

Notes to Editor and Referee:

We thank the Referee for providing very insightful and helpful comments and suggestions.

1. We have highlighted all the changes made to the final submission in blue. These include the changes suggested by the Referee.
2. Below we provided a point-by-point response to the Referee' comments.

Referee #1

Dear Editor:

This is a theoretical work which calculates related rate coefficients and analyzes temperature-dependent kinetics for a few systems of sesquiterpene ozonolysis. The main mechanism is copied below.

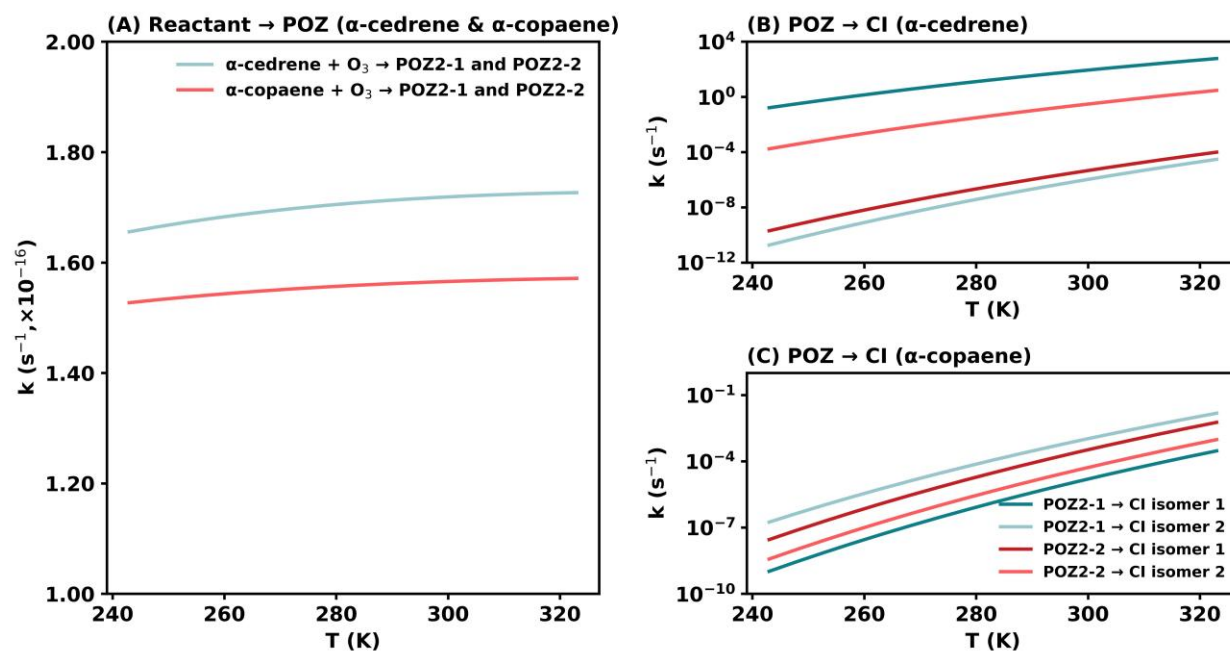
Terpene + O₃ { $k_1 \rightleftharpoons k_{-1}$ } SPCs

SPCs { $k_2 \rightarrow$ } POZs

POZs { $k_3 \rightarrow$ } CIs

While the estimation for k_1 , k_{-1} , and k_2 in this work does not seem unreasonable, the very small values of k_3 (as given in Figure 3 (B) and (C)) are surprising. Note: the y-axis unit is strange; k_3 should be first-order.

Response: We thank the referee for pointing out the issue of the y-axis. We agree that k_3 should be a first-order rate constant, so the unit should be s⁻¹. The revised Figure 3 (the current Figure 4 in the revised manuscript) is shown below.



“Figure 4. Temperature dependence of (A) the ozonolysis rate constants (k_{oz}) of α-cedrene and α-copaene and the decomposition rate constants (k_3) of thermalized POZs that produce (B) α-cedrene-derived CIs and (C) α-copaene-derived CIs.”

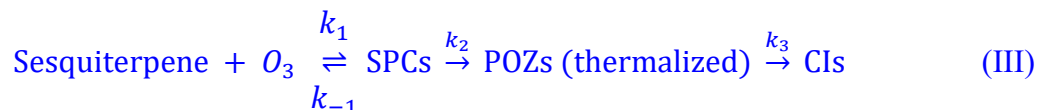
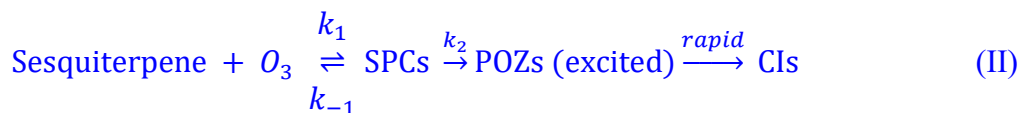
It appears to me that this work assumes that the primary ozonide (POZ) is fully thermalized and calculates k_3 accordingly. However, it is well known that the POZ formation is highly exothermic and the large energy release leads to ultrafast decomposition of the POZ. Unless under a very high pressure, thermalized POZ is not expected.

Response: We appreciated the referee for the critical comment. We agree that the formation of POZ is a highly exothermic process, and we also agree that, for small alkenes in general, POZs should undergo ultrafast decomposition and thus the thermalized POZ is not expected unless the pressure is very high.

However, whether or not the thermalized POZ exists depends on the size of the precursor. Figure 6 of Chuong et al. (2004) shows that under atmospherically relevant conditions (10^{10} s^{-1} at the x axis), the ozonolysis of 4-butyl-5-pentylcyclohexene (the surrogate compound of sesquiterpenes) produces a ~10% yield of thermalized POZs. We realize that only a small fraction of sesquiterpene-derived POZs can be fully thermalized in the atmosphere, so the CI kinetic relaxation is not a universal phenomenon, and its significance should be narrowed down. To clarify this, we rewrote part of the Introduction section, and further revision is provided below after the referee's comments.

Rewritten part in the Introduction section:

“The value of k_{CI} is generally assumed equal to the ozonolysis rate constant (k_{oz}) in the literature (Taatzes et al., 2014; Cox et al., 2020). In principle, terpene ozonolysis first forms stabilized prereactive complexes (SPCs) and subsequently generates primary ozonides (POZs), which further decompose into CIs (Donahue et al., 2011; Vereecken and Francisco, 2012; Taatzes et al., 2014). The quantity k_{CI} refers to the projection from the reactants (sesquiterpenes and O_3 in this study) to CIs (Scheme I), and k_{oz} refers to the projection from the reactants to POZs (Ou and Chen, 2025; Ou et al., 2026). Given the high exothermic energy ($\sim 50\text{--}60 \text{ kcal mol}^{-1}$) from O_3 addition to the $C=C$ double bond (Nangia and Benson, 1980; Cremer, 1981; Chuong et al., 2004; Johnson and Marston, 2008), POZs are typically in their vibrationally excited states to rapidly produce CIs under normal atmospheric conditions (Chuong et al., 2004; Hakala and Donahue, 2023). In this case, the conversion from POZs to CIs is expected to be far from thermal equilibrium so that the reaction proceeds more like SPCs overcoming the energy barrier corresponding to k_2 and directly produce CIs (Scheme II).



However, if POZs are fully thermalized, k_{CI} and k_{oz} are not necessarily interchangeable (Scheme III). This will not happen for all of the small alkenes and even C_{10} molecules (e.g., monoterpenes) in the air, but for C_{15} molecules such as sesquiterpenes, a fraction of them can be thermalized under atmospheric conditions (Chuong et al., 2004). In this case, there is no guarantee that k_{CI} can be

equal to k_{oz} . The influence of k_3 on k_{CI} is largely overlooked from the thermalized POZs. To address this concern, the community may require a rigorous approach to resolving the rate constant of CI formation by explicitly considering the POZ-to-CI conversion.”

“We selected CIs from sesquiterpene ozonolysis as our case study for three reasons: (1) the rate constants of sesquiterpene ozonolysis mostly show no dependence on air pressure in the troposphere; (2) the large molecular size of sesquiterpenes may keep the SPCs collisionally stabilized (Wong et al., 2003; Yao et al., 2017; Ou and Chen, 2025); (3) sesquiterpenes are C_{15} molecules such that their ozonolysis yields a fraction of thermalized POZs under atmospherically relevant conditions (Chuong et al., 2004).”

At lines 242-244, the authors claimed:

“Once formed, sesquiterpene-derived POZs rapidly stabilize by colliding with the surrounding gas molecules (Chuong et al., 2004; Hakala and Donahue, 2023), mainly nitrogen and oxygen in the air, which inhibits rapid decomposition.”

However, both Chuong et al., 2004 and Hakala and Donahue, 2023 do not support this claim at all. The former mentions:

“... ozone adds to the double bond in a concerted [2 + 3] cycloaddition to produce a vibrationally excited primary ozonide (POZ), which then quickly decomposes to yield an excited carbonyl oxide [Criegee intermediate (CI)] and a carbonyl compound. The excited CI may either undergo further unimolecular reactions or be collisionally stabilized.”

And the later mentions:

“Here, we focus on gas-phase systems, where POZ decomposition is rapid, and also assume that concerted scission of C–C and O–O bonds gives bimolecular (or for endocyclic alkenes, unimolecular) products with unit yields.”

Therefore, I feel that the basic assumption of this work is in doubt. The authors should carefully consider the energy content of POZ, which has been addressed in a number of publications, but fully neglected in this work.

Response: We appreciated the referee’s critical comment. We have deleted the inappropriate statement and reevaluated the energy content of POZs as well as the impact of excess energy on CI formation kinetics by conducting the RRKM-ME computation. Our RRKM-ME results show much higher rate constants for POZ decomposition, while certain sesquiterpenes (e.g., β -caryophyllene) still show non-negligible relaxation timescale in the CI formation kinetics. To clarify all these points in detail, we rewrote the entire Abstract, added the methodology of RRKM-ME computation, revised the discussions in Section 3.3 about the k_3 values of thermalized POZs, added the discussions about the results of RRKM-ME computation in Section 3.4, and revised the statement in the Conclusion section.

Rewritten Abstract:

“Sesquiterpene ozonolysis contributes to secondary organic aerosol (SOA) formation through the production of Criegee intermediates (CIs) via primary ozonide (POZ) decomposition. Although POZs are in general vibrationally excited to rapidly produce CIs, a fraction of sesquiterpene-derived POZs can be fully thermalized; yet the kinetics of CI formation from these thermalized POZs has received little attention. This study reports the overlooked kinetic relaxation during CI

formation from thermalized POZs of representative sesquiterpenes, including α -cedrene, α -copaene, β -caryophyllene, α -farnesene, and β -farnesene. We found that, for thermalized POZs, the apparent CI formation rate constant is initially unstable but gradually approaches a plateau, which equals the rate constant of sesquiterpene ozonolysis. Our results revealed that kinetic relaxation is sensitive to temperature variations, as cold surges extend the relaxation timescale from minutes to hours (or hours to days) while heatwaves reversely diminish the relaxation timescale. We further examined the CI formation kinetics from non-thermalized POZs, which suggested that kinetic relaxation may still occur for those derived from β -caryophyllene. The relaxation timescale is longer than the ozonolysis lifetime of β -caryophyllene under tropospheric O₃ concentrations. Our findings demonstrate that, for sesquiterpenes, neglecting kinetic relaxation may overestimate the rate of their CI formation and thus the resultant oxidation capacity.”

RRKM/ME setup in the Method section:

“The decomposition rate constant of non-thermalized POZs was estimated using the RRKM/ME calculations (i.e., Rice–Ramsperger–Kassel–Marcus theory/master equation) by the Multiwell 2023 program (Barker, 2009, 2001). The pressure was set as 1.0 atm, and the surrounding collider was nitrogen gas (N₂) with the Lennard–Jones (LJ) parameters (σ and ε / k_B) of 3.70 Å and 85 K (Weaver and Alexeenko, 2015). Since the LJ parameters for the studied POZs are unavailable, our calculations assumed 6.77 Å and 365 K for α -cedrene, α -copaene, β -caryophyllene (hydrocarbons with several alkyl branches) and 8.02 Å and 362 K for α -farnesene and β -farnesene (long-chain hydrocarbons) (Hippler et al., 1983). The exponential model was employed for deactivation collision (Tardy and Rabinovitch, 1977; Barker et al., 2001), with the energy loss of deactivation collision set to 500 cm⁻¹ (Chuong et al., 2004). The density of states was computed by the DenSum code incorporated in the program. The “DELTA” keyword was used to input the excess energy from the exothermic POZ production. All the calculations were also simplified by neglecting (1) the reverse reaction from CIs to POZs (keyword “NOREV”), (2) the tunneling in the POZ-to-CI conversion (keyword “NOTUN”), (3) the effects of intramolecular vibrational energy redistribution (IVR) which is expected to be slow (keyword “FAST”), and (4) the centrifugal correction (keyword “NOCENT”). For each POZ decomposition, 1000 simulations were conducted using the “LOGT” keyword to set the simulation timescale. The decomposition rate constant of non-thermalized POZs was estimated by applying the first-order decay model to fit the decreasing POZ concentration as a function of simulation time. Although the decomposition rate constant of non-thermalized POZs may in principle vary with time, the time-independent value obtained from our fitting can still support a meaningful comparison with mVTST-calculated k_3 .”

Revised discussion in Section 3.3:

“The value of k_3 for thermalized POZs increases by 3–6 orders of magnitude as the temperature increases from 243 to 323 K (Fig. 4B and 4C).”

“Our findings reveal that the kinetics of sesquiterpene-derived CI formation from thermalized POZs are far more sensitive to temperature variations than the sesquiterpene ozonolysis kinetics. The strong temperature dependence arises from the high activation energies associated with the decomposition of thermalized POZs (Fig. S7). It is noted that only a small fraction of sesquiterpene-derived POZs can be thermalized by colliding with the surrounding gas molecules

in the atmosphere (Chuong et al., 2004; Hakala and Donahue, 2023). For the large fraction of non-thermalized POZs, whether their CI formation may experience kinetic relaxation in the atmosphere will be discussed below along with the thermalized cases.”

RRKM/ME results in Section 3.4:

“It bears reiterating that all the calculated values of relaxation timescales above are based on entirely thermalized POZs. For non-thermalized POZs, their k_3 values would be much higher. If we assume that the decomposition rate constants of non-thermalized POZs at atmospherically relevant temperatures are close to the values at 400 K, as justified by the numerical instability in matrix inversions of RRKM/ME computation at lower temperatures (Chuong et al., 2004), the calculated value of k_3 would be on the order of 10^3 – 10^5 s⁻¹ for α -cedrene, α -farnesene and β -farnesene (Tables S5 and S6). The corresponding relaxation timescales would then be around 10^{-5} – 10^{-3} s, which is too short to be neglected in the atmosphere. The value of k_3 is ~ 50 s⁻¹ for α -copaene at 423 K and thus would be close to ~ 10 s⁻¹ at 400 K since k_3 decreases with decreasing temperature (Table S5). The k_3 for β -caryophyllene-derived CIs is also ~ 10 s⁻¹ but at 523 K; although k_3 values for β -caryophyllene-derived CIs were not successfully obtained at lower temperatures owing to the extremely high computational cost, the k_3 value for β -caryophyllene-derived CIs at 400 K is expected to be smaller.

The extent to which k_3 at 400 K for β -caryophyllene-derived CIs is smaller may be evaluated according to the trend of RRKM/ME-computed k_3 along with the simulation temperature. We found that the RRKM/ME-computed k_3 data points for all the studied sesquiterpene-derived POZs can be well fitted by the modified Arrhenius equation (Figs. S9–S11). If extrapolated, the k_3 value for non-thermalized β -caryophyllene-derived POZ decomposition is expected to be $\sim 10^{-3}$ – 10^{-2} s⁻¹ at 400 K (Fig. S9), and the corresponding relaxation timescale is around 2–17 minutes. This is longer than the ozonolysis lifetime of β -caryophyllene (~ 1 –2 minutes) under an O₃ concentration of ~ 30 –60 ppb (Shu and Atkinson, 1994; Ou and Chen, 2025).

We note that further extrapolation of RRKM/ME-computed k_3 to 273 K and 298 K could be barely reliable; at these temperatures k_3 values for non-thermalized POZs are very close to those computed for the thermalized POZs at atmospherically relevant temperatures (Table S7). Even at 400 K, the extrapolated values may have considerable uncertainty, but the trend of RRKM/ME-computed k_3 with the simulation temperature (Tables S5 and S6) still suggests that the k_3 values of non-thermalized β -caryophyllene-derived POZs are much smaller compared to those derived from other sesquiterpenes at atmospherically relevant conditions. Collectively, our analysis of the RRKM/ME-computed results indicates that kinetic relaxation is a non-negligible phenomenon for CI formation from non-thermalized β -caryophyllene-derived POZs.”

Table S5. RRKM/ME-computed formation rate constant (unit: s⁻¹) of α -cedrene-derived, α -copaene-derived, and β -caryophyllene-derived CIs from non-thermalized POZ decomposition.*

T(K)	α -cedrene-derived CI1	α -cedrene-derived CI2	α -copaene-derived CI1	α -copaene-derived CI2	β -caryophyllene-derived CI1	β -caryophyllene-derived CI2
323	2.29×10^2	/	/	/	/	/

373	6.45×10^3	1.99×10^2	/	/	/	/
423	9.76×10^4	4.26×10^3	6.13×10^1	4.28×10^1	/	/
473	7.42×10^5	4.77×10^4	9.75×10^2	9.30×10^2	/	/
523	4.29×10^6	3.34×10^5	9.75×10^3	1.06×10^4	1.51×10^1	/
573	1.44×10^7	1.95×10^6	6.93×10^4	8.54×10^4	1.63×10^2	4.37×10^2
623	2.98×10^7	6.03×10^6	3.48×10^5	4.43×10^5	1.25×10^3	2.98×10^3
673	3.80×10^7	1.23×10^7	1.22×10^6	1.75×10^6	6.56×10^3	1.49×10^4
723	5.58×10^7	2.16×10^7	3.13×10^6	4.42×10^6	2.96×10^4	6.03×10^4

*Some values are not computed owing to the highly extensive simulation time.

Table S6. RRKM/ME-computed formation rate constant (unit: s^{-1}) of α -farnesene-derived and β -farnesene-derived CIs from non-thermalized POZ decomposition.*

T(K)	α -farnesene-derived CI1	α -farnesene-derived CI2	β -farnesene-derived CI1	β -farnesene-derived CI2
323	/	/	/	/
373	5.56×10^3	/	2.24×10^3	/
423	9.05×10^4	7.88×10^3	3.69×10^4	1.93×10^3
473	9.17×10^5	7.03×10^4	3.87×10^5	2.34×10^4
523	6.29×10^6	4.73×10^5	2.63×10^6	2.02×10^5
573	2.07×10^7	1.94×10^6	1.07×10^7	1.12×10^6
623	3.39×10^7	5.89×10^6	2.32×10^7	3.93×10^6
673	7.09×10^7	1.18×10^7	4.26×10^7	1.01×10^7
723	7.22×10^7	1.94×10^7	4.90×10^7	1.68×10^7

*Some values are not computed owing to the highly extensive simulation time.

Table S7. Comparisons of k_3 from mVTST computation and RRKM/ME-based extrapolation.

Sesquiterpene-derived CIs	k_3 from mVTST computation		k_3 from RRKM/ME-based extrapolation	
	273 K	298 K	273 K*	298 K*
α -cedrene-derived CI1	6.10×10^0	7.26×10^1	6.88×10^{-1}	1.49×10^1
α -cedrene-derived CI2	1.28×10^{-2}	2.42×10^{-1}	2.75×10^{-3}	9.83×10^{-2}
α -copaene-derived CI1	2.67×10^{-5}	8.19×10^{-4}	9.69×10^{-6}	4.14×10^{-4}
α -copaene-derived CI2	6.34×10^{-6}	2.54×10^{-4}	1.13×10^{-6}	7.79×10^{-5}

β -caryophyllene-derived CI1	2.38×10^{-10}	1.84×10^{-8}	2.15×10^{-10}	1.71×10^{-8}
β -caryophyllene-derived CI2	2.32×10^{-9}	1.40×10^{-7}	1.26×10^{-9}	9.18×10^{-8}

*Translational temperature of the colliders

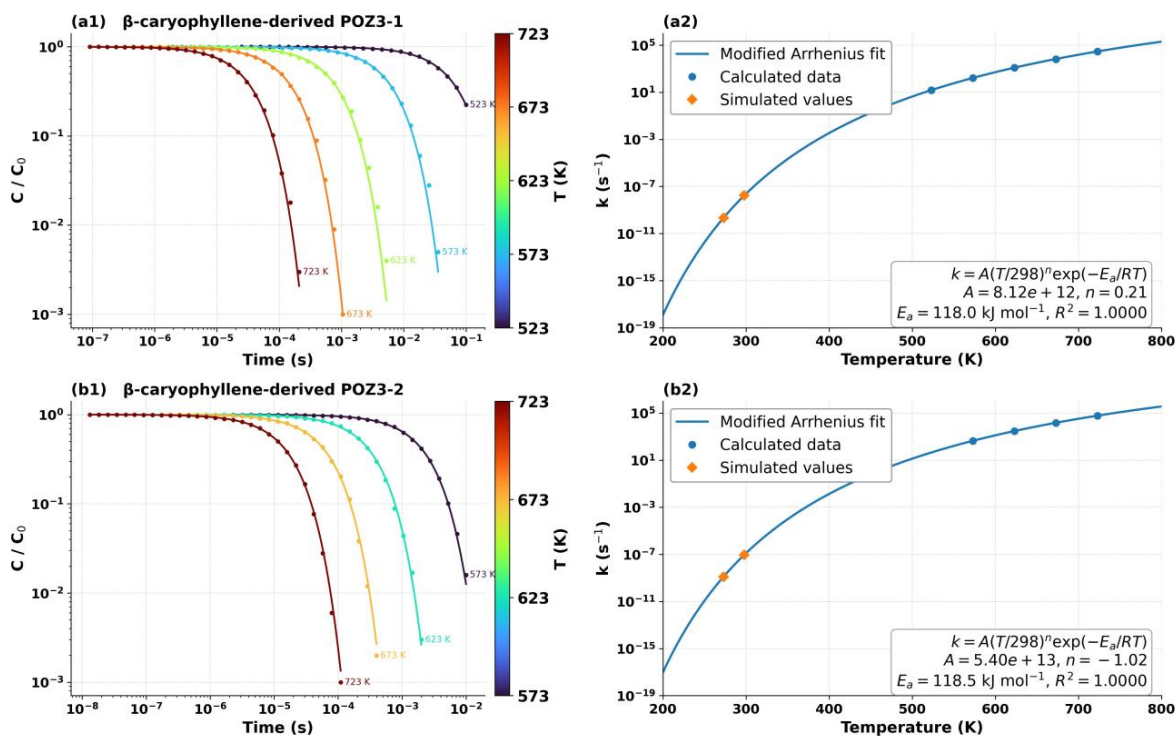


Figure S9. The normalized concentration (C / C_0) of β -caryophyllene-derived POZ3-1 (a1) and β -caryophyllene-derived POZ3-2 (b1) at different temperatures as directly output from the RRKM/ME computation. The structures of β -caryophyllene-derived POZ3-1 and POZ3-2 are obtained from our previous study (Ou and Chen, 2025); their decomposition produce β -caryophyllene-derived CI1 and CI2, respectively. The fitting k_3 results (a2-d2) are visualized with same order as the panels on the left.

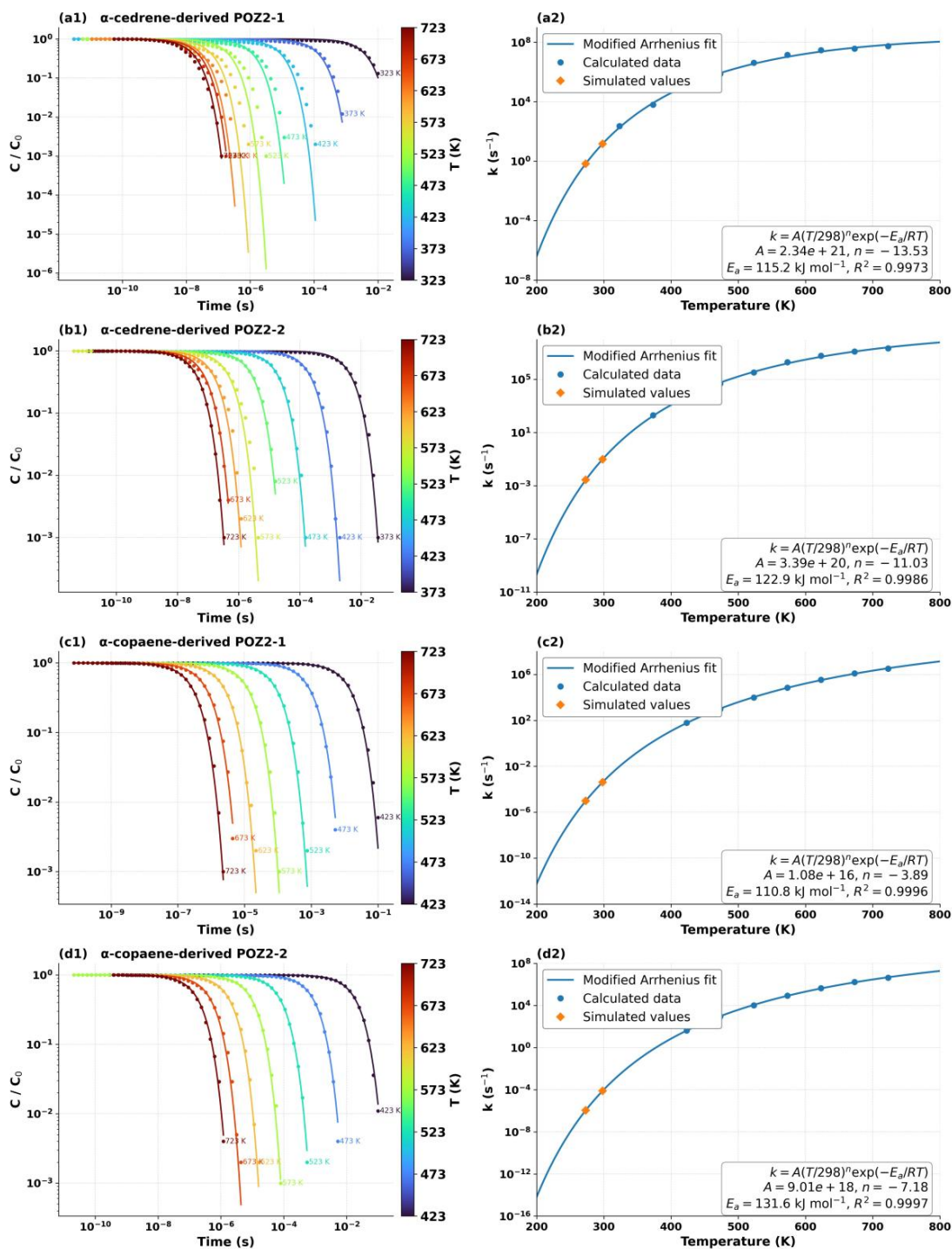


Figure S10. The normalized concentration (C/C_0) of α -cedrene-derived POZ2-1 (a1), α -cedrene-derived POZ2-2 (b1), α -copaene-derived POZ2-1 (c1) and α -copaene-derived POZ2-1 (d1) at different temperatures as directly output from the RRKM/ME computation. The fitting k_3 results (a2-d2) are visualized with same order as the panels on the left.

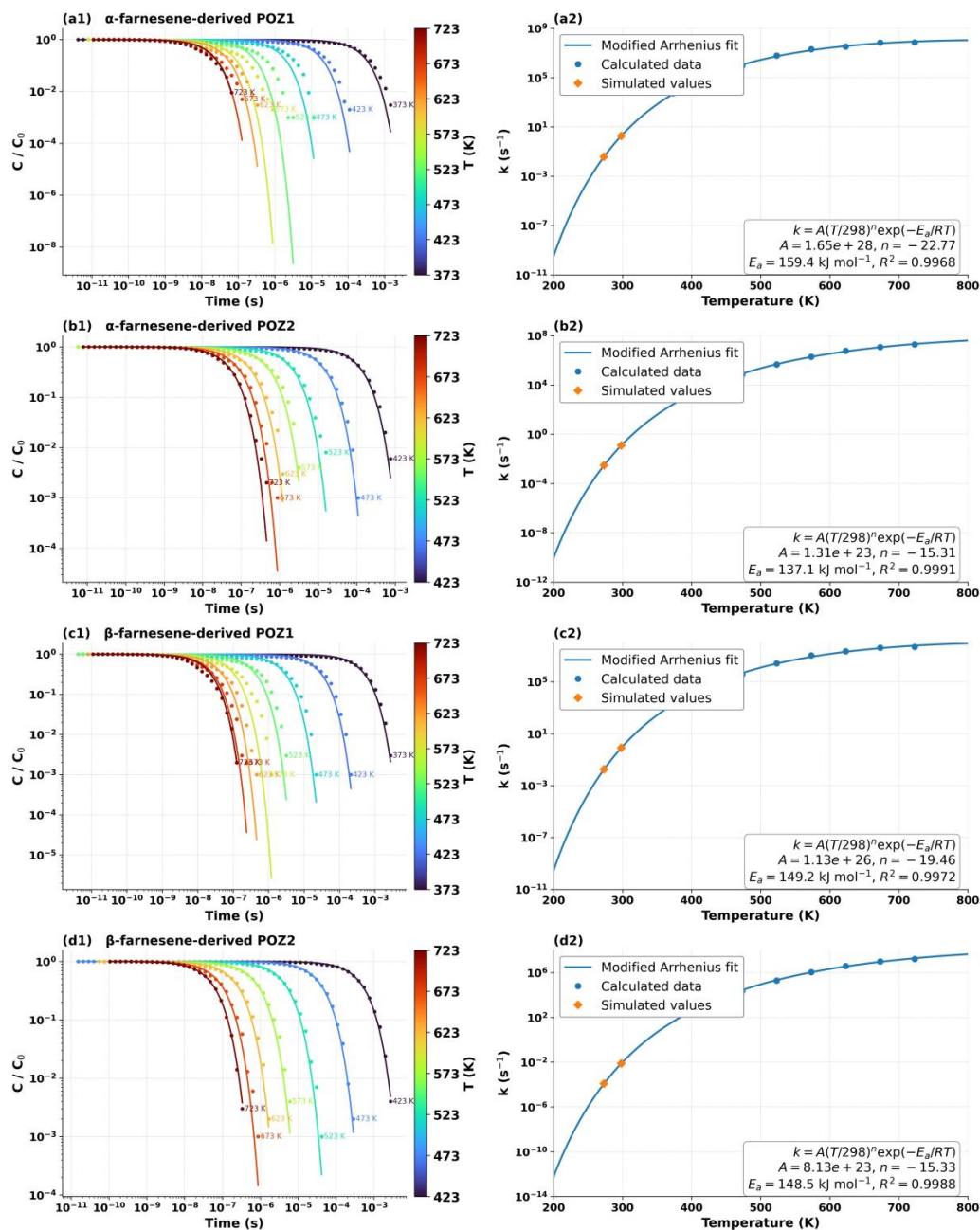


Figure S11. The normalized concentration (C / C_0) of α -farnesene-derived POZ1 (a1), α -farnesene-derived POZ2 (b1), β -farnesene-derived POZ1 (c1) and β -farnesene-derived POZ2 (d1) at different temperatures as directly output from the RRKM/ME computation. The fitting k_3 results (a2-d2) are visualized with same order as the panels on the left.

In the Conclusion section:

“This relaxation arises from the thermalized sesquiterpene-derived POZs and potentially from non-thermalized POZs derived from certain sesquiterpenes such as β -caryophyllene.”

Referee #2

In this manuscript, the authors have evaluated “kinetic relaxation” in the ozonolysis process in atmospheric sesquiterpenes using computational methods. Here, they compared the reaction rate for forming primary ozonide (POZ) versus that for forming the Criegee intermediates (CIs). In both reactions, the reactants are the sesquiterpenes and ozone. The authors defined kinetic relaxation as the ratio of CI formation rate versus POZ formation rate. They performed theoretical calculations using M06-2X/def2-TZP geometries with DLPNO-CCSD(T) energy corrections.

The key issue in this manuscript is that the authors considered thermal POZ formation from ozone and sesquiterpene and CI formation from thermally equilibrated POZ as two independent processes for the calculation. I suggest that the authors properly show the calculated energies in Figures 2C and 2D. Whether POZ will be in equilibrium or not after passing the transition state from ozone and sesquiterpene depends on the exothermic energy of POZ relative to the reactants, ozone and sesquiterpenes. Many previous studies have mentioned that ozonolysis will produce “vibrationally excited” POZ, which can quickly produce CI under atmospheric pressure conditions. Therefore, the difference in the POZ formation rate and the CI formation rate is assumed to be small in atmospheric conditions.

Response: We appreciated the referee’s the critical comment. We agree that treating POZ formation from sesquiterpene ozonolysis and CI formation from POZs as two independent processes is inappropriate in general, since the latter is affected by the exothermic energy released in the former. Under atmospheric conditions (e.g., 1 atm and 300 K), only ~10% of POZs derived from C₁₅ precursors like sesquiterpenes can be fully thermalized (Chuong et al., 2004), so our computation is only valid for a small fraction of the sesquiterpene-derived POZ population. The majority of POZs remain in their vibrationally excited states, and we agree that, for these non-thermalized POZs, the difference in POZ formation rate constant and CI formation rate constant is reasonably assumed to be small.

In the revised manuscript, we highlight that only a small fraction of sesquiterpene-derived POZs can be fully thermalized in the atmosphere, so the CI kinetic relaxation is not a universal phenomenon, and its significance should be narrowed down. To clarify all these points, we rewrote the entire Abstract and part of the Introduction section, and revised the discussions in Section 3.3 about the k_3 values of thermalized POZs. We also explicitly show the calculated energies in the new Figure 2.

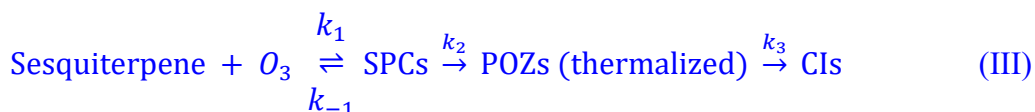
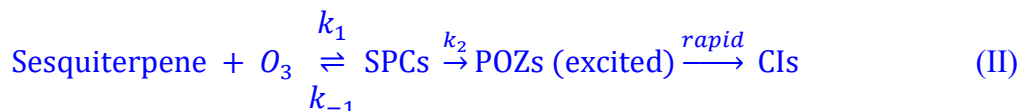
Rewritten Abstract:

“Sesquiterpene ozonolysis contributes to secondary organic aerosol (SOA) formation through the production of Criegee intermediates (CIs) via primary ozonide (POZ) decomposition. Although POZs are in general vibrationally excited to rapidly produce CIs, a fraction of sesquiterpene-derived POZs can be fully thermalized; yet the kinetics of CI formation from these thermalized POZs has received little attention. This study reports the overlooked kinetic relaxation during CI formation from thermalized POZs of representative sesquiterpenes, including α -cedrene, α -copaene, β -caryophyllene, α -farnesene, and β -farnesene. We found that, for thermalized POZs, the apparent CI formation rate constant is initially unstable but gradually approaches a plateau, which

equals the rate constant of sesquiterpene ozonolysis. Our results revealed that kinetic relaxation is sensitive to temperature variations, as cold surges extend the relaxation timescale from minutes to hours (or hours to days) while heatwaves reversely diminish the relaxation timescale. We further examined the CI formation kinetics from non-thermalized POZs, which suggested that kinetic relaxation may still occur for those derived from β -caryophyllene. The relaxation timescale is longer than the ozonolysis lifetime of β -caryophyllene under tropospheric O_3 concentrations. Our findings demonstrate that, for sesquiterpenes, neglecting kinetic relaxation may overestimate the rate of their CI formation and thus the resultant oxidation capacity.”

Rewritten part in the Introduction section:

“The value of k_{CI} is generally assumed equal to the ozonolysis rate constant (k_{oz}) in the literature (Taatjes et al., 2014; Cox et al., 2020). In principle, terpene ozonolysis first forms stabilized prereactive complexes (SPCs) and subsequently generates primary ozonides (POZs), which further decompose into CIs (Donahue et al., 2011; Vereecken and Francisco, 2012; Taatjes et al., 2014). The quantity k_{CI} refers to the projection from the reactants (sesquiterpenes and O_3 in this study) to CIs (Scheme I), and k_{oz} refers to the projection from the reactants to POZs (Ou and Chen, 2025; Ou et al., 2026). Given the high exothermic energy ($\sim 50\text{--}60\text{ kcal mol}^{-1}$) from O_3 addition to the $C=C$ double bond (Nangia and Benson, 1980; Cremer, 1981; Chuong et al., 2004; Johnson and Marston, 2008), POZs are typically in their vibrationally excited states to rapidly produce CIs under normal atmospheric conditions (Chuong et al., 2004; Hakala and Donahue, 2023). In this case, the conversion from POZs to CIs is expected to be far from thermal equilibrium so that the reaction proceeds more like SPCs overcoming the energy barrier corresponding to k_2 and directly produce CIs (Scheme II).



However, if POZs are fully thermalized, k_{CI} and k_{oz} are not necessarily interchangeable (Scheme III). This will not happen for all of the small alkenes and even C_{10} molecules (e.g., monoterpenes) in the air, but for C_{15} molecules such as sesquiterpenes, a fraction of them can be thermalized under atmospheric conditions (Chuong et al., 2004). In this case, there is no guarantee that k_{CI} can be equal to k_{oz} . The influence of k_3 on k_{CI} is largely overlooked from the thermalized POZs. To address this concern, the community may require a rigorous approach to resolving the rate constant of CI formation by explicitly considering the POZ-to-CI conversion.”

“We selected CIs from sesquiterpene ozonolysis as our case study for three reasons: (1) the rate constants of sesquiterpene ozonolysis mostly show no dependence on air pressure in the troposphere; (2) the large molecular size of sesquiterpenes may keep the SPCs collisionally stabilized (Wong et al., 2003; Yao et al., 2017; Ou and Chen, 2025); (3) sesquiterpenes are C_{15}

molecules such that their ozonolysis yields a fraction of thermalized POZs under atmospherically relevant conditions (Chuong et al., 2004).”

Description related to the new Figure 2:

“Taking α -cedrene and α -copaene as examples, both molecules have only one C=C double bond and both have two sites for ozonolysis (Fig. 2A). Since each POZ has two conformers, there are totally four POZs can be formed for α -cedrene or α -copaene (Fig. S2). The POZ production tendency is quantified by the ratio $k_2 / (k_{-1} + k_2)$ (Fig. S3 and S4), wherein the predominant channels for POZ production as well as CI formation are shown here (Fig. 2B and 2C). The comparisons of activation energies ($E_a(k_{-1})$ and $E_a(k_2)$) from the Arrhenius fitting can help a clear analysis of temperature dependence (Fig. 3, Table S1).”

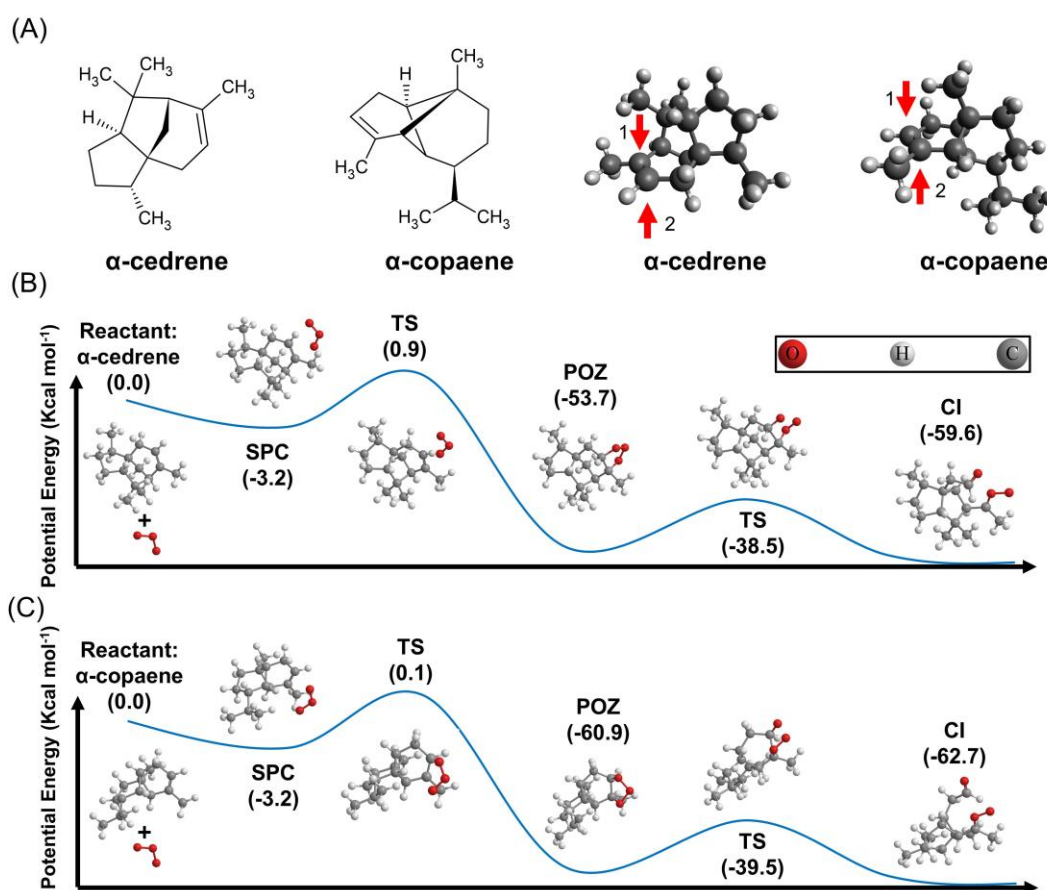


Figure 2. Examples of sesquiterpene ozonolysis kinetics: (A) Molecular structures of α -cedrene and α -copaene with the labels of ozonolysis site 1 and 2; the “double-well” potential energy surface of the formation of (B) an α -cedrene-derived CI and (C) an α -copaene-derived CI.

Reference:

Chuong, B., Zhang, J., and Donahue, N. M.: Cycloalkene Ozonolysis: Collisionally Mediated Mechanistic Branching, *J. Am. Chem. Soc.* **2004**, 126, 12363-12373. DOI: 10.1021/ja0485412

Instead of using thermal approximation for each process, one should use energy-based master's equation with buffer gas collision for energy activation and deactivation. Such protocols are available in the multiwell package that the authors used for calculating thermal rate coefficients.

Response: We thank the referee for the constructive comment. We conducted the RRKM/ME calculations, which handle the CI formation kinetics by considering the energy activation and deactivation with collisions between the non-thermalized POZs and buffer gas. Our RRKM/ME results show much higher rate constants for POZ decomposition, while certain sesquiterpenes (e.g., β -caryophyllene) still show non-negligible relaxation timescale in the CI formation kinetics. The description RRKM/ME methodology as well as computational results have been added to the revised manuscript and the revised Supporting Information. The content is also attached below.

RRKM/ME setup in the Method section:

“The decomposition rate constant of non-thermalized POZs was estimated using the RRKM/ME calculations (i.e., Rice–Ramsperger–Kassel–Marcus theory/master equation) by the Multiwell 2023 program (Barker, 2009, 2001). The pressure was set as 1.0 atm, and the surrounding collider was nitrogen gas (N_2) with the Lennard–Jones (LJ) parameters (σ and ϵ / k_B) of 3.70 Å and 85 K (Weaver and Alexeenko, 2015). Since the LJ parameters for the studied POZs are unavailable, our calculations assumed 6.77 Å and 365 K for α -cedrene, α -copaene, β -caryophyllene (hydrocarbons with several alkyl branches) and 8.02 Å and 362 K for α -farnesene and β -farnesene (long-chain hydrocarbons) (Hippler et al., 1983). The exponential model was employed for deactivation collision (Tardy and Rabinovitch, 1977; Barker et al., 2001), with the energy loss of deactivation collision set to 500 cm^{-1} (Chuong et al., 2004). The density of states was computed by the DenSum code incorporated in the program. The “DELTA” keyword was used to input the excess energy from the exothermic POZ production. All the calculations were also simplified by neglecting (1) the reverse reaction from CIs to POZs (keyword “NOREV”), (2) the tunneling in the POZ-to-CI conversion (keyword “NOTUN”), (3) the effects of intramolecular vibrational energy redistribution (IVR) which is expected to be slow (keyword “FAST”), and (4) the centrifugal correction (keyword “NOCENT”). For each POZ decomposition, 1000 simulations were conducted using the “LOGT” keyword to set the simulation timescale. The decomposition rate constant of non-thermalized POZs was estimated by applying the first-order decay model to fit the decreasing POZ concentration as a function of simulation time. Although the decomposition rate constant of non-thermalized POZs may in principle vary with time, the time-independent value obtained from our fitting can still support a meaningful comparison with mVTST-calculated k_3 .”

RRKM/ME results in Section 3.4:

“It bears reiterating that all the calculated values of relaxation timescales above are based on entirely thermalized POZs. For non-thermalized POZs, their k_3 values would be much higher. If we assume that the decomposition rate constants of non-thermalized POZs at atmospherically relevant temperatures are close to the values at 400 K, as justified by the numerical instability in matrix inversions of RRKM/ME computation at lower temperatures (Chuong et al., 2004), the calculated value of k_3 would be on the order of 10^3 – 10^5 s^{-1} for α -cedrene, α -farnesene and β -farnesene (Tables S5 and S6). The corresponding relaxation timescales would then be around 10^{-5} – 10^{-3} s, which is too short to be neglected in the atmosphere. The value of k_3 is ~ 50 s^{-1} for α -

copaene at 423 K and thus would be close to $\sim 10 \text{ s}^{-1}$ at 400 K since k_3 decreases with decreasing temperature (Table S5). The k_3 for β -caryophyllene-derived CIs is also $\sim 10 \text{ s}^{-1}$ but at 523 K; although k_3 values for β -caryophyllene-derived CIs were not successfully obtained at lower temperatures owing to the extremely high computational cost, the k_3 value for β -caryophyllene-derived CIs at 400 K is expected to be smaller.

The extent to which k_3 at 400 K for β -caryophyllene-derived CIs is smaller may be evaluated according to the trend of RRKM/ME-computed k_3 along with the simulation temperature. We found that the RRKM/ME-computed k_3 data points for all the studied sesquiterpene-derived POZs can be well fitted by the modified Arrhenius equation (Figs. S9–S11). If extrapolated, the k_3 value for non-thermalized β -caryophyllene-derived POZ decomposition is expected to be $\sim 10^{-3}$ – 10^{-2} s^{-1} at 400 K (Fig. S9), and the corresponding relaxation timescale is around 2–17 minutes. This is longer than the ozonolysis lifetime of β -caryophyllene (~ 1 –2 minutes) under an O_3 concentration of ~ 30 –60 ppb (Shu and Atkinson, 1994; Ou and Chen, 2025).

We note that further extrapolation of RRKM/ME-computed k_3 to 273 K and 298 K could be barely reliable; at these temperatures k_3 values for non-thermalized POZs are very close to those computed for the thermalized POZs at atmospherically relevant temperatures (Table S7). Even at 400 K, the extrapolated values may have considerable uncertainty, but the trend of RRKM/ME-computed k_3 with the simulation temperature (Tables S5 and S6) still suggests that the k_3 values of non-thermalized β -caryophyllene-derived POZs are much smaller compared to those derived from other sesquiterpenes at atmospherically relevant conditions. Collectively, our analysis of the RRKM/ME-computed results indicates that kinetic relaxation is a non-negligible phenomenon for CI formation from non-thermalized β -caryophyllene-derived POZs.”

Table S5. RRKM/ME-computed formation rate constant (unit: s^{-1}) of α -cedrene-derived, α -copaene-derived, and β -caryophyllene-derived CIs from non-thermalized POZ decomposition.*

T(K)	α -cedrene-derived CI1	α -cedrene-derived CI2	α -copaene-derived CI1	α -copaene-derived CI2	β -caryophyllene-derived CI1	β -caryophyllene-derived CI2
323	2.29×10^2	/	/	/	/	/
373	6.45×10^3	1.99×10^2	/	/	/	/
423	9.76×10^4	4.26×10^3	6.13×10^1	4.28×10^1	/	/
473	7.42×10^5	4.77×10^4	9.75×10^2	9.30×10^2	/	/
523	4.29×10^6	3.34×10^5	9.75×10^3	1.06×10^4	1.51×10^1	/
573	1.44×10^7	1.95×10^6	6.93×10^4	8.54×10^4	1.63×10^2	4.37×10^2
623	2.98×10^7	6.03×10^6	3.48×10^5	4.43×10^5	1.25×10^3	2.98×10^3
673	3.80×10^7	1.23×10^7	1.22×10^6	1.75×10^6	6.56×10^3	1.49×10^4
723	5.58×10^7	2.16×10^7	3.13×10^6	4.42×10^6	2.96×10^4	6.03×10^4

*Some values are not computed owing to the highly extensive simulation time.

Table S6. RRKM/ME-computed formation rate constant (unit: s^{-1}) of α -farnesene-derived and β -farnesene-derived CIs from non-thermalized POZ decomposition.*

T(K)	α -farnesene-derived CI1	α -farnesene-derived CI2	β -farnesene-derived CI1	β -farnesene-derived CI2
323	/	/	/	/
373	5.56×10^3	/	2.24×10^3	/
423	9.05×10^4	7.88×10^3	3.69×10^4	1.93×10^3
473	9.17×10^5	7.03×10^4	3.87×10^5	2.34×10^4
523	6.29×10^6	4.73×10^5	2.63×10^6	2.02×10^5
573	2.07×10^7	1.94×10^6	1.07×10^7	1.12×10^6
623	3.39×10^7	5.89×10^6	2.32×10^7	3.93×10^6
673	7.09×10^7	1.18×10^7	4.26×10^7	1.01×10^7
723	7.22×10^7	1.94×10^7	4.90×10^7	1.68×10^7

*Some values are not computed owing to the highly extensive simulation time.

Table S7. Comparisons of k_3 from mVTST computation and RRKM/ME-based extrapolation.

Sesquiterpene-derived CIs	k_3 from mVTST computation		k_3 from RRKM/ME-based extrapolation	
	273 K	298 K	273 K*	298 K*
α -cedrene-derived CI1	6.10×10^0	7.26×10^1	6.88×10^{-1}	1.49×10^1
α -cedrene-derived CI2	1.28×10^{-2}	2.42×10^{-1}	2.75×10^{-3}	9.83×10^{-2}
α -copaene-derived CI1	2.67×10^{-5}	8.19×10^{-4}	9.69×10^{-6}	4.14×10^{-4}
α -copaene-derived CI2	6.34×10^{-6}	2.54×10^{-4}	1.13×10^{-6}	7.79×10^{-5}
β -caryophyllene-derived CI1	2.38×10^{-10}	1.84×10^{-8}	2.15×10^{-10}	1.71×10^{-8}
β -caryophyllene-derived CI2	2.32×10^{-9}	1.40×10^{-7}	1.26×10^{-9}	9.18×10^{-8}

*Translational temperature of the colliders

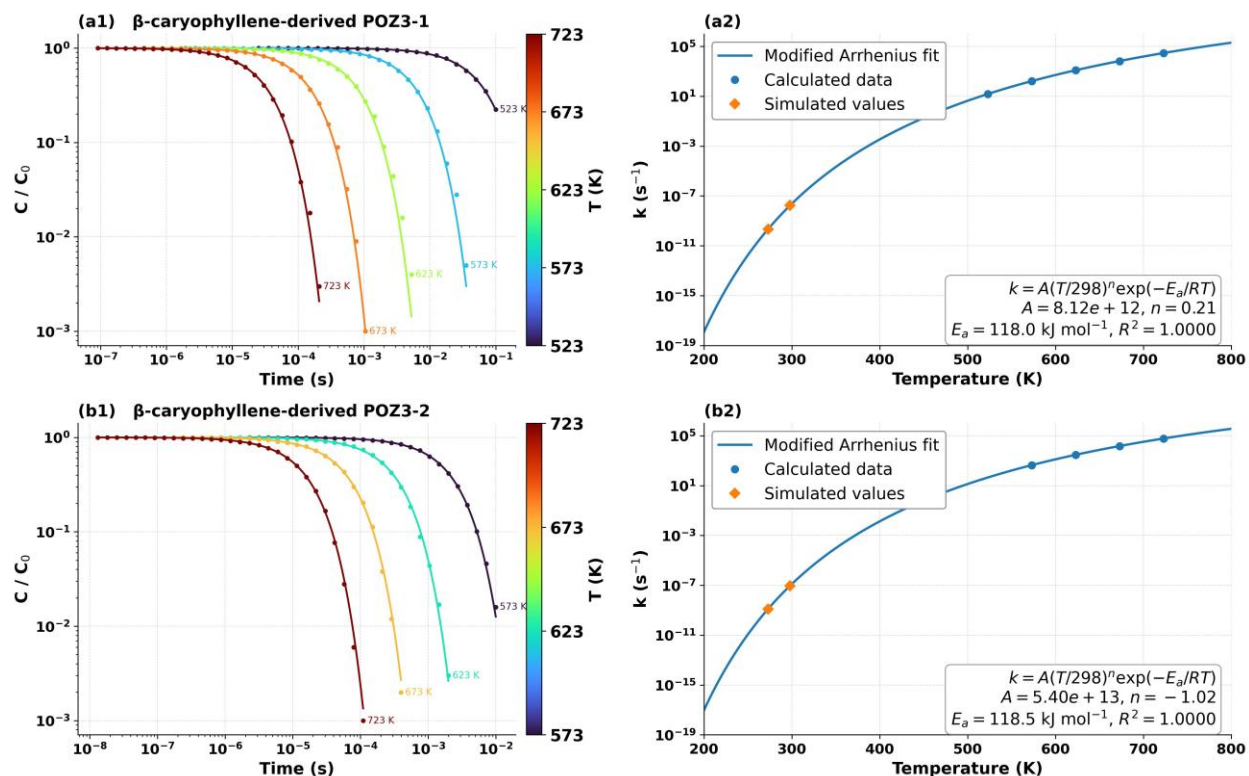


Figure S9. The normalized concentration (C/C_0) of β -caryophyllene-derived POZ3-1 (a1) and β -caryophyllene-derived POZ3-2 (b1) at different temperatures as directly output from the RRKM/ME computation. The structures of β -caryophyllene-derived POZ3-1 and POZ3-2 are obtained from our previous study (Ou and Chen, 2025); their decomposition produce β -caryophyllene-derived CI1 and CI2, respectively. The fitting k_3 results (a2-d2) are visualized with same order as the panels on the left.

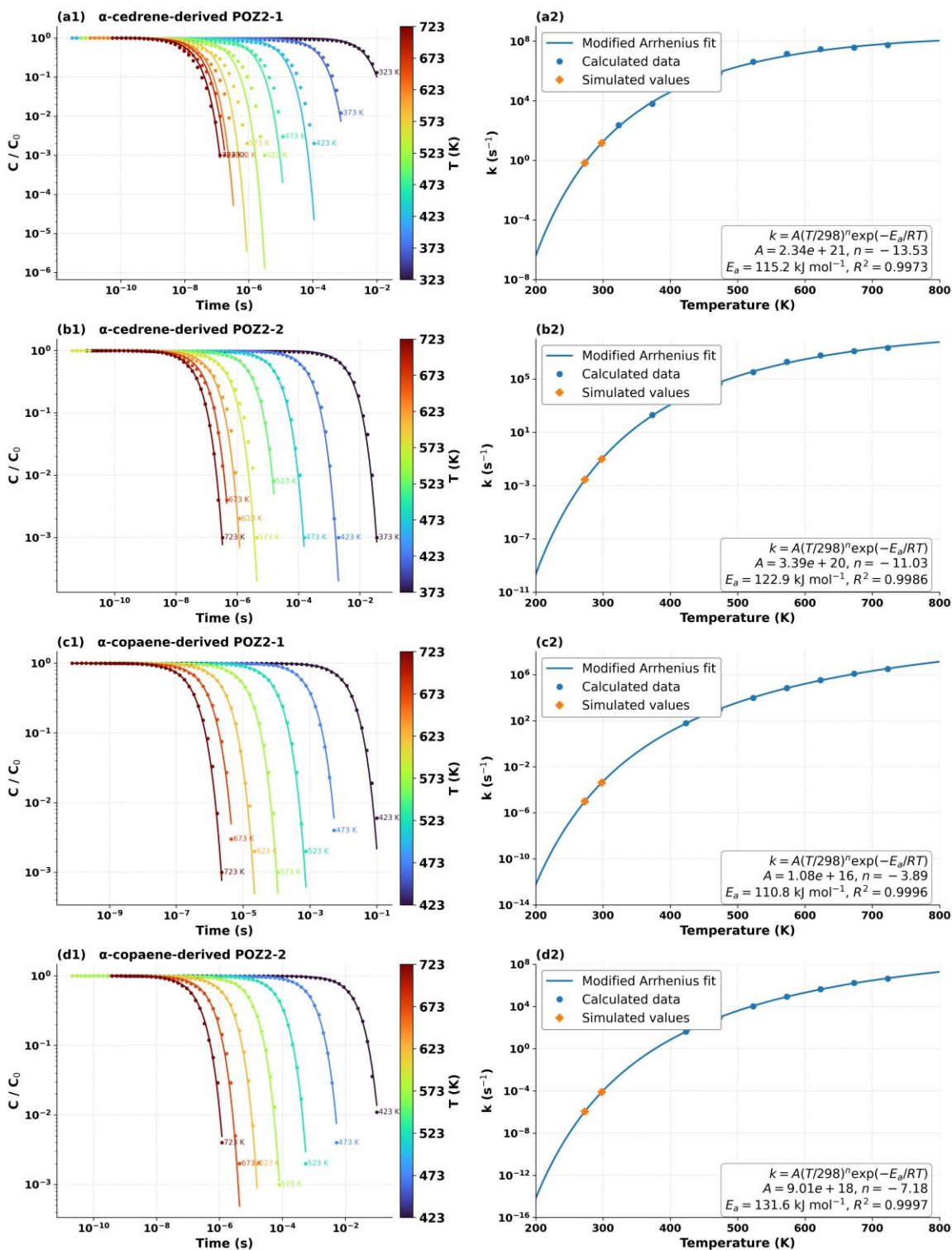


Figure S10. The normalized concentration (C / C_0) of α -cedrene-derived POZ2-1 (a1), α -cedrene-derived POZ2-2 (b1), α -copaene-derived POZ2-1 (c1) and α -copaene-derived POZ2-1 (d1) at different temperatures as directly output from the RRKM/ME computation. The fitting k_3 results (a2-d2) are visualized with same order as the panels on the left.

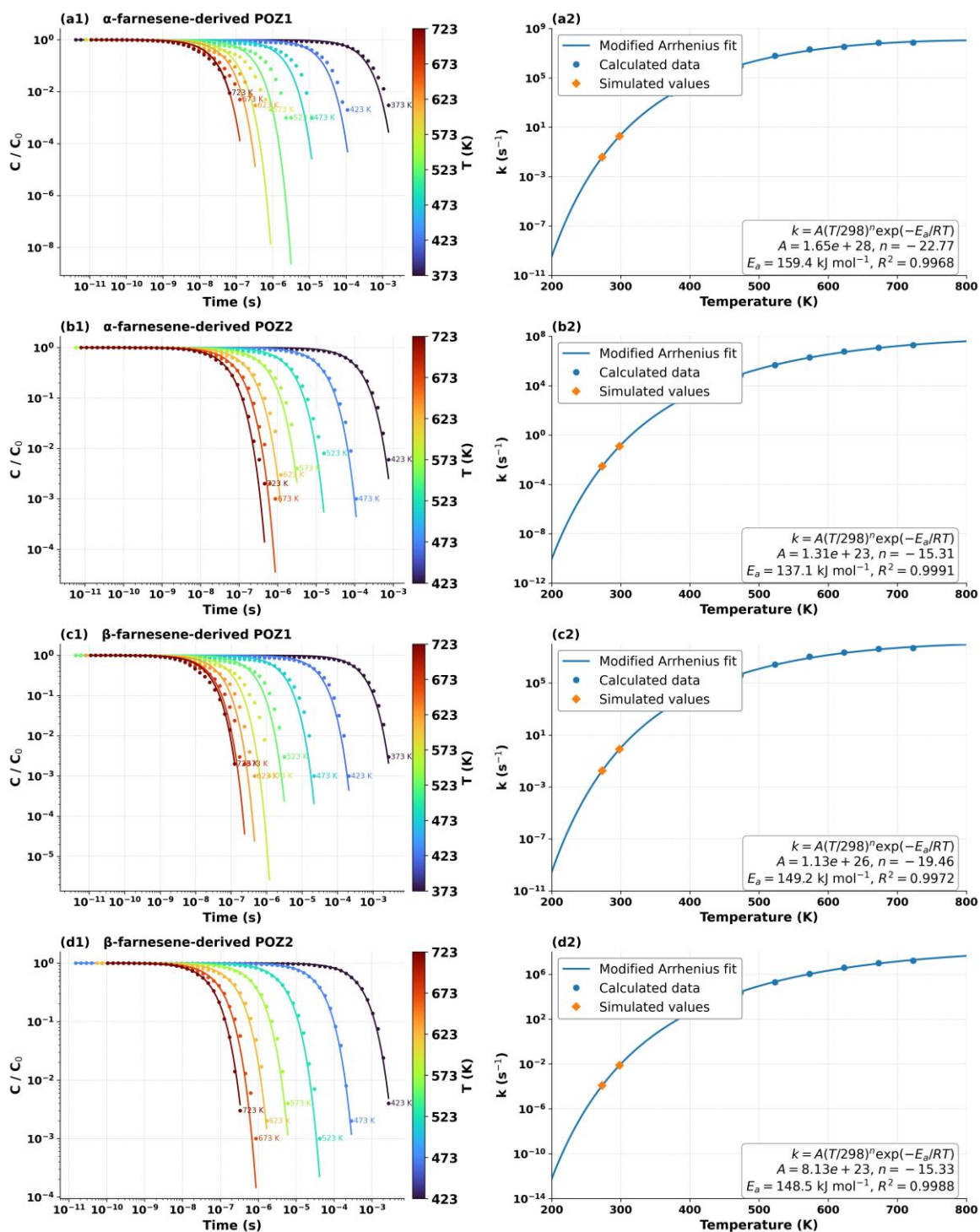


Figure S11. The normalized concentration (C / C_0) of α -farnesene-derived POZ1 (a1), α -farnesene-derived POZ2 (b1), β -farnesene-derived POZ1 (c1) and β -farnesene-derived POZ2 (d1) at different temperatures as directly output from the RRKM/ME computation. The fitting k_3 results (a2-d2) are visualized with same order as the panels on the left.

In the Conclusion section:

“This relaxation arises from the thermalized sesquiterpene-derived POZs and potentially from non-thermalized POZs derived from certain sesquiterpenes such as β -caryophyllene.”

In addition, schematic geometries of intermediates and CIs should be presented in the main text. Labels such as SPC1-1, SPC1-2, or CI isomer 1 are hard to follow without molecular structures in the main text.

Response: We currently split the initial Figure 2 into a new Figure 2 and a new Figure 3 in the revised manuscript. The new Figure 3 currently shows the geometries of SPC1-1, SPC1-2, SPC2-1, and SPC2-2. We also add a new figure (Figure 5) to the revised manuscript to show the structures of CI isomer 1 and CI isomer 2, and how these CI isomers are produced from POZ decomposition. These figures are also attached below.

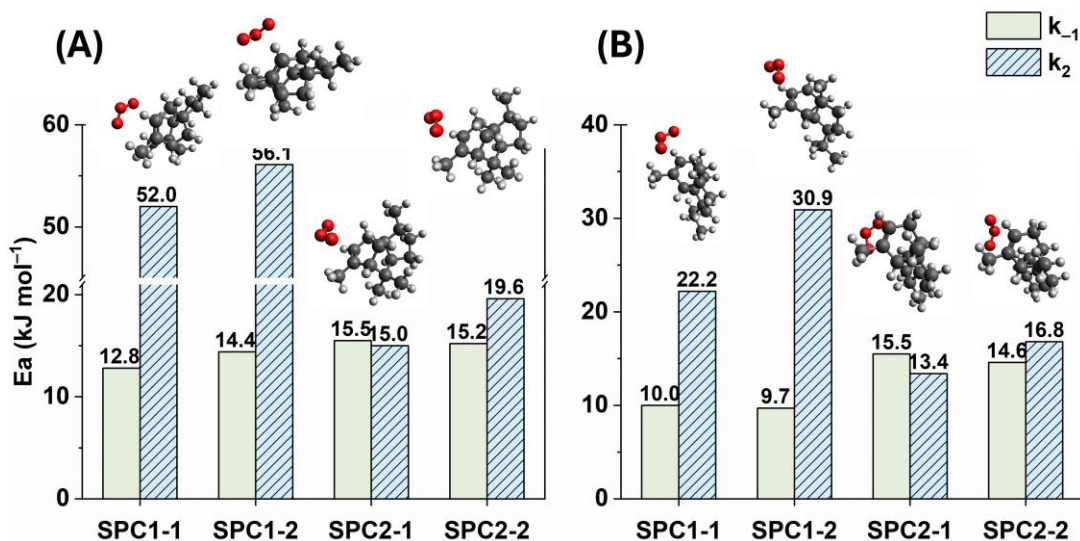


Figure 3. Fitted activation energy of k_{-1} and k_2 for all the SPCs from ozonolysis of (A) α -cedrene and (B) α -copaene.

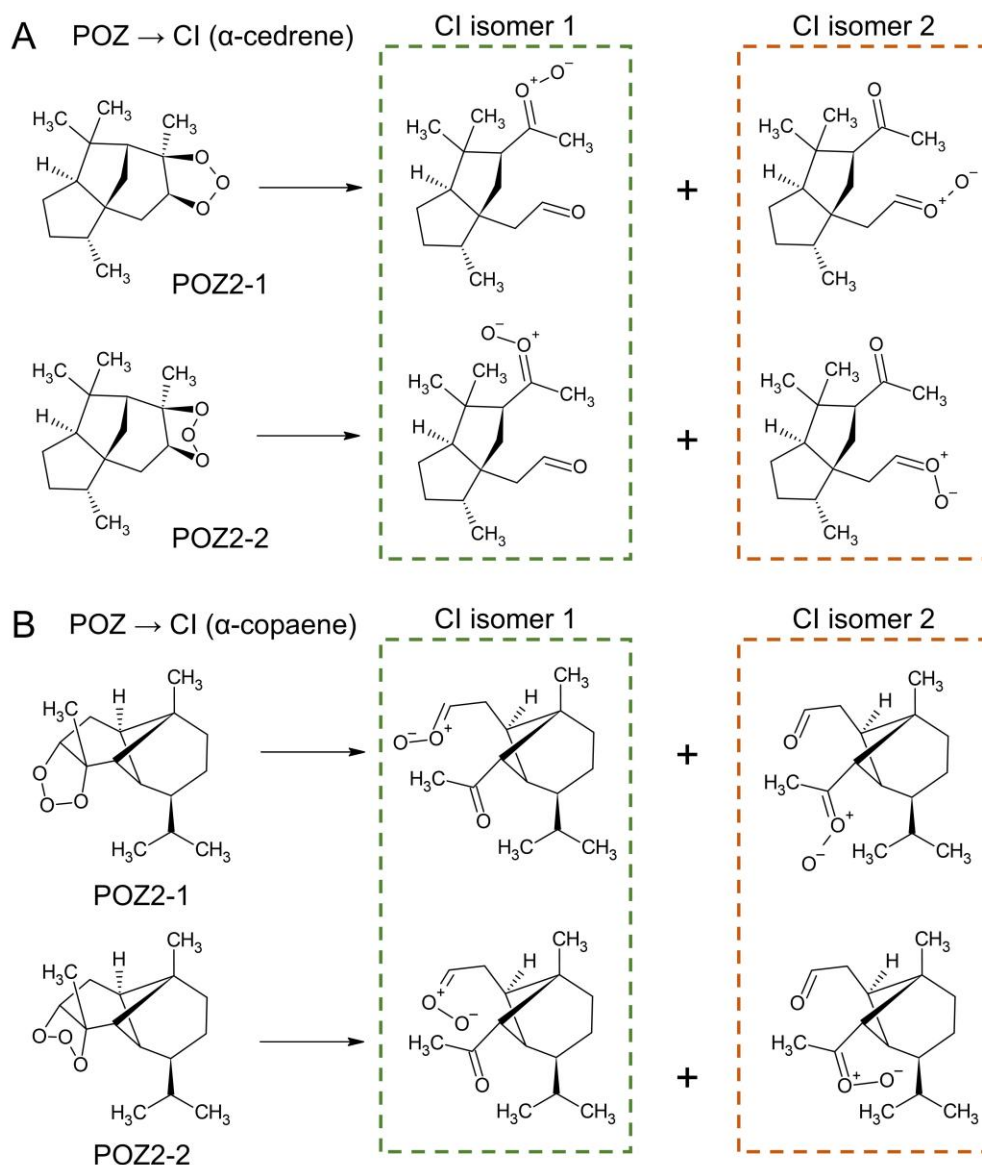


Figure 5. Structures of the predominant POZs derived from α -cedrene and α -copaene, and of the CIs produced by the decomposition of POZs.

“Although each POZ can decompose via two channels to form two CI isomers (Fig. 5), our results reveal that only one pathway clearly dominates.”

Some conditions mentioned in the main text are not necessary. For example, on page 8, the authors assume steady-state SPC concentration for the reaction forming POZ. However, forming POZ from the reactants of ozone and sesquiterpene can occur by directly reaching the TS through collision.

Response: We appreciated the referee for the critical comment. We agree that it is possible to directly reach the TS through collisions between the reactants, but under atmospheric conditions, it may play a very minor role. Direct access to the TS proceeds from excited prereactive complexes,

which have higher energy compared to the SPCs (and thus the SPCs are skipped) and may play a major role only at high temperatures. For example, SPCs can be entirely skipped at over 450 K for OH-initiated oxidation of acetone (Yamada et al., 2003; Davis et al., 2005). If the steady-state concentration of SPCs is assumed, the resultant kinetic model can fit the experimental data of OH-initiated oxidation kinetics of acetone across different temperatures (237–353 K) pretty well (Talukdar et al., 2003). It is also similar in sesquiterpene ozonolysis; our previous study shows that, if β -caryophyllene ozonolysis is assumed to proceed mainly via SPCs, the resultant steady-state SPC concentrations can enable a computational simulation that reproduces the experimentally observed temperature dependence of β -caryophyllene ozonolysis within 243–313 K (Ou and Chen, 2025). All the evidence collectively supports that under atmospheric conditions the reactants tend to form SPCs. To clarify this point, we revised the statement in the manuscript, as shown below.

“The kinetic relaxation was found when we explicitly derived the kinetic model of CI formation. As suggested in the literature (Taatjes et al., 2014; Cox et al., 2020), the rate constant for CI formation was previously assumed to be equal to that of ozonolysis. Such an assumption treats the process from sesquiterpene ozonolysis to CI formation as a balance of inflow and outflow, but since this process is a consecutive reaction intermediated by SPCs and POZs, the rate of sesquiterpene consumption and the rate of CI formation are in principle not always the same. Stepwise kinetics related to SPCs and POZs should be explicitly handled.

The main assumption in this study is the steady-state concentration of SPCs (Fig. 1A). Prior studies proposed that assuming steady-state SPC concentrations can fit the experimental data of OH-initiated oxidation kinetics of acetone across different temperatures within 237–353 K (Talukdar et al., 2003). Although the reaction may proceed from excited prereactive complexes (thereby skipping the SPCs) to directly reach the transition states, excited prereactive complexes may play a major role only at high temperatures (e.g., over 450 K for acetone) such that under atmospheric conditions the reactants tend to form SPCs (Yamada et al., 2003; Davis et al., 2005). The assumption of steady-state SPC concentrations also enables a computational simulation that reproduces the experimentally observed temperature dependence of β -caryophyllene ozonolysis within 243–313 K (Ou and Chen, 2025). The agreement between the experimental data and the simulation suggests that the collision between reactants may primarily yield the SPCs.”

Reference:

- Talukdar, R. K., Gierczak, T., McCabe, D. C., and Ravishankara, A. R.: Reaction of Hydroxyl Radical with Acetone. 2. Products and Reaction Mechanism, *J. Phys. Chem. A* **2003**, 107, 5021-5032. DOI: 10.1021/jp0273023
- Yamada, T., Taylor, P. H., Goumri, A., and Marshall, P.: The reaction of OH with acetone and acetone-d₆ from 298 to 832 K: Rate coefficients and mechanism, *J. Chem. Phys.* **2003**, 119, 10600-10606. DOI: 10.1063/1.1619950
- Davis, M. E., Drake, W., Vimal, D., and Stevens, P. S.: Experimental and theoretical studies of the kinetics of the reactions of OH and OD with acetone and acetone-d₆ at low pressure, *J. Photochem. Photobiol. A Chem.* **2005**, 176, 162-171. DOI: 10.1016/j.jphotochem.2005.08.030
- Ou, H. and Chen, K.: Atmospheric Temperature Dependence of β -Caryophyllene Ozonolysis Kinetics Is Governed by Stabilized Prereactive Complexes, *J. Phys. Chem. A* **2025**, 129, 9982-9990. DOI: 10.1021/acs.jpca.5c05523

CC 1

The authors applied a kinetic model based on thermal equilibrium to a reaction system far from thermal equilibrium. The results are misleading.

Response: We appreciate the referee for providing critical comments. We agree that our results related to POZs and k_3 are misleading in the manuscript, as we did not separate the thermal equilibrium and non-equilibrium cases in the kinetic discussions. We now realize that only a small fraction of sesquiterpene-derived POZs can be fully thermalized in the atmosphere, so the CI kinetic relaxation is not a universal phenomenon, and its significance should be narrowed down.

In the revised manuscript, we separated the discussion about k_3 into the scenarios of thermalized POZs and non-thermalized POZs. More details can be found in the point-to-point response below.

(1) The kinetic model assumed thermal equilibrium for SPCs and POZs, and ignored collisional energy transfer within each species. This may be true for SPCs, and is invalid for POZs. POZs are formed with high excitations as POZs, which can undergo prompt isomerization to CIs*. The authors calculated k_3 using the equilibrium energy distribution in POZs. This is invalid unless the reactions are under extremely high pressure.*

The kinetic processes are more often modelled using RRKM-ME method. Due to the large size of reaction system, there might be a fraction of POZ being thermalized by collision before their prompt isomerization.*

Response: We appreciate the referee's insightful comment and detailed explanation. We agree that POZs are formed in their excited states and can generate CIs that are also highly excited. We also agree that our computational approach is only valid for all the POZs if the pressure is extremely high. Under atmospheric conditions (e.g., 1 atm and 300 K), only ~10% of POZs derived from C₁₅ precursors like sesquiterpenes can be fully thermalized (refer to Figure 6 in Chuong et al., 2004; the full reference is provided below), which agrees with the referee's comment about “a fraction of POZ* being thermalized by collision”.

For the non-thermalized POZs, we conducted RRKM-ME computations for their decomposition kinetics and added the results to the revised manuscript as well as the Supporting Information. Our RRKM/ME results show much higher rate constants for POZ decomposition, while certain sesquiterpenes (e.g., β -caryophyllene) still show non-negligible relaxation timescale in the CI formation kinetics. To clarify all these points, we rewrote the entire Abstract and part of the Introduction section, added the methodology of RRKM-ME computation, revised the discussions in Section 3.3 about the k_3 values of thermalized POZs, added the discussions about the results of RRKM-ME computation in Section 3.4, and revised the statement in the Conclusion section.

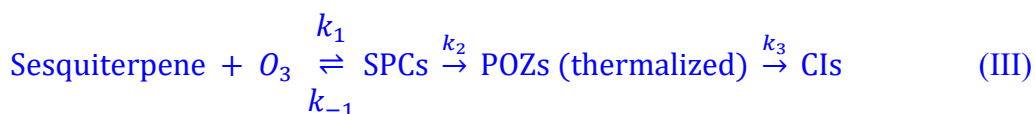
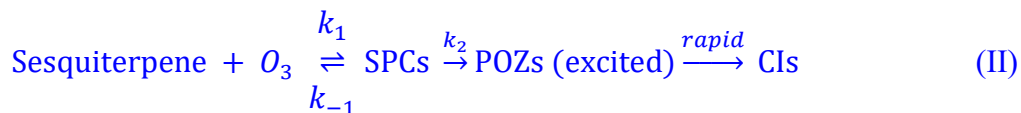
Rewritten Abstract:

“Sesquiterpene ozonolysis contributes to secondary organic aerosol (SOA) formation through the production of Criegee intermediates (CIs) via primary ozonide (POZ) decomposition. Although POZs are in general vibrationally excited to rapidly produce CIs, a fraction of sesquiterpene-

derived POZs can be fully thermalized; yet the kinetics of CI formation from these thermalized POZs has received little attention. This study reports the overlooked kinetic relaxation during CI formation from thermalized POZs of representative sesquiterpenes, including α -cedrene, α -copaene, β -caryophyllene, α -farnesene, and β -farnesene. We found that, for thermalized POZs, the apparent CI formation rate constant is initially unstable but gradually approaches a plateau, which equals the rate constant of sesquiterpene ozonolysis. Our results revealed that kinetic relaxation is sensitive to temperature variations, as cold surges extend the relaxation timescale from minutes to hours (or hours to days) while heatwaves reversely diminish the relaxation timescale. We further examined the CI formation kinetics from non-thermalized POZs, which suggested that kinetic relaxation may still occur for those derived from β -caryophyllene. The relaxation timescale is longer than the ozonolysis lifetime of β -caryophyllene under tropospheric O_3 concentrations. Our findings demonstrate that, for sesquiterpenes, neglecting kinetic relaxation may overestimate the rate of their CI formation and thus the resultant oxidation capacity.”

Rewritten part in the Introduction section:

“The value of k_{CI} is generally assumed equal to the ozonolysis rate constant (k_{oz}) in the literature (Taatjes et al., 2014; Cox et al., 2020). In principle, terpene ozonolysis first forms stabilized prereactive complexes (SPCs) and subsequently generates primary ozonides (POZs), which further decompose into CIs (Donahue et al., 2011; Vereecken and Francisco, 2012; Taatjes et al., 2014). The quantity k_{CI} refers to the projection from the reactants (sesquiterpenes and O_3 in this study) to CIs (Scheme I), and k_{oz} refers to the projection from the reactants to POZs (Ou and Chen, 2025; Ou et al., 2026). Given the high exothermic energy ($\sim 50\text{--}60\text{ kcal mol}^{-1}$) from O_3 addition to the $C=C$ double bond (Nangia and Benson, 1980; Cremer, 1981; Chuong et al., 2004; Johnson and Marston, 2008), POZs are typically in their vibrationally excited states to rapidly produce CIs under normal atmospheric conditions (Chuong et al., 2004; Hakala and Donahue, 2023). In this case, the conversion from POZs to CIs is expected to be far from thermal equilibrium so that the reaction proceeds more like SPCs overcoming the energy barrier corresponding to k_2 and directly produce CIs (Scheme II).



However, if POZs are fully thermalized, k_{CI} and k_{oz} are not necessarily interchangeable (Scheme III). This will not happen for all of the small alkenes and even C_{10} molecules (e.g., monoterpenes) in the air, but for C_{15} molecules such as sesquiterpenes, a fraction of them can be thermalized under atmospheric conditions (Chuong et al., 2004). In this case, there is no guarantee that k_{CI} can be equal to k_{oz} . The influence of k_3 on k_{CI} is largely overlooked from the thermalized POZs. To address this concern, the community may require a rigorous approach to resolving the rate constant of CI formation by explicitly considering the POZ-to-CI conversion.”

“We selected CIs from sesquiterpene ozonolysis as our case study for three reasons: (1) the rate constants of sesquiterpene ozonolysis mostly show no dependence on air pressure in the troposphere; (2) the large molecular size of sesquiterpenes may keep the SPCs collisionally stabilized (Wong et al., 2003; Yao et al., 2017; Ou and Chen, 2025); (3) sesquiterpenes are C₁₅ molecules such that their ozonolysis yields a fraction of thermalized POZs under atmospherically relevant conditions (Chuong et al., 2004).”

RRKM/ME setup in the Method section:

“The decomposition rate constant of non-thermalized POZs was estimated using the RRKM/ME calculations (i.e., Rice–Ramsperger–Kassel–Marcus theory/master equation) by the Multiwell 2023 program (Barker, 2009, 2001). The pressure was set as 1.0 atm, and the surrounding collider was nitrogen gas (N₂) with the Lennard–Jones (LJ) parameters (σ and ε / k_B) of 3.70 Å and 85 K (Weaver and Alexeenko, 2015). Since the LJ parameters for the studied POZs are unavailable, our calculations assumed 6.77 Å and 365 K for α -cedrene, α -copaene, β -caryophyllene (hydrocarbons with several alkyl branches) and 8.02 Å and 362 K for α -farnesene and β -farnesene (long-chain hydrocarbons) (Hippler et al., 1983). The exponential model was employed for deactivation collision (Tardy and Rabinovitch, 1977; Barker et al., 2001), with the energy loss of deactivation collision set to 500 cm⁻¹ (Chuong et al., 2004). The density of states was computed by the DenSum code incorporated in the program. The “DELTA” keyword was used to input the excess energy from the exothermic POZ production. All the calculations were also simplified by neglecting (1) the reverse reaction from CIs to POZs (keyword “NOREV”), (2) the tunneling in the POZ-to-CI conversion (keyword “NOTUN”), (3) the effects of intramolecular vibrational energy redistribution (IVR) which is expected to be slow (keyword “FAST”), and (4) the centrifugal correction (keyword “NOCENT”). For each POZ decomposition, 1000 simulations were conducted using the “LOGT” keyword to set the simulation timescale. The decomposition rate constant of non-thermalized POZs was estimated by applying the first-order decay model to fit the decreasing POZ concentration as a function of simulation time. Although the decomposition rate constant of non-thermalized POZs may in principle vary with time, the time-independent value obtained from our fitting can still support a meaningful comparison with mVTST-calculated k_3 .”

Revised discussion in Section 3.3:

“The value of k_3 for thermalized POZs increases by 3–6 orders of magnitude as the temperature increases from 243 to 323 K (Fig. 4B and 4C).”

“Our findings reveal that the kinetics of sesquiterpene-derived CI formation from thermalized POZs are far more sensitive to temperature variations than the sesquiterpene ozonolysis kinetics. The strong temperature dependence arises from the high activation energies associated with the decomposition of thermalized POZs (Fig. S7). It is noted that only a small fraction of sesquiterpene-derived POZs can be thermalized by colliding with the surrounding gas molecules in the atmosphere (Chuong et al., 2004; Hakala and Donahue, 2023). For the large fraction of non-thermalized POZs, whether their CI formation may experience kinetic relaxation in the atmosphere will be discussed below along with the thermalized cases.”

RRKM/ME results in Section 3.4:

“It bears reiterating that all the calculated values of relaxation timescales above are based on entirely thermalized POZs. For non-thermalized POZs, their k_3 values would be much higher. If we assume that the decomposition rate constants of non-thermalized POZs at atmospherically relevant temperatures are close to the values at 400 K, as justified by the numerical instability in matrix inversions of RRKM/ME computation at lower temperatures (Chuong et al., 2004), the calculated value of k_3 would be on the order of 10^3 – 10^5 s⁻¹ for α -cedrene, α -farnesene and β -farnesene (Tables S5 and S6). The corresponding relaxation timescales would then be around 10^{-5} – 10^{-3} s, which is too short to be neglected in the atmosphere. The value of k_3 is ~ 50 s⁻¹ for α -copaene at 423 K and thus would be close to ~ 10 s⁻¹ at 400 K since k_3 decreases with decreasing temperature (Table S5). The k_3 for β -caryophyllene-derived CIs is also ~ 10 s⁻¹ but at 523 K; although k_3 values for β -caryophyllene-derived CIs were not successfully obtained at lower temperatures owing to the extremely high computational cost, the k_3 value for β -caryophyllene-derived CIs at 400 K is expected to be smaller.

The extent to which k_3 at 400 K for β -caryophyllene-derived CIs is smaller may be evaluated according to the trend of RRKM/ME-computed k_3 along with the simulation temperature. We found that the RRKM/ME-computed k_3 data points for all the studied sesquiterpene-derived POZs can be well fitted by the modified Arrhenius equation (Figs. S9–S11). If extrapolated, the k_3 value for non-thermalized β -caryophyllene-derived POZ decomposition is expected to be $\sim 10^{-3}$ – 10^{-2} s⁻¹ at 400 K (Fig. S9), and the corresponding relaxation timescale is around 2–17 minutes. This is longer than the ozonolysis lifetime of β -caryophyllene (~ 1 –2 minutes) under an O₃ concentration of ~ 30 –60 ppb (Shu and Atkinson, 1994; Ou and Chen, 2025).

We note that further extrapolation of RRKM/ME-computed k_3 to 273 K and 298 K could be barely reliable; at these temperatures k_3 values for non-thermalized POZs are very close to those computed for the thermalized POZs at atmospherically relevant temperatures (Table S7). Even at 400 K, the extrapolated values may have considerable uncertainty, but the trend of RRKM/ME-computed k_3 with the simulation temperature (Tables S5 and S6) still suggests that the k_3 values of non-thermalized β -caryophyllene-derived POZs are much smaller compared to those derived from other sesquiterpenes at atmospherically relevant conditions. Collectively, our analysis of the RRKM/ME-computed results indicates that kinetic relaxation is a non-negligible phenomenon for CI formation from non-thermalized β -caryophyllene-derived POZs.”

Table S5. RRKM/ME-computed formation rate constant (unit: s⁻¹) of α -cedrene-derived, α -copaene-derived, and β -caryophyllene-derived CIs from non-thermalized POZ decomposition.*

T(K)	α -cedrene-derived CI1	α -cedrene-derived CI2	α -copaene-derived CI1	α -copaene-derived CI2	β -caryophyllene-derived CI1	β -caryophyllene-derived CI2
323	2.29×10^2	/	/	/	/	/
373	6.45×10^3	1.99×10^2	/	/	/	/
423	9.76×10^4	4.26×10^3	6.13×10^1	4.28×10^1	/	/
473	7.42×10^5	4.77×10^4	9.75×10^2	9.30×10^2	/	/

523	4.29×10^6	3.34×10^5	9.75×10^3	1.06×10^4	1.51×10^1	/
573	1.44×10^7	1.95×10^6	6.93×10^4	8.54×10^4	1.63×10^2	4.37×10^2
623	2.98×10^7	6.03×10^6	3.48×10^5	4.43×10^5	1.25×10^3	2.98×10^3
673	3.80×10^7	1.23×10^7	1.22×10^6	1.75×10^6	6.56×10^3	1.49×10^4
723	5.58×10^7	2.16×10^7	3.13×10^6	4.42×10^6	2.96×10^4	6.03×10^4

*Some values are not computed owing to the highly extensive simulation time.

Table S6. RRKM/ME-computed formation rate constant (unit: s^{-1}) of α -farnesene-derived and β -farnesene-derived CIs from non-thermalized POZ decomposition.*

T(K)	α -farnesene-derived CI1	α -farnesene-derived CI2	β -farnesene-derived CI1	β -farnesene-derived CI2
323	/	/	/	/
373	5.56×10^3	/	2.24×10^3	/
423	9.05×10^4	7.88×10^3	3.69×10^4	1.93×10^3
473	9.17×10^5	7.03×10^4	3.87×10^5	2.34×10^4
523	6.29×10^6	4.73×10^5	2.63×10^6	2.02×10^5
573	2.07×10^7	1.94×10^6	1.07×10^7	1.12×10^6
623	3.39×10^7	5.89×10^6	2.32×10^7	3.93×10^6
673	7.09×10^7	1.18×10^7	4.26×10^7	1.01×10^7
723	7.22×10^7	1.94×10^7	4.90×10^7	1.68×10^7

*Some values are not computed owing to the highly extensive simulation time.

Table S7. Comparisons of k_3 from mVTST computation and RRKM/ME-based extrapolation.

Sesquiterpene-derived CIs	k_3 from mVTST computation		k_3 from RRKM/ME-based extrapolation	
	273 K	298 K	273 K*	298 K*
α -cedrene-derived CI1	6.10×10^0	7.26×10^1	6.88×10^{-1}	1.49×10^1
α -cedrene-derived CI2	1.28×10^{-2}	2.42×10^{-1}	2.75×10^{-3}	9.83×10^{-2}
α -copaene-derived CI1	2.67×10^{-5}	8.19×10^{-4}	9.69×10^{-6}	4.14×10^{-4}
α -copaene-derived CI2	6.34×10^{-6}	2.54×10^{-4}	1.13×10^{-6}	7.79×10^{-5}
β -caryophyllene-derived CI1	2.38×10^{-10}	1.84×10^{-8}	2.15×10^{-10}	1.71×10^{-8}
β -caryophyllene-derived CI2	2.32×10^{-9}	1.40×10^{-7}	1.26×10^{-9}	9.18×10^{-8}

*Translational temperature of the colliders

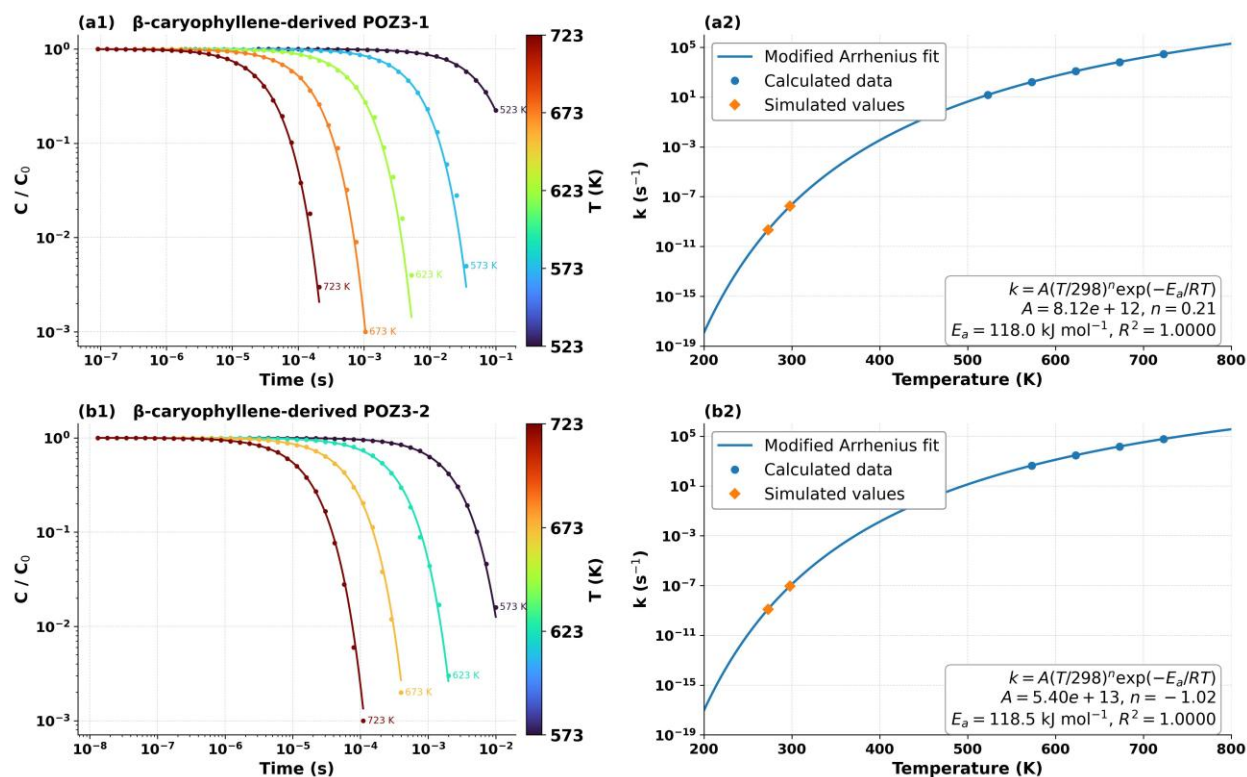


Figure S9. The normalized concentration (C / C_0) of β -caryophyllene-derived POZ3-1 (a1) and β -caryophyllene-derived POZ3-2 (b1) at different temperatures as directly output from the RRKM/ME computation. The structures of β -caryophyllene-derived POZ3-1 and POZ3-2 are obtained from our previous study (Ou and Chen, 2025); their decomposition produce β -caryophyllene-derived CI1 and CI2, respectively. The fitting k_3 results (a2-d2) are visualized with same order as the panels on the left.

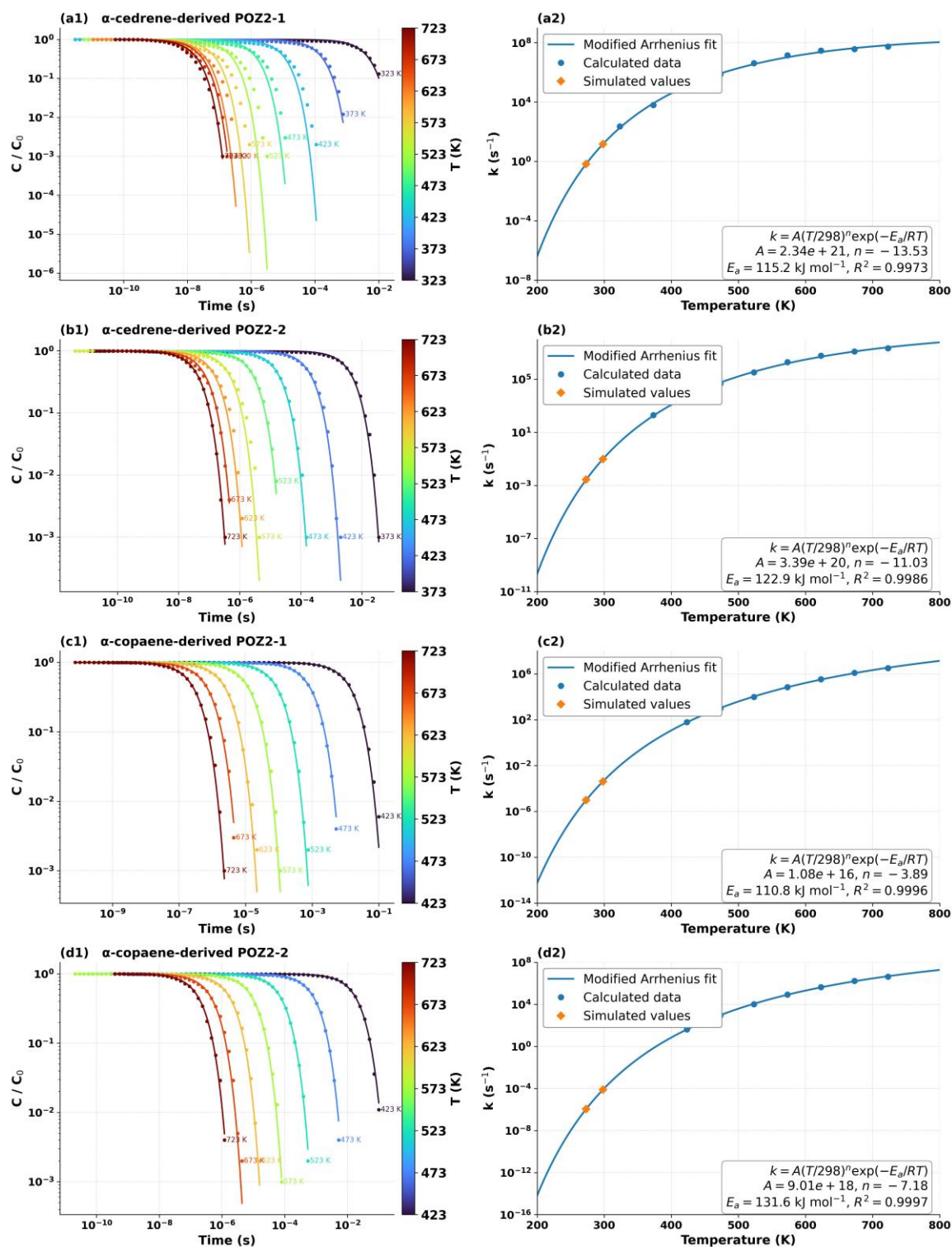


Figure S10. The normalized concentration (C / C_0) of α -cedrene-derived POZ2-1 (a1), α -cedrene-derived POZ2-2 (b1), α -copaene-derived POZ2-1 (c1) and α -copaene-derived POZ2-1 (d1) at different temperatures as directly output from the RRKM/ME computation. The fitting k_3 results (a2-d2) are visualized with same order as the panels on the left.

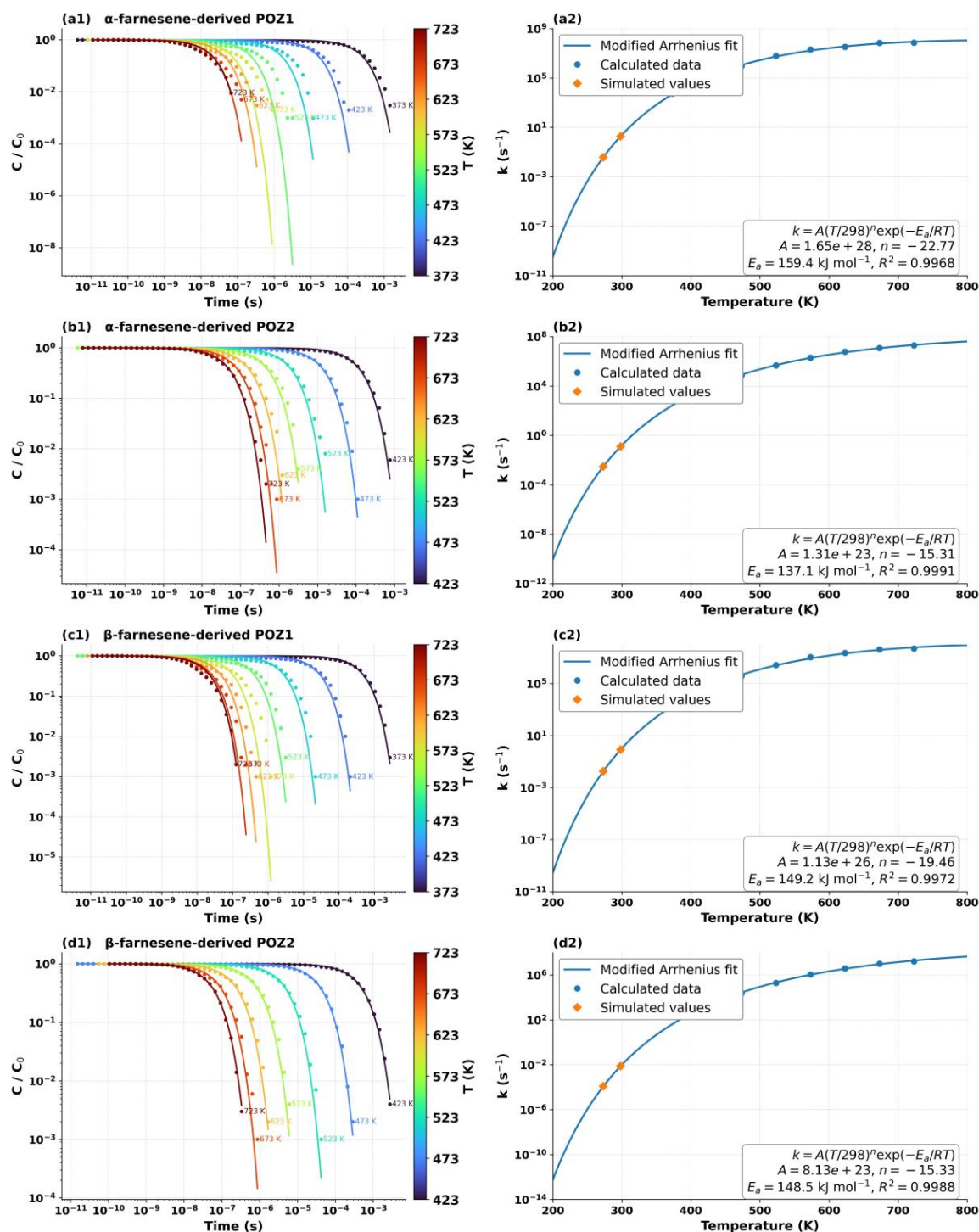


Figure S11. The normalized concentration (C / C_0) of α -farnesene-derived POZ1 (a1), α -farnesene-derived POZ2 (b1), β -farnesene-derived POZ1 (c1) and β -farnesene-derived POZ2 (d1) at different temperatures as directly output from the RRKM/ME computation. The fitting k_3 results (a2-d2) are visualized with same order as the panels on the left.

In the Conclusion section:

“This relaxation arises from the thermalized sesquiterpene-derived POZs and potentially from non-thermalized POZs derived from certain sesquiterpenes such as β -caryophyllene.”

Reference:

Chuong, B., Zhang, J., and Donahue, N. M.: Cycloalkene Ozonolysis: Collisionally Mediated Mechanistic Branching, *J. Am. Chem. Soc.* **2004**, 126 (39), 12363-12373. DOI: 10.1021/ja0485412

(2) *The kinetic model is simply an example of consecutive reaction as “Reactant $\rightarrow$ Intermediate $\rightarrow$ Product” in all Physical Chemistry textbooks. The rate of reactant consumption and the rate of product formation are NOT always the same. This is a commonsense, particularly when “Intermediate $\rightarrow$ Product” is slow. It is NOT a black box.*

Response: We thank the referee for the clarification. We agree that in textbooks the consecutive reaction is common sense instead of a black box, while in the literature of atmospheric chemistry, the rate constant for CI formation was previously assumed to be equal to that of ozonolysis. The process from sesquiterpene ozonolysis to CI formation was treated as a balance of inflow and outflow. We would like to highlight that stepwise kinetics related to SPCs and POZs should be explicitly handled for a more appropriate kinetic model of CI formation. To clarify this, we revised the statement in the manuscript, as also shown below.

“The kinetic relaxation was found when we explicitly derived the kinetic model of CI formation. As suggested in the literature (Taates et al., 2014; Cox et al., 2020), the rate constant for CI formation was previously assumed to be equal to that of ozonolysis. Such an assumption treats the process from sesquiterpene ozonolysis to CI formation as a balance of inflow and outflow, but since this process is a consecutive reaction intermediated by SPCs and POZs, the rate of sesquiterpene consumption and the rate of CI formation are in principle not always the same. Stepwise kinetics related to SPCs and POZs should be explicitly handled.”

(3) *Note that rate coefficient is an empirical parameter, and it is well-defined only for reactants with steady-state energy distribution (such as equilibrium distribution under high pressures). For system far from steady-state energy distribution such as POZ* here, the rate coefficient is just a phenomenological parameter and would vary with time.*

Response: We appreciated the referee’s insightful comment and detailed explanation. We agree that k_3 may become a time-dependent parameter for non-thermalized POZs, and after we conducted the RRKM/ME computation, we found that the phenomenological k_3 could be approximated as a time-independent parameter when fitting the POZ concentration as a proportional function of the decomposition time. Even though the fitting may not be well in some cases, the fitted value still gains some sense of the expected magnitude of k_3 values for non-thermalized POZs. In this case, we may explore the extent to which kinetic relaxation may be suppressed if the CI formation is from non-thermalized POZ decomposition. To clarify this, we add the following paragraph to the revised manuscript.

“It is worth noting that thermalized POZs are typically the prerequisite for deriving Eq. (3), since k_3 becomes a time-independent constant only when POZs maintain a steady-state energy distribution. For non-thermalized POZs (i.e., those in their vibrationally excited states), k_3 may become a time-dependent parameter. However, if the phenomenological k_3 could be approximated as a time-independent parameter when fitting the POZ concentration as a proportional function of the decomposition time, Eq. (3) may still be a useful tool for describing the kinetic relaxation associated with the CI formation from non-thermalized POZ decomposition. In this case, we may still gain some sense of the expected magnitude of k_3 values for non-thermalized POZs and the extent to which kinetic relaxation may be suppressed. All these results will be further discussed in Section 3.4.”

(4) Line 167: “ k_{CI} is in principle proportional to the POZ concentration”. This statement is incorrect. k_{CI} , if exist as stated in (3), should be a parameter of molecule and energy distribution. It is “the Formation Rate of CI is proportional to the POZ concentration”. Figure 1C is incorrectly interpreted.

Response: We appreciated the referee for the critical comment. We revised the interpretation of Figure 1C in the manuscript, as shown below.

“So, in principle, k_{CI} should be a parameter of energy distribution of POZs.”