

Alkoxy Radical Bond Scissions Explain the Anomalously Low Secondary Organic Aerosol and Organonitrate Yields From α -Pinene + NO_3

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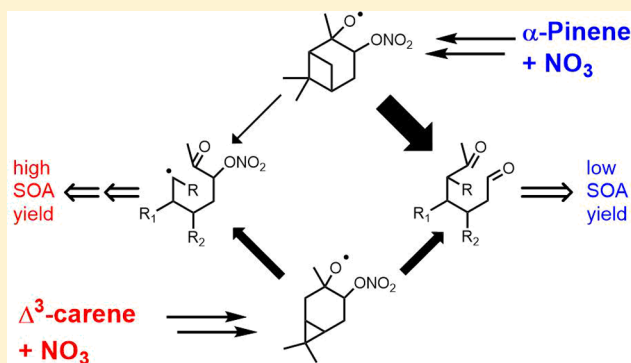
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Supporting Information

ABSTRACT: Oxidation of monoterpenes ($\text{C}_{10}\text{H}_{16}$) by nitrate radicals (NO_3) constitutes an important source of atmospheric secondary organic aerosol (SOA) and organonitrates. However, knowledge of the mechanisms of their formation is incomplete and differences in yields between similar monoterpenes are poorly understood. In particular, yields of SOA and organonitrates from α -pinene + NO_3 are low, while those from Δ^3 -carene + NO_3 are high. Using computational methods, we suggest that bond scission of the nitrooxy alkoxy radicals from Δ^3 -carene lead to the formation of reactive keto-nitrooxy-alkyl radicals, which retain the nitrooxy moiety and can undergo further reactions to form SOA. By contrast, bond scissions of the nitrooxy alkoxy radicals from α -pinene lead almost exclusively to the formation of the relatively unreactive and volatile product pinonaldehyde ($\text{C}_{10}\text{H}_{16}\text{O}_2$), thereby limiting organonitrate and SOA formation. This hypothesis is supported by laboratory experiments that quantify products of the reaction of α -pinene + NO_3 under atmospherically relevant conditions.



Plants emit enormous quantities of highly reactive biogenic alkenes to the atmosphere. Monoterpenes ($\text{C}_{10}\text{H}_{16}$),¹ contribute approximately 11% of these emissions, with α -pinene as the dominant (35%) contributor.² The subsequent oxidation of these compounds in the atmosphere impacts both aerosol and ozone levels.

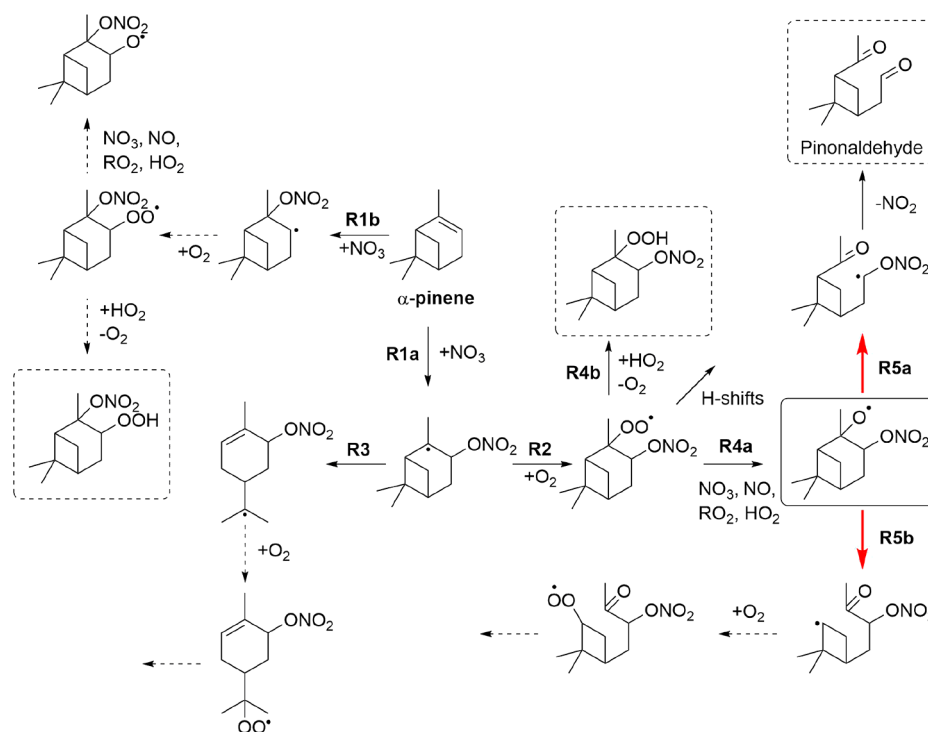
Atmospheric aerosol particles play a key role in regulating our climate,³ and are responsible for most air pollution-related mortality.⁴ A large fraction of these particles consists of secondary organic aerosol (SOA) material formed by oxidation of large organic molecules such as monoterpenes. It is this chemistry, for example, that is responsible for the haze that makes the US Smoky Mountains “smoky”.⁵ Despite its importance, the mechanisms for SOA formation from biogenically produced alkenes are poorly understood.

Ozone is a significant component of photochemical smog and is associated with pulmonary impacts in humans as well as being an antagonist for plants. Formation of ozone occurs in the troposphere via the oxidation of organic hydrocarbons in the presence of nitric oxide (NO). The highly reactive monoterpenes can contribute significantly to this process. However, oxidation of these biogenic compounds can also reduce ozone formation via production of organonitrates that serves to reduce the level of rapidly interconverting nitrogen oxide free radicals (NO_x) here defined as the sum of NO , NO_2 ,

Received: April 28, 2017

Accepted: June 6, 2017

Published: June 6, 2017

Scheme 1. Reaction Pathways for the α -Pinene + NO_3 System^a

^aReactions studied here are labeled, while likely subsequent reactions not investigated in this study are indicated by dashed arrows. To evaluate the calculated branching ratios, the yields of the hydroperoxy nitrates and pinonaldehyde (shown in dashed boxes) are quantified experimentally. The key β -nitrooxy-alkoxy radical is shown in the solid box with the bifurcating reactions highlighted with red arrows.

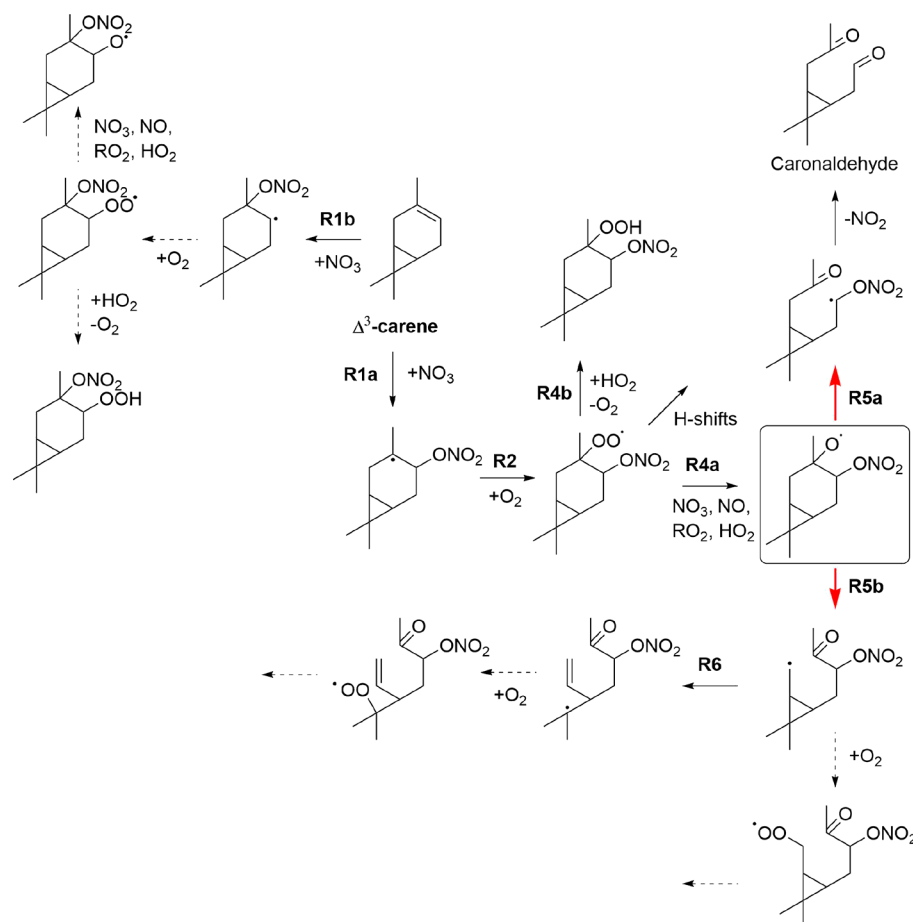
and NO_3 . The impact on NO_x and thus ozone formation, therefore depends on the yield of the organonitrates and whether during their subsequent degradation the NO_x is recycled.⁶

Recent global modeling studies of organic aerosol^{7–9} suggest that a large contribution to SOA production arises from the oxidation of biogenic organic compounds by the nitrate radical (NO_3). This contribution is potentially larger than that following their oxidation by ozone or OH .¹⁰ Though typically thought of as a nighttime process, NO_3 oxidation has recently been shown to play a role also during the day.^{11,12} In addition, field analyses of organonitrate diurnal variation^{13–16} illustrate that NO_3 oxidation chemistry is a major pathway for the production of organonitrates.¹⁷ Depending on their subsequent photochemistry, these nitrates constitute a large NO_x reservoir or sink. Improved understanding of the mechanistic basis for the differing yields of SOA and organonitrates from oxidation of biogenic compounds following their oxidation by NO_3 is thus essential.

SOA levels are typically underestimated by current atmospheric chemistry models.^{18,19} Recent research^{20–22} indicates that peroxy radical (RO_2) hydrogen shift rearrangements (H-shifts)—particularly important in monoterpene chemistry—may be responsible for part of the underestimate. According to these studies, sequential RO_2 H-shifts and O_2 addition reactions (often termed autoxidation) rapidly lead to highly oxidized multifunctional products (HOMs) that end up in the aerosol phase via equilibrium partitioning. The prerequisite for atmospheric autoxidation is that the initial oxidant-hydrocarbon reaction leads to an RO_2 radical that can access C–H bonds weak enough to allow H-shifts to compete with bimolecular reactions.^{23–25}

Much research on monoterpene oxidation in the context of SOA and organonitrate formation has focused on α -pinene, as it accounts for about 35% of total global monoterpene emissions.^{2,26} The organonitrate and SOA yield varies with both the monoterpene and the oxidant. These variations are reasonably well understood for OH - and O_3 -initiated oxidation. For example, exocyclic alkenes often have lower HOM or SOA yields from ozonolysis than analogous endocyclic alkenes.²⁷ The variations in yields in the NO_3 -initiated oxidation of different monoterpenes are less well understood. For example, the $\text{NO}_3 + \alpha$ -pinene reaction has a low organonitrate yield and leads to little or no SOA formation.^{28–31} By contrast, the yields of both organonitrates and SOA from NO_3 -initiated oxidation of every other monoterpene studied are considerably higher.¹⁰ For example, both the organonitrate and SOA yields from Δ^3 -carene have been measured to be larger than 50%, despite the similar structures of Δ^3 -carene and α -pinene (see Schemes 1 and 2).²⁸ Previous laboratory studies of the reaction of α -pinene + NO_3 have found high yields of carbonyls and low yields of organonitrates.²⁹ The opposite has been shown to apply to the Δ^3 -carene + NO_3 reaction.^{10,28}

Here we show that the key to understanding the disparate organonitrate and SOA yields in these very similar monoterpenes arises from a bifurcation in the fragmentation of the β -nitrooxy-alkoxy radicals (nitrooxy and alkoxy groups on neighboring carbon atoms) produced following addition of NO_3 . In the case of α -pinene, scission of the bond between these groups releases NO_2 and yields the highly volatile pinonaldehyde. In Δ^3 -carene, by contrast, this bond is more likely to remain intact, yielding a nitrooxy-peroxy radical that is able to undergo further reactions. We use computational methods (see section S1 in the Supporting Information (SI) for

Scheme 2. Reaction Pathways for the Δ^3 -Carene + NO_3 System^a

^aReactions studied here are labeled, while likely subsequent reactions not investigated in this study are indicated by dashed arrows. The reaction equivalent to R3 in Scheme 1 is not possible for Δ^3 -carene. The key β -nitrooxy-alkoxy radical is shown in the solid box with the bifurcating reactions highlighted with red arrows.

full details), to investigate the reason for the vast difference in SOA, nitrate, and carbonyl yields between the NO_3 -initiated oxidation of α -pinene and Δ^3 -carene (the “+” enantiomers). We test the hypotheses arising from these computations with experimental data on the α -pinene + NO_3 reaction under simulated atmospheric conditions.

The reaction pathways for α -pinene + NO_3 and Δ^3 -carene + NO_3 are illustrated in Schemes 1 and 2, respectively. The most likely first step of both reactions is the addition of nitrate to the double bond to form a nitrooxy-alkyl radical, with the major addition pathway forming the tertiary alkyl radical with a greater degree of substitution (reaction R1a in Schemes 1 and 2). The branching ratios for the two addition pathways in the α -pinene + NO_3 system have been recommended to be 0.65 and 0.35.^{32,33} See section S2 in the SI for thermodynamics of the addition reactions, and section S3 for a discussion of key reactions along the minor addition pathway (R1b).

Under atmospheric conditions, alkyl radicals will usually undergo O_2 addition reactions (reaction R2 in Schemes 1 and 2), to form peroxy radicals, at pseudounimolecular rates on the order of 10^7 s^{-1} .³⁴ Each nitrooxy-peroxy radical has four isomers, as illustrated in Figure 1 for α -pinene, and in Figure S1 for Δ^3 -carene. For both monoterpenes, the most thermodynamically favorable NO_3 and O_2 addition channels are those forming the S,S isomer.

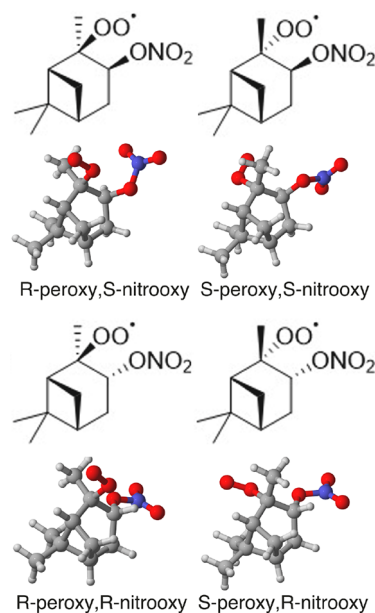


Figure 1. Structures of the four different isomers of the nitrooxy-peroxy radical formed in the oxidation of α -pinene by NO_3 , assuming initial radical addition to the secondary carbon atom. Color coding: gray = C, white = H, red = O, blue = N.

Table 1. Barriers (Zero-Point Corrected Transition State - Reactant Electronic Energy Differences) and Multi-Conformer Transition State Theory (MC-TST) Reaction Rate Coefficients (298.15 K) Computed at the ω B97X-D/aug-cc-pVTZ Level for the Bond Scission Reactions R5a and R5b of the Nitrooxy-Alkoxy Radicals Formed in the α -Pinene + NO₃ and Δ^3 -Carene + NO₃ Systems^a

alkoxy radical isomer	barrier for R5a ^b (kcal/mol)	rate coefficient for R5a (s ⁻¹)	barrier for R5b ^c (kcal/mol)	rate coefficient for R5b (s ⁻¹)
α -pinene, R-alkoxy, S-nitrooxy	4.8	1.5×10^9	9.4	3.6×10^6
α -pinene, S-alkoxy, S-nitrooxy	8.6	2.2×10^6	10.5	1.0×10^5
α -pinene, R-alkoxy, R-nitrooxy	6.1	1.7×10^8	10.6	1.3×10^5
α -pinene, S-alkoxy, R-nitrooxy	6.7	7.3×10^7	10.4	3.7×10^5
Δ^3 -carene, R-alkoxy, S-nitrooxy	9.2	1.7×10^6	8.3	8.4×10^6
Δ^3 -carene, S-alkoxy, S-nitrooxy	8.6	2.6×10^6	8.1	9.0×10^6
Δ^3 -carene, R-alkoxy, R-nitrooxy	8.4	8.2×10^6	7.4	2.7×10^7
Δ^3 -carene, S-alkoxy, R-nitrooxy	8.4	3.3×10^6	8.4	6.2×10^6

^aSee Figure 2 for lowest-energy transition state structures for the lowest-energy S,S isomers. ^bC–C(ONO₂) bond scission. ^cC–C(H) bond scission in α -pinene and C–C(H₂) bond scission in Δ^3 -carene.

For the hydroxyl-alkyl radical formed by OH addition to α -pinene at the secondary carbon, a ring-breaking bond scission pathway leading to a hydroxyl-alkenyl radical has also been proposed.^{35,36} This bond scission has a barrier of about 12 kcal/mol, making its thermal rate uncompetitive with O₂ addition, but excess energy from the OH addition (around 30 kcal/mol) may facilitate the reaction.³⁵ We have identified an analogous reaction in the α -pinene + NO₃ system (reaction R3 in Scheme 1). Due to the slightly higher barrier (around 14 kcal/mol), and the significantly lower exothermicity of the NO₃ addition reaction (around 20 kcal/mol), our modeling (SI, section S5) indicates that this reaction is not competitive with O₂ addition. A corresponding channel does not exist for the Δ^3 -carene + NO₃ adduct. Nitrooxy-alkyl radical bond scissions can thus not explain the differences in SOA, nitrate, or carbonyl yields following addition of NO₃ to either α -pinene or Δ^3 -carene.

We considered possible H-shift reactions of the first-generation nitrooxy-peroxy radicals. The constraints imposed by the two rings in each system prevent the OO group from reaching most hydrogens, as can be seen from Figure 1. The remaining H atoms are all difficult to abstract due to steric strain in the transition states and/or high C–H bond strengths. We investigated all accessible H-shifts for each peroxy radical (see section S6 in the SI for details). All calculated H-shift rate coefficients were below 10^{-4} s⁻¹ for both monoterpenes. As the computational method employed likely overestimates the H-shift rates,³⁷ the peroxy radicals thus almost certainly have lifetimes long enough to undergo bimolecular reactions, which occur on a time scale of between 0.01 and 100 s under most atmospheric conditions.³⁸

In the atmosphere, the peroxy radicals produced at night from NO₃ chemistry will typically react with HO₂ or other RO₂ radicals,³⁹ and during daytime the reaction with NO will contribute significantly. Understanding the products of this nitrooxy-peroxy radical chemistry is important, as it will determine the subsequent pathways. Alkoxy radicals will be produced by reactions of RO₂ with NO or other radicals (R4a), while hydroperoxides are typically major products of the reaction with HO₂ (R4b).

Due to the large radical concentrations in most laboratory investigations of the oxidation of hydrocarbons by NO₃, the peroxy radicals typically react with NO₃ or themselves, leading primarily to the production of alkoxy radicals.³⁸ It is thus unclear to what extent these previous investigations are relevant for the atmosphere, where HO₂ radicals play such an important

role. An α -pinene + NO₃ experiment conducted as part of the FIXCIT chamber study⁴⁰ and analyzed here for the first time (see section S11) provides evidence for large production of RO from the reaction of HO₂ with the RO₂ radicals produced via α -pinene + NO₃. We find that the hydroperoxy nitrate yield is only ~30%—much lower than, for example, in the equivalent chemistry of isoprene.⁴¹ The carbon budget is balanced by formation of pinonaldehyde (~70%), with essentially no SOA being observed (molar yield of less than 1%). Together, these yields suggest that the majority of the atmospheric bimolecular chemistry following addition of the nitrate radical to α -pinene leads to the formation of the nitrooxy-alkoxy radicals even under atmospherically relevant HO₂ dominated conditions (R4a). To our knowledge, however, there is no equivalent HO₂-dominated laboratory study for Δ^3 -carene + NO₃.

By analogy with the OH-initiated oxidation of α -pinene,⁴² perhaps it is not too surprising that the reaction of the tertiary peroxy radicals with HO₂ has such a large yield of alkoxy radicals (R4a). The computed Gibbs free energy (at 298.15 K and 1 atm reference pressure) for the RO₂ + HO₂ → RO + OH + O₂ reaction (SI section S7) varies between –1.4 kcal/mol and –5.2 kcal/mol for the four NO₃-RO₂ isomers from the α -pinene + NO₃ reaction, and –2.3 kcal/mol and –6.4 kcal/mol for those from Δ^3 -carene + NO₃. The alkoxy-forming pathway is thus thermodynamically favorable for all RO₂ radicals studied here.

A recent review of organic peroxy radical chemistry noted that, while chain-terminating formation of hydroperoxides (ROOH) is dominant for simple alkylperoxy radicals, greater substitution favors alkoxy-forming channels.³⁸ Consistent with this suggestion, it would be expected that the hydroperoxide yield from the less substituted peroxy radical from R1b is higher than that from R1a. We note that the measured yield of hydroperoxy nitrate in the α -pinene + NO₃ system is very close to the estimate of the branching ratio (R1a vs R1b), suggesting that perhaps R1b is the route to most of the observed hydroperoxide.

The retention of the nitrate group and the high yields of SOA produced following formation of the alkoxy radical in Δ^3 -carene + NO₃ system compared to α -pinene results from differences in the alkoxy radical scissions. Alkoxy radicals located on ring systems are known to undergo rapid ring-breaking reactions (C–C bond scissions).^{23,35,36,43} Each alkoxy radical studied here has two possible bond scission pathways that lead to ring breaking. Breaking the bond to the nitrooxy carbon (β -nitrooxy-alkoxy scission, R5a in Schemes 1 and 2)

leads to the formation of keto aldehydes (pinonaldehyde for α -pinene and caronaldehyde for Δ^3 -carene) and recycling of NO_2 .⁴⁴ The alternative scission (R5b) leads to a keto-nitrooxy-alkyl radical. A pathway similar to R5a but involving O_2 addition and subsequent prompt HO_2 loss exists in the OH oxidation system.^{35,36}

The barriers and estimated rate coefficients for reactions R5a and R5b are given in Table 1, with the lowest-energy transition states for the thermodynamically most favorable isomers illustrated in Figure 2. See SI section S8 for other isomers,

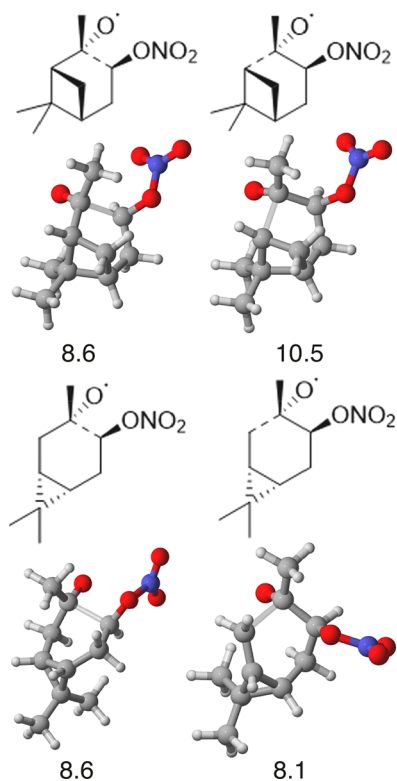


Figure 2. Transition states for the bond scission reactions of the *S,S* isomers of the nitrooxy-alkoxy radicals formed in the oxidation of α -pinene (top) and Δ^3 -carene (bottom) by NO_3 , assuming initial radical addition to the secondary carbon atom. The reaction barriers (zero-point corrected $\omega\text{B97X-D/aug-cc-pVTZ}$ electronic energy differences between the lowest-energy transition states and reactants) in kcal/mol are given under each structure. See Table 1 for details. Left column: transition states for reaction R5a. Right column: transition states for reaction R5b. Color coding as in Figure 1.

and section S9 for data on the α -pinene + OH and Δ^3 -carene + OH systems. Alkoxy bond scission pathways typically compete with H-shift reactions.^{45,46} For the nitrooxy-alkoxy radicals studied here, steric strain prevents most of these H-shifts from occurring. However, in the *S*-alkoxy isomers, the hydrogens on one of the methyl groups attached to the C_3/C_4 ring are accessible. Alkoxy H-shifts from primary hydrogen atoms typically have rate coefficients of around 10^4 – 10^6 s^{-1} at room temperature,^{45,46} which suggests that these are not dominating. If these alkoxy H-shifts are faster than suggested they could be competitive for the *S,S* isomer leading to additional minor products.

The α -pinene + NO_3 system shows a strong preference for $\text{C}-\text{C}(\text{ONO}_2)$ scission (R5a), with differences in barrier heights between the two scission pathways varying between 1.9 and 4.6 kcal/mol, depending on the isomer, which corresponds to a

difference of at least a factor of 20 in the reaction rates. By contrast, the relative barriers for the two pathways are within 1 kcal/mol of each other for the Δ^3 -carene + NO_3 system, with a slight preference for $\text{C}-\text{C}(\text{H}_2)$ scission (R5b). This leads to a significantly different product distribution for the two monoterpenes. Our prediction for α -pinene + NO_3 is in qualitative agreement with the structure–activity relationship (SAR) of Vereecken and Peeters,⁴⁷ which also predicts a lower barrier for R5a compared to R5b. For Δ^3 -carene + NO_3 , naive application of the SAR would predict R5a to be faster than R5b, but this is likely due to the treatment of the complex substituent on the β -carbon atom of the product alkyl radical (γ to the original alkoxy carbon) as a simple alkyl group. For the OH oxidation systems (SI section S9) we find, as also predicted by the SAR,⁴⁷ a preference for $\text{C}-\text{C}(\text{OH})$ scission in both α -pinene and Δ^3 -carene systems; however, more pronounced in the α -pinene + OH system. Our theoretical results on α -pinene + OH agree with previous investigations.^{35,36}

Because of the large difference between the bond scission rates, we find, consistent with laboratory data, that the nitrooxy-alkoxy radicals formed in the α -pinene + NO_3 system will almost exclusively form pinonaldehyde. By contrast, both the formation pathways of caronaldehyde and the keto-nitrooxy-alkyl radical are accessible in high yield in the Δ^3 -carene + NO_3 system. The keto-nitrooxy-alkyl radical can undergo further reactions to form HOM that can partition to SOA.

Subtle differences in the stabilities of the radicals formed by the $\text{C}-\text{C}$ scission reactions determine the fate of the nitrooxy alkoxy radicals formed in the NO_3 -initiated oxidation of monoterpenes. In the α -pinene case, the unfavorable formation of a radical center on the C_4 ring^{48–50} in reaction R5b drives the NO_2 loss and pinonaldehyde formation (R5a). In the Δ^3 -carene case, our results indicate that both scission pathways are competitive, likely due to the added stabilization of the primary alkyl radical formed in reaction R5b by the cyclopropyl derived substituent. Of the other atmospherically relevant monoterpenes² with cyclic structures, β -pinene and sabinene contain exocyclic double bonds, and their NO_3 oxidation will likely lead predominantly to nitrooxy alkoxy radicals where the nitrooxy group is not located on the ring. Their scission reactions will thus lead almost exclusively to products retaining the nitrooxy group.⁴⁷ Limonene contains both an endo- and an exocyclic double bond. NO_3 attack on the former would lead to nitrooxy alkoxy radicals similar to those formed in the Δ^3 -carene + NO_3 reaction. However, due to the lack of the extra stabilization of the primary alkyl radical formed in the analogue of reaction R5b, the branching ratio of the two bond scission pathways may be more weighted toward the NO_2 loss pathway. In comparison, the observed organic nitrate molar yield for limonene was 30%,⁵¹ compared to 70% for Δ^3 -carene.^{28,29}

Analogous bifurcation in β nitrooxy-alkoxy radical scission occurs in the oxidation of the two major organonitrates produced in the oxidation of isoprene by OH in the presence of NO. In this system, experiments show that decomposition of the nitrooxy-alkoxy radical leads to minimal NO_x recycling for a secondary nitrooxy group.⁵² We present calculations (SI section S12) that show, however, that the NO_x recycling is likely much higher for the structurally similar tertiary nitrooxy-alkoxy radical. Again, this illustrates that the competition between β scission of the nitrooxy-alkoxy radical and alternative fragmentation pathways that retain this bond is sensitive to subtle structural differences.

As established previously for α -pinene + OH,^{23,35,36} we predict that the hydroxy alkoxy radicals formed in the α -pinene + OH and Δ^3 -carene + OH systems will almost exclusively form pinonaldehyde and caronaldehyde, respectively (SI section S9). The reported SOA formation in these systems therefore likely involves either further OH reactions of the aldehydes with oxidation products undergoing for example oligomerization, or competing reaction steps earlier in the oxidation mechanism, such as alkyl radical bond scission, or H-abstraction by OH rather than addition.⁵³ Since alkyl radical bond scission is not available to the Δ^3 -carene + OH system, it could therefore be expected to have a smaller SOA yield than α -pinene + OH. This is consistent with the generally higher SOA yields reported for α -pinene + OH (e.g., 24–28% for 60–70 $\mu\text{g m}^{-3}$ of total OA)⁵⁴ compared to those for Δ^3 -carene + OH (e.g., 14–16% for 55–65 $\mu\text{g m}^{-3}$ of total OA).⁵⁵

The observed²⁸ high SOA and nitrate yields, and low keto aldehyde (caronaldehyde) yields, from NO₃-initiated Δ^3 -carene oxidation are likely explained by further reactions of the keto-nitrooxy-alkyl radical formed by reaction R5b. This radical may add O₂ either directly, or after a second ring-breaking reaction forming a more highly substituted alkyl radical (reaction R6 in Scheme 2). We find a barrier of around 6 kcal/mol for R6 (SI, section S10), implying that R6 and direct O₂ addition may both be competitive. Due to their greater flexibility, both keto-nitrooxy-peroxy radicals may undergo H-shifts much faster than the first-generation nitrooxy-peroxy radicals. Alternatively, bimolecular reactions could form reactive keto-nitrooxy-alkoxy radicals—in both cases ultimately leading to more oxidized and less volatile organonitrate products.

Our results illustrate how minor structural differences between monoterpenes can lead to very different reaction mechanisms, product distributions, and atmospheric impacts. Extrapolating or generalizing measurement results from a single terpene to all monoterpenes can thus lead to serious errors in predicted SOA and organonitrate yields in model simulations, especially if the terpene used is α -pinene, as its reaction mechanism is likely unique among the monoterpenes.

METHODS

Computational. To calculate reaction rates, we applied a modified version of our recently published approach using both multiconformer transition state theory (MC-TST) and the lowest energy conformer TST (LC-TST) methods.³⁷ This involves an initial systematic conformational search using the MMFF force field⁵⁶ in the Spartan'14 program,⁵⁷ followed by B3LYP/6-31+G(d) optimizations,^{58,59} and finally ω B97X-D/aug-cc-pVTZ^{60–62} optimizations using Gaussian 09⁶³ and adding Eckart tunneling⁶⁴ corrections. We investigated all conformers and calculated LC-TST rates for most reactions, while for the central reactions (R5a and R5b in Schemes 1 and 2) we calculated MC-TST rates. ROHF-ROCCSD(T)-F12a/VDZ-F12 single-point calculations⁶⁵ on reaction R3 were performed using Molpro 2012.1.⁶⁶ Reaction dynamic modeling for R3 was performed using the MESMER program (see SI section S5).⁶⁷ Details on the computational approach are given in SI section S1.

Experimental. In the FIXCIT chamber experiment,⁴⁰ α -pinene was added to a darkened 24 m³ chamber containing NO₂, O₃ (and consequently NO₃ and N₂O₅), and H₂CO (and consequently HO₂). The chamber was first filled with NO₃ and HO₂ radicals produced via addition of \sim 75 ppb O₃, \sim 150 ppb NO₂, and \sim 8 ppm formaldehyde, into which a volume of α -

pinene was gradually injected equivalent to \sim 35 ppb. The consumption of α -pinene and production of pinonaldehyde was monitored by a switchable reagent ion high-resolution time-of-flight mass spectrometer (SRI-ToF-MS) using H₃O⁺ reagent. The hydroperoxynitrate production was monitored by a time-of-flight chemical ionization mass spectrometer (ToF-CIMS) using CF₃O⁻ reagent, and the organic aerosol production was monitored by an aerosol mass spectrometer (AMS). After 3 h of reaction, \sim 20 ppb of α -pinene had been depleted and \sim 4 ppb of hydroperoxynitrate formed. The branching ratio for the NO₃-RO₂ + HO₂ \rightarrow NO₃-ROOH + O₂ channel was 30% (15–45%), which includes a correction for the fraction of α -pinene reaction that reacted with O₃ (see SI section S11 for more experimental details and description of uncertainties). Approximately 17 ppb of pinonaldehyde is produced during the same period. Minimal SOA production is observed (\sim 1.5 $\mu\text{g m}^{-3}$ organic aerosol, unseeded).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.7b01038.

Full computational details; thermodynamics of the initial radical and O₂ addition reactions; data on selected further reactions along the minor NO₃ addition pathway to α -pinene; pictures of Δ^3 -carene + NO₃ nitrooxy-peroxy radical isomers; reaction kinetic modeling of the alkyl radical bond scission reaction in the α -pinene - NO₃ adduct; H-shift rates for nitrooxy-peroxy radicals formed in the nitrate oxidation of α -pinene and Δ^3 -carene; thermodynamics of nitrooxy-alkoxy formation from reaction of nitrooxy-peroxy radicals with HO₂; pictures of transition states for all isomers for the alkoxy radical bond scission reactions in the α -pinene + NO₃ and Δ^3 -carene + NO₃ systems; data on alkoxy radical bond scission reactions in the α -pinene + OH and Δ^3 -carene + OH systems; transition states and energetics for reaction R6 (bond scission in the keto-nitrooxy-alkyl radical formed in the Δ^3 -carene + NO₃ system by reaction R5b); detailed description of experimental instrumentation; alkoxy bond breaking reactions in isoprene-derived nitrooxy-alkoxy radicals. (PDF)

Gaussian.log files and Molpro.out files (ZIP)

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The authors declare no competing financial interest.

ACKNOWLEDGMENTS

From the FIXCIT campaign, we thank Matthew Coggon and John Seinfeld for AMS data, Jeong-Hoo Park, Allen Goldstein, John Mak, and Alex Guenther for the PTR-MS data, John Crouse, Alex Teng and Kelvin Bates for the ToF-CIMS data and their work organizing and conducting the experiment. We also thank Alan Shusterman, Catherine Neshyba, Katie Stellmach, Rasmus V. Otkjær, Noora Hyttinen, Camilla Mia Tram, and Benjamin N. Frandsen for helpful discussions. T.K. thanks the Academy of Finland (266388) for funding and the CSC IT Center for Science in Espoo, Finland, for computing time. H.G.K. and K.H.M. thank the Center for Exploitation of Solar Energy, University of Copenhagen and the Danish Center for Scientific Computing for funding. POW thanks the NSF for funding (Grant No. CHE-1508526 and AGS-1240604). J.L.F. gratefully acknowledges sabbatical support from the U.S. Fulbright Scholar Program and research funding from the NOAA Climate Program Office's AC4 program (Grant No. NA13OAR4310070). The National Center for Atmospheric Research is sponsored by the National Science Foundation.

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