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Computational Investigation of $\text{RO}_2 + \text{HO}_2$ and $\text{RO}_2 + \text{RO}_2$ Reactions of Monoterpene Derived First-Generation Peroxy Radicals Leading to Radical Recycling

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Abstract

The oxidation of biogenically emitted volatile organic compounds (BVOC) plays an important role in the formation of secondary organic aerosols (SOA) in the atmosphere. Peroxy radicals (RO_2) are central intermediates in the BVOC oxidation process. Under

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clean (low- NO_x) conditions, the main bimolecular sink reactions for RO_2 are with the hydroperoxy radical (HO_2) and with other RO_2 radicals. Especially for small RO_2 , the $\text{RO}_2 + \text{HO}_2$ reaction mainly leads to closed-shell hydroperoxide products. However, there exist other known $\text{RO}_2 + \text{HO}_2$ and $\text{RO}_2 + \text{RO}_2$ reaction channels that can recycle radicals and oxidants in the atmosphere, potentially leading to lower-volatility products and enhancing SOA formation. In this work, we present a thermodynamic overview of two such reactions: **a)** $\text{RO}_2 + \text{HO}_2 \rightarrow \text{RO} + \text{OH} + \text{O}_2$ and **b)** $\text{R}'\text{O}_2 + \text{RO}_2 \rightarrow \text{R}'\text{O} + \text{RO} + \text{O}_2$ for selected monoterpene + oxidant derived peroxy radicals. The monoterpenes considered are α -pinene, β -pinene, limonene, trans- β -ocimene, and Δ^3 -carene. The oxidants considered are the hydroxyl radical (OH), the nitrate radical (NO_3), and ozone (O_3). The reaction Gibbs energies were calculated at the DLPNO-CCSD(T)/def2-QZVPP// ω B97X-D/aug-cc-pVTZ level of theory. All reactions studied here were found to be exergonic in terms of Gibbs energy. Based on a comparison with previous mechanistic studies, we predict that reaction **a** and reaction **b** are likely most important for first-generation peroxy radicals from O_3 oxidation (especially for β -pinene), while less so for most first-generation peroxy radicals from OH and NO_3 oxidation. This is because both reactions are comparatively more exergonic for the O_3 oxidized systems than their OH and NO_3 oxidized counterparts. Our results indicate that bimolecular reactions of certain complex RO_2 may contribute to an increase in radical and oxidant recycling under high HO_2 conditions in the atmosphere, which can potentially enhance SOA formation.

Introduction

Biogenically emitted volatile organic compounds (BVOCs) play a critical role in the formation and growth of atmospheric secondary organic aerosol particles (SOA).¹⁻⁴ Once they have grown to sufficient sizes (on the order of ~ 100 nm), aerosol particles can affect the Earth's climate both directly, by reflecting solar radiation, and indirectly, by serving as cloud condensation nuclei, and thus modifying cloud properties such as reflectivity and lifetime.⁵

Isoprene (C_5H_8) and monoterpenes, a class of VOCs with the chemical formula $C_{10}H_{16}$, are the most abundant BVOC emissions, accounting for about 69% and 11% of the total global BVOC emission, respectively.⁶ These molecules undergo gas-phase reactions with the atmospheric oxidants such as the hydroxyl radical (OH), the nitrate radical (NO_3) and ozone (O_3), forming peroxy radicals (RO_2). Unimolecular reaction pathways of peroxy radicals have recently been demonstrated to be important, especially for the formation of highly oxidized multifunctional organic compounds (HOM) through the process of autooxidation.^{4,7} HOMs can have very low volatilities, allowing them to condense and form particles very effectively. Other peroxy radical reaction pathways generally lead to less oxidized and more volatile products, which may nevertheless also contribute to the growth of particulate matter.

α -pinene, β -pinene, limonene, trans- β -ocimene, and Δ^3 -carene together account for close to 90% of the global monoterpene emissions.⁶ The reaction of monoterpenes with the atmospheric oxidants initiates the process that leads to the formation of a range of products, including the multi-functionalized HOMs. OH initiated oxidation of alkenes can involve either OH radical addition to one of the olefinic carbon atoms, or the abstraction of an aliphatic hydrogen atom. In both cases, the product is an alkyl radical. O_2 can rapidly add to alkyl radicals to form a peroxy radical RO_2 .⁸ For simple alkyl radicals, a pseudo-unimolecular rate of $\sim 10^7 s^{-1}$ is often assumed for the $O_2 + \text{alkyl}$ reaction when the O_2 partial pressure is approximately 0.2 atm.^{9,10} NO_3 oxidation also involves addition to one of the olefinic carbon atoms of the alkene (though, in some cases, hydrogen atom abstraction may compete^{11,12}), followed by the O_2 addition to the subsequent alkyl radical to form the RO_2 . The RO_2 contains an ONO_2 functionality, and closed-shell reaction products retaining this group are commonly called organonitrates. Organonitrates are important in the atmosphere as they can serve as a NO_x (where, $x=1,2$) reservoir.¹³ Ambient measurements have discovered that organonitrates make up a significant fraction of SOA.^{14,15}

Ozone oxidation produces peroxy radicals that are structurally different from the peroxy radicals formed following OH or NO₃ oxidation. There are multiple known channels for alkene + ozone reactions. For RO₂ formation, the main channel involves the formation and subsequent decomposition of a vinylhydroperoxide (VHP). Ozonolysis of alkenes (see Figure 2) is initiated by addition of O₃ across the double bond, forming a primary ozonide (POZ). The POZ then rapidly decomposes, forming a Criegee intermediate (CI; a carbonyl oxide) and a carbonyl group. In the case of endocyclic alkenes, such as α -pinene, limonene, and Δ^3 -carene, the CI and carbonyl groups remain within the same molecule. For exocyclic, or acyclic alkenes, such as β -pinene and trans- β -ocimene, POZ decomposition leads to fragmentation of the molecule. In the VHP channel, the CI forms a VHP following a 1,4 hydrogen shift (VHP formation may or may not be preceded by collisional stabilization of the CI¹⁶). The VHP quickly loses an OH, forming a vinoxy radical, which adds O₂ to form the first-generation RO₂.

Monoterpenes (and other alkene VOCs) are thus eventually converted to peroxy radicals by all the main atmospheric oxidants. A myriad of possible unimolecular and bimolecular reactions in the atmosphere determine the fate of these radicals. The chemistry of simpler RO₂ has been explored in detail previously (Orlando et al. 2012¹⁷ and references therein). Over regions with significant anthropogenic emissions, NO can react with RO₂ to produce alkoxy radicals (organonitrate formation is a competing, but generally minor, channel).¹⁷ This is a radical propagating channel, leading also to NO₂, which contributes to the formation of O₃ and ultimately OH (and HO₂).¹⁸ In more pristine conditions that are relatively unaffected by anthropogenic emissions, RO₂ are more likely to react with HO₂ or other RO₂, or undergo unimolecular reactions.

The RO₂ + HO₂ channel becomes relevant in low NO_x conditions, where the lifetime of RO₂ is long enough to react with the HO₂ radical. The RO₂ + HO₂ reaction is usually

assumed to be a radical sink process, forming (mostly) stable hydroperoxides¹⁹ (reaction 1). However, other known $RO_2 + HO_2$ reaction channels (reaction 2 and reaction 3) can potentially be important and result in radical and oxidant recycling in the atmosphere:

Reaction 2 leads to the formation of alkoxy radicals. These radicals can continue oxidation in the atmosphere^{20,21} and may lead to products with lower volatilities than the ROOH product of reaction 1. Since the reaction also serves to recycle OH, it can enhance VOC oxidation. Studies of the branching ratios of the two reactions have only been performed for relatively small hydrocarbons (up to 3 carbon atoms).^{19,22,23}

The $RO_2 + RO_2$ reaction has three known channels:

Reactions 4 and 6 are both radical termination reactions. Reaction 6 is generally unimportant for small RO_2 , but it has been suggested as a mechanism for the lowest-volatility "dimer" reaction products observed in experiments on e.g. monoterpenes.^{1,24} Reaction 5 is a radical propagation reaction, and leads to reactive alkoxy radicals analogously to reaction 2. The branching between the competing reaction pathways for both $RO_2 + HO_2$ and $RO_2 + RO_2$ reactions are thus important for the radical recycling of the atmosphere.

In this work, we carry out a thermodynamic study of the favorability of the radical-recycling reactions 2 and 5 for a set of the most common monoterpenes and oxidants in the atmosphere. Only the first generation RO_2 is considered, i.e., the RO_2 formed by the first O_2 addition to the alkyl radical following oxidation. Despite this restriction, our study encompasses 83 different RO_2 species, and a total of 3486 possible reactions for reaction 5. We also compute thermodynamic parameters for reaction 3, which has previously been observed for carbonyl-containing acyl peroxy radicals.^{19,22,23} It is unlikely that any of the non-acyl peroxy radicals studied here will undergo direct bimolecular reactions with HO_2 to form O_3 , as no mechanism has been identified for this in the literature. However, the reaction might conceivably occur in the presence of catalysts, either in the gas-phase via clustering, or in the atmospheric condensed phase. The reaction Gibbs energies for this reaction are provided in Table S1 in the SI. The transition states and associated rates of reactions for the oxidized monoterpenes were not studied in this work because of the large set of reactions and the size of the individual reactants and products considered here.

Methods

The computational methods employed here have been described in detail previously.^{8,25,26} The systems studied here possess multiple different isomers, each with a large number of potential conformers. In this context, isomers are defined as compounds with the same chemical elemental composition (and in this case also the same functional groups), but differing in their bonding patterns (i.e. positional isomers). Interconversion of different isomers typically involves the breaking of covalent bonds, and is thus associated with high barriers. Conformers, on the other hand, have identical bonding patterns, and differ only in the three-dimensional arrangement of atoms. Conformers can be interconverted by rotations around torsional angles, which typically have low energy barriers in comparison to reactions breaking and forming

bonds.

The conformer sampling for each isomer was carried out by a systematic conformer search using the MMFF force field,^{27–32} followed by single-point energy calculations and geometry optimizations at the B3LYP/6-31+G(d) level of theory.^{33–38} Spartan '14 and '16 were used to carry out these computations.^{39,40} For the RO₂s and the ROs, the keyword "FFHINT=O_x ~6" (*x*=radical oxygen atom number as labeled by the Spartan program) was used to denote the radical oxygen and to specify its atom type to "generic divalent O", which was found to yield good results for peroxy radicals.^{38,41} Following initial single-point calculations on all the conformers, those within 5 kcal/mol in relative electronic energies of the lowest-energy conformer were optimized at the B3LYP/6-31+G(d) level. Conformers within 2 kcal/mol in relative electronic energy following the optimization were then optimized at the ωB97X-D/aug-cc-pVTZ^{42–44} level using the Gaussian 09 program.⁴⁵ The calculations were performed using an ultrafine integration grid. Since there were multiple conformers for every reactant and product isomer, the reaction energies were calculated using conformationally averaged Gibbs energies. The equation for calculating the conformationally averaged Gibbs energy, *G*, is:⁴⁶

$$G = -k_B T \ln \left(e^{-\beta g_0} \sum_k e^{-\beta (g_k - g_0)} \right), \quad (7)$$

where, *g*₀ is the Gibbs energy of the most energetically favorable conformer, $\beta = 1/k_B T$, *g*_{*k*} is the Gibbs energy of the *k*th conformer relative to *g*₀, *k*_B is the Boltzmann constant, and *T* is the temperature. The Gibbs energies for each individual conformer was computed using the standard rigid rotor and harmonic oscillator approximations, with the temperature set to 298.15 K and with a reference pressure of 1 atm (values at different conditions can be computed using the log files provided in a supplementary information file). The conformationally averaged Gibbs energies were then corrected using DLPNO-CCSD(T)/def2-QZVPP single point energies calculated using the ORCA program.^{47,48} The DLPNO-CCSD(T)/def2-QZVPP single point calculation was performed on the lowest energy conformer geometry and the

conformationally averaged Gibbs energy was corrected by the difference between the DFT and DLPNO-CCSD(T) electronic energies of the lowest energy conformer. DLPNO stands for domain-based local pair natural orbitals. Instead of canonical delocalized orbitals, the method uses pair natural orbitals that are then localized and classified into domains for sorting and selection of the most important excitations that account for electronic correlation. The DLPNO-CCSD(T) method also differs from corresponding canonical methods when evaluating the triples, using the T_0 approximation which neglects the elements outside the diagonal in the Fock Matrix. This greatly reduces the calculation time. The accuracy of the DLPNO-CCSD(T) method has been tested previously by comparing the DLPNO-CCSD(T) calculated formation enthalpies with accurate formation enthalpies for a set of 113 molecules and found to have a mean absolute error of 1.6 kcal/mol.⁴⁹

Test calculation were performed on small systems with the same functionalities as the molecules studied here to determine the transition state energies for the reaction $\text{RO}_2 + \text{HO}_2 \rightarrow \text{RO} + \text{OH} + \text{O}_2$ (reaction 2). The transition states were calculated for $\text{CH}_2(\text{OH})\text{CH}_2\text{OO}$ and $\text{CH}_2(\text{ONO}_2)\text{CH}_2\text{OO}$ systems (analogous to those formed from OH and NO_3 oxidation) at the CBS/QB3 level,⁵⁰ which was used by Hasson et al.²³ for similar systems. These transition states are open-shell singlets and were therefore calculated using unrestricted UCBS-QB3 with the Guess=(mix,always) keyword. This mixes the HOMO and the LUMO so as to destroy the α and β spatial symmetries and requests a new initial guess to be generated at each point in the optimization. The spin contamination in the UHF steps in the CCSD(T) and MP2 calculations in UCBS-QB3 were ~ 1.05 before and ~ 0.9 after annihilation. The energetics of the intermediate complex of reaction $\text{RO}'_2 + \text{RO}_2 \rightarrow \text{R}'\text{O} + \text{RO} + \text{O}_2$ (reaction 5) was studied by optimizing $\text{CH}_3\text{CH}_2\text{O} \cdots \text{O}_2 \cdots \text{OCH}_2\text{CH}_3$ at the M11/6-31+G(d,p)^{35,51-53} level of theory employed in Lee et al.⁵⁴

The reaction Gibbs energies for reactions 2, 3 and 5 were calculated by subtracting the

Gibbs energies of the free products from the Gibbs energies of the free reactants:

$$\Delta G(\text{Reaction } 2) = [G(RO) + G(OH) + G(O_2)] - [G(RO_2) + G(HO_2)] \quad (8)$$

$$\Delta G(\text{Reaction } 3) = [G(ROH) + G(O_3)] - [G(RO_2) + G(HO_2)] \quad (9)$$

$$\Delta G(\text{Reaction } 5) = [G(R'O) + G(RO) + G(O_2)] - [G(R'O_2) + G(RO_2)] \quad (10)$$

The structures of the monoterpenes studied here are shown in Figure 1. For α -pinene and β -pinene, the "-" enantiomers were considered, while for limonene and Δ^3 -carene the "+" enantiomers were considered. As the other enantiomers are mirror images, their energetics are identical. For ocimene, trans- β -ocimene was studied as it makes up the majority of the biogenic ocimene emission.⁶

Figure 1: Monoterpene isomers investigated in this study. a) α -pinene, b) β -pinene, c) limonene, d) trans- β -ocimene, and e) Δ^3 -carene.

Depending on which olefinic carbon is attacked by the oxidants, multiple isomers of the first-generation RO_2 are possible. For RO_2 s from OH and NO_3 oxidation, we generally consider only those isomers formed by addition to the double bond where the initial alkyl radical is formed on the most substituted (tertiary) carbon atom. However, for β -pinene, which has a very limited number of RO_2 isomers from OH and NO_3 oxidation, all first-

generation isomers were calculated to see the effect on the reaction energy. All possible first-generation isomers were also calculated for trans- β -ocimene, including resonance isomers from ozone oxidation. Oxidation via H-abstraction by OH is possible (and can account for a significant fraction of OH oxidation products of monoterpenes according to Rio et al. 2010⁵⁵). However, we decided to limit our study to only oxidation via OH addition as, according to current knowledge, it is still the dominant OH oxidation pathway for monoterpenes.^{55,56}

For the ozonolysis reaction, the RO₂ radicals with more than one carbon atom formed via the VHP pathway were considered. The mechanism for trans- β -ocimene is illustrated in Figure 2. For limonene, we only consider ozone attack on the endocyclic double bond, as it has been reported to be 35 times more favorable than the attack on the exocyclic double bond.⁵⁷ β -pinene is an exocyclic alkene and thus does not undergo a ring-opening reaction, but instead loses the CH₂ group in the form of formaldehyde (CH₂O) in the POZ decomposition. The CI formed by ozone attack on the terminal double bond of trans- β -ocimene can not form a VHP (as there is no H atom to abstract in a 1,4 H-shift), and this reaction site was thus omitted from our study. Since ozonolysis leads to the breaking of a C=C bond, the RO₂ products of limonene ozonolysis are acyclic, while those of α -pinene and Δ^3 -carene have lost their 6-membered rings, but retain their 4- and 3-membered rings, respectively.

Figure 2: Ozonolysis reaction of trans- β -ocimene over one of the double bonds. The primary ozonide (POZ) can decompose via two possible Criegee intermediate (CI) and carbonyl compound forming channels. The CI forms a vinyl hydroperoxide (VHP) by a 1,4 hydrogen shift, followed by OH loss to form a vinoxy radical. The vinoxy radical then adds an oxygen molecule, forming a peroxy radical.

Results

$\text{RO}_2 + \text{HO}_2$ reaction for RO_2 radicals from OH and NO_3 oxidation

The general mechanisms for the initial steps of oxidation via OH and NO_3 addition to double bonds are identical, and the results for the HO_2 reactions with OH and NO_3 -derived RO_2 radicals are therefore presented in the same section. The schematic of the lowest energy RO_2 radical isomer is shown in Table 1 for the OH oxidized case and in Table 2 for the NO_3 oxidized case, with the range (maximum-minimum) of Gibbs energies given for the full set of isomers. All reaction Gibbs energies are provided in Tables S4-S8 in the SI. The log files needed to compute them are also provided in the supplementary zip archive.

Table 1: Range of Reaction Gibbs Energies (ΔG) in kcal/mol for Different Isomers For the OH Oxidized Monoterpenes in the $\text{RO}_2 + \text{HO}_2 \rightarrow \text{RO} + \text{OH} + \text{O}_2$ Reaction

Monoterpene	Isomer ^a	ΔG^b
α -pinene		-0.12 to -6.40
β -pinene		-2.03 to -4.88
Trans- β -ocimene		-1.47 to -3.85
Limonene		-1.11 to -2.61
Δ^3 -carene		-1.34 to -4.70

^a Lowest energy RO_2 isomer (in terms of Gibbs energy at 298.15 K).

^b Gibbs energies (at 298.15 K and 1 atm reference pressure) are conformationally averaged and calculated at the DLPNO-CCSD(T)/def2-QZVPP// ω B97X-D/aug-cc-pVTZ level.

Table 2: Range of Reaction Gibbs Energies (ΔG) in kcal/mol for Different Isomers For the NO_3 Oxidized Monoterpenes in the $\text{RO}_2 + \text{HO}_2 \rightarrow \text{RO} + \text{OH} + \text{O}_2$ Reaction

Monoterpene	Isomer ^a	ΔG^b
α -pinene		-1.79 to -5.25
β -pinene		-1.74 to -4.88
Trans- β -ocimene		-1.78 to -5.52
Limonene		-1.63 to -4.40
Δ^3 -carene		-2.13 to -5.75

^a Lowest energy RO_2 isomer (in terms of Gibbs energy at 298.15 K).

^b Gibbs energies (at 298.15 K and 1 atm reference pressure) are conformationally averaged and calculated at the DLPNO-CCSD(T)/def2-QZVPP// ω B97X-D/aug-cc-pVTZ level.

$\text{RO}_2 + \text{HO}_2$ reaction for RO_2 from ozonolysis

The range (maximum-minimum) of the reaction Gibbs energies for the different isomers of the ozonolysis derived RO_2 s are given in Table 3, with the schematic of the lowest energy RO_2 also shown. The ozonolysis of trans- β -ocimene leads to the formation of peroxy radicals with different elemental compositions which are not isomers of each other. Therefore, the reaction energies for each of the different trans- β -ocimene derived RO_2 s are shown separately in Table 4.

Table 3: Range of Reaction Gibbs Energies (ΔG) in kcal/mol For Different Isomers for the O_3 Oxidized Monoterpenes in the $RO_2 + HO_2 \rightarrow RO + OH + O_2$ Reaction

Monoterpene	Isomer ^a	ΔG^b
α -pinene		-4.03 to -4.16 (-26.64,-25.42) ^c
β -pinene		-4.24 to -7.16
Trans- β -ocimene		-2.38 to -4.68
Limonene		-4.02 to -4.70
Δ^3 -carene		-2.09 to -4.70

^a Lowest energy RO_2 isomer (in terms of Gibbs energy at 298.15 K).

^b Gibbs energies (at 298.15 K and 1 atm reference pressure) are conformationally averaged and calculated at the DLPNO-CCSD(T)/def2-QZVPP// ω B97X-D/aug-cc-pVTZ level.

^c Includes alkoxy ring-breaking step as no alkoxy radical minimum could be found.

Table 4: Reaction Gibbs Energies (ΔG) in kcal/mol for All The Trans- β -Ocimene Ozonolysis Isomers Considered In This Study in the $RO_2 + HO_2 \rightarrow RO + OH + O_2$ Reaction

RO ₂	Isomer	ΔG^a
1		-2.70
2		-2.37
3		-4.03
4		-2.37
5		-1.97
6		-4.68

^a Gibbs energies (at 298.15 K and 1 atm reference pressure) are conformationally averaged and calculated at the DLPNO-CCSD(T)/def2-QZVPP// ω B97X-D/aug-cc-pVTZ level.

The RO_2 s from α -pinene ozonolysis with the radical group located on the ring were excluded from the study due to a previously reported ring-breaking reaction that occurs spontaneously upon formation of the RO product,⁸ making the alkoxy forming channel significantly exergonic. In this reaction, the alkoxy oxygen forms a carbonyl group, breaking the four-member cyclobutyl ring in the process, forming a second-generation alkyl radical, as shown in Figure 3. Reaction thermodynamics for the other two RO_2 s formed in α -pinene ozonolysis are comparable to the other monoterpenes.

Figure 3: Ring breaking reaction observed during the optimization of the RO product for the most favorable RO₂ isomer product following ozonolysis of α-pinene.

R'O₂ + RO₂ → R'O + RO + O₂ reaction

For reaction 5, 83 self-reactions + (83×82)/2 cross-reactions were possible, giving a total of 3486 reactions when all the monoterpene + oxidant combinations were considered. The reaction Gibbs energies varied from a maximum of -2.86 kcal/mol to a minimum of -16.96 kcal/mol. Table 5 shows the reaction Gibbs energies of a select few reactions categorized into reaction energy ranges of 0 to -5, -5 to -10, and -10 to -17 kcal/mol. Reaction Gibbs energy ranges were used to point out important RO₂/RO features that were found to strongly influence the reaction Gibbs energies. The complete set of reaction Gibbs energies is provided as an Excel spreadsheet in the supplementary material.

Table 5: Reaction Gibbs Energies (ΔG) in kcal/mol for Selected $R'O_2 + RO_2 \rightarrow R'O + RO + O_2$ Reactions

Range		Isomer		ΔG^a
		$R'O_2$	RO_2	
0 to -5	a			-2.86
	b			-3.86
	c			-4.08
-5 to -10	d			-5.90
	e			-7.63
	f			-9.91
-10 to -17	g			-12.40
	h			-14.78
	i			-16.96

^a Gibbs energies (at 298.15 K and 1 atm reference pressure) are conformationally averaged and calculated at the DLPNO-CCSD(T)/def2-QZVPP// ω B97X-D/aug-cc-pVTZ level.

The reaction Gibbs energies of reaction 5 point to low favorability for the reactions involving the OH-oxidized α -pinene isomer with the RO_2 functional group and OH functional group on the opposite sides of the ring. The first six entries in Table 5 all have this isomer as

the R'O₂ reactant to help illustrate how the identity of the other peroxy radical changes the reaction thermodynamics.

Discussion and Atmospheric Implications

All reactions studied here had standard Gibbs energies below 0. However, while important, this is not a sufficient condition for a reaction to be competitive under atmospheric conditions. The atmospheric importance of a reaction depends on its reaction rate. While reaction rates cannot be determined from the thermodynamic parameters reported here, some general guidelines can help illustrate which reactions might be competitive in atmospheric conditions, and which can be ruled out.

Most of the reactions studied here likely involve transition states, or at least reactant complexes or reaction intermediates, which suffer from an entropy penalty compared to the free reactants (or products) due to the loss of translational and rotational degrees of freedom. This is especially important for reaction 2 and reaction 5, where two reactants first combine, and then separate to form three products, with an associated gain in entropy. Our discussion here focuses on parameters computed at 298.15 K. The rates of bimolecular radical reactions in the atmosphere are typically not very temperature-sensitive (as the enthalpy barriers of competitive reaction channels are inevitably fairly close to zero), and the general conclusions drawn here can thus likely be applied to most of the lower troposphere. Thermodynamic parameters at other temperatures can be computed from the data in the log files (provided as a supplementary material zip archive).

The overall entropy gain in reaction 2 translates to a difference of around 9-10 kcal/mol between the reaction enthalpies and the reaction Gibbs energies (computed at the ω B97X-

D/aug-cc-pVTZ level as the thermal contributions to the Gibbs energy are available only at this level). Similarly, the entropy contributions to the Gibbs energies ($-T\Delta S$) of the transition states and/or intermediates for reaction 2 must be around 20 kcal/mol higher than those of the products. If the transition states and products were isoenergetic in terms of the enthalpy, a reaction Gibbs energy of 0 kcal/mol would thus imply a barrier of about 20 kcal/mol – making the reaction much too slow to matter in the atmosphere.

In reality, the transition states and separated products are not isoenergetic – either can contain both stabilizing and destabilizing interactions that are lacking in the other. Hasson et al.²³ found that for ethyl peroxy and acetonyl peroxy radicals, the rate-limiting transition states for reaction 2 were 7.5 and 13.7 kcal/mol below the separated products in enthalpies, respectively (the transition states can be lower than the products due to the presence of multiple intermediates or product complexes on the reaction path).

The entropy contribution to the Gibbs energy of the transition state relative to the products, and the stabilization of the transition state due to inter-molecular interactions, were further investigated for reaction 2 by performing test calculations on small systems with the same functionalities as the OH and NO₃ oxidized RO₂ (two-carbon systems CH₂(OH)CH₂OO and CH₂(ONO₂)CH₂OO). The analogous system for O₃ oxidation is the acetonyl peroxy radical, which was already studied by Hasson et al.²³ The enthalpies, entropy contributions ($-T\Delta S$), and Gibbs energies for key stationary points of the CH₂(OH)CH₂OO + HO₂ → CH₂(OH)CH₂O + OH + O₂ reaction are shown in Figure 4. Only the rate limiting transition state energy is shown. There are multiple intermediates and transition states between intermediate 2 (INT₂ in Figure 4) and the separated products. Hasson et al.²³ provide the entire reaction pathway for alkyl, acyl, and acetonyl type RO₂s. The transition states for the OH- and NO₃-oxidized systems were found to be 12.4 kcal/mol and 13.2 kcal/mol lower in enthalpies, respectively, than the corresponding free products (these values were calculated

at the same computational level employed in Hasson et al.- CBS-QB3²³). This is very similar to the value of 13.7 kcal/mol found for the acetyl peroxy radical, indicating that transition states for all RO₂ + HO₂ reactions studied here are stabilized (in enthalpy, compared to the free products) by roughly similar amounts. The entropy contribution to the Gibbs energy of the transition state relative to the free products was 21.5 and 21.8 kcal/mol for OH- and NO₃-oxidized systems, respectively (and 23.6 kcal/mol for the acetyl peroxy radical²³). In terms of Gibbs energy (accounting for both the entropy contribution to the transition state Gibbs energy and the stabilization of the transition state due to favorable intra-molecular interactions) the transition states were thus 9.4, 8.0, and 9.9 kcal/mol above the reactants for the OH-, NO₃, and O₃ oxidized systems, respectively.

Figure 4: Reaction stationary points for the RO₂ + HO₂ reaction, where the RO₂ = CH₂(OH)CH₂OO, in terms of a) enthalpies and c) Gibbs energies. b) shows the entropy contribution ($-T\Delta S$ at 298.15 K) to the Gibbs energies calculated at the CBS-QB3 level of theory. INT = intermediate, TS = transition state.

The overall rates (including all channels) for RO₂ + HO₂ reactions are typically on the order of 10⁻¹¹ cm³ molecules⁻¹ s⁻¹, and they typically increase with the size of the RO₂.⁵⁸ For a particular reaction channel (such as reaction 2) to be competitive, its rate can thus not be much lower than this. Using elementary transition state theory, a rate of 10⁻¹¹ cm³ molecules⁻¹ s⁻¹ corresponds to a Gibbs energy barrier of approximately 5 kcal/mol. Based on our test calculations and Hasson et al.,²³ for the two-carbon systems, the entropy penalty to the Gibbs energy of the transition states is about 22 kcal/mol relative to the products, while

the TS enthalpies are about 13 kcal/mol below the products of reaction 2 due to favorable intra-molecular interactions. Thus, for the Gibbs energy barrier to be 5 kcal/mol or less, the Gibbs energy of reaction 2 should not be higher than -4 kcal/mol. While our test systems have the same functional groups as the molecules in this study, the calculated $-T\Delta S$ and enthalpic contributions to the transition state Gibbs energy of reaction 2 cannot be assumed to be directly applicable to all the monoterpene derived reactants and products studied here. However, test calculations on one α -pinene derived RO_2 (see section S3 in the SI) indicate that our "rule of thumb" may be reasonably valid also for larger systems, and can thus be helpful in gauging what reactions are likely to be competitive. We can conclude therefore that any example of reaction 2 with an overall Gibbs energy much above -4 kcal/mol is unlikely to be competitive in the atmosphere. As seen from tables 1 to 4, this includes most (though not all) of the OH and NO_3 derived 1st generation RO_2 , and some of the RO_2 from O_3 oxidation of trans- β -ocimene and Δ^3 -carene. On the other hand, for each monoterpene + oxidant combination except limonene + OH, at least one isomer can be found for which the Gibbs energy of reaction 2 is around or below -4 kcal/mol.

Intra-molecular hydrogen bonds generally lower the Gibbs energy of molecules. A lower reactant RO_2 energy (for example, due to hydrogen bonding) will increase the reaction energy, while a lower product RO energy will decrease the reaction energy. The alkoxy RO product from the OH-oxidized RO_2 isomer for α -pinene shown in Table 1 has the alkoxy oxygen on the opposite side of the ring to the OH-group and is therefore unable to form an intra-molecular hydrogen bond. The RO_2 group in the reactant is more flexible and is able to form a weak hydrogen bond with the OH group. This results in a high reaction 2 Gibbs energy of -0.12 kcal/mol. The reaction Gibbs energy corresponding to the reactant RO_2 isomer where the OH-group is on the same side as the peroxy radical is significantly more exergonic (-6.40 kcal/mol) due to a strong intra-molecular hydrogen bond between the alkoxy oxygen and the OH group in the product, and a relatively weaker interaction between the RO_2 group and

the OH group in the reactant. Figure 5 shows the two alkoxy radical isomers schematically. Isomer b in the figure can form an intra-molecular hydrogen bond between the alkoxy-oxygen and the OH-group and is consequently about 5 kcal/mol lower in Gibbs energy than the RO isomer a.

Figure 5: Alkoxy products of OH-oxidized α -pinene a) OH down, O up, b) OH down, O down. $\Delta\Delta G$ denotes the relative Gibbs energies of the alkoxy isomers and $\Delta G(R_2)$ is the Gibbs energy of reaction 2 producing this product. All values are in kcal/mol.

In the case of OH-derived RO_2 , the reaction rate may ultimately be controlled by the degree of hydrogen bonding stabilization of the transition states, which cannot be directly deduced from the overall reaction energies. In other words, our "rule of thumb" of an overall reaction Gibbs energy not much above -4 kcal/mol being necessary for an efficient reaction 2 may have the largest uncertainty for the OH-oxidized cases.

In the case of NO_3 oxidation, the difference between the reaction Gibbs energies of different isomers for each monoterpene is controlled mainly by the stability of the reactant RO_2 , as the differences in Gibbs energies between the RO_2 isomers is larger than the difference in Gibbs energies of the corresponding RO. For trans- β -ocimene, the most energetically favorable RO_2 isomer (shown in Table 2) was 3.68 kcal/mol lower in Gibbs energy than the next best RO_2

isomer. This showed in the reaction Gibbs energies for reaction 2, where the most favorable RO₂ isomer lead to the highest (least negative) reaction Gibbs energy. The RO₂ isomer that has the O₂ and ONO₂ functional groups in opposite positions compared to the lowest Gibbs energy RO₂ isomer had a relative Gibbs energy of 4.77 kcal/mol and a reaction 2 Gibbs energy of -5.52 kcal/mol. The two isomers are shown schematically in Figure 6. Similarly, the Δ_3 -carene NO₃ oxidized RO₂ isomer that is 2.60 kcal/mol (**b** in Figure 7) higher in Gibbs energy than the most energetically favorable isomer (**a** in Figure 7) has a reaction 2 Gibbs energy of -5.75 kcal/mol compared to -2.13 kcal/mol for the latter.

Figure 6: Two of the RO₂ isomers for NO₃ oxidized trans- β -ocimene that were studied. $\Delta\Delta G$ denotes the relative Gibbs energy in kcal/mol. **a)** Is the most energetically favorable RO₂ isomer, while **b)** is an isomer that is 4.77 kcal/mol higher in Gibbs energy. $\Delta G(R_2)$ is the Gibbs energy of reaction 2 involving this reactant.

Figure 7: Two of the RO₂ isomers for NO₃ oxidized Δ^3 -carene that were studied. $\Delta\Delta G$ denotes the relative Gibbs energy in kcal/mol. **a)** Is the most energetically favorable RO₂ isomer and **b)** is an isomer that is 3.25 kcal/mol higher in Gibbs energy. $\Delta G(R_2)$ is the Gibbs energy of reaction 2 involving this reactant.

The Gibbs energies of reaction 2 for the O₃ oxidized systems were on average slightly lower than for the OH and NO₃-oxidized cases. The variation of Gibbs energies (both for different RO₂ isomers from the same monoterpene, and between monoterpenes) was also generally slightly smaller, possibly due to weaker direct interactions between the carbonyl group and the radical centers compared to the ONO₂ or OH cases. Crucially, most RO₂ isomers derived from O₃ oxidation of monoterpenes had Gibbs energies just around or below -4 kcal/mol for reaction 2, implying that they could be competitive in the atmosphere. The main exceptions to this trend are some RO₂ isomers from trans- β -ocimene and Δ^3 -carene ozonolysis, which have reaction Gibbs energies between -2 and -3 kcal/mol, and one of the RO₂ isomers from β -pinene ozonolysis, which has an anomalously low reaction Gibbs energy of -7.16 kcal/mol. This last isomer has the RO₂ (and subsequent RO) group located on a tertiary carbon atom, leading to an exceptionally low energy for the RO product. While spontaneous breaking of the cyclo-butyl ring by the oxy-radical on the tertiary carbon was expected (and was observed at the lower-level B3LYP/6-31+G* optimization), a direct optimization at the higher ω B97X-D/aug-cc-pVTZ level found an alkoxy radical minimum (note that the ring-breaking reaction is still likely to have a low barrier, and occur before any other reaction in atmospheric conditions). The three RO isomers of ozone oxidized β -pinene along with the

difference in relative Gibbs energies are shown in Figure 8. It should be noted that isomer **a** is unlikely to form in the atmosphere as the initial hydrogen abstraction by the Criegee intermediate required to form the preceding RO₂ has a barrier of 25 kcal/mol.⁵⁹

Figure 8: The three RO isomers for O₃ oxidized β -pinene. $\Delta\Delta G$ denotes the relative Gibbs energy in kcal/mol. **a)** Is the isomer with the oxy radical on the tertiary carbon atom, while **b)** and **c)** are the isomers with the oxy radical on the secondary carbon atom. $\Delta G(R_2)$ is the Gibbs energy of reaction 2 producing this product.

Reaction 3 was found to be consistently exergonic, by -13 to -25 kcal/mol, see Table S1 in the SI for full details. The most favorable reaction Gibbs energies were observed for the isomers where the alcohol product formed an intra-molecular hydrogen bond with the O-atom of the OH, NO₃, and the carbonyl O functional groups from the three different oxidized systems, respectively. If (likely catalytic) kinetically competitive reaction mechanisms exist for reaction 3 also for the non-acyl peroxy radicals studied here, then thermodynamic factors will not prevent the reaction from occurring.

The mechanism of reaction 5 is currently uncertain. The most recent and theoretically rigorous computational study by Lee et al.⁵⁴ proposes (in agreement with a multireference study by Ghigo et al. from 2003⁶⁰) that all RO₂ + RO₂ reactions proceed via an RO $\cdots$ O₂ $\cdots$ RO complex, where the two RO are coupled as a triplet, coupling to the triplet O₂ to give an overall singlet. Branching between the three different pathways (reactions 4, 5 and 6)

is then controlled by a competition between hydrogen abstraction, fragmentation of the complex and intersystem crossing (and subsequent barrierless recombination of the two RO), respectively. The thermodynamic parameters computed here can thus not be used to assess relative probabilities of reaction 5 compared to the two other channels. However, analogous to reaction 2, the $\text{RO} \cdots \text{O}_2 \cdots \text{RO}$ complex also suffers from an entropy penalty to its Gibbs energy compared to the separated products (in terms of the $-T\Delta S$ contribution to the Gibbs energy at 298 K). For example, the entropy contribution to the Gibbs energy of the $\text{CH}_3\text{CH}_2\text{O} \cdots \text{O}_2 \cdots \text{OCH}_2\text{CH}_3$ complex was found to be 17 kcal/mol relative to the separated products (calculated at M11//6-31+G(d,p) level employed by Lee et al.⁵⁴). Since the entropy penalty to the Gibbs energy of the $\text{RO} \cdots \text{O}_2 \cdots \text{OR}$ complex and the transition state (or states) associated with its formation are likely quite similar (see Figure 4 **b** for the analogous case for reaction 2), the overall $\text{RO}_2 + \text{RO}_2$ reaction is thus associated with a Gibbs energy barrier around 17 kcal/mol higher than the reaction Gibbs energy computed here, plus or minus any stabilizing or destabilizing enthalpic contributions, for example from H-bonding or bond-breaking (respectively). Lee et al.⁵⁴ suggest (based on CCSD(T) energy corrections) that the rate-limiting transition state for the $\text{CH}_3\text{CH}_2\text{OO} + \text{CH}_3\text{CH}_2\text{OO}$ reaction is almost 13 kcal/mol above the $\text{RO} \cdots \text{O}_2 \cdots \text{OR}$ complex in enthalpy. This would lead to negligibly low overall reaction rates for the gas-phase $\text{CH}_3\text{CH}_2\text{OO} + \text{CH}_3\text{CH}_2\text{OO}$ reaction, in disagreement with observations.¹⁷ CASPT2 calculations by Ghigo et al.⁶⁰ for the $\text{CH}_3\text{OO} + \text{CH}_3\text{OO}$ system suggest that the rate-limiting transition state is less than 2 kcal/mol above the complex in enthalpy, leading to much better agreement with experiments. Here, we use computed properties for a few model $\text{RO} \cdots \text{O}_2 \cdots \text{OR}$ and $\text{RO} \cdots \text{OR}$ complexes, together with our computed overall reaction Gibbs energies, to estimate lower limits for the barrier heights for the $\text{RO}_2 + \text{RO}_2$ reactions. If the rate-limiting transition states are much higher in enthalpy than the $\text{RO} \cdots \text{O}_2 \cdots \text{OR}$ complex, the barriers would be correspondingly higher. However, as long as the reaction proceeds via the $\text{RO} \cdots \text{O}_2 \cdots \text{OR}$ complex, the rate-limiting barrier cannot not be lower than the free energy of the complex.

428

429 If we consider that the stabilization of the $\text{RO}\cdots\text{O}_2\cdots\text{OR}$ complex is mostly from the
430 favorable interaction of the two RO, we can estimate this stabilization by looking at the
431 binding energy of $\text{RO}\cdots\text{RO}$. We considered a simple two-carbon model ROs for each of the
432 OH-, NO_3 , and O_3 -oxidized system. The calculation was done for an overall triplet state, as
433 the Lee et al.⁵⁴ mechanism indicates the two RO are initially coupled as a triplet (and ROOR
434 formation from two RO likely occurs spontaneously on the singlet surface). The binding
435 enthalpy (at the DLPNO/def2-QZVPP// ω B97X-D/aug-cc-pVTZ level of theory) for the
436 OH-, NO_3 - and O_3 oxidized $\text{RO}\cdots\text{RO}$ is 4.4, 3.9 and 2.7 kcal/mol, respectively. Considering
437 an entropy penalty to the transition state Gibbs energy of around 17 kcal/mol, a stabilization
438 of around 4 kcal/mol would mean that the rate limiting transition state (or intermediate) for
439 reaction 5 is at least around 13 kcal/mol above the separated products. For example, for a
440 reaction Gibbs energy of around -10 kcal/mol (implying that the products are 10 kcal/mol
441 below the reactants), the transition state would then be about 3 kcal/mol in Gibbs energy
442 above the reactants.

443

444 The reaction Gibbs energies of reaction 5 showed that the reaction was less favorable
445 when one of the reacting peroxy radicals was the OH-oxidized α -pinene isomer with the RO_2
446 functional group and the OH functional group on the opposite sides of the ring (see rows
447 **a** to **f** in Table 5). This is due to the previously discussed stabilization of the OH-oxidized
448 α -pinene RO_2 by a weak H-bond between the hydrogen atom of the OH group and the
449 RO_2 group and the absence of such an interaction in the corresponding RO product (see
450 Figure 9). For the reactions in the range of -5 to -10 kcal/mol, the lowering of the OH-oxidized
451 α -pinene peroxy radical isomer due to the interaction between the RO_2 and OH groups were
452 compensated by the relatively high energies of the second RO_2 reactant in the reaction. The
453 NO_3 -oxidized trans- β -ocimene RO_2 isomer in row **d** in Table 5 is 4.4 kcal/mol higher in
454 Gibbs energy compared to the most favorable NO_3 -oxidized trans- β -ocimene RO_2 isomer.

Similarly, the OH-oxidized β -pinene RO₂ in row **e** in the table has the peroxy radical group on a secondary carbon, and is consequently 1 kcal/mol higher in Gibbs energy relative to the lowest energy OH-oxidized β -pinene RO₂ isomer. While 1 kcal/mol should not significantly affect the overall reaction Gibbs energy on its own, the ΔG is augmented by the low energy of the corresponding RO product of this OH-oxidized β -pinene RO₂ isomer in row **e**, which is the most favorable RO isomer of the four considered in this study. For the third case in this energy range, the ΔG is significantly influenced by the previously discussed low RO Gibbs energy of the O₃-oxidized β -pinene isomer in row **f** in Table 5. In the -10 to -17 kcal/mol energy range in Table 5, the NO₃-oxidized α -pinene R'O₂ and OH-oxidized β -pinene RO₂ in row **g** are both less favorable isomers (2.8 kcal/mol and 2 kcal/mol higher than the most favorable NO₃-oxidized α -pinene and OH-oxidized- β -pinene RO₂s, respectively), translating to lower overall ΔG s. In row **h**, in addition to the OH-oxidized α -pinene and NO₃-oxidized Δ^3 -carene being unfavorable by 1.4 and 2.6 kcal/mol, respectively, relative to their corresponding most favorable RO₂ isomer, the low ΔG can be explained by the low energy of the RO products of the two isomers (the lowest energy OH-oxidized RO isomer in the α -pinene case, and only 0.3 kcal/mol higher than the lowest energy NO₃ oxidized RO isomer in the Δ^3 -carene case). Finally, the lowest ΔG was found for the reaction between the two O₃-oxidized β -pinene RO₂s (row **i**) due to the low energy of the corresponding RO product.

Figure 9: Distances between the OH group and the RO₂ group (a) and the OH group and the RO group (b). The interaction between the OH group and the RO₂ group in (a) translates to a lower RO₂ energy.

Conclusion

Multiple channels compete for RO₂ + HO₂ and RO₂ + RO₂ reactions. The thermodynamics of the two radical propagation reactions involving monoterpene derived RO₂s were studied here. This is the first time such a study has been carried out for a large set of atmospherically relevant monoterpenes and oxidants. The reaction Gibbs energies were exergonic for all cases. However, the RO₂ + HO₂ → RO + OH + O₂ channel (reaction 2) was found to be only barely so for some of the OH and the NO₃ oxidized systems, especially for the lowest-energy RO₂ isomers. Using our simple "rule of thumb" that the reaction Gibbs energy cannot be much higher than -4 kcal/mol for reaction 2 to be competitive, we can rule out this reaction for most OH and NO₃-derived first generation monoterpene RO₂ isomers. However, for each monoterpene-oxidant combination except limonene + OH, at least one RO₂ isomer can be found for which the Gibbs energy of reaction 2 is around or below -4 kcal/mol. These RO₂ isomers could thus conceivably have non-negligible yields for reaction 2. The ozone-derived RO₂s, especially from β -pinene, have somewhat lower reaction Gibbs energies, and for many of their isomers reaction 2 may be feasible.

The $R'O_2 + RO_2 \rightarrow R'O + RO + O_2$ reaction (reaction 5) Gibbs energies varied from a maximum of ~ -3 kcal/mol for the α -pinene-OH system to a minimum of ~ -17 kcal/mol for the β -pinene- O_3 system. The structure of the reactant RO_2 and the product RO strongly affect the reaction Gibbs energies. $RO_2 + RO_2$ self-reaction rates as low as 3×10^{-17} cm³ molecule⁻¹ s⁻¹ have been observed for systems similar to those studied here (tertiary C₄H₉O₂ radical, in this case).⁶¹ Assuming that the overall mechanism proposed by Ghigo et al.⁶⁰ and Lee et al.⁵⁴ for $RO_2 + RO_2$ reactions is correct, all RO_2 s studied here should have self-reaction rates faster than the slowest observed rate. We can qualitatively conclude, however, that O_3 -derived monoterpene RO_2 are generally likely to have higher, and OH-derived RO_2 lower, overall self- and cross-reaction rates, with NO_3 -derived RO_2 representing an intermediate case between the other two.

Supporting information

The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org/> and includes reaction Gibbs energies for the studied reactions for all isomers. Output files (.log and .out) for all studied systems are provided in a zip file archived at: <https://doi.org/10.5281/zenodo.1476995>

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