

Response to the comments of Anonymous Referee #3

General comments:

The manuscript by Zhang et al. investigated the effect of relative humidity (RH) on the formation of secondary organic aerosols (SOA) from structurally distinct monoterpenes from a molecular-level perspective. They observed a significant difference between limonene and Δ^3 -carene SOA formation on RH dependence. Further, they proposed potential chemical reaction mechanisms and pathways based on mass spectrometry analysis to explain the observed increase in limonene SOA and the decrease in Δ^3 -carene SOA. They suggested that the exocyclic double bond in limonene plays an important role in multi-generation reactions, contributing to the formation of lower volatile compounds under high RH conditions. Compared to many previous studies on the RH effects of SOA formation from monoterpenes, this study provides important insights into the multi-generation reactions that drive SOA formation by applying high-resolution MS analysis. The findings of this manuscript have significant implications for a better understanding of the mechanism of monoterpene oxidation reactions and the generation of secondary organic aerosols. This manuscript is well-written and I recommend publication in Atmospheric Chemistry and Physics after addressing the following minor concerns.

Response: We thank the Referee for the valuable comments and suggestions regarding our manuscript. We have made revisions to address these issues and believe that the updated version significantly improves the quality and meet the standard of ACP. The major revisions are as follows:

1. We have conducted low precursor concentration experiments to investigate the influence of SOA loading on multi-generation reactions of limonene.
2. We have supplemented the distribution of mass spectrum of Δ^3 -carene to provide a more comprehensive understanding for the increase of number concentration under low RH.

The responses are listed below in blue color text and the associated revisions to the manuscript are shown in red color text.

Specific comments:

1. The authors used high precursor concentrations in the experiments. It would be more convincing if similar results can be found with lower precursor concentrations.

Response: We have added the low-concentration limonene ozonolysis experiment (Fig. S6). The details are updated in the revised manuscript at Page 18, Line 339-348.

“To investigate the multi-generation reactions of limonene under low-concentration conditions, we conducted low-concentration limonene ozonolysis experiments, and the results are shown in Figure S6. In these experiments, the limonene and O₃ concentrations were 20.5 ppb and 5.7 ppm, respectively. According to the experimental results, the number concentration of SOA formed from limonene ozonolysis increased by approximately 1.4 times under high RH, which is similar to the increase observed under high-loading conditions. The mass concentration increased by

approximately 1.3 times at a precursor concentration of 20.5 ppb. The relatively small increase in mass concentration compared to the high-concentration conditions may be attributed to the less pronounced distribution of SVOCs at low mass concentrations. This result indicates that the enhancement effect on limonene SOA by high RH is still valid for low precursor concentrations.”

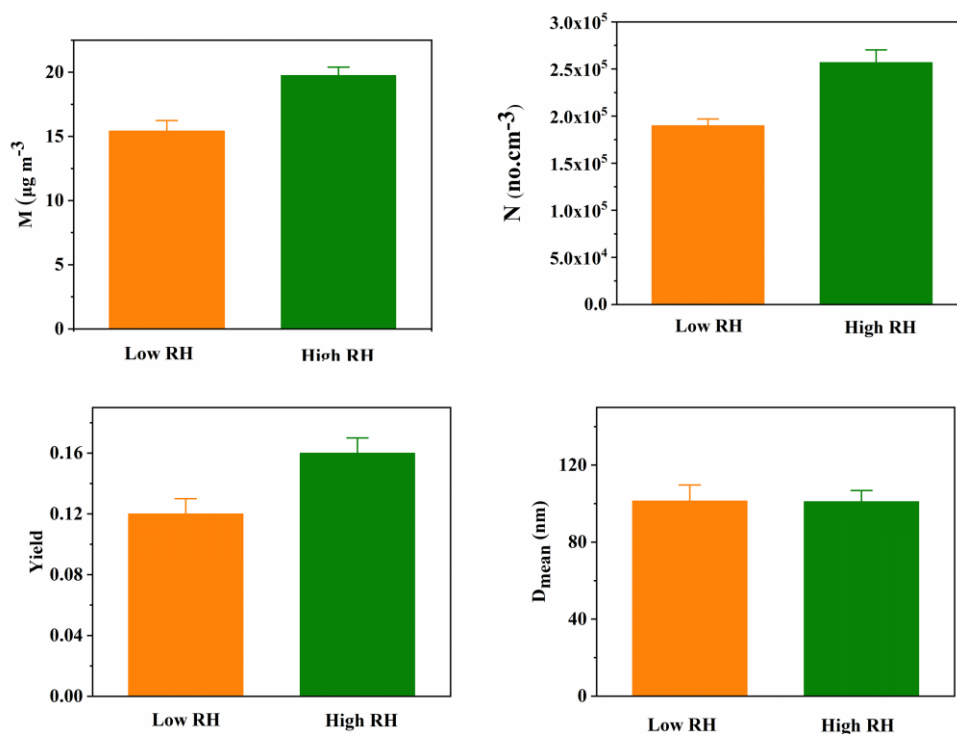


Figure S6. The SOA formation of low-concentration limonene under low and high RH (a) mass concentration (b) number concentration (c) SOA yield (d) mean diameter.

2. The authors have extensively described the mass spectrometry analysis of limonene, while only briefly providing the distribution of high oxygenated compounds and dimers in Δ^3 -carene. It would be beneficial to include additional analysis of Δ^3 -carene mass spectrometry.

Response: Like limonene, we have analyzed the number and intensity proportion of four groups for Δ^3 -carene. The details have given in Table S2 in the Supplement, and the distribution is similar to that of limonene-SOA, i.e., most of the SOA molecules are monomers (~70%) (Fig. 2b) and dimers (~25%), while trimers and tetramers contribute to very small fractions (~2% and <1%). The corresponding discussion was changed in the revised manuscript (Page 11, Line 200-203): “Correspondingly, the distribution of Δ^3 -carene-SOA can be divided into four groups (Fig. S4), comparable to that of limonene-SOA. Most of the SOA molecules are monomers (~70%) and dimers (~25%), while trimers and tetramers contribute to smaller proportions (~2% and <1%, respectively) (Table S2).”

Table S2. The number and intensity proportion of four groups for Δ^3 -carene.

Groups	Monomers	Dimers	Trimers	Tetramers
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Number (L)^a	239	178	76	4
Number (H)^b	216	151	26	1
Intensity proportion (L)^a	69.8%	28.6%	1.6%	0.5%
Intensity proportion (H)^b	72.5%	26.9%	2.0%	0.2%

^a L means under low RH. ^b H means under high RH.

3. Method: what is the temperature ramp program in liquid chromatography?

Response: The temperature ramp program was: 0–3min with 0%–3% phase B, 3–25min with 3%–50% phase B, 25–43min with 50%–90% phase B, 43–48 min with 90%–3% phase B, 48–60min with 3% phase B. The corresponding content has been added in the revised manuscript at Page 6, Line 138-140.

R4: Page 5, Line116: “limonene-” should be “limonene-SOA”.

Response: Revised.

R5: Page 7, Line 156: the authors have pointed out that the OH scavenger will produce additional products which may influence the reactions of target precursors, so what about the 2-butanol and cyclohexane discussed in this article?

Response: Though there is no difference between 2-butanol and cyclohexane in the scavenging ability of OH radical, 2-butanol will produce more HO₂· than cyclohexane and, consequently, R· will react with HO₂· to produce more hydroxyl acids and hydroxyl per-acid products, most of which have low volatility, thus high partitioning into the particle phase. The corresponding content has been revised in Page 7, Line 161-165: “For example, there is no difference between 2-butanol and cyclohexane in the scavenging ability of OH radical, though 2-butanol will produce more HO₂· than cyclohexane and, consequently, R· will react with HO₂· to produce more hydroxyl acids and hydroxyl per-acid products, most of which have low volatility and, thus high partitioning into the particle phase.”

R6: Page12, Line 238-239: specify the condition of the increase and decrease of C₉H₁₄O₃ and C₁₀H₁₆O₂, respectively.

Response: In order to avoid ambiguity, we have revised the sentence to “This mechanism can well explain the decrease in the relative intensity of C₁₀H₁₆O₂ from high RH to low RH and the increase in the relative intensity of C₉H₁₄O₃ from low RH to high RH (Table S3)”.

R7: Supplement, Page 11: there were two (K) in Table S6.
Response: Revised.