

Molecular Dynamics-Guided Reaction Discovery Reveals Endoperoxide-to-Alkoxy Radical Isomerization as Key Branching Point in α -pinene Ozonolysis

Huan Yang^{1†#*}, Umberto Raucci^{2†*}, Siddharth Iyer^{3†}, Galib Hasan⁴, Thomas Golin Almeida⁴, Shawon Barua³, Anni Savolainen³, Juha Kangasluoma¹, Matti Rissanen^{3,4}, Hanna Vehkamäki¹, Theo Kurtén^{4*}

¹ Institute for Atmospheric and Earth System Research/Physics, University of Helsinki, FI-00014 Helsinki, Finland

² Atomistic Simulations, Italian Institute of Technology, 16156 Genova, Italy

³ Aerosol Physics Laboratory, Tampere University, FI-33720 Tampere, Finland

⁴ Department of Chemistry, University of Helsinki, FI-00014 Helsinki, Finland

Current Address: Max Planck Institute for Chemistry, DE-55122 Mainz, Germany

Contributed equally (†)

Corresponding authors (*)

Huan Yang: Huan.yang@mpic.de

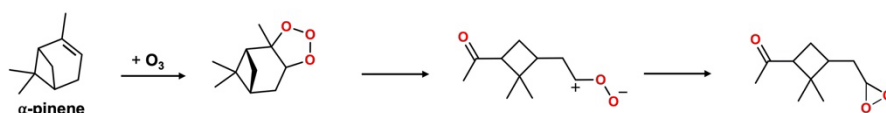
Umberto Raucci: Umberto.raucci@iit.it

Theo Kurtén: Theo.Kurten@helsinki.fi

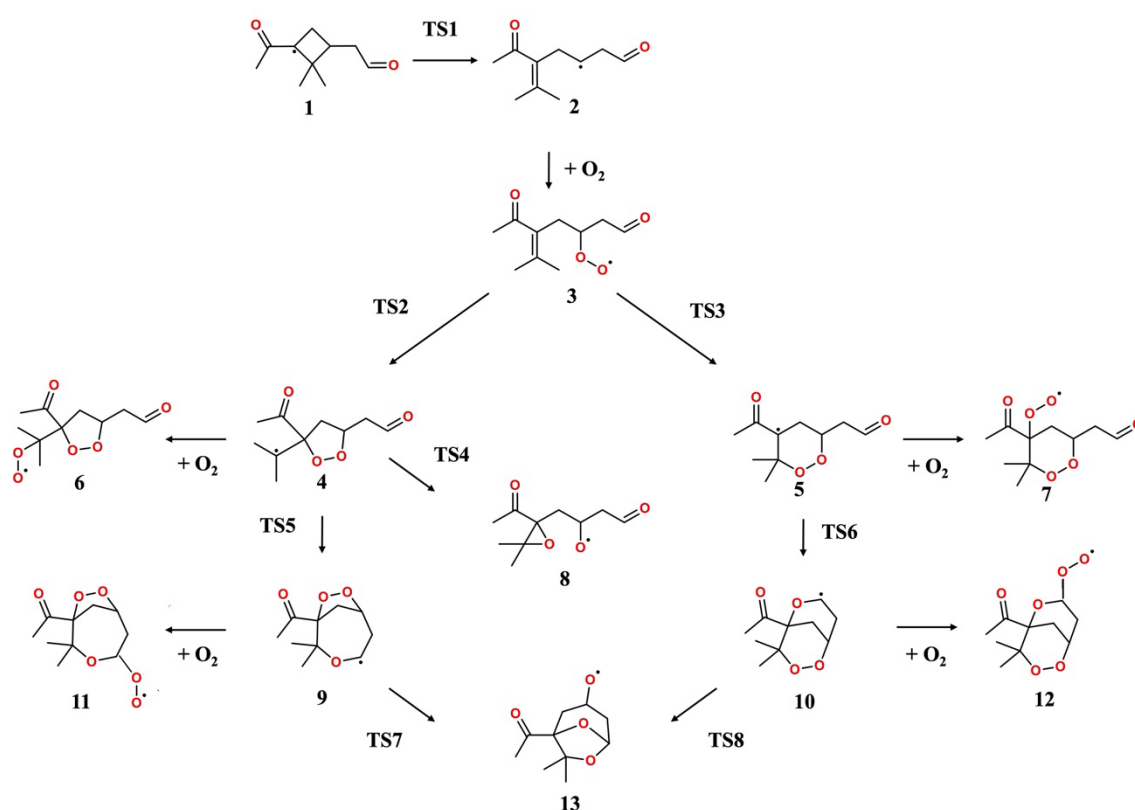
Supplementary Materials

Supplementary Note 1. The “anti” CI isomer pathway and the ring-breaking channel of Vinox-y-c

a



b



Supplementary Figure 1. (a) The “anti” CI isomer pathway. (b) The ring-breaking channel following Vinox-y-c and the subsequent reactions discovered by the reaction discovery procedure.

Supplementary Table 1. Absolute energies in Hartrees for molecules and transition states in Supplementary Figure 1b. DFT = B3LYP/6-31+G(d); ZPE = Zero-point corrected energy; EE = Electronic energy

Molecules	DFT – EE	DFT – ZPE
1	-540.4914868	-540.263667
2	-540.4810716	-540.254762
3	-690.8609052	-690.623713
4	-690.8608552	-690.624757
5	-690.8755678	-690.637808
6	-841.2316064	-840.985552
7	-841.2276893	-840.981571
8	-690.9047139	-690.669548
9	-690.8486988	-690.609219
10	-690.8554690	-690.615338
11	-841.2296696	-840.980095
12	-841.2312360	-840.981366
13	-690.9353919	-690.694465
TS1	-540.4398134	-540.213930
TS2	-690.8424494	-690.607143
TS3	-690.8431023	-690.606806
TS4	-690.8447998	-690.610703
TS5	-690.8329306	-690.596094
TS6	-690.8333641	-690.595225
TS7	-690.8283924	-690.591625
TS8	-690.8329583	-690.595241
O ₂	-150.3275756	-150.323839

Supplementary Table 2. Relative energies in kcal/mol for molecules and transition states in Supplementary Figure 1b. DFT = B3LYP/6-31+G(d); ZPE = Zero-point corrected energy; EE = Electronic energy

Molecules	DFT – EE	DFT – ZPE
1+2O ₂	0	0
2+2O ₂	6.54	5.59
3+O ₂	-26.26	-22.72
4+O ₂	-26.22	-23.38
5+O ₂	-35.46	-31.56
6	-53.32	-46.56
7	-50.86	-44.07
8+O ₂	-53.75	-51.48
9+O ₂	-18.60	-13.62
10+O ₂	-22.85	-17.46
11	-52.10	-43.14
12	-53.09	-43.94
13+O ₂	-73.00	-67.12
TS1+2O ₂	32.43	31.21
TS2+O ₂	-14.68	-12.32
TS3+O ₂	-15.09	-12.11
TS4+O ₂	-16.15	-14.56
TS5+O ₂	-8.70	-5.39
TS6+O ₂	-8.97	-4.84
TS7+O ₂	-5.85	-2.58
TS8+O ₂	-8.72	-4.85

Supplementary Note 2. Excess energy dissipation and its effects on endoperoxy-alkyl radical rearrangement

Free molecular heat dissipation model

The activation of the endoperoxy-alkyl radical rearrangement reaction channel relies on the large amount of excess energy from preceding steps. The net effect of the excess energy is intricately tied to its rate of dissipation, particularly during the bottleneck $\text{RB} + \text{O}_2$ step. To investigate this phenomenon, we employ a free molecular heat dissipation (FM-HD) model¹ that is specifically designed to analyze heat dissipation of nanoclusters much smaller than the mean free path of the carrier gas.

In the FM-HD model, the heat flux onto/out of the nanocluster surface is governed by:

$$\frac{dE_c}{dt} = \dot{q}, \quad (\text{S1})$$

where $E_c = \gamma T_c$ denotes the internal energy of the nanocluster and $\dot{q} = \bar{A} \bar{c} n_g \langle E_o - E_i \rangle$ represents the heat flux onto the nanocluster surface. In these expressions, γ stands for the specific heat of the nanocluster, T_c represents the effective temperature of the nanocluster, $\bar{A}$ denotes the rotationally averaged collision area of the nanocluster, $\bar{c}$ represents the mean thermal speed of the carrier gas, n_g denotes the number concentration of the carrier gas, and $\langle E_o - E_i \rangle$ represents the average heat exchange per carrier gas-nanocluster collision. This average energy exchange is typically characterized using the so-called Thermal Accommodation Coefficient (TAC), defined as $\alpha = \langle E_o - E_i \rangle / \langle E_o - E_i \rangle_{\text{max}}$. Here, the denominator represents the maximum energy transfer allowed by the second law of thermodynamics, which occurs if gas molecules equilibrated completely with the nanocluster surface after collision. $\langle E_o - E_i \rangle_{\text{max}}$ can be derived based on kinetic gas theory, and $\langle E_o - E_i \rangle_{\text{max}} = 3k_B(T_g - T_c)$ for diatomic gases² like N_2 , where k_B represents the Boltzmann constant and T_g denotes the temperature of the carrier gas. The substitution of these expressions into Equation S1 gives:

$$\gamma \frac{dT_c}{dt} = 3\alpha k_B \bar{A} \bar{c} n_g (T_g - T_c). \quad (\text{S2})$$

The solution for Equation S2 is readily available:

$$T_c(t) - T_g = [T_{c0}(t_0) - T_g] e^{-3\alpha k_B \bar{A} \bar{c} n_g t / \gamma}. \quad (\text{S3})$$

Note that the excess energy of the nanocluster is defined as $E_{\text{excess}}(t) = \gamma [T_c(t) - T_g]$.

Therefore, according to Equation S3:

$$E_{\text{excess}}(t) = E_{\text{excess}}(t_0) e^{-3\alpha k_B \bar{A} \bar{c} n_g t / \gamma}. \quad (\text{S4})$$

We used Equation S4 to assess the dissipation of excess energy for RB in a N₂ environment at 298 K and 1 atm. Parameters required in Equation S4 are summarized in Supplementary Table 3. Special attention was paid to the determination of three essential parameters: the rotationally averaged collision area of RB ($\bar{A}$), the specific heat of RB (γ), and the RB-N₂ TAC (α). The value of $\bar{A}$ was computed by randomly orienting RB in three-dimensional space and projecting it onto a two-dimensional surface to determine average projected areas. This process involved repeated iterations to calculate an averaged projected area^{3,4}, which was then considered as $\bar{A}$. To determine γ , molecular dynamics simulations were employed, wherein the translation and internal energy of a free RB molecule were computed at various temperatures using the PM6 empirical force field (the choice is because of computational efficiency). The slope of the "translational + internal energy" versus "temperature" curve was extracted as γ . The only remaining parameter was the TAC (α).

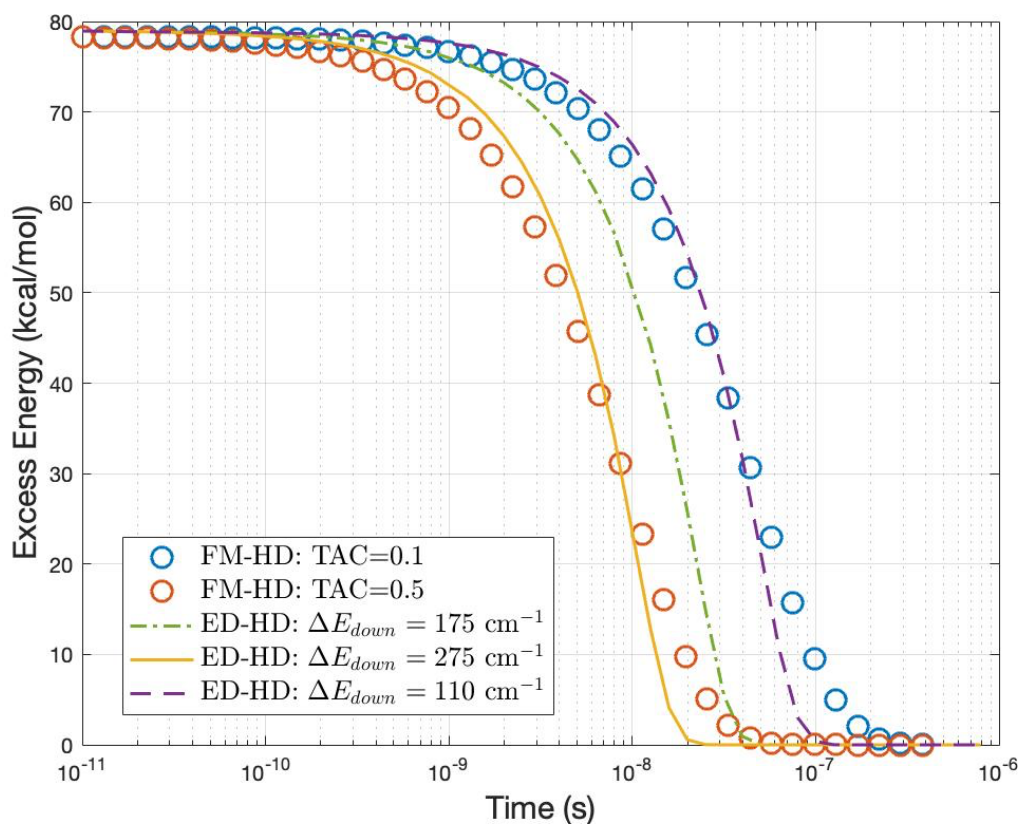
Supplementary Table 3. Numerical values for the parameters used in Equation S4.

$\bar{A}$	γ	α	$\bar{c}$	n_g
5.03e-19 m ²	1.12e-21 J/K	0.1 – 0.5	466 m/s	2.46e25 m ⁻³

The Thermal Accommodation Coefficient (TAC) has been extensively studied through experiments and molecular dynamics simulations and was found to be insensitive to the temperature. Despite its theoretical range from 0 to 1, reported values in literature indicate that TAC values rarely exceed 0.5 in practical scenarios.⁵⁻⁹ Various studies have reported TAC values involving N₂ as the carrier gas. For instance, Daun et al.⁸ documented a TAC range of 0.2 to 0.3 for N₂ with soot surfaces. Additionally, Yang et al.⁷ reported TAC values of 0.1 for N₂ with gold nanoclusters and 0.13 for N₂ with copper nanoclusters. It is worth noting that higher TAC values correspond to increased heat dissipation rates and diminished effects of excess energy in activating reactions.

We used a TAC range of 0.1 to 0.5 to evaluate the predictive capabilities of the FM-HD model for our RB-N₂ case. The evaluation was done by comparing the FM-HD model with the exponential down heat dissipation (ED-HD) model implemented in the MESMER code. Results are depicted in Figure S2. In the ED-HD model, the parameter governing the rate of excess energy dissipation is denoted as ΔE_{down} . MESMER proposes a range for ΔE_{down} with N₂ carrier gas, spanning from 175 cm⁻¹ to 275 cm⁻¹. Notably, this entire range falls within the

scope of the FM-HD model when considering a TAC range of 0.1 to 0.5. Thus, the FM-HD model offers a more conservative estimate for the range of excess energy dissipation rates.

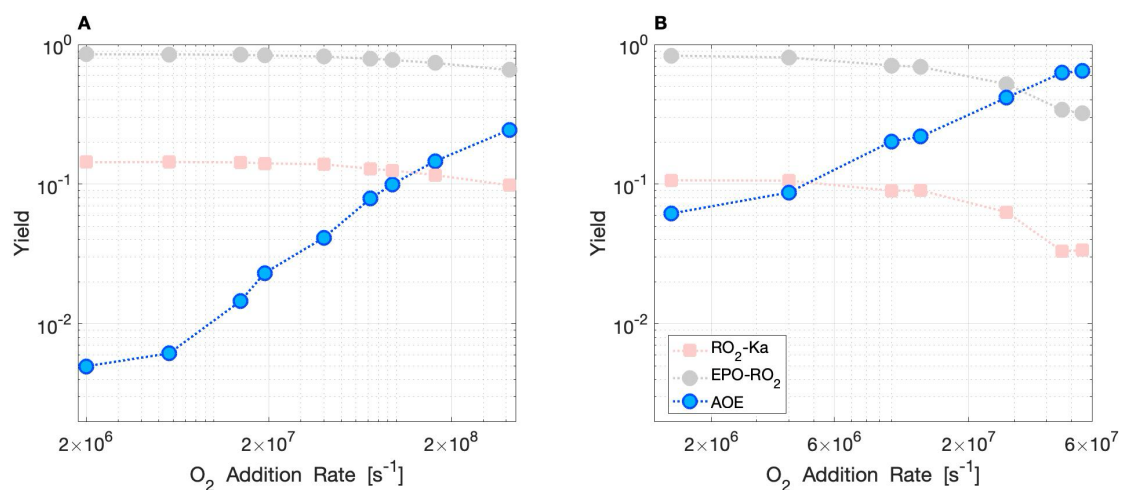


Supplementary Figure 2. RB excess energy dissipation predicted by the FM-HD and ED-HD model.

Influence of excess energy on the endoperoxy-alkyl radical rearrangement

Based on the discussion in the previous section, we opt to use a moderate value of TAC = 0.25 to model the RB excess energy dissipation rate in the main text. However, both the lower and upper extremes of TAC = 0.1 and TAC = 0.5 were explored to evaluate their influence on the yield of the endoperoxy-alkyl radical rearrangement reaction. The FM-HD model was not directly invoked in the MESMER simulation. Instead, the ED-HD model implemented in the MESMER code was used with its ΔE_{down} value determined by fitting to the FM-HD model. Consequently, $\Delta E_{\text{down}} = 175 \text{ cm}^{-1}$ (corresponding to TAC = 0.25) was adopted in the main text, while ΔE_{down} values of 110 cm^{-1} and 275 cm^{-1} (corresponding to TAC = 0.1 and 0.5) were tested to assess the lower and upper extremes of the yield. The results are illustrated in Fig. S3. For the fastest excess energy dissipation rate, the yield of the endoperoxy-alkyl radical rearrangement reaction ranges from 1% to approximately 10% within the O_2 addition rate range of 10^7 s^{-1} to 10^8 s^{-1} . In contrast, for the slowest excess energy dissipation

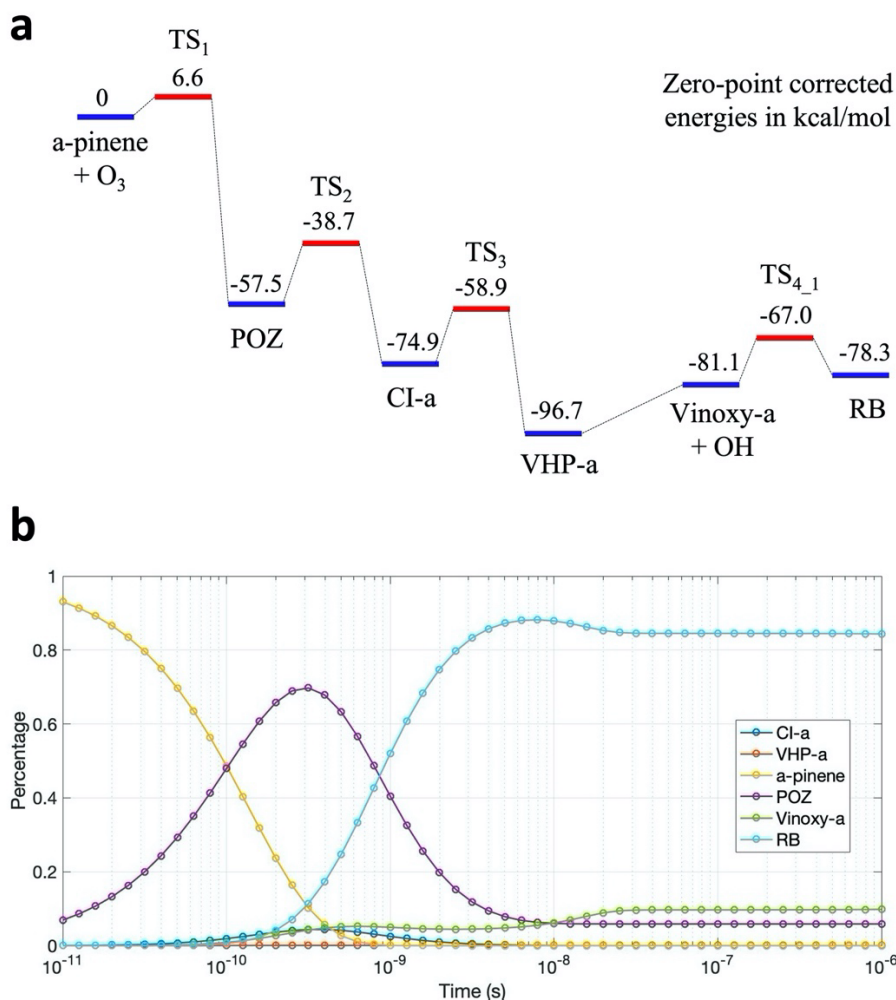
rate, the yield already exceeds 20% at an O_2 addition rate of 10^7 s^{-1} . These yields represent a highly conservative estimation, as the extremes of the TACs tested correspond to energy dissipation rates that are significantly faster or slower than what is typically observed in realistic scenarios.



Supplementary Figure 3. Yield of the endoperoxy-alkyl radical rearrangement reaction (AOE) compared to its competing channels at the low and high extremes of heat dissipation rates. (A) high heat dissipation rate with $\Delta E_{\text{down}} = 275 \text{ cm}^{-1}$. (B) low heat dissipation rate with $\Delta E_{\text{down}} = 110 \text{ cm}^{-1}$.

Supplementary Note 3. Majority of RB forms approximately 2 ns after the initial ozonolysis

To elucidate the temporal dynamics of RB formation, we conducted kinetic master equation simulations using a reduced potential energy surface, as depicted in the panel A of Supplementary Figure 4. All reaction steps were configured identically to those in the main text, with the exception of employing the MESMER-ILT method, available within the MESMER program, for the initial alpha-pinene + Ozone bimolecular step. In contrast, the main text simulations utilized the SimpleRRKM method for this reaction. The utilization of the MESMER-ILT method enabled us to manually set a high rate for the alpha-pinene + Ozone bimolecular reaction, allowing for visualization of the concentration evolution of subsequent intermediates at the nanosecond scale. It is important to note that the alpha-pinene + Ozone bimolecular reaction does not influence the yield of subsequent products. As illustrated in the panel B of Figure S4, over 75% of RB was produced approximately 2 ns after the initial ozonolysis. According to the excess energy dissipation analysis in section 2, only a small portion of excess energy is expected to dissipate within the 2 ns timeframe. This observation confirms that RB produced during the ozonolysis process retains a substantial portion of the excess energy from preceding reaction steps.

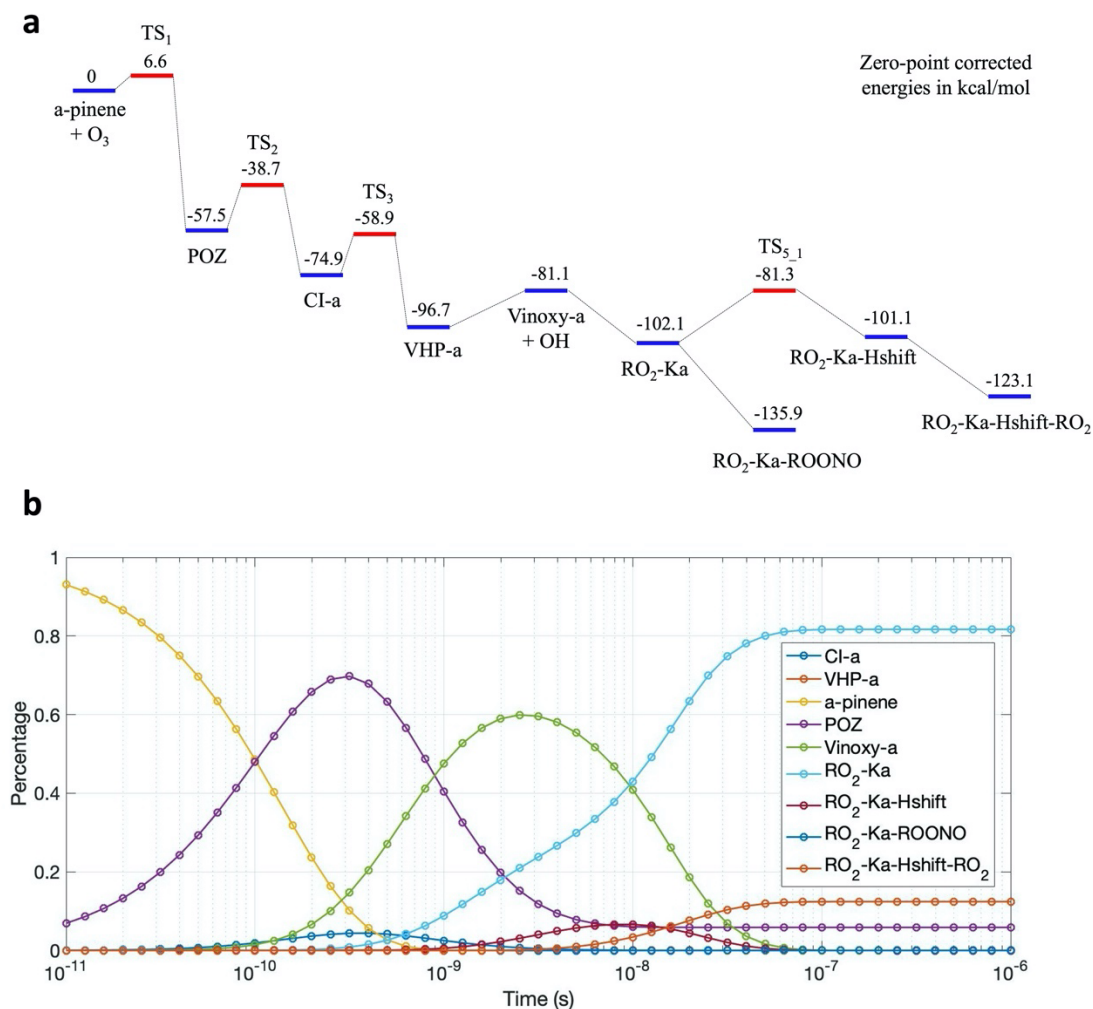


Supplementary Figure 4. Kinetic master equation simulations performed on the reduced potential energy surface reveal that the majority of RB was produced approximately 2 ns following the initial ozonolysis. A high a-pinene + ozone bimolecular rate was used here, facilitating the visualization of concentration profile evolutions at the nanosecond scale. (a) Potential energy surface used in the kinetic master equation simulation. (b) Percentage of the reactant, intermediates, and products during the simulation period.

Supplementary Note 4. Excess energy could also lead to the rapid (at nanosecond scale) H-shifts for the first generation RO₂ product

To evaluate the role of excess energy in facilitating this H-shift reaction, targeted kinetic master equation simulations were conducted along the potential energy surface of one of the Vinoxys studied in the main text (Vinoxy-a), as depicted in panel A of Supplementary Figure 5. The setup for all reaction steps leading up to RO₂-Ka remained consistent with that of the main text, with the exception of utilizing the MESMER-ILT method for the initial alpha-pinene + O₃ bimolecular step. With a similar purpose as in the previous section, this modification aimed to utilize a high bimolecular reaction rate to speed up barrier passage and enable the visualization of dynamics at the nanosecond scale. Properties of the RO₂-Ka H-shift product (RO₂-Ka-Hshift), including the coupled cluster energy, were sourced from Kurten et al.¹⁰ RO₂-Ka-ROONO was introduced as a sink to control the RO₂-Ka lifetime (set at 1 s), while RO₂-Ka-Hshift-RO₂, the O₂ addition product of RO₂-Ka-Hshift, was also introduced as a sink, with an O₂ addition rate of 7.5e7 s⁻¹ fixed for test simulations. For the O₂ addition step of the Vinoxys, we used a model transition state with variable energies (while the O₂ concentration was fixed at 5×10¹⁸ cm⁻³) to control the effective pseudo-first-order O₂ addition rate at 7.5e7 s⁻¹.

As illustrated in panel B of Supplementary Figure 5, 12.4% of a-pinene following the Vinoxys pathway underwent the H-shift reaction, converting to RO₂-Ka-Hshift-RO₂ within less than 100 ns, indicating that the conversion is driven by the excess energy. It should be noted that the actual yield of RO₂-Ka-Hshift-RO₂ is expected to be lower than 12.4%, as a significant portion of Vinoxys should undergo the competing ring-breaking channel forming RB-RO₂ under realistic conditions (in the model simulations of this section, this competing ring-breaking channel is not included). Nevertheless, the H-shift reaction remains noteworthy in a-pinene ozonolysis, given the absence of the ring-breaking channel in other Vinoxys pathways. Notably, these unstudied Vinoxys pathways lead to RO₂ products exhibiting comparable barriers for their H-shift reactions¹⁰ as RO₂-Ka.

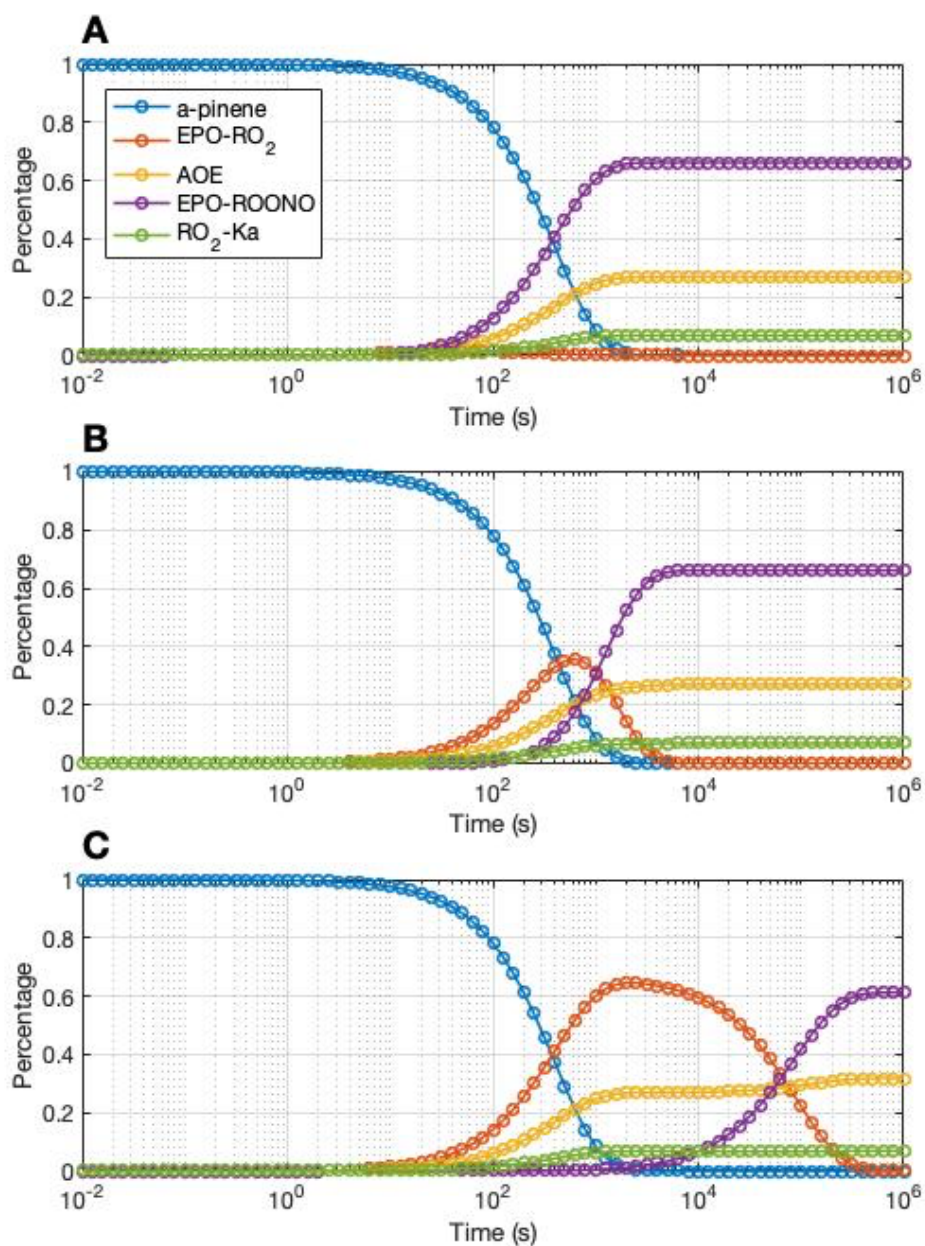


Supplementary Figure 5. (a) Representation of the potential energy surface employed in the kinetic master equation simulation to investigate the influence of excess energy on the H-shift reaction for one of the first generation RO₂ product (RO₂-Ka) in alpha-pinene ozonolysis. The simulation utilized a high alpha-pinene + ozone bimolecular rate, enabling the elucidation of concentration profile dynamics at the nanosecond time scale. (b) Temporal evolution of concentration profiles observed in the kinetic master equation simulation.

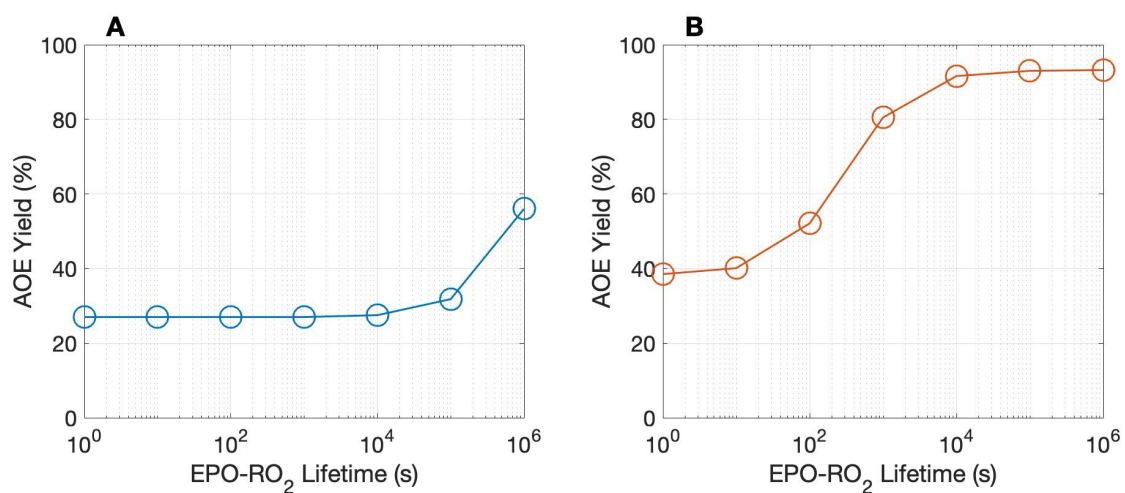
Supplementary Note 5. EPO-RO₂ lifetime impacts the yield of endoperoxy-alkyl radical rearrangement

The back-reaction of O₂ addition for EPO has the potential to enhance the overall yield of the endoperoxy-alkyl radical rearrangement reaction. The significance of this back-reaction depends on the lifetime of the O₂ addition product (EPO-RO₂). To assess the influence of EPO-RO₂ lifetime on the final yield of the endoperoxy-alkyl radical rearrangement reaction, simulations were conducted using MESMER across the entire ozonolysis potential energy surface starting with α -pinene + O₃. The simulation setup is identical to those employed in the main text, except for: (1) Instead of treating the O₂ addition step of EPO using the "Simple Bimolecular Sink", we used the SimpleRRKM method employing a model transition state that led the O₂ addition rate of EPO to be $7e7\text{ s}^{-1}$ at 298 K and 1 atm. This way, the potential back-reaction of EPO O₂ addition can be included. (2) We added a bimolecular "EPO-RO₂ + NO $\rightarrow$ EPO-ROONO" sink reaction to control the lifetime of EPO-RO₂ (varied between 1 s to 10^8 s), which was achieved using the "Simple Bimolecular Sink" method by adjusting the bimolecular loss rate coefficient from $2e-19\text{ cm}^3\text{ s}^{-1}$ to $2e-11\text{ cm}^3\text{ s}^{-1}$ (the concentration of the NO was fixed at $5e10\text{ molecules cm}^{-3}$).

Supplementary Figure 6 shows the concentration profile for key species on the potential energy surface. Notably, a non-negligible increase in the yield of AOE is observed only when the EPO-RO₂ lifetime exceeds 10^5 s (Supplementary Figure 7 panel A). Beyond this threshold, the concentration profile of AOE reveals two distinct stages of increase, attributed to excess energy and the back-reaction, respectively. It is evident, however, that this lifetime significantly surpasses the realistic range of EPO-RO₂ lifetimes (1 s – 100 s) in the atmosphere. Nevertheless, if the energy of the transition state TS6 is lowered to approximately 14 kcal/mol, the back-reaction can enhance the overall yield of AOE within a realistic EPO-RO₂ lifetime range (1 s – 100 s), as depicted in Supplementary Figure 7 panel B.



Supplementary Figure 6. Temporal concentration profiles using different EPO-RO₂ lifetime. Simulations using the complete alpha-pinene ozonolysis potential energy surface (PES) in Figure 3 of the main text, but with different EPO-RO₂ lifetimes controlled by the bimolecular sink EPO-ROONO: (A) EPO-RO₂ lifetime = 10 s, (B) 10³ s, and (C) 10⁵ s.



Supplementary Figure 7. AOE yield as a function of EPO-RO₂ lifetime. (A) Simulations using the complete alpha-pinene ozonolysis PES in Figure 3 of the main text. (B) Simulations using the PES in Figure 3 of the main text, but with TS6 energy adjusted to be 14 kcal/mol.

Supplementary Note 6. Effects of “excess energy” and the “back-reaction of O₂ addition” on the yield of (AOE) the endoperoxy-alkyl radical rearrangement for compounds with lower rearrangement barriers and lower amount of available excess energy

In the main text, we modeled the full potential energy surface (PES) for alpha-pinene + O₃, where the TS6 barrier height is 17.9 kcal/mol, with an available excess energy of 115.5 kcal/mol (though a portion of the energy will dissipate before it can take effect). Because of the high excess energy value, the yield of the endoperoxy-alkyl radical rearrangement (AOE) is solely attributed to excess energy in the case of the main text. On the other hand, due to the high TS6 barrier, the EPO-RO₂ will primarily be consumed by bimolecular sink reactions before it can revert and cross TS6 to yield AOE. Lowering TS6 to around 14 kcal/mol is essential for the back reaction to impact AOE yield.

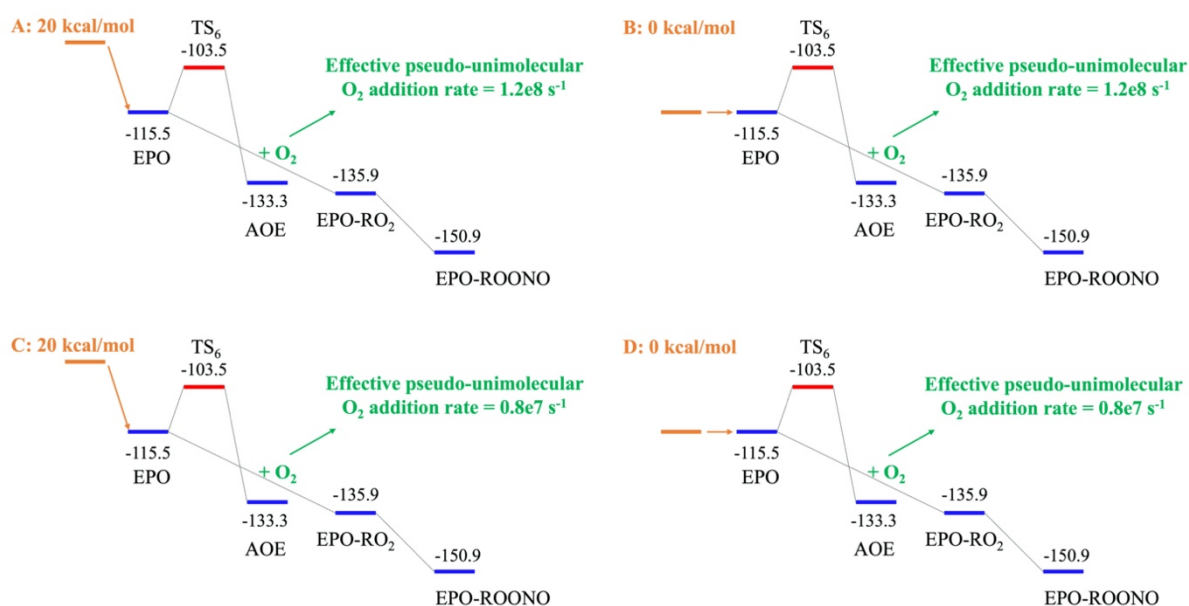
In this section, we performed additional simulations on a reduced PES, where TS6 barrier height is varied between 6 and 14 kcal/mol, and the excess energy for EPO is set to either 0 or 20 kcal/mol. This section aims to provide context for the endoperoxy-alkyl radical rearrangement reactions that may occur in other atmospheric compounds, which likely have lower rearrangement barriers and lower excess energy from previous steps. We found that the contributions of "excess energy" and the "back-reaction of O₂ addition" differ significantly in these cases compared to the full PES scenario discussed in the main text.

Although simulations performed in this section target other atmospheric compounds, the PESs were constructed by referencing several alpha-pinene intermediates for convenience. The simulations start with EPO, and the subsequent reaction of EPO involves two competing pathways: O₂ addition and the endoperoxy-alkyl radical rearrangement reaction. Four sets of model simulations were carried out, encompassing a cross-combination of two different O₂ addition rates and considering scenarios with either 0 kcal/mol excess energy or 20 kcal/mol excess energy derived from preceding reaction steps (see Supplementary Figure 8). For each of the four simulations, the barrier for the endoperoxy-alkyl radical rearrangement reaction ranged from 6 kcal/mol to 16 kcal/mol. Additionally, within each simulation, results were collected for two different conditions where O₂ addition was assumed to be reversible and irreversible, respectively. For cases where the O₂ addition was assumed to be reversible, the EPO-RO₂ lifetime was set at 100 s controlled by a bimolecular sink EPO-ROONO. For cases where the O₂ addition was assumed to be irreversible, EPO-RO₂ itself was modelled as a bimolecular sink. For cases where the O₂ addition was assumed to be reversible, we used a model transition state with variable energies (while the O₂ concentration was fixed at 5×10¹⁸

cm⁻³) to control the effective pseudo-first-order O₂ addition rate of EPO at either 0.8e7 s⁻¹ or 1.2e8 s⁻¹.

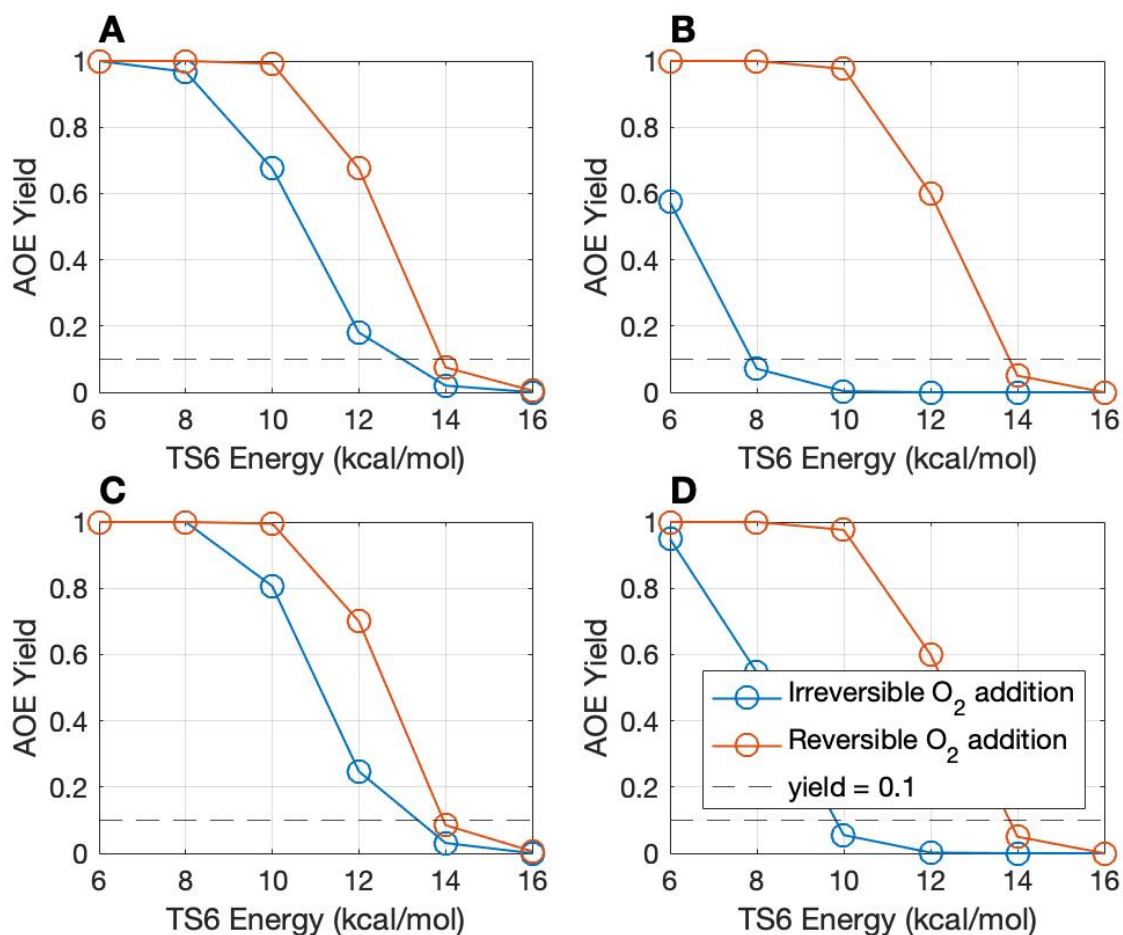
The results are summarized in Figure S9. For these simulations on a reduced PES, where the TS₆ barrier height varies between 6 kcal/mol to 14 kcal/mol and the excess energy for EPO is set to either 0 or 20 kcal/mol, we found that cases where O₂ addition was treated reversibly produced much higher yields than those treated irreversibly. Additionally, the influence of reversible O₂ addition was significantly more pronounced than that of excess energy. The effects of excess energy were only noticeable under irreversible conditions.

Overall, with no excess energy, the endoperoxy-alkyl radical rearrangement reaction is competitive to O₂ addition only if the reaction barrier is less than 8 kcal/mol – 10 kcal/mol, however, with 20 kcal/mol of excess energy, the barrier for the endoperoxy-alkyl radical rearrangement reaction to be competitive is elevated to 12 kcal/mol – 13 kcal/mol. This barrier height range is relevant to large portion of the similar reactions discovered for other atmospherically relevant systems (see Supplementary Note 7 of this document).



Supplementary Figure 8. Potential energy surfaces used in the 4 sets of model simulations. This section aims to provide context for the endoperoxy-alkyl radical rearrangement reactions that may occur in other atmospheric compounds, which likely have lower rearrangement barriers and lower excess energy from previous steps. For cases where the O₂ addition was assumed to be reversible, we used a model transition state with variable energies (while the O₂ concentration was fixed at $5 \times 10^{18} \text{ cm}^{-3}$) to control the effective pseudo-

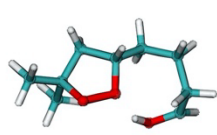
first-order O_2 addition rate of EPO at either $0.8\text{e}7\text{ s}^{-1}$ or $1.2\text{e}8\text{ s}^{-1}$. For cases where the O_2 addition was assumed to be irreversible, EPO- RO_2 was modelled as a bimolecular sink. (A) O_2 addition rate of $1.2\text{e}8\text{ s}^{-1}$ and 20 kcal/mol excess energy added to the reactant. (B) O_2 addition rate of $1.2\text{e}8\text{ s}^{-1}$ and 0 excess energy added to the reactant. (C) O_2 addition rate of $0.8\text{e}7\text{ s}^{-1}$ and 20 kcal/mol excess energy added to the reactant. (D) O_2 addition rate of $0.8\text{e}7\text{ s}^{-1}$ and 0 excess energy added to the reactant.



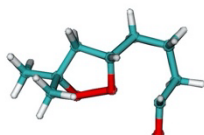
Supplementary Figure 9. Model simulation results that show the effects of “excess energy” and the “back-reaction of O_2 addition” on the yield of the endoperoxy-alkyl radical rearrangement reaction. Irreversible O_2 addition: without considering the back-reaction of O_2 addition; Reversible O_2 addition: with considering the back-reaction of O_2 addition. The EPO- RO_2 lifetime is set to be 100 s for simulations where O_2 addition is reversible. (A) O_2 addition rate of $1.2\text{e}8\text{ s}^{-1}$ and 20 kcal/mol excess energy added to the reactant. (B) O_2 addition rate of $1.2\text{e}8\text{ s}^{-1}$ and 0 excess energy added to the reactant. (C) O_2 addition rate of $0.8\text{e}7\text{ s}^{-1}$ and 20 kcal/mol excess energy added to the reactant. (D) O_2 addition rate of $0.8\text{e}7\text{ s}^{-1}$ and 0 excess energy added to the reactant.

Supplementary Note 7. Endoperoxy-alkyl radical rearrangement barrier (CCSD(T)) is lowered by the presence of the OH substituent

1. Endoperoxy-alkyl-5-6-ring with -OH substituent
Reaction barrier: 14.5 kcal/mol

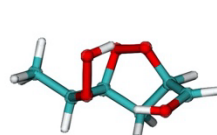


Reactant

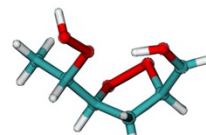


TS

4. Endoperoxy-alkyl-5-3-ring from '1-4-hexadiene + OH'
Reaction barrier: 13.4 kcal/mol

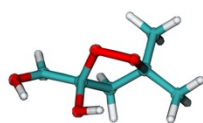


Reactant

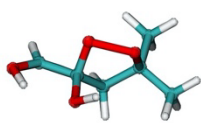


TS

2. Endoperoxy-alkyl-5-3-ring with 2 -OH substituents
Reaction barrier: 12.8 kcal/mol

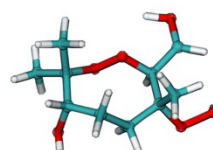


Reactant

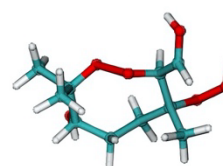


TS

5. Endoperoxy-alkyl-8-3-ring from 'geraniol + OH'
Reaction barrier: 11 kcal/mol

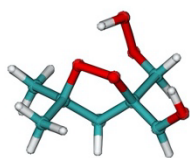


Reactant

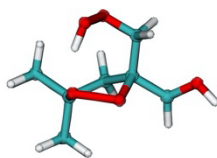


TS

3. Endoperoxy-alkyl-5-3-ring with -OH-CH₂-OOH substituents
Reaction barrier: 11.4 kcal/mol

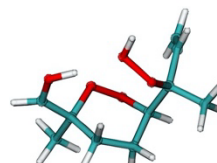


Reactant

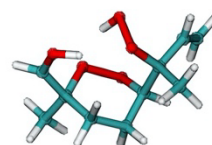


TS

6. Endoperoxy-alkyl-6-3ring from 'alpha-ocimene + OH'
Reaction barrier: 3.05 kcal/mol



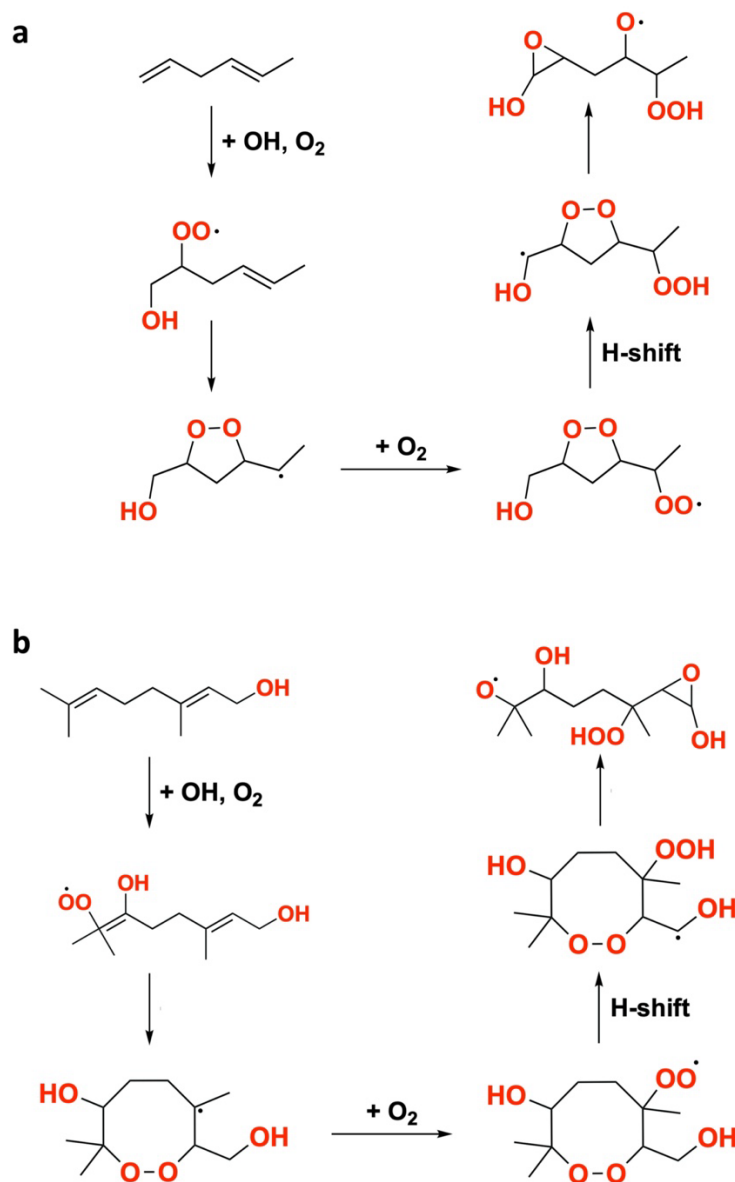
Reactant



TS

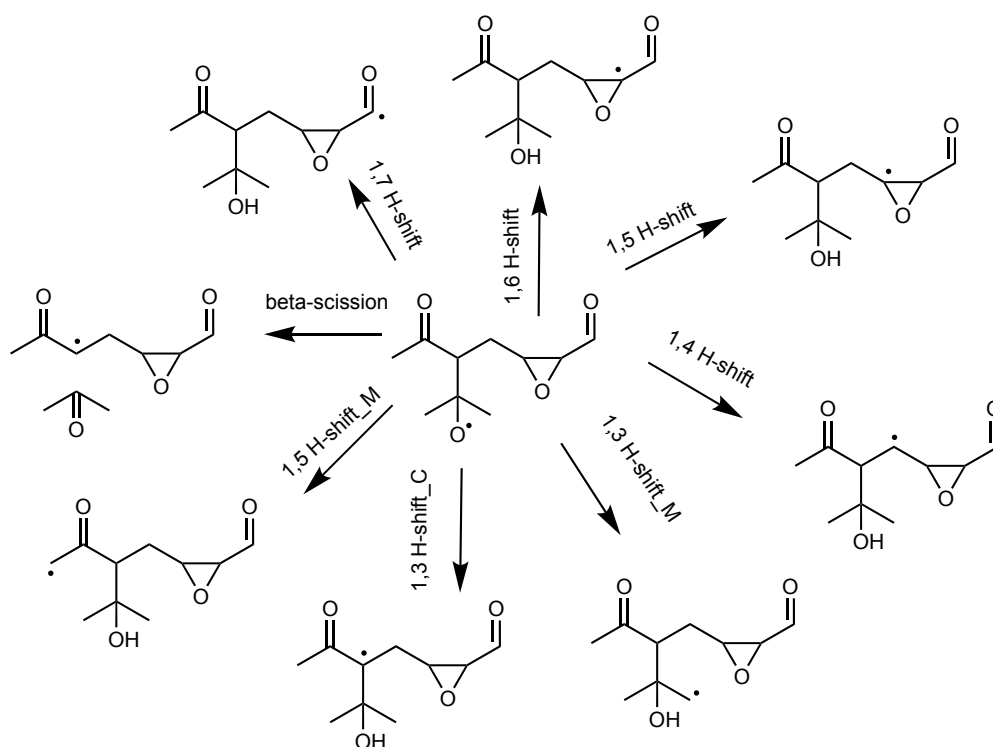
Supplementary Figure 10. Systems where the endoperoxy-alkyl radical rearrangement reaction barrier is lowered by the presence of OH substituent.

Supplementary Note 8. Biogenic and anthropogenic molecules with the newly discovered endoperoxy-alkyl radical rearrangement mechanism



Supplementary Figure 11. (a) The endoperoxy-alkyl radical rearrangement reaction channel found in the 1,4 hexadiene + OH system. (b) The endoperoxy-alkyl radical rearrangement reaction channel found in the geraniol + OH system.

Supplementary Note 9. Potential subsequent reactions for the AOE



Supplementary Figure 12. Possible unimolecular reactions of the endoperoxy-alkyl radical rearrangement product AOE.

Supplementary Table 4. Barriers in zero-point corrected energies of the different unimolecular reactions of Molecule-3

Reaction	$\Delta E^\ddagger$, kcal/mol	$\Delta E^\ddagger$, kcal/mol
	ω B97X-D/6-31+G(d)	ω B97X-D/aug-cc-pVTZ
1,3 H-shift_C	27.1	-
1,3 H-shift_M	29.3	-
1,4 H-shift	19.0	-
1,5 H-shift	11.4	9.8
1,6 H-shift	14.7	-
1,7 H-shift	11.3	9.3
Beta-scission	8.6	7.5
1,5 H-shift_M	12.4	-

Supplementary Note 10. Yield of AOE on a reduced potential energy surface

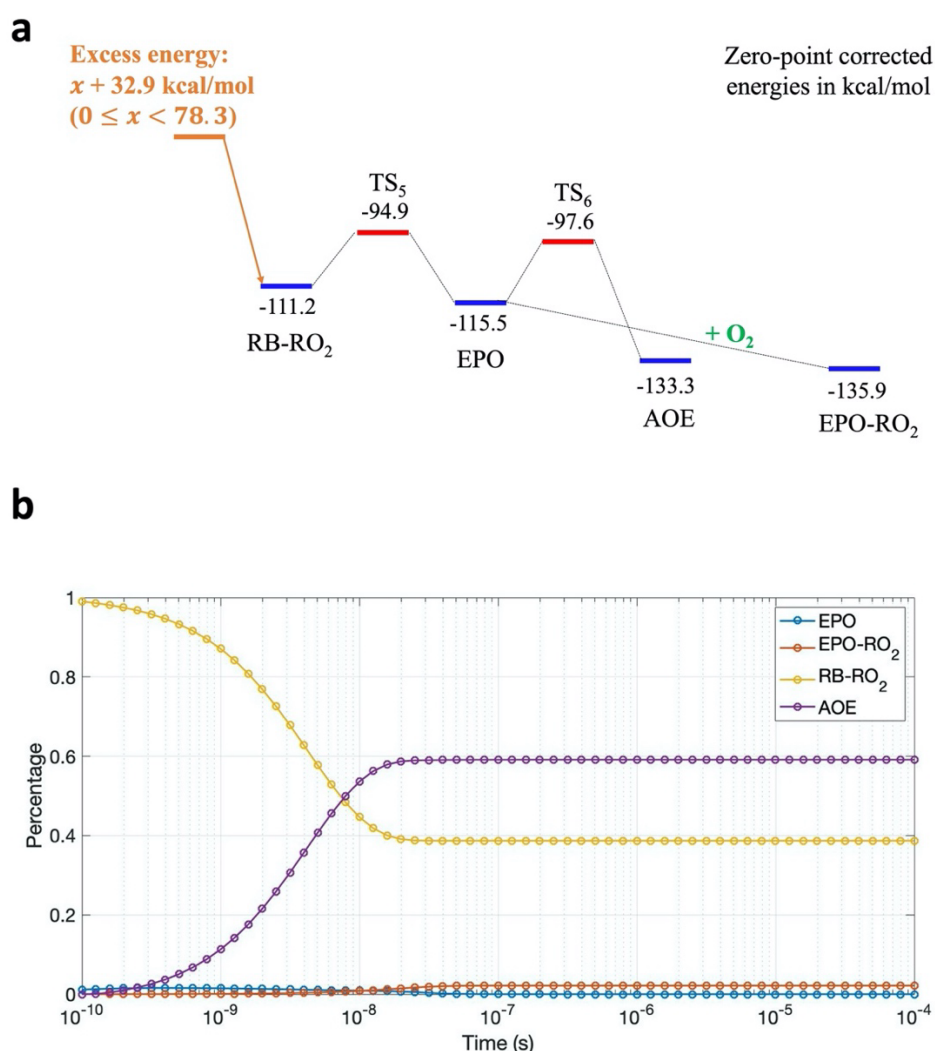
In the main text Figure 3, we performed MESMER simulation on a full PES with a model transition state for the $\text{RB} + \text{O}_2$ to RB-RO_2 step. The model transition state has an assumed barrier that was not explicitly calculated. Optimizing transition states for O_2 addition reactions to alkyl radicals is difficult. However, a TS is nevertheless needed for the SimpleRRKM method in MESMER. While the assumed barrier was arbitrary, it was constrained by the rate of the O_2 addition, which was kept within the ambient relevant range of 10^7 s^{-1} to 10^8 s^{-1} as described in the manuscript.

We would like to clarify that the assumptions made regarding the model transition state do not directly affect the AOE yield. Instead, the yield is ultimately governed by the conversion rate of $\text{RB} + \text{O}_2$ to RB-RO_2 . This rate controls the amount of excess energy retained in RB-RO_2 —the faster the production rate, the less excess energy is dissipated. In turn, this retained excess energy influences whether subsequent isomerization steps are activated. This argument is further illustrated in the following example, where we estimate the AOE yield over the first 7 nanoseconds without resorting to the model transition state, assuming a moderate RB-RO_2 production rate of $7.1 \times 10^7 \text{ s}^{-1}$ and a moderate heat dissipation rate ($\Delta E_{\text{down}} = 175 \text{ cm}^{-1}$, Figure S2):

- In the first 2 nanoseconds, over 70% of RB is produced from the reaction of α -pinene with O_3 , as determined by the MESMER simulation (Figure S4).
- In the following 5 nanoseconds (i.e., between 2 and 7 nanoseconds), the 70% of RB produced in the first 2 nanoseconds will result in at least 50% RB-RO_2 , based a pseudo-first-order rate process: $70\% \times \{1 - \exp[-(5 \times 10^{-9} \text{ s}) \times (7.1 \times 10^7 \text{ s}^{-1})]\} = 50\%$.
- According to the ED-HD model shown in Figure S2, RB is expected to retain about 60 kcal/mol of excess energy at 7 nanoseconds. This implies that the 50% RB-RO_2 produced within this timeframe should retain at least $(60 + 32.9) \text{ kcal/mol}$ of excess energy (the 32.9 kcal/mol is from the $\text{RB} + \text{O}_2$ step).
- We performed additional MESMER simulations on a reduced PES (Figure S13) starting from RB-RO_2 to determine the AOE yield, factoring in various levels of excess energy on RB-RO_2 . This approach bypasses the use of the model transition state on the full PES. The results (Supplementary Table 5) indicate that with $(60 + 32.9) \text{ kcal/mol}$ of excess energy on RB-RO_2 , the branching ratio between AOE and EPO-RO_2 is 59% vs. 41%.

- e. Therefore, based on points c and d, the estimated AOE yield over the first 7 nanoseconds is $50\% \times 59\% = 29.5\%$. This value is quite close to the 26% yield (with an O_2 addition rate of $7.1 \times 10^7 \text{ s}^{-1}$) calculated in Figure 3 from the MESMER simulation on the full PES. The slightly higher yield in this estimation arises because the excess energy lost due to OH in the VHP decomposition step is not accounted for.

This estimation example utilizes a moderate RB-RO₂ production rate of $7.1 \times 10^7 \text{ s}^{-1}$ and a moderate heat dissipation rate ($\Delta E_{\text{down}} = 175 \text{ cm}^{-1}$, Figure S2). The lower and upper limits of both the RB-RO₂ production rate and the heat dissipation rate were explored and shown in Figure 3 and Figure S3 (using the full PES). These simulations underscore the significance of the newly identified pathway.



Supplementary Figure 13. (A) Representation of the reduced potential energy surface employed in the kinetic master equation simulation to investigate the influence of excess energy on the AOE yield. (B) Temporal evolution of concentration profiles observed in the

kinetic master equation simulation for the case of Total Excess Energy = 60 kcal/mol + 32.9 kcal/mol, where 60 kcal/mol is the assumed amount from the “ α -pinene to RB” step (whose maximum amount is 78.3 kcal/mol) and 32.9 kcal/mol comes from the “RB to RB-RO₂”. In this case, the amount of excess energy from the “ α -pinene to RB” step needs to be assumed because it is expected to be partially dissipated during the RB + O₂ step.

Supplementary Table 5. Effect of the total excess energy possessed by RB-RO₂ on the yield of AOE

Total Excess Energy, kcal/mol (“ α -pinene to RB” + “RB to RB-RO ₂ ”)	AOE yield	EPO-RO ₂ yield
30 + 32.9	0.076	0.924
40 + 32.9	0.198	0.802
50 + 32.9	0.381	0.619
60 + 32.9	0.594	0.406

Supplementary Note 11. Effect of the pseudo first-order O₂ addition rate for “Vinoxy-a + O₂” and “EPO + O₂” on AOE yield

Supplementary Table 6. Effect of the pseudo first-order O₂ addition rate for “Vinoxy-a + O₂” on AOE yield. MESMER simulations were performed on the full potential energy surface shown in Figure 3 of the main text. The other two pseudo first-order O₂ addition rates for “EPO + O₂” and “RB + O₂” were fixed at 7.1×10^7 s⁻¹.

O ₂ addition rate, s ⁻¹ (Vinoxy-a + O ₂)	AOE yield	EPO-RO ₂ yield	RO ₂ -Ka yield
10 ⁷	0.266	0.693	0.041
2×10 ⁷	0.266	0.689	0.045
4×10 ⁷	0.265	0.681	0.054
6×10 ⁷	0.264	0.672	0.064
8×10 ⁷	0.263	0.665	0.072
10 ⁸	0.262	0.658	0.080

Supplementary Table 7. Effect of the pseudo first-order O₂ addition rate for “EPO + O₂” on AOE yield. MESMER simulations were performed on the full potential energy surface shown in Figure 3 of the main text. The other two pseudo first-order O₂ addition rates for “Vinoxy-a + O₂” and “RB + O₂” were fixed at 7.1×10^7 s⁻¹.

O ₂ addition rate, s ⁻¹ (EPO + O ₂)	AOE yield	EPO-RO ₂ yield	RO ₂ -Ka yield
10 ⁷	0.269	0.663	0.068
2×10 ⁷	0.268	0.664	0.068
4×10 ⁷	0.266	0.666	0.068
6×10 ⁷	0.265	0.667	0.068
8×10 ⁷	0.263	0.669	0.068
10 ⁸	0.261	0.671	0.068

Supplementary Note 12. Absolute and relative energies for the molecules shown in Figure 3 of the main text

Supplementary Table 8. Absolute energies in Hartrees for molecules shown in Figure 3 of the main text.

ZPE = Zero-point corrected energy; EE = Electronic energy. Note that “ZP correction” is calculated at the wB97X-D/aug-cc-pVTZ level of theory.

Molecules	ZP correction	CCSD(T) – E	CCSD(T) – ZPE
AP	0.237260	-390.0658103	-389.8285503
POZ	0.252126	-615.3704567	-615.1183307
CI-a	0.247038	-615.3930726	-615.1460346
VHP-a	0.246846	-615.4276444	-615.1807984
Vinox-y-a	0.229910	-539.7314706	-539.5015606
RO ₂ -Ka	0.238798	-689.9454328	-689.7066348
RB	0.227132	-539.7242497	-539.4971177
RB-RO ₂	0.237990	-689.9590600	-689.7210700
EPO	0.239707	-689.9676416	-689.7279346
AOE	0.238038	-689.9943714	-689.7563334
EPO-RO ₂	0.249011	-840.1809889	-839.9319779
TS ₁	0.247577	-615.2637538	-615.0161768
TS ₂	0.248896	-615.3371465	-615.0882505
TS ₃	0.242706	-615.3631863	-615.1204803
TS ₄	0.227312	-539.7065330	-539.4792210
TS ₅	0.237363	-689.9325584	-689.6951954
TS ₆	0.237206	-689.9365995	-689.6993935
O ₂	0.003884	-150.1754180	-150.1715340
OH	0.008603	-75.66287400	-75.65427100
O ₃	0.007811	-225.2059050	-225.1980940

Supplementary Table 9. Relative energies in kcal/mol for molecules shown in Figure 3 of the main text.

ZPE = Zero-point corrected energy; EE = Electronic energy

Molecules	CCSD(T) – EE	CCSD(T) – ZPE
α -pinene+O ₃ +2O ₂	0	0
POZ+2O ₂	-62.0	-57.5
CI-a+2O ₂	-76.2	-74.9
VHP-a+2O ₂	-97.9	-96.7
Vinoxy-a+2O ₂ +OH	-77.0	-81.1
RO ₂ -Ka+O ₂ +OH	-101.1	-102.1
RB+2O ₂ +OH	-72.4	-78.3
RB-RO ₂ +O ₂ +OH	-109.7	-111.2
EPO+O ₂ +OH	-115.1	-115.5
AOE+O ₂ +OH	-131.9	-133.3
EPO-RO ₂ +OH	-138.9	-135.9
TS ₁ +2O ₂	5.0	6.6
TS ₂ +2O ₂	-41.1	-38.7
TS ₃ +2O ₂	-57.4	-58.9
TS ₄ +2O ₂ +OH	-61.3	-67.0
TS ₅ +O ₂ +OH	-93.1	-94.9
TS ₆ +O ₂ +OH	-95.6	-97.6

Supplementary Note 13. Multi-conformer effects

We performed full conformational sampling to obtain the lowest-energy conformers of the different stationary points along the PES, but multiple conformers were not considered in our RRKM-ME simulations. MESMER does not account for multiple conformers explicitly, but the use of the HinderedRotorQM1D method allows for the implicit consideration of conformers. To assess effects of multiple conformers, we used Gaussian 16 to run DFT calculations (wb97X-D/aug-cc-pVTZ) with Freq=HinderedRotor to identify the hindered rotors + the periodicities and barriers of all “non-sink” molecules along the PES in Figure 3. We successfully identified hindered rotors for all intermediates and transition states except TS₅. Hindered rotor calculations with Gaussian is imperfect and often fails to identify the internal rotational modes of complex transition states, such as TS₅. The following table compares the rate coefficients derived from MESMER for the rigid-rotor harmonic oscillator (RRHO) model versus the hindered rotor model. As shown, the rate coefficients are quite similar between the two cases (within a factor of ~2), except for the EPO → AOE step, where the hindered rotor model yields a rate coefficient approximately one order of magnitude higher than the RRHO model (this higher value from hindered rotor model favors the proposed endoperoxide rearrangement pathway). We also compared the fraction of alpha-pinene molecules that follow the Vinox-y-a → RB path (as opposed to the Vinox-y-a → RO₂-Ka path), which contributes to the subsequent endoperoxide rearrangement pathway. Using MESMER simulations with pseudo-first-order O₂ addition rate coefficients of 7.1e7 s⁻¹ (RRHO) and 8.2e7 s⁻¹ (hindered rotor), we found similar results: 93.2% for the RRHO model and 96.8% for the hindered rotor model. These comparable values suggest that including or excluding multiple conformer effects will not alter our conclusions.

Supplementary Table 10. MESMER derived rate coefficients at thermalized conditions: RRHO v.s. hindered rotor.

	RRHO (s ⁻¹)	Hindered rotor (s ⁻¹)
AP → POZ	2.043e-5	4.484e-5
POZ → CI-a	0.144	0.142
CI-a → VHP-a	299.67	173.37
VHP-a → Vinox-y-a	1470.06	1420.20
Vinox-y-a → RB	282.73	122.72
EPO → AOE	0.882	7.938

Supplementary References

- 1 Liu, F., Daun, K., Snelling, D. R. & Smallwood, G. J. Heat conduction from a spherical nano-particle: status of modeling heat conduction in laser-induced incandescence. *Applied physics B* **83**, 355-382 (2006).
- 2 Filippov, A. & Rosner, D. Energy transfer between an aerosol particle and gas at high temperature ratios in the Knudsen transition regime. *International journal of heat and mass transfer* **43**, 127-138 (2000).
- 3 Gopalakrishnan, R., Thajudeen, T. & Hogan, C. J. Collision limited reaction rates for arbitrarily shaped particles across the entire diffusive Knudsen number range. *The Journal of chemical physics* **135** (2011).
- 4 Gopalakrishnan, R., McMurtry, P. H. & Hogan Jr, C. J. The bipolar diffusion charging of nanoparticles: A review and development of approaches for non-spherical particles. *Aerosol Science and Technology* **49**, 1181-1194 (2015).
- 5 Daun, K. Thermal accommodation coefficients between polyatomic gas molecules and soot in laser-induced incandescence experiments. *International Journal of Heat and Mass Transfer* **52**, 5081-5089 (2009).
- 6 Daun, K., Sipkens, T., Titantah, J. & Karttunen, M. Thermal accommodation coefficients for laser-induced incandescence sizing of metal nanoparticles in monatomic gases. *Applied Physics B* **112**, 409-420 (2013).
- 7 Yang, H., Song, G. & Hogan Jr, C. J. A molecular dynamics study of collisional heat transfer to nanoclusters in the gas phase. *Journal of Aerosol Science* **159**, 105891 (2022).
- 8 Daun, K., Smallwood, G. & Liu, F. Investigation of thermal accommodation coefficients in time-resolved laser-induced incandescence. (2008).
- 9 Sipkens, T. & Daun, K. Effect of surface interatomic potential on thermal accommodation coefficients derived from molecular dynamics. *The Journal of Physical Chemistry C* **122**, 20431-20443 (2018).
- 10 Kurten, T. *et al.* Computational study of hydrogen shifts and ring-opening mechanisms in α -pinene ozonolysis products. *The Journal of Physical Chemistry A* **119**, 11366-11375 (2015).