**Interactive comment on “Understanding the oxidants transition and SOA property in limonene ozonolysis: Role of different double bonds, radical chemistry, and water” by Yiwei Gong et al.**

**Anonymous Referee #2**

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Summary “Understanding the oxidants transition and SOA property in limonene ozonolysis: Role of different double bonds, radical chemistry, and water” describes a range of aspects of SOA formation from limonene ozonolysis. Experiments were carried out in a flow tube reactor with varying oxidant to limonene ratios and humidity. Scavengers were used to reduce OH concentrations during oxidation. Measurements were based on filter-based methods and collection of gas phase compounds in a coil collector. Peroxides were formed in significant amounts that increased with higher ozone to limonene ratio, suggesting the importance of the ozonolysis of the exo double bond in their formation. The formation and partitioning of carbonyls was also determined, and the partition coefficients (Kp) were found to be orders of magnitude larger than predicted. The sustained production of H2O2 from sampled particles over the course of several days suggests varying ability of the limonene ozonolysis products to form oxidants in aerosol. Humidity was shown to consistently increase the formation of products that could evolve hydrogen peroxide in the particle phase. Small peroxide formation (e.g. peroxyformic acid) had increased production with higher RH. There were small effects of humidity on formation of larger peroxides in particles and a general decrease in gas-phase larger peroxide formation with increasing RH. The stability of peroxides formed was estimated based on total peroxides and hydrogen peroxide evolution after SOA formation. This manuscript present a number of interesting results and could be published with significant improvement in clarity and presentation.

General Comments:

- It seems that “SOA property” should be replaced by SOA composition.
- 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.
- 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.
- Add a clearer discussion/explanation of why the two OH scavengers had different effects. Add a clearer discussion of measurement techniques, particular the coil collector, with diagrams of the flow reactor and coil collector in the supplement.
- 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.

C1
and only state differences if they can be supported statistically, otherwise characterize them as similar.

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)

Too often the past tense is used incorrectly. For example, line 288 should read “Figure 3 shows…”. 

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.

Specific Comments

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)

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).

C3

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

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.

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.

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

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

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

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

Line 504 Awkward sentence. What does “chemical effect” mean in this case?

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

13 – “radical chemistry” 25 “Considerable generation of H2O2 from SOA in the aqueous phase” 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...”

References