

## **Response to reviewers' comments on "Elucidation of the myrcene ozonolysis mechanism from a Criegee Chemistry perspective"**

Dear Reviewers,

The authors thank the reviewers for their thoughtful evaluation of the manuscript entitled "**Elucidation of the myrcene ozonolysis mechanism from a Criegee Chemistry perspective**" (egusphere-2025-4310). We greatly appreciate the constructive comments and suggestions provided. Enclosed are our detailed, point-by-point responses to each comment, and the corresponding revisions have been incorporated into the revised manuscript and Supporting Information. For clarity, the reviewers' comments are reproduced first, followed by our responses shown in blue. All textual changes in the manuscript are highlighted in red, and the reference numbering has been updated accordingly in both the manuscript and Supporting Information.

### **Response to Reviewer #2**

This manuscript provides significant insights into the atmospheric oxidation of the multifunctional monoterpene myrcene, highlighting the pivotal role of CIs in forming low-volatility products. It integrates complementary techniques including matrix isolation FTIR spectroscopy, smog chamber experiments, and quantum chemical calculations, to establish a coherent molecular-level framework. This integrated approach itself represents a novel methodological framework for investigating CIs. The experimental design is sound, and the chosen computational methods have been appropriately validated against established benchmarks for CIs systems.

By synthesizing results from these approaches, the work clarifies how the distinct fates of myrcene-derived CIs govern SOA formation. While research on this important, polyunsaturated acyclic terpene has been limited, this study introduces chemical mechanisms, specifically, CIs-involved oligomerization and its synergy with RO<sub>2</sub> autoxidation. These pathways are potentially generalizable and may improve the predictive modeling of the contribution of CIs to SOA formation for a broader range of

unsaturated compounds.

Overall, the manuscript presents a logically clear narrative, supported by detailed experimentation and reliable conclusions, making it suitable for the broad readership of ACP.

The authors sincerely thank the reviewer for their positive assessment and for recognizing the significance of our work. We also wish to express our deep gratitude for the reviewer's patient and meticulous examination of the manuscript. Each comment has been addressed point by point; our responses are highlighted in blue, while the corresponding revisions in the manuscript are indicated in red. All updates have been clearly marked within the revised version of the manuscript.

#### Minor Comments

Lines 42, how is the term "smaller-sized SCIs" specifically defined?

**The author's answer:** Thank you for your comments. This phenomenon is further elucidated in the text. Lines 42-43, we added the explanation to the term, "smaller-sized SCIs (species with carbon numbers  $C \leq 4$ )".

Lines 61-62, "The yields of SCIs obtained from monoterpene ozonolysis ranges from approximately 0.2 to 0.60 (Sipila et al., 2014; Zhang and Zhang, 2005; Gong and Chen, 2021; Cox et al., 2020; Newland et al., 2018). The high yield leads to the occurrence of numerous SCIs-related reactions." Why is high? In my view, a yield of 0.20 is not particularly high.

**The author's answer:** Thank you for your comments. We changed "high yield" to "production of SCIs".

Lines 97, "freezing pump – thawing" this expression contains a grammatical error.

**The author's answer:** Thank you for your comments. We modified "freezing pump – thawing" to "freeze-pump-thaw".

Lines 96 and 115, the description of ozone generation is repeated in two sections and could be consolidated or streamlined.

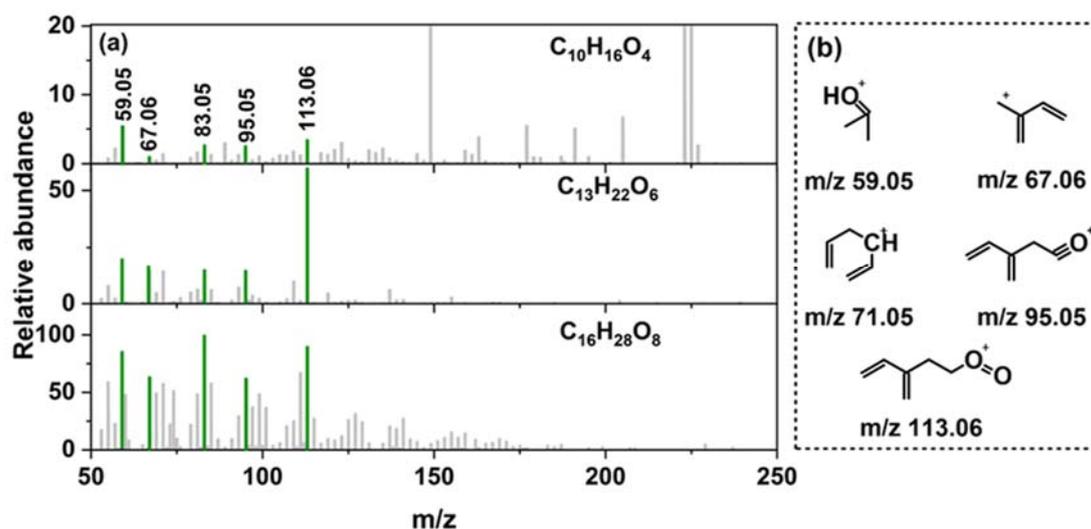
**The author's answer:** Thank you for your comments. Lines 96, we changed “The O<sub>2</sub>/O<sub>3</sub> mixture was produced by a high-voltage discharge type ozone generator (Beijing Tonglin Technology Co., LTD).” to “An O<sub>2</sub>/O<sub>3</sub> mixture was generated by passing high-purity O<sub>2</sub> (≥99.999%) at a flow rate of 200 mL/min through an ozone generator (Beijing Tonglin Technology Co., Ltd.).”.

Lines 115, we changed “An O<sub>2</sub>/O<sub>3</sub> mixture was generated by passing high-purity O<sub>2</sub> (≥99.999%) at a flow rate of 200 mL/min through an ozone generator (Beijing Tonglin Technology Co., Ltd).” to “The O<sub>2</sub>/O<sub>3</sub> mixture was generated in the same manner as described above.”.

Lines 302-311, this part dedicates a detailed discussion to the MS/MS spectrum corresponding to Sequence 2. However, the relevant figure is currently placed in the Supporting Information. Given that ACP does not impose strict limits on the number of figures or manuscript length, it would be more appropriate and convenient for readers if this spectrum were moved into the main text.

**The author's answer:** Thank you for your comments. Figures S3 and S4 in the Supporting Information present the MS/MS spectra for Sequence 1 and Sequence 2, respectively. Given that the fragmentation patterns shown in these figures exhibit redundant structural units with the chemical formulas proposed in Equations R7 and R8, Figures S3 and S4 have been assigned to the Supporting Information for conciseness.

Upon review, we identified and addressed inconsistencies in the font sizes in Figure S4. The revised version, which now adheres to a uniform style, is presented below for your review.



**Figure S4** The MS/MS of  $C_7H_9O_3$  + n-C3-SCIs +  $RO_2$  sequence (a) and chemical structures of ions corresponding to major fragment peaks in MS/MS spectra (b).

Lines 320. "...oligomerized compound ( $C_{19}H_{34}O_{10}$ ) was detected. Water...". There is a missing space between the two sentences.

**The author's answer:** Thank you for your comments. Lines 320, we added the space.

Lines 391, "secondary organic aerosol" should be abbreviated as "SOA".

**The author's answer:** Thank you for your comments. We modified "secondary organic aerosol" to "SOA".

In the Supplement, in the explanatory notes section of Table S1, there is no "Table R1". And in this part, you should delete "and incorporated the necessary revisions".

**The author's answer:** Thank you for your comments. In the Supplement, we changed "Table R1" to "Table S1".