



1 Impact of HO₂/RO₂ ratio on highly oxygenated α -pinene 2 photooxidation products and secondary organic aerosol formation 3 potential

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14 **Abstract.** Highly oxygenated molecules (HOM) from the atmospheric oxidation of biogenic volatile organic compounds are
15 important contributors to secondary organic aerosol (SOA). Organic peroxy radicals (RO₂) and hydroperoxy radicals (HO₂)
16 are key species influencing the HOM product distribution. In laboratory studies experimental requirements often result in
17 overemphasis of RO₂ cross-reactions compared to reactions of RO₂ with HO₂. We analyzed the photochemical formation of
18 HOMs from α -pinene and their potential to contribute to SOA formation under high ($\approx 1/1$) and low ($\approx 1/100$) HO₂/RO₂
19 conditions. As HO₂/RO₂ > 1 is prevalent in the daytime atmosphere, sufficiently high HO₂/RO₂ is crucial to mimic
20 atmospheric conditions and to prevent biases by low HO₂/RO₂ on the HOM product distribution and thus SOA yield.
21 Experiments were performed under steady-state conditions in the new, continuously stirred tank reactor SAPHIR-STAR at
22 Forschungszentrum Jülich. The HO₂/RO₂ ratio was increased by adding CO, while keeping the OH concentration constant.
23 We determined the HOM's SOA formation potential, considering their fraction remaining in the gas phase after seeding with
24 (NH₄)₂SO₄ aerosol. Increase of HO₂/RO₂ led to a reduction in SOA formation potential, with the main driver being a $\approx 60\%$
25 reduction in HOM-accretion products. We also observed a shift in HOM-monomer functionalization from carbonyl to
26 hydroperoxide groups. We determined a reduction of the HOM's SOA formation potential by $\approx 30\%$ at HO₂/RO₂ $\approx 1/1$.
27 Particle phase observations measured an about according decrease in SOA mass and yield. Our study showed that too low
28 HO₂/RO₂ ratios compared to the atmosphere can lead to an overestimation of SOA yields.



Introduction

In the atmosphere highly oxidized products from the oxidation of biogenic or anthropogenic volatile organic compounds (VOCs) are an important source of secondary organic aerosol (SOA) (Roldin et al., 2019; Mohr et al., 2019). SOA is an important contributor to the overall ambient aerosol and of interest because of its impact on climate, visibility, and human health (Hallquist et al., 2009).

Recently, many studies (Pullinen et al., 2020; Berndt et al., 2016; Bianchi et al., 2017) have focused on understanding the oxidation pathways of VOCs that yield highly oxygenated molecules (HOMs), as these are expected to be of low enough volatility to condense into the particle phase. One important tool for the investigation of VOC degradation and SOA formation is the utilization of experiments in atmospheric simulation chambers (Hidy, 2019). Such experiments have also helped to elucidate key processes in the HOM formation, i.e. the process of autoxidation.

After an initial oxidant attack and the formation of a peroxy radical (RO_2), autoxidation adds oxygen to the molecule via an internal H-shift to the peroxy group, forming a hydroxy peroxide group and an alkyl radical, to which O_2 immediately adds, reestablishing the peroxy functionality. This process can be repeated multiple times yielding almost instantaneously highly oxygenated peroxy radicals (HOM-RO_2) which are terminated to a series of HOM closed-shell products (Bianchi et al., 2019; Ehn et al., 2014; Crounse et al., 2013).

Chamber studies often work with a singular compound and operate at higher precursor concentrations than those observed in the atmosphere for experimental reasons. These experiments cannot represent the complex mixture of VOCs and oxidized VOCs present in the atmosphere (McFiggans et al., 2019). Higher precursor concentrations can lead per se to higher SOA yields than observed in the atmosphere (a well characterized phenomenon (see Henry et al. (2012), Shilling et al. (2009)) and to a general preference of higher order processes which may not be important in the atmosphere. One example is that chamber studies tend to overestimate the role of cross reactions between organic peroxy radicals (RO_2) owing to high precursor concentrations of a single VOC. In chambers, reactions of HOM-RO_2 with other organic peroxy radicals terminate the autoxidation chain, leading typically to multifunctional carbonyl and alcohol compounds. In comparison, in the atmosphere termination by HO_2 is more likely, leading to multifunctional hydroperoxides. In presence of sufficient NO , termination to multifunctional organic nitrates may be more important (Schervish and Donahue, 2021).

Another possible termination reaction of HOM-RO_2 with HOM-RO_2 and less oxidized RO_2 leads to the formation of accretion products, which are expected to be extremely low volatile organic compounds (ELVOCs) and are therefore expected to contribute to new particle formation and SOA formation (Ehn et al., 2014; Berndt et al., 2018). Schervish and Donahue (2021) raised awareness that chamber studies could overestimate the SOA formation potential from the oxidation of terpenes such as α -pinene compared to the atmosphere, because of missing HO_2 and small RO_2 (e.g. CH_3O_2), which favors accretion product formation.



In chamber studies the use of higher VOC concentrations is often an unavoidable necessity either to match the sensitivity of the analytical instrumentation or to overcome chamber related effects. The question remains, how can conditions dictated by the chamber be steered towards more realistic chemical pathways and higher atmospheric relevance?

In this study we address this overestimated importance of peroxy radical cross reactions. We studied the photooxidation of α -pinene in a series of steady-state experiments in the newly built continuously stirred tank reactor SAPHIR-STAR (a modernized version of JPAC, see Mentel et al. (2009)).

In these experiments, after an initial α -pinene photooxidation phase as a reference, CO was added to the oxidation system to represent small, oxidized VOCs in the atmosphere that can produce HO_2 by reaction with OH (compare Schervish and Donahue (2021)). Presence of CO shifts the HO_2 to RO_2 ratio, increasing the importance of the RO_2 termination with HO_2 . However, McFiggans et al. (2019) showed that one limiting factor in mixture experiments is oxidant scavenging: the products and their yields in mixed systems change, because there is less OH available to the individual VOC. Thus, after the CO addition the OH production in the chamber was increased to compensate for the oxidant scavenging. The OH levels in the system before and after the CO addition were approximately the same, keeping the α -pinene OH turnover, as well as the primary peroxy radical production approximately constant.

Furthermore, the addition of seed particles ($(\text{NH}_4)_2\text{SO}_4$) allowed us to observe the condensation behavior of the HOM-products and to compare our gas phase observations directly with particulate phase measurements of the condensed organic mass.

In this study we will address two central questions: How does the shift in HO_2/RO_2 impact the oxidation mechanism of α -pinene, especially the HOM formation pathway? And what is the subsequent impact on the SOA formation potential of the α -pinene photooxidation system? As the central analysis tool, we will use high resolution time of flight mass spectrometry with chemical ionization (HR-TOF-CIMS).

1 Methods

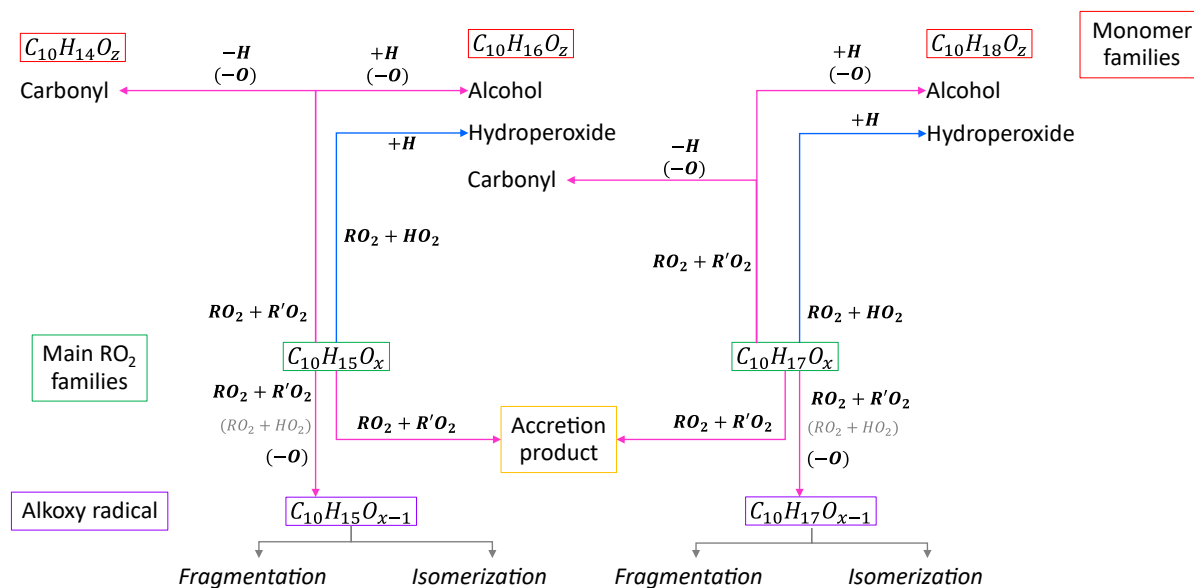
1.1 Generic α -pinene HOM peroxy radical chemistry

The chemical mechanistic information for the basic oxidation scheme of α -pinene was taken from the Master Chemical Mechanism MCM v3.3.1 (Jenkin et al., 1997; Saunders et al., 2003) (<http://mcm.york.ac.uk>). The main peroxy radicals expected from α -pinene photooxidation are $\text{C}_{10}\text{H}_{17}\text{O}_x$ and $\text{C}_{10}\text{H}_{15}\text{O}_x$. $\text{C}_{10}\text{H}_{17}\text{O}_x$ is formed by the addition of OH to α -pinene, followed by O_2 (starting RO_2 : $\text{C}_{10}\text{H}_{17}\text{O}_3$) (MCM v3.3.1 (Jenkin et al., 1997; Saunders et al., 2003)). Studies showed that the autoxidation can start from $\text{C}_{10}\text{H}_{17}\text{O}_3$ with the four-member ring in α -pinene opened (Berndt, 2021; Xu et al., 2019).

For $\text{C}_{10}\text{H}_{15}\text{O}_x$ the autoxidation chain is assumed to start with $\text{C}_{10}\text{H}_{15}\text{O}_4$, which can be formed directly from ozonolysis via the vinyl hydroperoxide path (Johnson and Marston, 2008; Iyer et al., 2021) or via H-abstraction from first-generation oxidation



90 products such as pinonaldehyde ($C_{10}H_{16}O_2$). (MCM v3.3.1 (Jenkin et al., 1997; Saunders et al., 2003; Fantechi et al., 2002).
 91 A recent study suggests direct H-abstraction by OH from α -pinene (Shen et al., 2022).
 92 The autoxidation process is rapid with H-shift rates of about $0.01 - 0.1 \text{ s}^{-1}$ and faster (Piletic and Kleindienst, 2022; Berndt,
 93 2021; Xu et al., 2019; Vereecken et al., 2007). Once the autoxidation process starts it quickly adds more oxygen to the
 94 molecule, until the difficulty in abstracting remaining H-atoms slows down the reaction sufficiently such that termination
 95 reactions can compete. In the absence of NO_x , the peroxy radicals have two major bimolecular termination channels: the
 96 reaction with another RO_2 or with HO_2 . A third pathway is the intramolecular termination (Rissanen et al., 2014).
 97 Based on the considerations above, we apply a simplified generic reaction scheme to analyze our observations. **Figure 1**
 98 shows an overview of the reaction pathways for the main peroxy radical families in the α -pinene photooxidation and the
 99 resulting product groups and families. The compounds can be separated into four classes; peroxy radicals (HOM- RO_2),
 100 monomers (HOM-Mon), accretion products (HOM-Acc) and fragments (HOM-Frag). The HOM- RO_2 class consists of all
 101 detected HOM- RO_2 , with special focus on the analysis of the C_{10} HOM- RO_2 family. The HOM-Mon class contains the
 102 closed-shell HOM- C_{10} products. The compounds in the fragment class contain less than ten carbon atoms, while all
 103 HOM-Acc compounds contain more than ten carbon atoms. The compound classes are further divided into groups and
 104 families. Here, the term group is used for compounds with the same carbon number, while a family contains all compounds
 105 with the same carbon and hydrogen number but a varying oxygen number.



106

107 **Figure 1: Overview of important reaction pathways of α -pinene RO_2 with other RO_2 and HO_2 .**



108 The termination of RO₂ with HO₂ will lead to hydroperoxide formation:



109 In the case of C₁₀H₁₅O_x, reaction **(R1)** will lead to multifunctional C₁₀H₁₆O_z hydroperoxides (wherein the notation
 110 “hydroperoxides” or “carbonyls”, “alcohols” etc. here and in the following relates to the functionality of the group formed by
 111 the termination reaction). For C₁₀H₁₇O_x it will lead to the formation of C₁₀H₁₈O_z hydroperoxides. The termination via
 112 RO₂+RO₂ can either result in the formation of accretion products or in the formation of carbonyls and alcohols. For the
 113 accretion product formation, it is assumed that the two RO₂ chemically bond eliminating O₂ from the molecule:



114 Recombination reactions of the main peroxy radical families C₁₀H₁₅O_x and C₁₀H₁₇O_x lead to the product families C₂₀H₃₀O_z
 115 (combination of two C₁₀H₁₅O_x), C₂₀H₃₂O_z (combination of C₁₀H₁₅O_x and C₁₀H₁₇O_x), and C₂₀H₃₄O_z (combination of two
 116 C₁₀H₁₇O_x).

117 However, due to reactions with smaller peroxy radicals, HOM-Acc families with smaller carbon and hydrogen numbers are
 118 also observed. Indeed, one reason why the RO₂+R'O₂ termination is expected to affect the SOA formation potential is the
 119 formation of accretion products by scavenging of less oxidized and smaller RO₂ by HOM-RO₂. Thus, the smaller RO₂ will
 120 also contribute to the SOA mass which would otherwise not be the case. For the HOM-RO₂ itself, it is expected that they
 121 contribute to SOA formation independently of the termination pathway, due to the low volatility of its expected termination
 122 products (Pullinen et al., 2020; McFiggans et al., 2019).

123 The second RO₂+R'O₂ termination pathway is the formation of a carbonyl and alcohol compound:



124 In this reaction both radicals lose an oxygen atom, and a hydrogen atom is transferred to the RO₂ forming the alcohol
 125 termination group. Preferences of RO₂ to form an alcohol or carbonyl compound are possible for individual reactions, but
 126 statistically carbonyl and alcohols should be formed with the same fractions. Since mass spectrometry can only determine
 127 formula composition, we cannot distinguish alcohols and hydroperoxides, which arise from RO₂ differing by one O atom.
 128 Therefore, details of balance of alcohol and carbonyl formation cannot be detected.

129 However, the formula composition can help to differentiate certain formation pathways. The C₁₀H₁₄O_z family contains only
 130 carbonyl formed from a C₁₀H₁₅O_x RO₂ while the alcohol will be part of the C₁₀H₁₆O_z family. The C₁₀H₁₆O_z family also
 131 contains the carbonyl produced from the RO₂+R'O₂ monomer termination of C₁₀H₁₇O_x, while the alcohol from this RO₂
 132 family will be found in the C₁₀H₁₈O_z family. So, from a diagnostic point of view, C₁₀H₁₄O_z as well as C₁₀H₁₈O_z are uniquely
 133 related to a precursor radical family.



134 The classification of the formation pathways of the monomers is helpful to analyze the effect of the HO₂/RO₂ ratio shift in
135 the experiments. Considering the termination pathways, a decrease in the C₁₀H₁₄O_z family and an increase of the C₁₀H₁₈O_z
136 family is expected with increasing HO₂/RO₂ because of increasing termination by HO₂ and decreasing termination by RO₂.
137 In case of C₁₀H₁₈O_z the increase of hydroperoxides is partially compensated by a decrease of the alcohol channel. For
138 C₁₀H₁₆O_z the situation is more complicated as it contains contributions from all termination pathways.

139 Besides closed-shell products, HOM-RO₂ can also form alkoxy radicals (HOM-RO). In general, alkoxy radicals (RO) are
140 important intermediates in the oxidation scheme of organics and are formed via **(R4)** and probably also via **(R5)** for specific
141 RO₂ (Jenkin et al., 2019):



142 In reaction **(R5)** OH will be formed. The importance of reaction **(R5)** compared to reaction **(R1)** is still unclear in the
143 literature, but functionalization of the RO₂ close to the peroxy functionality possibly enables this reaction (Iyer et al., 2018;
144 Eddingsaas et al., 2012; Hasson et al., 2005; Jenkin et al., 2019). If reaction **(R5)** is of negligible importance, the reaction
145 scheme will simplify and the effect of increased HO₂/RO₂ is easier to diagnose.

146 We are interested in the importance of alkoxy radical formation as (HOM)-RO tend to fragment, leading to the formation of
147 smaller products (Vereecken et al., 2007). In the context of SOA formation, these fragments are less likely to contribute to
148 SOA mass because of their higher volatility. Since alkoxy radicals are too unstable to be detected directly we use two
149 diagnosis tools to judge the importance of HOM-RO. Firstly, HOM-RO fragmentation can lead to HOM-RO₂ with less than
150 10 carbon atoms which may also continue the autoxidation chain. Therefore, the abundance of HOM with less than 10
151 carbon atoms (HOM-Frag) indicates the importance of alkoxy steps. Secondly, with increasing functionalization, H-shifts
152 retaining the carbon backbone become more likely (Vereecken et al., 2007) which will lead to a next generation of C₁₀-
153 HOM-RO₂. Such alkoxy peroxy steps can continue the autoxidation chain (Mentel et al., 2015). Interestingly, by coupling of
154 an alkoxy and a peroxy step, the parity of the number of oxygen atoms in the HOM-RO₂ changes, while in pure autoxidation
155 steps the oxygen parity remains the same. Therefore, a parity change of the oxygen number can be used as an indication of
156 alkoxy step abundance (Kang, 2021).

157 In summary we will use the changes in contribution and relative signal of the different families and classes to judge the
158 impact of shifting from low to high HO₂/RO₂ on the α-pinene photooxidation pathway.



159 1.2 Control of α -pinene OH turnover

160 One important concept of the conducted experiments is the constant OH availability to α -pinene in the mixtures with CO to
 161 avoid effects of oxidant scavenging (McFiggans et al., 2019). Therefore, after each change in the HO₂/RO₂ regime by CO
 162 addition, the OH level was readjusted to yield the same α -pinene OH turnover and compensate for the OH consumed by CO.
 163 This OH adjustment ensures that the primary α -pinene chemistry was kept the same and enables a direct comparison.

164 However, since experiments could only be performed at *about* the same OH levels, a normalization by the actual α -pinene
 165 OH turnover is applied to the data. This compensates for the slight experimental imperfections and enables better
 166 comparison of experiment series with different boundary conditions. The turnover in steady state is given in **Eq. (1)**. Here
 167 the subscript “SS” denotes steady state condition for the concentrations of α -pinene and OH, k_{OH} is the α -pinene OH reaction
 168 rate constant.

$$turnover_{\alpha\text{-pinene}+OH} = k_{OH} * [\alpha\text{-pinene}]_{SS} * [OH]_{SS} \quad (1)$$

169 This normalization also directly shows the yield of certain oxidation product or product group per α -pinene consumed by
 170 OH.

171 1.3 Derivation of effect on condensable mass from gas-phase measurement

172 A simple proxy for the condensable mass from HOM products can be calculated from the steady-state HOM-signals
 173 measured by the NO₃-CIMS, assuming condensation for all low volatility HOM-compounds and no back evaporation into
 174 the gas phase. To only take low volatility products into account we used all detected formula compositions with
 175 $M > 230 \text{ g mol}^{-1}$ and weighted them with their molar mass. The reasoning behind this threshold can be found in **Sect. 4.4**. All
 176 contributions were summed up and normalized with the α -pinene OH turnover for the comparison between the low and high
 177 HO₂/RO₂ cases (**Eq. (2)**).

$$mass\ weighted\ signal\ sum = \frac{\sum_{i=0}^i S_i * M_i}{turnover_{\alpha\text{-pinene}+OH}} \quad (2)$$

178 We also estimated the expected SOA mass formed using the calibration factor obtained for sulfuric acid for our NO₃-CIMS
 179 instrument in a calibration setup (see supplement **Sect. S1**). From this we calculated an upper boundary concentration of
 180 detected HOM-compounds in the gas phase under the assumption that sulfuric acid clusters with nitrate at the collision limit,
 181 yielding maximum sensitivity (a common approach, see for example Ehn et al. (2014), Pullinen et al. (2020)).
 182 The calculated gas phase concentration was then used in the steady state equation describing the relationship between gas
 183 and particle phase concentrations of a single compound i shown in **Eq. (3)**.

$$m_{i,seed}(p) = \frac{m_{i,seed}(g) * k_{cond,i}}{k_{particleLoss} + k_{evap,i}} \quad (3)$$



Equation (3) shows that the steady state particle phase (mass) concentration $m_{i,seed}(p)$ of compound i in presence of seed in the chamber is only dependent on the steady state gas phase concentration $m_{i,seed}(g)$, the condensation rate and evaporation rate constants $k_{cond,i}$, $k_{evap,i}$ of i (to and from the particles) and the particle loss rate constant $k_{particleLoss}$ in the chamber. The condensation rate can be calculated (see supplement **Sect. S6**), and the particle loss rate constant was measured by observation of the particle loss in the chamber after ending the seed addition (details in the supplement **Sect. S2**). The evaporation rate was assumed to be negligible for the investigated HOM-compounds. For the SOA yield calculation, we calculate a corrected organic mass m_{SOA} from the organic mass m_{AMS} measured by aerosol mass spectrometry (AMS) and the fraction expected to be lost on the seed particles compared to the overall loss on particles and chamber wall as shown in **Eq. (4)** (McFiggans et al., 2019).

$$m_{SOA} = m_{AMS} * \frac{k_{cond} + k_{wall}}{k_{cond}} \quad (4)$$

In **Eq. (4)** we use the condensation rate constant k_{cond} calculated for one major HOM-product ($C_{10}H_{16}O_7$) and the average HOM-Mon wall loss rate k_{wall} which was determined by switching off the UVC light and observing the decay of photooxidation products in the NO_3 -CIMS. The wall loss determination, as well as SOA mass correction were described before in Sarrafzadeh et al. (2016) and McFiggans et al. (2019).

2 Experimental methods

2.1 Chamber setup

Experiments were conducted in the Jülich SAPHIR STAR chamber, which is the modern successor of the JPAC setup (Mentel et al., 2009). The basic concepts are the same as in JPAC, but each parameter is set, controlled, and monitored in a program. The chamber was operated as a continuously stirred tank reactor. It is a borosilicate glass cylinder ($l=2.5$ m, $d=1$ m) with a volume of 2000 L and all equipment inside the chamber is either glass or glass coated steel (SilcoTek GmbH).

With an inflow of 32 L min^{-1} , the residence time in the chamber was approximately 63 minutes with a fan ensuring mixing within minutes. In contrast to the JPAC chamber, the stirring is conducted perpendicular to the cylinder axis, as opposed to coaxial. Chamber inflow is split into two humidified clean air flows (mixed from N_2 and O_2) of about equal volume, one with added oxidant (here O_3), the other with added VOC and other trace gases (here α -pinene and CO). All experiments were performed at a relative humidity of 50 % and at 20°C . Temperature stability is ensured by the climate-controlled surrounding of the chamber.

α -Pinene ($\geq 99\%$ purity, Sigma-Aldrich Merck KGaA) was introduced via liquid injection with a syringe pump (Fusion 4000, CHEMYX Inc.) into a heated glass bulb and flushed by a stream of 1 L min^{-1} into the chamber. CO was added from a



211 gas bottle (10% CO in N₂, Messer SE & Co. KGaA). Ozone was directly produced photolytically before injection with a
 212 self-built ozone generator.

213 OH is produced in the chamber by ozone photolysis using two UV-C lamps with a wavelength of 254 nm and subsequent
 214 reaction of O(¹D) with water vapor. The lamps are mounted in closed quartz cylinders in the middle of the chamber,
 215 vertically to the cylinder axis and light intensity can be varied with a movable shielding installed around the lamps. The
 216 shielding allows an exact percentage of the lamp to be covered, thus controlling the amount of OH produced in the chamber.

217 The OH radical concentration after CO addition was adjusted by setting the shielding of the UVC lamps and a slight
 218 adjustment of O₃ inflow. The applied J(O¹D) values in different phases were calculated to be in the range of 0.8·10⁻³ to
 219 2.4 ·10⁻³ s⁻¹.

220 In some of the experiments, ammonium sulfate (≥99 % purity, Merck KGaA) seed particles were added to the system to
 221 provide a surface for the condensation of organic material. The aerosol was produced with a modified TSI atomizer (Model
 222 3076, TSI GmbH) and dried to 50% relative humidity.

223 VOC concentrations in the chamber were measured using proton-transfer-reaction mass spectrometry (PTR-TOF-MS;
 224 Ionicon GmbH). CO₂, CO, H₂O (G2401 Cavity Ringdown Spectrometer, Picarro Inc.), NO, NO_x (NCLD899, Eco Physics
 225 GmbH with a home-built photolytic converter) and O₃ (O342e, Envea GmbH) were additionally monitored. Particle
 226 distribution and concentration were measured with a condensation particle counter (CPC, Model 3788, TSI GmbH) and a
 227 scanning mobility particle sizer (SMPS; Model 3080, TSI GmbH) with a CPC (Model 3788, TSI GmbH). The aerosol
 228 composition was measured with a high-resolution aerosol mass spectrometer (HR-TOF AMS; Aerodyne Inc.).

229 In all experiments, VOC, O₃, and SMPS+CPC sampling switched between inlet and outlet of the chamber to measure the
 230 input concentrations as well as the concentrations in the reactor. The flow control system of the chamber adapts to these
 231 switches so that the inflow into the chamber stays constant.

232 All results discussed here were observed under steady-state conditions when all parameters were constant. For each steady
 233 state, the OH concentration was calculated from the decay of α-pinene as described by Kiendler-Scharr et al. (2009).
 234 **Equation (5)** is derived from the mass balance of α-pinene at steady state. The steady state OH concentration [OH]_{ss}
 235 depends on the amount of α-pinene consumed by reaction with OH and the reaction with O₃, as well as the flush out.

$$[OH]_{ss} = \frac{F}{V} * \frac{[VOC]_{in} - [VOC]_{ss} - k_{O_3} * [O_3]_{ss}}{k_{OH}} \quad (5)$$

236 Here, F is the total flow and V the volume of the chamber. The subscript “SS” indicates steady-state concentrations, while
 237 [VOC]_{in} represents the α-pinene concentration entering the chamber. k_{O₃} and k_{OH} represent the reaction rate constants of α-
 238 pinene with the corresponding oxidant. We applied rate coefficients of k_{O₃}=5.36·10⁻¹¹ cm³·s⁻¹ (Atkinson and Arey, 2003) and



$k_{OH}=9.25 \cdot 10^{-17} \text{ cm}^3 \cdot \text{s}^{-1}$ (Cox et al., 2020) at 20 °C. The uncertainty of the OH calculation was estimated as 20 % by Wildt et al. (2014).

2.2 Experiment conditions

An overview of the experiments and their boundary conditions can be found in **Table 1**. Four experiments were performed in total. In two of the experiments ammonium sulfate seeds were added leading to a total particle surface in the chamber on the order of $8 \cdot 10^{-4} \text{ m}^2 \text{ m}^{-3}$ and organic loadings of about 3 ug m^{-3} in the photooxidation stage. The *Exp2* experiment is a consecutive combination of a seeded, followed by a non-seeded experiment to provide direct insight into the effect of seed presence on the system.

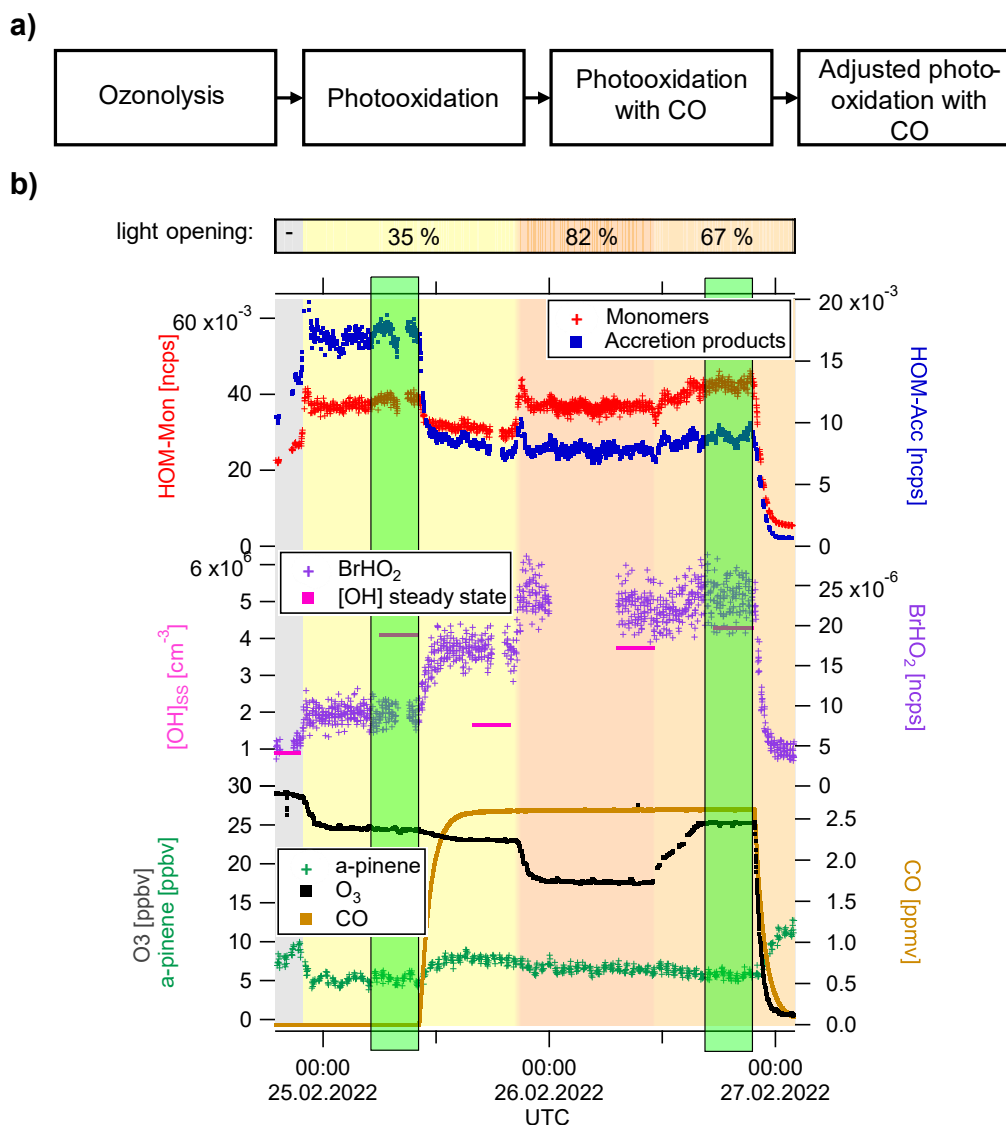
As the OH radical is produced by photolysis of ozone and α -pinene reacts with ozone, it is important to know the relative contribution of the α -pinene consumption by OH and by O_3 . This is achieved by comparing the turnover of α -pinene with OH and O_3 respectively. The results can be found in **Table 1**. The listed results are for the low HO_2/RO_2 conditions, but nearly identical values were reached after the HO_2/RO_2 shift.

Table 1. Overview of experimental conditions

Name	Experiment description	[VOC] _{in}	[CO] _{in}	[OH] _{ss} at low HO_2/RO_2	Contribution of OH to turnover at low HO_2/RO_2	Particle surface at low HO_2/RO_2	Organic mass concentration at low HO_2/RO_2
<i>Exp1</i>	<i>pure gas phase (1)</i>	10 ppbv	2.5 ppmv	$4.1\text{E}+6 \text{ cm}^{-3}$	80 %	-	-
<i>Exp2.1</i>	<i>seeded (1)</i>	10 ppbv	2.5 ppmv	$1.0\text{E}+7 \text{ cm}^{-3}$	91 %	$8.7\text{E}-4 \text{ m}^2 \text{ m}^{-3}$	3.4 ug m^{-3}
<i>Exp2.2</i>	<i>unseeded (2)</i>	10 ppbv	2.5 ppmv	$1.3\text{E}+7 \text{ cm}^{-3}$	93 %	-	-
<i>Exp3</i>	<i>seeded (2)</i>	10 ppbv	2.5 ppmv	$1.4\text{E}+7 \text{ cm}^{-3}$	79 %	$6.8\text{E}-4 \text{ m}^2 \text{ m}^{-3}$	2.7 ug m^{-3}



253 2.3 Experimental procedure



254

255 **Figure 2: a) Experiment flow scheme b) Exemplary timeseries of *Exp1* experiment showing HOM-Mon and HOM-Acc**
 256 **product sum (top panel), calculated OH concentration and BrHO₂ signal (middle panel), and ozone, α -pinene and CO**
 257 **concentrations (bottom panel). Background color represents light intensity. Highlighted in green are the low HO₂/RO₂**
 258 **steady state and the steady state at high HO₂/RO₂ (addition of CO and adjusted oxidant level).**

259 All experiments started with α -pinene ozonolysis followed by illumination of the UVC-lights to induce the reaction with
 260 OH. A general flow scheme of the experiment can be found in **Fig. 2**, together with one exemplary timeseries of the
 261 unseeded experiment *Exp1*. After the photooxidation steady state, CO was added to the system. In the displayed *Exp1*
 262 experiment the OH concentration was adjusted in three steps to approach the desired value. First the UVC-light opening was
 263 adjusted and then O₃ was added, and the UVC-light opening was adjusted again. In some experiments initially the effect of



CO on the unchanged system was observed, before the adjustment of OH. In other experiments (*Exp2.2*, *Exp3*) the adjustment of the α -pinene OH turnover via ozone concentration and UVC-light opening were made simultaneously with the CO addition. Highlighted in green are the steady states with the “same” OH concentration characterized by low and high HO_2/RO_2 , which were used for analysis and interpretation.

2.4 Model calculation for HO_2/RO_2 ratio estimation

Box model calculations were performed applying the MCM v3.3.1 chemistry (Jenkin et al., 1997; Saunders et al., 2003) under the boundary conditions of the SAPHIR-STAR chamber. All calculations were performed with the institute software package EASY which uses FACSIMILE to solve the differential equations (EASY Version 5.69b). More details about the model parameters can be found in the supplement **Sect. S3**. The model calculations reproduced the primary observables α -pinene, O_3 , CO, and OH within the experimental uncertainties. The box-model results were used to characterize the HO_2/RO_2 ratio of the chemical systems, as no direct measurement of these parameters was available. The observed cluster signal BrHO_2^- follows the modelled HO_2 concentration (**Fig. 3**).

The model predicts a shift of the HO_2/RO_2 ratio from about 0.01 to about 1 by CO addition and oxidant adjustment, an increase by two orders of magnitude. Owing to lack of observations to verify model results, we will consider only the magnitude of HO_2/RO_2 here. The model results show that indeed a major shift from RO_2+RO_2 to RO_2+HO_2 reactions can be expected.

We further used the modelled RO_2 and HO_2 concentrations to estimate the relative importance of pathways for individual (observed) HOM- RO_2 . For that we applied two generic rate coefficients $k_{\text{RO}_2\text{HO}_2}$ and $k_{\text{RO}_2\text{RO}_2}$. As the rate coefficient for the RO_2+HO_2 termination to a hydroperoxide $k_{\text{RO}_2\text{HO}_2}$ we used the value specified in the MCM ($1.85 \cdot 10^{-11} \text{ cm}^3 \cdot \text{s}^{-1}$ at 20°C (Jenkin et al., 1997; Saunders et al., 2003)). We chose a $k_{\text{RO}_2\text{RO}_2}$ of $5 \cdot 10^{-12} \text{ cm}^3 \cdot \text{s}^{-1}$ as the approximated reaction rate of the RO_2+RO_2 reactions. This value applies to all possible reactions (accretion product, monomer, and alkoxy formation) and is in the range of $k_{\text{RO}_2\text{RO}_2}$ utilized by Roldin et al. (2019) in the PRAM model.

2.5 Determination of oxidized VOCs, HOMs and HO_2

Chemical ionization mass spectrometry (HR-TOF-CIMS) techniques were used to detect a range of gaseous compounds. For this, two atmospheric pressure interface time of flight mass spectrometers (APi-TOF-MS; ToFwerk AG) with different inlet systems were used simultaneously. General information about the APi-TOF-MS instrument can be found in Junninen et al. (2010).

A long TOF (LTOF) (Resolution ~ 8500 for peaks at $>200 \text{ m/Q}$) was coupled with the multi-scheme ionization inlet (MION; Karsa Oy). The setup of the inlet is described in detail by Rissanen et al. (2019). The distinctive feature of the MION inlet is the switching between two reagent ions. Here, nitrate was used to detect closed-shell HOMs, as well as HOM- RO_2 . Bianchi et al. (2019) suggested to define HOM as products stemming from autoxidation containing more than 6 oxygen. In our



overall analysis we decided to also include fragments and monomers containing 5 or in a few cases 4 oxygens (see peaklist in supplement **Sect. S4**) as we are interested to see if the importance of these less oxidized (but still with NO_3 -CIMS detectable) products increases at higher HO_2/RO_2 . However, in all considerations regarding SOA formation we furthermore set a molar weight threshold which automatically excluded any products with less 6 oxygens.

As the second reagent ion, bromide was used to detect less oxidized products and the HO_2 radical (Albrecht et al., 2019; Sanchez et al., 2016). The nitrate ion source had a reaction time of 600 ms, while the bromide ion source had a shorter reaction time of 60 ms. For all experiments an inlet flow of 10 L min^{-1} was used and the ionization scheme was switched every 10 minutes.

In the data evaluation the first step was the separation of the timeseries of the two reagent ions. The data was subsequently processed with Tofware (Version 3.2.3, Tofwerk AG) using the high resolution timeseries workflow. No transmission correction was performed as previous measurements showed an approximately flat relative transmission curve in the mass region of interest. The analyte signals were normalized with the reagent ion signal (NO_3^- and $\text{HNO}_3\text{NO}_3^-$ for nitrate and Br^- and BrH_2O^- for bromide).

Since no direct HO_2 calibration was available, the HO_2 signal in the Br-MION-CIMS was used to compare the levels of HO_2 relative to each other in the different phases of the experiment. The comparison of the measured HO_2 signal to the modelled HO_2 concentration shows a good linear relation between the model predictions and observations.

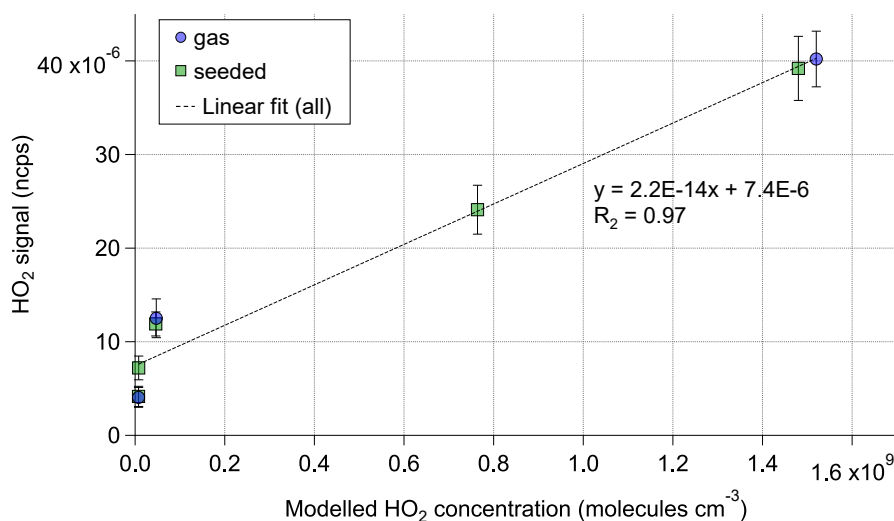


Figure 3: Modelled HO_2 concentration vs. normalized HO_2 signal for each steady state of Exp2. HO_2 is measured as the BrHO_2 cluster and is normalized with the sum of the reagent ion Br^- and its water cluster. The dotted line shows the linear fit to all (gas phase and seeded) measurement points.

Figure 3 illustrates this for the example of the Exp2 experiment. A background signal of around $\sim 1 \cdot 10^{-5}$ is observed as soon as VOC and ozone are present in the reactor. The background HO_2 signal was not observed when only O_3 or only VOC were



in the system. As shown by the MCM modelling results HO_2 production of this strength is not expected in the α -pinene ozonolysis phase but this background phenomenon was observed before (Albrecht et al., 2019) and is not fully understood.

For the HOM molecules measured by the NO_3 -MION-CIMS the relative changes between different experiment phases are compared. For all detected HOM products the same detection sensitivity is assumed. Hyttinen et al. (2018) showed in quantum chemical calculations that HOMs containing 6 or more oxygen atoms have comparable sensitivity with the nitrate reagent ion. At this degree of oxidation it can be expected that the HOMs already contain multiple hydroperoxyl and/or hydroxy functional groups (Bianchi et al., 2019) prior to the termination step, making it unlikely that the sensitivity is strongly influenced by the termination group. Thus, the signal strength reflects the correct ranking of the observations and relative comparisons do not require calibration. Pullinen et al. (2020) studied the mass balance between condensable HOMs and formed particle mass and were able to find closure within a factor of 2.

A second CI-API-TOF was used to measure less oxidized species. It was configured with a CI inlet based on the design of Eisele and Tanner (1993) coupled to an HTOF (Resolution ~ 2700 for peaks at >200 m/Q) (ToFwerk AG) and was operated in positive mode with propylamine ($\text{C}_3\text{H}_7\text{NH}_2$, Sigma-Aldrich, purity $\geq 99\%$) to detect the early generation RO_2 and oxidation products (Berndt et al., 2018). The propylamine was purified and added as an amine- N_2 mixture (flow: 0.12 mL min^{-1}) to the 30 L min^{-1} sheath flow. Furthermore, the sheath flow air is humidified to optimize ionization. The instrument sampled 0.1 L min^{-1} from the chamber, which was diluted with 9.9 L min^{-1} for a sample flow of 10 L min^{-1} . The dilution was necessary to reduce depletion of the primary ion (Hantschke, 2022).

3 Results and Discussion

In order to understand the effect of HO_2/RO_2 on the gas phase product composition, we will present and compare two cases: The steady state without CO (low HO_2/RO_2) and the steady state with CO addition and OH adjustment by $\text{J}(\text{O}^1\text{D})$ and O_3 (high HO_2/RO_2). The modelling results predicted HO_2/RO_2 of about 1/100 and of about 1/1 for these two cases respectively. The modelling results show that the HO_2/RO_2 ratio changes by two orders of magnitude, because $[\text{RO}_2]$ was reduced by about a factor of three, while $[\text{HO}_2]$ was increased by a factor of 30. Consequently, HO_2 reactions were almost negligible at low HO_2/RO_2 while RO_2+RO_2 reactions can still contribute at high HO_2/RO_2 .

Assuming correctly modelled $[\text{HO}_2]$ and $[\text{RO}_2]$, we calculated the competition between HO_2 and RO_2 reactions for each (observed) RO_2 expressed in form of pseudo first order rate coefficients in $k_{\text{RO}_2\text{HO}_2} \cdot [\text{HO}_2]$ or $k_{\text{RO}_2\text{RO}_2} \cdot [\text{RO}_2]$. Herein $[\text{RO}_2]$ is the sum of all RO_2 species as defined in the MCM v3.3.1. For all experiments the results of our calculations indicate that the sink for HOM- RO_2 is dominated by RO_2+RO_2 reactions at low HO_2/RO_2 ($\sim 98\%$ contribution), while at high HO_2/RO_2 RO_2+HO_2 contributed $\sim 75\%$. As the rate coefficients are not well known and we cannot verify the modelling results for HO_2 and RO_2 our calculations serve solely as an indication of expected trends in the chemical system.



3.1 Impact on overall HOM-formation

The top panel of **Fig. 2** shows the timeseries of HOM-Mon and HOM-Acc products. The HOM-Mon signal recovers after the oxidant adjustment, while the HOM-Acc signal is significantly suppressed at high HO_2/RO_2 . This indicates that the shift from low to high HO_2/RO_2 substantially impacts the termination reactions, shifting formation from the HOM-Acc product channel (RO_2+RO_2) to the HOM-Mon channel.

An overview of the results for the product classes defined in the method section is shown in **Fig. 4**. Plotted are the average ratios of signal in the NO_3 -CIMS in the high HO_2/RO_2 steady state compared to the low HO_2/RO_2 steady state. For better comparison, all experiment phases were normalized to the actual α -pinene OH turnover. The overall HOM-signal was lower at high HO_2/RO_2 showing a reduction of about 20 %. Most distinctive, the HOM-Acc were strongly reduced by about 60 %. A reduction of HOM-Acc by addition of CO was observed before by McFiggans et al. (2019), however there the OH concentration was not kept constant. The HOM-Frag ($5 \leq C < 10$) also show a reduction of about 20 %. At high HO_2/RO_2 C_{10} -HOM- RO_2 were also reduced significantly by about 40 %.

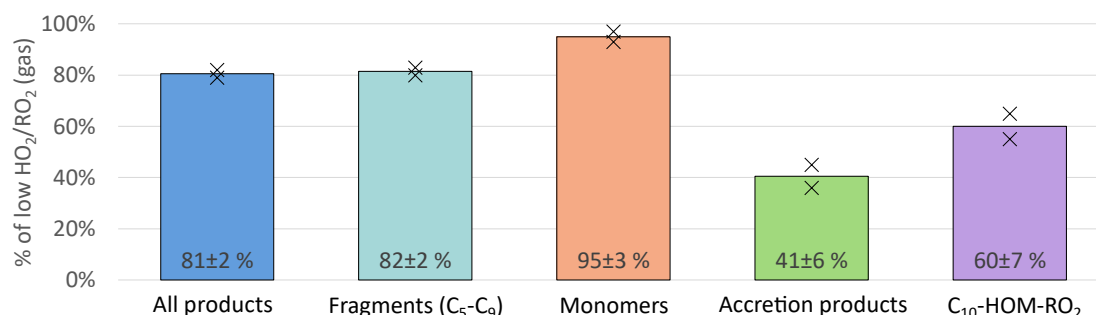


Figure 4: Overview of average, relative change in product classes detected in NO_3 -CIMS between low and high HO_2/RO_2 case (both normalized to α -pinene OH turnover) for pure gas phase experiments. Bars represent average of the two experiments, markers represent individual experiments.

The HOM-Mon signal level remained about the same at low and high HO_2/RO_2 . Without reduction in the HOM- RO_2 precursors a reduction of HOM-Acc should lead to an increase in HOM-Mon, as each HOM-Acc is formed from one HOM- RO_2 ($\text{HOM-RO}_2+\text{RO}_2$) or potentially even two HOM- RO_2 ($\text{HOM-RO}_2+\text{HOM-RO}_2$). Of course, the presence of HO_2 could reduce the alkoxy formation, and thus fragmentation of HOM- RO_2 . This missing sink could lead to an additional HOM-Mon source compared to the low HO_2/RO_2 case. However, the distribution of the product classes at low and high HO_2/RO_2 (**Fig. 5**) shows that contributions are shifted from HOM-Acc to HOM-Mon, while the contribution of HOM-Frag remains constant.

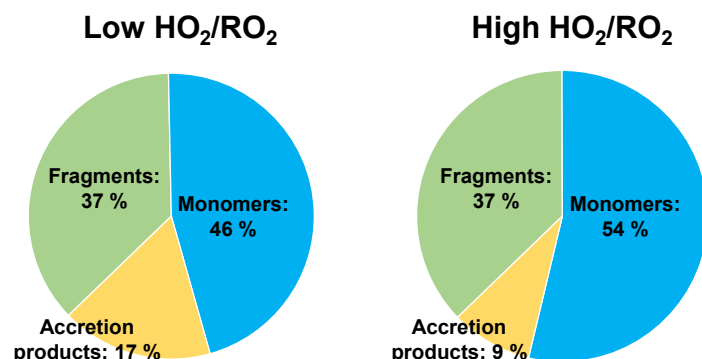


Figure 5: Average contribution of the closed shell product classes to overall HOM-product signal in the low and high HO_2/RO_2 cases (pure gas phase experiments).

Further changes in the product distribution become evident when considering the individual HOM-Mon families as shown in **Fig. 6**. The $\text{C}_{10}\text{H}_{15}\text{O}_x$ peroxy radical family and the related $\text{C}_{10}\text{H}_{14}\text{O}_z$ family (carbonyl compounds) show the strongest suppression with a decrease of about 40 % at high HO_2/RO_2 . For the $\text{C}_{10}\text{H}_{17}\text{O}_x$ peroxy radical family the suppression was less pronounced with a 17 % reduction. In contrast, the $\text{C}_{10}\text{H}_{16}\text{O}_z$ family remained about the same while the $\text{C}_{10}\text{H}_{18}\text{O}_z$ family showed a strong increase at high HO_2/RO_2 .

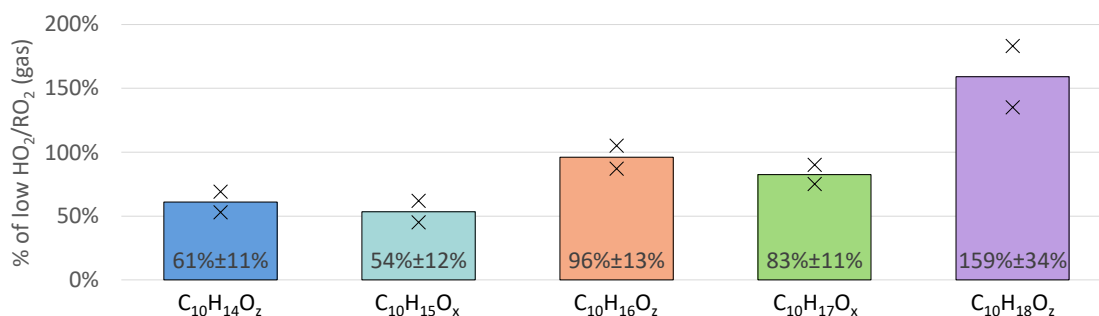


Figure 6: Overview of average, relative change in monomer families detected in NO_3 -CIMS between low and high HO_2/RO_2 case (both normalized to α -pinene OH turnover) for pure gas phase experiments. Bars represent average of the two experiments, markers represent individual experiments.

The suppression of C_{10} -HOM- RO_2 of only about 40 % compared to the reduction of overall $[\text{RO}_2]$ by ~70 % in the model calculations shows that in many instances the autoxidation is too efficient to be out-competed by the $\text{RO}_2 + \text{HO}_2$ termination reaction, which is several times faster than $\text{RO}_2 + \text{RO}_2$ reactions.

Furthermore, the signal weighted O/C ratio of the monomer class does not change between low and high HO_2/RO_2 (0.70 ± 0.01). If the HO_2 termination would interrupt the autoxidation chain, a lower oxidation level would be expected at high HO_2/RO_2 . The unchanged oxidation level and the suppression of HOM-Acc, indicate that the average autoxidation rate must be faster than $k_{\text{RO}_2\text{HO}_2}[\text{HO}_2]$, while the average accretion rate for $k_{\text{HOM-RO}_2+\text{RO}_2}[\text{RO}_2]$ must be slower. In conclusion, the change in HO_2/RO_2 should essentially impact the distribution of the HOM- RO_2 termination products.



3.2 Impact on HOM-RO₂

C₁₀-HOM-RO₂ are key to understand the changes in the HOM product distribution. Therefore, we will first discuss the changes in the HOM-RO₂ and then the changes in the closed shell products.

The C₁₀ peroxy radical class consists of the C₁₀H₁₅O_x and C₁₀H₁₇O_x families which were reduced to 54 % and 83 %, respectively when comparing the high and low HO₂/RO₂ cases (**Fig. 6**, light blue and green bars). The observed reduction in C₁₀-HOM-RO₂ is significantly smaller than the overall RO₂ concentration reduction predicted by the MCM model results (reduction to ~30 %). In the following paragraphs, we present a plausibility consideration to assess if these observed changes are consistent with our expectations from modelling results and reaction rates.

The change in the steady state concentration of a compound is always defined by the changes in its sources and sinks. The source of a HOM-RO₂ is the intramolecular reaction of a precursor RO₂ and thus the HOM-RO₂'s source is reduced if the steady state concentration of the precursor RO₂ is reduced. However, assuming the source term of the precursor RO₂ is the same in low and high HO₂/RO₂ (due to the constant α -pinene OH turnover) and the precursor RO₂'s sink term is dominated by the fast autoxidation in both cases, then the RO₂'s steady state concentration would not be significantly changed. This consideration is only applicable for RO₂ where autoxidation dominates the sink term at low and high HO₂/RO₂. However, the unchanged oxidation level of the HOM-Mon indicates that once the autoxidation is initiated it out-competes the possible termination reactions.

In this case, the change in steady state concentration of the HOM-RO₂ will be defined by the changes in the sink terms. Owing to the faster reaction of RO₂+HO₂ compared to RO₂+RO₂ the chemical sink for all RO₂ including HOM-RO₂ with slower autoxidation rates increased, which leads to a reduction in the steady state concentration of RO₂ in general, despite holding the primary RO₂ source term constant.

For steady state conditions, we can estimate the expected effect of high and low HO₂/RO₂ on the RO₂ ratio for those HOM-RO₂ with production directly linked to the primary production ($k_{OH}\cdot[OH]\cdot[\alpha\text{-pinene}]$) with negligible further autoxidation. The necessary equations and assumptions can be found in supplement **Sect. S5**. We assume the same primary production at low and high HO₂/RO₂ and that the reaction with HO₂, the reaction with RO₂ and the wall loss are the only significant loss pathways. At high HO₂/RO₂, a reduction to 80 % is expected if the rate coefficient $k_{RO_2HO_2}$ ($1.85\cdot 10^{-11} \text{ cm}^3\cdot\text{s}^{-1}$ at 20 °C (Jenkin et al., 1997; Saunders et al., 2003)) is 5 times faster than $k_{RO_2RO_2}$ (leading to $k_{RO_2RO_2}=3.7\cdot 10^{-12} \text{ cm}^3\cdot\text{s}^{-1}$). A reduction to 60 % is expected if $k_{RO_2HO_2}$ is 8 times faster than $k_{RO_2RO_2}$. These reductions are in the range of what is observed for the C₁₀-HOM-RO₂. Of course, the approach of using generalized bulk rate constants is limited, but the resulting values for $k_{RO_2RO_2}$ were clearly within the range of rate coefficients expected for HOM-RO₂+RO₂ reactions (Roldin et al., 2019) showing that the increased chemical sink is a plausible explanation for our observations.

The C₁₀H₁₅O_x family is on average reduced by around 30 % more than the C₁₀H₁₇O_x family (see **Fig. 6**). C₁₀H₁₅O_x peroxy radicals are either formed by sequential oxidation of α -pinene, e.g. from oxidation products like pinonaldehyde, or directly



422 from α -pinene via the H-abstraction pathway (Shen et al., 2022). Formation of pinonaldehyde and, even more so HOM
423 formation via the H-abstraction channel, involve alkoxy steps. However, alkoxy radicals should be reduced at high HO_2/RO_2
424 since they are mainly formed by RO_2+RO_2 reactions in the absence of NO_x . Thus, missing source terms add to the increased
425 chemical sink by HO_2 for $\text{C}_{10}\text{H}_{15}\text{O}_x$ peroxy radicals.

426 Amine CIMS measurements enabled detection of the formula composition $\text{C}_{10}\text{H}_{16}\text{O}_2$ (e.g. pinonaldehyde). $\text{C}_{10}\text{H}_{16}\text{O}_2$ was
427 reduced on average to $71\% \pm 1\%$ at high HO_2/RO_2 compared to low HO_2/RO_2 . This supports that a fraction of the $\text{C}_{10}\text{H}_{15}\text{O}_x$
428 radical decrease at high HO_2/RO_2 arose from suppression of $\text{C}_{10}\text{H}_{16}\text{O}_2$ first generation products. In addition, a further
429 suppression of HOM formation via the H-abstraction channel is likely. It should be noted that the reduction of $\text{C}_{10}\text{H}_{16}\text{O}_2$ is
430 smaller than that expected by the MCM model results. This might indicate that HO_2 can also enable alkoxy radical steps to a
431 certain degree as summarized by Jenkin et al. (2019) and postulated by e.g. Eddingsaas et al. (2012) as a source of
432 pinonaldehyde in HO_2 dominated systems.

433 According to the model calculations the pseudo first order rate coefficient $k_{\text{RO}_2\text{HO}_2}[\text{HO}_2]$ is expected to be about 0.03 s^{-1} for
434 the RO_2+HO_2 reaction at high HO_2/RO_2 . Consequently, only such HOM- RO_2 with autoxidation rates of $\leq 0.03 \text{ s}^{-1}$ will be
435 significantly lost by reaction with HO_2 at the higher HO_2 concentrations. However, typical isomerization rates of peroxy
436 radicals in autoxidation are of the order of 0.1 s^{-1} and many are faster (Piletic and Kleindienst, 2022; Berndt, 2021).
437 Therefore, reduction in a HOM- RO_2 is only expected when the faster termination rate of $k_{\text{RO}_2\text{HO}_2}[\text{HO}_2]$ can compete with the
438 autoxidation rate, i. e. when the autoxidation slows as the degree of oxidation increases on the specific HOM- RO_2 .

439 The increase in chemical sink strength by going from RO_2 termination to HO_2 termination is the main expected reason for
440 the decrease in $\text{C}_{10}\text{H}_{17}\text{O}_x$. As discussed, the $\text{C}_{10}\text{H}_{15}\text{O}_x$ family is subject to an additional decrease in the precursors due to the
441 alkoxy steps necessary in the formation pathway. Since $\text{C}_{10}\text{H}_{15}\text{O}_x$ were the main contributors to the C_{10} -HOM- RO_2 class
442 their stronger reduction is reflected in the overall reduction of C_{10} -HOM- RO_2 .

443 3.2.1 Contribution of $\text{C}_{10}\text{H}_{15}\text{O}_x$ and $\text{C}_{10}\text{H}_{17}\text{O}_x$ families to HOM- RO_2

444 In the pure gas phase experiments, the contribution of the $\text{C}_{10}\text{H}_{17}\text{O}_x$ family to the C_{10} -HOM- RO_2 class is $23\% \pm 2\%$ on
445 average in the low HO_2/RO_2 case. In the high HO_2/RO_2 case the contribution increases to $31\% \pm 4\%$ on average. As
446 discussed above the suggested pathways to $\text{C}_{10}\text{H}_{15}\text{O}_x$ HOM- RO_2 may be additionally suppressed due to a decrease of alkoxy
447 steps at high HO_2/RO_2 reducing the entry channel into $\text{C}_{10}\text{H}_{15}\text{O}_x$ HOM- RO_2 .

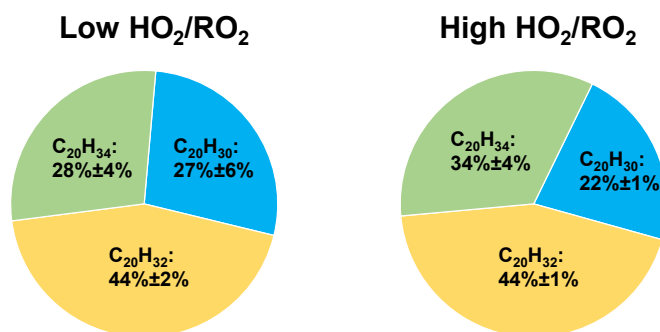
448 Nevertheless, the contribution of $\text{C}_{10}\text{H}_{15}\text{O}_x$ is substantial in both experiment stages. Kang (2021) and Shen et al. (2022)
449 reported that, in the photooxidation of α -pinene, the HOM- RO_2 detected by NO_3 -CIMS are dominated by the $\text{C}_{10}\text{H}_{15}\text{O}_x$
450 family, while $\text{C}_{10}\text{H}_{17}\text{O}_x$ formation is the main expected OH reaction pathway described in literature (Berndt, 2021; Berndt et
451 al., 2016; Xu et al., 2019).



452 This hints towards an effective pathway to HOM via $C_{10}H_{15}O_x$. A reason may be the fast opening of both carbon-rings in the
453 bicyclic α -pinene (Shen et al., 2022), or a four-ring opening in pinonaldehyde or similar compounds, for easy autoxidation.
454 From our observations increasing the HO_2/RO_2 ratio does increase the relative importance of the $C_{10}H_{17}O_x$ family, but the
455 change is less than 10 % in contribution.

456 Contribution of the two peroxy radical families to the HOM formation is also reflected in the composition of C_{20} HOM-Acc.
457 **Figure 7** shows the average contributions of the $C_{20}H_{30}O_z$, $C_{20}H_{32}O_z$, and $C_{20}H_{34}O_z$ families in the low and high HO_2/RO_2
458 cases. Although the absolute amount of HOM-Acc was suppressed by 60 % the family distribution was similar, $C_{20}H_{32}O_z$
459 dominated, while $C_{20}H_{30}O_z$ was lowest. $C_{20}H_{30}O_z$ is formed from two members of the $C_{10}H_{15}O_x$ family, while $C_{20}H_{34}O_z$ is
460 formed by two members of the $C_{10}H_{17}O_x$ family. $C_{20}H_{32}O_z$ is then a combination of a $C_{10}H_{15}O_x-RO_2$ and $C_{10}H_{17}O_x-RO_2$.

461 Families that require one or two $C_{10}H_{17}O_x$ peroxy radicals for their formation have a higher contribution than the $C_{10}H_{17}O_x$
462 family's contribution to C_{10} -HOM- RO_2 . Here, it is important to note that not only HOM- RO_2 can participate in HOM-Acc
463 formation, but also traditional, less oxidized RO_2 radicals (Berndt et al., 2018; Pullinen et al., 2020; McFiggans et al., 2019),
464 which are not detectable by NO_3^- -CIMS. However, more oxidized peroxy radicals exhibit faster accretion rates (Berndt et al.,
465 2018).



466
467 **Figure 7: Average contribution of the $C_{20}H_{30}O_z$, $C_{20}H_{32}O_z$, and $C_{20}H_{34}O_z$ family to the C_{20} HOM-Acc group signal in the low and**
468 **high HO_2/RO_2 cases (pure gas phase experiments). Not pictured is $C_{20}H_{28}O_z$ due to its negligible signal (contribution ~1 %).**

469 The large contributions of $C_{20}H_{32}O_z$ and $C_{20}H_{34}O_z$ thus clearly show the general importance of the $C_{10}H_{17}O_x$ peroxy radicals.
470 The largest fraction, the $C_{20}H_{32}O_z$ family reflects the importance of HOM- $C_{10}H_{15}O_x$ and the high abundance of lower
471 oxidized $C_{10}H_{17}O_x$ peroxy radicals. The fraction of $C_{20}H_{34}O_z$ is smaller because their formation requires HOM- $C_{10}H_{17}O_x$
472 radicals which are less abundant compared to HOM- $C_{10}H_{15}O_x$, while the small fraction of $C_{20}H_{30}O_z$ indicates that, despite the
473 importance of HOM- $C_{10}H_{15}O_x$, lower oxidized $C_{10}H_{15}O_x$ are less important.

474 These results indicate the importance of mixed HOM-Acc formation by cross reactions of HOM- RO_2 and a lower oxidized
475 RO_2 . The importance of mixed HOM-Acc is supported by the relatively small fractions of HOM-Acc products with very
476 high oxygen numbers, which more likely stem from HOM- RO_2 +HOM- RO_2 . For example, C_{20} -HOM-Acc with 12 or more



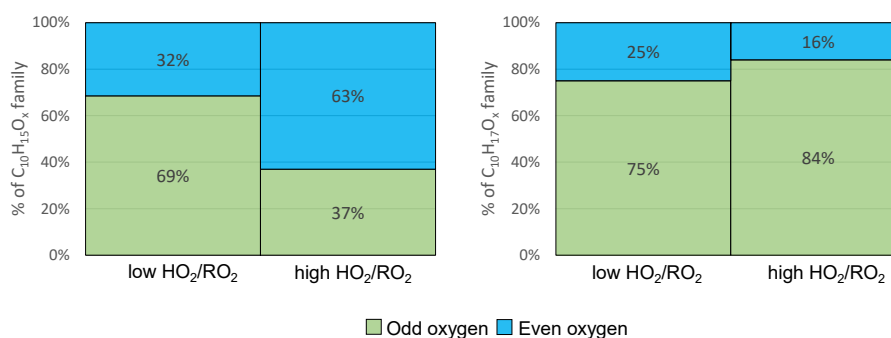
oxygen atoms contribute only around 30 % (low HO_2/RO_2 : 26 % $\pm$ 4 %, high HO_2/RO_2 : 31 % $\pm$ 2 %) of the signal in the product group.

Although the effect of the changed HO_2/RO_2 ratio is small, a tendency to higher $\text{C}_{20}\text{H}_{34}\text{O}_z$ contribution was observed. This is consistent with the observation of a slightly higher $\text{C}_{10}\text{H}_{17}\text{O}_x$ contribution to the C_{10} -HOM RO_2 . The stronger suppression of the $\text{C}_{10}\text{H}_{15}\text{O}_x$ family at high HO_2/RO_2 is the first indication for, and can be explained by, a reduction in the alkoxy radical formation.

3.2.2 Impact on HOM-Alkoxy radical formation

Alkoxy radicals (RO) are the second important radical type in the oxidation chain of α -pinene. RO cannot be detected directly as they are highly unstable and thus have very low concentrations. However, as explained in Sect. Fehler! V erweisquelle konnte nicht gefunden werden. the parity change in the HOM- RO_2 families can be used as a diagnosis tool for the abundance of alkoxy steps (Kang, 2021). A second indicator for alkoxy steps is the abundance of HOM products with less than 10 C-atoms.

Figure 8 shows the average contribution of $\text{C}_{10}\text{H}_{15}\text{O}_x$ and $\text{C}_{10}\text{H}_{17}\text{O}_x$ with an even and odd number of oxygens at low and high HO_2/RO_2 . $\text{C}_{10}\text{H}_{15}\text{O}_x$ radicals with an even number of oxygens contribute on average 32 % at low HO_2/RO_2 . For $\text{C}_{10}\text{H}_{15}\text{O}_x$, the autoxidation chain is expected to start from an even number of oxygen either from $\text{C}_{10}\text{H}_{15}\text{O}_4$ (pinonaldehyde-like) (MCM v3.3.1 (Jenkin et al., 1997; Saunders et al., 2003) or from $\text{C}_{10}\text{H}_{15}\text{O}_2$ ($\text{C}_{10}\text{H}_{16}$ H-abstraction) (Berndt, 2021; Shen et al., 2022). Therefore, without the involvement of an alkoxy step, the parity of the oxygen number in the observed $\text{C}_{10}\text{H}_{15}\text{O}_x$ HOM- RO_2 is expected to be even. Due to the average contribution of $\text{C}_{10}\text{H}_{15}\text{O}_{\text{odd}}$ of 69 % we conclude that at least one alkoxy step (or any odd number of alkoxy steps) must have taken place in most of the cases at low HO_2/RO_2 .



Legend: ■ Odd oxygen ■ Even oxygen

Figure 8: Average contribution of O_{odd} and O_{even} to the HOM- RO_2 families $\text{C}_{10}\text{H}_{15}\text{O}_x$ (left) and $\text{C}_{10}\text{H}_{17}\text{O}_x$ (right) signal in the low and high HO_2/RO_2 cases (pure gas phase experiments).

At high HO_2/RO_2 $\text{C}_{10}\text{H}_{15}\text{O}_{\text{even}}$ contributed 63 % and the $\text{C}_{10}\text{H}_{15}\text{O}_{\text{odd}}$ contribution was reduced to 37 %. This demonstrates a change in the number of alkoxy steps along the formation pathway of the observed HOM- RO_2 radicals. The increased contribution of $\text{C}_{10}\text{H}_{15}\text{O}_{\text{even}}$ at high HO_2/RO_2 lets us infer an even number of alkoxy steps as more common (0,2,4...). In the

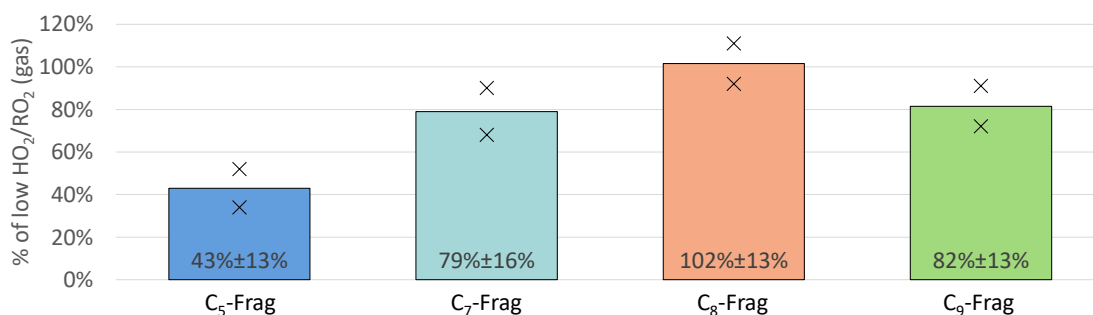


simplest case 1 or 2 alkoxy step take place at low HO_2/RO_2 due to HOM-RO formation from $\text{HOM-RO}_2 + \text{RO}_2$ reactions, while no or 1 alkoxy step take place at high HO_2/RO_2 , because $\text{HOM-RO}_2 + \text{HO}_2$ produces none or less HOM-RO than $\text{HOM-RO}_2 + \text{RO}_2$.

For $\text{C}_{10}\text{H}_{17}\text{O}_x$ the entry channel into autoxidation is $\text{C}_{10}\text{H}_{17}\text{O}_3$ with an odd number of oxygen atoms. Therefore, in autoxidation without alkoxy steps the oxygen parity is expected to be odd. At low HO_2/RO_2 $\text{C}_{10}\text{H}_{17}\text{O}_{\text{odd}}$ species contribute 75 % to the total $\text{C}_{10}\text{H}_{17}\text{O}_x$ signal indicating that either none or an even number (2,4,...) of alkoxy steps occurred. At high HO_2/RO_2 the odd contribution increases to 84 % (see **Fig. 8**). This result could indicate a low occurrence of alkoxy steps even at low HO_2/RO_2 , with a further decrease of alkoxy formation at high HO_2/RO_2 . However, the observed shift is minor.

In any case the different responses of the $\text{C}_{10}\text{H}_{15}\text{O}_x$ and $\text{C}_{10}\text{H}_{17}\text{O}_x$ families to the reduction of HOM-RO₂ formation from $\text{HOM-RO}_2 + \text{RO}_2$ at high HO_2/RO_2 indicate that there could be fundamental differences in the autoxidation chains of $\text{C}_{10}\text{H}_{15}\text{O}_x$ and $\text{C}_{10}\text{H}_{17}\text{O}_x$ (or the limit of the parity analysis). The parity analysis indicates a decrease in alkoxy steps at high HO_2/RO_2 , but it cannot be directly inferred with certainty. However, decrease in alkoxy steps at high HO_2/RO_2 is supported by the observation of changes in HOM-Frag products.

On average the sum of all HOM-Frag products (detected compounds with $5 \leq \text{C} < 10$ by NO_3^- -CIMS) showed a reduction of around 20 % (pure gas phase experiments, see **Fig. 4**). Further trends become recognizable when separating the species according to their carbon number. **Figure 9** shows the C_5 , C_7 , C_8 , and C_9 HOM-Frag at high HO_2/RO_2 compared to the low HO_2/RO_2 case, normalized to the α -pinene OH turnover. The fragment group with C_6 compounds is not included, as it contributed less than 5 % of the fragment signal and contained few detected compounds.



520

521 **Figure 9: Overview of average, relative change in C_5 , C_7 , C_8 , C_9 fragment groups detected in NO_3 -CIMS between high and low**
 522 **HO_2/RO_2 case (both normalized to α -pinene OH turnover) for pure gas phase experiments. Bars represent average of the two**
 523 **experiments, markers represent individual experiments.**

524 **Figure 9** shows a significant reduction in HOM-Frag with shorter carbon chain length: C_5 HOM-Frag are reduced by around
 525 60 % compared to the low HO_2/RO_2 case. If we assume that the fragmentation of C_{10} compounds happens in consecutive
 526 steps via scission of HOM-RO radicals (analogously to the MCM), this observation is in accord with decreasing importance
 527 of alkoxy radical formation at high HO_2/RO_2 .



Overall, all observations indicate strong involvement of RO in HOM formation as well as a reduced, but still significant, involvement of RO at high HO_2/RO_2 , when HO_2 chemistry dominates: This is supported by the change of the oxygen parity in C_{10} -HOM- RO_2 , and the decrease of fragmentation products, especially with lower carbon number, as well as the only moderate reduction in the observed $\text{C}_{10}\text{H}_{16}\text{O}_2$ product (pinonaldehyde) and the still substantial importance of the $\text{C}_{10}\text{H}_{15}\text{O}_x$ HOM- RO_2 family at high HO_2/RO_2 .

3.3 Impact on carbonyl and hydroperoxide formation

Increased HO_2/RO_2 should shift the product distribution by reduction of alcohol and carbonyl compounds from the so-called molecular channel in the RO_2+RO_2 reaction (see reaction **(R3)**), in favor of hydroperoxide formation from RO_2+HO_2 termination (reaction **(R1)**). This effect can be best observed in the $\text{C}_{10}\text{H}_{18}\text{O}_z$ family, which contains the hydroperoxide and alcohol termination products arising from $\text{C}_{10}\text{H}_{17}\text{O}_x$. $\text{C}_{10}\text{H}_{18}\text{O}_z$ significantly increased to on average 159 % (see **Fig. 6**). This supports an increased hydroperoxide formation, however, with some uncertainty due to the alcohol termination products from $\text{C}_{10}\text{H}_{17}\text{O}_x$ (by reaction with RO_2). To elucidate this further the contribution of individual species to the $\text{C}_{10}\text{H}_{18}\text{O}_z$ family was examined.

Formation of an alcohol via the molecular path (reaction **(R3)**) leads to the loss of one oxygen atom compared to the precursor $\text{C}_{10}\text{H}_{17}\text{O}_x$ radical, while in the hydroperoxide formation (reaction **(R1)**) the oxygen number remains the same. The most abundant member of the $\text{C}_{10}\text{H}_{17}\text{O}_x$ family was $\text{C}_{10}\text{H}_{17}\text{O}_7$ with a contribution of 72 % $\pm$ 6 % at low HO_2/RO_2 , and a contribution of 82 % $\pm$ 1 % at high HO_2/RO_2 . $\text{C}_{10}\text{H}_{17}\text{O}_7$ terminates to $\text{C}_{10}\text{H}_{18}\text{O}_z$ products either as an alcohol with sum formula $\text{C}_{10}\text{H}_{18}\text{O}_6$, or as a hydroperoxide with sum formula $\text{C}_{10}\text{H}_{18}\text{O}_7$. These products have additional sources from $\text{C}_{10}\text{H}_{17}\text{O}_6$ and $\text{C}_{10}\text{H}_{17}\text{O}_8$ but due to the dominant contribution of $\text{C}_{10}\text{H}_{17}\text{O}_7$ to the $\text{C}_{10}\text{H}_{17}\text{O}_x$ family we expect any other production channels to be of minor importance.

Figure 10 shows the HOM product distribution within the $\text{C}_{10}\text{H}_{18}\text{O}_z$ family at low and high HO_2/RO_2 . The sum of the O_6 and O_7 product did not change significantly in the two regimes (about 88 %), showing that these are the major products, and agreeing well with the observation of $\text{C}_{10}\text{H}_{17}\text{O}_7$ being the major $\text{C}_{10}\text{H}_{17}\text{O}_x$ HOM- RO_2 . At low HO_2/RO_2 the O_6 product has a larger contribution of 64 % $\pm$ 8 %, while at high HO_2/RO_2 ~30% of signal is shifted to the O_7 product. This shows that the increase in the $\text{C}_{10}\text{H}_{18}\text{O}_z$ is matched with an increase of hydroperoxide formation.

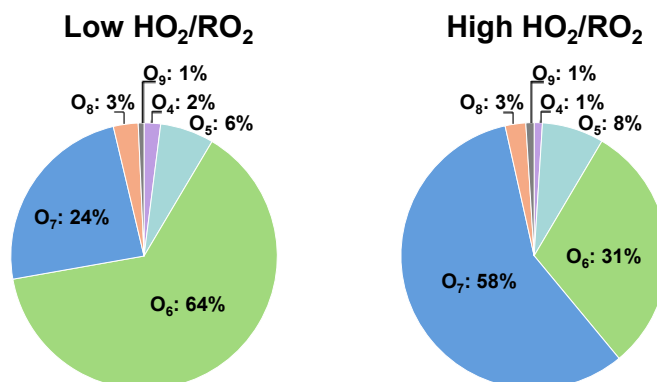


Figure 10: Average contribution of the individual compounds to the $\text{C}_{10}\text{H}_{18}\text{O}_2$ family signal at low and high HO_2/RO_2 (pure gas phase experiments).

An indicator for carbonyl formation is the $\text{C}_{10}\text{H}_{14}\text{O}_z$ family as it only contains the carbonyl products arising from $\text{C}_{10}\text{H}_{15}\text{O}_x\text{-RO}_2$. The $\text{C}_{10}\text{H}_{14}\text{O}_z$ family was reduced on average to 61 % at high HO_2/RO_2 , however this decrease matches the decrease in the $\text{C}_{10}\text{H}_{15}\text{O}_x$ precursor family. If the reaction of a $\text{C}_{10}\text{H}_{15}\text{O}_x\text{-HOM-RO}_2$ with a second RO_2 were the main formation pathway for $\text{C}_{10}\text{H}_{14}\text{O}_z$ a stronger reduction would be expected as both precursor species were decreased significantly. Instead, it appears that $\text{C}_{10}\text{H}_{14}\text{O}_z$ is mainly impacted by the decrease in $\text{C}_{10}\text{H}_{15}\text{O}_x$ as their reductions are similar. A possible explanation could be that intramolecular termination is a major reaction pathway for $\text{C}_{10}\text{H}_{15}\text{O}_x\text{-RO}_2$, forming $\text{C}_{10}\text{H}_{14}\text{O}_x\text{-carbonyls}$. Intramolecular termination of the autoxidation chain has been discussed in the literature for different VOCs (Shen et al., 2021; Guo et al., 2022), Rissanen et al. (2014) discussed the possible importance of the unimolecular termination via an H-shift, followed by formation of a carbonyl functional group and OH loss in the autoxidation chain of cyclohexene. Piletic and Kleindienst (2022) calculated fast reaction rate constants in the range of $1\text{-}30\text{ s}^{-1}$ for such intramolecular termination reactions to carbonyls for some $\text{C}_{10}\text{H}_{17}\text{O}_5$ in the α -pinene photooxidation, indicating that this pathway could also be significant for $\text{C}_{10}\text{H}_{15}\text{O}_x$. However, more investigation is necessary.

The overall contributions of the $\text{C}_{10}\text{H}_{14}\text{O}_z$, $\text{C}_{10}\text{H}_{16}\text{O}_z$, and $\text{C}_{10}\text{H}_{18}\text{O}_z$ families to the HOM-Mon class at high HO_2/RO_2 are shifted as shown in **Fig. 11**.

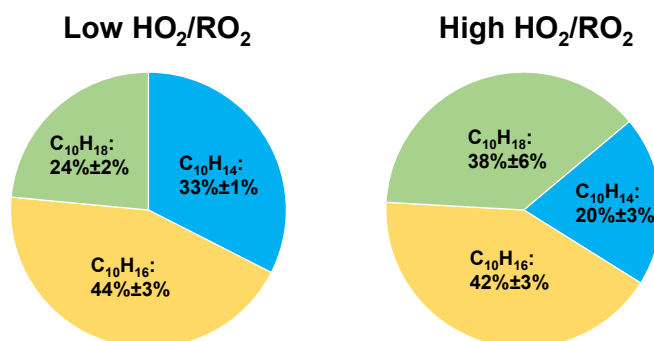


Figure 11: Average contribution of the $C_{10}H_{14}O_z$, $C_{10}H_{16}O_z$, and $C_{10}H_{18}O_z$ family to the monomer class signal at low and high HO_2/RO_2 (pure gas phase experiments).

The contribution of $C_{10}H_{16}O_z$ is largest and remains similar in both cases, matching the already shown unchanged signal level in **Fig. 6**. This is the case because the $C_{10}H_{16}O_z$ family contains the alcohols from $C_{10}H_{15}O_x + RO_2$, carbonyls from $C_{10}H_{17}O_x + RO_2$ and hydroperoxides from $C_{10}H_{15}O_x + HO_2$ (see **Fig. 1**). A separation of the effects of enhanced HO_2 on this monomer family is difficult, as for the case where RO_2 termination dominates vs. the case where HO_2 termination dominates, the loss of carbonyls and alcohols is partially compensated by the gain of hydroperoxides. A strong gain in hydroperoxides is clearly reflected in the strong increase of $C_{10}H_{18}O_z$ at high HO_2/RO_2 .

Inspection of the $C_{10}H_{14}O_z$ and $C_{10}H_{18}O_z$ families shows that ~13 % of the contribution by $C_{10}H_{14}O_z$ are lost (carbonyls, 33 % at low HO_2/RO_2) and are present instead as $C_{10}H_{18}O_z$ (hydroperoxides), giving $C_{10}H_{18}O_z$ a contribution of 38 % at high HO_2/RO_2 .

3.4 Impact on condensable organic mass

In the previous sections we demonstrated a shift of the product distribution by the shift from low to high HO_2/RO_2 conditions. We also showed that the changes could be rationalized by generic mechanistic considerations. We added $(NH_4)_2SO_4$ seed aerosol in two experiments to determine how the shift in the product distribution affects the condensable organic mass by determining the fraction which remained in the gas-phase after seeding.

Figure 12 shows the fraction remaining for the sum of all products as well as for the individual product classes for the high and the low HO_2/RO_2 case. In both cases a significant reduction of products in the gas phase was observed with seed present. Overall, the sum of all products was reduced by around 60 %, with a slightly higher reduction in the low HO_2/RO_2 case. This can be attributed to the larger importance of HOM-Acc in the low HO_2/RO_2 case, as well as to a 10 % lower reduction of the HOM-Frag in the high HO_2/RO_2 case. In both cases a reduction of the HOM- RO_2 is observed, which indicates that the provided particle sink could have affected HOM formation chemistry, however only moderately.

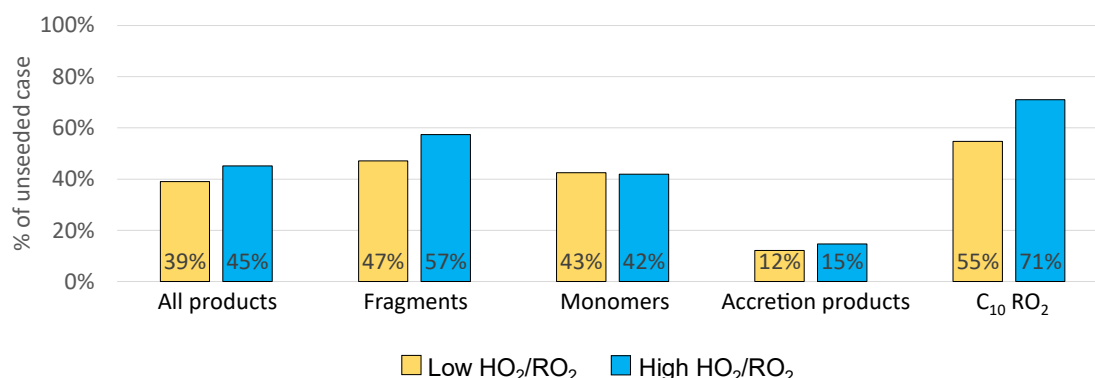


Figure 12: Overview of average, relative change in product classes signal between gas phase only and seeded system. Blue shows the high HO₂/RO₂ case, yellow the low HO₂/RO₂ case. (All are normalized to α -pinene OH turnover, *Exp2* experiment)

The total organic particulate mass was determined by AMS measurements and was 2.0 $\mu\text{g m}^{-3}$ and 3.4 $\mu\text{g m}^{-3}$ at high and low HO₂/RO₂ in the experiment (*Exp2*) displayed in **Fig. 12**. A reduction of condensed organic mass to 73 % $\pm$ 3 % at high HO₂/RO₂ (orange bar in **Fig. 14**) was observed on average. Since non-seeded and seeded experiments were conducted at otherwise the same conditions and we did not observe significant new particle formation, the gas-phase compositions can be directly compared. Therefore, we conclude that the shift in the product distribution led to a reduction of condensable material at the same α -pinene turnover with OH (and O₃).

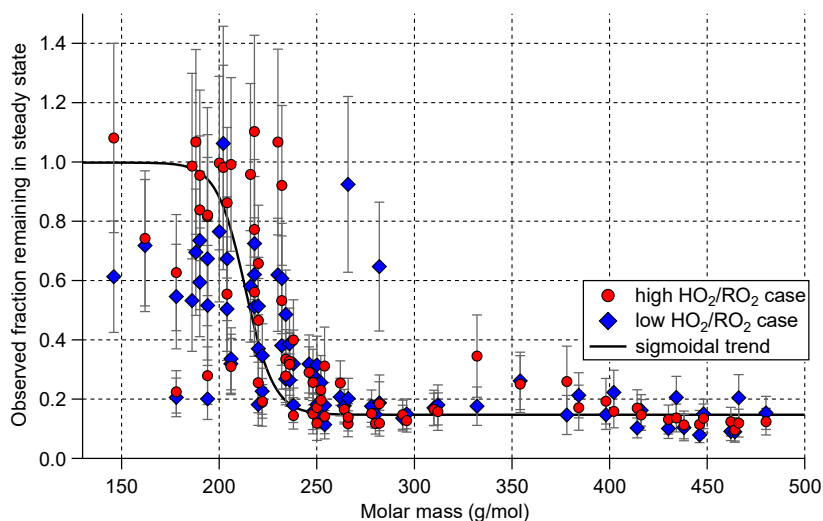
We calculated the wall loss corrected SOA yields with the corrected SOA mass as shown in **Eq. (4)** and as described by Sarrafzadeh et al. (2016). To this end we used C₁₀H₁₆O₇ as the lead HOM compound. In the two experiments with seed present (*Exp2.1* and *Exp3*) we had SOA yields of 7.3 % and 10.0 % at high HO₂/RO₂ and 10.0 % and 12.8 % at low HO₂/RO₂. The difference in the SOA yields between experiments can be explained by the slightly different OH concentrations and subsequent difference in contribution by photooxidation (see **Table 1**). Overall, our yields are in the lower range in comparison with the SOA yields reported by McFiggans et al. (2019) for the α -pinene photooxidation. However, our experiments were also performed at 5 °C higher temperature (20 °C compared to 15 °C in McFiggans et al. (2019)). The SOA yields show an absolute reduction of ~3 % at high HO₂/RO₂ compared to low HO₂/RO₂ (relative a reduction of about 30%). A reduction of the SOA yield of α -pinene by addition of CO was described before by McFiggans et al. (2019), however, there the α -pinene OH turnover was not held constant.

The change from low to high HO₂/RO₂ regime favored termination reactions to protic termination groups, as we observed less carbonyl compounds and more hydroperoxides. This could overall shift the product distribution to products with lower vapor pressures and favor SOA formation, since protic groups can act as hydrogen bond donors as well as hydrogen bond acceptors. (as exemplified by the comparison of ethanol (boiling point (b.p) 78 °C) and ethane hydroperoxide (b.p. 93-97 °C) with acetaldehyde (b.p. 20 °C) (Richter et al., 1955)). However, the effect of the termination group should be small for HOM as they likely contain multiple hydroperoxide groups (compare Pullinen et al. (2020)). The reduction in HOM-Acc is



618 expected to decrease the condensable mass, since the HOM-Acc scavenge non-HOM-RO₂, that would otherwise not partition
619 into the particle phase.

620 Which of the measured compounds contribute significantly to the organic particle mass can be inferred by comparing their
621 signal from the pure gas phase cases to their signal with seed in the system. Under the assumptions that, for most HOM-
622 compounds re-evaporation to the gas phase is negligible and that the precursor chemistry is not substantially disturbed by
623 seed addition, the fraction of signal remaining with seed in the system reflects to which degree the compound is condensing.
624 **Figure 13** shows the fraction remaining with seed in the system plotted against the molar mass of each individual compound.
625 The plot includes all closed shell products that were measured with a relative standard deviation of less than 30% for all
626 measurement phases and depicts the results for both the high and low HO₂/RO₂ case.



627

628 **Figure 13: Gas-phase fraction remaining in presence of seed (normalization of all data with α -pinene OH turnover) for the low**
629 **(blue) and high (red) HO₂/RO₂ case. Displayed points represent all closed-shell compounds that were detected with relative**
630 **standard deviation <30 % in all four experiment phases. Error bars represent result of error propagation (see supplement**
631 **Sect. S7)**

632 Overall, in both cases we observed the same trend. Lighter compounds are not affected by the presence of seed particles, but
633 with increasing molar mass the fraction remaining in the gas phase is reduced. A difference between the low and high
634 HO₂/RO₂ case can be observed in the low molar mass range: In the high HO₂/RO₂ case many fragmentation products show a
635 higher gas-phase fraction remaining up to 1. (In some cases, values larger than 1 were observed, however within the error
636 limits. For the error estimation see supplement **Sect. S7**). Fractions remaining larger than 1 beyond error could be an
637 indication that such products have a particle-phase production source. **Figure 13** also shows a critical SVOC/LVOC region
638 for molar masses between 175 g mol⁻¹ and 250 g mol⁻¹ where neither a fraction remaining of 1 nor complete condensation is
639 observed. The position of this region on the molar mass scale depends on the provided organic mass concentration. The large
640 variation of the fraction remaining in this small range of molar masses shows that the partitioning coefficients are dependent



on the detailed structure of the compounds and not simply on their molar mass. The semi-volatile and low volatility products represent mainly higher oxidized fragments and HOM-Mon with less than 8 oxygen.

For compounds with a molar mass larger than 250 g mol^{-1} a constant fraction remaining is reached in steady state, which is due to an ongoing production of the compounds. From the condensation behavior shown in **Fig. 13** we conclude that the compounds heavier than 230 g mol^{-1} are expected to be of sufficiently low volatility to be mainly found in the particle phase for the organic mass present in the system and therefore contribute significantly to the SOA mass formation. Our finding agrees with the threshold used for low volatility HOM products in Pullinen et al. (2020).

Therefore, the signal of all compounds with a molar mass heavier than 230 g mol^{-1} was weighted with their molar mass and summed (see **Eq. (2)**). The ratio of this weighted signal sum at low and high HO_2/RO_2 is then a measure of expected SOA mass loss. The calculation leads to an expected reduction of 72 % (blue bar, **Fig. 14**). This simplified approach leads to a good agreement with the AMS measurements and can thus explain the reduced particulate organic mass within the errors.

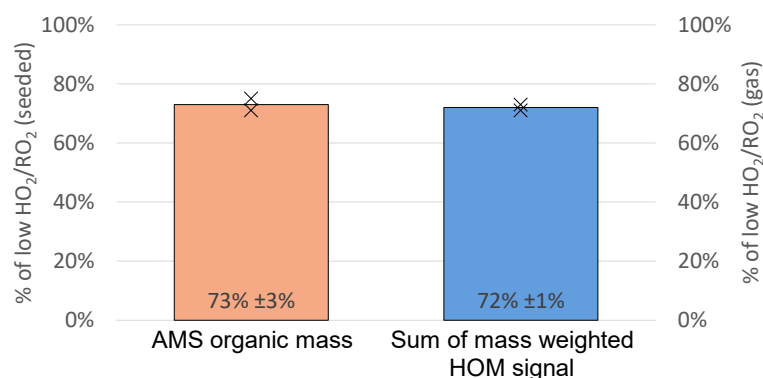


Figure 14: Overview of the average, relative change in organic mass observed in the AMS (left y-axis, seeded experiments) and the mass weighted HOM signal observed in the NO_3 -CIMS (right y-axis, pure gas phase experiments) between the low and high HO_2/RO_2 case (both normalized to α -pinene OH turnover).

To test for closure between HOM lost and particulate organic mass measured we approximated the upper limit of HOM concentration in the condensed phase. For this calculation we used the calibration factor determined for sulfuric acid for our NO_3 -MION-CIMS ($7.0 \cdot 10^9 \text{ molecules cm}^{-3} \text{ ncps}^{-1}$) and the relationship between gas and particulate concentration of a compound in the SAPHIR STAR chamber described in **Eq. (3)**. Again, we considered all compounds with $M > 230 \text{ g mol}^{-1}$ in our calculation. The summed mass concentration lost from the gas phase was then compared to the SOA mass measured in the AMS. This comparison yields a good agreement within the uncertainties. The detailed calculation results can be found in the supplement (**Fig. S3**). Overall, an agreement within 40 % is achieved for all measurement stages.



663 The comparisons presented above show that we understand the processes governing the SOA formation in our chamber and
664 that the NO_3 -CIMS measurements are well suited to observe the critical changes to understand the reduction in condensable
665 organic material when shifting from low to high HO_2/RO_2 .

666 4 Conclusion

667 In the presented series of experiments, we achieved a shift from a RO_2+RO_2 dominated chemistry to a more atmospherically
668 relevant HO_2/RO_2 ratio under constant α -pinene OH turnover. It was shown that moving towards atmospheric HO_2/RO_2 ratio
669 affected the SOA formation potential, with the observed organic mass being reduced at high HO_2/RO_2 . This is in support of
670 the potential bias towards high SOA yields in chamber studies at low HO_2/RO_2 as discussed by Schervish and Donahue
671 (2021). The gas-phase observations showed that the SOA reduction at high HO_2/RO_2 was mainly due to a reduced
672 HOM-Acc formation which were formed by RO_2+RO_2 cross reactions in the low HO_2/RO_2 cases. This prevented
673 contribution to SOA by less oxidized RO_2 which were scavenged in the HOM-Acc at low HO_2/RO_2 . Under atmospheric
674 condition such cross reactions are less important, and such (mixed) accretion products would contribute less to SOA.

675 The overall observed HOM-products were reduced slightly, showing that under certain circumstances RO_2+HO_2 termination
676 can impede the HOM formation, mainly by reducing the precursor RO_2 levels and less by impeding the autoxidation itself.
677 The autoxidation chain (once initiated) runs to a similar oxidation level at both high and low HO_2/RO_2 . The observed
678 HOM-Mon products shift significantly between monomer families due to the different termination reaction. A decrease in
679 carbonyl and alcohol formation from RO_2+RO_2 and an increase in hydroperoxide formation from RO_2+HO_2 was observed at
680 high HO_2/RO_2 .

681 Furthermore, a reduction in HOM-Frag products, especially with lower carbon numbers, as well as the parity of the $\text{C}_{10}\text{H}_{15}\text{O}_x$
682 HOM- RO_2 show a reduction in alkoxy radical formation at high HO_2/RO_2 . The moderate reduction in larger HOM-Frag
683 products and pinonaldehyde, however, suggest that some alkoxy radical steps are still important. This raises the question of
684 whether alkoxy radical formation can be facilitated by HO_2 . In the atmosphere such effects are most often overcome
685 whenever RO_2+NO is the major alkoxy radical source.

686 Overall, the observed changes in the gas phase could be well explained with the presented generic mechanistic understanding
687 of HOM formation in the α -pinene system. The addition of seed demonstrated that the shift towards high HO_2/RO_2 reduced
688 the condensable organic mass, stressing the importance of controlling higher order reactions of peroxy radicals which lead to
689 overemphasis of HOM-Acc product formation at low HO_2/RO_2 ratios.

690 Furthermore, the seed addition allowed us to determine which products were contributing to the SOA formation and show
691 that their volatility is a function of molar mass and detailed molecular structure. This revealed a critical mass region in which
692 compounds have significant fractions in gas and particulate phase. Based on absorptive partitioning theory the volatilities at
693 which this critical region is found should depend on the organic mass present in the system.



694 Valuable insight about the condensed phase can be gained from HOM gas phase measurements. We inferred conclusions
695 about the particulate phase from the gas phase measurements and compared them to the direct particle phase observations,
696 finding good agreements between our expectations and the measurements.

697 **Data availability**

698 All presented data will be available in a repository before the submission of the final manuscript.

699 **Author contribution**

700 TFM, MH and GM conceptualized the study and TFM, YB, SK and SRZ designed the experiments and developed the
701 analysis methodology. The experiments were performed by YB, SK, VG and SRZ. Instrument deployment and/or data
702 analysis were performed by YB, SK, HW, RW, JX, AZ, QH, TZ and VG. YB did model calculations of the experiments.
703 AV, SPO, TJB, MG and MH provided counsel on experiment design and data interpretation. The compiled data set was
704 interpreted by YB and TFM, and the results were discussed by all co-authors. YB visualized the data and YB and TFM
705 prepared the manuscript. All co-authors reviewed the manuscript.

706 **Competing interests**

707 The authors declare that they have no conflict of interest.

708 **Financial support**

709 This research has received funding from the European Union's Horizon 2020 research and innovation programme under the
710 FORCeS grant agreement No 821205, the Federal Ministry of Education and Research (BMBF) Germany under the FONA
711 Strategy "Research for Sustainability" as part of the implementation of ACTRIS-D under the funding code 01LK200010,
712 Vetenskapsrådet (VR, grant agreement No. 2018-04430), Svenska Forskningsrådet Formas (grant agreement No. 2019-586)
713 and the Natural Environment Research Council (NERC) UK under the grant agreement No. NE/V012665/1.



714 References

- 715 Albrecht, S. R., Novelli, A., Hofzumahaus, A., Kang, S., Baker, Y., Mentel, T., Wahner, A., and Fuchs, H.: Measurements of
716 hydroperoxy radicals (HO₂) at atmospheric concentrations using bromide chemical ionisation mass spectrometry, *Atmos.*
717 *Meas. Tech.*, 12, 891-902, <https://doi.org/10.5194/amt-12-891-2019>, 2019.
- 718 Atkinson, R. and Arey, J.: Atmospheric degradation of volatile organic compounds, *Chem. Rev.*, 103, 4605-4638,
719 <https://doi.org/10.1021/cr0206420>, 2003.
- 720 Berndt, T.: Peroxy Radical Processes and Product Formation in the OH Radical-Initiated Oxidation of α -Pinene for Near-
721 Atmospheric Conditions, *J. Phys. Chem. A*, 125, 9151-9160, <https://doi.org/10.1021/acs.jpca.1c05576>, 2021.
- 722 Berndt, T., Mentler, B., Scholz, W., Fischer, L., Herrmann, H., Kulmala, M., and Hansel, A.: Accretion product formation
723 from ozonolysis and OH radical reaction of α -pinene: mechanistic insight and the influence of isoprene and ethylene,
724 *Environ. Sci. Technol.*, 52, 11069-11077, <https://doi.org/10.1021/acs.est.8b02210>, 2018.
- 725 Berndt, T., Richters, S., Jokinen, T., Hyttinen, N., Kurtén, T., Otkjaer, R. V., Kjaergaard, H. G., Stratmann, F., Herrmann,
726 H., Sipila, M., Kulmala, M., and Ehn, M.: Hydroxyl radical-induced formation of highly oxidized organic compounds, *Nat.*
727 *Commun.*, 7, 13677, <https://doi.org/10.1038/ncomms13677>, 2016.
- 728 Bianchi, F., Garmash, O., He, X. C., Yan, C., Iyer, S., Rosendahl, I., Xu, Z. N., Rissanen, M. P., Riva, M., Taipale, R.,
729 Sarnela, N., Petäjä, T., Worsnop, D. R., Kulmala, M., Ehn, M., and Junninen, H.: The role of highly oxygenated molecules
730 (HOMs) in determining the composition of ambient ions in the boreal forest, *Atmos. Chem. Phys.*, 17, 13819-13831,
731 <https://doi.org/10.5194/acp-17-13819-2017>, 2017.
- 732 Bianchi, F., Kurtén, T., Riva, M., Mohr, C., Rissanen, M. P., Roldin, P., Berndt, T., Crounse, J. D., Wennberg, P. O., Mentel,
733 T. F., Wildt, J., Junninen, H., Jokinen, T., Kulmala, M., Worsnop, D. R., Thornton, J. A., Donahue, N., Kjaergaard, H. G.,
734 and Ehn, M.: Highly Oxygenated Organic Molecules (HOM) from Gas-Phase Autoxidation Involving Peroxy Radicals: A
735 Key Contributor to Atmospheric Aerosol, *Chem. Rev.*, 119, 3472-3509, <https://doi.org/10.1021/acs.chemrev.8b00395>, 2019.
- 736 Cox, R. A., Ammann, M., Crowley, J. N., Herrmann, H., Jenkin, M. E., McNeill, V. F., Mellouki, A., Troe, J., and
737 Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VII – Criegee intermediates,
738 *Atmos. Chem. Phys.*, 20, 13497-13519, <https://doi.org/10.5194/acp-20-13497-2020>, 2020.
- 739 Crounse, J. D., Nielsen, L. B., Jørgensen, S., Kjaergaard, H. G., and Wennberg, P. O.: Autoxidation of organic compounds in
740 the atmosphere, *J. Phys. Chem. Lett.*, 4, 3513-3520, <https://doi.org/10.1021/jz4019207>, 2013.
- 741 Eddingsaas, N., Loza, C., Yee, L., Seinfeld, J., and Wennberg, P.: α -Pinene photooxidation under controlled chemical
742 conditions – Part 1: Gas-phase composition in low- and high-NO_x environments, *Atmos. Chem. Phys.*, 12, 6489-6504,
743 <https://doi.org/10.5194/acp-12-6489-2012>, 2012.
- 744 Ehn, M., Thornton, J. A., Kleist, E., Sipila, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B.,
745 Lopez-Hilfiker, F., Andres, S., Acir, I. H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J.,
746 Nieminen, T., Kurtén, T., Nielsen, L. B., Jørgensen, S., Kjaergaard, H. G., Canagaratna, M., Maso, M. D., Berndt, T., Petaja,
747 T., Wahner, A., Kerminen, V. M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-
748 volatility secondary organic aerosol, *Nature*, 506, 476-479, <https://doi.org/10.1038/nature13032>, 2014.
- 749 Eisele, F. and Tanner, D.: Measurement of the gas phase concentration of H₂SO₄ and methane sulfonic acid and estimates of
750 H₂SO₄ production and loss in the atmosphere, *J. Geophys. Res. Atmos.*, 98, 9001-9010, <https://doi.org/10.1029/93JD00031>,
751 1993.
- 752 Fantechi, G., Vereecken, L., and Peeters, J.: The OH-initiated atmospheric oxidation of pinonaldehyde: Detailed theoretical
753 study and mechanism construction, *Phys. Chem. Chem. Phys.*, 4, 5795-5805, <https://doi.org/10.1039/B205901K>, 2002.
- 754 Guo, Y., Shen, H., Pullinen, I., Luo, H., Kang, S., Vereecken, L., Fuchs, H., Hallquist, M., Acir, I. H., Tillmann, R., Rohrer,
755 F., Wildt, J., Kiendler-Scharr, A., Wahner, A., Zhao, D. F., and Mentel, T. F.: Identification of highly oxygenated organic
756 molecules and their role in aerosol formation in the reaction of limonene with nitrate radical, *Atmos. Chem. Phys.*, 22,
757 11323-11346, <https://doi.org/10.5194/acp-22-11323-2022>, 2022.
- 758 Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George,
759 C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L.,
760 Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D.,
761 Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging
762 issues, *Atmos. Chem. Phys.*, 9, 5155-5236, <https://doi.org/10.5194/acp-9-5155-2009>, 2009.



- 763 Hantschke, L. L.: Oxidation of monoterpenes studied in atmospheric simulation chambers, Forschungszentrum Jülich
764 GmbH, Zentralbibliothek, Verlag, 2022.
- 765 Hasson, A. S., Kuwata, K. T., Arroyo, M. C., and Petersen, E. B.: Theoretical studies of the reaction of hydroperoxy radicals
766 (HO₂) with ethyl peroxy (CH₃CH₂O₂), acetyl peroxy (CH₃C(O)O₂), and acetonyl peroxy (CH₃C(O)CH₂O₂) radicals, J.
767 Photochem. Photobiol. A, 176, 218-230, <https://doi.org/10.1016/j.jphotochem.2005.08.012>, 2005.
- 768 Henry, K. M., Lohaus, T., and Donahue, N. M.: Organic aerosol yields from α -pinene oxidation: bridging the gap between
769 first-generation yields and aging chemistry, Environ. Sci. Technol., 46, 12347-12354, <https://doi.org/10.1021/es302060y>,
770 2012.
- 771 Hidy, G.: Atmospheric chemistry in a box or a bag, Atmos., 10, 401, <https://doi.org/10.3390/atmos10070401>, 2019.
- 772 Hyttinen, N., Otkjær, R. V., Iyer, S., Kjaergaard, H. G., Rissanen, M. P., Wennberg, P. O., and Kurtén, T.: Computational
773 comparison of different reagent ions in the chemical ionization of oxidized multifunctional compounds, J. Phys. Chem. A,
774 122, 269-279, <https://doi.org/10.1021/acs.jpca.7b10015>, 2018.
- 775 Iyer, S., Reiman, H., Möller, K. H., Rissanen, M. P., Kjaergaard, H. G., and Kurtén, T.: Computational investigation of
776 RO₂+ HO₂ and RO₂+ RO₂ reactions of monoterpene derived first-generation peroxy radicals leading to radical recycling, J.
777 Phys. Chem. A, 122, 9542-9552, <https://doi.org/10.1021/acs.jpca.8b09241>, 2018.
- 778 Iyer, S., Rissanen, M. P., Valiev, R., Barua, S., Krechmer, J. E., Thornton, J., Ehn, M., and Kurtén, T.: Molecular mechanism
779 for rapid autoxidation in α -pinene ozonolysis, Nat. Commun., 12, 878, <https://doi.org/10.1038/s41467-021-21172-w>, 2021.
- 780 Jenkin, M. E., Saunders, S. M., and Pilling, M. J.: The tropospheric degradation of volatile organic compounds: a protocol
781 for mechanism development, Atmos. Environ., 31, 81-104, [https://doi.org/10.1016/S1352-2310\(96\)00105-7](https://doi.org/10.1016/S1352-2310(96)00105-7), 1997.
- 782 Jenkin, M. E., Valorso, R., Aumont, B., and Rickard, A. R.: Estimation of rate coefficients and branching ratios for reactions
783 of organic peroxy radicals for use in automated mechanism construction, Atmos. Chem. Phys., 19, 7691-7717,
784 <https://doi.org/10.5194/acp-19-7691-2019>, 2019.
- 785 Johnson, D. and Marston, G.: The gas-phase ozonolysis of unsaturated volatile organic compounds in the troposphere,
786 Chem. Soc. Rev., 37, 699-716, <https://doi.org/10.1039/B704260B> 2008.
- 787 Junninen, H., Ehn, M., Petäjä, T., Luosujärvi, L., Kotiaho, T., Kostianinen, R., Rohner, U., Gonin, M., Fuhrer, K., Kulmala,
788 M., and Worsnop, D. R.: A high-resolution mass spectrometer to measure atmospheric ion composition, Atmos. Meas.
789 Tech., 3, 1039-1053, <https://doi.org/10.5194/amt-3-1039-2010>, 2010.
- 790 Kang, S.: Formation of highly oxygenated organic molecules from α -pinene photochemistry, Forschungszentrum Jülich
791 GmbH, 2021.
- 792 Kiendler-Scharr, A., Wildt, J., Maso, M. D., Hohaus, T., Kleist, E., Mentel, T. F., Tillmann, R., Uerlings, R., Schurr, U., and
793 Wahner, A.: New particle formation in forests inhibited by isoprene emissions, Nature, 461, 381-384,
794 <https://doi.org/10.1038/nature08292>, 2009.
- 795 McFiggans, G., Mentel, T. F., Wildt, J., Pullinen, I., Kang, S., Kleist, E., Schmitt, S., Springer, M., Tillmann, R., Wu, C.,
796 Zhao, D., Hallquist, M., Faxon, C., Le Breton, M., Hallquist, A. M., Simpson, D., Bergstrom, R., Jenkin, M. E., Ehn, M.,
797 Thornton, J. A., Alfarra, M. R., Bannan, T. J., Percival, C. J., Priestley, M., Topping, D., and Kiendler-Scharr, A.: Secondary
798 organic aerosol reduced by mixture of atmospheric vapours, Nature, 565, 587-593, <https://doi.org/10.1038/s41586-018-0871-y>, 2019.
- 800 Mentel, T., Springer, M., Ehn, M., Kleist, E., Pullinen, I., Kurtén, T., Rissanen, M., Wahner, A., and Wildt, J.: Formation of
801 highly oxidized multifunctional compounds: autoxidation of peroxy radicals formed in the ozonolysis of alkenes—deduced
802 from structure–product relationships, Atmos. Chem. Phys., 15, 6745-6765, <https://doi.org/10.5194/acp-15-6745-2015>, 2015.
- 803 Mentel, T. F., Wildt, J., Kiendler-Scharr, A., Kleist, E., Tillmann, R., Dal Maso, M., Fisseha, R., Hohaus, T., Spahn, H.,
804 Uerlings, R., Wegener, R., Griffiths, P. T., Dinar, E., Rudich, Y., and Wahner, A.: Photochemical production of aerosols
805 from real plant emissions, Atmos. Chem. Phys., 9, 4387-4406, <https://doi.org/10.5194/acp-9-4387-2009>, 2009.
- 806 Mohr, C., Thornton, J. A., Heitto, A., Lopez-Hilfiker, F. D., Lutz, A., Riipinen, I., Hong, J., Donahue, N. M., Hallquist, M.,
807 Petaja, T., Kulmala, M., and Yli-Juuti, T.: Molecular identification of organic vapors driving atmospheric nanoparticle
808 growth, Nat. Commun., 10, 4442, <https://doi.org/10.1038/s41467-019-12473-2>, 2019.
- 809 Piletic, I. R. and Kleindienst, T. E.: Rates and yields of unimolecular reactions producing highly oxidized peroxy radicals in
810 the OH-induced autoxidation of α -pinene, β -pinene, and limonene, J. Phys. Chem. A, 126, 88-100,
811 <https://doi.org/10.1021/acs.jpca.1c07961>, 2022.



- 812 Pullinen, I., Schmitt, S., Kang, S., Sarrafzadeh, M., Schlag, P., Andres, S., Kleist, E., Mentel, T. F., Rohrer, F., Springer, M.,
813 Tillmann, R., Wildt, J., Wu, C., Zhao, D., Wahner, A., and Kiendler-Scharr, A.: Impact of NO_x on secondary organic aerosol
814 (SOA) formation from α -pinene and β -pinene photooxidation: the role of highly oxygenated organic nitrates, *Atmos. Chem.*
815 *Phys.*, 20, 10125-10147, <https://doi.org/10.5194/acp-20-10125-2020>, 2020.
- 816 Richter, F., Ostertag, R., Ammerlahn, G., Behrle, E., Baumann, M., and Kobel, M.: Beilstein's handbook of organic
817 chemistry. Third supplement, covering the literature from 1930-1949, 1955.
- 818 Rissanen, M. P., Mikkilä, J., Iyer, S., and Hakala, J.: Multi-scheme chemical ionization inlet (MION) for fast switching of
819 reagent ion chemistry in atmospheric pressure chemical ionization mass spectrometry (CIMS) applications, *Atmos. Meas.*
820 *Tech.*, 12, 6635-6646, <https://doi.org/10.5194/amt-12-6635-2019>, 2019.
- 821 Rissanen, M. P., Kurtén, T., Sipilä, M., Thornton, J. A., Kangasluoma, J., Sarnela, N., Junninen, H., Jorgensen, S.,
822 Schallhart, S., Kajos, M. K., Taipale, R., Springer, M., Mentel, T. F., Ruuskanen, T., Petaja, T., Worsnop, D. R., Kjaergaard,
823 H. G., and Ehn, M.: The formation of highly oxidized multifunctional products in the ozonolysis of cyclohexene, *J. Am.*
824 *Chem. Soc.*, 136, 15596-15606, <https://doi.org/10.1021/ja507146s>, 2014.
- 825 Roldin, P., Ehn, M., Kurtén, T., Olenius, T., Rissanen, M. P., Sarnela, N., Elm, J., Rantala, P., Hao, L., Hyttinen, N.,
826 Heikkinen, L., Worsnop, D. R., Pichelstorfer, L., Xavier, C., Clusius, P., Öström, E., Petäjä, T., Kulmala, M., Vehkamäki,
827 H., Virtanen, A., Riipinen, I., and Boy, M.: The role of highly oxygenated organic molecules in the Boreal aerosol-cloud-
828 climate system, *Nat. Commun.*, 10, 4370, <https://doi.org/10.1038/s41467-019-12338-8>, 2019.
- 829 Sanchez, J., Tanner, D. J., Chen, D., Huey, L. G., and Ng, N. L.: A new technique for the direct detection of HO₂ radicals
830 using bromide chemical ionization mass spectrometry (Br-CIMS): initial characterization, *Atmos. Meas. Tech.*, 9, 3851-
831 3861, <https://doi.org/10.5194/amt-9-3851-2016>, 2016.
- 832 Sarrafzadeh, M., Wildt, J., Pullinen, I., Springer, M., Kleist, E., Tillmann, R., Schmitt, S. H., Wu, C., Mentel, T. F., Zhao,
833 D., Hastie, D. R., and Kiendler-Scharr, A.: Impact of NO_x and OH on secondary organic aerosol formation from β -pinene
834 photooxidation, *Atmos. Chem. Phys.*, 16, 11237-11248, <https://doi.org/10.5194/acp-16-11237-2016>, 2016.
- 835 Saunders, S. M., Jenkin, M. E., Derwent, R., and Pilling, M.: Protocol for the development of the Master Chemical
836 Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, *Atmos. Chem. Phys.*,
837 3, 161-180, <https://doi.org/10.5194/acp-3-161-2003>, 2003.
- 838 Schervish, M. and Donahue, N. M.: Peroxy radical kinetics and new particle formation, *Environ. Sci. Atmos.*, 1, 79-92,
839 <https://doi.org/10.1039/d0ea00017e>, 2021.
- 840 Shen, H., Vereecken, L., Kang, S., Pullinen, I., Fuchs, H., Zhao, D., and Mentel, T. F.: Unexpected significance of a minor
841 reaction pathway in daytime formation of biogenic highly oxygenated organic compounds, *Sci. Adv.*, 8, eabp8702,
842 <https://doi.org/10.1126/sciadv.abp8702>, 2022.
- 843 Shen, H., Zhao, D., Pullinen, I., Kang, S., Vereecken, L., Fuchs, H., Acir, I. H., Tillmann, R., Rohrer, F., Wildt, J., Kiendler-
844 Scharr, A., Wahner, A., and Mentel, T. F.: Highly Oxygenated Organic Nitrates Formed from NO(3) Radical-Initiated
845 Oxidation of β -Pinene, *Environ. Sci. Technol.*, 55, 15658-15671, <https://doi.org/10.1021/acs.est.1c03978>, 2021.
- 846 Shilling, J. E., Chen, Q., King, S. M., Rosenoern, T., Kroll, J. H., Worsnop, D. R., DeCarlo, P. F., Aiken, A. C., Sueper, D.,
847 Jimenez, J. L., and Martin, S. T.: Loading-dependent elemental composition of α -pinene SOA particles, *Atmos. Chem.*
848 *Phys.*, 9, 771-782, <https://doi.org/10.5194/acp-9-771-2009>, 2009.
- 849 Vereecken, L., Müller, J.-F., and Peeters, J.: Low-volatility poly-oxygenates in the OH-initiated atmospheric oxidation of α -
850 pinene: impact of non-traditional peroxy radical chemistry, *Phys. Chem. Chem. Phys.*, 9, 5241-5248,
851 <https://doi.org/10.1039/b708023a>, 2007.
- 852 Wildt, J., Mentel, T. F., Kiendler-Scharr, A., Hoffmann, T., Andres, S., Ehn, M., Kleist, E., Müsgen, P., Rohrer, F., Rudich,
853 Y., Springer, M., Tillmann, R., and Wahner, A.: Suppression of new particle formation from monoterpene oxidation by
854 NO_x, *Atmos. Chem. Phys.*, 14, 2789-2804, <https://doi.org/10.5194/acp-14-2789-2014>, 2014.
- 855 Xu, L., Møller, K. H., Crounse, J. D., Otkjær, R. V., Kjaergaard, H. G., and Wennberg, P. O.: Unimolecular reactions of
856 peroxy radicals formed in the oxidation of α -pinene and β -pinene by hydroxyl radicals, *J. Phys. Chem. A*, 123, 1661-1674,
857 <https://doi.org/10.1021/acs.jpca.8b11726>, 2019.