Response to Reviewer 2

We gratefully thank you for your constructive comments and thorough review. Below are our responses to your comments.

(Q=Question, and A=Answer)

General Comments:

Q1. It seems that "SOA property" should be replaced by SOA composition.

A: We have revised it.

Q2. It seems that "oxidation transition" should be replaced by "oxidation regime" or something similar. Do you mean to indicate the effect of adding OH scavenger? Please clarify.

A: Thanks for your suggestion and "oxidation regime" is used in the revised manuscript. In this study, the objective of investigating the oxidation regime of alkene ozonolysis is to understand the formation of the oxidizing products in limonene ozonolysis. These compounds, including OH radicals, stabilized Criegee intermediates, and peroxides, are critical to atmospheric oxidation processes since they own the power of oxidizing other species. We clarify this in the revised introduction.

Q3. There are a number of places where introductory material shows up in the results and discussion, such as the historical perspective on OH formation in section 3.3. Please move this material to the introduction. The introduction itself needs a much clearer/more logical flow of ideas.

A: We follow the advice of the reviewer and all of the introductory materials shown in the Sect. 3.2, Sect. 3.3, and Sect. 3.4 are now moved to the introduction. The introduction has been restructured and shortened.

Q4. Add a clearer discussion/explanation of why the two OH scavengers had different effects.

A: The reviewer concerns the effect of two OH scavengers hence the following content has been added into the Sect. 3.5.4 of the revised text.

Researches before have provided evidence for OH radicals formation in ozonolysis experiments and OH scavenger is often used to avoid the disturbance of OH reaction. 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 (HO_2) and alkylperoxy (RO_2) radicals and higher $[HO_2]/[RO_2]$ is observed when 2-butanol is used (Docherty and Ziemann, 2003; Jonsson et al., 2008). 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 with cyclohexane suggested that the increase of HO_2 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.

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 reactions. 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 supposed to be affected by OH scavenger since both of the peroxides and carbonyl compounds observed in the gas phase did not show large differences when 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 $[HO_2]/[RO_2]$. Keywood et al. (2004) indicated that the OH scavenger impacted the HO_2 reaction with acylperoxy radicals forming acid and peracid products, which were considered

to have low volatility. With higher HO_2 concentration, the SOA yield in the presence of 2-butanol was higher than that in the presence of cyclohexane, since the HO_2-acylperoxy reactions contributed to some low-volatility products. However, the RO_2 radicals formed from cyclohexane may also participate into reactions and help produce more unstable peroxycarboxylic acids which could partition into the particle phase.

Q5. Add a clearer discussion of measurement techniques, particular the coil collector, with diagrams of the flow reactor and coil collector in the supplement.

A: We have better explained the measurement techniques in the revised manuscript. 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) and is controlled at a temperature of 4 °C with H_3PO_4 solution (pH 3.5) serving as the rinsing solution. The diagrams of the flow tube reactor, the coil collector, and the Horibe tube are added in the Supplement.

Q6. The differences in yields are often overstated or exaggerated. For example, the peroxide mass fraction was determined in the three scavenger cases and discussed as if there were significant differences among these cases (Lines 484-487). But in fact, the differences were fairly small. Please check over all comparisons in the manuscript and only state differences if they can be supported statistically, otherwise characterize them as similar.

A: We have revised it and other comparisons in the text are also checked.

Q7. A theme of the paper is the different effects from each of the two double bonds in limonene reacting with ozone. But your discussion of the ozonolysis of the endo and exo double bonds (e.g, Lines 320-323) is misleading, because the ozonolysis of the endo-DB will generally precede ozonolysis of the exo-DB. Your experiments can only isolate the ozonolysis of the endo-DB due to the discrepancy in reaction rates, which you do state. The ozonolysis of what was originally the exo-DB may not occur on the exo-DB of limonene, but

rather on the remaining DB in an ozonolysis product of limonene. This is clearly stated in the final paragraph of Herrmann et al. "It should be noted that the measured OH-radical yield of the second double bond is the sum of all possible products formed from the reaction of ozone with the first double bond of the monoterpene."(1)

A: We regret that in the previous version we did not clarify well enough. We have added an explanation in Sect. 3.2 for that. The SCIs yield of exocyclic DB ozonolysis estimated here was not for a specific product formed from endocyclic DB ozonolysis, but the sum of first-generation products with a remaining double bond.

Q8. Too often the past tense is used incorrectly. For example, line 288 should read, "Figure 3 shows . . ."

A: We have revised it and other similar mistakes are also corrected.

Q9. Calculated values are rarely supported by equations that clearly show how the calculation was done (however simple they may be). Add equations, either in the main text or supplement, that show how all yields are calculated.

A: We follow the advice of the reviewer and in the Supplement a summary of the calculation equations have been added, which includes the equations to calculate the wall loss fraction, the molar yield of products, the molar yield of SCIs, the SOA yield, and the mass fraction of particulate peroxides.

Specific Comments:

Q10. Figures 1 and 2. Neither of these needs to be in the main manuscript, both should be moved to supplemental. You should replace these with a scheme that indicates what chemistry you are investigating, particularly to show that the second DB oxidized is part of the products from the initial ozonolysis (such as Fig.2 from Herrmann et al.). (1)

A: Figure 1 and Figure 2 have been moved to the Supplement and a scheme of endocyclic and exocyclic double bonds of limonene reaction with ozone (Figure 2) is added in the revised manuscript.

Q11. Figure 3. The different markers are hard to distinguish. Please change the markers you use to make it

easier to determine what experiment each line corresponds to. You might also label the two groups of lines (low and high ratios of ozone to limonene).

A: Thanks for your suggestion. We have changed the markers and labeled the two groups of lines in Figure 1 and Figure 3 in the revised text.

Q12. Figure 6. The lines are not helpful, please use just markers for each data point.

A: We have revised it.

Q13. Lines 75-79 The ability of SCI to react with water is grossly overstated, even though it may be an important source of peroxides in the case of limonene. Review the discussions and add references to publications such as Long et al.(2) and Drozd et al.(3) that discuss lifetimes of SCI for bimolecular reaction and unimolecular decomposition.

A: We thank the reviewer for pointing us to these references, which we now include in the revised paper. Besides, we have clarified in the Sect. 3.2 that considering that a portion of SCIs might undergo unimolecular decomposition, the SCIs yield estimated here represented a lower limit. In the Sect. 3.3 the results demonstrated that the OH yield was not obviously affected by RH, we speculated that the fraction of SCIs that decomposed and formed OH radicals was small.

Q14. Line 265-267 Specify the lifetimes for each loss process. You need to define "relatively long lifetime" with current quantitative estimates and relate this to unimolecular decomposition.

A: Thanks for your suggestion and we have defined the lifetimes of SCIs in the Sect. 3.2. In previous studies, the unimolecular decomposition of SCIs and the reactions of SCIs with water showed strong structure dependence. For CH_2OO and anti-CH_3CHOO, the atmospheric lifetimes of their bimolecular reactions with H_2O and $(H_2O)_2$ were less than 1 ms, while their lifetimes of unimolecular reaction were much longer (Lin et al., 2016; Sheps et al., 2014; Taatjes et al., 2013; Welz et al., 2012). For syn-CH_3CHOO and $(CH_3)_2COO$, the

atmospheric lifetimes of their bimolecular reactions with H_2O and $(H_2O)_2$ were more than 100 ms, while their lifetimes of unimolecular reaction were just 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 H_2O and $(H_2O)_2$ were not quantified. Tillmann et al. (2010) inferred that about 46% ECIs formed from α-pinene ozonolysis would stabilize and at 44% RH about 65% SCIs formed H_2O_2 after reacting with water and 28% 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 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.

Q15. Line 310 What reactions were suppressed? Support or contrast this result with literature on SCI reactivity.

A: We regret for the unclear expression and we have better explained this in the revised manuscript. These suppressed reaction channels include the unimolecular decomposition of SCIs and the reactions of SCIs with other products in the system. For SCIs containing three or less carbon atoms, their unimolecular decomposition and reactions with water showed strong structure dependence, which have been clarified in the revised text. However, as for large SCIs their reaction pathways are still not clear. Tillmann et al. (2010) inferred that about 46% ECIs formed from α-pinene ozonolysis would stabilize and at 44% RH about 65% SCIs formed H_2O_2 after reacting with water and 28% 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. The results in this study indicated that at high RH the unimolecular decomposition of

limonene SCIs could be suppressed by their bimolecular reactions with water monomer and water dimer.

Q16. Line 317. You need to add equations that show how you calculate these yields, possibly in the supplemental.

A: We have added equations in the Supplement.

Q17. Section 3.5.3 You need to show in an equation how you calculate the relative amounts of stable and unstable peroxides.

A: We have added the equation in Sect. 3.5.3.

Q18. Line 479 Why was a MW of 300 g/mol assumed? Support with references or appropriate justification.

A: The average molecular weight of peroxides in particles is assumed to be 300 g/mol, which is 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). We clarify this in the revised manuscript.

Q19. Line 504 Awkward sentence. What does "chemical effect" mean in this case?

A: We are sorry for not explaining that clearly. The chemical effect means the effect of water participating in some gas-phase and particle-phase reactions resulting in more low-volatility peroxides formation. This is now better explained in the revised text.

Q20. There are many grammatical errors and awkward sentences. Below is a partial list of these. Check over the entire manuscript again.

13 – "radical pha chemistry" 25 "Considerable generation of H2O2 from SOA in the aqueous se" 28 "SOA composition" (and throughout paper) 39-40 "suggest that the. . .need further study" 45 "Total monoterpene emissions are estimated to be.." 47 "non-negligible. . ." 64 "esters" 79 "reactions of alkenes. . ." 103 "Due to abundant water vapor..." 169 "first generation" 222 "constituents were generated" 280 "prior to generating

aldehyde" 293 "There was little to no effect of scavenger" 385 "chamber studies" 516"HACE might be generated. . ."

A: Thanks for your suggestion and we have revised all of these mistakes mentioned above. We also check over the manuscript seriously and correct other errors.

References

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