



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 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 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 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 SO_2 , 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 SO_2 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 SO_2 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
55 (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;
60 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
65 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
70 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
75 (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), indicating that this mechanism may be important for heterogeneous oxidation of aerosols, but the contribution to SO₂ sink is likely small.



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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) 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
135 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
140 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
145 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. 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
150 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

155 Prior to chemical analysis, the SOA extract was concentrated to $0.5\text{--}1\ \text{mg mL}^{-1}$ 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,
TOFWERK, hereafter referred to as IMS-TOF). 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



160 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 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:

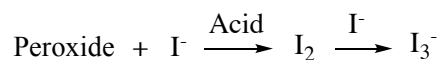
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$$K = \frac{1}{t_d} \frac{L_d^2}{V_d}$$

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
170 mbar). Generally, small and compact molecules have shorter ion drift times and higher ion mobilities than
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,
175 TOFWERK).

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
180 orange-brown color complex which absorbs strongly at 470 nm.



Peroxide content was measured for limonene SOA formed under humid conditions. Limonene SOA
185 (LSOA) extract was concentrated to around 2 mg mL^{-1} and added into a 96 well UV plate ($160 \mu\text{L/well}$,



No. 655801, Greiner Bio-One). 20 μL Formic acid ($\geq 98\%$, 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 ($\geq 99\%$, Sigma-Aldrich) into MilliQ water ($18.2 \text{ M}\Omega\cdot\text{cm}$). The plate was sealed with a UV transparent film (EdgeBio) to eliminate contact with ambient O_2 . After 1 h at room temperature, the absorbance of
190 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 $242.23 \text{ g mol}^{-1}$ (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.

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2.5 Bulk solution SO_2 bubbling experiments

In addition to chamber and flow tube experiments, the reaction of SO_2 with peroxides was also investigated in bulk solutions. LSOA was collected from flow tube experiments mentioned previously and extracted using a methanol/ H_2O (1:1) solution. The solution was divided into two and added into
200 glass bottles. SO_2 (5.2 ppm balanced by N_2) was bubbled through one of the solutions at a flowrate of 0.02 L min^{-1} for 2.5 h. N_2 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
205 with SO_2 and N_2 in parallel in the same manner.

2.6 Chamber experiments with SO_3

Experiments were also conducted to investigate the reactivity of SO_3 with organic compounds. The chamber was cleaned and filled with limonene (63 ppb) before experiment. Relative humidity in the
210 chamber was maintained at 10-12%, which is similar to the LSOA experiments under dry conditions in Table 1 (Exp. #4-10). SO_3 was generated by blowing fuming sulfuric acid (20% free SO_3 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.

215 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
220 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
225 SO₂, more limonene was added into the chamber at $t = 175$ min and both SO₂ consumption and particle formation resumed immediately. 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.

230 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 [SO₂] > 140 ppb, it appears that SO₂ has no further effect on SOA yields with initial [Limonene] ~ 30 ppb. Here we expect that the observed enhancement in total aerosol formation by SO₂ is the result of formation and condensation of sulfuric acid and/or increased SOA formation owing to
235 increased particle acidity (Gao et al., 2004; Jang et al., 2002). Based on the measured loss of SO₂, we calculate the maximum contribution of condensed sulfuric acid to the increased aerosol mass by assuming all of the reacted SO₂ 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 SO₂ (Exp. #7) and in the absence of SO₂ (Exp. #1). In Exp.
240 #7, we observed a 5.7 ppb decay in SO₂ concentration, which would add a maximum of 14.7 μm³ 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
245 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 SO₂ decay and limonene SOA formation under humid conditions (RH ~ 47-55%)

250 SO₂ 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 SO₂ 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
255 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
before the SMPS particle sampling inlet to remove water and eliminate the influence of condensed water
260 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
should also be noted that in all the experiments, particle volume concentration instead of mass



265 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 initial SO₂ concentration of 141 ppb, only 6 ppb of SO₂ was consumed under dry conditions (Exp. #8, 270 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 conducted further experiments in which the experimental conditions were systematically varied to probe 275 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 oxidants of SO₂ in the atmosphere (Mauldin III et al., 2012; Vereecken et al., 2012; Huang et al., 2015). 280 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 has lower reaction rate constants with water and water dimer ($<1.5 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ and $<1.3 \times 10^{-13} \text{ cm}^3$ 285 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.

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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. S1 (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. S1A and S1B). 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.

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. S1B and S1C), 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 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 by bubbling SO_2 into a solution of LSOA extract. Shown in Fig. S2 (left panel), the peroxide fraction
320 decreased significantly after SO_2 was bubbled through the LSOA solution, when compared to the negative control experiment using N_2 bubbling to account for potential evaporation and/or decomposition at room temperature. As a positive control, experiments were conducted by bubbling SO_2 through a solution of 2-butanone peroxide. Again, a significant decrease in the peroxide content was observed (Fig. S2, right panel), confirming that organic peroxides are reactive towards SO_2 .

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Since the observed SO_2 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 SO_2 first dissolves into the aqueous particle and the reaction proceeds in the aqueous phase. It is well known that the aqueous phase reaction of hydrogen peroxide is the dominant sink of SO_2 in the atmosphere (Seinfeld
330 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 SO_2 under atmospherically relevant RH conditions. With the iodometric-spectrophotometric method used in this study, we cannot distinguish between different types of peroxides, specifically ROOH and ROOR. Previous work has shown that ROOH are important products of
335 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-type peroxides (Ng et al., 2008). Further work should focus on the mechanisms and kinetics of reaction
340 between SO_2 and different types of organic peroxides, which are ubiquitous in the atmosphere.

3.3.3 Other mechanisms of SO_2 reactions: $\text{SO}_2 + \text{ozone}$, $\text{SO}_2 + \text{OH}$

Experiments were also conducted to rule out other possible explanations for SO_2 decay. Aqueous phase SO_2 has been shown to react with dissolved ozone at appreciable rates at $\text{pH} \geq 5$ (Seinfeld and Pandis,



345 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. S3A), suggesting that reactions between SO₂ and ozone either in the gas or particle phase have negligible effects
350 on SO₂ consumption. 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 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,
355 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, 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
360 role in SO₂ oxidation in this study.

3.4 Organosulfate formation

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
365 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.

Shown in Fig. 5A and 5B, eight parent ion peaks were matched to HSO₄⁻ and CH₃SO₄⁻ fragment ion peaks
370 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. S4 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.

380 It should be noted that the number of organosulfate ions identified increased with increasing SO₂ concentrations. Shown in Fig. S5, 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 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. S4, 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 SO₂ 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 SO₂. For example, peroxide may react with bisulfite in the particle phase instead of forming peroxyhemiacetals, that will affect MW distribution.

395 In all experiments, the average carbon oxidation state (OS_c = 2 O/C - H/C) of SOA was observed to increase with SO₂. It is noted that since the negative mode in ESI is sensitive only to acidic species, the effects of SO₂ on relative signal fractions and oxidation states observed here may only be valid for these species.



400 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 SO₂. The relative signal fraction of high-MW products measured in the IMS-TOF was reduced compared to when SO₂ was not present, suggesting that SO₂ may reduce oligomer formation, which may decrease SOA yields. However, we also observe that the presence of SO₂ (which is then converted to
405 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
410 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)
415 (Fig. S6) 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
420 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. On the other hand, first-generation oxidation products from α -pinene ozonolysis may be too volatile to condense, and the presence
425 of SO₂ reduces oligomerization and prevents any 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. S3B, SO₃ reacted rapidly with H₂O to form sulfuric acid once injected, even at 11% RH, the lowest RH among all the experiments
430 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
435 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, assuming that sCI yield is unity and sCI only reacts with SO₂). Therefore, it is likely that the reaction
440 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 suggest that both sCI and organic peroxides formed from monoterpene ozonolysis may play crucial roles
445 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, we observed reduced oligomerization for semivolatile oxidation products relative to increased low-MW
450 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



into aerosol liquid water to form HSO_3^- , and we present evidence to suggest that HSO_3^- can further react
455 with organic peroxides produced from monoterpene ozonolysis. This mechanism is consistent with the
greater SO_2 consumption observed under humid conditions, since more aerosol water was available for
both SO_2 and peroxides to partition.

In order to evaluate the relative contributions of sCI and peroxides as reactive sinks for SO_2 in our
460 experiments, we formulate a simplified kinetic model to attribute observed SO_2 loss to each process. We
note that without detailed knowledge of the SO_2 uptake mechanisms, the heterogeneous reaction of SO_2
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
simplified model to apportion the observed SO_2 loss under the experimental conditions employed in this
465 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 S6).

In this model, we calculated the relative contributions of the two pathways under two humidities (10%
470 and 50%) and under two initial concentrations of SO_2 . As our laboratory observation suggests, SO_2
consumption increases with increasing humidity (Fig. 8A and 8B). In the high SO_2 scenario (Fig. 8A,
 $[\text{SO}_2] > [\text{limonene}]$), both interactions with sCI and peroxide play important roles in SO_2 oxidation. A
major fraction of SO_2 consumption can be attributed to the reaction with sCI under dry conditions. At
50% RH, the amount of SO_2 consumed by the sCI pathway drops slightly (from 3 to 2 ppb in this
475 scenario). On the other hand, the relative importance of reactive uptake by peroxides become dominant
at 50% RH, accounting for 87% of the total SO_2 consumption. In the low SO_2 emission scenario (Fig. 8B,
 $[\text{SO}_2] < [\text{limonene}]$), sCI does not react with SO_2 at appreciable amounts, owing to the competition from
reactions with water and water dimer. Therefore, sCI chemistry does not contribute significantly to the
 SO_2 sink, and SO_2 consumption is dominated by reactions with peroxides and other reactive
480 intermediates. To identify when the transition from “low SO_2 ” to “high SO_2 ” occurs, simulations were
performed for a range of SO_2 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 peroxides is modelled as a simplified bimolecular reaction to match the observed SO₂ decay in our
485 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 compounds will need to be measured. Despite these missing parameters, our simplified model highlights
490 the importance of the reactive uptake pathway, and suggests further studies are warranted to elucidate the reaction rates and mechanisms for this reaction.

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
495 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 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
500 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 that the uptake coefficient of SO₂ on the aqueous particle through reacting with peroxides from limonene
505 ozonolysis is $1-5 \times 10^{-5}$ (Supporting Information, Section S7). 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), O₃ (Docherty et al., 2005) and NO₃ (Ng et al., 2008). Results from our study therefore suggest a new



510 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.

The importance of the reaction pathways (sCI and reactive uptake) proposed in this study imply that
515 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 anthropogenic emissions on atmospheric chemistry.

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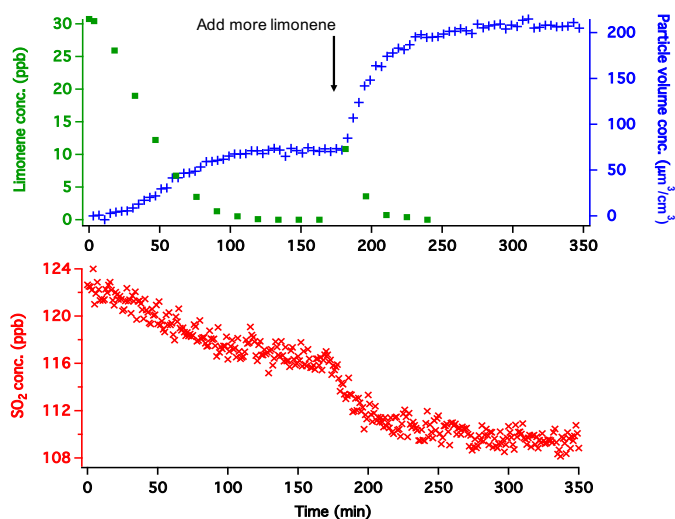
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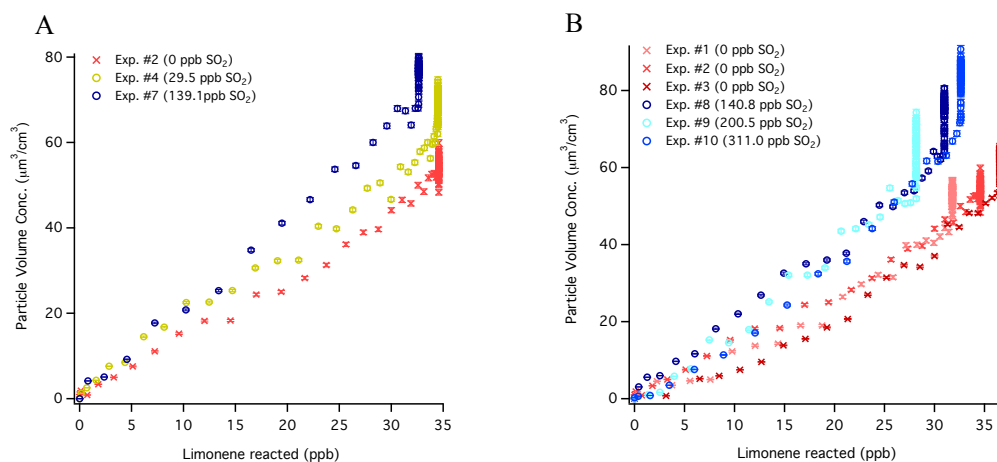
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Figure 1 Particle volume concentration, limonene concentration and SO_2 concentration as a function of experimental time. After 105 min, the limonene concentration was below 1 ppb, and the particle volume concentration and SO_2 concentration began to stabilize. At $t = 170$ min, additional limonene was injected into the chamber, and particle formation and SO_2 decay resumed. The timescale of SO_2 consumption matches that of SOA formation suggesting that there are synergistic effects between LSOA formation and SO_2 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 SO_2 injection concentration (0 ppb, 30 ppb and 139 ppb) under dry conditions (panel A). The enhancement reached a plateau as more SO_2 was injected (panel B).



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%

770 ^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.

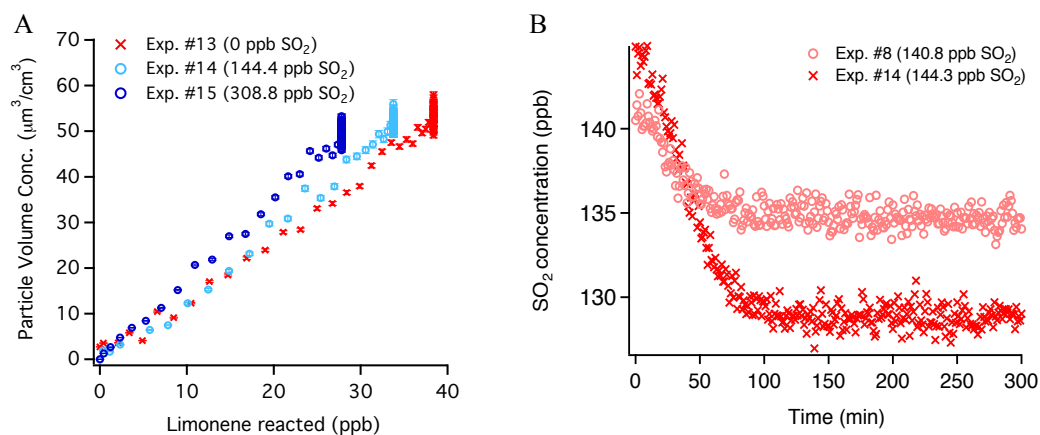
^c: Twice the amount of cyclohexane was added in Exp. #16 and #17 to examine the reaction between SO₂ and OH.

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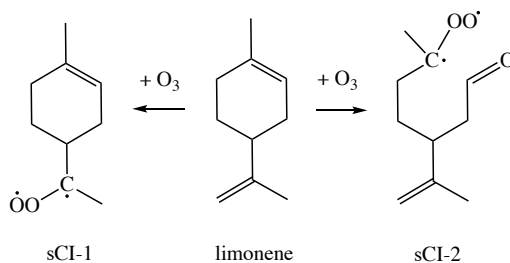
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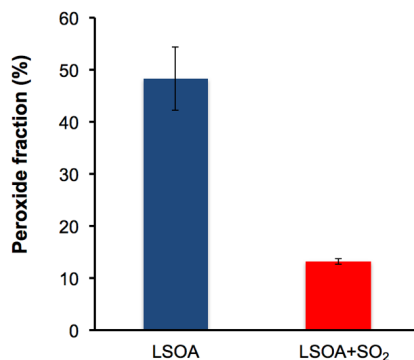
Figure 3 A) Particle volume concentration as a function of limonene reacted under humid conditions. Enhanced particle mass formation was observed with increasing SO_2 concentration. B) Greater consumption of SO_2 was observed under humid conditions than under dry conditions. By comparing Exp. #14 (humid) 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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Scheme 1 Formation of di-substituted sCI from limonene ozonolysis

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810 **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.

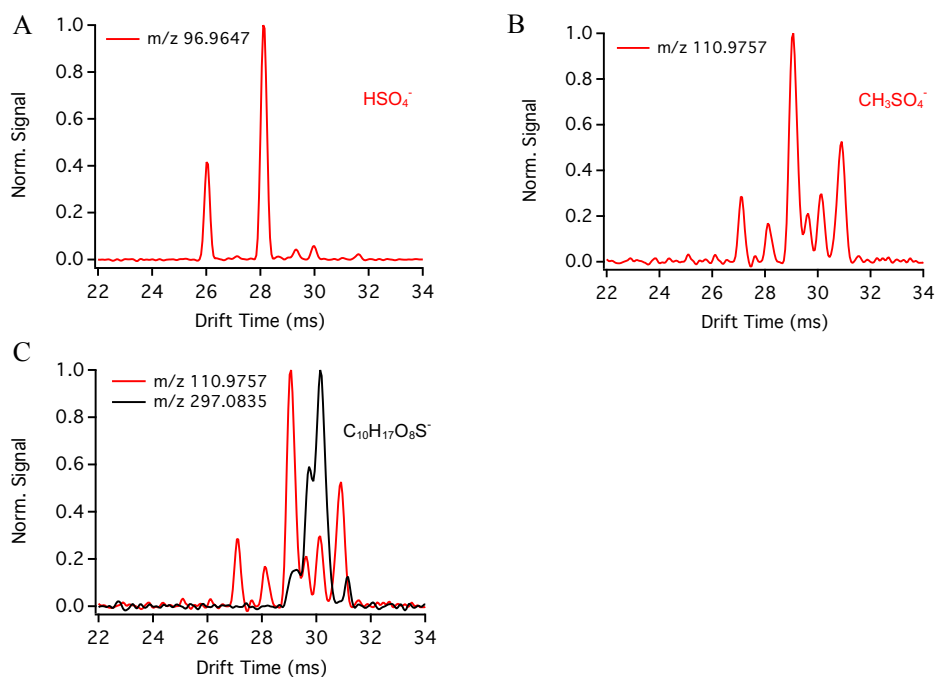
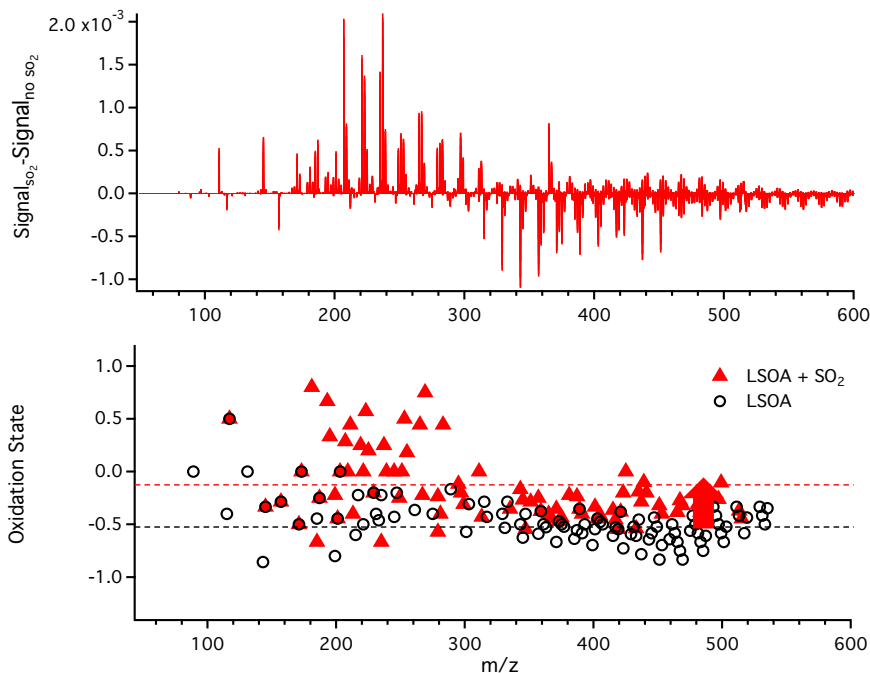


Figure 5 Organosulfate identification using IMS-TOF: A) Drift time of HSO₄⁻ (m/z 96.9647); B) Drift time of CH₃SO₄⁻ (m/z 110.9757); C) Drift time of CH₃SO₄⁻ and m/z 297.0835 (assigned to C₁₀H₁₇O₈S⁻). Overlapping of the drift times at 30.14 ms between the two mass-to-charge ratios indicates that the daughter ion CH₃SO₄⁻ is a fragment ion of the parent ion C₁₀H₁₇O₈S⁻.



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825 **Figure 6** Difference of normalized mass spectra between LSOA in the presence and absence of SO₂ (top panel). Signal of HSO₄⁻ (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 + SO₂ (red dashed line).

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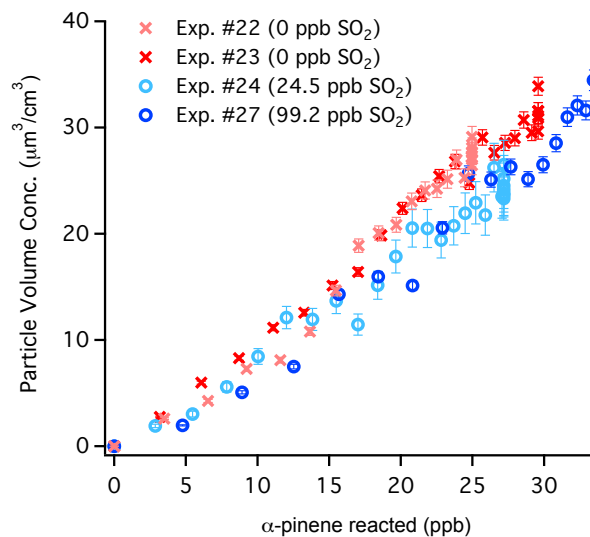
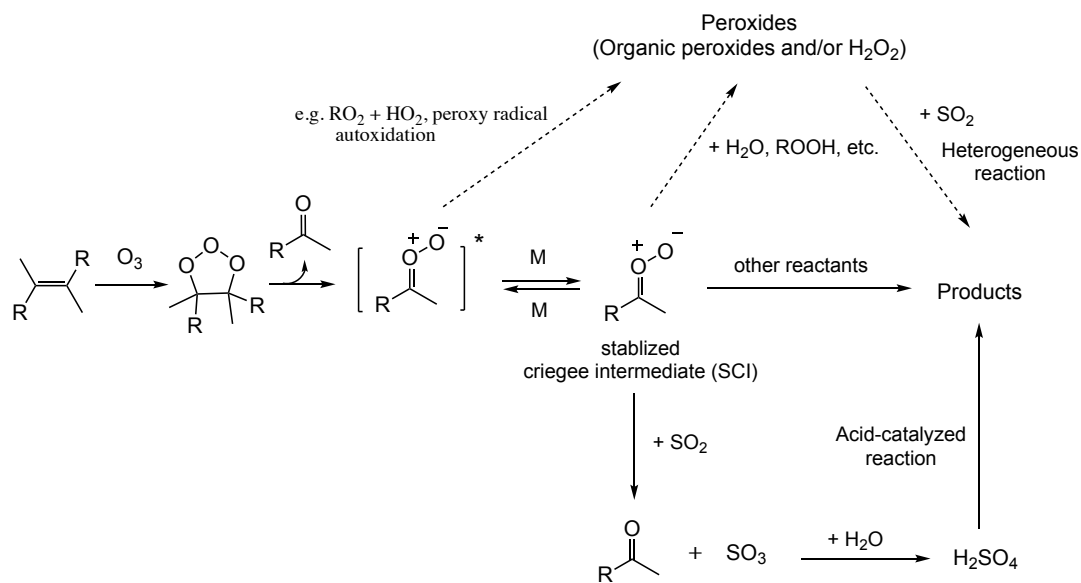


Figure 7 Growth of particle volume concentration as a function of reacted α -pinene under dry conditions. No significant change of SOA formation was observed.

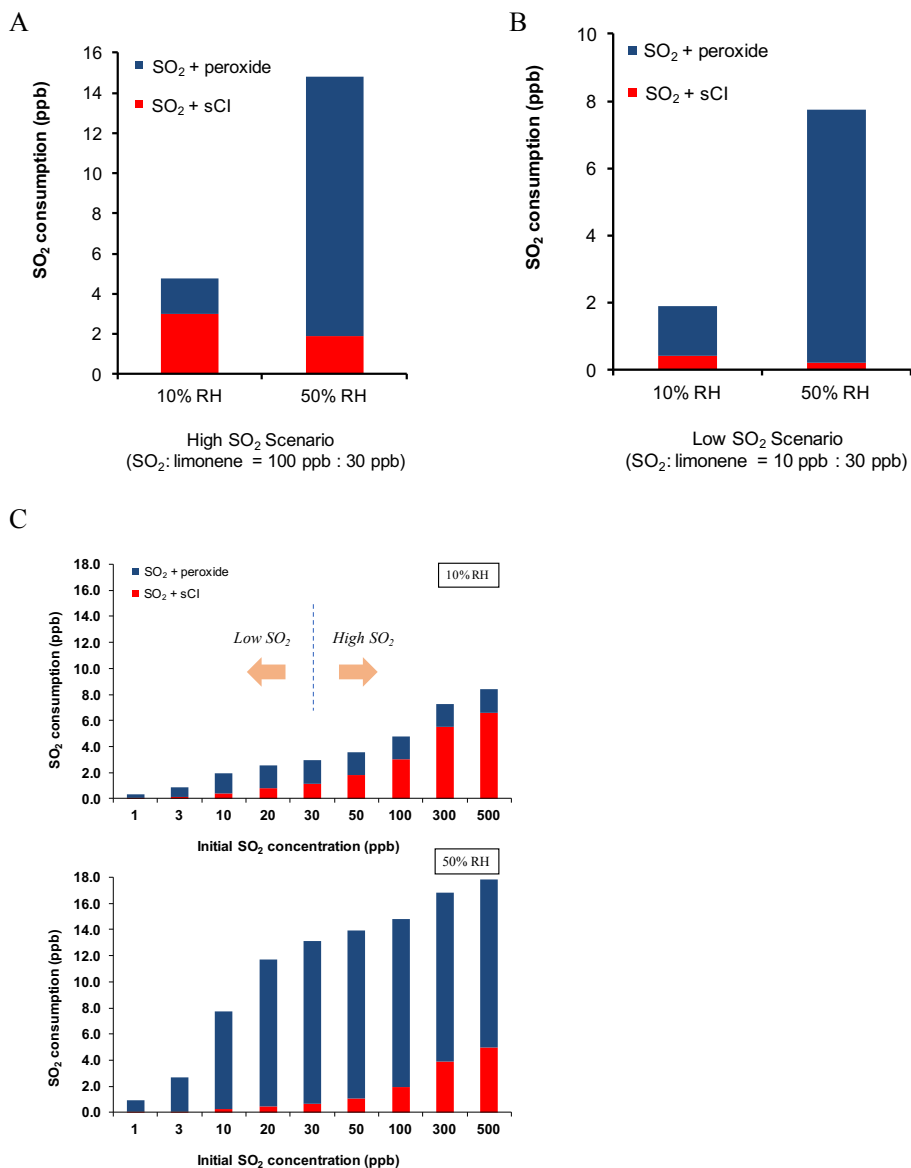
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Scheme 2 The proposed reaction mechanisms for SO_2 and reactive intermediates in monoterpene ozonolysis.



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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).