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α -pinene Autoxidation Products May not Have Extremely Low Saturation Vapor Pressures Despite High O:C Ratios

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ABSTRACT

COSMO-RS (COnductor-like Screening MOdel for Real Solvents) and three different group-contribution methods were used to compute saturation (subcooled) liquid vapor pressures for 16 possible products of ozone-initiated α -pinene autoxidation, with elemental compositions $C_{10}H_{16}O_{4-10}$ and $C_{20}H_{30}O_{10-12}$. The saturation vapor pressures predicted by the different methods varied widely. COSMO-RS predicted relatively high saturation vapor pressures values in the range of 10^{-6} to 10^{-10} bar for the $C_{10}H_{16}O_{4-10}$ “monomers”, and 10^{-11} to 10^{-16} bar for the $C_{20}H_{30}O_{10-12}$ “dimers”. The group-contribution methods predicted significantly (up to 8 order of magnitude) lower saturation vapor pressures for most of the more highly oxidized monomers. For the dimers, the COSMO-RS predictions were within the (wide) range spanned by the three group-contribution methods. The main reason for the discrepancies between the methods is likely that the group-contribution methods do not contain the necessary parameters to accurately treat autoxidation products containing multiple hydroperoxide, peroxy acid or peroxide functional groups, which form intramolecular hydrogen bonds with each other. While the COSMO-RS saturation vapor pressures for these systems may be overestimated, the results strongly indicate that despite their high O:C ratios, the volatility of the autoxidation products of α -pinene (and possibly other atmospherically relevant alkenes) are not necessarily extremely low. In other words, while autoxidation products are able to adsorb onto aerosol particles, their evaporation back into the gas phase cannot be assumed to be negligible, especially from the smallest nanometer-scale particles. Their observed effective contribution to aerosol particle growth may therefore involve rapid heterogeneous reactions (reactive uptake) rather than effectively irreversible physical absorption.

Introduction

Conversion of volatile organic compounds (VOC) into less-volatile products is a major topic in atmospheric chemistry. Organic vapors, often classified by volatility into subgroups such as semi-volatile (SVOC), low-volatility (LVOC) or extremely low-volatility (ELVOC) organic compounds¹, are responsible for the formation of secondary organic aerosol (SOA).² Aerosol particles, of which SOA is a key component, in turn play a significant role in regulating Earth's climate, and are responsible for most air-pollution related mortality and other adverse health effects.³

The main chemical mechanism responsible for the formation of low-volatility material in the atmosphere is the addition of polar oxygen-containing functional groups to a carbon backbone through oxidation reactions.^{4,5} Oxidation of closed-shell molecules in the troposphere is always initiated by radical formation, which can occur either via direct photolysis, or (more commonly) via reaction with one of a small number of photochemically generated oxidants, such as OH, O₃, Cl and NO₃.⁶ The resulting radicals almost always then react with molecular oxygen, O₂, to form a peroxy radical (RO₂). The subsequent reactions of those peroxy radicals have long been recognized as a key branching point in atmospheric photochemical mechanisms,⁷ and recently the complexity at the RO₂ node has become even more interesting. Until recently, it was generally assumed that under atmospheric conditions unimolecular or bimolecular termination reactions inevitably prevented the addition of more than 4 oxygen atoms to a carbon backbone of an organic radical during one "generation" of chemistry from a stable molecular precursor to a stable molecular product.⁸ In order for large VOC molecules (such as biogenic monoterpenes with 10 carbon atoms) to be extensively oxidized, multiple reactions with low-concentration oxidants would therefore be required, making the process slow (taking hours or days).

Recent experimental^{9,10,11,12,13,14,15,16} and theoretical^{9,11,17,18} research has demonstrated that for suitable VOC – oxidant combinations, a process called autoxidation can lead to very rapid (second-timescale) formation of highly oxidized molecules (denoted “HOM”) after just a single initial reaction with an oxidant. Key to this autoxidation mechanism is a chain of sequential unimolecular peroxy radical hydrogen shifts (H-shifts) and O₂ additions within peroxy radicals, eventually followed by either unimolecular or bimolecular termination reactions. The total molar yields of HOMs are relatively small, between a few and ten percent,^{11,13} but they may have an outsized influence on aerosol formation. Due to their high O:C ratios and multitude of hydrogen-bonding functional groups, the HOMs formed by autoxidation have been assumed to be ELVOCs, implying¹⁹ saturation vapor pressures around or below about 10⁻¹⁴ bar for compounds with molar masses of a few hundred atomic mass units. It is important to note that while compounds with saturation vapor pressures in the LVOC regime, roughly 10^{-10...-14} bar, have negligible evaporation rates from bulk solutions or large aerosol particles, their evaporation from nanometer-sized aerosol particles is significant due to the Kelvin effect. Thus, saturation vapor pressures that are too low to measure by many experimental methods may still be too high to allow homogeneous nucleation, or even effective contributions to nanoparticle growth.²⁰ The difference between LVOC and ELVOC is thus crucial for the smallest particle sizes, as the former evaporate from nanoparticles while the latter do not.

Much of the research on HOM/ELVOC formation has focused on ozone-initiated oxidation, either of model compounds such as simple cyclic alkenes like cyclohexene, or of the more complex but also more atmospherically relevant α -pinene, one of the main monoterpenes emitted by vegetation, and a crucial SOA precursor. OH-initiated autoxidation of α -pinene has recently also been shown to produce significant amounts of HOM – compounds (unpublished results).

The HOMs formed through both O_3 - and OH-initiated peroxy radical autoxidation represent a new and hitherto unknown class of compounds in the atmosphere. HOMs formed from the ozonolysis of endocyclic alkenes likely contain one or two peroxyacid ($C(O)OOH$) functionalities, together with additional ketone ($C=O$), hydroperoxide ($C-OOH$) and possibly also alcohol ($C-OH$) or carboxylic acid ($C(O)OH$) groups.¹² In addition, reactions with NO_x or NO_3 may produce nitrate functional groups. Experimental observations, including the fact that these molecules are detected in the first place, indicate that HOMs have gas-phase lifetimes long enough to permit condensation (defined here as the uptake of gas molecules into a liquid phase of any composition). Even the RO_2 radical intermediates of the autoxidation process likely have lifetimes on the order of seconds or more, and might thus possibly participate in, or initiate, condensed-phase reactions.¹³ HOMs may therefore affect aerosol properties and growth, and contribute to SOA formation. However, the subsequent condensed-phase reactions of these highly functionalized polyperoxides are probably rapid, and likely include both decomposition reactions (which increase volatility), oligomerization reactions (which decrease volatility), and photolysis (which leads to new highly reactive intermediates). Due to this high reactivity, HOM-type compounds are difficult, dangerous and potentially even impossible to synthesize in pure form. The industrial chemicals most closely related to the proposed HOMs are polyperoxides such as triacetone triperoxide, TATP – a well-known and notoriously hazardous high explosive. The lack of easily available pure compound samples presents severe challenges both for calibration of HOM detection methods, and for experimentally obtaining reliable estimates of their crucial properties such as saturation vapor pressures.

Predicting the equilibrium phase partitioning of specific organic compounds requires accurate knowledge of their saturation vapor pressures as well as activity coefficients within the complex amorphous condensed phase comprising atmospheric organic particulate matter. A challenge is that the condensed-phase composition is poorly constrained. Simple bulk properties of the condensed phase such as the oxygen to carbon ratio (O:C) or the effective oxidation state of carbon ($O_{Sc} = 2 O:C - H:C$) are generally known,²¹ but even a single 100 nm particle may contain 1 million organic molecules, and in all probability more than 100,000 individual organic compounds, most of which have not been synthesized yet.^{19,21} The working hypothesis of highly simplified frameworks for atmospheric chemistry is that, on average, the complex distribution of functional groups within the organic condensed phase will result in equilibrium phase partitioning that is highly correlated first and foremost with the saturation vapor pressure.

Reliable information on the saturation vapor pressures of HOMs is thus a crucial precondition for determining their further reaction pathways, ultimate fate, and health and climate impact. While the large number of hydrogen-bonding functional groups of HOMs has been assumed to lead to low saturation vapor pressures, reliable data on their volatilities and solubilities do not exist. Quantum chemical calculations²² on clusters containing HOM-candidates from cyclohexene ozonolysis (*e.g.* a $C_6H_8O_7$ ketodiperoxoic acid) show that their cluster-forming ability is much lower than expected, indicating (though not proving or quantifying) a surprisingly high volatility. Unfortunately, the basis datasets of existing group-contribution-based empirical parameterizations for determining saturation vapor pressures of organic molecules (*e.g.* SIMPOL²³, or the widely used and generally successful Nannoolal *et al.* approach²⁴) do not contain complex polyhydroperoxides (or multiply substituted peroxy acids), and the parameterizations may therefore not be reliable for HOMs. While Compernolle *et al.*^{25,26} have

extended the Nannoolal method to include hydroperoxides and peroxy acids, their dataset includes only monofunctional molecules of these types, and they indeed explicitly caution²⁵ that the missing group-interaction parameters “can be especially important for the hydrogen-bonding hydroperoxide and peracid groups”. The EVAPORATION method developed by Compennolle *et al.*²⁶ does include a limited number of peroxides and peroxy acids in its parameterization dataset, but the errors of the predicted saturation vapor pressures are the largest precisely for these particular groups of compounds. In a recent intercomparison, O’Meara *et al.*²⁷ found that the EVAPORATION method provided the most reliable saturation vapor pressures for the compounds to which it was applicable, with Nannoolal²⁴ providing the lowest mean bias error for a larger set of compounds. However, EVAPORATION had a tendency to “increasingly underestimate vapour pressure with decreasing vapour pressure”. According to Valorso *et al.*²⁸, this is a common feature of group-contribution methods: all the methods in their comparison were found to underestimate the saturation vapor pressure of the multifunctional semivolatile species. Valorso *et al.* also found differences of several orders of magnitude in the saturation vapor pressures estimated by three different group-contribution approaches (including Nannoolal²⁴) for low-volatility products of α -pinene OH-oxidation including up to four different functional groups.

In this study, we use the COSMO-RS (Conductor-like Screening Model for Real Solvents) method,^{29,30} as implemented in the Turbomole^{31,32} and COSMOTerm programs³³, to evaluate the (subcooled) liquid saturation vapor pressures of HOM candidate structures from α -pinene ozonolysis, based on quantum chemical calculations, thus avoiding the need for system-specific empirical fitting parameters. COSMOTerm has previously been successfully applied to predict

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3 equilibrium gas-particle partitioning coefficients for alkane oxidation products relevant to SOA
4 formation.³⁴
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9 Within the COSMO-RS framework, saturation vapor pressures are computed as follows. First,
10 quantum chemical calculations are performed on the molecule of interest both in “vacuum” (to
11 obtain the reference gas-phase energy) and using COSMO, which is a type of continuum solvent
12 model (CSM).³⁵ The COSMO – calculation yields the screening charge surface (known as the σ -
13 surface) of the molecule, which is converted into a distribution function (known as the σ -profile)
14 giving the relative amount of the molecule’s surface with a certain polarity. We show an
15 illustrative σ -surface and σ -profile for the lowest-energy conformer of one of the molecules
16 studied in this work in Figure 1. The intermolecular electrostatic, hydrogen bonding and van der
17 Waals interactions between surface segments with different σ values (polarities) can then be
18 computed using various parameterizations. These are specific to the quantum-chemical method
19 but not to the actual chemical system – though the numerical values of the parameters are
20 obtained by fitting to large sets of experimental data. Multiple molecular conformations for each
21 chemical may need to be included if they have significantly different polarities and/or hydrogen
22 bonding patterns, and thus different σ -profiles. Once the molecular interactions are described, the
23 chemical potential can be computed, and together with the gas-phase energy, the saturation vapor
24 pressure can be obtained. For multicomponent mixtures, an additional parameterized
25 combinatorial term is required, but this is not relevant for the pure-compound saturation vapor
26 pressures we consider here.
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Figure 1. Top: screening charge surface (σ -surface) for the lowest-energy conformer of the $C_{10}H_{16}O_9$ molecule investigated in this study. Red regions indicate positive charge density, blue areas negative charge density. Hydrogen-bonding polar functional groups are clearly visible in the σ -surface. Bottom: the σ -profile computed from this surface, showing the relative amount of molecular surface with a certain polarity.

For compounds resembling those in the parameterization dataset of group-contribution methods, the absolute saturation vapor pressures predicted by COSMO-RS are likely somewhat less reliable than those predicted by those group-contribution methods. However, for compounds very different from the parameterization datasets, the COSMO-RS approach is more reliable, as it contains no system-specific parameters, and represents (albeit imperfectly and approximately) all of the chemical interactions present in the real chemical system.

Computational Methods

We conducted initial conformational sampling for the HOM-candidate molecules using the Spartan 14 program³⁶, following the approach described in Rissanen *et al.*¹¹ First, we performed systematic conformer sampling (for the monomers, i.e. the autoxidation products with 10 carbon

atoms) or Monte-Carlo sampling (for the dimers, i.e. the autoxidation products with 20 carbon atoms) using the MMFF force-field, in order to produce a representative set of unique conformers. Next, we computed the B3LYP/6-31+G(d) single-point energy of these structures. We then performed B3LYP/6-31+G(d) optimizations on up to 100 structures with B3LYP/6-31+G(d) single-point energies within 5 kcal/mol of the lowest-energy conformer. All MMFF and B3LYP calculations were performed on Spartan '14.

We selected the best 20 of the optimized structures for each HOM candidate (based on the energy of the B3LYP-optimized structure) for COSMO-RS calculations using Turbomole version 6.6³¹, followed by saturation vapor pressure calculations using COSMOTerm (version 15.0.2)³³. We visually inspected the structures to ensure that we included conformers with different hydrogen-bonding patterns in the saturation vapor pressure calculations (though the very large number of conformers especially for the larger HOM-candidates prevented a complete selection of all possible potential H-bonding patterns). We carried out comprehensive test calculations, which indicated that the saturation vapor pressure values were essentially converged with respect to the number of conformers once we included 10-20 of the lowest-energy conformers. We also tested the effect of including higher-energy conformers lacking, or having a smaller number of, internal H-bonds (which could potentially be more stable in the liquid phase due to increased capacity for intermolecular hydrogen bonding, and thus contribute to the saturation vapor pressures despite higher gas-phase energies). These tests indicated that the effect of such conformers on the saturation vapor pressure was negligible. For the test-set molecules (see below), we first generated the full list of conformers using Spartan '14 as described above. We then manually arranged conformers into groups with distinctly different hydrogen bonding patterns and dipole moments, and we selected the lowest-energy conformer

from each group (for a maximum of five groups per molecule) for the saturation vapor pressure calculations. As discussed in the COSMOTerm documentation³⁷, alkyl group conformational differences do not significantly affect saturation vapor pressures, so this approach is likely to give a reasonable picture of the effect of including multiple conformers on the predicted saturation vapor pressure.

We performed the COSMOTerm/Turbomole calculations using the default settings recommended by the program manuals. We first performed gas-phase and COSMO calculations using Turbomole, either at the BP/TZVP level or the BP/TZVPD-FINE level. These yielded the .cosmo input files for subsequent COSMOTerm saturation vapor pressure calculations (See the Supporting Information for the .cosmo input files for all studied HOM-candidate species). Here, “BP/TZVP” refers to a RI-DFT calculation using the B88-VWN-P86 functional, the TZVP basis set³⁸ and the associated auxiliary basis set for the RI expansion, and the default settings for the COSMO cavity construction. Similarly, “BP/TZVPD-FINE” refers to a RI-DFT single-point energy calculation on top of the BP/TZVP geometry, performed using the same density functional but the larger TZVPD basis set (and associated auxiliary basis set), and using a finer grid for the surface cavity construction in the COSMO calculations. The parameter set for the COSMOTerm chemical potential calculations using the BP/TZVPD-FINE σ -profiles contains additional terms for hydrogen bonding and van der Waals dispersion, and according to the COSMOTerm documentation often improves accuracy for systems where the default BP/TZVP approach performs poorly.³⁹ Due to the computational expense (caused primarily by the lack of parallelized versions of some of the Turbomole modules required for the BP/TZVPD-FINE calculations), we only computed the BP/TZVPD-FINE vapor pressures for the test-set molecules and the “HOM dimers” (with 20 carbon atoms) for the lowest-energy conformer of each studied

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3 system. We note that due (presumably) to small differences in the implementation of the
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5 BP/TZVPD-FINE parameterization of COSMO-RS in different Turbomole versions (*e.g.* 6.6 vs
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7 7.0), the BP/TZVPD-FINE saturation vapor pressures predicted (for identical molecular
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9 structures, using the same version of COSMOTerm) may differ by some tens of percent
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11 depending on the Turbomole version used to generate the .cosmo files. All saturation vapor
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13 pressures in this study are computed using .cosmo files generated by the same version
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15 (Turbomole v 6.6.) and are therefore intercomparable.
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21 We evaluated the Nannoolal *et al.*²⁴ and EVAPORATION²⁶ group-contribution saturation
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23 vapor pressures using the UManSysProp online system⁴⁰, in the former case using the Nannoolal
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25 *et al.*⁴¹ boiling point parameterization, as recommended *e.g.* by O'Meara *et al.*²⁷ The
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27 EVAPORATION method does not require a boiling point parameterization (despite the
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29 requirement to select one in the UManSysProp input). We note that using Nannoolal *et al.*²⁴
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31 together with the older boiling point parameterizations available in UManSysProp led to very
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33 different (and physically unreasonably low, *e.g.* 10^{-32} bar) saturation vapor pressure values for
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35 some of the HOM candidates. We generated the SMILES – strings required by UManSysProp
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37 from the xyz co-ordinate files produced by Spartan using the OpenBabel conversion program⁴²
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39 in order to eliminate errors from incorrect structure assignments (the Spartan program produced
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41 incorrect SMILES strings for some of the peroxide compounds in this study).
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48 We derived the SIMPOL saturation vapor pressures using chemical group-contribution
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50 parameters from Pankow and Asher.²³ The SIMPOL method is based on nonlinear regression
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52 least-square fitting to measured saturation vapor pressures of 272 organic compounds, with
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54 saturation vapor pressures spanning 14 orders of magnitude. Only seven of these compounds
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56 contain hydroperoxide- or peroxyacid functional groups. In total SIMPOL considers 30 first- or
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second-order chemical groups of which the number of carbon atoms, non-aromatic rings (second-order), hydroxyl-, aldehyde-, ketone-, carboxylic acid-, peroxide-, hydroperoxide- and carbonylperoxyacid groups are relevant for the 16 HOMs candidate structures considered in this work.

Results and discussion

Testing COSMOTerm saturation vapor pressure predictions for atmospherically relevant molecules

The performance of COSMO-RS/COSMOTerm has been extensively validated for several liquid-phase thermodynamic parameters such as partition coefficients, activity coefficients and solvation free energies (see *e.g.* Klamt⁴³ for a review). Absolute saturation vapor pressures (in the absence of experimental data) are unfortunately not the main focus on COSMO-RS theory development, and systematic benchmarking or validation studies on the accuracy of COSMOTerm – computed saturation vapor pressures are therefore scarce. According to Eckert and Klamt³⁰, the maximum deviation for the saturation vapor pressure predicted for the parameterization dataset of 310 compounds is a factor of 3.7. However, the accuracy of the saturation vapor pressure predictions, unlike the activity coefficient, Henry's law coefficient and excess free energy predictions, are not subsequently evaluated on a larger test-set, making the quantitative assessment of error margins difficult. In a MSc thesis work, A. Gasawi⁴⁴ found that for a test-set of 71 pure compounds, the COSMOTerm saturation vapor pressures between 300 and 500 K were between 3% and 142% of the experimental values. The accuracy of saturation vapor pressure predictions can also be estimated from the accuracy of the COSMOTerm solvation free energies, which are generally⁴⁵ better than 1 kcal/mol for the standard BP/TZVP

parameterization – implying that the saturation vapor pressure is accurate to about a factor of 5 or better (though with significantly larger errors possible for some outliers, as indicated already by the work of Gasawi⁴⁴). The BP/TZVPD-FINE saturation vapor pressure predictions have recently been tested on an extremely large saturation vapor pressure dataset of 21607 data points⁴⁶ (including some of the molecules of the parameterization dataset), with a RMS deviation of a factor of 1.5 and a maximum deviation of a factor of 50 (private communications, Dr. Jens Reinisch).

Before computing the saturation vapor pressures of HOM candidate structures, we used COSMOTerm to compute the saturation vapor pressures for a small set of atmospherically relevant organic compounds with O:C ratios ranging from 0 to 0.8, for which experimental saturation vapor pressures are known. These molecules were fluoranthene, 4-tert-butylcatechol, adipic acid, pimelic acid and levoglucosan (see Figure S1 in the Supporting Information for molecular structures). In addition to confirming the order-of-magnitude applicability of the COSMOTerm approach to atmospherically relevant systems, the purpose of these calculations was to test whether or not there is a systematic trend in the errors of the predicted saturation vapor pressure with respect to the oxidation state of the molecules. We also calculated the saturation vapor pressures of peroxyformic and peroxyacetic acid in order to assess the performance of COSMOTerm for the peroxy acids formed by autoxidation.

The results, presented in Table 1, are more or less in line with literature benchmarking studies. While far from quantitative, the COSMOTerm saturation vapor pressure predictions are within a factor of 50 of the measured values. This is roughly comparable to the performance of the group-contribution methods, which are within a factor of 20 of the experimental values for most of the molecules (pimelic acid, adipic acid, levoglucosan, peroxyacetic acid; see Table S1 in the

Supporting Information). The worst mismatch between SIMPOL²³ and experimental data was a factor of 72, comparable to the performance of COSMOTerm. On the other hand, the other two group-contribution methods had much more extreme outliers than COSMOTerm, namely an overestimation of the saturation vapor pressure of fluoranthene by a factor of 6600 by Nannoolal²⁴/Nannoolal⁴¹, and an overestimation of the saturation vapor pressure of 4-tertbutylcatechol by a factor of 3.8×10^6 by EVAPORATION.²⁶ These large outliers may be illustrative of the danger of using group-contribution methods for chemical compounds far from their parameterization dataset. For example, the EVAPORATION method is not parameterized for aromatic compounds,²⁷ so the poor performance for 4-tertbutylcatechol should not be surprising. See the Supporting Information (Table S1) for saturation vapor pressures computed with the three group-contribution methods used in this study for the molecules in Table 1.

In contrast to the test-set of Gasawi⁴⁴, where the largest overprediction by COSMOTerm was less than a factor of 1.5, overprediction was both more frequent and more extreme than underprediction for our limited test-set: the only molecule for which the saturation vapor pressure was underpredicted was 4-tert-butylcatechol. Apart from this, we could discern no systematic trends in the size or direction of the error, for example with respect to the O:C ratio. The saturation vapor pressure of peroxyacetic acid is overestimated by about an order of magnitude by all the COSMOTerm approaches. We were unable to find a genuine experimental value for the saturation vapor pressure of peroxyformic acid; *e.g.* the value quoted in the PubChem database turned out to be a modeled estimate rather than an experimental result.

Including multiple conformers in the calculations always decreased the saturation vapor pressures for this dataset, but by less than an order of magnitude. This improved the agreement with experiments for all molecules except 4-tert-butylcatechol: however, for this molecule the

difference between single- and multiconformer results was also very small, as it has little conformational flexibility. Using the BP/TZVPD-FINE parameterization instead of the standard BP/TZVP parameterization for a single conformer could either increase or decrease the predicted saturation vapor pressure, but again by less than an order of magnitude. Using the BP/TZVPD-FINE parameterization for a single conformer did not systematically reduce the error of the predicted saturation vapor pressures (in the sense of always decreasing the difference between the predicted and measured values). This indicates that for a rough order-of-magnitude estimate of the saturation vapor pressure, a BP/TZVP calculation on a single low-energy conformer may be sufficient and cost-effective, though including multiple conformers is likely to improve the accuracy of the result. Also, we tentatively conclude that the COSMOTerm – predicted saturation vapor pressures for the molecules in this study are more likely to be too high than too low – in contrast to the group-contribution methods.²⁸

Table 1. Modeled and measured saturation vapor pressures for a set of test compounds (all values in bar, and at 298.15 K).

molecule	p _{sat} , single conformer, BP/TZVP	p _{sat} , multiple conformers, BP/TZVP	p _{sat} , single conformer, BP/TZVPD-FINE	Experimental	Reference
Fluoranthene	5.4×10^{-7}	5.4×10^{-7}	4.9×10^{-7}	1.2×10^{-8}	47
4-t.butylcatechol	1.5×10^{-6}	1.4×10^{-6}	3.4×10^{-6}	3.7×10^{-6}	48
Pimelic acid	5.0×10^{-8}	2.0×10^{-8}	2.2×10^{-8}	2.7×10^{-9}	49
Adipic acid	6.9×10^{-8}	3.6×10^{-8}	3.6×10^{-8}	2.1×10^{-9}	49
Levogluconan	1.6×10^{-8}	8.5×10^{-9}	9.5×10^{-8}	1.9×10^{-9}	49

Peroxyformic acid	6.0×10^{-1}	4.9×10^{-1}	1.1×10^0	-	-
Peroxyacetic acid	1.3×10^{-1}	1.2×10^{-1}	2.3×10^{-1}	1.9×10^{-2}	50

Selecting HOM candidate structures

For this study, we have selected 16 different potential HOM autoxidation products, all of which could possibly be formed in the O₃-initiated autoxidation of α -pinene. The precise reaction pathway of this process is as yet unknown. High-resolution mass spectrometric measurements, combined with *e.g.* H/D exchange experiments, yield the elemental composition and the number of acidic (OH or OOH) hydrogen atoms in the autoxidation products, but no other information on their actual molecular structures. High-level quantum chemical calculations⁵¹ on the H-shifts of the first-generation RO₂ radicals formed in α -pinene ozonolysis (with the elemental composition C₁₀H₁₅O₄) strongly indicate that in order to add more than 4-5 oxygen atoms to the carbon backbone through autoxidation, the cyclobutyl ring left intact by the ozonolysis reaction must be broken, either by bimolecular reactions forming alkoxy radicals (which subsequently undergo prompt ring-breaking), or via more speculative unimolecular channels. Ring-breaking reactions inevitably increase the conformational flexibility of the carbon backbone significantly, and allow for H-shifts from several different sites, including not only the aldehydic groups, but also tertiary carbon atoms and carbon atoms adjacent to ketone groups, which are known to enhance H-shift rates.⁵²

Once RO₂ radicals with at least one OOH group are formed, ultra-fast COO...H...OOC hydrogen shifts⁵³ very likely “scramble” the position of the radical group, further increasing the number of possible structures and reaction paths. Bimolecular reactions (with *e.g.* HO₂, NO or other RO₂) can either propagate the reaction chain through alkoxy radical formation, or terminate it through several possible channels (including “dimer” formation, possibly through direct or indirect reactions of the type RO₂ + RO₂ ⇒ ROOR + O₂). Unimolecular termination reactions via OH loss are also possible, mainly after H-shifts from carbon atoms with hydroperoxy groups.

This multitude of reactions and reaction pathways means that, despite the combined experimental and theoretical constraints, there are hundreds of possible HOM structures in the α-pinene + O₃ system alone. In this study, we have attempted to model a representative sample of these possible structures, shown in Figure 2 (with three-dimensional structures of the lowest-energy conformers shown in Figure 3). The set of HOM-candidate structures included in the study are not intended to correspond only to the “most probable” HOM structures (which, based on our current limited mechanistic understanding, contain mainly ketone, hydroperoxy and peroxy acid functional groups), but also to include chemically more diverse functionalities, including also alcohol, carboxylic acid and endoperoxy (C-O-O-C) groups. The formation of some of the studied HOM-candidate structures thus requires fairly speculative reaction mechanisms, such as ring-opening via Criegee Intermediates,⁵⁴ or peroxy radical ring closure to form endoperoxides.^{Error! Bookmark not defined.} We provide brief descriptions of possible reaction paths leading to all 16 studied compounds in the Supporting Information.

Figure 2. HOM-candidate structures investigated in this study. a) $C_{10}H_{16}O_4$ -iso1, b) $C_{10}H_{16}O_4$ -iso2, c) $C_{10}H_{16}O_4$ -iso3, d) $C_{10}H_{16}O_5$, e) $C_{10}H_{16}O_6$ -iso1, f) $C_{10}H_{16}O_6$ -iso2, g) $C_{10}H_{16}O_7$ -iso1, h) $C_{10}H_{16}O_7$ -iso2, i) $C_{10}H_{16}O_8$ -iso1, j) $C_{10}H_{16}O_8$ -iso2, k) $C_{10}H_{16}O_8$ -iso3, l) $C_{10}H_{16}O_9$, m) $C_{10}H_{16}O_{10}$, n) $C_{20}H_{30}O_{10}$ -iso1, o) $C_{20}H_{30}O_{10}$ -iso2, p) $C_{20}H_{30}O_{12}$.

Figure 3. Lowest-energy conformers of the HOM-candidate structures shown in Figure 2, at the BP/TZVP level with COSMO-RS. Color coding: green=carbon, red=oxygen, white=hydrogen.

a) $\text{C}_{10}\text{H}_{16}\text{O}_4$ -iso1, b) $\text{C}_{10}\text{H}_{16}\text{O}_4$ -iso2, c) $\text{C}_{10}\text{H}_{16}\text{O}_4$ -iso3, d) $\text{C}_{10}\text{H}_{16}\text{O}_5$, e) $\text{C}_{10}\text{H}_{16}\text{O}_6$ -iso1, f) $\text{C}_{10}\text{H}_{16}\text{O}_6$ -iso2, g) $\text{C}_{10}\text{H}_{16}\text{O}_7$ -iso1, h) $\text{C}_{10}\text{H}_{16}\text{O}_7$ -iso2, i) $\text{C}_{10}\text{H}_{16}\text{O}_8$ -iso1, j) $\text{C}_{10}\text{H}_{16}\text{O}_8$ -iso2, k) $\text{C}_{10}\text{H}_{16}\text{O}_8$ -iso3, l) $\text{C}_{10}\text{H}_{16}\text{O}_9$, m) $\text{C}_{10}\text{H}_{16}\text{O}_{10}$, n) $\text{C}_{20}\text{H}_{30}\text{O}_{10}$ -iso1, o) $\text{C}_{20}\text{H}_{30}\text{O}_{10}$ -iso2, p) $\text{C}_{20}\text{H}_{30}\text{O}_{12}$.

Saturation vapor pressures of HOM candidates

The saturation vapor pressures of the HOM candidates computed using COSMOTerm are given in Table 2. For comparison, we give values computed using the Nannoolal *et al.*,²⁴ EVAPORATION²⁶ and SIMPOL²³ group-contribution based parameterizations in Table 3.

Table 2. Saturation vapor pressures (in bar) at 298.15 K for HOM-candidate structures, using COSMOTerm and the BP/TZVP or BP/TZVPD-FINE parameterizations for COSMO-RS, and either one or 20 conformers.^a

Molecule	p _{sat} , single conformer BP/TZVP	p _{sat} , multiple conformers, BP/TZVP	p _{sat} , single conformer BP/TZVPD-FINE	p _{sat} , multiple conformersBP/TZVPD- FINE
C ₁₀ H ₁₆ O ₄ -iso1	2.6×10 ⁻⁷	1.1×10 ⁻⁷	1.1×10 ⁻⁶	5.2×10 ⁻⁷
C ₁₀ H ₁₆ O ₄ -iso2	2.4×10 ⁻⁸	6.3×10 ⁻⁸	4.7×10 ⁻⁸	1.5×10 ⁻⁷
C ₁₀ H ₁₆ O ₄ -iso3 ^a	1.6×10 ⁻⁷	1.7×10 ⁻⁷	2.2×10 ⁻⁷	2.1×10 ⁻⁷
C ₁₀ H ₁₆ O ₅	8.0×10 ⁻⁷	6.0×10 ⁻⁷	1.0×10 ⁻⁶	8.5×10 ⁻⁷
C ₁₀ H ₁₆ O ₆ -iso1	6.4×10 ⁻⁷	8.7×10 ⁻⁸	3.5×10 ⁻⁶	3.6×10 ⁻⁷
C ₁₀ H ₁₆ O ₆ -iso2	1.3×10 ⁻⁸	1.1×10 ⁻⁸	8.3×10 ⁻⁹	9.3×10 ⁻⁹
C ₁₀ H ₁₆ O ₇ -iso1	3.2×10 ⁻⁷	1.7×10 ⁻⁷	1.2×10 ⁻⁶	7.0×10 ⁻⁷
C ₁₀ H ₁₆ O ₇ -iso2	2.8×10 ⁻⁹	3.1×10 ⁻⁹	1.5×10 ⁻⁹	1.7×10 ⁻⁹
C ₁₀ H ₁₆ O ₈ -iso1	5.6×10 ⁻⁹	2.4×10 ⁻⁹	9.1×10 ⁻⁹	9.4×10 ⁻¹⁰
C ₁₀ H ₁₆ O ₈ -iso2	1.0×10 ⁻⁷	6.1×10 ⁻⁸	4.1×10 ⁻⁷	1.5×10 ⁻⁷
C ₁₀ H ₁₆ O ₈ -iso3	1.3×10 ⁻⁹	1.9×10 ⁻⁹	7.7×10 ⁻⁹	1.2×10 ⁻⁸
C ₁₀ H ₁₆ O ₉	4.3×10 ⁻⁸	6.2×10 ⁻⁸	2.4×10 ⁻⁷	2.3×10 ⁻⁷
C ₁₀ H ₁₆ O ₁₀	1.9×10 ⁻⁹	1.6×10 ⁻¹⁰	3.5×10 ⁻⁸	1.7×10 ⁻⁹
C ₂₀ H ₃₀ O ₁₀ -iso1	3.2×10 ⁻¹⁶	9.0×10 ⁻¹⁵	1.3×10 ⁻¹²	-

C ₂₀ H ₃₀ O ₁₀ -iso2	1.0×10 ⁻¹³	1.6×10 ⁻¹²	5.7×10 ⁻¹³	-
C ₂₀ H ₃₀ O ₁₂	9.4×10 ⁻¹²	3.0×10 ⁻¹²	7.1×10 ⁻¹¹	-

a) Only ten unique conformers were found for the C₁₀H₁₆O₄-iso3 structure.

Table 3. Saturation vapor pressures (in bar) at 298.15 K for HOM-candidate structures, using the Nannoolal *et al.* vapor pressure parameterization²⁴ with the Nannoolal *et al.* boiling point parameterization⁴¹ (Nannoolal/Nannoolal), the EVAPORATION parameterization²⁶, or the SIMPOL²³ parameterization.

Molecule	p _{sat} , Nannoolal/Nannoolal	p _{sat} , EVAPORATION	p _{sat} , SIMPOL
C ₁₀ H ₁₆ O ₄ -iso1	1.8×10 ⁻⁶	9.5×10 ⁻⁷	7.6×10 ⁻⁸
C ₁₀ H ₁₆ O ₄ -iso2	3.3×10 ⁻⁶	1.5×10 ⁻⁶	7.6×10 ⁻⁸
C ₁₀ H ₁₆ O ₄ -iso3	7.2×10 ⁻⁷	7.5×10 ⁻⁷	7.6×10 ⁻⁸
C ₁₀ H ₁₆ O ₅	5.8×10 ⁻⁸	1.8×10 ⁻⁸	9.3×10 ⁻⁹
C ₁₀ H ₁₆ O ₆ -iso1	1.1×10 ⁻⁸	1.1×10 ⁻⁸	1.3×10 ⁻⁹
C ₁₀ H ₁₆ O ₆ -iso2	8.3×10 ⁻¹¹	3.4×10 ⁻¹¹	6.0×10 ⁻¹¹
C ₁₀ H ₁₆ O ₇ -iso1	3.9×10 ⁻¹⁰	3.2×10 ⁻¹⁰	7.2×10 ⁻¹⁰
C ₁₀ H ₁₆ O ₇ -iso2	2.6×10 ⁻¹⁴	1.1×10 ⁻¹²	3.9×10 ⁻¹³
C ₁₀ H ₁₆ O ₈ -iso1	4.6×10 ⁻¹⁶	2.2×10 ⁻¹⁴	2.2×10 ⁻¹³
C ₁₀ H ₁₆ O ₈ -iso2	1.9×10 ⁻¹³	1.1×10 ⁻¹¹	4.7×10 ⁻¹²
C ₁₀ H ₁₆ O ₈ -iso3	2.0×10 ⁻⁹	6.7×10 ⁻¹⁰	2.4×10 ⁻⁹
C ₁₀ H ₁₆ O ₉	3.9×10 ⁻¹⁵	2.2×10 ⁻¹³	2.6×10 ⁻¹²
C ₁₀ H ₁₆ O ₁₀	4.4×10 ⁻¹⁴	1.8×10 ⁻¹³	8.7×10 ⁻¹²
C ₂₀ H ₃₀ O ₁₀ -iso1	8.3×10 ⁻¹⁰	2.1×10 ⁻¹⁴	9.5×10 ⁻¹⁸
C ₂₀ H ₃₀ O ₁₀ -iso2	2.5×10 ⁻¹¹	1.4×10 ⁻¹⁵	8.0×10 ⁻¹⁶

$C_{20}H_{30}O_{12}$	2.3×10^{-12}	1.9×10^{-17}	2.9×10^{-18}
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We used four levels of theory to compute the saturation vapor pressure with COSMOTerm: BP/TZVP σ -profiles for the single lowest-energy conformer; BP/TZVP σ -profiles for the 20 lowest-energy conformers; BP/TZVPD-FINE σ -profiles for the single lowest-energy conformer; or BP/TZVPD-FINE σ -profiles for the 20 lowest-energy conformers excluding the “dimers”. The four sets of saturation vapor pressures computed by COSMOTerm are within a factor of 100 of each other for all cases except for $C_{10}H_{16}O_{10}$ and $C_{20}H_{30}O_{10}$ -iso1, for which the ratio between the highest and lowest predicted saturation vapor pressures are around 200 and 4000, respectively. There is no clear systematic relation between the four sets of COSMOTerm predictions. Increasing the number of conformers can either increase or decrease the predicted saturation vapor pressures of the HOM-candidate molecules, with decreases being somewhat more frequent in the studied set (9 cases of lower and 7 cases of higher vapor pressures at the BP/TZVP level, and 9 cases of lower and 4 cases of higher vapor pressures at BP/TZVPD-FINE level). Using the BP/TZVPD-FINE parameterization instead of the default BP/TZVP parameterization usually increases the predicted saturation vapor pressures, but in a few cases we observe the opposite (14 cases of higher and 2 cases of lower vapor pressures for the single-conformer predictions, and 10 cases of higher and 3 cases of lower vapor pressures for the multi-conformer predictions). The two improvements to the BP/TZVP single-conformer predictions thus often act in opposite directions.

The three group-contribution methods mostly predict lower saturation vapor pressures than the four COSMOTerm – based approaches. The maximum difference between all three group-contribution predictions and any of the four COSMOTerm saturation vapor pressure

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3 datasets is 7-8 orders of magnitude. The largest differences are observed for the most highly
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5 oxidized monomers, and for the dimers. For the least oxidized monomers (the three $C_{10}H_{16}O_4$
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7 isomers), both Nannoolal/Nannoolal and EVAPORATION actually predict somewhat higher
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9 saturation vapor pressures than most of the COSMOTerm approaches, though all methods are
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11 in reasonable agreement for these species. The Nannoolal/Nannoolal method also predicts
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13 higher saturation vapor pressures for the dimers than most of the COSMOTerm approaches, in
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15 contrast to the trend observed for the more oxidized monomers.
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21 The three group-contribution methods are within 3 orders of magnitude of each other for
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23 the monomers, but disagree by up to 8 orders of magnitude for the dimers (with the
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25 Nannoolal/Nannoolal and SIMPOL predictions of the saturation vapor pressure for $C_{20}H_{30}O_{10}$ -
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27 iso1 being 8.3×10^{-10} bar and 9.5×10^{-18} bar, respectively). Even the somewhat more sophisticated
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29 Nannoolal/Nannoolal and EVAPORATION methods disagree by 4-5 orders of magnitude for the
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31 dimer saturation vapor pressures.
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36 To illustrate the spread in the saturation vapor pressure predictions of the different
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38 methods, Figure 4 shows the saturation vapor pressures predicted by two of the COSMOTerm
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40 approaches and the EVAPORATION method, plotted against the SIMPOL saturation vapor
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42 pressures.
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Figure 4. Comparison of saturation vapor pressure predictions (in bar, at 298 K) by various methods, versus the group-contribution method SIMPOL. Values are given for COSMOTerm using the BP/TZVP parameterization and multiple conformers (blue diamonds), COSMOTerm using the BP/TZVPD-FINE parameterization and a single conformer (red squares) and the EVAPORATION group-contribution method (green triangles). A 1:1 line is shown in black to aid the comparison.

Compared to the group-contribution methods, COSMOTerm predicts larger differences between positional isomers (where the same functional groups are located on different positions on the carbon chain, *e.g.* the three C₁₀H₁₆O₄ isomers), but generally somewhat smaller

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3 differences between functional group isomers (with the same elemental composition but different
4 functional groups, *e.g.* the three $C_{10}H_{16}O_8$ isomers). Especially the former result is unsurprising,
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6 given the limited ability of group-contribution methods to distinguish between positional
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8 isomers. By construction, SIMPOL does not distinguish between positional isomers at all. For
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10 the HOM monomers, SIMPOL predicts differences between functional group isomers that are
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12 mostly larger than those predicted by COSMOTerm, but smaller than those predicted by
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14 Nannoolal/Nannoolal or EVAPORATION.
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20 All methods agree that the hydroperoxycarboxylic acids $C_{10}H_{16}O_6$ -iso2 and $C_{10}H_{16}O_8$ -
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22 iso1 have lower saturation vapor pressures than their hydroxyperoxy acid isomers $C_{10}H_{16}O_6$ -iso1
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24 and $C_{10}H_{16}O_8$ -iso2, respectively, and that the hydroxy-hydroperoxy-carboxylic acid $C_{10}H_{16}O_7$ -
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26 iso2 has a lower saturation vapor pressure than its hydroperoxy-peroxy acid isomer $C_{10}H_{16}O_7$ -
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28 iso1. In contrast, the methods disagree on the effect of endoperoxide groups on the saturation
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30 vapor pressure: Nannoolal/Nannoolal, EVAPORATION, SIMPOL and COSMOTerm using
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32 multiple conformers and the BP/TZVPD-FINE parameterization predict that the $C_{10}H_{16}O_8$ -iso3
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34 structure containing an endoperoxide functional group has a saturation vapor pressure 4×10^6 ,
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36 3×10^4 , 1×10^4 or 13 times higher, respectively, than the $C_{10}H_{16}O_8$ -iso1 isomer, while the three
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38 remaining COSMOTerm approaches predict the opposite (though by less than a factor of 5).
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45 All methods also agree that replacing a carboxylic acid group by a peroxy acid group (*i.e.*
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47 going from $C_{10}H_{16}O_6$ -iso2 to $C_{10}H_{16}O_7$ -iso1, from $C_{10}H_{16}O_7$ -iso2 to $C_{10}H_{16}O_8$ -iso2, or from
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49 $C_{10}H_{16}O_8$ -iso1 to $C_{10}H_{16}O_9$) increases the saturation vapor pressure. According to the group-
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51 contribution methods, replacing an alcohol group by a hydroperoxide group (*i.e.* going from
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53 $C_{10}H_{16}O_7$ -iso2 to $C_{10}H_{16}O_8$ -iso1, from $C_{10}H_{16}O_8$ -iso2 to $C_{10}H_{16}O_9$, or from $C_{20}H_{30}O_{10}$ -iso1 to
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55 $C_{20}H_{30}O_{12}$) always lowers the saturation vapor pressure. The differences between OH/OOH pairs
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predicted by Nannoolal/Nannoolal and EVAPORATION are larger than those predicted by SIMPOL. With COSMOTerm, the effect of the OH/OOH substitution depends on the exact approach (single or multiple conformers, BP/TZVP or BP/TZVP-FINE) and the molecules in question. For the monomers, COSMOTerm usually predict fairly small (less than a factor of 2) changes in either direction upon substitution of OH groups by OOH groups. In contrast, COSMOTerm predicts the $C_{20}H_{30}O_{12}$ dimer structure with two OOH groups to have a much higher saturation vapor pressure than the corresponding $C_{20}H_{30}O_{10}$ -iso1 structure with two OH groups.

As expected, all methods qualitatively predict that the saturation vapor pressure usually tends to decrease with increasing oxidation state. However, the magnitude of this decrease is much smaller (and much more frequently reversed) for the COSMOTerm – based approaches than for the group-contribution methods. For example, the decrease in saturation vapor pressure in going from $C_{10}H_{16}O_4$ -iso3 to $C_{10}H_{16}O_9$, which represent different termination products of the same autoxidation chain (see Fig 12 in Kurtén *et al.*⁵¹) is less than a factor of 10 according to COSMOTerm (with the BP/TZVPD-FINE - based approaches actually predicting a small increase), but a factor of 2×10^8 , 3×10^6 and 3×10^4 according to Nannoolal/Nannoolal, EVAPORATION and SIMPOL, respectively. In Figure 5 we illustrate the different trends with respect to oxidation state in a two-dimensional volatility-oxidation space,¹⁹ plotting the average carbon oxidation states against the saturation vapor pressures predicted by four of the methods for the different ROOH termination products of the same autoxidation chain. The average carbon oxidation state we use here is the empirical formulation easily derived from mass-spectrometer observations ($O_{Sc} = 2 O:C - H:C$), though the actual oxidation state of carbon is much lower for

–OOH functional group addition (the second oxygen atom does not increase the carbon oxidation state).

Figure 5. The average carbon oxidation state ($\overline{OS}_c$, see text for definition) of four autooxidation products ($\text{C}_{10}\text{H}_{16}\text{O}_4\text{-iso3}$, $\text{C}_{10}\text{H}_{16}\text{O}_5$, $\text{C}_{10}\text{H}_{16}\text{O}_7\text{-iso1}$ and $\text{C}_{10}\text{H}_{16}\text{O}_9$) plotted against the logarithms of the saturation vapor pressure (in bar, at 298 K) predicted by four different methods: COSMOTerm using the BP/TZVP parameterization and multiple conformers (blue diamonds), COSMOTerm using the BP/TZVPD-FINE parameterization and a single conformer (red squares), the EVAPORATION group-contribution method (green triangles), and the SIMPOL group-contribution method (purple crosses). The four products (shown schematically in the right-hand-side of the figure) are all ROOH termination products of the same autooxidation chain

(shown in Fig 12 in Kurtén *et al.*⁵¹), which involves one bimolecular step forming an alkoxy radical (which promptly leads to ring opening and formation of a keto-alkyl radical) in addition to the peroxy radical H-shifts and O₂ additions.

A large part of the difference between COSMOTherm and the other methods is very likely due to its more detailed treatment of intramolecular hydrogen bonds. These tend to stabilize the gas-phase molecules relative to the liquid phase (or even relative to small clusters²²), and thus increase the saturation vapor pressure. In this particular system, breaking of the cyclobutyl ring (in going from C₁₀H₁₆O₄ to the more highly oxidized products) increases the flexibility of the molecule, and allows for more intramolecular H-bonding as more and more polar functional groups are added. This is illustrated by the difference in saturation vapor pressures of C₁₀H₁₆O₄-iso3 and C₁₀H₁₆O₅ (see also Figure 5), which differ only by the absence of a cyclobutyl ring and the presence of a ketone group in the latter structure. All COSMOTherm-based approaches predict an increase in the saturation vapor pressure in going from C₁₀H₁₆O₄-iso3 to C₁₀H₁₆O₅, as the increased capacity for intramolecular hydrogen bonding outweighs the effect of the ketone group. The group-contribution methods do not account for this increased H-bonding, and thus predict a significant decrease in the saturation vapor pressure.

Due to the intramolecular H-bonds, the decrease in saturation vapor pressures as a function of oxidation state for the studied set of α -pinene autoxidation products can be expected to be much smaller than that predicted by the group-contribution methods. The latter are well-known^{27,28} to overestimate the decrease in volatility due to increasing functionalization, in part due to the limited ability of these methods to account for effects such as intramolecular H-bonding. As can be seen from Figure 3, the HOM candidates in this study contain between 1 and

3 intramolecular hydrogen bonds. Assuming that each bond stabilizes the molecule in the gas phase (with respect to the liquid phase) by 2-4 kcal/mol in terms of the free energy, this would imply an increase in the saturation vapor pressure of between a factor of 30 and 900 per H-bond, or by over 8 orders of magnitude for molecules with three internal H-bonds. Due to the lack of group-interaction terms describing the H-bonding of peroxide or peroxy acid groups in the group-contribution methods used here, this effect is entirely neglected in their saturation vapor pressure predictions. The increasing disagreement between COSMOtherm and the group-contribution methods as a function of the oxidation state of the HOM monomers (see *e.g.* Figure 5) could thus in principle be entirely due to the neglect of the effect of internal H-bonds by the group-contribution methods.

In the absence of measured saturation vapor pressure data on any HOM-type molecules, it is difficult to evaluate which set of predictions is more reliable in an absolute sense. In addition to the arguments presented above, another possible approach for evaluating the reliability of the different families of predictions is to examine whether or not they are even internally consistent, for example by comparing the effects of small structural changes on the saturation vapor pressures. The Nannoolal/Nannoolal saturation vapor pressure dataset in particular seems to contain some unrealistic predictions. For example, adding just a single OOH group to C₁₀H₁₆O₈-iso3 to form C₁₀H₁₆O₁₀ should, according to this method, result in a decrease of the saturation vapor pressure by a factor of 45 000. The single-conformer COSMOtherm predictions of a saturation vapor pressure increase upon OOH addition are similarly unrealistic, though the magnitude of the effect is much smaller. The multiconformer COSMOtherm and SIMPOL predictions of a decrease of about a factor of 10 and 300, respectively, seem more plausible, while the EVAPORATION prediction of a decrease by a factor of 3700, while high, is not

completely implausible. Other odd predictions by Nannoolal/Nannoolal include the 15 000 – fold difference in saturation vapor pressures predicted for the two $C_{10}H_{16}O_7$ isomers (for which all other approaches predict more reasonable differences of 2-3 orders of magnitude), the above-mentioned 4×10^6 – fold difference in vapor pressures between $C_{10}H_{16}O_8$ -iso3 and $C_{10}H_{16}O_8$ -iso1, and – perhaps oddest of all – the prediction that the saturation vapor pressure of the C_{20} dimers are considerably higher than that of the C_{10} monomers, despite having twice the number of carbon atoms and an equal or greater number of oxygen atoms. The strange behavior of the Nannoolal/Nannoolal method is likely due to the fact that parameters describing hydroperoxide, endoperoxide or peroxy acid groups are entirely missing from the Nannoolal *et al.* parameterization,²⁴ as also noted (and cautioned) by Compennolle *et al.*²⁵ The Nannoolal/Nannoolal method can therefore not be expected to produce reliable results for molecules containing multiple (or even any) such groups. The parameterization dataset of SIMPOL does not contain multifunctional hydroperoxides or peroxyacids either, but due to its greater simplicity, the method is likely more robust – as indicated by the lack of serious internal inconsistencies in the SIMPOL – predicted saturation vapor pressures. The EVAPORATION method²⁵ does contain parameters describing the effect of single hydroperoxide or peroxy acid groups, but does not have sufficient data in the parameterization dataset to describe their interactions with each other (or with other groups). It can therefore be expected to be fairly accurate for the less functionalized monomers, and while it neglects *e.g.* the effect of intramolecular H-bonds in the more oxidized monomers, its predictions are internally consistent. The more advanced (multiconformer and/or BP/TZVP-FINE) COSMOTerm – based predictions are also free from obvious major internal inconsistencies in the monomer saturation vapor pressures, unless the exceptionally small change in saturation vapor pressure in going from

$C_{10}H_{16}O_4$ -iso3 to $C_{10}H_{16}O_9$ is counted as such. For the dimers, the large (between 50-fold and 30 000-fold depending on the method) increase in saturation vapor pressure in going from $C_{20}H_{30}O_{10}$ -iso1 to $C_{20}H_{30}O_{12}$ could be considered an inconsistency, as the COSMOTerm results for the monomers indicate that replacement of OH by OOH groups should not lead to enormous changes in saturation vapor pressures in either direction. This increase is also hard to justify solely in terms of the intramolecular H-bonds of $C_{20}H_{30}O_{12}$, as also the $C_{20}H_{30}O_{10}$ -iso1 molecule contains two internal H-bonds, though these might – especially relative to the intermolecular bonds in the liquid phase - be weaker due to the more limited flexibility of the OH groups. It seems likely that while the group-contribution methods neglect the effects of intramolecular H-bonds on the HOM saturation vapor pressures, COSMOTerm may be overestimating these effects, possibly due to its limited ability to model the rearrangement of molecular structures toward their optimal intermolecular H-bonding patterns in the liquid phase. This is supported by the observation that COSMOTerm somewhat overestimates the saturation vapor pressures of all the molecules in our test-set (Table 1) which possess both conformational flexibility, and the ability to form intramolecular H-bonds.

Based on a cautious interpretation of the literature benchmarks and our limited atmospherically relevant test-set (Table 1), the error margins of the COSMOTerm saturation vapor pressures for the exotic multifunctional HOM molecules are probably at least around a factor of 100, with overprediction being more likely than underprediction. As the SIMPOL method neglects any position-dependent interactions between functional groups (*e.g.* intramolecular H-bonds, which are certainly present in these systems, as indicated by Figure 3), it likely has at least a similar error margin for these multifunctional compounds. The Nannoolal/Nannoolal predictions, as mentioned above, should probably be disregarded due to

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3 this method's lack of parameters describing the studied functional groups. The EVAPORATION
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5 predictions for these compounds should certainly be better than the Nannoolal/Nannoolal ones,
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7 but as suggested by Valorso *et al.*²⁸ and O'Meara *et al.*²⁷, they likely significantly underestimate
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9 the saturation vapor pressures of the most highly oxidized (and thus functionalized) compounds,
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11 in this case mainly due to the neglect of intramolecular H-bonds. The same very probably applies
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13 also to SIMPOL. The error margin of the EVAPORATION method is thus unlikely to be any
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15 smaller than that of COSMOTerm or SIMPOL, at least for the more highly oxidized monomers,
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17 or for the dimers.
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23 The COSMOTerm, EVAPORATION and SIMPOL saturation vapor pressure
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25 predictions for the monomers are thus all compatible with each other, in the sense of their
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27 (admittedly large) likely error margins overlapping. For the dimers, the differences between the
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29 COSMOTerm-based and group-contribution predictions (ignoring the probably unreliable
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31 Nannoolal/Nannoolal method) are both larger, and harder to explain in terms of structural
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33 features. In contrast to the most highly oxidized monomers with three intramolecular H-bonds,
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35 C₂₀H₃₀O₁₀-iso2 contains only one, and the two other dimers two, intramolecular H-bonds. It
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37 therefore seems unlikely that these would account for all of the (at worst over 10⁷ – fold)
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39 differences between the COSMOTerm-based predictions and the group-contribution methods.
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41 Also, as mentioned previously, the COSMOTerm predictions for the dimers are internally
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43 somewhat inconsistent. In the absence of any convincing explanations for the differences
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45 between the predicted saturation vapor pressures for the HOM dimers, we can only note that they
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47 are chemically quite different from any of the molecules in the parameterization datasets of any
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49 of the methods used here (including COSMO-RS), and that saturation vapor pressure data for
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51 molecules of this size (and likely volatility) are in general very scarce.²⁰ The error margins of all
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of the methods may therefore be even larger for the dimers than for the monomers. Nevertheless, due to the likelihood of COSMOTerm overpredicting and EVAPORATION (or SIMPOL) underpredicting the saturation vapor pressures, the true saturation vapor pressures of both the monomers and the dimers should very probably lie between the minimum and maximum values presented in Tables 2 and 3.

Wania *et al.*³⁴ suggest that the partitioning coefficient $K_{i,WIOM}$ for an organic compound i between the gas phase and a phase composed of water-insoluble organic matter (WIOM) may be a more robust predictor of the gas-particle partitioning behavior of the compound than its saturation vapor pressure, as predictions by different methods for $K_{i,WIOM}$ generally vary less than the predicted saturation vapor pressures. Using COSMOTerm, $K_{i,WIOM}$ can be calculated either directly (as a Henry's Law constant in the desired WIOM phase), or indirectly, by computing separately the saturation vapor pressures and the activity coefficients in a suitable (single- or multicomponent) WIOM phase, as described by Arp and Goss (Eq 5 in their study).⁵⁵ The results of the two approaches are identical. As we have already computed the saturation vapor pressures, we employed the indirect approach in this study. Using the standard BP/TVZP parameterization and multiple conformers, we computed the activity coefficients of all 16 products shown in Figure 2 in a WIOM phase composed of the model compound "B" proposed by Kalberer *et al.*⁵⁶, and also used in both Arp and Goss⁵⁵ and Wania *et al.*³⁴ (We included all six conformers found for this molecule in the calculations.) The activity coefficients (at infinite dilution and 298 K) of the autoxidation products in the model WIOM phase varied between 0.59 and 2.01, with the more oxidized structures generally tending to have lower activity coefficients. This small variation indicates that for the particular set of compounds studied here, and assuming order-of-magnitude validity of the result that the computed activity coefficients are close to unity, using

partitioning coefficients instead of saturation vapor pressures is unlikely to significantly reduce the differences between the predictions on the extent of gas-particle partitioning. The results further suggest that equilibrium phase partitioning is likely to be strongly correlated with the saturation vapor pressure also for atmospheric autoxidation products. The activity coefficients in water, computed with the same approach, varied between 220 and 12 000 for the “monomers” and between 93 000 and 790 000 for the “dimers”, indicating that especially the latter are indeed water-insoluble, and that $K_{i,WIOM}$ is thus the appropriate coefficient to describe their partitioning.

Conclusions and atmospheric implications

For evaluating the atmospheric fate and impact of HOMs and other autoxidation products, one crucial question is whether or not their saturation vapor pressures are low enough to qualify them as ELVOCs, or alternatively LVOCs. Vapors with saturation vapor pressures around or below 10^{-14} bar are usually considered to be effectively non-volatile (i.e. “ELVOC”), whereas saturation vapor pressures much higher than this generally prevent homogeneous nucleation due to the Kelvin effect, and also indicate that re-evaporation back into the gas phase can not be neglected from nanometer-scale particles.¹⁹ Saturation vapor pressures around 10^{-10} bar, on the other hand, are sufficient to contribute to the growth of larger aerosol particles.

According to the COSMOTherm results, none of the autoxidation products studied here (with the possible exception of $C_{20}H_{30}O_{10}$ -iso1) are genuine ELVOCs. If we account for the fact that the COSMOTherm predictions for these molecules are likely overestimates (by up to a factor of 100 or so), and that the true saturation vapor pressures are probably found somewhere between the COSMOTherm and the group-contribution predictions, then all of the HOM dimers may well be ELVOCs. In contrast, none of the studied “HOM monomer” structures are ELVOCs

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3 according to any of the reliable methods used here. The Nannoolal/Nannoolal predictions for
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5 HOM – type molecules, as discussed above, should likely be disregarded – and it is worth noting
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7 that if they were to be accepted at face value, then the HOM dimers would no longer be
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9 ELVOCs, and some dimers would hardly even be LVOCs. However, the more oxidized
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11 monomers are likely still LVOCs, as their saturation vapor pressures, after accounting for the
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13 probable overestimation by COSMOTerm, are likely roughly around 10^{-10} bar.
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19 While the COSMOTerm saturation vapor pressures are not quantitatively reliable, the
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21 benchmarking performed both here and in literature studies indicates that they are unlikely to be
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23 wrong by many orders of magnitude, as COSMOTerm - unlike the group-contribution methods
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25 when applied to systems very different to their parametrization dataset - models the actual
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27 chemical interactions of the real molecular systems, including the crucially important
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29 intramolecular hydrogen bonds. Thus, we can state the following tentative conclusions:
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34 1)Group-contribution methods very likely generally underestimate the volatility of atmospheric
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36 autoxidation products, largely by ignoring intramolecular H-bonds. Conversely, COSMOTerm
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38 may somewhat overestimate the effect of these H-bonds and thus the saturation vapor pressures.
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40 Without any other basis for recommendation, we suggest using a geometric average of
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42 COSMOTerm and SIMPOL saturation vapor pressures for autoxidation products, with the
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44 COSMOTerm representing the likely maximum and SIMPOL the likely minimum saturation
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46 vapor pressure.
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51 2)“HOM” monomers formed in α -pinene autoxidation are unlikely to be ELVOCs (i.e. have
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53 saturation vapor pressures around or below 10^{-14} bar) even when their O:C ratios are close to 1.
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However, they are likely to be LVOCs (i.e. have saturation vapor pressures around or below 10^{-10} bar).

3) The less oxidized products of α -pinene autoxidation are highly unlikely to be ELVOCs, and may not even be LVOCs.

4) HOM dimers may well be ELVOCs, but even this should not be assumed with certainty.

The relatively high saturation vapor pressures computed here do not rule out a significant contribution of HOMs to SOA formation and/or aerosol growth, nor do they contradict the many experimental indications of such a contribution. Laboratory experiments¹⁰ demonstrate that HOMs formed in α -pinene ozonolysis condense (adsorb) effectively onto both chamber walls and seed particles, and both HOMs and their decomposition products have recently been detected in the particle phase.¹⁶ If HOMs indeed turn out not to be ELVOCs, this simply suggests either that HOMs mainly contribute to the condensational growth of larger particles (with diameters well above a few nanometers), and/or that the mechanism by which HOMs contribute to particle growth involves chemical reactions in addition to simple physical condensation or absorption. Recent AMS measurements indicate that HOMs undergo rapid chemical reactions after partitioning into particles.⁵⁷ Provided that these reactions convert the HOMs into less volatile form, such reactive uptake could significantly increase their contributions to particle growth.

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ASSOCIATED CONTENT

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

Structures and group-contribution saturation vapor pressures for the test molecules, description of the chemical reactions leading from α -pinene ozonolysis to the studied molecules, zip archive with cosmo files and gas-phase energies for all studied compounds.

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⁵⁷ Zhang, X.; McVay, R.; Huang, D. D.; Dalleska, N. F.; Aumont, B.; Flagan, R. C.; Seinfeld, J. H. Formation and evolution of molecular products in α -pinene secondary organic aerosol. *Proc. Natl. Acad. Sci.* **2015**, *112*, 14168-14173.

Table of Contents (TOC) Image

Figure 1
50x64mm (300 x 300 DPI)

Figure 3
169x237mm (300 x 300 DPI)

Figure 4
296x209mm (300 x 300 DPI)

Figure 5
296x209mm (300 x 300 DPI)

TOC image
46x27mm (300 x 300 DPI)