https://doi.org/10.5194/egusphere-2026-3255
Preprint. Discussion started: 6 July 2026

An Overlooked Kinetic Relaxation in the Formation of Sesquiterpene-Derived Criegee Intermediates

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https://doi.org/10.5194/egusphere-2026-3255
Preprint. Discussion started: 6 July 2026

Abstract

Criegee intermediates (CIs) from sesquiterpene ozonolysis contribute to secondary organic aerosol (SOA) formation. The ozonolysis rate constants of typical sesquiterpenes have been measured by prior experiments, but whether these values can represent the formation rate constants of sesquiterpene-derived CIs remains questionable. This study reports the overlooked kinetic relaxation in the CI formation from representative sesquiterpenes, including α-cedrene, α-copaene, β-caryophyllene, α-farnesene and β-farnesene. We found that the apparent formation rate constant of sesquiterpene-derived CIs is initially unstable but gradually approaches a plateau, which equals the rate constant of sesquiterpene ozonolysis. Such behavior arises because CI formation cannot instantaneously respond to sesquiterpene ozonolysis due to the finite time for the production of primary ozonides (POZs). Our results also reveal that the kinetic relaxation is sensitive to temperature variations, as cold surges extend the relaxation timescale from minutes to hours (or hours to days) for most sesquiterpenes while heatwaves reversely diminish the relaxation timescale. Exceptionally, β-caryophyllene exhibits the longest relaxation timescale (at least 2.6 days) even during the heatwaves. Our findings demonstrate that neglecting this kinetic relaxation may substantially overestimate the rate of sesquiterpene-derived CI formation and thus the CI-driven atmospheric oxidation capacity under extreme temperature conditions.

Keywords

ozone, volatile organic compounds, primary ozonide, relaxation, extreme temperature

https://doi.org/10.5194/egusphere-2026-3255
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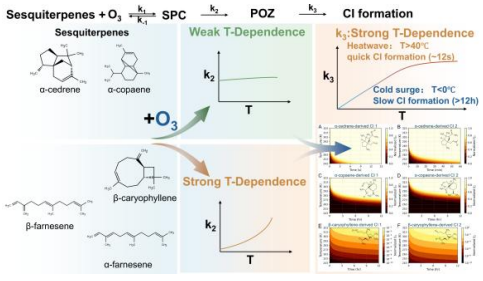
43 

https://doi.org/10.5194/egusphere-2026-3255
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1. Introduction

Atmospheric Criegee intermediates (CIs) are produced from the ozonolysis of airborne alkenes such as terpenes (Criegee, 1975; Johnson and Marston, 2008), but whether the formation rate of CIs equals the rate of ozonolysis is still a question. The formation of CIs from reactions between terpenes and ozone (O_3) contributes to the atmospheric oxidation capacity (Khan et al., 2018; Chhantyal-Pun et al., 2020), which governs the formation of O_3-initiated secondary organic aerosols (SOAs) (Zhao et al., 2015; Zhao et al., 2016; Gong and Chen, 2021). CI chemistry produces hydroxyl radicals and organic hydroperoxides (ROOHs) (Docherty et al., 2005; Reinnig et al., 2009; Donahue et al., 2011; Iyer et al., 2021), which further boost the formation of oxygenated species (e.g., carbonyls, alcohols) with high molecular weights in SOAs (Dekermenjian et al., 1999; Jaoui et al., 2003; Jaoui et al., 2004; Kanawati et al., 2008; Reinnig et al., 2009; Jaoui et al., 2013; Jaoui et al., 2017). The formation rate of CIs is determined not only by the concentrations of O_3 and terpenes but also by the formation rate constant (k_{CI}). The value of k_{CI} is always assumed equal to the ozonolysis rate constant (k_{oz}) in the literature (Taatjes et al., 2014; Cox et al., 2020).

However, k_{CI} and k_{oz} are not necessarily interchangeable. In principle, terpene ozonolysis directly produces stabilized prereactive complexes (SPCs) and subsequently primary ozonides (POZs), which further decompose into CIs (Donahue et al., 2011; Vereecken and Francisco, 2012; Taatjes et al., 2014). By definition, k_{CI} refers to the projection from the reactants (i.e., terpenes and O_3) to CIs (Scheme I), but k_{oz} refers to the projection from the reactants to POZs (Scheme II) (Ou and Chen, 2025; Ou et al., 2026), so there is no guarantee that k_{CI} can be equal to k_{oz}. Even if k_{CI} equals k_{oz} at some temperatures, k_{oz} is analytically expressed as a function of k_1, k_{-1} and k_2 (Ou and Chen, 2025; Ou et al., 2026), whereas k_{CI} is not only related to k_1, k_{-1} and k_2 but also k_3. Since k_1, k_{-1}, k_2, and k_3 possess their own temperature dependence, k_{CI} may exhibit a more complicated

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response to temperature variations compared to k_{oz}. To date, the field lacks a kinetically rigorous framework for resolving the rate constants of CI formation.

$$\text{Terpene} + O_3 \xrightarrow{k_{CI}} \text{CIs} \quad \text{(I)}$$

$$\text{Terpene} + O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{SPCs} \xrightarrow{k_2} \text{POZs} \xrightarrow{k_3} \text{CIs} \quad \text{(II)}$$

This study discloses a previously unrecognized phenomenon, termed "kinetic relaxation", by explicitly elucidating the relationship between k_{CI} and k_{oz}. Kinetic relaxation refers to a transient deviation of k_{CI} from k_{oz}. We chose CIs from sesquiterpene ozonolysis as the study case because (1) the rate constants of sesquiterpene ozonolysis mostly show no dependence on air pressure in the troposphere, and (2) the large molecular size of sesquiterpenes renders SPCs and POZs collisionally stable (Wong et al., 2003; Yao et al., 2017; Ou and Chen, 2025). The sesquiterpene-derived CIs thus serve as a simplified system that maintains a clear "double-well" potential energy surface along the CI formation mechanism (Donahue et al., 2011; Vereecken and Francisco, 2012; Taatjes et al., 2014), which is key to understanding the kinetic relaxation. The studied sesquiterpenes involve α-cedrene, α-copaene, β-caryophyllene, α-farnesene and β-farnesene, which are representative in the troposphere and emitted from vegetation in forests and farms (Lwande et al., 1989; Arey et al., 1995; Duhl et al., 2008; Yee et al., 2018; Frazier et al., 2022; Chen et al., 2024). Ozonolysis represents the predominant fate of these compounds (Shu and Atkinson, 1995; Richters et al., 2015; Frazier et al., 2022), and most of their CIs (e.g., ~88% for α-cedrene and >60% for β-caryophyllene) can be stabilized in the atmosphere (Winterhalter et al., 2009; Nguyen et al., 2009; Yao et al., 2014). We estimated all the kinetic parameters with a computational approach that can replicate the temperature-dependent ozonolysis rate constants of α-cedrene (Fig. S1 in the supporting information) and β-caryophyllene (Ou and Chen, 2025). The

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influence of temperature variations on sesquiterpene ozonolysis kinetics as well as the relaxation timescale is also explored. The atmospheric implications of kinetic relaxation in the sesquiterpene-derived CI formation kinetics are further discussed.

2. Methods

2.1 Kinetics of Sesquiterpene Ozonolysis

The rate constant of sesquiterpene ozonolysis (k_{oz}) can be expressed by Eq. (1), as presented in our previous studies (Ou and Chen, 2025; Ou et al., 2026).

$$k_{oz} = k_1 \cdot \sum_i \left[p_i \cdot \left(\frac{k_{2,i}}{k_{-1,i} + k_{2,i}} \right) \right] \quad (1)$$

Here k_1 is the bimolecular collision rate constant of the sesquiterpene molecule and O_3, which is calculated by the collision theory; p_i is the branching ratio of the i-th SPC arisen from the bimolecular collisions, which is also corresponding to the i-th POZ; $k_{-1,i}$ and $k_{2,i}$ are the rate constants of the backward dissociation of the i-th SPC and the forward formation of the i-th POZ, respectively. All these quantities can be affected by temperature variations, and the ratio $k_{2,i} / (k_{-1,i} + k_{2,i})$ serves as the main factor to control the temperature dependence of the i-th POZ formation kinetics (Ou and Chen, 2025). Since the temperature-dependent ozonolysis rate constants of β-caryophyllene, α-farnesene and β-farnesene have been quantified by previous experimental measurements (Kim et al., 2011; Gao et al., 2022), Eq. (1) was employed to estimate the temperature-dependent ozonolysis rate constants of α-cedrene and α-copaene.

2.2 Kinetics of CI Formation

The computation of k_{CI} is based on the steady-state concentration of SPCs (Text S1), which is supported by experimental measurements (Talukdar et al., 2003; Davis et al., 2005; Ou and Chen, 2025). The expression of k_{CI} is approximated by Eq. (2), wherein $f_{CI,i}$ is the projection factor for the i-th CI, as given by Eq. (3), if the initial concentrations of all POZs are zero.

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$$k_{CI} \approx k_{oz} \cdot \sum_i f_{CI,i} \quad (2)$$

$$f_{CI,i} = r_i \cdot (1 - e^{-k_{3,i} \cdot t}) \quad (3)$$

In Eq. (3), t is time after ozonolysis starts, r_i is the steady-state branching ratio of the i-th CI formation, which satisfies $\sum_i r_i = 1$ (Text S1), and $k_{3,i}$ is the rate constant of the i-th CI formation from POZ decomposition. When the initial concentrations of POZs are not zero, $f_{CI,i}$ should be implemented with a scale factor s_i (Text S2). Eq. (3) also shows that, when t equals0, $f_{CI,i}$ also equals 0 (Text S1); if the i-th POZ pre-exists before the ozonolysis (i.e., s_i shows up in $f_{CI,i}$), the value of $f_{CI,i}$ will equal $r_i \cdot s_i$ when t equals 0 (Text S2). Regardless of the s_i, if t is infinitely large, $f_{CI,i}$ will equal 0 so that k_{CI} will converge with k_{oz} (Text S1 and S2). Eqs. (2) and (3) show that k_{CI} is not equal to k_{oz} at the beginning of ozonolysis, but k_{CI} approaches k_{oz} after a period of relaxation. The projection factors $f_{CI,i}$ represent the kinetic relaxation of each CI generated from sesquiterpene ozonolysis.

2.3 Thermodynamic and Kinetic Computation

The thermodynamic parameters such as zero-point energy (ZPE) and vibrational frequencies were computed by the ORCA 5.0.4 software (Neese, 2012). Vibrational analysis based on the optimized structures was conducted by the density functional theory (DFT) with the M06-2X functional (Zhao and Truhlar, 2008) and the def2-TZVP basis set (Weigend and Ahlrichs, 2005). The RIJCOSX approximation was also employed to accelerate all the calculations (Neese et al., 2009). Single-point energy was computed by using the DLPNO-CCSD(T) method with the def2-TZVPP basis set (Riplinger and Neese, 2013; Weigend and Ahlrichs, 2005), accelerated by the RIJCOSX algorithm as well. For benchmarking, the same DLPNO-CCSD(T) method was also applied with the cc-pVTZ basis set (Dunning, 1989; Weigend et al., 2002), and the resulting energy barriers were 0.3−0.5 kcal mol^{-1} higher than those obtained by using def2-TZVPP (Table S4). The

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thermodynamic parameters were used to calculate p_i, $k_{-1,i}$, $k_{2,i}$, and $k_{3,i,j}$ within the temperature range of 243−323 K and the temperature increment of 5 K using the J-resolved microcanonical variational transition state theory (mVTST) incorporated in the Multiwell 2023 program (Barker, 2009, 2001). Detailed computation procedures and accuracy tests were described in our previous study (Ou and Chen, 2025).

2.4 Arrhenius Fitting of Temperature Dependence

The computed $k_{-1,i}$, $k_{2,i}$, and $k_{3,i,j}$ were further fitted by the Arrhenius equation $k(T) = A \cdot exp(-E_a / (RT))$, wherein A is the pre-exponential factor, E_a is the activation energy, and R is the ideal gas constant. The temperature dependence of $k_{-1,i}$, $k_{2,i}$, and $k_{3,i,j}$ is controlled by the value of E_a. The computed k_{oz} was fitted by the modified Arrhenius equation (Eq. (4)).

$$k_{oz} \approx F_{oz} \cdot \left(\frac{T}{298}\right)^{m} \cdot e^{\Theta/T} \quad (4)$$

Here F_{oz} is the temperature-independent constant for ozonolysis, m is the constant for temperature dependence of the power-law factor, and Θ is the constant for temperature dependence of the exponential factor.

3. Results and Discussions

3.1 The Origin of Kinetic Relaxation

The kinetic relaxation was found when we opened the "black box" kinetic model of CI formation. The rate constant for CI formation is assumed equal to that of ozonolysis, as previously suggested (Taatjes et al., 2014; Cox et al., 2020). Such assumption treats the processes from sesquiterpene ozonolysis to CI formation as a “black box” in which inflow and outflow are considered balanced. As we open the kinetic model, SPCs and POZs lay inside and a more reliable foundation comes up, which is to assume the steady-state SPC concentrations (Fig. 1A). This is an assumption consolidated by the experimental measurements of temperature-dependent kinetics

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(Talukdar et al., 2003; Davis et al., 2005; Ou and Chen, 2025). Under the steady-state SPC concentrations, we find that the concentrations of POZs are time-dependent (Text S1). The concentration of each POZ is initially zero, subsequently increases along with ozonolysis time, and asymptotically approaches a plateau value that represents the steady-state POZ concentration (Fig. 1B).

The time-dependent concentration of POZs causes k_{CI} to also vary with time (Text S1). The well-established mechanism of CI formation indicates that CIs are not directly generated from the reactive collision between alkenes and O_3 but from the decomposition of POZs (Criegee, 1975; Donahue et al., 2011; Taatjes et al., 2014; Vereecken and Francisco, 2012). So, in principle, k_{CI} is in principle proportional to the POZ concentration. At the beginning of ozonolysis, k_{CI} is also zero unless pre-existing POZs are present before the ozonolysis (Text S2). The value of k_{CI} increases over time and asymptotically approaches its plateau value (Fig. 1C), which is exactly k_{oz} (Text S1). Our deductive results suggest that only when both SPCs and POZs are at their steady-state concentrations can k_{CI} be equal to k_{oz}.

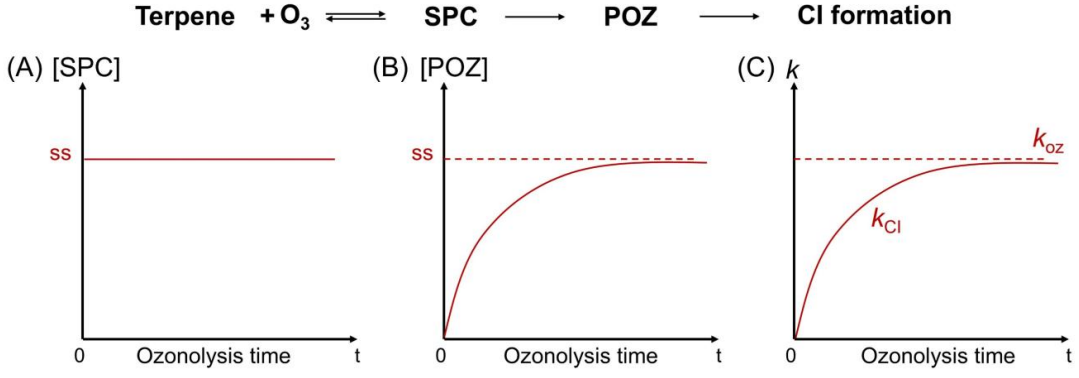

Figure 1. The origin of kinetic relaxation of CI formation: (A) steady-state (ss) SPC concentration; (B) time-dependent POZ concentration; (C) time-dependent CI formation rate constant (k_{CI}), which ultimately reaches a stable value equal to the ozonolysis rate constant (k_{oz}).

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3.2 Competition Between SPC Dissociation and POZ Production

The kinetic relaxation of CI formation is based on the steady-state concentrations of SPCs, which is balanced by the kinetic competition between SPC dissociation (k_{-1}) and POZ production (k_2). The POZ production tendency is quantified by the ratio $k_2 / (k_{-1} + k_2)$ (Fig. S2 and S3), and 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. 2E and 2F, Table S1).

Taking α-cedrene and α-copaene as examples, both molecules have only one C=C double bond (Fig. 2A), and both have two sites for ozonolysis (Fig. 2B). Since each POZ has two conformers (Ou and Chen, 2025; Ou et al., 2026), there are totally four POZs can be formed for α-cedrene or α-copaene (Fig. S4). For α-cedrene, site 2 dominates POZ production with the branching ratio at SPC2-1 of >89% (Table S2). The values of $E_a(k_2)$ and $E_a(k_{-1})$ are comparable at site 2, with SPC2-1 uniquely showing $E_a(k_2) < E_a(k_{-1})$ (Fig. 2E). The resultant $k_2 / (k_{-1} + k_2)$ shows different temperature dependence for SPC2-1 and SPC2-2 (Fig. S2C and 2D), with the case in SPC2-1 remaining largely stable across temperatures. Similarly, POZ production from α-copaene exclusively occurs at site 2, with the SPC2-1: SPC2-2 branching ratio of ~3:1 at 243 K and ~3:2 at 323 K (Table S2). The ratio $k_2 / (k_{-1} + k_2)$ at site 2 does not decrease significantly with declining temperature (Fig. S3C and S3D).

Our findings reveal that, if $E_a(k_2)$ is higher than $E_a(k_{-1})$, SPC dissociation is favored so that ozonolysis through this SPC is infeasible. Conversely, if $E_a(k_2)$ is lower than $E_a(k_{-1})$, POZ formation is feasible and the associated ozonolysis channel is highly efficient. Since branching ratios of all the SPCs minorly vary with temperature (Table S2), the ozonolysis channels of α-cedrene and α-copaene are very stable across a wide temperature range. Such a robust ozonolysis mechanism directly identifies representative POZs responsible for further CI formation.

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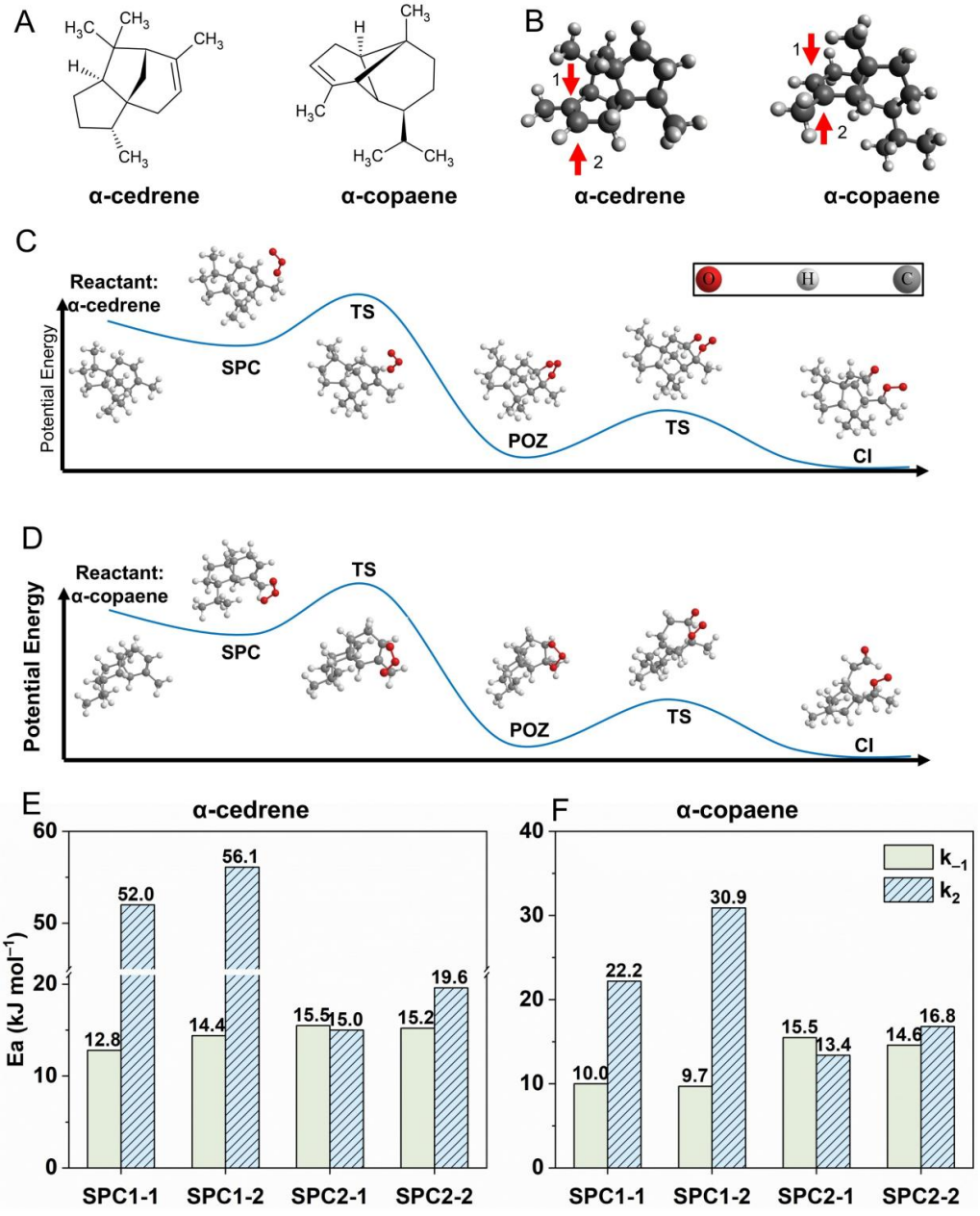

Figure 2. Examples of sesquiterpene ozonolysis kinetics: (A) Molecular structures of α-cedrene and α-copaene; (B) ozonolysis site 1 and 2 labelled on the molecular structures; the "double-well" potential energy surface of the formation of (C) an example of α-cedrene-derived CI and (D) an example of α-copaene-derived CI; fitted activation energies of k_{-1} and k_2 among the ozonolysis SPCs of (E) α-cedrene and (F) α-copaene.

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3.3 Temperature-Dependent Kinetics of Ozonolysis and POZ Decomposition

The kinetic competition between SPCs and POZs only affects the value of k_{oz}, while the value of k_{CI} not only depends on k_{oz} but also the decomposition rate constant of POZs (k_3). Here we examine the temperature-dependent ozonolysis kinetics of the studied sesquiterpenes, with particular attention to the anomalous behavior of α-cedrene and α-copaene. The ozonolysis kinetics of α-cedrene and α-copaene exhibit only weak temperature dependence (Fig. 3A). Despite the wide temperature range, their k_{oz} remain within a narrow interval (~$1.5-1.7 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}). The analytical fitting based on the modified Arrhenius equation gives $k_{oz} = 3.8 \times 10^{-16} \times (T / 298)^{-0.7} \times \exp(-236.6 / T)$ for α-cedrene and $k_{oz} = 2.5 \times 10^{-16} \times (T / 298)^{-0.4} \times \exp(-139.6 / T)$ for α-copaene (Fig. S5). In these expressions, the exponential terms increase with temperature, whereas the temperature-dependent pre-exponential factors decrease (Fig. S6). This phenomenon is different from those of β-caryophyllene and farnesenes, wherein β-caryophyllene exhibits an increasing exponential factor as temperature increases, while farnesenes show decreasing exponential factors (Fig. S6) (Kim et al., 2011; Gao et al., 2022). Notably, their pre-exponential factors remain unchanged along with the temperature variations, in contrast to the compensating trends observed for α-cedrene and α-copaene (Fig. S6). Among the studied sesquiterpenes, α-cedrene and α-copaene are very resistant to temperature variations regarding their k_{oz} values. The resistant k_{oz} indicates that the POZ production flux is correspondingly stable.

Unlike the weak temperature dependence of k_{oz} for α-cedrene and α-copaene, their POZ decomposition kinetics (represented by k_3) show a much more dramatic response to temperature. The value of k_3 increases by 3−6 orders of magnitude as the temperature increases from 243 to 313 K (Fig. 3B and 3C). Although each POZ can decompose via two channels to form two CI isomers, our results reveal that only one pathway clearly dominates. For α-cedrene, POZ2-1 mainly produces its CI isomer 1, while POZ2-2 mainly produces its CI isomer 2 (Fig. 3B). For α-copaene,

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POZ2-1 favors the formation of its CI isomer 2 whereas POZ2-2 favors the formation of its CI isomer 1 (Fig. 3C). For each POZ, the rate constant for producing the predominant CI consistently exceeds that of the other CI at every temperature within 243−323 K by multiple orders of magnitude.

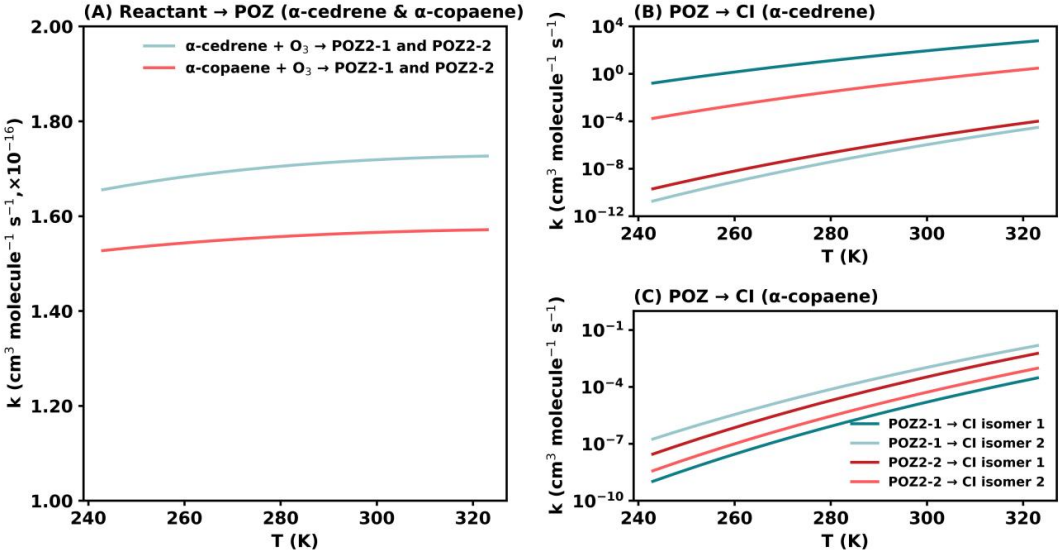

Figure 3. Temperature dependence of (A) ozonolysis rate constants (k_{oz}) of α-cedrene and α-copaene, and POZ decomposition rate constants (k_3) for (B) α-cedrene-derived CIs and (C) α-copaene-derived CIs.

The strong temperature dependence arises from the high activation energies associated with POZ decomposition (Fig. S7). 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. The level of collisional stabilization may also depend on air pressure, so that the value of k_3 could potentially show pressure dependence. Nevertheless, our findings reveal that the formation kinetics of sesquiterpene-derived CIs are far more sensitive to temperature variations than the sesquiterpene ozonolysis kinetics.

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3.4 Relaxation Timescale of CI Formation

We further explore the temperature-dependent relaxation of CI formation kinetics. The kinetic relaxation at different temperatures can be visualized by the contour of "normalized f_{CI}" (i.e., $f_{CI,i} / r_i$ as referred to Eq. (2)) (Fig. 4), and the relaxation timescale is estimated by $1 / k_3$ (Tables 1 and S3). Taking α-cedrene as an example, the normalized f_{CI} for CI isomer 1 reaches unity in less than 1 s at temperatures above 273 K, while it approaches unity within 6 s at 243 K (Fig. 4A). The relaxation timescale is within 0.1 minutes at the studied temperatures (Table 1). In contrast, for α-cedrene-derived CI isomer 2, the normalized f_{CI} reaches unity in ~1 min at temperatures above 273 K but requires more than 1 hour at 243 K (Fig. 4B). The relaxation timescale is negligibly short at 323 K but extended to 96.9 minutes at 243 K (Table 1). These results reveal that different CIs derived from the same sesquiterpene may exhibit divergent relaxation timescales.

If the relaxation timescale extends to half a day or even longer, kinetic relaxation will considerably reduce the formation rate constants of CIs. Taking α-copaene as an example, when the temperature falls below 273 K, the relaxation timescales are over 10 hours and 40 hours for its CI1 and CI2, respectively (Table 1). The normalized f_{CI} is below 0.1 for more than 1 hour, meaning that the formation rate constants for both CIs are less than 10% of their steady-state values for a non-negligible timescale (Fig. 4C and 4D). However, during heatwaves over 313 K, the relaxation timescales are hugely reduced to less than 10 minutes (Table 1). These findings reveal that heatwaves can diminish kinetic relaxation to a negligible level for the α-copaene-derived CIs.

Moreover, an identical CI may be produced from structurally similar sesquiterpenes, but the relaxation timescales are different. Taking α-farnesene and β-farnesene as examples, their ozonolysis proceeds predominantly from the same C=C double bonds (Kourtchev et al., 2009;

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Jaoui et al., 2017), yielding the same CI (CI1 in Fig. S8A and S8C). During cold surges at 243 K, the relaxation timescale in α-farnesene ozonolysis is 3 orders of magnitude larger than that in β-farnesene ozonolysis, but during heatwaves, the CI1 from both farnesenes has a negligible relaxation timescale (Table S3). The dramatic decrease in relaxation timescale also holds for other CIs generated from α-farnesene and β-farnesene (Fig. S8B and S8D). Our results suggest that kinetic relaxation may be more general during cold surges.

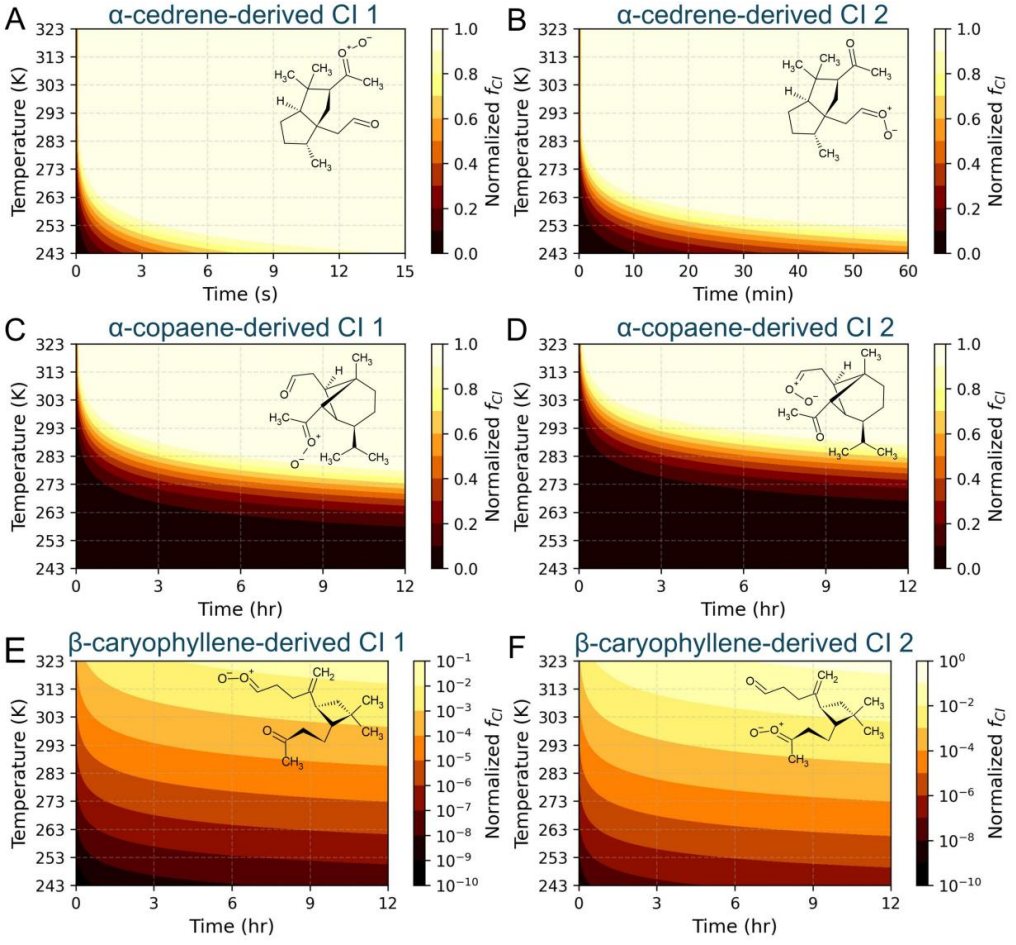

Figure 4. Kinetic relaxation of the temperature-dependent formation rate constant of (A) α-cedrene-derived CI isomer 1; (B) α-cedrene-derived CI isomer 2; (C) α-copaene-derived CI isomer 1; (D) α-copaene-derived CI isomer 2; (E) β-caryophyllene-derived CI isomer 1; (F) β-caryophyllene-derived CI isomer 2.

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Table 1. Relaxation timescale of CI formation from the ozonolysis of α-cedrene, α-copaene, and β-caryophyllene.

T (K)	α-cedrene (unit: minutes)		α-copaene (unit: hours)		β-caryophyllene (unit: days)	
	CI1	CI2	CI1	CI2	CI1	CI2
243	0.1	96.9	1576.1	9791.6	2.8×10^7	2.1×10^6
248	0.1	44.0	628.5	3635.0	9.0×10^6	6.8×10^5
253	0.0	20.6	259.7	1402.5	2.9×10^6	2.4×10^5
258	0.0	9.9	111.0	561.1	9.7×10^5	8.3×10^4
263	0.0	4.9	49.0	232.3	3.5×10^5	3.2×10^4
268	0.0	2.5	22.3	99.4	1.3×10^5	1.3×10^4
273	0.0	1.3	10.4	43.8	4.9×10^4	5000.0
278	0.0	0.7	5.0	19.9	1.9×10^4	2083.3
283	0.0	0.4	2.5	9.3	7638.9	902.8
288	0.0	0.2	1.2	4.4	3263.9	388.9
293	0.0	0.1	0.6	2.2	1388.9	180.6
298	0.0	0.1	0.3	1.1	631.9	83.3
303	0.0	0.0	0.2	0.6	284.7	39.6
308	0.0	0.0	0.1	0.3	131.9	19.4
313	0.0	0.0	0.06	0.2	64.6	9.7
318	0.0	0.0	0.03	0.1	31.9	4.9
323	0.0	0.0	0.02	0.05	16.0	2.6

Surprisingly, β-caryophyllene-derived CIs show substantial kinetic relaxation regardless of the temperature variations (Fig. 4E and 4F). Across the entire temperature range, the normalized f_{CI} remains 1−10 orders of magnitude lower than unity, showing much stronger temperature dependence driven by the high activation energies of k_3 (Fig. S7). Even under the heatwaves at 323 K, the relaxation timescales are at least 2.6 days (Table 1). It is again highlighted that the calculated values of k_3 as well as the relaxation timescale are based on entirely collisional stabilization of POZs. In the real atmosphere, as air pressure changes spatiotemporally, different levels of incomplete collisional stabilization may occur, such that the value of k_3 could be higher

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and the relaxation timescale correspondingly shorter. Even so, β-caryophyllene still has the longest relaxation timescales among the studied sesquiterpenes. Neglecting such prolonged relaxation may systematically overestimate the formation rate of β-caryophyllene-derived CIs.

It is also noted that our results above are based on simplified cases where the pre-existing POZs are absent. Our supplemental simulations with the POZ scale factors show that the value of normalized f_{CI} can be amplified but the relaxation timescales remain almost unchanged (Fig. S9). Our findings collectively demonstrate that relaxation timescales and their response to temperature variation can be highly distinct for different sesquiterpenes. Relaxation may be negligible in long-term modeling studies for most sesquiterpenes during heatwaves, but it may still be a great concern in cold surge simulations.

4. Conclusions

Kinetic relaxation is a previously unrecognized behavior in the formation of CIs from sesquiterpene ozonolysis. This relaxation arises from the finite time for POZ production, which hinders an instantaneous response of CI formation to sesquiterpene ozonolysis. The relaxation timescale is sensitive to temperature variations and may be amplified during cold surges and suppressed during heatwaves. Under future warming scenarios (Perkins-Kirkpatrick and Lewis, 2020; Martinez-Villalobos et al., 2025) as well as less frequent cold surges (Nie et al., 2025; Blackport and Fyfe, 2024), kinetic relaxation could become less important on average, although substantial regional and seasonal variability is expected. It is also worth noting that the global trend does not necessarily represent spatiotemporal variations of temperatures; the low temperatures at high latitudes and intense cooling at night may still be possible to induce considerable kinetic relaxation. Under such conditions, ignoring kinetic relaxation may lead to overestimation of CI

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concentrations and therefore potentially overestimate the oxidation rates of trace gases such as SO_2 and NO_2 (Welz et al., 2012; Mauldin Iii et al., 2012; Chhantyal-Pun et al., 2020).

This study also provides an additional perspective for estimating the impact of temperature variation on SOA formation. CI chemistry can contribute to SOA formation through the production of highly oxygenated organic molecules (HOMs) with extremely low volatility (Zhao et al., 2015; Richters et al., 2016a; Richters et al., 2016b). The rate of HOMs formation from sesquiterpene ozonolysis may be considerably affected by the CI formation kinetics. Temperature variations could modulate the formation rate of HOMs by inducing different levels of kinetic relaxation in CI formation. A more comprehensive analysis of SOA formation should integrate detailed reaction mechanisms, temperature-dependent sesquiterpene emission factors, temperature-dependent gas-particle partitioning, and potentially new particle formation events. Among these complex factors, kinetic relaxation uniquely offers a new aspect on the CI supply flux. Overall, our study demonstrates that kinetic relaxation should be considered in atmospheric chemistry models when simulating CI chemistry under conditions characterized by strong temperature variability or low temperatures.

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Acknowledgments

The authors would like to acknowledge computational resources in Tsinghua University as well as those inherited from the late Professor Jun Zhao. Jingkun Jiang acknowledges support from the National Natural Science Foundation of China (22536004). Hengjia Ou acknowledges the funding from the Key Innovation Team of Guangdong Meteorological Bureau (No. GRMCTD202506-ZD06). Yao Li acknowledges the funding from Talent Recruitment Special Project of the Shandong Meteorological Bureau (No. 2025SDRCYJ07).

Author Contribution

Hengjia Ou, Yao Li, and Kunpeng Chen contributed to conceptualization, computational methodology, investigation, formal analysis, and visualization. Yuqing Sha and Kunpeng Chen contributed to equation derivation. Kunpeng Chen supervised the study. Jingkun Jiang, Hengjia Ou, and Yao Li contributed to funding acquisition. Hui Zhou, Hengjia Ou and Yao Li contributed to computational resources. Hengjia Ou, Yao Li, Yuqing Sha, and Kunpeng Chen contributed to original draft writing. All authors contributed to draft review and editing.

Data Availability

All the data are available in the main text or the supplementary information.

Competing Interest

The authors declare no competing financial interest.

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