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

Response to Reviewer #1

This study employs a combined approach of matrix isolation Fourier transform infrared spectroscopy (MI-FTIR) and smog chamber experiments to elucidate the mechanisms of myrcene ozonolysis from the perspective of Criegee chemistry, thus significantly enhancing our understanding of oxidation processes in acyclic monoterpenes.

The manuscript presents research of high quality, with sound methodology and clearly described experimental processes. The findings are of considerable significance and are generally well-articulated and convincing. The methods applied are appropriate, and the reaction mechanisms are described in a detailed and clear manner. This work merits publication in Atmospheric Chemistry and Physics after the authors address the minor revisions outlined below.

The authors greatly thank the reviewer for the careful review of our manuscript and the valuable feedback. All the comments are addressed point by point, with our responses in blue, and the corresponding revisions to the manuscript in red *italics*. All updates are marked in the revised manuscript. According to the comments, we have added new analysis to strengthen our work.

Specific comments:

1. It is recommended to provide additional clarification on the calculation method of SOA yield in Table 2, such as whether corrections were made for particle wall loss.

The author's answer： Thank you for your comments. In our study, the SOA yield was calculated according to the following formula.

$$\mathrm{Y_{SOA}}=\frac{\mathrm{M_{SOA}}}{\Delta\mathrm{M_{VOC}}}$$

Here, Y_{SOA} represented the SOA yield, M_{SOA} denoted the maximum mass concentration of particle after wall-loss correction during the reaction process, and ΔM_{VOC} referred to the total consumption mass concentration of VOCs throughout the reaction.

In this study, wall-loss corrections for SOA were applied. Specifically, ammonium sulfate particles were introduced smog chamber under identical environmental conditions (e.g., relative humidity (RH) and temperature), and their wall-loss rate was used to correct the SOA mass concentration. Table R1 presented the wall-loss rates of ammonium sulfate particles measured under different RH conditions. And in supplement Figure S2 presented the corrected SOA volume concentration.

Table R1 Wall-loss rate of ammonium sulfate as a function of relative humidity.

	RH	**Rate/(min^{-1})**
1	RH<0.5 %	$0.00165 \pm 7.83 \times 10^{-5}$
2	RH= ~20%	$0.0019 \pm 7.47 \times 10^{-5}$
3	RH= ~50%	$0.00301 \pm 8.97 \times 10^{-5}$

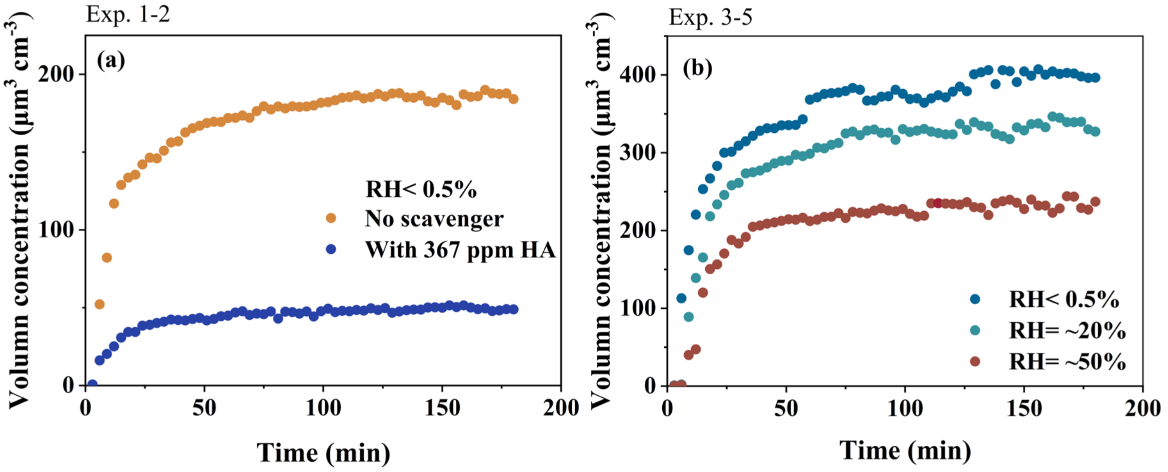

Figure S2 Time series of particle volume concentration in myrcene ozonolysis under different condition. (a) depict particle formation processes in Exp. 1-2 from Table 2, while (b) illustrate particle formation processes in Exp. 3-5 of Table 2.

Lines 123-126, we added "*The specific equation was as follows.*

$$Y_{SOA}=\frac{M_{SOA}}{\Delta M_{VOC}}$$

Here, Y_{SOA} *represented the SOA yield,* M_{SOA} *denoted the maximum mass concentration of particle after wall-loss correction during the reaction process, and* ΔM_{VOC} *referred to the total consumption mass concentration of VOCs throughout the reaction.*".

2. In the MI-FTIR experiment, the characteristic peak of C7-CIs (905 cm^{-1}) overlaps with that of myrcene itself. How was interference from the parent compound ruled out in this case?

The author's answer： Thank you for your comments. The spectra of a single precursor (myrcene/Ar or O_3/Ar) were conducted at different temperatures. The results showed that temperature variation did not alter the intensity of the infrared characteristic peak of myrcene or O_3 at 905 cm^{-1} as shown in Figure S1(a). To assess and minimize computational errors, we compared the accuracy of several commonly calculational levels used for calculating POZs and CIs infrared spectra in VOC ozonolysis. This comparison identified B3LYP/6-311G++(d,2p) as the optimal method for CIs, which we accordingly used to recalculate all infrared spectra. Based on a re-examination of the characteristic IR peaks of C7-CIs, we concluded that no such peaks were observed in our experiments. However, in the spectrum from the twin-jet experiment at 55 K, the relative peak intensity at 905 cm^{-1} increased significantly. This indicated the formation of new species exhibiting a characteristic vibration at this location. The characteristic IR bands of C3-CIs could only be detected at 55 K, and the intensity change of the peak at 905 cm^{-1} followed this consistent behavior. Therefore, the 905 cm^{-1} position might be attributed to the 4-vinyl-4-pentenal (C7-aldehyde).

Lines 187-192, we modified "The calculated O-O stretching vibrations of C7-CIs were located at 892 (syn-C7-CIs) and 923 (anti-C7-CIs) cm^{-1}, which were covered by the main characteristic infrared vibration peaks of myrcene. Consequently, it was challenging to directly observe the strongest characteristic infrared vibration peaks belonging to C7-CIs. In addition to the -COO group, C7-CIs also possessed conjugated double bonds as characteristic functional groups. In both syn- and anti-C7-CIs, the second most intense infrared vibration band consistently corresponded to the wagging vibration of the $=CH_2$ group on the conjugated moiety. The calculated position of this vibration agreed with that of myrcene. Position 905 cm^{-1} was the infrared characteristic peak generated by the wagging vibration of myrcene $=CH_2$, as obtained by twin-jet method. In the spectra, a significant relative increase at the 905 cm^{-1} position was observed after annealing to 55 K. This increase might be attributable to the generation of C7-CIs. The characteristic infrared peaks of C3- and C7-CIs were both generated after 55 K annealing." to "*The calculated O-O stretching vibrations of C7-CIs were located at 882 (syn-C7-CIs) and 910 (anti-C7-CIs)* cm^{-1}*. According to Table S1, the calculated IR peaks of CIs were consistently overestimated by over 10* cm^{-1} *relative to experimental values, with the deviation being most pronounced for anti-CIs. Notably, no distinct new peaks appeared below 882* cm^{-1} *in the experiment. This absence suggested that very few stabilized C7-CIs were likely generated during the ozonolysis of myrcene. Instead, most C7-CIs were consumed via unimolecular decay pathways, this conclusion which was also supported by our subsequent analysis.*".

Lines 148-149, we changed "The products generated along with C7-CIs and C3-CIs were acetone and 4-vinyl-4-pentental with yields of 0.27 and 0.73, respectively." to "*The products generated along with C7-CIs and C3-CIs were acetone and 4-vinyl-4-pentental (C7-aldehyde) with yields of 0.27 and 0.73, respectively.*".

Lines 195-196, we added "*The peak at 905 cm^{-1} coincided in temperature with the C3-CIs peaks and suggested its assignment to the =CH$_2$ wagging vibration of the C7-aldehyde.*".

3. In this study, the conclusion regarding the role of C7-CIs in SOA formation primarily relies on their degradation product C7-RO$_2$. Could this potentially underestimate the direct involvement of C7-CIs themselves in other bimolecular reactions, such as those with organic acids?

The author's answer: Thank you for your comments. For CIs, the unimolecular and bimolecular reactions were competing processes. In mass spectrometric analysis, the signals corresponding to the products of C7-CIs ($C_7H_9O_3$) unimolecular degradation exhibited significant intensity (Top 4), both in the presence and absence of OH scavengers. Furthermore, anti-C7-CIs could react via a unimolecular degradation pathway to produce C7-acid ($C_7H_{10}O_2$). No observable products ($C_{14}H_{20}O_4$, m/z= 253.142, relative abundance=1.73%) from the reaction between C7-CIs and C7-acid were detected in the system. Thus, we considered unimolecular degradation to be the primary loss process for C7-CIs in the myrcene ozonolysis system.

Both excited-state and stabilized Criegee intermediates (SCIs) were susceptible to unimolecular degradation. However, only the SCIs could participate in rapid bimolecular reactions with organic acids. Our analysis detected no oligomeric sequences with C7-CIs as repeating units in the particles. This suggested that C7-CIs were predominantly removed via unimolecular degradation in their excited state, with only a minor fraction surviving to the stabilized form. Consequently, bimolecular reactions made a negligible contribution to particle formation for C7-CIs in myrcene ozonolysis.

4. In the Results and Discussion section, it is mentioned that for C10-CIs produced by cyclic monoterpenes such as α-pinene and limonene, they may more closely resemble C7-CIs in being incorporated into the particle phase through monomeric reactions rather than oligomerization. This inference tends to rely more on molecular size analogy. Are there any literature sources that provide direct experimental observations or quantum chemical calculations to support this view?

The author's answer: Thank you for your comments. Currently, no literature has elucidated the contribution mechanisms of CIs of different sizes to SOA formation from the perspective of molecular size. This study presented this concept for the first time. However, indirect evidence supporting our hypothesis existed in the literature. First, the unimolecular reactions of CIs could generate OH radicals. As shown in Table R2, the main monoterpene ozonolysis reactions generally exhibited higher OH radical yields (≤0.97), which was consistent with the inference that most CIs undergo unimolecular reactions. Second, existing studies on the limonene ozonolysis mechanism have identified the monomer as the dominant contributor to SOA (Zhang et al., 2023).

Table R2 Summary of OH yields for reactions of O_3 with monoterpene at 298 K and 1 bar.

Monoterpene	OH yield	References [a]
α-pinene	0.80±0.10	(Cox et al., 2020)
β-pinene	0.30±0.06	
limonene	0.66±0.04	
camphene	≤0.18	
2-carene	0.81±0.11	
3-carene	0.86±0.11	
myrcene	0.63±0.09	
β-ocimene	0.55±0.09	
β-phellandrene	0.29±0.05	
sabinene	0.33±0.05	
α-terpinene	0.32±0.06	
γ-terpinene	0.81±0.11	
terpinolene	0.70±0.08	

Note: [a] This table is sourced from a review on CIs.

Lines 342-343, we added "*Currently, no literature has elucidated the contribution mechanisms of CIs of different sizes to SOA formation from the perspective of molecular size. This study presented this concept for the first time.*".

5. This study mentions that "the contribution of C7-CIs oligomerization is negligible." Is this due to their low reactivity or the high volatility of the reaction products? It is recommended to briefly explain this in the discussion.

The author's answer： Thank you for your comments. As shown in Figure 4(c), oligomers derived from the addition of two or more C7-CIs were not observed. Notably, even the monomeric adduct $C_{17}H_{28}O_7$, might resulting from the reaction of C10-R'O_2 with a single C7-CIs, displayed only weak signal intensity. $C_{17}H_{28}O_7$ was classified as a low-volatility organic compound (LVOCs, as calculated by the formula below), which readily partitioned into the particle phase. But its low abundance implied that oligomerization via C7-CIs is not a major process. The primary sink for C7-CIs was their competing unimolecular degradation, as evidenced by the high-intensity signals of their decomposition products ($C_7H_{10}O_2$) detected in experiments both with and without an OH scavenger as shown in Figure 4(a) and (d).

The saturation mass concentration (C^0, µg m^{-3}) of $C_{17}H_{28}O_7$ was also calculated based on its elemental composition using the following expression:

$$\log_{10}C_i^0=\left(n_C^0-n_C^i\right)b_C-n_O^ib_O-2\frac{n_C^in_O^i}{n_C^i+n_O^i}b_{CO}$$

Where n_C^0 was the reference carbon number; n_C^i and n_O^i, represented the numbers of carbon and oxygen atoms, respectively; b_C and b_O denoted the contribution of each carbon and oxygen atom; and b_{CO} was the carbon–oxygen nonideality. LVOCs defined by saturation mass concentrations of 0.3-3×10^{-4} µg m^{-3}.

Lines 272-274, we changed "$C_{17}H_{28}O_7$ did not appear as a dominant product in the mass spectra." to *"$C_{17}H_{28}O_7$ was classified as a low-volatility organic compound (LVOCs) (Donahue et al., 2012; Donahue et al., 2011), which readily partitioned into the particle phase. But its low abundance implied $C_{17}H_{28}O_7$ did not appear as a dominant product.*".

6. Some sentences in the text are quite lengthy; it is suggested to appropriately break them down to enhance the readability of the article.

The author's answer: Thank you for your comments. Following the reviewers' suggestions, we have made some revisions to some of the long sentences in the manuscripts. The details are as follows:

Lines 14-15, we changed "Ordered oligomers with C3-CIs serving as chain units, formed via RO_2 + n C3-CIs + HO_2/RO_2 mechanisms, are detected as significant components in secondary organic aerosol (SOA)." to "*Ordered oligomers, which contain C3-CIs as chain units, are detected as significant components in secondary organic aerosol (SOA). These oligomers are formed via RO_2 + n C3-CIs + HO_2/RO_2 mechanisms.*".

7. Is the synergistic mechanism discovered in this study universal in other monoterpene or alkene systems beyond the myrcene system?

The author's answer: Thank you for your comments. Our findings established that the synergistic mechanism emerged from the coexistence of smaller (C3-CIs) and larger-sized CIs (C7-CIs) during monoterpene ozonolysis as shown in Figure 5(c). Such a coexistence of CIs of varying molecular sizes might also occur in other monoterpenes besides myrcene, including ocimene (C3-CIs and C7-CIs). Although the results and analysis within the manuscript suggested the probable occurrence of this synergy in these systems, its definitive verification remained a subject for future experimental investigation.

Lines 357-358, we added “*The structural similarity of ocimene to myrcene meant its ozonolysis might also lead to CIs of varying sizes, potentially allowing for this synergistic mechanism.*”.

References

Cox, R. A., Ammann, M., Crowley, J. N., Herrmann, H., Jenkin, M. E., McNeill, V. F., Mellouki, A., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VII - Criegee intermediates, Atmos. Chem. Phys., 2020, 13497-13519, 10.5194/acp-2020-472, 2020.

Donahue, N. M., Epstein, S. A., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics, Atmos. Chem. Phys., 11, 3303-3318, 10.5194/acp-11-3303-2011, 2011.

Donahue, N. M., Kroll, J. H., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set - Part 2: Diagnostics of organic-aerosol evolution, Atmos. Chem. Phys., 12, 615-634, 10.5194/acp-12-615-2012, 2012.

Zhang, S., Du, L., Yang, Z., Tchinda, N. T., Li, J., and Li, K.: Contrasting impacts of humidity on the ozonolysis of monoterpenes: insights into the multi-generation chemical mechanism, Atmos. Chem. Phys., 23, 10809-10822, 10.5194/acp-23-10809-2023, 2023.