

## Response to Reviewer #1

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)

5 General Comments: Gong and Chen report the experimental study on the formation of SOA during the ozonolysis of limonene, a class of important biogenic VOC in the atmosphere. They used flow tube reactors under different relative humidity (RH) to investigate the mechanism of SOA formation, especially the role of stabilized Criegee intermediates (SCIs). Their findings imply the different mechanisms of SOA formation  
10 at dry vs humid condition. The subject is within the scope of ACP and some findings seem important from the viewpoint of atmospheric aerosol chemistry. However, I am concerned about some critical issues that should be addressed.

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

15 Specific Comments:

Q1. I am most concerned about the side reaction of SCIs with 2- butanol. In page 10, the authors wrote “The rate constants of CH<sub>2</sub>OO reaction with methanol and ethanol were measured to be about 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K (McGillen et al., 2017)”, but this statement is incorrect. Actually, McGillen et al. (ACS Earth Space  
20 Chem. 2017, 1, 664–672) experimentally determined the rate constants  $k \sim 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for CH<sub>2</sub>OO + CH<sub>3</sub>OH/C<sub>2</sub>H<sub>5</sub>OH and  $k \sim 4 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for (CH<sub>3</sub>)<sub>2</sub>COO + CH<sub>3</sub>OH at ~ 298 K. Furthermore, Tadayon et al. (J. Phys. Chem. A 2018, 122, 1, 258–268) reported the rate constants of  $(1.9 \pm 0.5) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the reaction of CH<sub>2</sub>OO with 2-propanol at 295 K. Hence, the  
25 assumption that the rate constant of limonene-derived SCIs reaction with 2-butanol is 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> seems to be inadequate. If the authors assumed the rate constant to be 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, then the ratio of the amount of SCIs reacted with 2-butanol to the amount of SCIs reacted with AA would be much larger than the value authors claimed. Thus, SCIs in the presence of an excess amount of 2-butanol  
30 would be exclusively converted into alpha-alkoxyalkyl-hydroperoxides, that may contribute to the observed SOA formation. The authors should discuss the issue for details.

A1: Thanks for your suggestion and we regret that we did not calculate the impact of adding 2-butanol correctly. We have reevaluated the effect of 2-butanol on SCIs  
35 reactions in the revised manuscript, and to better understand the structure-dependent

reactivity of SCIs, the chemical structures of SCIs formed from endo-DB and exo-DB ozonolysis are provided in the Supplement. Besides, we also conducted experiments with cyclohexane and lower concentration of 2-butanol to confirm the impact of 2-butanol.

40 C1: Lines 307–331 in Sect. 3.3.2:

Previous studies reported that as for the reactions of SCIs with alcohols, the substitution group of alcohols had little effect on the reactions, while the structures of SCIs showed an obvious influence. The rate constants of CH<sub>2</sub>OO reaction with alcohols were about 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K (Tadayon et al., 2018), and it was slower for  
45 (CH<sub>3</sub>)<sub>2</sub>COO reaction with alcohols, whose rate constants were reported to be 10<sup>-15</sup> ~ 10<sup>-14</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Aroeira et al., 2019; McGillen et al., 2017). Watson et al. (2019) computed that the rate constant of *syn*-CH<sub>3</sub>CHOO + CH<sub>3</sub>OH was about 10<sup>-17</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, which was much smaller than that of about 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for *anti*-CH<sub>3</sub>CHOO + CH<sub>3</sub>OH at 298 K. In limonene ozonolysis, several kinds of  
50 SCIs were produced and their structures were shown in Fig. S7. A mono-substituted SCIs and a di-substituted SCIs were formed from endo-DB ozonolysis, and exo-DB ozonolysis produced CH<sub>2</sub>OO and a di-substituted SCIs. When assuming the rate constant of SCIs reaction with 2-butanol as 10<sup>-14</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, it was estimated that in terms of the concentrations of AA used in experiments, the ratio of the amount  
55 of SCIs reacted with 2-butanol to the amount of SCIs reacted with AA ranged from 0.06 to 1.25, and this ratio might be higher in exo-DB oxidation because of the formation of CH<sub>2</sub>OO. This meant that part of SCIs could react with 2-butanol, producing  $\alpha$ -alkoxyalkyl-hydroperoxides and contributing to the observed SOA, especially when using low concentrations of AA and water. To figure out whether the  
60 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, and the details were described in the Supplement. It was found that with the use of cyclohexane, SCIs reactions still accounted for more than 60% in SOA formation and according to the fitting results, the SOA formation potentials of SCIs  
65 were even a bit larger than those with the use of 2-butanol, and their deviations were within 12%. This phenomenon was speculated to be due to the higher concentration of RO<sub>2</sub> radicals when using cyclohexane, promoting the reactions of SCIs with RO<sub>2</sub>. 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  
70 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

75 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.

Q2. Adding AA and water (increasing relative humidity) should change the acidity of SOA. It is known that the pH dramatically influences the fates of ozonation products in condensed phase. See Zhao et al. J. Phys. Chem. A 2018, 122, 5190 and Qiu et al. Environ. Sci. Technol. 2020, doi.org/10.1021/acs.est.0c03438 for example. How does  
80 the change of SOA acidity influence the results?

A2: Thanks for your suggestion. The acidity of aerosols is an issue needing consideration and we have added a discussion on the effect of SOA acidity on the results in the revised manuscript.

C2: Lines 344–361 in Sect. 3.3.3:

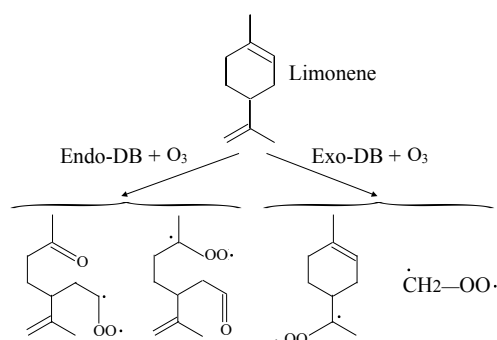
85 In this study, with the addition of AA the acidity of aerosols would change, and some reactions that happened in bulk phase were influenced, especially under high-humidity conditions. In view of this, the effect of SOA acidity on particle-phase reactions was considered. Zhao et al. (2018) investigated the aqueous-phase hydrolysis of  $\alpha$ -acyloxyalkyl-hydroperoxides, which were produced from reactions of SCIs and organic  
90 acids. It was found that  $\alpha$ -acyloxyalkyl-hydroperoxides decomposed promptly when pH was larger than 5 in aqueous phase. The aqueous decomposition of  $\alpha$ -hydroxyalkyl-hydroperoxides was also reported to be accelerated by acids, and the rate coefficients of decay increased with decreasing pH (Qiu et al., 2020a). These studies implied that  
95 in liquid particles and might reduce the amount of SOA. However, the effect of acidity on bulk-phase reactions was found to be complicated, and Iinuma et al. (2004) reported that acidity promoted the formation of large molecules in particles. Some reactions, which produced peroxyacetals, esters, aldols, etc., and contributed to SOA formation, could be catalyzed by acids and  $H^+$  in aqueous phase (Ziemann and Atkinson, 2012),  
100 while the rate coefficients of these reactions with varying pH were not clear. Actually, we could not evaluate the effect of acidity on the formation of SOA accurately because the acidity of aerosols might impact a series of reactions, and the mechanisms and rates of these reactions at different pH were vague. It was noted that Chen et al. (2008) found that in the aqueous-phase ozonolysis of methacrolein and methyl vinyl ketone, the  
105 yields of products were almost independent of pH, and Zhang et al. (2009) also observed this phenomenon in the ozonolysis of  $\alpha$ -pinene and  $\beta$ -pinene in aqueous phase. Thus the effect of the particle acidity on the results might also be limited here, and the accurate estimates of this issue still needed further research.

Q3. It has been reported that water accelerates the decomposition of alpha-  
110 hydroxyalkyl-hydroperoxides (formed by SCIs + water) and alpha-acyloxy-  
hydroperoxides (formed by SCIs + carboxylic acids) [see Zhao et al. J. Phys. Chem. A  
2018, 122, 5190, Qiu et al. Environ. Sci. Technol. 2020, 54, 3890–3899]. Could this  
humidity-assisted decomposition of ROOH explain the observed RH effects on SOA  
yield? The authors should comment on the issue in the text.

115 A3: Thanks for your suggestion. Water could accelerate the decomposition processes  
of  $\alpha$ -acyloxyalkyl-hydroperoxides and  $\alpha$ -hydroxyalkyl-hydroperoxides in aqueous  
phase, resulting in the formation of  $H_2O_2$ . The reactions of  $H_2O_2$  in particles have been  
thought to be important and may impact the aerosols formation. A discussion about this  
issue was provided in the revised manuscript.

120 C3: Lines 368–377 in Sect. 3.3.3:

On the other hand, a significant amount of  $H_2O_2$  formed from SCIs reaction with water  
was observed in ozonolysis under high-humidity conditions (Chen et al., 2016; Jiang et  
al., 2013), and water was reported to accelerate the decomposition of  $\alpha$ -acyloxyalkyl-  
hydroperoxides and  $\alpha$ -hydroxyalkyl-hydroperoxides in aqueous phase, resulting in the  
125 formation of  $H_2O_2$  (Qiu et al., 2019, 2020b; Zhao et al., 2018).  $H_2O_2$  was reported to  
play an important role in the nonradical oxidation of carbonyls in aqueous phase  
(Galloway et al., 2011; Herrmann et al., 2015), producing hydroxyhydroperoxides and  
promoting SOA formation (Zhao et al., 2012, 2013). The  $H_2O_2$  oxidation of carbonyls  
was speculated to mainly occur in surface liquid layer of aerosols, resulting in the  
130 generation of organic peroxides and high-molecular-weight oligomers (Sui et al., 2017;  
Zhang et al., 2019). The impact of  $H_2O_2$  reactions at air-liquid interface might be  
another reason for the performances of SCIs in SOA formation under high-humidity  
conditions.



135 **Figure S7.** Structures of limonene-derived SCIs formed from endo-DB and exo-DB  
ozonolysis.

## References

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