Response to Reviewer #2

We gratefully thank you for your constructive comments and through review. Below are our point-by-point responses to your comments.

(Q=Question, A= Answer, C=Change in the revised manuscript)

General Comments: This manuscript by Gong and Chen describes a series of laboratory experiments, aiming to elucidate the contribution of stabilized Criegee intermediates (SCIs) to the formation of SOA from limonene. The authors used a creative flow tube setup to investigate SCIs arising from ozonation of the endo- and exo-double bonds (DBs) separately. By employing an SCI scavenger in the system, the authors claimed that they have quantified the contribution of SCI chemistry towards the SOA yields as a function of RH. The major conclusion is that water plays a complex role in the reaction system, suppressing SOA formation under low RH, while facilitating SOA formation at high RH. Over the past few years, the importance of SCI chemistry in the atmosphere has become evident. With SCI being a reactive intermediate that is difficult to detect, quantitative evaluations for the importance of SCI is lacking. This manuscript aims to provide quantitative information that fills our gap in understanding. The topic is timely and is within the scope of ACP. The writing and data analyses were conducted with caution. However, I have concerns regarding a few approaches and assumptions that authors employ in the study. I recommend a major revision before publication on ACP.

A: We highly appreciate your comments and suggestions. The questions you mentioned are answered as follows.

Major comments:

Q1. I'm afraid that the contribution of SCI to the SOA formation may be exaggerated in the current setup due to the presence of a high concentration of butanol (OH scavenger). The authors provided an estimate that 12.5% of SCI has reacted with butanol, using a lower-band estimate for the SCI reactivity with alcohol. It is not convincing that the effect of butanol is "not important (Line 304)". Can the author perform an experiment with an aprotic OH scavenger (e.g., hexane) to experimentally confirm their assumption?

A1: Thanks for your suggestion. Here to evaluate whether the addition of 2-butanol made obvious impacts on the results, we conducted experiments with cyclohexane as OH scavenger, and the results were discussed as follows.

Part of SCIs might react with 2-butanol, producing α-alkoxyalkyl-hydroperoxides and contributing to the observed SOA, especially when using low concentrations of AA and water. To figure out whether the SOA formation potentials of SCIs estimated here were higher than those under the situation without 2-butanol, the experiments with cyclohexane as OH scavenger were carried out. Here three representative conditions: dry conditions, 40% RH (representing low-humidity conditions) and 80% RH (representing high-humidity conditions), were analyzed in the endo-DB ozonolysis. The abilities of 2-butanol and cyclohexane on scavenging OH radicals were similar (Chew and Atkinson, 1996), however, the use of different OH scavengers brought different impacts on the reaction system. When 2-butanol was used, higher $[HO_2]/[RO_2]$ was observed, which was thought to be more similar to the atmospheric conditions, while adding cyclohexane resulted in a lower $[HO_2]/[RO_2]$ (Docherty and Ziemann, 2003; Jonsson et al., 2008). In view of this, this study chose 2-butanol as OH scavenger, while the use of cyclohexane could provide a contrast to help us better understand the mechanisms in the reaction system.

In the experiments with cyclohexane, the concentrations of limonene and O_3 were about 90 ppbv and 270 ppbv, and the reaction time was 240 s. Around 400 ppmv of cyclohexane was added to scavenge OH radicals. With the addition of cyclohexane, the SOA yields were found to be lower than those with the addition of 2-butanol, suggesting that higher concentration of HO_2 radicals promoted aerosols formation (Keywood et al., 2004). Through adding different concentrations of AA (24–480 ppbv), the amount of SCIs in the reaction system was regulated and calculated as elaborated in Sect. 3.1, and the dependence of SOA mass concentration on the amount of SCIs was shown in Fig. S8. The SCIs reactions still accounted for more than 60% in SOA formation and according to the fitting results, the SOA formation potentials of SCIs under the use of cyclohexane were even a bit larger than those under the use of 2-butanol, and the deviations were within 12%. This phenomenon was speculated to be due to the higher concentration of RO_2 radicals when using cyclohexane, promoting the reactions of SCIs with RO_2.

To further determine the impact of 2-butanol, we also conducted experiments with the concentration of 2-butanol as about 150 ppmv, which was half of the previous concentration of 2-butanol used in experiments and was estimated to be sufficient for scavenging more than 99% OH radicals. It was observed that the amount of SOA formation was not impacted by the concentration of 2-butanol, and the SOA formation potentials of SCIs under a lower concentration of 2-butanol were similar with those under a higher concentration of 2-butanol. Based on the results elaborated above, we confirmed that the effect of 2-butanol on the results was limited. We have added the details on the experiments with cyclohexane in the Supplement.

Q2. The fraction of SCI reacting with water (SCI_I) was estimated solely from the formation of H_2O_2.

- How did the authors measure H_2O_2? Was it the gas phase H_2O_2 or particle phase?

- Although I agree that H_2O_2 is the major decomposition product of α-hydroxyhydroperoxides (product of SCI + H_2O), the decomposition of α-hydroxyhydroperoxides is an equilibrium process and may not always proceed completely.

- α-hydroxyhydroperoxides are not the only source of H_2O_2. It's known that H_2O_2 is generated in SOA extracts, likely due to the decomposition of larger organic peroxides.

- In particular, Zhao et al. 2018, J. Phys. Chem. A reported H_2O_2 arising from the decomposition of hydroperoxyester, which is formed from SCI + organic acids. Although the mechanism is not completely clear, this implies that the product of SCI + AA may also give rise to H_2O_2.

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A2: Thanks for your suggestions. When we estimated the yield of SCI_I in limonene ozonolysis, the formation of gas-phase H_2O_2 was measured, which was elaborated in our previous study (Gong et al., 2018). For the detection of gas-phase H_2O_2, the gas samples passing through the PTFE filter were collected in a glass coil collector at a temperature of 4 °C with H_3PO_4 solution (pH 3.5) serving as the rinsing solution. After the collection, solutions containing peroxides were analyzed by HPLC (Agilent 1100, USA) coupled with post-column derivatization and fluorescence detection online. Peroxides separated by column chromatography reacted with *p*-hydroxyphenylacetic acid (POPHA) to form POPHA dimers under the catalysis of hemin, and then the dimers were quantified using a fluorescence detector. With the increase of RH, it was observed that the yield of H_2O_2 increased significantly from dry conditions to 70% RH, and the H_2O_2 yield approached the limiting value above 70% RH, suggesting that reaction with water suppressed other reactions of SCI_I. In the exo-DB oxidation, the formation of hydroxymethyl hydroperoxide was also taken into consideration. Through the box model simulation, the contribution of HO_2 self-reaction to H_2O_2 formation was estimated to be limited. As for the reaction of SCIs with water, the products α-hydroxyalkyl hydroperoxides were reported to be preferential to decompose and generate H_2O_2 (Chen et al., 2016; Kumar et al., 2014). Although theoretical calculations indicated that the decomposition of α-hydroxyalkyl hydroperoxides was slow, some studies proved that water and acids could significantly catalyze the process (Anglada et al., 2002, 2011; Aplincourt and Anglada, 2003; Crehuet et al., 2001), and H_2O_2

formation occurred rapidly (Chen et al., 2016; Winterhalter et al., 2000). In addition, few α-hydroxyalkyl hydroperoxides larger than hydroxymethyl hydroperoxide were identified in gas phase, and the decomposition of α-hydroxyalkyl hydroperoxides was speculated to be totally completed.

The generation of H_2O_2 from aerosols in aqueous phase, which is mainly due to the decomposition of some compounds, has received attentions in recent years (Wang et al., 2011; Zhao et al., 2018). Here only the gas-phase H_2O_2 was detected to estimate the yield of SCI_I, while it was still needed to analyze whether the formation of H_2O_2 in SOA could impact the results. Zhao et al. (2018) reported the aqueous decomposition rate coefficients of α-acyloxyalkyl hydroperoxides, whose lifetime was estimated to be about 24 min in liquid aerosols. As the reaction time in flow tube reactors was around 4 min, the H_2O_2 formation from aerosols was not considered to contribute much to gas-phase H_2O_2 in this study. In addition, it was found that the dependence of H_2O_2 yield on RH could be well simulated with the gas-phase mechanisms, confirming that the particle-phase formation of H_2O_2 did not make obvious impact on the results. We have added the discussion about the formation and measurement of H_2O_2 in the Supplement.

Q3. The flow tube experiments employ tens of ppb of limonene with an excess amount of O_3 for reactions. While these concentrations are rather typical for flow tube experiments, I think the author should discuss the feasibility of extrapolating their flow tube results to the real environment. As the authors point out, limonene mixing ratios are at the sub-ppb level for forest and urban environments. In my opinion, SCIs will predominantly react with water when organic concentrations are low. Thus, the SOA formation potential of SCIs they determine in the flow tube may or may not be applicable to the ambient conditions.

A3: Thanks for your suggestion and a discussion on the effect of the concentrations of reactants has been added in the Supplement. In this study, to get enough products for analysis in a short reaction time, both of the concentrations of limonene and O_3 used in experiments were higher than those in the real atmosphere, and it was needed to consider the effect of concentrations of reactants. In the atmosphere, the concentrations of organic compounds formed from limonene ozonolysis are much smaller than those in flow tube reactors, while it should be noted that limonene-derived SCIs would not only react with the compounds formed from limonene, they could also react with other compounds in the ambient air. In this study, we determined the rate of SCIs isomerization and reaction with other products. In the atmosphere, the organic compounds that SCIs could react with are generally carboxylic acids, carbonyls, alcohols, and RO_2 radicals, and the concentrations of these compounds in forest are about 10^{11} molecule cm^{-3}, 10^{11} molecule cm^{-3}, 10^{11} molecule cm^{-3}, and 10^{9} molecule

cm^{-3}, respectively. In urban area, the concentrations of carbonyls and alcohols were reported to be higher because of the anthropogenic emissions (Vereecken et al., 2012). The rate coefficients of SCIs reaction with carboxylic acids, carbonyls, alcohols, and RO_2 radicals were reported to be around 10^{-10} molecule cm^3 s^{-1}, 10^{-12} molecule cm^3 s^{-1}, 10^{-14} molecule cm^3 s^{-1}, and 10^{-11} molecule cm^3 s^{-1}, respectively (Khan et al., 2018; Lin and Chao, 2017; Zhao et al., 2017). It was estimated that the sum of the rate of SCIs isomerization and reaction with organic compounds in the atmosphere was on the same order of magnitude as that in experiments, and thus the results obtained here were considered to be feasible to the ambient conditions. We declare that further studies on different concentrations of reactants with the coexistence of other organic compounds would make the results more concise.

Minor and Technical Comments:

Q4. Line 155 “that” to “than”

A4: We have revised that.

Q5. Line 307 the sentence: “The reactions of SCIs with the compounds formed from SCIs scavengers would not compensate the effect of the consumption of SCIs on SOA formation.” is unclear. Please rephrase.

A5: Thanks for your suggestion. We have revised this sentence as follows.

C5: Lines 335–336 in Sect. 3.3.2:

The major role of SCIs scavengers was consuming SCIs in the reaction system, and the effect of products formed from SCIs scavengers on SCIs reactions was not expected to be important.

Q6. I’m supportive of the authors’ idea to provide an atmospheric implication of their findings by simulating three scenarios: forest, urban, and indoor. Instead of investigating all the RH for each scenario, I wonder if authors can constrain the RH to ranges that are more relevant to each scenario? For instance, the most comfortable RH range for human occupancy in an indoor environment is between 30 to 60%. It is unlikely we see an indoor that are extremely dry or wet.

A6: Thanks for your suggestion. The relevant RH under each scenario was considered and provided in the revised manuscript.

C6: Lines 413–418 in Sect. 3.4:

In forest, the typical RH is higher than 60%, and for urban and indoor area, they are usually under low-humidity conditions (Carslaw, 2017; Vereecken et al., 2012). According to the SOA formation potential of SCIs, it is estimated that the typical contribution of limonene-derived SCIs to SOA formation is $(8.21 \pm 0.15) \times 10^{-2}$ μg m^{-3} h^{-1} in forest, $(4.26 \pm 0.46) \times 10^{-2}$ μg m^{-3} h^{-1} in urban area, and $(2.52 \pm 0.28) \times 10^{-1}$ μg m^{-3} h^{-1} in indoor area.

Q7. Acid anhydrides can be hydrolyzed to form organic acids. By any chance, can the acid anhydrides arising from SCI + AA be hydrolyzed at higher RH, regenerating AA?

A7: Thanks for your suggestion. Some acid anhydrides were stable against water (Rong et al., 2020), and some others could be hydrolyzed to form organic acids in aqueous phase (Fritzler et al., 2014). The hydrolysis reactions of acid anhydrides were usually accelerated significantly by some catalysts (Faria et al., 2008). In the gas phase, α-acyloxyalkyl hydroperoxides formed from SCIs reaction with AA could dehydrate and form acid anhydrides (Long et al., 2009), and the reintroduction of water on anhydrides might not be easy to happen. The hydrolysis of acid anhydrides was expected to occur after anhydrides were taken up into atmospheric liquid water (Taatjes et al., 2019). Considering that the reaction time in this study was just a few minutes, this process was not predicted to be important.

Q8. Line 391-392 - “On the other hand” is repeated in the same sentence.

A8: Thanks for your suggestion. We have revised that in the manuscript.

Q9. Line 173 - k(other) - I wonder if wall loss of SCIs should be included in k(other)?

A9: Yes. Although the wall loss of SCIs was difficult to estimate and was not discussed in detail, we think the rate of wall loss of SCIs could be included in $k_{(\text{other})}$.

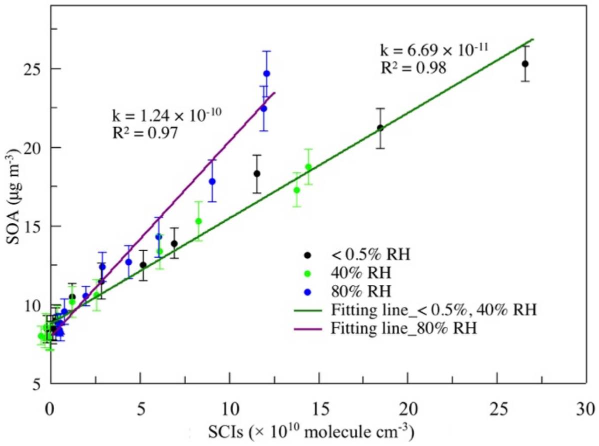

Figure S8. The dependence of SOA mass concentration on the amount of SCIs at different relative humidity (RH) in the first-generation oxidation with cyclohexane as OH scavenger.

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