ACP Editor

Dear Prof. Markus Ammann,

Enclosed please find our revised manuscript entitled "The oxidation regime and SOA composition in limonene ozonolysis: Roles of different double bonds, radicals, and water", revised supplement and the response to the comments by you and the two anonymous referees. We have corrected the technical errors and the English. A native English speaker has helped us to polish the English language.

Detailed changes made in the manuscript can be seen in the marked-up version in this response.

Thanks for your time.

Sincerely yours,

Zhongming Chen and co-authors

Response to Referee 1

We gratefully thank the reviewer for the comments and we have polished the language and checked the grammar. Below are our responses to the comments and the responses are in blue. Other corrections are shown in the revised manuscript.

28: specify the 0.2 and 0.4-0.6 are yields

We have clarified in the abstract that these numbers represent the mass fraction of particulate peroxides in SOA.

69-70: add references

We add the relevant references in the revised text.

87: needs

Yes, we have revised it.

95: include more recent references here

We have added more recent references in the revised manuscript.

97: have paid

Yes, we have revised it.

99-101: rewrite without the phrases "on the one hand" and "on the other hand"

We follow the advice of the reviewer and the sentence is rewritten.

151-152: processes

Yes, we have revised it.

162: we take the peroxides.... to be HMW peroxides

Yes, we have revised it.

241: discussed?

We have changed that to "investigated".

251-252 (and throughout paper): Do not use the term "molar number" use number of moles Thanks for your suggestion and we have changed such expressions throughout the paper.

275: is slow

Yes, we have revised it.

297-298: remove this sentence

Yes, we have removed the sentence.

301: generated

Yes, we have revised it.

303 (and throughout): change to "SCI yield"

Yes, we have changed that throughout the paper.

317: was generated

Yes, we have revised it.

320: yield the same as

Yes, we have revised it.

322: show a clear dependence

Yes, we have revised it.

346: PFA and PAA were mainly formed through ECI isomerization

Yes, we have revised it.

354: "similar formation mechanisms"

Yes, we have revised it.

361: radical generation

Yes, we have revised it.

379: inclined to have

Yes, we have revised it.

394: remove concretely

Yes, we have removed it.

398: for six days

Yes, we have revised it.

401: under dry conditions

Yes, we have revised it.

414-416: change to number of moles

Yes, we have revised it.

423: may have hydrolyzed to form

Yes, we have revised it.

455: "not supposed to be.." I believe you mean "was not considered to be"

Yes, we have revised it.

490: we are the first to report

Yes, we have revised it.

500: degree of oxidation

Yes, we have revised it.

503: the effect of water

Yes, we have revised it.

508-511: rewrite without the phrases "on the one hand" and "on the other hand"

We follow the advice of the reviewer and the sentence is rewritten.

552: Figure 6 shows

Yes, we have revised it.

564: oxidizing products including

Yes, we have revised it.

583: Limonene is unique in many aspects because of its different DBs, suggesting that terpenes with multiple double bonds may have more complex effects on the atmosphere than previously thought.

We follow the advice of the reviewer and the sentence is rewritten.

585 degree of oxidation

Yes, we have revised it.

Response to Referee 2

We gratefully thank the reviewer for the comments we have polished the language and checked the grammar. Below are our responses to the comments and the responses are in blue. Other corrections are shown in the revised manuscript.

1. Lines 38-40: grammar

We have rewritten that sentence in the revised manuscript.

2. Line 58: isomers

Yes, we have revised it.

3. Line 82: references needed

We add the relevant references in the revised text.

4. Line 282: quantify

Yes, we have quantified the precision.

5. Line 448-449: grammar

We have rewritten the sentence in the revised manuscript.

6. Line 518-520: grammar

We have rewritten the sentence in the revised manuscript.

7. Line 556: grammar

We have rewritten the sentence in the revised manuscript.

The oxidation regime and SOA composition in limonene ozonolysis: Roles of different double bonds, radicals, and water

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Abstract. Volatile organic compounds (VOCs) play an important role in air quality and climate change, largely because they contributeof their contribution to the formation of oxidizing compounds and secondary organic aerosol (SOA). In this study, a series of products, including peroxides and carbonyl compounds in both gaseous and particulate phases, were simultaneously detected to help us investigate the oxidation regime and SOA composition in limonene ozonolysis. The roles of different double bonds (DBs), radicals, and water were also examined discussed. In our first investigation For the first issue, we were focused on the representative oxidizing compounds produced in limonene ozonolysis, including stabilized Criegee intermediates (SCIs), OH radicals, and peroxides. The dependence of H₂O₂ and hydroxymethyl hydroperoxide (HMHP) formation on RH demonstrates demonstrated that the reaction with water is was an important reaction pathway for limonene SCIs, and the lower-limit SCIsSCI yields of endocyclic and exocyclic DBs were estimated to be ~ 0.24 and ~ 0.43 , respectively. The OH yield was determined by adding sufficient amounts of an OH scavenger, and the OH yields of endocyclic and exocyclic DBs were ~0.65 and ~0.24, respectively. These The results indicate indicated that in limonene ozonolysis the endocyclic DB iswas inclined to generate OH radicals through hydroperoxide channel, while the exocyclic DB has ahad higher fraction of forming SCIs. Besides, other gas-phase and particle-phase peroxides were also studied in this work. The formation of peroxyformic acid (PFA) and

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peroxyacetic acid (PAA) waswere promoted significantly by the increasing RH and the degree of oxidation degree, and the discrepancy between the experimental and model results suggested some missing formation pathways. Considerable generation of H_2O_2 from SOA in the aqueous phase was observed, especially at high [O₃]/[limonene], which was mainly attributed to the hydration and decomposition of unstable peroxides in SOA such as peroxycarboxylic acids and peroxyhemiacetals. Different DBs and OH scavengers had a large were found to have a great-impact on the particulate peroxides, whose stabilities and their stability indicated that the types of peroxides in SOA-were changed under different conditions. As for the contribution of peroxides to SOA, the results demonstrated that peroxides could account for less than 0.2 in limonene SOA-the mass fraction of particulate peroxides in limonene SOA was less than 0.2 at low $[O_3]$ /[limonene], while the mass fraction was 0.4-0.6 at high $[O_3]/[Iimonene]$ -peroxides could account for 0.4-0.6 in SOA. The partitioning behavior of peroxides showed that multi-generation oxidation helped produce more low-volatility peroxides, which partially explained the provided some explanation for higher SOA yield. The partitioning behavior of carbonyls was also examined discussed and the experimental partitioning coefficients (K_n) were found to be typically usually several orders of magnitude higher than the theoretical values. This study provided new insights into the oxidation regime and SOA composition in limonene ozonolysis, and limonene showed its specificity in many aspects when both endocyclic and exocyclic DBs were ozonated. We suggestsuggested that the atmospheric implications of terpenes containing more than one DB and the SOA composition, especially particulate peroxides, need further study.

40 **1 Introduction**

As an important monoterpene, limonene has a high emission rate-both from both biogenic and anthropogenic sources, which that is only second only to pinene (Atkinson and Arey, 2003; Clausen et al., 2001; Fellin and

Otson, 1994; Griffin et al., 1999; Guenther et al., 1995; Lamb et al., 1993; Seifert et al., 1989; Sindelarova et al., 2014; Wolkoff et al., 2000). Total monoterpene emissions are estimated to be 50 Tg C yr⁻¹, and limonene might comprise about 20% of that (Stroud et al., 2005). In addition to the-massive emissions from vegetation, theits extensive utilization of limonene in household and industrial processes-also makes itlimonene non-negligible in the atmosphere. Compared with its isomerisomers α -pinene and β -pinene, an obvious structural feature of limonene in structure is that it hasowns two different double bonds (DBs), an endocyclic DBone and an exocyclic DBone, which complicatesmakes the behavior and the fate of limonene in the atmosphere complicated. Ozonolysis is an important reaction pathway of limonene and it serves as a source of free radicals, intermediate products, and aerosol. The first step inof alkene ozonolysis is the addition of O₃ to the carbon-carbon double bond, forming an energy-rich primary ozonide (POZ), The POZ which decomposes intoto two sets of carbonyls plus carbonyl oxides, which are called excited Criegee intermediates (ECIs) (Criegee, 1975; Fenske et al., 2000; Gutbrod et al., 1996, 1997; Kroll et al., 2001a, b). ECIs can isomerize through the

55 hydroperoxide channel followed by OH production, rearrange to esters with subsequent decomposition, or undergo collisional stabilization forming stabilized Criegee intermediates (SCIs) (Cremer et al., 1993; Presto and Donahue, 2004; Richard et al., 1999; Wegener et al., 2007).

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In the last few years, the oxidizing compounds formed in alkene ozonolysis have received much attention because they are able to removeown the power of removing a series of trace gases and contribute-much to atmospheric oxidation capacity (Möller, 2009; Prinn, 2003; Taatjes et al., 2013). Representatives The representatives of these compounds include OH radicals, SCIs, peroxides, etc. Investigations into Investigating the oxidation regime of alkene ozonolysis areis essential to understandunderstanding the formation of these critical products and evaluating evaluate the actual impact of this reaction in the atmosphere. As an important source of OH radicals needed for to make OH-initiated reactions occurring continue in darkness the dark (Kroll et

65 al., 2001a, b), OH formation pathways in alkene ozonolysis have been extensively studied and the major pathway is considered to be the unimolecular decomposition of ECIs, FurthermoreBesides, some studies suggestsuggested that SCIs could also generate OH radicals through self-decomposition or reactions with other species (Anglada et al., 2002; Hasson et al., 2003; Kroll et al. 2001a, b; Tillmann et al., 2010; Zhang and Zhang, 2005). SCIs generated during the process have been shownprove to have asufficient lifetime, which is usually 70 on the order of sub-seconds (Kroll et al., 2001a, b; Long et al., 2018; Mauldin et al., 2012), that is sufficiently long to react with other trace species, such as H₂O, SO₂, NO₂, carbonyls, alcohols, and carboxylic acids, etc. (Sakamoto et al., 2017; Sipilä et al. 2014; Yao et al., 2014). There have been numbers A number of studies have focused focusing on the reactions of SCIs containing 3 or fewerless carbon atoms, and their unimolecular decomposition and reactions with water show strong structure dependence. The reactions with water monomer 75 and water dimer are the main reaction pathways for CH₂OO and *anti*-CH₂CHOO, while the unimolecular decomposition would be more important for svn-CH₃CHOO and (CH₃)₂COO the unimolecular decomposition would be more important (Huang et al., 2015; Lin et al., 2016; Welz et al., 2012, 2014; Taatjes et al., 2013). However, As the reaction mechanisms for larger SCIs formed from biogenic alkenes ozonolysis, their reaction mechanisms are still unclear, since it is difficult to synthesis and observe them directly. Furthermore, reactions 80 of alkenes with ozone can also generate a considerable amount of peroxides, which are considered to be important due to their oxidizability and role as a radicals reservoir. H₂O₂ is the most crucial oxidant to oxidize S (IV), forming sulfuric acid and sulfate in the aqueous phase (Calvert et al., 1985; Penkett et al., 1979; Peña et al., 2001). And as a species accounting for 40%-50% of the total global organic peroxides (Crounse et al., 2006; Khan et al., 2015), peroxycarboxylic acids (RC(O)OOH) play an important role in promoting atmospheric oxidation capacity and enhancing the acidity of the aqueous phase.

One important reason whyfor limonene chemistry has attracted drawing much attention is its high SOA

90 gas-particle partitioning, there are still large discrepancies between the model and experimental results (Cocker et al., 2001; Griffin et al., 1999; Hoffmann et al., 1997; Odum et al., 1996; Pankow, 1994; Presto et al., 2005; Pye and Seinfeld, 2010). Laboratory studies of about SOA formation in limonene ozonolysis mainly focused on 95 100

the aerosol yields under different conditions and the identification of identifying some products in the particle phase (Calogirou et al., 1999; Glasius et al., 2000; Grosjean et al., 1992, 1993; Leungsakul et al., 2005; Ng et al., 2006; Pathak et al., 2012), however, the composition of limonene SOA still needneeds detailed study, especially when it comes to the effect of different DBs. As a double-unsaturated terpene, the SOA formation process of limonene could be more complicated than that for single-unsaturated terpene, since as the multi-generation oxidation has significant influence on SOA. In this study, two classes of species.- peroxides and carbonyls are studied forchosen to study their behaviors in limonene SOA formation. Over the pastIn the last few years, analyses of organic peroxides suggest that they are have been analyzed and suggested to be an important componentcomposition in aerosol (Docherty et al., 2005; Heaton et al., 2007; Li et al., 2016; Mertes et al., 2012; Pathak et al., 2012), and particulate peroxides could cause negative health effects when they penetrateafter penetrating into lungs (Chen et al., 2011; Fischer and Maier, 2015; Gupta et al., 2014; Verma et al., 2009; Wragg et al., 2016). The reactive uptake and particle-phase reactions of carbonyls are believed to be responsible 105 for fractions of aqueous SOA formation (Ervens et al., 2011; Mcneill et al., 2012), especially for the dicarbonyls glyoxal and methylglyoxal. Until Up to now, there has been little research intofew researches pay attention to the contribution of peroxides and carbonyls to limonene SOA and their behaviors in aerosol formation are only vaguely understood, <u>in to the best of our knowledge</u>.

formation potential, which is proven to be higher than that of α -pinene since because limonene is doubly

unsaturated (Andersson-Sköld and Simpson 2001; Kroll and Seinfeld, 2008; Lane et al., 2008; Lee et al., 2006).

Although progress has been made inover the past years on simulating SOA formation with the theory of

The focus of this study is to investigate the oxidation regime and SOA composition in limonene ozonolysis, especially for the roles of different DBs, radicals, and water. On the one hand, through We considerdetermining the generation of SCIs, OH radicals, and peroxides in discussions of, the oxidation regime in the reaction system is discussed. On the other hand, Furthermore, peroxides and carbonyls are taken as representatives to study their behaviors in SOA formation.

2 Experimental

115 **2.1 Chemicals**

This study used the following: R-(+)-Limonene (Sigma-Aldrich, ≥ 99.0%), 2-butanol (Sigma-Aldrich, 99.5%), cyclohexane (Alfa Aesar, ≥ 99.9%), potassium iodide (KI, Alfa Aesar, 99.9%), hydrogen peroxide (H₂O₂, Alfa Aesar, 35wt.%), ortho-phosphoric acid (H₃PO₄, Fluka, 85–90%), hemin (Sigma, ≥ 98.0%), 4-hydroxyphenylacetic acid (Alfa Aesar, 99%), formaldehyde (Sigma-Aldrich, 37wt.%), acetaldehyde
120 (Amethyst Chemicals, 40wt.%), acetone (Fluka, ≥ 99.7%), hydroxyacetone (Sigma-Aldrich, 90%), glyoxal (Sigma-Aldrich, 40wt.%), methylglyoxal (Sigma-Aldrich, 40wt.%), 2-butanone (Alfa Aesar, ≥ 99%), acetonitrile (Alfa Aesar, ≥ 99.7%), 2,4-dinitrophenyl hydrazinel (DNPH, TCI, 50wt.%), ammonia solution (NH₃·H₂O, Beijing Tongguang Fine Chemicals Company, ≥ 99.5%), sulfuric acid (H₂SO₄, Xilong Chemical Company, 95.0–

125 98.0%), ultrapure water (18MΩ, Millipore), N₂ (≥ 99.999%, Beijing Haikeyuanchuang Practical Gas Company Limited, Beijing, China), O₂ (≥ 99.999%, Beijing Haikeyuanchuang Practical Gas Company Limited, Beijing, China), polytetrafluoroethylene (PTFE) filter membrane (Whatman Inc., 47_mm in diameter), and quartz microfiber filters (Whatman Inc.)-were used in this study.

2.2 Apparatus and procedures

- 130 A flow tube reactor (2 m length, 70 mm inner diameter, quartz wall)₂ equipped with a water jacket for controlling <u>the</u> temperature₂ was used to investigate the ozonolysis of limonene. All the experiments were conducted at 298±0.5 K in <u>darknessthe-dark</u>. O₃ was generated by O₂ photolysis in a 2 L quartz tube with a low-pressure Hg lamp, and the detailed quantification method of O₃ was described in our previous study (Chen et al., 2008). H₂O₂ produced by UV irradiation of O₂ and trace water was measured in control experiments and
- deducted from the results. Limonene gas was generated by passing N₂ flow over liquid limonene in a diffusion
 tube at the selected temperature₂ and OH scavenger (2-butanol or cyclohexane) gas was generated with a
 bubbler. The concentrations of limonene and the OH scavenger were determined by gas chromatography with <u>a</u>
 flame ionization detector (GC-FID, Agilent 7890A, USA). Water vapor was generated by passing N₂ through a
 water bubbler, which contained a carborundum disc <u>submergedsubmerging</u> in ultrapure water (18 MΩ). The
 mixing gas₂ including limonene, OH scavenger, ozone, and dry or wet synthetic air (80% N₂ and 20% O₂), was
 successively introduced into the reactor₂, and with With a total flow rate of 2 standard L min⁻¹, the residence
 time was estimated to be 240 s.

To explore the reaction mechanism of endocyclic and exocyclic DBs ozonolysis; and the effect of multi-generation oxidation in limonene ozonolysis, <u>we conducted</u> two sets of experiments with different ratios of ozone to limonene concentration<u>were</u>-conducted. In the following<u>-content</u>, [O₃] <u>denotes</u><u>denoted</u> the concentration of ozone, [limonene] <u>denotes</u><u>denoted</u> the concentration of limonene, and [O₃]/[limonene] <u>denotes</u><u>denoted</u> the concentration. In the low [O₃]/[limonene]-set of experiments, the initial concentrations of limonene and ozone were ~280 ppbv and ~500 ppbv, respectively<u>-In₃</u> <u>whereas in the high [O₃]/[limonene]-set of</u> experiments, the initial concentrations of limonene and ozone were ~

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cyclohexane were added to scavenge OH radicals in the RH range of 0%–90%. In the tables and figures, the low-ratio and high-ratio-ratio sets of experiments arewere denoted by with marks L and H, respectively, and the conditions in the absence of scavenger, in the presence of 2-butanol, and in the presence of cyclohexane are denoted were represented by No-sca, 2-But, and C-hex, respectively. The experimental Experimental conditions arewere listed in Table 1.

According to previous studies, in limonene ozonolysis the rate constant of the endocyclic DB reaction with ozone in limonene ozonolysis iswas 2×10^{-16} cm³ molecule⁻¹ s⁻¹ (Atkinson, 1990; Shu and Atkinson, 1994), while the exocyclic DB reaction with ozone iswas about 30 times slower than the endocyclic DB reaction (Zhang et al., 2006). Based on those rate constants, we estimated that at low [O₃]/[limonene], less than 1% exocyclic DB iswas ozonated, so this situation mainly represents represented the first-generation oxidation. In this circumstance, because the ozone concentration iswas low, the OH reaction would impact the amount of limonene consumed by O₃. In the presence of OH scavenger, ~-42% endocyclic DB reacted with O₃, while in the absence of scavenger, ~-38% endocyclic DB reacted with O₃. At high [O₃]/[limonene], more than 99% endocyclic DB and about 51% exocyclic DB reacted with ozone, and since the ozone concentration in this situation was high, the OH effect on the ozonolysis was presumed to be unimportant. The latter condition, which contained multi-generation oxidation processprocesses, was more likely to occurhappen since the ratio of [O₃] to [limonene] was similar to the ratio in the real atmosphere.

It should be noted that one advantage of flow tube reactor <u>iswas</u> that the wall would be in equilibrium with the gas phase after a stationary period, <u>and according According</u> to our observations, this process usually <u>requiresneeded</u> about 2 h. <u>Thus, In order</u> to stabilize the system and diminish the wall effect to the extentas much as possible, <u>we ran</u> the reactor was usually aged for 2 h prior to <u>taking measurements</u>. <u>and And</u> after the experiments, the reactor was rinsed-out with ultrapure water and blown-to dry with N₂.

2.3 Products analysis

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To better investigate the gas-particle partitioning of products formed in limonene ozonolysis, we analyzed the gas-phase and particle-phase products simultaneously. We measured total Total peroxides and a series of low-molecule-weight (LMW) peroxides, were measured here, and in In the following discussion we regarded those the peroxides that could be detected by high performance liquid chromatography (HPLC) to been LMW peroxides, while eonsidered took the peroxides undetermined by HPLC asto be high-molecule-weight (HMW) peroxides. For particle-phase peroxides detection, a PTFE filter was used for the SOA collection, and the mass of SOA was measured by semi-micro balance (Sartorius, Germany). Since the control experiment-results showed that a long-duration time collection led to the loss of some peroxides in particles, the collection time was controlled to be 3 h for each filter, and the accuracy of the particulate products analysis was discussed in the Supplement. Each loaded PTFE filter was extracted with 20 mL H₃PO₄ solution (pH 3.5) using a shaker (Shanghai Zhicheng ZWY 103D, China) at 180 rpm and 4 °C for 15 min₃ and the extraction efficiency was confirmed in our previous work (Li et al., 2016). For gas-phase peroxides detection, the air samples through the

- confirmed in our previous work (Li et al., 2016). For gas-phase peroxides detection, the air samples through the filter were collected in a glass coil collector at a temperature of 4 °C with H₃PO₄ solution (pH 3.5) serving as the rinsing solution. The coil collector is around 30 cm long and its effective length is about 100 cm. The coil is similar with that used in earlier studies (Grossmann et al., 2003; Sauer et al., 1996, 1997)_a and the diagram of the thermostatic coil collector is provided shown in the Supplement.
- The detection method for detecting theof peroxides was reported in our previous studies (Hua et al., 2008; Li et al., 2016), so and is only a briefly described description was given here. LMW peroxides were analyzed by HPLC (Agilent 1100, USA) coupled with post-column derivatization and fluorescence detection on line. Peroxides separated by column chromatography reacted with *p*-hydroxyphenylacetic acid (POPHA) under the catalysis of hemin forming POPHA dimers, and then the dimers were quantified by fluorescence detector. The

195 standard solution of peroxides was prepared and used for calibration in each measurement. The detection limit for theof gas-phase LMW peroxides was about 22 ppty, and in the particle phase the detection limit was around 0.068 ng/ug for H₂O₂. The accuracy of this method was estimated to be around 7% with and the precision of the measurement results was usually within 20%. The concentration of total peroxides (H_2O_2 , ROOH, and ROOR') was determined by the iodometric spectrophotometric method, which is based on the reaction of peroxides and 200 iodide ions (Docherty et al., 2005; Mutzel et al., 2013). Briefly, excessive KI solution was added tointo samples purged of Q₂, after After remaining staying 12 24 h in the darkdarkness 12–24 h for the derivatization, the produced I₃⁻ ions-produced were quantified at 420 nm by UV/VIS spectrophotometer (SHIMADZU UV-1800, Japan). The efficiency of the total peroxides measurement was discussed in our previous work (Li et al., 2016) and the detection limit of the total peroxides was about 0.92 ppby in the gas phase and 0.025 $\mu g/\mu g$ in the particle phase. The accuracy of this method was estimated to be 10% withand the precision of the measurement 205 results was usually within 20%.

To measure the particle-phase carbonyls, SOA was collected onto a quartz microfiber filter for 3 h.- after After collection, the filter was placedput upside down in a conical flask, and then- 5 mL acetonitrile, 1 mL DNPH saturated solution, and 50 μ L H₂SO₄ solution (0.25 M) were added into the flask in sequence. -the flask was 210 then shaken at 180 rpm and 4 °C for 3 h and kept in darkness for 12–24 h prior to waiting for detection afterwards. For the gas-phase carbonyls measurement, gas through the filter was directly introduced into a Horibe tube, which was placed in a cold trap (Beijing Tiandijingyi TH-95-15-G, China) at about -98 °C to freeze the products in the tube. The Horibe tube was composed is made of an inlet tube (25 cm length, 4 cm O.D.), a coil (7 laps, 1 cm O.D.), and an outlet tube with a carborundum disc. The diagram of the Horibe tube is shown in the Supplement. After collection, 10 mL acetonitrile was added to rinse the inside of the Horibe tube inside to dissolve carbonyl compounds, and then the solution was mixed with DNPH saturated solution and

H₂SO₄ solution to derivatize for 12–24 h in the darkness. <u>The derived samples Samples derived</u> were analyzed by HPLC with UV detection (Agilent 1100, USA), and details of the process could be found <u>Details of this</u> process are provided in our previous <u>reportwork</u> (Wang et al., 2009). The detection limit of carbonyl compounds

was about 0.3 ppbv in the gas phase, and in the particle phase it was 0.15 ng/µg in terms of formaldehyde (FA). The accuracy of this method was estimated to be 8% and the precision of the measurement results was within 30%. Since the yields of bothFor acetone (ACE) and methylglyoxal (MGL), since the yields of both were low, especially under some conditions, their uncertainty might be high-during the analysis and the precision was within 80%.

225 2.4 Wall loss experiments

To increase the accuracy of themake results more accurate, we designed and conducted a series of control experiments to quantify the wall loss effect, including gaseous products and aerosol wall loss evaluation. Gas containing peroxide constituents was generated by passing N₂ through a diffusion tube, at a controlled temperature of at 4 °C, which contained certain peroxide solution in it. The synthetic method of multiple organic peroxides was described in our previous work (Huang et al., 2013). Gas containing carbonyl constituents was prepared by injecting liquid substance into an evacuated steel canister (15 L, Entech Instrument), and then Then N₂ was added constantly until the pressure in the canister reached 30 psi. The outlet of the canister was linked with a mass flow controller thatto regulated the gas flow rate. The gas containing peroxides or carbonyls was mixed with synthetic air at different RH levels and introduced into the reactor atwith a rate of 2 standard L min⁻¹, and the concentrations of peroxides and carbonyls were controlled to be at the similar to the concentrations of level with the products observed in limonene ozonolysis. After the gas mixture was introduced into the flow tube, a period of approximately around 2 h was needed for the gas and wall to become balanced, and then the

measurements were begun would start. The aerosol wall loss experiment used two-stage reaction equipment that contained containing two flow tube reactors. Because we wanted In order to explore the wall loss effect on pure SOA, the first reactor was used to generate aerosol where limonene and O_3 had sufficient time to react completely. The gas containing aerosol out of the first reactor was mixed with synthetic air at different RH

levels and introduced into the second reactor with a rate of 2 standard L min⁻¹. The particles at the inlet and

outlet of the second reactor were collected on PTFE filters and measured by balance to calculate the SOA concentration. The wall loss fraction of the gas-phase constituent or SOA was determined as the difference between the inlet and outlet concentrations divided by the inlet concentration as Eq. (S1) (in the Supplement). The wall loss experiments were conducted in the RH range of 0%–90%, and the profiles of loss fractions as a function of RH could be used to correctfor correcting products and SOA yields to diminish the wall loss effect.

3 Results and discussion

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3.1 Wall loss correction

- 250 The wall loss fractions of LMW peroxides increased with increasing RH, and this tendency was especially obvious for peroxyformic acid (PFA) and peroxyacetic acid (PAA), whose loss fractions increased successively with RH. For H₂O₂ and hydroxymethyl hydroperoxide (HMHP), their wall loss fractions went up quickly above 50% RH, yet they did notdidn²t have a large change below 50% RH. Generally speaking, HMHP had the highest wall loss fraction, which could reaching ~0.25 at 90% RH, while PFA had the lowest wall loss fraction.
- 255 The average of these LMW peroxides loss fractions was used to correct the wall loss effect for gas-phase HMW peroxides.

As for carbonyl compounds, the variation of their wall loss fractions with RH was not very obvious. The loss

curves of FA, acetaldehyde (AA), and ACE were somewhatkind of irregular. The wall loss fractions of For hydroxyacetone (HACE), glyoxal (GL), and MGL, their wall loss fractions were lowest at 10% RH, and then

260 they gradually arose with increasing water vapor concentration. The higher loss fractions of GL and MGL compared with other carbonyls could be attributed to their inclination towards hydration. FA had the lowest wall loss fraction around 0.03, while MGL had the highest loss fraction around 0.12.

The wall loss effect on SOA was also discussed investigated from 0% to 90% RH. The SOA wall loss fraction was ~ 0.06 at the dry condition, then it increased slightly with water vapor concentration. At 50% RH the The SOA loss fraction was ~0.11 and ~0.17, and at 50% RH and at 90% RH, respectively. the SOA loss fraction was - 0.17. The dependencies of the peroxides, carbonyls, and SOA wall loss fractions on RH are provided were definitely shown in the Supplement.

3.2 SCIs generation

The reaction between SCIs and water, which produces α -hydroxyalkyl hydroperoxides (HAHPs) decomposing 270 to H₂O₂, carbonyls, and carboxylic acids, is thought to be an essential source of these compounds and serves as a principle source of H₂O₂ formation without light (Becker et al., 1990, 1993; Gäb et al., 1985; Sauer et al., 1999). Figure 1 shows the dependence of H_2O_2 yield and HMHP yield on RH, and the six profiles in each subgraph represents conditions at low or high $[O_3]/[limonene]$ in the presence or absence of the OH scavenger (2-butanol or cyclohexane). The molar yield used here is defined as the ratio of the product's-molar number of moles to the molar number of moles of limonene consumed, as given by Eq. (S2) (in the Supplement). It was obvious that, even although in different cases, the variations of H_2O_2 yield and HMHP yield with RH had similar tendenciestendency, both of which increased significantly from 0% RH to 70% RH, and then they approached the limiting values. There was little effect of OH scavenger. At low $[O_3]/[limonene]$, the maximum H₂O₂ yield

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was ~-24.00% without OH scavenger, ~-24.60% with 2-butanol, and ~-22.95% with cyclohexane, respectively. At high $[O_3]$ /[limonene], the maximum H₂O₂ yield reached ~-41.20% without OH scavenger, ~-41.80% with 2-butanol, and $\sim 40.50\%$ with cyclohexane. As for HMHP, its yield was much higher at high $[O_3]/[limonene]$ (~ 5.43%) than at low $[O_3]/[limonene]$ (~ 0.62%), withand the specific information-could be found in the following picture. It is usually believed that H_2O_2 has two generation pathways: , one is HO_2 self-reaction, and the other one is HAHPs decomposition. The former pathway is considered as a main contributor to H_2O_2 during daytime, while the latter is regarded to occur as a route-without photochemistry. In the reaction system discussed here, when we applied a box model coupled with the limonene reaction mechanism extracted from-the Master Chemical Mechanism (MCM) v3.3 (website: http://mcm.leeds.ac.uk/MCMv3.3.1) to simulate the reaction, it was estimated that the yield of H_2O_2 formed from the HO₂ self-reaction was estimated to be less than 0.1% under both dry and wet conditions. When the 2-butanol or cyclohexane reaction mechanism was taken into consideration, the contribution of this pathway to H₂O₂ formation was still very limited, hence, it was assumed that the HO₂ self-reaction was not important for H_2O_2 generation in this reaction system. Under dry condition, a small amount of water vapor might desorb from the flow tube wall and participated in reactions resulting in a small amount of little H_2O_2 formation. Thus, the high H_2O_2 yield observed here might be mainly attributed to SCIs reaction with water.

295 From 0% to 70% RH, both theof H₂O₂ yield and HMHP yield were promoted significantly by the increasing RH, indicating that the reaction with water gradually became turned to be dominant for limonene SCIs. Jiang et al. (2013) suggested that the formation of HAHPs was the most favorable pathway for limonene SCIs reaction with H_2O_2 , and the subsequent decomposition of HAHPs was thought to be prior to generating aldehyde and H_2O_2 (Chen, 2016; Kumar, 2014). Although theoretical calculation results indicated that HAHPs decomposition wasis 300 slow, some studies proved that water and acid molecules could greatly promote the decomposition process

(Anglada et al., 2002; Anglada et al., 2011; Aplincourt and Anglada, 2003; Crehuet et al., 2001), and the H₂O₂ formation from HAHPs decomposition occurs very rapidlywas very fast (Chen et al., 2016; Winterhalter et al., 2000). The fact that few HAHPs larger than HMHP were identified in alkene ozonolysis also provided evidence for the rapid decomposition of large HAHPs. Above 70% RH, the appearance of the limiting values of H_2O_2 yield and HMHP yield suggested that the water vapor concentration was high enough that to make the bimolecular reaction of SCIs and H₂O suppressed the unimolecular decomposition of SCIs and the reactions of SCIs with other products. In previous studies, the unimolecular decomposition of SCIs and the reactions of SCIs with water showed strong structure dependence. For CH₂OO and *anti*-CH₃CHOO, the atmospheric lifetimes of their bimolecular reactions with H_2O and $(H_2O)_2$ were less than 1 ms, while their lifetimes of unimolecular 310 reaction were much longer (Lin et al., 2016; Sheps et al., 2014; Taatjes et al., 2013; Welz et al., 2012). For syn-CH₃CHOO and (CH₃)₂COO, the atmospheric lifetimes of their bimolecular reactions with H₂O and (H₂O)₂ were more than 100 ms, while their lifetimes of unimolecular reaction were just a few milliseconds at 298 K (Drozd et al., 2017; Huang et al., 2015; Long et al., 2018; Sheps et al., 2014; Taatjes et al., 2013; Welz et al., 2014). For larger SCIs their atmospheric lifetimes of unimolecular reaction and bimolecular reactions with H₂O and $(H_2O)_2$ were not quantified. Tillmann et al. (2010) inferred that about 46% of ECIs formed from α -pinene ozonolysis would stabilize and at 44% RH about 65% of SCIs formed H2O2 after reacting with water and 28% of SCIs decomposed. Yao et al. (2014) showed that a large fraction of ECIs formed from α -cedrene were stabilized and the unimolecular decomposition of SCIs was suppressed by their bimolecular reactions. Although we could not estimate the rates of SCIs decomposition and their reaction with water, the results here proved that the reaction with water was an essential route for limonene SCIs, and the rapid decomposition of HAHPs made an important contribution to H_2O_2 formation. At high RH, the unimolecular decomposition of limonene SCIs could be suppressed by their bimolecular reactions with water monomer and water dimer.

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325 generationgenerated in the ozonolysis of different DBs-ozonolysis. The predicted SCIsSCI yield was derived by combining the limiting yields of H₂O₂ and HMHP together, as in Eq. (S3) (in the Supplement), based on the assumption that the limiting yield of H₂O₂ was equal towith the large SCIsSCI yield (Hasson, 2001a, b). Considering that a portion of SCIs might undergo unimolecular decomposition a lower-limit yield of SCIs formed in limonene ozonolysis was estimated here. Additionally, as described in Sect. 3.3, the results demonstrated that the OH yield was not obviously affected by RH, and we speculated that the fraction of SCIs that decomposed and formed OH radicals was small. It was observed that the OH scavenger did notn²t have a largehuge impact on the SCIs measurement results, while big difference existed between the ozonolysis of two DBs ozonolysis. The SCIsSCI yield of the endocyclic DB ozonolysis was around 24.45%, yet the exocyclic DB ozonolysis had a larger stabilization fraction of ECIs, which was about 42.90%. It should be noted that, since

endocyclic DB ozonolysis, but was the sum of first-generation products with a remaining double bond, as shown in the Fig. 2. The results meant that, even though exocyclic DB ozonolysis is was much slower than endocyclic DB, it playsplayed a non-negligible role in generating SCIs in limonene ozonolysis.

According to the experimental conditions elaborated in Sect. 2.2, we tried to calculate the contribution of

endocyclic DB and exocyclic DB ozonolysis to H₂O₂ and HMHP formation, and furthermore, infer the SCIs

340 3.3 OH radicals generation

In this study, OH yield was determined by adding sufficient 2-butanol as <u>a</u> scavenger and measuring how much 2-butanone <u>was</u> generated. Aschmann et al. (2002) suggested that using 2-butanol to measure OH formation would be more accurate than using cyclohexane. The yield of 2-butanone formed from the reaction of 2-butanol

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and OH was had been detected previously (Aschmann et al., 2002; Baxley and Wells, 1998; Chew and Atkinson, 1996), and we used 0.66, which is the as an average of the reported values (Forester and Wells, 2011), to calculate OH radicals yield as the same as Forester and Wells (2011). The results showed that the yield of OH radicals produced from endocyclic DB ozonolysis was 0.65 ± 0.21 , while for exocyclic DB, the OH yield was 0.24 ± 0.13 . The OH generation did notn't show evidenta clear dependence on water vapor concentration. the The OH yield of endocyclic DB ozonolysis was within the range of published values published, while the OH yield of exocyclic DB ozonolysis was determined to be higher than that reported by Herrmann et al. (2010) reported. The effect of water on OH formation in alkene ozonolysis is still under debate as there are because of the discrepancies among the existing publications. Anglada et al. (2002) used quantum mechanical calculations to indicated that water could increase OH production, using quantum mechanical calculations and Tillmann et al. (2010) reported higher OH vield under humid condition. Nevertheless, more studies showed that OH formation was independent of water vapor concentration (Aschmann et al., 2002; Atkinson and Aschmann, 1993; Atkinson et al., 1992; Berndt et al., 2003; Forester and Wells, 2011; Hasson et al., 2003). The fact that the OH yields of both unsaturated bonds were not obviously affected by RH suggestssuggested that the major pathway of OH generation in limonene ozonolysis is the was decomposition of ECIs through hydroperoxide channel. The possibility that other OH formation pathways also existed could cannot not be totally excluded, but we speculated that the contribution of any other pathways to OH formation was are not significant. Hence, it could be concluded that in limonene ozonolysis, the endocyclic DB iswas inclined to generate OH radicals through ECIs decomposition, while the exocyclic DB has ahad higher fraction of stabilization forming SCIs.

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3.4 Peroxycarboxylic acids generation

In our experiments, two kinds of peroxycarboxylic acids PFA (CH(O)OOH) and PAA (CH₃C(O)OOH) were

- 365 observed, and the yields of PFA and PAA both showed large discrepancies between the low-ratio and highratio sets of experiments (Fig. 3). The yields of PFA and PAA at high $[O_3]/[limonene]$ were about three times as much as those at low $[O_3]/[limonene]$. When the exocyclic DB was ozonated, the generation of PFA and PAA waswere enhanced to a large extent compared with only endocyclic DB ozonolysis, indicating that exocyclic DB ozonolysis had an important impact on PFA and PAA. As far as we know, this was the first time that such 370 high yields of PFA and PAA in alkene ozonolysis have beenwere reported. For both of PFA and PAA, the highest molar yields were observed when no OH scavenger was used, demonstrating that the OH reaction contributed to part of their formation. When OH radicals were scavenged, we speculated that PFA and PAA formation were mainly formed through ECIs isomerization and decomposition following the generation of HC(O)OO and CH₃C(O)OO radicals generation. These radicals could further react with HO₂ forming 375 peroxycarboxylic acids, which provided a plausible explanation for the higher yields of PFA and PAA observed in experiments with 2-butanol instead of than with cyclohexane.
- The yields of PFA and PAA had a positive relationship with water vapor concentration in all the cases, reaching the highest level at 90% RH. Model simulation results significantly underestimated the PAA formation and ignored the RH effect, indicating some missing pathways of PAA generation related to with water. Because of 380 the deficiency of PFA mechanism in MCM, we did notn't simulate the PFA formation., however, However, the similar variation tendency of PFA and PAA yields could provide some evidence for the assumption that they might have similar forming mechanism formation mechanisms. In previous studies, the dominant formation pathway of PAA was considered to beas the reaction of $CH_3C(O)OO$ radicals with HO₂ radicals (Groß et al., 2014; Lightfoot et al., 1992; Winiberg et al., 2016), while the formation pathway of PFA had notn²t been 385 identified yet and was speculated to be the reaction of HC(O)OO radicals with HO₂ radicals (Liang et al., 2015).

The rate constant of the RO₂ reaction with HO₂ washad been investigated in a series of studies and was thought

to be unaffected by water (Atkinson et al., 1999; Lightfoot et al., 1992; Tyndall et al., 2001; Wallington et al., 1992). Therefore, the increase of PFA and PAA yields with RH might be attributed to the promoting effect of water on HC(O)OO and $CH_3C(O)OO$ radicals radical generation. Because the highly reactive peroxides were easy to lose on the wall, chamber studies, which usually last for hours, might be hard to observe these peroxycarboxylic acids. In field observations, PAA is widelyare reported widely in remote and urban areas (Lee

et al., 2000; Liang et al., 2013; Zhang et al., 2010), yet there are few reports on about PFA existence in the

atmosphere (Liang et al., 2015). The results here demonstrated that limonene ozonolysis could contribute to

PFA and PAA formation, and although itsthe high instability and reactivity makes-made PFA difficult to

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395 observe, it may might have a short stay in the atmosphere.

3.5 Particulate peroxides and H₂O₂ generation

3.5.1 H₂O₂ evolution at low [O₃]/[limonene]

 H_2O_2 generation from SOA in the aqueous phase is thought to be a possible way of producing H_2O_2 in cloud water or releasing H₂O₂ continuously after inhalation. Here, we provided the quantitatively measured measurement of H₂O₂ generation from SOA produced in limonene ozonolysis in different cases. Considering that some unstable constituents would decay rapidly when SOA extract solution was kept at room temperature (298 K)-some unstable constituents would decay rapidly, we chose to keep the SOA solution at 4 °C to maintain the stability of the samples and prolong their storage time. In the low--ratio set of experiments, the concentration of total peroxides in solution nearly maintained stable in 48 h. The H_2O_2 concentration went through a brief 405 period of increase and then became stable. and H₂O₂ concentration could reach a steady state after going through a short rising period. After the aqueous H_2O_2 concentration reached a plateau, the amount of particulate H₂O₂ per particle mass formed in different cases, from 0% to 90% RH, was calculated and shown in Table 2.

Regardless of whether the No matter-OH scavenger was used or not, SOA produced at higher RH was inclined to ownhave a higher capacity of producing H_2O_2 . When no OH scavenger was used, the lowest H_2O_2 content per particle mass was ~ -1.13 ng/µg at dry condition, and the highest value was ~ -2.45 ng/µg at 90% RH. When 2-butanol was used the changing trend of H_2O_2 generation resembled the condition without scavenger, and the minimum was ~-1.33 ng/µg at 0% RH, while the maximum was ~-2.89 ng/µg at 80% RH, which was a little higher than the valuethat at 90% RH. It was interesting to note that, in the presence of cyclohexane, the trend of H_2O_2 generation in SOA solution differed greatly from both of the above. Even under dry condition, the H_2O_2 content per particle mass could reach \sim 3.22 ng/µg, and the maximum was \sim 4.63 ng/µg at 90% RH.

3.5.2 H₂O₂ evolution at high [O₃]/[limonene]

In the experiments of high [O₃]/[limonene], SOA produced with different scavengers was found to have different rates of generating H₂O₂ generation in solution at 4 °C, according to which we determined appropriate detection frequency and total duration for the three kinds of SOA. SOA produced without OH scavenger had the

- 420 lowest rate of generating H₂O₂ generation, so an eight-day measurement result was reported here. For SOA produced in the presence of 2-butanol, it was a little faster than the former on generating H_2O_2 generation was a little faster than the former and reached the limiting value within six days. However, SOA produced with cyclohexane had a much faster rate than both of the above, and the H₂O₂ concentration in solution became stable within three days. For all of the three typeskinds of SOA, the total peroxides concentration decreased slightly in the analysis duration, which was-concretely clarified in the Supplement.
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It is obvious that SOA produced in the high-ratio set of experiments has greater ability of generating H_2O_2 , and Fig. 4 shows the time profiles of H₂O₂ evolution of different kinds of SOA. When no OH scavenger was used, H₂O₂ concentration in solution rose constantly in about for six days then became stable. The limiting value of the

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 H_2O_2 generation was influenced by RH, which was ~-5.28 ng/µg at 0% RH, then increased gradually with increasing RH until 80% RH (~ 14.45 ng/µg). In the experiments with 2-butanol, the H₂O₂ concentration kept rising in the first four days, then it became stable. At dry condition Under dry conditions, the limiting value of the H₂O₂ content was ~-7.60 ng/µg, then it increased until 50% RH. SOA produced above 50% RH did notn²t show any obvious difference, and the highest H₂O₂ content was ~-15.50 ng/µg. When cyclohexane was added, the H₂O₂ concentration in solution increased rapidly rose up quickly in the first day then tended to become stable. The limiting value of H₂O₂ generation was also affected by water vapor concentration, yet the promoting effect was not very significant, and no largebig difference was observed above 30% RH. The limiting H₂O₂ content per particle mass was ~-16.64 ng/µg at dry condition and was ~-30.00 ng/µg above 30% RH.

3.5.3 Different stabilities of particulate peroxides

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$$\varphi_i = \frac{N_i}{N_{total}} \tag{1}$$

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where φ_i is the molar fraction of stable or unstable peroxides in particles, N_i (mol) is the molar number of moles of stable or unstable peroxides in particles, and N_{total} (mol) is the molar number of moles of total peroxides in particles. At low $[O_3]/[limonene]$, the molar fraction of unstable peroxides in SOA was around 0.11-0.13 in the case of adding no scavenger, which was similar towith the case of adding 2-butanol. In the presence of cyclohexane, the molar fraction of unstable peroxides would increase to 0.20-0.32. At high

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 $[O_3]/[limonene]$, the molar fractions of unstable peroxides in the case of adding no scavenger and adding 2-butanol were also similar, with both of them ranged in the range 0.13–0.25, yet this value would reach ~ 0.50 when cyclohexane was used. Detailed information <u>is provided was shown</u> in the Supplement. Model results showed that most peroxides produced in the reaction were ROOH and R(O)OOH, in addition, some studies proposed that peroxyhemiacetals also made important contribution to aerosol (Tobias and Ziemann, 2000; Tobias et al., 2000). The acetal reaction producing peroxyhemiacetals <u>wasis</u> reversible, so part of the peroxyhemiacetals in SOA were possible to hydrolyze andmay have hydrolyzed to form some peroxides. To investigate the stabilities of ROOH and R(O)OOH, we synthesized methyl hydroperoxide (MHP) and ethyl hydroperoxide (EHP) to represent ROOH. As for R(O)OOH, PFA and PAA were used to represent R(O)OOHas representative. All the synthesis solutions were stored at 4_°C, which was the same <u>aswith</u> the experimental condition. PFA and PAA were found to decompose and generate H₂O₂ within several days, yet MHP and EHP maintained stable. Hence₂ we speculated that peroxycarboxylic acids and peroxyhemiacetals might be the main components of unstable peroxides in particles, and they contribute to H₂O₂ generation in the aqueous phase.

The amount of H_2O_2 generation at low $[O_3]/[limonene]$ measured here was comparable with the published value of H_2O_2 produced from α -pinene SOA in solution (Li et al., 2016; Wang et al., 2011). However, at high $[O_3]/[limonene]$, the H_2O_2 generation level increased significantly, which proved that the multi-generation oxidation improved the formation of peroxycarboxylic acids and peroxyhemiacetals in particles. These results demonstrated that SOA produced in limonene ozonolysis could behave as an important source of H_2O_2 in the aqueous phase, and they also showed the difference between the SOA formed from single-unsaturated monoterpene ozonolysis and double-unsaturated monoterpene ozonolysis.

3.5.4 The effect of OH scavenger

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Prior researches Researches before have provided evidence for OH radicals formation in ozonolysis experiments.

and OH scavenger is often used to avoid the disturbance of the_OH reaction. Both_2-butanol and cyclohexane used here-_are-both commonly used OH scavengers, and Chew and Atkinson (1996) showed that there was no difference in their abilities to scavenge OH radicals. However, it should be noted that OH scavenger could convert OH radicals into a mixture of hydroperoxy (HO₂) and alkylperoxy (RO₂) radicals and a_higher $[HO_2]/[RO_2]$ is observed when 2-butanol is used (Docherty and Ziemann, 2003; Jonsson et al., 2008a). As shown in the Sect. 3.6.1, the fact that both at low and high $[O_3]/[limonene]$, the SOA yield was higher with 2-butanol than cyclohexane suggested that the increase inof HO₂ concentration promoted the SOA formation. This result is consistent with that suggested by Keywood et al. (2004) who observed the higher $[HO_2]/[RO_2]$ resulting in higher SOA yield in cyclohexene ozonolysis, while Docherty and Ziemann (2003) showed that increased $[HO_2]/[RO_2]$ inhibited aerosol formation in β-pinene ozonolysis.

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Some studies demonstrated that acid and peroxide products were sensitive to OH scavengers (Ahmad et al., 2017; Henry and Donahue, 2011; Ma et al., 2008). Here through investigating the stabilities of particulate peroxides formed in different conditions, we showed that the choice of OH scavenger would influence the types of particulate peroxides produced in the reaction. In the Sect. 3.5.3, we suggest that peroxycarboxylic acids and peroxyhemiacetals be the main components of unstable peroxides in particles. The peroxyhemiacetals formed by heterogeneous reactions of peroxides and aldehydes could dissociate into these species, yet the formation of peroxyhemiacetals was not supposedconsidered to be affected by the OH scavenger since both of the peroxides and carbonyl compounds observed in the gas phase did not show large differences when the OH scavenger changed. We speculate that the impact of OH scavenger on particulate peroxides could be mainly attributed to the formation of peroxycarboxylic acids under different [HO₂]/[RO₂]. Keywood et al. (2004) indicated that the OH scavenger impacted the HO₂ reaction with acylperoxy radicals forming acid and peracid products, which were considered to have low volatility. With higher HO₂ concentration, the SOA yield in the presence of

2-butanol was higher than that in the presence of cyclohexane, since the HO₂-acylperoxy reactions contributed to some low-volatility products. However, the RO₂ radicals formed from cyclohexane may also participate into reactions and help produce more unstable peroxycarboxylic acids which could partition into the particle phase.

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3.6 Contribution of peroxides to SOA

3.6.1 SOA formation

The yield of SOA produced from limonene ozonolysis in different cases <u>ranging_from 0%</u> to 90% RH was measured. The SOA yield is defined as the ratio of aerosol mass concentration to the mass concentration of limonene consumed, as <u>given by Eq.</u> (S4) (in the Supplement). In the six different cases, SOA yield was determined to be unaffected by water, yet it showed strong dependence on the reactants ratio and the use of OH scavenger, <u>as_which_was_shown</u> in Table 3. Whether at low or high $[O_3]/[limonene]$, the case of none OH scavenger had the highest SOA yield, which suggested the effect of OH reaction on aerosol formation, and the order of SOA yield was no scavenger > 2-butanol > cyclohexane. The case <u>with_owning_the</u> highest SOA yield was high $[O_3]/[limonene]$ without OH scavenger (0.511 ± 0.097), while the lowest SOA yield was detected at

low $[O_3]/[limonene]$ with cyclohexane (0.288 ± 0.038) .

3.6.2 Peroxides mass fraction

In this study, <u>we used</u> the iodometric method was used to analyze the particle-phase total peroxides content in limonene ozonolysis. The iodometric method is commonly regarded as a standard method <u>forof</u> detecting total peroxides and it could almost quantify all kinds of peroxides (Bonn et al., 2004; Jenkin, 2004). The mass fraction used here is defined as the ratio of particulate peroxides mass to SOA mass, as <u>given in</u> Eq. (S5) (in the Supplement). The average molecular weight of peroxides in particles is assumed to be 300 g/mol, which is

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estimated to be slightly less than the molecular weight of peroxyhemiacetals, and this value has been used to calculate the mass of particulate peroxides in some studies (Docherty et al., 2005; Nguyen et al., 2010; Surratt et al., 2006). The mass fractions of peroxides in the six cases from 0% to 90% RH <u>arewere</u> summarized in Table 3. In each case, the peroxides mass fraction in SOA increased slightly with RH, and <u>there was a significant</u> difference-existed between the low-<u>ratio</u> and high-<u>ratio</u> sets of experiments, while the <u>there was little</u> effect of the_OH scavenger-was-little. The mass fraction of peroxides at low $[O_3]/[limonene]$ was usually below 0.2, however, at high $[O_3]/[limonene]$ the peroxides mass fraction increased to 0.4–0.6. Docherty et al. (2005) reported that the peroxides mass fraction in α -pinene SOA was ~0.47, while for β -pinene SOA the fraction was ~-0.85. Li et al. (2016) observed that peroxides could account for ~-0.21 in α -pinene SOA. Here we first reported-We are the first to report the mass fraction of peroxides in SOA derived from limonene ozonolysis, highlighting the important role of organic peroxides in SOA composition, especially when multi-generation oxidation happenshappened.

525 **3.6.3 Peroxides partitioning**

The molar yields of HMW peroxides in both gas phase and particle phase were determined in different cases. There was little effect of RH and OH scavenger, while <u>underat</u> high $[O_3]/[limonene]$ the HMW peroxides yield increased by ~ 10% in contrast with the <u>yield atcondition of</u> low $[O_3]/[limonene]$. Furthermore, the gas-phase HMW peroxides and particle-phase HMW peroxides were discussed separately, which was shown in Fig. 5. For

gas-phase HMW peroxides, the molar yield showed a decreasing tendency with increasing RH, which was obvious at high [O₃]/[limonene]. For particle-phase HMW peroxides, the molar yield showed a slight increasing dependence on RH and their yield was promoted significantly by <u>oxidizing-the</u> degree_of oxidation. A possible explanation for the RH effect was that the water content in aerosol would increase when RH increased, and this

promoted the uptake of some compounds into particles. However, some researches proved that water the effect of water on the partitioning of organic products seemed to be small especially when no inorganic seed particles were used (Jonsson et al., 2006, 2008a, b), so Thus, we proposed that the promoting effect of water on particulate HMW peroxides cancould be mainly attributed to the effect of water participating in some gas-phase and particle-phase reactions resulting in the formation of more low-volatility peroxides-formation. The contribution of multi-generation -oxidation products to SOA formation in limonene ozonolysis had been stated 540 by some studies (Hoffmann et al., 1997; Ng et al., 2006), and the results here indicated that organic peroxides proportion might account for considerable of those products. On the one hand. а multi-generation Multi-generation oxidation helpsed produce more low-volatility peroxides in the gas phase that could partition into particles. What's moreand on the other hand, it could also accelerate accelerates the occurrence of some heterogeneous reactions bythrough providing more reactive species.

545 3.7 Contribution of carbonyls to SOA

3.7.1 Carbonvls formation

Carbonyl compounds including HACE, FA, AA, ACE, GL, and MGL were detected in the reaction. Unlike peroxides, whose generation often showed obvious increasing dependence on RH, only FA vield would increase with RH and the production of other carbonyls production were not significantly affected by water. The yields

of HACE, AA, ACE, GL, and MGL in different cases were summarized in Table 4. The fact that HACE formed 550 without OH scavenger but did not form when cyclohexane was used indicated that HACE might be generated from OH reactions. As for AA and ACE, both of their yields in the presence of cyclohexane were found to be lower than the case without scavenger, especially at low $[O_3]/[limonene]$. This suggested that OH reaction contributed to a potion of their formation and the endocyclic DB ozonolysis did not tend to generate AA and ACE. It was speculated that these three kinds of carbonyls could also generate from the reaction of 2-butanol or HO₂ radicals promoted their formation, so the presence of 2-butanol increased their yields. As regards GL and MGL, RH and OH scavenger did not <u>have a large make big</u>-influence, and both of their yields at high [O₃]/[limonene] were higher than the condition of low [O₃]/[limonene]. The generation of FA had a positive dependence on RH, which was specifically-illustrated in the Supplement and the total variation range could be found in Table 4.

3.7.2 Experimental and theoretical partitioning coefficients

A parameter that has been used widely to describe the partitioning feature of a compound is described as follows (Pankow, 1994; Pankow and Bidleman, 1992):

$$K_{p,i} = \frac{F_i / TSP}{A_i} \tag{2}$$

- 565 where $K_{p,i}$ (m³ µg⁻¹) is the partitioning coefficient of compound i, *TSP* (µg m⁻³) is the concentration of total suspended particulate matter, F_i (µg m⁻³) and A_i (µg m⁻³) are the particulate and gaseous concentrations of compound i, respectively. The measured partitioning coefficients of FA, AA and ACE were on the magnitude of 10⁻⁵ m³ µg⁻¹, and the partitioning coefficients of HACE, GL, and MGL were on the magnitude of 10⁻⁴ m³ µg⁻¹.
- 570 Theoretical gas-particle partitioning coefficients of these compounds were calculated using the absorption equilibrium equation defined by Pankow (1994), which <u>has beenwas</u> used widely to estimate the ability of a substance to partition into the particulate phase and <u>to predict SOA yield in models</u> (Griffin et al., 1999; Hohaus et al., 2015; Odum et al., 1996; Yu et al., 1999):

$$K_{p,i} = \frac{760 R T f_{om}}{MW_{om} \, 10^6 \, \zeta_i \, p_{L,i}^0} \tag{3}$$

where Where R is the ideal gas constant (8.206 × 10⁻⁵ m³ atm mol⁻¹ K⁻¹), T is the temperature (K), f_{om} is the mass fraction of TSP that is the absorbing organic material (om) and is equal to 1, which is 1 here, MW_{om} (g mol⁻¹) is the mean molecular weight of the om phase, which is estimated to be 130 g mol⁻¹ in this study, ζ_i is the activity coefficient of compound i in the om phase, which is assumed to be unity, and $p_{L,i}^0$ (Torr) is the vapor pressure of compound i, which is predicted by the method of Moller et al. (2008). The calculated gas-particle partitioning coefficients of HACE, FA, AA, ACE, GL, and MGL were 3.972×10^{-8} m³ μ g⁻¹, $2.096 \times 10^{-11} \text{ m}^3 \text{ }\mu\text{g}^{-1}\text{, } 1.624 \times 10^{-10} \text{ }\text{m}^3 \text{ }\mu\text{g}^{-1}\text{, } 6.192 \times 10^{-10} \text{ }\text{m}^3 \text{ }\mu\text{g}^{-1}\text{, } 5.476 \times 10^{-10} \text{ }\text{m}^3 \text{ }\mu\text{g}^{-1}\text{, } \text{and } 1.246 \times 10^{-9} \text{ }\text{m}^3 \text{ }\mu\text{g}^{-1}\text{, } 1.624 \times 10^{-10} \text{ }\text{m$ 580 respectively, at 298K. The experimental K_p value of HACE was about 10,000 times larger bigger than the theoretical value, and for other carbonyls, the experimental K_p was about 100,000 times bigger larger than the theoretical value. The gap between the experimental K_p and predicted K_p of GL and MGL we estimated was comparable with the results of Healy et al. (2008, 2009), but it was higher than that of Ortiz et al. (2013). The fact that the gas-particle partitioning coefficients of carbonyls observed were much higher than the theoretical values indicated that carbonyl compounds made a more important contribution tofor SOA formation than estimated. Although the partitioning coefficients measured in experiments showed huge difference with the calculated values, <u>a</u>some relationship between the measured K_p and the vapor pressure of carbonyl compounds was observed. Figure 6 showed shows the dependence of the measured $lg(K_p)$ and predicted $lg(K_p)$ on $lg(p^0)$, and their linear fitting curves. The slope of the linear fitting equation of the predicted $lg(K_p)$ versus $lg(p^0)$ was -0.964, and R² was 0.998. The slope of the linear fitting equation of measured $lg(K_p)$ versus $lg(p^0)$ was -0.484, and R² was 0.750, which indicated that the $lg(K_p)$ of carbonyls observed in laboratory also had <u>a</u> negative correlation with $lg(p^0)$. A plausible explanation for the large difference between the

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measured and predicted K_p was that carbonyl compounds were easy to polymerize and react with other species on particles, resulting in that these carbonyls existing existed in the forms of hydrates and oligomers in SOA (Corrigan et al., 2008; Hastings et al., 2005; Kroll et al., 2005; Volkamer et al., 2007). The hydrates and oligomers of carbonyls have much lower vapor pressures than their precursors, and they could reversibly return to their carbonyl monomers during analysis (Healy et al., 2008; Ortiz et al., 2013; Toda et al., 2014).

4 Conclusions and implications

600 This work reports on anAn experimental study of about the oxidation regime and SOA composition in limonene ozonolysis with respect to the roles of different DBs, radicals, and water-was reported in this work. A series of oxidizing products owning the oxidizing capacity including SCIs, OH radicals, and peroxides in both gaseous and particulate phases were detected. Based on the variation of H_2O_2 and HMHP generation on RH, the importance of the reaction of limonene SCIs reaction with water was confirmed and the yield of SCIs could be 605 estimated as, which was ~ -0.24 for endocyclic DB and ~ -0.43 for exocyclic DB. OH yields of endocyclic and exocyclic DBs were indirectly determined to be ~ -0.65 and ~ -0.24 , demonstrating the different reaction mechanisms of different DBs in limonene ozonolysis. The formation of two peroxycarboxylic acids PFA and PAA was observed, and their high yields were first reported in alkene ozonolysis. The yields of PFA and PAA increased with RH and oxidizing the degree of oxidation, showing the effect of water and the exocyclic DB 610 oxidation on their formation. The H_2O_2 generation from SOA in solution provided evidence for the ability of SOA to contribute oxidants in the aqueous phase. And through investigating the stabilities of particulate peroxides formed underin different conditions, we showed that the choice of the OH scavenger would influence the types of particulate peroxides produced in the reaction. The partitioning behaviors of peroxides and carbonyls were discussed in this paper, and the results showed their importance to SOA formation. Particulate

peroxides could account for less than 0.2 in limonene SOA at low [O₃]/[limonene] and 0.4–0.6 at high 615 [O₃]/[limonene], which proved the important role of peroxides in SOA composition especially when multi-generation oxidation happened. Due to their ability to polymerize and react with other species on particles. the carbonyl compounds often exist in SOA in forms of hydrates and oligomers whose vapor pressures are much lower than that of their precursors. The partitioning coefficients of carbonyls observed in laboratory were 620 always several orders of magnitude higher than the theoretical values, indicating that their contribution to SOA was higher than estimated. the estimation. Limonene shows its specificity in many aspects because of its different DBs, suggesting that some influence of terpenes containing more than one DB in the atmosphere might be underestimated before. Limonene is unique in many aspects because of its different DBs, suggesting that terpenes with multiple double bonds may have more complex effects on the atmosphere than previously thought. 625 The results demonstrated the effect of oxidizing the degree of oxidation, radical chemistry, and water on limonene SOA composition, while some particulate products especially peroxides should be studied further. The implications of limonene chemistry in the atmosphere are were close with the multi-generation oxidation that occurshappened on its different DBs, and whether the phenomena could be observed in other terpenes oxidation that containeontained more than one DB needsneeded more laboratory evidence.

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Exp.	[Limonene]	[O ₃]		[OH Scavenger]	RH
	(ppbv)	(ppbv)	OH Scavenger	(ppmv)	(%)
L(No-sca)	280	500		_	0–90
L(2-But)	280	500	2-butanol	350	0–90
L(C-hex)	280	500	cyclohexane	420	0–90
H(No-sca)	183	19000		—	0–90
H(2-But)	183	19000	2-butanol	350	0–90
H(C-hex)	183	19000	cyclohexane	420	0–90

 Table 1. Experimental Conditions.

Note: L, low [O₃]/[limonene]ratio; H, high [O₃]/[limonene]ratio; No-sca, none scavenger; 2-But, 2-butanol; C-hex,

cyclohexane; RH, relative humidity.

1030 **Table 2.** H_2O_2 generation per particle mass (ng/ug) in SOA formed with different OH scavengers in the relative humidity (RH) range of 0%–90% at<u>under</u> low $[O_3]/[limonene]$ ratio.

	0% RH	10% RH	30% RH	50% RH	70% RH	80% RH	90% RH
No-sca	1.13±0.22	$1.42{\pm}0.40$	1.53±0.28	1.88±0.16	2.24±0.42	2.26±0.44	2.45 ± 0.48
2-But	1.33±0.15	1.56±0.18	1.77±0.12	2.02 ± 0.65	2.55±0.43	$2.89{\pm}0.42$	2.66±0.57
C-hex	3.22±0.52	3.95±0.43	4.12±0.40	4.22±0.33	4.63±0.24	4.26±0.33	4.63±0.96

Note: No-sca, none scavenger; 2-But, 2-butanol; C-hex, cyclohexane.

	L(No-sca)	L(2-But)	L(C-hex)	H(No-sca)	H(2-But)	H(C-hex)
0% RH	0.065 ± 0.006	0.101 ± 0.009	$0.087 {\pm} 0.011$	0.401±0.016	$0.502{\pm}0.008$	$0.477 {\pm} 0.010$
10% RH	0.091 ± 0.010	0.124±0.013	0.113±0.009	0.436±0.009	$0.534 {\pm} 0.009$	$0.502{\pm}0.013$
30% RH	0.125±0.010	0.147 ± 0.011	0.143±0.015	0.458±0.020	0.553±0.015	$0.506{\pm}0.011$
50% RH	0.149 ± 0.007	0.174 ± 0.011	0.161±0.016	0.466±0.016	0.571±0.009	$0.512{\pm}0.007$
70% RH	0.155±0.009	0.178 ± 0.009	0.169±0.014	0.486±0.023	0.576±0.010	$0.503{\pm}0.011$
80% RH	0.169±0.013	0.189±0.010	0.189±0.012	0.492±0.015	0.580±0.013	$0.502{\pm}0.014$
90% RH	0.156±0.010	0.183±0.013	0.189±0.013	0.492 ± 0.017	0.580 ± 0.018	0.506 ± 0.016
SOA Yield	0.379±0.039	0.337±0.048	0.288±0.038	0.511±0.097	0.479 ± 0.044	0.401 ± 0.068

Table 3. The SOA yield and mass fraction of particulate peroxides at low or high [O₃]/[limonene] ratio in the presence or absence of OH scavenger from 0% to 90% relative humidity (RH).

Note: L, low [O₃]/[limonene]ratio; H, high [O₃]/[limonene]ratio; No-sca, none scavenger; 2-But, 2-butanol; C-hex,

cyclohexane.

Table 4. Yields (%) of carbonyls at low or high [O₃]/[limonene] ratio in the presence or absence of OH scavenger.

	HACE	FA	AA	ACE	GL	MGL
L(No-sca)	2.04 ± 0.48	7.02±0.90-10.58±0.94	1.32±0.24	0.22±0.15	0.89±0.25	0.56±0.34
L(2-But)	3.94±0.55	$4.90 \pm 0.86 - 7.77 \pm 0.86$	3.98±0.60	0.35±0.18	$0.69{\pm}0.25$	0.55±0.44
L(C-hex)	—	5.21±0.66-8.25±0.55	—	—	0.81 ± 0.24	0.67±0.56
H(No-sca)	4.45±0.52	13.11±0.63-27.00±1.56	2.16±0.84	0.79±0.22	1.33±0.41	1.35±0.61
H(2-But)	10.15±2.11	11.03±0.77-23.33±0.62	7.86±1.32	$1.00{\pm}0.28$	1.25±0.36	1.31±0.21
H(C-hex)	—	10.80±1.28-23.32±1.21	1.89±1.22	$0.60{\pm}0.47$	1.25±0.51	1.23±0.22

Note: —, below detection limit; L, low [O₃]/[limonene]ratio; H, high [O₃]/[limonene]ratio; No-sca, none scavenger; 2-But,

2-butanol; C-hex, cyclohexane; HACE, hydroxyacetone; FA, formaldehyde; AA, acetaldehyde; ACE, acetone; GL, glyoxal;

MGL, methylglyoxal.



Figure 1. Dependence of (a) H₂O₂ yield and (b) HMHP yield on relative humidity (RH) at low or high [O₃]/[limonene] ratio in the presence or absence of OH scavenger (2-butanol or cyclohexane). H₂O₂, hydrogen peroxide; HMHP, hydroxymethyl hydroperoxide; L, low [O₃]/[limonene]ratio; H, high [O₃]/[limonene]ratio; No-sca, none scavenger; 2-But, 2-butanol; C-hex, cyclohexane.



Figure 2. The reaction scheme of endocyclic and exocyclic double bonds in limonene ozonolysis



Figure 3. Dependence of (a) PFA yield and (b) PAA yield on relative humidity (RH) at low or high [O₃]/[limonene] ratio in the presence or absence of OH scavenger (2-butanol or cyclohexane). PFA, peroxyformic acid; PAA, peroxyacetic acid; L, low [O₃]/[limonene]ratio; H, high [O₃]/[limonene]ratio; No-sca, none scavenger; 2-But, 2-butanol; C-hex, cyclohexane.



1065Figure 4. Time profiles of H_2O_2 evolution per particle mass of different SOA formed (a) without OH scavenger, (b) with2-butanol, and (c) with cyclohexane in the relative humidity (RH) range of 0–90% atunder high $[O_3]/[limonene]$ ratio. H_2O_2 ,hydrogen peroxide; No-sca, none scavenger; 2-But, 2-butanol; C-hex, cyclohexane.



Figure 5. The variation of (a) gas-phase and (b) particle-phase high-molecular-weight peroxides molar yields with relative humidity (RH) at low or high [O₃]/[limonene] ratio in the presence or absence of OH scavenger (2-butanol or cyclohexane).
L, low [O₃]/[limonene]ratio; H, high [O₃]/[limonene]ratio; No-sca, none scavenger; 2-But, 2-butanol; C-hex, cyclohexane.



Figure 6. The relationship of measured and predicted partitioning coefficients ($\mathbf{m}^3 \ \mu g^{-1} \mathbf{K}_p$) versus vapor pressure (\mathbf{atmp}^{θ}) of carbonyls produced in limonene ozonolysis. \mathbf{K}_p , partitioning coefficients, \mathbf{p}^0 , vapor pressure, HACE, hydroxyacetone; FA, formaldehyde; AA, acetaldehyde; ACE, acetone; GL, glyoxal; MGL, methylglyoxal.