ESI is sensitive only to acidic species, the effects of SO_2 on relative signal fractions and oxidation states observed here may only be valid for these species. It should also be noted that compared to chamber experiments, SOA formed in the flow tube may be less oxidized due to the short residence time. However, this does not affect our conclusions regarding the effects of SO_2 on the change of SOA composition. The observations of organosulfate formation and increased SOA oxidation state in the presence of SO_2 , are still valid despite the differences in residence time between the chamber and the flow tube experiments.

3.6 Potential mechanisms of SOA yield enhancement: comparison to α -Pinene

As mentioned earlier, enhanced SOA formation was observed from limonene ozonolysis in the presence of SO_2 . The relative signal fraction of high-MW products measured in the IMS-TOF was reduced compared to when SO_2 was not present, suggesting that SO_2 may reduce oligomer formation, which may decrease SOA yields. However, we also observe that the presence of SO_2 (which is then converted to sulfate via previously mentioned mechanisms) increases organosulfate formation, and the average carbon oxidation state of low-MW products also increases. Our results therefore suggest that for limonene ozonolysis, the effect of functionalization (formation of organosulfate and increase in oxidation state) exceeds that of decreased oligomerization, leading to an overall increase in SOA yields. It should be noted that previous studies have focused mostly on the effect of acidic sulfate on SOA yields, which likely

promotes both functionalization and oligomerization reactions. Here we show that while SO₂ leads to a decrease in oligomerization, but there is still an overall increase in SOA yields from limonene ozonolysis.

To further compare the effects of oligomerization and functionalization, SOA formation from α -pinene ozonolysis was examined in the presence of SO₂. The IMS-TOF mass spectra of α -pinene SOA (ApSOA) (Fig. S7) show a similar decrease in the high m/z signal fraction when SO₂ is present, suggesting that SO₂ has a similar effect of decreasing oligomerization in this system. However, unlike in limonene ozonolysis, α -pinene SOA yields did not change significantly under different SO₂ concentrations under both dry and humid conditions (Fig. 7 and Table 1). It is likely that any enhancement in SOA yield by SO₂ through functionalization is masked by reduced oligomerization. As a result, there is little overall change in SOA yields from α -pinene ozonolysis. It is likely that the difference between the two systems can be explained by the number of double bonds and the extent of functionalization. Limonene has two double bonds. If SO₂ prevents oligomerization of the first-generation products, these products can still react further with ozone to add another oxidized functional groups to form condensable products. As a comparison, α -pinene only have one double bond. The presence of SO₂ reduces oligomerization and limits enhancements in SOA yields.

Under dry conditions, SO₂ can be oxidized by sCI to SO₃, which may be reactive towards organic compounds and may change the formation mechanism of SOA. As shown in Fig. S4B, SO₃ reacted rapidly with H₂O to form sulfuric acid once injected, even at 11% RH, the lowest RH among all the experiments conducted. During the experiment, around 7 ppb (11% of initial) limonene was reacted, which can be attributed to the reactive uptake of limonene onto sulfuric acid seed. This is consistent with the experimental observation from Liggio and Li (2008) in which significant uptake of monoterpenes onto highly acidic seed was observed in chamber studies under various humidity conditions. It is noted that the SO₃ concentration was very high (estimated to be ~24 ppm) during this experiment, which can be inferred from the rapid formation of new particles ($2.8 \times 10^6 \text{ # cm}^{-3}$ and volume concentration of $1.1 \times 10^4 \text{ } \mu\text{m}^3 \text{ cm}^{-3}$), which are likely nucleated sulfuric acid particles. The concentration of SO₃ used in this test (~24 ppm) was expected to be much higher than those generated in the experiments shown in Table

1 (an estimated upper limit of 60 ppb SO₃ formation with initial limonene concentration of 30 ppb,
455 assuming that sCI yield is unity and sCI only reacts with SO₂). Therefore, it is likely that the reaction
between SO₃ and organic compounds do not play an important role in SOA formation under the
experimental conditions in this study.

4. Implications

Our combined experimental observations of SO₂ consumption and formation of LSOA and ApSOA
460 suggest that both sCI and organic peroxides formed from monoterpene ozonolysis may play crucial roles
in SO₂ oxidation under atmospherically relevant humidity levels. We propose the simplified mechanisms
shown in Scheme 2 to summarize our findings. Under dry conditions, sCI reacted with SO₂ to form SO₃
which quickly reacts with water to form sulfuric acid. In the presence of sulfuric acid in the particle phase,
SOA formation can be enhanced through acid-catalyzed reactions (Jang et al., 2002). At the same time,
465 we observed reduced oligomerization for semivolatile oxidation products relative to increased low-MW
compounds by SO₂. As more SO₂ was added, the formation of sulfuric acid was limited by the initial
monoterpene concentration, resulting in little change in particle acidity and, consequently, SOA yields.
On the other hand, under atmospherically relevant humidity conditions, most of the sCI is scavenged by
water and/or water dimer, and the sCI + SO₂ reaction is likely insignificant. However, SO₂ can partition
470 into aerosol liquid water to form HSO₃⁻, and we present evidence to suggest that HSO₃⁻ can further react
with organic peroxides produced from monoterpene ozonolysis. This mechanism is consistent with the
greater SO₂ consumption observed under humid conditions, since more aerosol water was available for
both SO₂ and peroxides to partition.

475 In order to evaluate the relative contributions of sCI and peroxides as reactive sinks for SO₂ in our
experiments, we formulate a simplified kinetic model to attribute observed SO₂ loss to each process. We
note that without detailed knowledge of the SO₂ uptake mechanisms, the heterogeneous reaction of SO₂
with condensed phase peroxide is simplified as a bimolecular reaction. This reaction may depend on many
factors, such as aerosol pH, aerosol liquid water content, and ionic strength. Nonetheless, we use this
480 simplified model to apportion the observed SO₂ loss under the experimental conditions employed in this

work to each process. In particular, we will use this model to illustrate the relative importance of the sCI reaction under the two different experimental RH. Results are shown in Fig. 8 and the details of the box model can be found in the supporting information (Section S7).

485 In this model, we calculated the relative contributions of the two pathways under two humidities (10% and 50%) and under two initial concentrations of SO₂. As our laboratory observation suggests, SO₂ consumption increases with increasing humidity (Fig. 8A and 8B). In the high SO₂ scenario (Fig. 8A, [SO₂] > [limonene]), both interactions with sCI and peroxide play important roles in SO₂ oxidation. A major fraction of SO₂ consumption can be attributed to the reaction with sCI under dry conditions. At
490 50% RH, the amount of SO₂ consumed by the sCI pathway drops slightly (from 3 to 2 ppb in this scenario). On the other hand, the relative importance of reactive uptake by peroxides become dominant at 50% RH, accounting for 87% of the total SO₂ consumption. In the low SO₂ emission scenario (Fig. 8B, [SO₂] < [limonene]), sCI does not react with SO₂ at appreciable amounts, owing to the competition from reactions with water and water dimer. Therefore, sCI chemistry does not contribute significantly to the
495 SO₂ sink, and SO₂ consumption is dominated by reactions with peroxides and other reactive intermediates. To identify when the transition from “low SO₂” to “high SO₂” occurs, simulations were performed for a range of SO₂ concentrations, shown in Fig. 8C. Based on these results, we identified that even at RH = 10%, sCI does not become an important sink of SO₂ until SO₂ exceeds 50 ppb (with 30 ppb limonene injection), and this threshold is likely greater than 500 ppb at RH = 50%. The reaction with
500 peroxides is modelled as a simplified bimolecular reaction to match the observed SO₂ decay in our experiments. Moving forward, more information about the reaction mechanism is needed to accurately model this reaction. In particular, the specific peroxide compounds that are reactive towards SO₂ need to be identified using advanced analytical techniques (Krapf et al., 2017; Reinnig et al., 2009). Also, since it is likely that the reaction is occurring in aqueous particles, the Henry’s Law constant of the peroxide
505 compounds will need to be measured. Despite these missing parameters, our simplified model highlights the importance of the reactive uptake pathway, and suggests further studies are warranted to elucidate the reaction rates and mechanisms for this reaction.

510 Currently, as a result of air quality control policies, SO₂ concentrations have significantly decreased in
many areas in the world during the past decades. For example, the annual national average SO₂
concentration has dropped to < 10 ppb in the U.S. (U.S. EPA, 2013) and 1.3 ppb in Canada (ECCC, 2016).
However, high SO₂ concentrations can still be observed, especially in some hot spots in North America
such as near oil sands operations in Northern Alberta (Hazewinkel et al., 2008), and in developing
515 countries like China where coal combustion is the main energy source. Hourly SO₂ concentrations
frequently exceed 100 ppb in some megacities in China during the winter season (Lin et al., 2011, Zhang
et al., 2015). Recent studies have shown that during heavy haze episodes, the rapid oxidation of SO₂ to
sulfate cannot be explained by known mechanisms (Guo et al., 2014; Wang et al., 2014), and while
heterogeneous reaction mechanisms have been proposed (Wang et al., 2016), these mechanisms require
relatively high pH to be plausible. Based on our experimental observations of SO₂ decay, we estimate
520 that the uptake coefficient of SO₂ on the aqueous particle through reacting with peroxides from limonene
ozonolysis is $1-5 \times 10^{-5}$ (Supporting Information, Section S8). These values are comparable to those from
heterogeneous uptake of SO₂ on mineral aerosol (Huang et al., 2015b, 2014; Adams et al., 2005; Ullerstam
et al., 2003) and sea salt (Gebel et al., 2000). It should be noted that organic peroxides are ubiquitous in
different SOA systems and can be formed from oxidation by OH (Surratt et al., 2006; Yee et al., 2012),
525 O₃ (Docherty et al., 2005) and NO₃ (Ng et al., 2008). Results from our study therefore suggest a new
pathway of SO₂ oxidation in the atmosphere, which may contribute to the missing mechanisms of high-
sulfate production in the polluted areas. Future work should investigate the role of peroxides from
different SOA systems in oxidizing SO₂ and the atmospheric importance of these reactions.

530 The importance of the reaction pathways (sCI and reactive uptake) proposed in this study imply that
oxidation of VOCs and reactions of SO₂ are tightly coupled. It is important to note that SO₂, the precursor
to sulfate, can directly influence the chemistry of SOA formation. And the oxidation of monoterpenes
provides viable pathways to act as SO₂ sinks and a source for sulfate in the atmosphere. Therefore,
oxidation of VOCs and SO₂ must be considered holistically in order to fully understand the impacts of
535 anthropogenic emissions on atmospheric chemistry.

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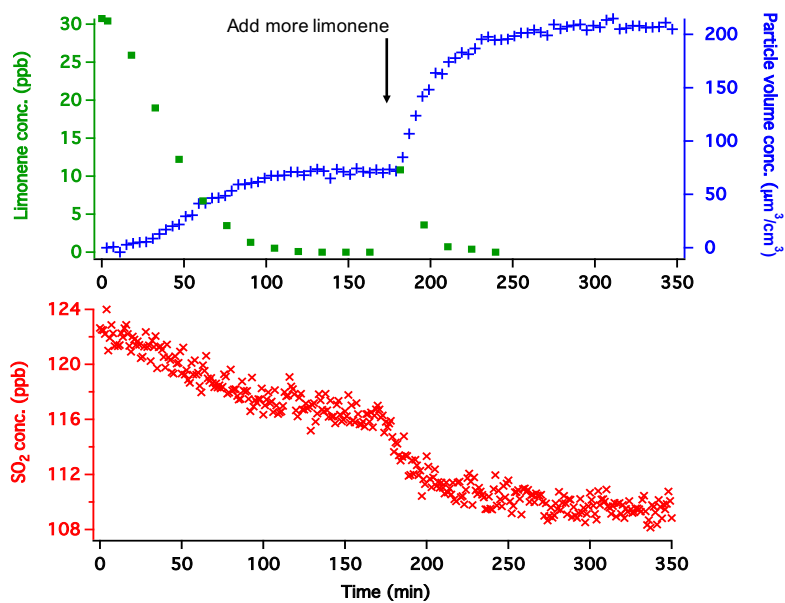
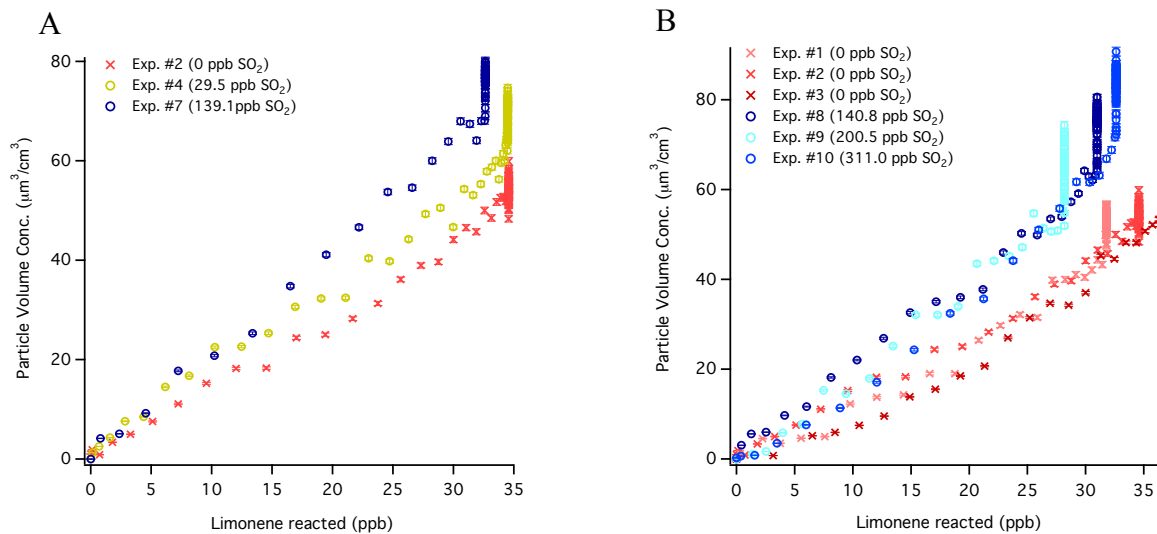


Figure 1 Particle volume concentration, limonene concentration and SO₂ concentration as a function of experimental time. After 105 min, the limonene concentration was below 1 ppb, and the particle volume concentration and SO₂ concentration began to stabilize. At $t = 170$ min, additional limonene was injected into the chamber, and particle formation and SO₂ decay resumed. The timescale of SO₂ consumption matches that of SOA formation suggesting that there are synergistic effects between LSOA formation and SO₂ oxidation.

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Figure 2 Growth of particle volume concentration as a function of limonene consumption under dry conditions. Particle concentration increased with increasing SO₂ injection concentration (0 ppb, 30 ppb and 139 ppb) under dry conditions (panel A). The enhancement reached a plateau as more SO₂ was injected (panel B).

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Table 1 Summary of conditions and results for limonene and α -pinene SOA experiments

Exp. #	HC reacted (ppb)	Initial SO ₂ conc. (ppb)	Δ SO ₂ (ppb)	HCOOH (ppm)	Seed volume conc. ^a ($\mu\text{m}^3 \text{cm}^{-3}$)	Final volume conc. ^a ($\mu\text{m}^3 \text{cm}^{-3}$)	ΔM ^b ($\mu\text{g cm}^{-3}$)	SOA yield	RH
Limonene									
1	31.8	0	0	0	67.0	121.9	71.4	39.6%	14%
2	34.6	0	0	0	82.3	137.3	71.5	36.5%	13%
3	36.5	0	0	0	46.9	110.7	82.9	40.1%	16%
4	34.5	29.5	2.7	0	59.8	132.1	94.0	48.1%	16%
5	31.1	110.3	5.2	0	46.8	116.9	91.1	51.7%	11%
6	30.4	122.2	5.9	0	65.5	136.8	92.7	53.8%	10%
7	31.0	139.1	5.7	0	89.8	166.3	99.5	56.6%	12%
8	32.6	140.8	6.1	0	42.9	119.9	100.1	54.2%	15%
9	28.2	200.5	5.5	0	122.6	193.1	91.7	57.4%	13%
10	32.6	311.0	7.3	0	68.2	151.5	108.3	58.6%	16%
11	31.5	0	0	0	68.1	115.1	61.1	34.2%	55%
12	37.3	0	0	0	59.0	118.3	77.0	36.4%	50%
13	38.4	0	0	0	70.9	125.8	71.4	32.8%	50%
14	33.7	144.3	15.5	0	57.4	110.5	69.0	36.1%	55%
15	27.8	308.8	15.2	0	78.5	130.0	67.0	42.5%	47%
16	35.0	137.4	7.4 ^c	0	56.9				16%
17	29.1	136.4	6.5 ^c	0	57.7				14%
18	34.7	251.6	2.2	13	65.0				12%
19	25.4	262.2	10.0	13	52.3				50%
20	28.3	605.4	12.4	13	117.5				52%
α-Pinene									
21	23.9	0	0	0	30.0	53.0	28.8	21.3%	14%
22	25.0	0	0	0	41.0	65.4	30.5	21.5%	14%
23	29.6	0	0	0	24.0	50.5	33.1	19.7%	12%
24	27.2	24.5	1.2	0	35.0	55.9	26.1	16.9%	13%
25	24.1	42.3	1.9	0	64.6	81.1	20.6	15.1%	10%
26	21.8	107.8	2.3	0	54.3	70.7	20.5	16.6%	12%
27	33.7	99.2	2.6	0	41.0	71.7	38.4	20.1%	12%
28	27.4	0	0	0	55.2	76.8	27.0	17.4%	49%
29	27.7	0	0	0	38.6	63.2	30.8	19.6%	48%
30	27.2	53.1	4.5	0	50.1	71.6	26.9	17.4%	46%

^a: Volume concentrations after particle wall loss correction.

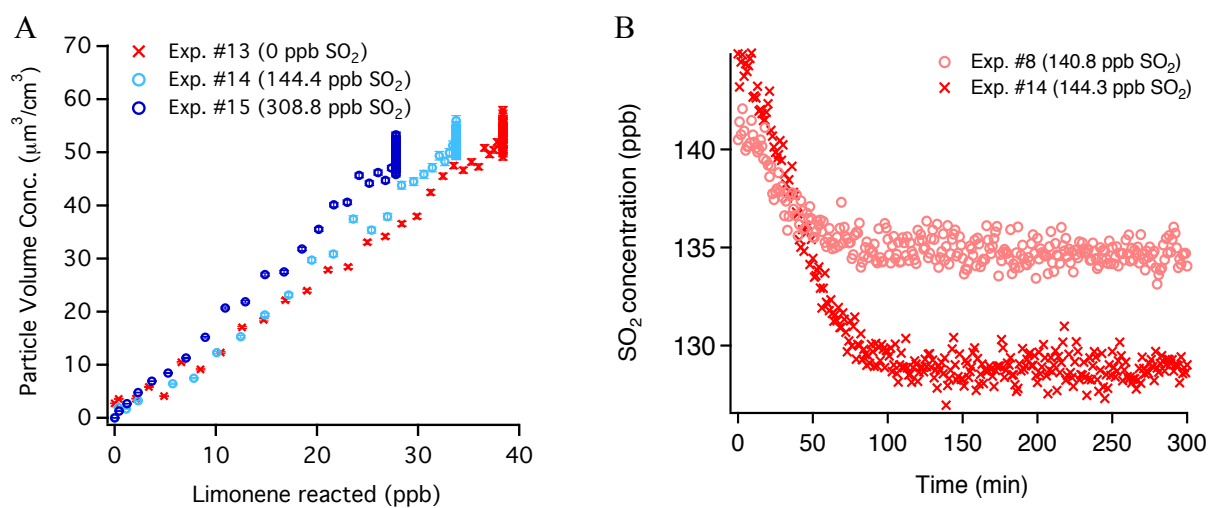
^b: Particle mass concentration formed during the experiments ($\Delta\text{M} = (\text{Final volume conc.} - \text{Seed volume conc.}) \times \rho$). A density of 1.30 and 1.25 g cm⁻³ was applied to calculate limonene and α -pinene SOA mass concentration, respectively.

^c: Twice the amount of cyclohexane was added in Exp. #16 and #17 to examine the reaction between SO₂ and OH.

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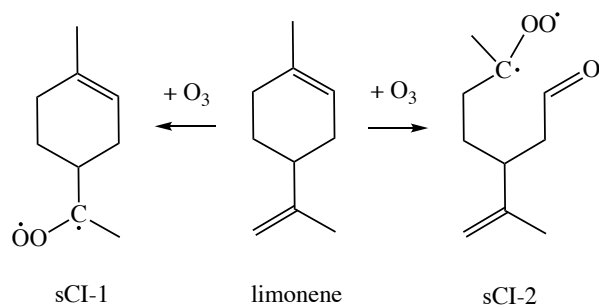
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815 **Figure 3** A) Particle volume concentration as a function of limonene reacted under humid conditions. Enhanced particle mass formation was observed with increasing SO_2 concentration. B) Greater consumption of SO_2 was observed under humid conditions than under dry conditions. By comparing Exp. #14 (humid) and Exp. #8 (dry), with similar initial SO_2 concentration, SO_2 consumption was more than two times greater under humid conditions.

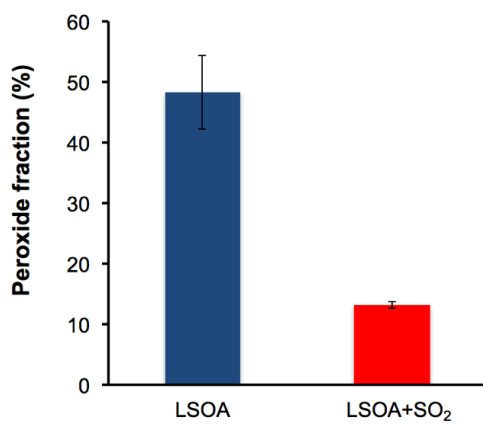
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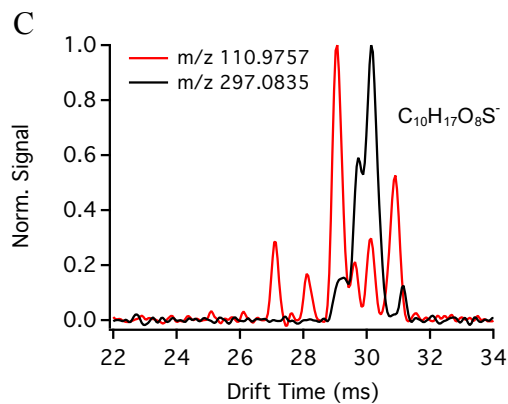
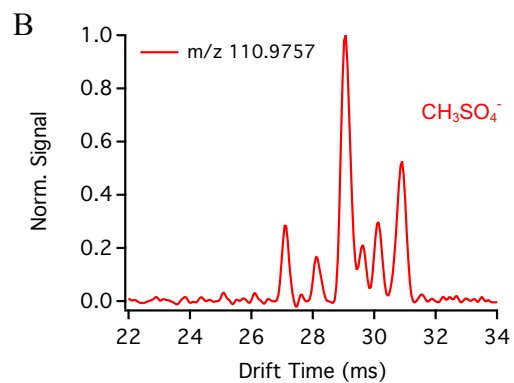
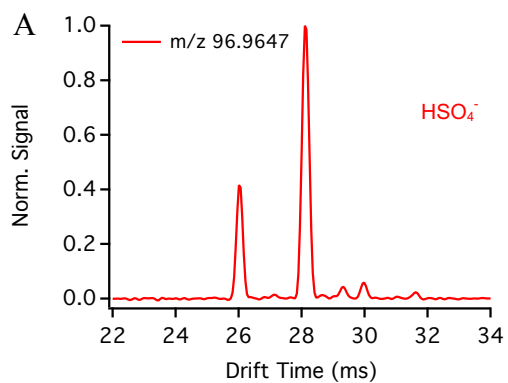
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Scheme 1 Formation of di-substituted sCI from limonene ozonolysis

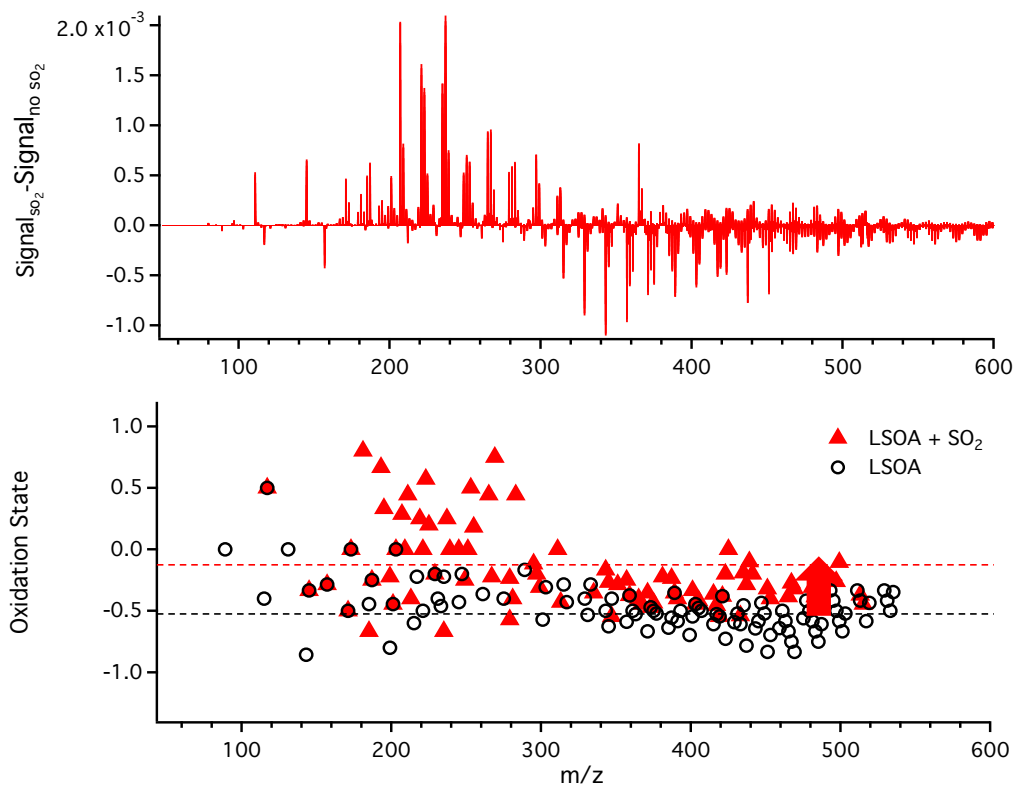
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835 **Figure 4** Mass fraction of peroxides in LSOA formed in the presence and absence of SO₂. Error bars represent measurements of three LSOA and three LSOA + SO₂ filters collected from different experiments. Peroxide measurement for each filter was repeated two times.



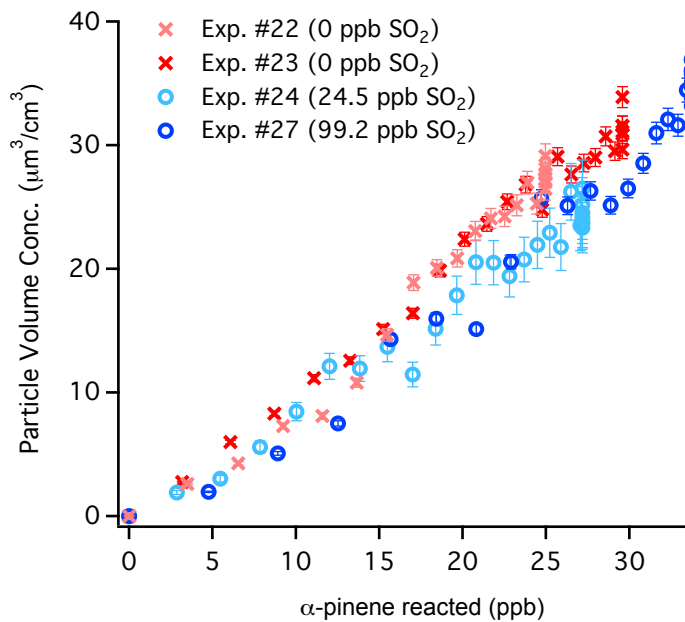
845 **Figure 5** Organosulfate identification using IMS-TOF: A) Drift time of HSO_4^- (m/z 96.9647); B) Drift time of CH_3SO_4^- (m/z 110.9757); C) Drift time of CH_3SO_4^- and m/z 297.0835 (assigned to $\text{C}_{10}\text{H}_{17}\text{O}_8\text{S}^-$). Overlapping of the drift times at 30.14 ms between the two mass-to-charge ratios indicates that the daughter ion CH_3SO_4^- is a fragment ion of the parent ion $\text{C}_{10}\text{H}_{17}\text{O}_8\text{S}^-$.



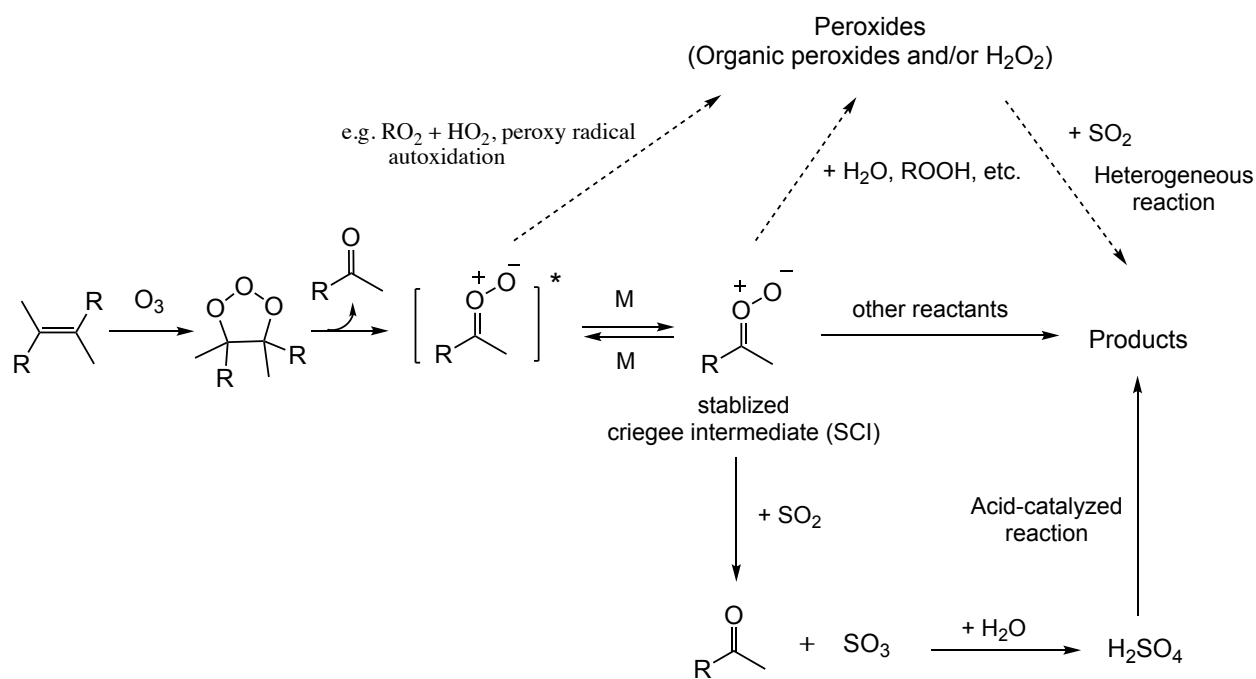
850 **Figure 6** Difference of normalized mass spectra between LSOA in the presence and absence of SO_2 (top panel). Signal of HSO_4^- (m/z 96.96) was excluded such that only organic mass spectra are compared. Bottom panel shows the average carbon oxidation state of each peak detected in IMS-TOF and the overall average carbon oxidation states of LSOA (black dashed line) and LSOA + SO_2 (red dashed line).

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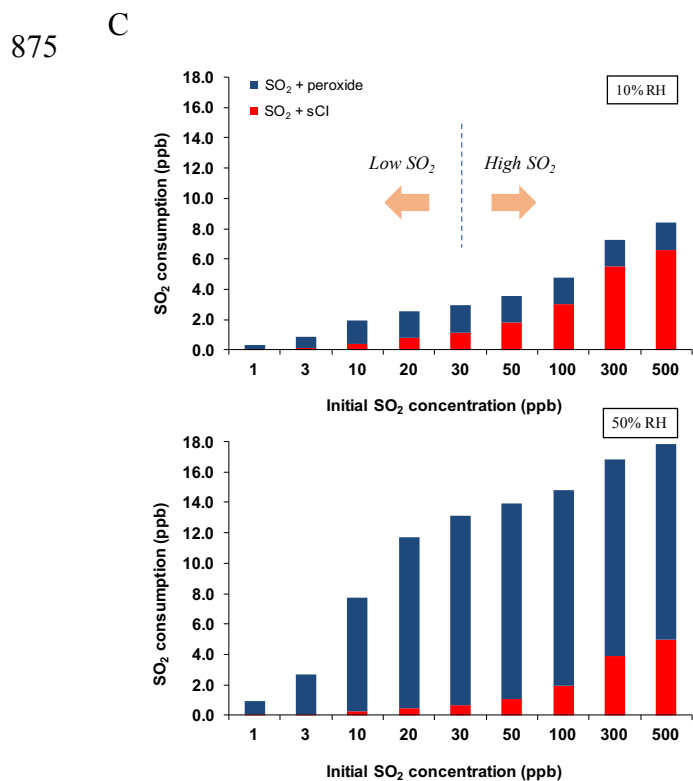
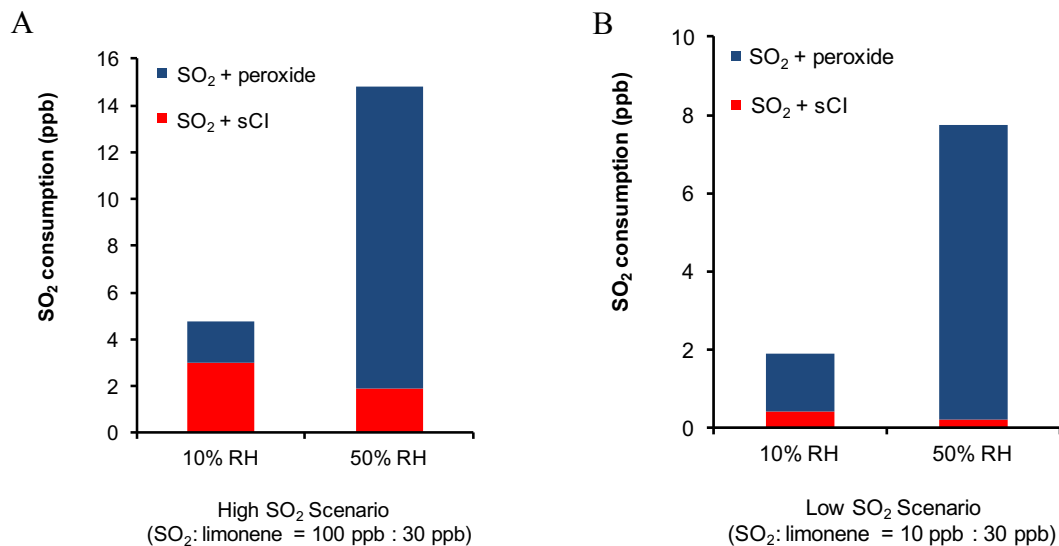
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865 **Figure 7** Growth of particle volume concentration as a function of reacted α -pinene under dry conditions. No significant change of SOA formation was observed.



870 **Scheme 2** The proposed reaction mechanisms for SO₂ and reactive intermediates in monoterpene ozonolysis.



880 **Figure 8** SO₂ consumption through reactions with sCl and peroxide under different humidity conditions in a high SO₂ scenario (100 ppb, panel A) and a low SO₂ scenario (10 ppb, panel B). And SO₂ consumption as a function of initial SO₂ concentration under different humidity conditions (panel C).

Response to Reviewer 1's comments:

We thank the reviewer for the comments. Below are our responses to the comments and corresponding
885 modifications to the manuscript.

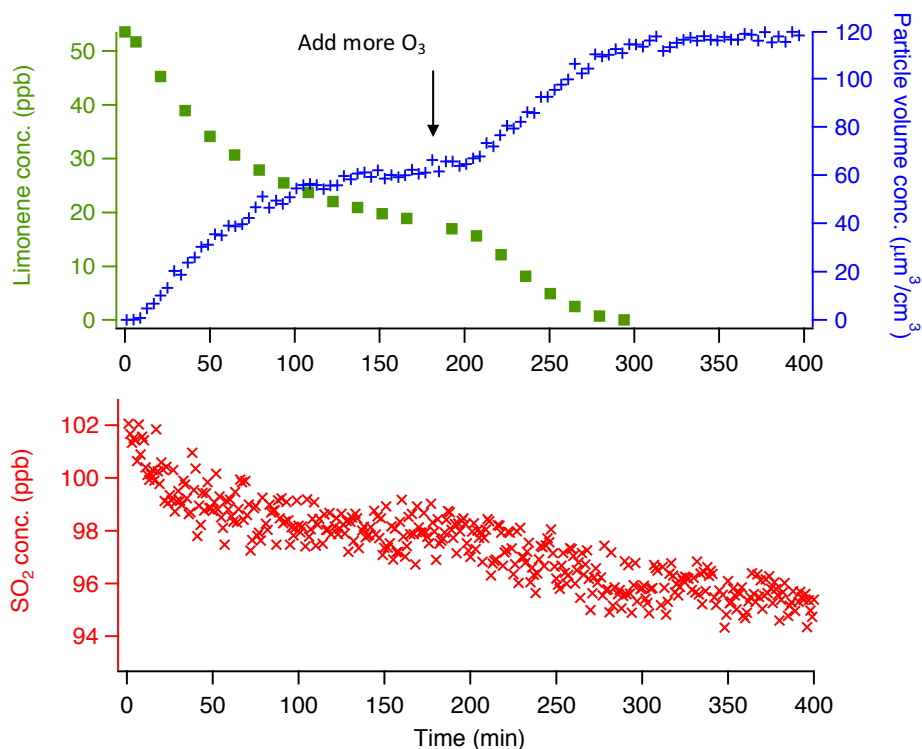
1. Experiments were made in presence of excess ozone to ensure the complete consumption of the terpenes. Have you performed tests experiments where this was not the case? Would expect any difference in the chemical regimes to SO₂ oxidation at lower ozone concentration? For instance, due to reduced
890 peroxy-functions productions, concomitant presence of unsaturations, etc:

Yes, we have performed chamber experiments with limited ozone injection, as shown in Fig. R1. Ozone was injected into the chamber that was prefilled with limonene until it reached ~ 50 ppb. Additional ozone was added at 180 min. As can be observed from the figure, SO₂ consumption coincides with limonene depletion and particle growth, further confirming the interactions between SO₂ and limonene oxidation
895 products. Comparing this result (e.g. the result of the 1st ozone injection) to the experiment conducted under ozone-rich conditions with similar SO₂ injection (Exp. #5, Table 1), lower SOA yield (41% vs. 52%) and smaller SO₂ consumption (4.0 ppb vs. 5.2 ppb) were observed, consistent with the results from other studies (Chen and Hopke, 2010; Leungsakul et al., 2005; Youssefi and Waring, 2014). This is likely
900 due to the incomplete oxidation of the two double bonds of limonene or high volatility of second-generation reactions under ozone-limited conditions. We have not examined the detailed chemical changes of SOA products between these two scenarios (ozone-rich vs. ozone-limit). However, based on our observations regarding SOA yields and SO₂ consumption, as also mentioned by the reviewer, reduced formation of Criegee intermediates and peroxides is expected, which may weaken the effect of SO₂ on limonene SOA formation. Unsaturated compounds may also be present when limited ozone was injected
905 (Maksymiuk et al., 2009).

The following content has been added and highlighted in the manuscript (Section 3.1):

“...Tests have also been performed by injecting ozone in two separate batches into the chamber prefilled

910 with limonene, as shown in Fig. S1. Similar to the experiments conducted under ozone-rich conditions (e.g. Fig. 1), synergistic effects have been observed. We therefore infer from the correlation between depletion rate of SO₂ and particle formation that similar species or processes are responsible for SO₂ reaction and LSOA formation.”



915

Figure R1 Particle volume concentration, limonene concentration and SO₂ concentration as a function of experimental time with stepwise ozone injection. Ozone was injected into the chamber that was prefilled with limonene until it reached around 50 ppb. Additional ozone was added at 180 min.

920

2. Maybe you could add in the experimental section 2.2, the ozone levels used in the flow tube experiments with, maybe, some indications how this compares to the chamber ones?

Thanks for the comments. The ozone concentration used in the flow tube experiments was around 3 ppm (in the absence of monoterpenes) as mentioned in Section 2.2. The inlet concentration of ozone was 6

925 times higher than those of monoterpenes. This concentration was chosen to achieve the greatest extent of

oxidation in the flow tube. Based on literature rate constants, the lifetimes of α -pinene and limonene were calculated to be around 3 min and 2 min at these ozone concentrations, respectively. The residence time of chemical species in the flow tube reactor was 4 min.

930 Compared to chamber experiments, the flow residence time in the flow tube reactor is shorter, which may lead to less-oxidized SOA formation in the flow tube. However, this does not affect our conclusions regarding the effects of SO₂ on the change of SOA composition. The observations of organosulfate formation and increased SOA oxidation state in the presence of SO₂, are still valid despite the difference between the chamber and the flow tube.

935

The following content has been added into Section 3.4 of the manuscript:

“...It should also be noted that compared to chamber experiments, SOA formed in the flow tube may be less oxidized due to the short residence time. However, this does not affect our conclusions regarding the effects of SO₂ on the change of SOA composition. The observations of organosulfate formation and increased SOA oxidation state in the presence of SO₂, are still valid despite the differences in residence time between the chamber and the flow tube experiments.”

940

3. You are making clear that limonene is needed to induce a SO₂ loss (line 225), but does this fully exclude that loss of SO₂ is not firstly physically driven by solubilization into the nascent aerosols? (Adding limonene would also affect such an equilibrium due to the growth rate of the particles).

945

Dissolution of SO₂ into the particles is governed by Henry's law. We calculated the dissolved SO₂ in two scenarios (acidic and neutral). pH = 5 is used for the calculation in acidic scenario because the pH for pure ammonium sulfate particle was estimated to be ~5 according to E-AIM Aerosol Thermodynamics

950 Model (Model II, Clegg et al., 1998).

The effective SO₂ Henry's law constants $H_{s(IV)}^*$ under these two scenarios were taken to be $1 \times 10^3 \text{ M atm}^{-1}$ (pH = 5) and $2 \times 10^5 \text{ M atm}^{-1}$ (pH = 7), respectively (Seinfeld and Pandis, 2006). Assuming an

initial SO₂ concentration of 600 ppb (the maximum SO₂ concentration used in this study), the concentrations of dissolved sulfur [S(IV)] in the aqueous phase can be calculated as 0.60 mM (pH = 5) and 120 mM (pH = 7). Assuming that the entire particle is aqueous, the aqueous mass concentration would be ~100 µg/m³, and dissolution of SO₂ would only result in a decrease of 1.5×10^{-3} ppb (pH = 5) and 0.3 ppb (pH = 7) gaseous SO₂, which is at least one order of magnitude less than observed. Therefore, we conclude that the loss of SO₂ into particle phase solely due to dissolution is negligible.

960

4. The paragraph starting at line 230 is slightly confusing to me. How do you conclude/affect to the growth effect to sulfuric acid? How would that acid be produced efficiently in your system? OH reaction can be excluded due to the presence of an OH scavenger and ozone reacts quite slowly under acidic conditions. Would all this just be linked to sCI chemistry? Maybe adding a few words of explanation would be helpful.

965

The formation of sulfuric acid was predicted based on the chemical mass balance. By assuming that all the loss of SO₂ leads to the formation of sulfuric acid, we can estimate the upper limit of sulfuric acid that was formed in the condensed phase in our experiments.

970 Oxidation of SO₂ by Criegee intermediates from monoterpene ozonolysis leads to efficient production of sulfuric acid (Sipilä et al., 2014). However, it is also observed in this study that SO₂ can be oxidized by organic peroxides in the particle phase, which may also contribute to the formation of sulfuric acid especially under humid conditions. The relative contributions of each pathway under dry and humid conditions are shown in Fig. 8A and 8B.

975

5. Humidity seems to reduce the SOA enhancement, as measured in the chamber. But what about the products distribution is humidity reducing the amount of organosulfate being produced? Also, as noted, an increased humidity leads to an increased particle phase pH and hence an increased reactivity of ozone toward SO₂ leading to sulfate production that may explain partly the observed enhanced SO₂ loss under humid conditions. Would that be a sign of a competition between ozone reactivity and peroxy-type chemistry leading to organosulfate production, as this exist for cloud processing of SO₂ (which is strongly

980

pH dependent)?

Thanks for the comments. The role of humidity in organosulfate formation can be complicated. On one hand, increased humidity reduces acidity in the particle phase. However, particle acidity was found to promote the formation of organosulfates. Surratt et al. (2008) demonstrated that sulfate formation (including inorganic sulfate and organosulfates) in isoprene and monoterpene oxidation system increased with increasing seed particle acidity. Chan et al. (2011) observed that the abundances of organosulfates from β -caryophyllene photooxidation correlates strongly with aerosol acidity. On the other hand, increased humidity enhances the interactions between SO_2 and organic peroxides as shown in this study. Conclusion cannot be drawn without detailed mechanism studies whether organosulfate can be formed through SO_2 /peroxide reactions. However, study is currently conducted in this group to examine the interactions between organic peroxide and SO_2 .

With regards to the effect of ozone, we have conducted control experiment by adding SO_2 , ozone, formic acid and ammonium sulfate into the chamber, as shown in Fig. S4A in the Supporting Information. No significant decrease of SO_2 was observed, indicating that dissolved ozone in the aqueous phase is not an important sink of SO_2 in this study. This is likely because that ammonium sulfate seed is slightly acidic (pH \sim 5, based on the calculation from E-AIM Aerosol Thermodynamic Model) that is less favorable for SO_2 oxidation by ozone in the aqueous phase. In addition, unlike SO_2 oxidation in a cloud droplet, the liquid water content in ammonium sulfate particles is limited. Therefore, little SO_2 depletion was observed. However, we agree with the reviewer that competition exists between SO_2 /ozone reaction and SO_2 /peroxide chemistry under high pH conditions and during cloud processing.

6. Line 76: please add the reference for the statement: “The reaction rate of particle phase $\text{SO}_2 + \text{RO}_2$ ”

Line 88: add also the reference to: Passananti, M.; Kong, L. D.; Shang, J.; Dupart, Y.; Perrier, S.; Chen, J. M.; Donaldson, D. J.; George, C. Organosulfate Formation through the Heterogeneous Reaction of Sulfur Dioxide with Unsaturated Fatty Acids and Long-Chain Alkenes. *Angewandte Chemie-International Edition* 2016, 55 (35), 10336-10339.

Thanks for the comments. The references were added into the manuscript.

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Youssefi, S. and Waring, M. S.: Transient secondary organic aerosol formation from limonene ozonolysis in indoor environments: Impacts of air exchange rates and initial concentration ratios, *Environ. Sci. Technol.*, 48(14), 7899–7908, doi:10.1021/es5009906, 2014.

045 **Response to Reviewer 2's comments:**

We thank the reviewer for the comments. Below are our responses to the comments and corresponding modifications to the manuscript.

050 1. OS vs. inorganic sulfate. OS and oligomers analyses are not quantitative, it is not easy to rely on their peak identifications to explain the difference in yields under wet and dry conditions.

We agree with the reviewer that the organosulfate and oligomer analyses based on the ESI mass spectra may not be quantitative. As mentioned in the manuscript, the negative mode in ESI is sensitive only to acidic species. Therefore, the effects of SO₂ on relative signal fractions and oxidation states observed in
055 this work may only be valid for these species. Though we observed increased total signal fraction of organosulfate ions with increased SO₂ concentration, since no authentic standards were available for quantification, no conclusions can be drawn about the difference in organosulfate amounts between the two experiments.

060 However, our qualitative analyses by linking the ion drift time and the Kendrick mass defect to the molecular formula of each peak in the ESI spectra highlights the formation of organosulfates. And the number of the organosulfates that were identified increased with increasing SO₂ injection.

2. Aerosol acidity has been used heavily to explain the results. Need better, at least, semi-quantitative
065 discussions, on aerosol acidity. Dissociation of H₂SO₄ under dry condition and influence of organics/SOAs on DRH of AS need to be discussed.

For aerosol acidity, please refer to the response to Comment 4 and Comment 7.

With regards to the influence of α -pinene and limonene SOA on the hygroscopicity of ammonium sulfate
070 particles, Takahama et al. (2007) observed that SOA from α -pinene and limonene ozonolysis has negligible effect on the efflorescence transitions of ammonium sulfate particles. Smith et al. (2011) demonstrated that both the deliquescence and efflorescence of ammonium sulfate were minimally

affected by SOA from α -pinene ozonolysis.

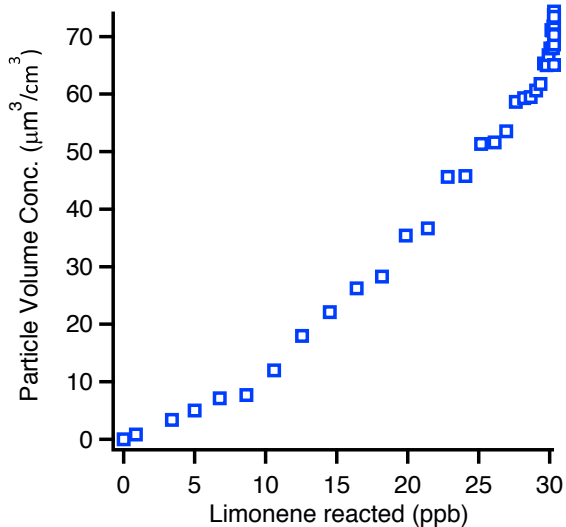
075 As discussed in Section 2.1 in the manuscript, under dry conditions, ammonium sulfate particles were generated from atomizer, followed by drying with silica gel diffusion dryers. The RH used in the experiments under dry conditions (~10%) were below the efflorescence relative humidity of ammonium sulfate. Therefore, we expect that particles remain in a solid phase with limited water content present. However, under humid conditions (~50%), no diffusion dryer was used before injecting ammonium
080 sulfate particles, suggesting that those particles are in a liquid form with higher liquid water content compared to those seeds under dry conditions.

3. Line 230

For all the experiments in Figure 2, when all the limonene was consumed, the particle volume
085 concentration seemed kept increasing, i.e., Exp.#7, dark blue markers vertically stacked at 30 ppb limonene. Does that mean that particle volume concentration kept increasing after limonene was completely consumed? This is inconsistent with Figure 1 that when all the limonene was consumed, the particle volume concentration reached a plateau.

Thanks for the comment. The particle volume concentration continued to increase even when the majority
090 of limonene was consumed. Fig. 1R plots the formation of particles as a function of limonene consumption shown in Fig. 1 (during the first limonene injection). Increased particle formation was observed even when the consumption of limonene was close to completion. This continued increase of particle mass concentration was also observed in studies by Ng et al. (2006) and Zhang et al. (2006) and was attributed to the multi-generation (first- and second-generation) oxidation and significantly slower
095 (rate-limiting) oxidation of the exocyclic double bond in limonene. However, it should be noted that both the first- and the second-generation reactions took place over the course of the experiment. The second-generation reaction of limonene SOA did not solely exist after limonene was completely consumed (i.e. after 30 ppb shown in Fig. 1R). The enhancement of particle volume concentration after the complete consumption of limonene varied slightly from experiment to experiment due to factors such as chamber
100 mixing, and/or particle wall loss correction and/or varied experimental conditions. However, this

difference could be minimized by calculating the overall SOA yields. As shown in Table 1, the overall SOA yields increased with increasing SO₂ concentrations.



105

Figure R1 The relationship between particle volume concentration and limonene consumption shown in Fig. 1 (for the first limonene injection only). Increased particle volume concentration was observed even when limonene was completely consumed.

110 4. Line 235 & Line 245

The authors attribute the increased SOA formation to increased particle acidity.

Experiments #1 - #10 were performed at RH below 16 %, where the particles might have less water. I'm not sure particle acidity is increased as it is a reflection of hydrogen activity, where aerosol water is needed. See comments earlier.

115 Enhanced SOA formation have been observed in the presence of acidic seeds under dry conditions (RH <= 20%) (Czoschke et al., 2003; Czoschke and Jang, 2006; Jang et al., 2002; Northcross and Jang, 2007). SOA yields from monoterpene ozonolysis were found to increase with increasing particle acidity.

We agree with the reviewer that under dry conditions, the particles might have less water. However, it should be noted that sulfuric acid is highly hygroscopic and it takes up water even at very low RH (Biskos

et al., 2009; Seinfeld and Pandis, 2006). Condensation of sulfuric acid increases the liquid water content in the particle phase. This amount of water helps the dissociation of sulfuric acid and increases hydrogen ion activity in the particle phase, which enables acid-catalyzed reactions. Under humid conditions, though increased liquid water content may potentially increase the dissociation of sulfuric acid, it may also dilute the molarity of hydrogen ion in the particle phase. As for the hydrogen ion activity and the pH value under dry conditions, please refer to Comment 7 for detailed discussion.

5. Line 270

SO₂ can dissolve into the aqueous droplets, what is its contribution to the measured SO₂ gas consumption?

130 Dissolution of SO₂ into the particles is governed by Henry's law. We calculated the dissolved SO₂ in two scenarios (acidic and neutral). pH = 5 is used for the calculation in acidic scenario because the pH for pure ammonium sulfate particle was estimated to be ~5 according to E-AIM Aerosol Thermodynamics Model (Model II, Clegg et al., 1998).

135 The effective SO₂ Henry's law constants $H_{S(IV)}^*$ under these two scenarios are taken to be $1 \times 10^3 \text{ M atm}^{-1}$ (pH = 5) and $2 \times 10^5 \text{ M atm}^{-1}$ (pH = 7), respectively (Seinfeld and Pandis, 2006). Assuming an initial SO₂ concentration of 600 ppb (the maximum SO₂ concentration used in this study), the concentrations of dissolved sulfur [S(IV)] in the aqueous phase can be calculated as 0.60 mM (pH = 5) and 120 mM (pH = 7). Assuming that the entire particle is aqueous, the aqueous mass concentration would be ~100 $\mu\text{g}/\text{m}^3$,
140 and dissolution of SO₂ would only result in a decrease of 1.5×10^{-3} ppb (pH = 5) and 0.3 ppb (pH = 7) gaseous SO₂, which is at least one order of magnitude less than observed. Therefore, we conclude that the loss of SO₂ into particle phase solely due to dissolution is negligible.

6. I understand the authors conducted flow tube experiments in order to collect more products for analysis.

145 But I'm not sure the flow tube experiments are exactly comparable to the chamber ones. The key issue is that OH scavenger is not added in the flow tube experiments. It is more efficient in producing peroxides in OH system than in O₃ system due to the RO₂ + HO₂ reactions. Therefore, the bulk experiments using the LSOA extracts without scavenger will bias the absorption of SO₂ high compared with the real chamber

SOA material where OH scavenger is present.

150 Thanks for the comment. OH scavenger was used in all the experiments, both in the flow tube and the chamber experiments. Therefore, the effect of OH on SOA formation in the flow tube was minimal. We apologize for not mentioning it clearly in the manuscript.

We have added the following content into Section 2.2:

155

“To collect sufficient SOA mass for offline chemical analysis, SOA was also produced in a quartz flow tube by reacting limonene or α -pinene with ozone (~ 3 ppm) in the presence or absence of SO_2 under dry (10-13% RH) and humid (55-60% RH) conditions. The flow tube has a diameter of 10.2 cm and length of 120 cm, and the residence time in the flow tube is 4 min. Cyclohexane was used as OH scavenger.

160 Limonene/cyclohexane (1:1500 v/v) and α -pinene/cyclohexane solution (1:500 v/v) was prefilled in a 1mL syringe (Hamilton) and injected into the flow tube using a syringe pump (Legato 100, KDS).”

7. Line 300

165 Even H_2SO_4 can be formed, I'm not sure in terms of the fate of “Sulfur”, which is formed more significantly H_2SO_4 and OS? This is related to the mechanism/yield of SOA formation under dry condition. The authors stated aerosol acidity increased SOA yield but what is the acidity of aerosols in dry condition? And the authors did observe quite some OS molecules, will this be the major reason for increased SOA yield? Please clarify.

170 Thanks for the comments. In this study, the formation of both sulfuric acid and organosulfates were observed, as displayed in the ESI spectra in Fig. S5 and the peak assignments of sulfur-containing ions in Table S1. For example, m/z 96.96 (HSO_4^-) and m/z 194.93 ($\text{H}_2\text{SO}_4 \cdot \text{HSO}_4^-$) show the evidence of the formation of sulfuric acid. This observation is consistent with the results from Sipilä et al. (2014) who also observed efficient sulfuric acid formation from monoterpene ozonolysis with SO_2 .

175 With regards to the contribution of organosulfates to SOA mass, Iinuma et al. (2007) demonstrated that organosulfates produced from limonene ozonolysis under acidic conditions contribute at least as much as

the first- and second-generation oxidation products to SOA mass. However, to what extent organosulfates contribute to the total particle-phase sulfur and SOA mass in this study is unknown without authentic standards. Further study is in progress in this group to quantify organosulfate formation using synthetic
180 standards.

In terms of aerosol acidity under dry conditions in this study, we did a simple estimation taking Exp. #6 as an example (both of SO₂ injection concentration and seed particle loading in Exp. #6 are in the middle range of all the experiments). Assuming all the consumed SO₂ resulting in sulfuric acid formation in the
185 particle phase, the formed sulfuric acid in the particle phase is calculated to be 0.24 μmol/m³. Ammonium sulfate seed concentration in Exp. #6 is 0.88 μmol/m³ with a density of 1.77 g/cm³. Based on the results from E-AIM Aerosol Thermodynamics Model (Model II; Clegg et al., 1998), the pH was then calculated using the following equations without considering the partitioning of NH₃ between the gas phase and the aqueous phase (Clegg et al., 1998):

190

$$\text{pH} = -\log [M_{H^+} \cdot \gamma_{H^+}]$$

where M_{H^+} and γ_{H^+} are the molarity and molarity-based activity coefficient of hydrogen ion in the aqueous phase, respectively.

195

Without taking the contribution of organic acids into account, the pH value was estimated to be ~1.2 at 10% RH, which is very acidic. And it is noted that if the partitioning of NH₃ is considered, the pH value will be even lower (i.e., even higher acidity).

200 8. Line 345

As the author said, aqueous reaction of SO₂ with O₃ in forming sulfate is proved to be quite efficient. What is the reason that SO₂ is not reacted efficiently with O₃ in these experiments? Any estimates for the rate constant of SO₂+O₃ in this experiment?

With regards to the effect of ozone, we have conducted control experiment by adding SO₂, ozone, formic

205 acid and ammonium sulfate into the chamber, as shown in Fig. S4A in the Supporting Information. No significant decrease of SO₂ was observed, indicating that dissolved ozone in the aqueous phase is not an important sink of SO₂ under the conditions in this study. This is likely because that ammonium sulfate seed is slightly acidic (pH ~ 5) that is less favorable for SO₂ oxidation by ozone in the aqueous phase. According to Seinfeld and Pandis (2006), the rate of SO₂ and ozone reaction in the aqueous phase at pH
210 = 4-5 is at the level of 10⁶ M⁻¹ s⁻¹. In addition, unlike SO₂ oxidation in a cloud droplet, the liquid water content in ammonium sulfate particles is limited. Therefore, little SO₂ depletion was observed.

The following content has been modified into Section 3.3.3:

215 “...suggesting that reactions between SO₂ and ozone either in the gas or particle phase have negligible effects on SO₂ consumption. This is likely because that ammonium sulfate seed is slightly acidic. The pH value calculated based on the E-AIM Aerosol Thermodynamic Model for ammonium sulfate at 50% RH is ~5 (Clegg et al., 1998; Wexler and Clegg, 2002). Under this pH condition, SO₂ oxidation by ozone is slow and less favorable in the aqueous phase. It is noted that the pH value was estimated without
220 considering the partitioning of trace gases (i.e. NH₃). Even lower pH (i.e. higher acidity) would be yielded if taking into account this effect. In addition, unlike SO₂ oxidation in a cloud droplet, the liquid water content in ammonium sulfate particles is limited. Therefore, little SO₂ depletion was observed.”

9. Line 370

225 What is the resolution of the mass spectrometers? I wonder if it can give four decimals for the detected m/z.

The resolution of the time-of-flight mass spectrometer is around 3500–4000 FWHM at m/z 250. When performing mass calibration, the accuracy of each calibrated mass and the overall calibration was constrained within 5 ppm. For example, if an ion of calculated m/z 250 is observed at m/z 250.001, the
230 mass accuracy is 4 ppm. Therefore, the mass detected by our instrument can be accurate to the third decimal place, with the fourth decimal point estimated.

This information of the mass spectral resolution and mass accuracy has been updated in the manuscript in Section 2.3:

235

“Particle composition was analyzed using electrospray ionization-ion mobility spectrometry-high resolution time-of-flight mass spectrometry (ESI-IMS-ToF, TOFWERK, hereafter referred to as IMS-ToF) with a mass spectral resolution of 3500-4000 FWHM at m/z 250. Mass calibration was performed before each measurement with a mass accuracy within 5 ppm of each calibration chemical. Details of the IMS-ToF technique are described in recent publications by Krechmer et al. (2016) and Zhang et al., (2016).”

10. Line 420

“first generation of oxidation products from alpha-pinene ozonolysis may be too volatile to condense...”

245 There are quite some studies (i.e., Ehn et al., Nature, 2014) showing that first generation of oxidation products were supposed to be HOMs, which are of extremely low vapor pressures and can condense easily. Please explain.

Thanks for the comment.

250 We have corrected the statements in the manuscript (Section 3.6):

“Limonene has two double bonds. If SO₂ prevents oligomerization of the first-generation products, these products can still react further with ozone to add another oxidized functional groups to form condensable products. As a comparison, α-pinene only have one double bond. The presence of SO₂ reduces oligomerization and limits enhancements in SOA yields.”

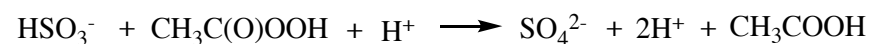
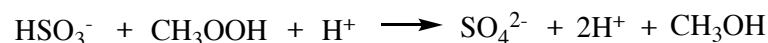
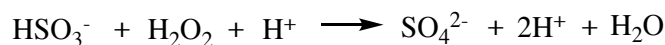
11. Line 455

“We present evidence to suggest that HSO₃⁻ can further react with organic peroxides produced from monoterpene ozonolysis” I don’t think the authors give any explanation before line 455 about reaction

260 between HSO₃⁻ with organic peroxides. The authors only show the evidence that organic peroxides

decreased when bubbling SO₂ into the solution. Please explain the reaction mechanism of HSO₃⁻ with organic peroxides.

Thanks for the comment. It is well known that dissolved SO₂ can be oxidized by peroxides (e.g., H₂O₂, methylhydroperoxide and peroxyacetic acid) to form sulfate (Lind et al., 1987), as also shown in the following equations:



The bubbling experiments conducted in this study have shown significant depletion of the total peroxide content when bubbling SO₂ into either limonene SOA extract or pure organic peroxide, suggesting that peroxides in SOA are reactive to dissolved SO₂. This is consistent with our experimental observations that greater SO₂ depletion was observed under humid conditions where more dissolved SO₂ was present. Further investigation is undertaken in this group to elucidate the mechanisms and kinetics of SO₂/peroxide reaction.

275

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