Molecular mechanism for rapid autoxidation in α-pinene ozonolysis

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Aerosol affects Earth’s climate and the health of its inhabitants. A major contributor to aerosol formation is the oxidation of volatile organic compounds. Monoterpenes are an important class of volatile organic compounds, and recent research demonstrate that they can be converted to low-volatility aerosol precursors on sub-second timescales following a single oxidant attack. The α-pinene + O₃ system is particularly efficient in this regard. However, the actual mechanism behind this conversion is not understood. The key challenge is the steric strain created by the cyclobutyl ring in the oxidation products. This strain hinders subsequent unimolecular hydrogen-shift reactions essential for lowering volatility. Using quantum chemical calculations and targeted experiments, we show that the excess energy from the initial ozonolysis reaction can lead to novel oxidation intermediates without steric strain, allowing the rapid formation of products with up to 8 oxygen atoms. This is likely a key route for atmospheric organic aerosol formation.
Aerosol affects the planet’s radiation budget, especially by affecting the formation and properties of clouds, and consequently the climate. However, uncertainties remain high in estimates of the radiative effects of aerosol\textsuperscript{1–13}. Epidemiological studies also show a clear link between high ambient aerosol concentration and increased mortality\textsuperscript{4,5}. Organic carbonaceous matter typically comprises 20–90% of the aerosol mass in the lower troposphere\textsuperscript{6}, and improving our understanding of the impact of aerosol on both climate and health therefore requires a detailed characterization of the sources and fates of organic aerosol mass. Secondary organic aerosol mass (SOA) is formed in situ through the oxidation of gas-phase volatile organic compounds (VOC). The oxidation process transforms VOC into less volatile products, which partition into aerosol\textsuperscript{7–9}, or in the case of the lowest-volatility products, even participate in new-particle formation. Recently, some VOC have been shown to undergo autoxidation\textsuperscript{10}, a series of sequential peroxy radical (RO\textsubscript{2}) hydrogen shifts (H-shifts) and O\textsubscript{2} additions to the hydrocarbon chain, leading to so-called highly oxygenated organic molecules (HOM) with very-low volatilities extremely rapidly\textsuperscript{9,11,12}. While the fastest VOC to HOM conversion hitherto measured has a reaction time of around 1.5 s\textsuperscript{12}, if sufficiently rapid RO\textsubscript{2} H-shift channels are available, autoxidation could allow some VOC to HOM conversion to occur even on sub-second timescales following a single oxidant attack under natural temperature and pressure (NTP) conditions. Formation of low-volatile HOM that contribute to aerosol formation and growth from a single bimolecular reaction of a VOC precursor with O\textsubscript{3} is the organic analog to the formation of sulfuric acid, which has already for over a century been known as the most important organic aerosol precursor, largely due to its efficient gas-phase formation via a single rate-limiting bimolecular reaction of volatile SO\textsubscript{2} with the OH radical\textsuperscript{13,14}.

Monoterpenes (C\textsubscript{10}H\textsubscript{16}) account for \~11% of the global biogenic VOC emission by mass, and contribute significantly to the global SOA budget\textsuperscript{15,16} because their oxidation products can have very low volatility. \(\alpha\)-pinene is the most emitted monoterpene, making up \~34% of the total monoterpene emission\textsuperscript{17}. It is a very efficient SOA precursor\textsuperscript{18}, and the \(\alpha\)-pinene + O\textsubscript{3} reaction in particular is one of the main SOA-forming systems in the atmosphere\textsuperscript{19–23}. This reaction has therefore been extensively studied over the past decades\textsuperscript{18,24–30}. However, no reaction pathway leading unambiguously from \(\alpha\)-pinene ozonolysis to HOM has been reported to date.

The conventional understanding of the initial steps of the \(\alpha\)-pinene + O\textsubscript{3} reaction is illustrated in Supplementary Fig. 1. Straight chain alkenes, like ethene, have an additional diradical pathway, which is not relevant to cyclic alkenes, such as \(\alpha\)-pinene (see Supplementary Methods). Briefly, the conventional mechanism involves the formation of four possible structural isomers of so-called Criegee intermediates (carbonyl oxides; CI), which then undergo rapid unimolecular reactions to form either vinyl hydroperoxides (VHP); in three of four cases), or a dioxirane. Further reactions of the VHP lead, via vinoxy radical intermediates, to four different peroxy radical (RO\textsubscript{2}) isomers. One of the RO\textsubscript{2} forming pathways is illustrated in detail in Fig. 1. This well-established reaction mechanism can unfortunately not explain the observed rapid SOA formation from \(\alpha\)-pinene + O\textsubscript{3}, as H-shifts in all of the four RO\textsubscript{2} isomers are hindered by the steric strain created by the intact cyclobutyl (CB) ring\textsuperscript{21}. Due to this strain, the barrier for the most favorable H-shift reaction is several kcal/mol higher than that of the corresponding H-shift in the cyclohexene + O\textsubscript{3} system (which lacks a CB ring).\textsuperscript{11,31}. The slow H-shift rates limit autoxidation, and therefore the rate of VOC to HOM conversion. Kurtén et al. considered an isomerization reaction available to the vinoxy intermediate that leads to a ring broken (RB) product (shown in Fig. 2), but found that it does not compete with O\textsubscript{2} addition under NTP conditions\textsuperscript{31}.

In this work, we show that excess energy from the initial ozonolysis of \(\alpha\)-pinene can activate otherwise inaccessable reaction pathways that lead to novel first-generation RO\textsubscript{2} without steric strain. Specifically, we model the effect of excess energy on the isomerization pathways available to one of the vinoxy intermediate isomers (see Fig. 2). Another ring-breaking isomerization reaction available to some CI isomers is also studied using multireference methods, as previously used computational methods have proved unreliable for describing this channel. Master equation calculations are carried out to estimate the fraction of RB products formed as a function of temperature and pressure.

**Fig. 1 Ozonolysis reaction of \(\alpha\)-pinene.** The addition of ozone to the double bond creates a primary ozonide (POZ). This breaks apart into a Criegee intermediate (CI; one out of four shown here). The CI can undergo a 1,4 H-shift, forming a vinyl hydroperoxide (VHP). The VHP will rapidly lose an OH radical and form a vinoxy radical, which then adds an O\textsubscript{2} to form a peroxy radical with an intact cyclobutyl ring (CB-RO\textsubscript{2}). Black dots indicate radical centers.

**Fig. 2 Ring-breaking isomerization reactions of the vinoxy radical shown in Fig. 1.** These reactions lead to alkyl radicals RB1 and RB2. Solid black circles indicate the atoms with radical centers. Color: carbon = gray, oxygen = red, hydrogen = white.
Finally, flow-tube experiments of α-pinene ozonolysis coupled to a nitrate-based chemical ionization mass spectrometer (nitrate-CIMS) are conducted to confirm that the formation of HOM does indeed occur at sub-second timescales.

### Results

The quantum chemically calculated reaction stationary points (minima and saddle points along the potential energy surface = PES) of the studied pathway of α-pinene ozonolysis are shown in Fig. 3. The initial ozone addition to α-pinene has a barrier of 6.6 kcal/mol. The overall exothermicity of the vinoxy formation is 81.1 kcal/mol, which is partitioned into the vinoxy and the spectator component OH. All unimolecular transition states leading to its formation are below the reactants in energy. The isomerization of the vinoxy radical to RB1 and RB2 have barriers corresponding to transition states TS4 and TS5, depicted with red and yellow traces in Fig. 3, respectively, and the products of these reactions will add O2 to form peroxy radicals RB1-RO2 and RB2-RO2, respectively. These two peroxy radicals were included in the master equation simulation because the reverse barriers going from the ring broken RB1 and RB2 to the ring intact vinoxy were lower than the barriers for their formation, and it was important to account for this reforming of the ring to accurately simulate the fraction of the RB RO2 produced. The direct ring-breaking isomerization of the CI to CI_RB in Fig. 3 was found to be endothermic by 29 kcal/mol, and has a barrier (TS6 in Fig. 3) of 44.1 kcal/mol (both relative to the energy of the CI). Optimized geometries along the CI ring-breaking isomerization channel and details of the method used are provided in Supplementary Methods.

The fractional populations of the products CB-RO2 and RB1-RO2 as a function of the precursor α-pinene concentration when 50% of the reaction exothermicity is partitioned into the density of states of the vinoxy (and 50% into the spectator component OH; details are provided in the following discussion section and in Supplementary Note 1) are shown in Fig. 4. The fractional populations of the products when the reaction exothermicity is unequally partitioned between the vinoxy and the OH, as well as other sensitivity tests indicating that the qualitative results are robust with respect to the likely error margins of the computational methods, are provided in Supplementary Notes 1 and 2.

### Discussion

Ideally, trajectory calculations are needed to accurately predict the amount of the available excess energy distributed to the rotovibrational modes of the vinoxy and the OH following the decomposition of the VHP intermediate. Since these are computationally too expensive to carry out at a sufficiently high level of theory, we instead controlled the fraction of the excess energy distributed to the vinoxy by introducing a parameter m (between 0 and 1) to be applied to the density of states of the vinoxy during the master equation simulation (see Supplementary Note 1). This procedure has been followed previously by Shannon et al. for a similar study on the fate of activated bimolecular products—the significantly exothermic glyoxal + OH reaction32. Due to the high barrier involved, the isomerization of the CI to ring broken CI_RB does not occur. However, a significant fraction of RB products produced via the vinoxy channel was observed. The vinoxy preferentially isomerizes to RB1 instead of RB2 because of the relatively lower barrier for the former. The product fraction of RB1-RO2 reached a maximum of ~82% for m = 0.45 and remained unchanged for higher m values. However, for 0.05 ≤ m ≤ 0.4, the RB1-RO2 fraction was reduced to between 33 and 81%, with a reciprocal increase in CB-RO2. For m = 0, only 12% of RB1-RO2 was observed, which is expected as the density of states of the vinoxy is replaced by a single classical harmonic oscillator in this extreme case. Including the hindrance potentials for the internal rotations for the intermediates and TSs along the PES (excluding the TS6 and CI_RB as this channel was found to be unimportant) in the simulation increased the RB1-RO2 fraction to ~89% (see Supplementary Note 2), indicating that the effect is small, likely due to the very large number of vibrational modes of the intermediates and products along the PES. Assuming that the four Criegee-forming channels of α-pinene + O3 have roughly equal yields, the 89% yield of RB1-RO2 from the single channel studied here translates into a total yield of RB products of about 22% of RB1-RO2 for the overall α-pinene ozonolysis reaction. It should be noted that the ~11% production of CB-RO2, which is formed from the thermalized fraction of the intermediates along the PES, is in qualitative, and very nearly quantitative agreement with the experimentally observed yield of 15% (±7%) of stabilized CI in α-pinene ozonolysis33.

The unimolecular H-shift pathways available to CB-RO2 are very slow31. In contrast, RB1-RO2 contains a double bond, and can consequently form an endoperoxide. Based on a comparison to similar reactions in the related α-pinene + OH system, this reaction likely has a high rate coefficient (around or above 1 s⁻¹)34. RB1-RO2 could also undergo an aldehydic H-abstraction, but this was found to be too slow to be competitive with the endoperoxide reaction (details in Supplementary Note 5). The endoperoxide reaction leads to a radical center on the adjacent carbon, which
which subsequently adds an O₂ to form a six-oxygen containing peroxy radical. This molecule can form a six-member endoperoxide via the transition state TS-endo, added D₂O, as inferred from earlier experiments of α-pinene ozonolysis that contains O₂.

The presence of an endoperoxide group in C₁₀H₁₅O₈ is supported by earlier experiments of α-pinene ozonolysis with an added D₂O flow. The H-to-D exchange in the observed mass spectra indicates the number of exchangeable H-atoms (in practice, –OH or –OOH groups) in the molecule. C₁₀H₁₅O₈ was found to undergo only a single H-to-D exchange, indicating only one H-shift reaction, thus necessitating other propagation pathways, likely endoperoxide formation. This is a strong experimental indicator that a fraction of the initial RO₂ following the aldehydic H-shift leads to the peroxy radical C₁₀H₁₅O₈. Thus, starting from RB₁-RO₂, one endoperoxide formation step and one aldehydic H-shift step, both rapid, can quickly form an eight-oxygen containing HOM RO₂. The steps are shown in Fig. 5.

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![Image](https://example.com/image.png)

**Fig. 5 Autodissociation steps available to ring-broken RB₁-RO₂.** The peroxy radical can form a six-member endoperoxide via the transition state TS-endo, which subsequently adds an O₂ to form a six-oxygen containing peroxy radical O₆-RO₂. This molecule can undergo a fast 1,4 aldehydic H-shift to form O₆-hydroperoxide via the transition state TS-1,4 H-shift, which subsequently adds an O₂ to form an eight-oxygen containing peroxy radical O₈-RO₂.
simulations. Test calculations were run with the more ambiently relevant \([O_3] = 1 \times 10^{12}\) molecules cm\(^{-3}\), and the ratio between CB-RO\(_2\) and RB1-RO\(_2\) fraction populations at the end of the simulation time was near identical to those at the higher \([O_3]\) values. This makes sense since, apart from the initial association reaction, the rest of the ozonolysis steps until the formation of the vinoxy radical are unimolecular. While the formation of the POZ does indeed depend on the initial ozone concentration, the remaining steps do not, and their rates remain the same for the different \([O_3]\) values. Giving a high initial ozone concentration thus allowed us to simulate the interplay between product fractions as a function of time, while keeping the simulation time (and therefore the computation time) feasible. See Supplementary Methods for more details.

**Chemical ionization time-of-flight mass spectrometry.** A nitrate-based high-resolution time-of-flight chemical ionization mass spectrometer (nitrate-CIMS) was used to detect the products of \(\alpha\)-pinene ozonolysis. \(\alpha\)-pinene was bubbled from a liquid reservoir using an \(\text{N}_2\) flow, and ozone was generated by flowing synthetic air through an ozone generator fitted with a 184.9-nm (Hg PenRay) lamp. The two precursors were allowed to react in the presence of \(\text{O}_2\) in a quartz tube reactor and the products were subsequently detected. The experiments were conducted under atmospheric conditions. The inlet flow rate was set to either 20 or 301 per minute to achieve rapid sub-second reaction times, which was made possible by the MION36 used in this work.

**Data availability**
Source data are provided with this paper. The ab initio output files (.log and .out) and the MESMER files that support the findings of the manuscript are provided at: https://doi.org/10.5281/zenodo.4297276. The mass spectrometry data are available upon request from the corresponding authors. Source data are provided with this paper.

**Code availability**
The scripts used to produce the plots are provided with this paper.

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**Author contributions**

M.P.R., T.K., M.E., and J.T. devised the experimental setup, S.I., S.B., and M.P.R. carried out the experiments, and S.I. analyzed the data. S.I. wrote the paper with contributions from all co-authors.

**Competing interests**

The authors declare no competing interests.

**Additional information**

**Supplementary information**

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