Answers to the Referees for “Molecular understanding of the suppression of new-particle formation by isoprene”, Heinritzi et al.

Manuscript number: acp-2020-51

We thank both referees for their comments, which are shown below in black font. Our replies are shown in blue.

Anonymous Referee #1

New particle formations (NPF) connected to RO2 radical chemistry from the OH oxidation of the monoterpenes are discussed extensively in recent studies especially after the findings of the autooxidation reactions. The isoprene was found to suppress new particle formation events in forested areas. And this is firstly explained by the suppression of the OH due to the addition of isoprene to the reaction system of monoterpene. Nevertheless, the OH concentration was found to be sustained or even enhanced within the isoprene oxidations. So other explanations for the isoprene suppression effects on the NPF are required.

As indicated by McFiggans et al., Nature, 2019 isoprene can actually suppress the SOA yield through scavenging of both the OH and the Monoterpenes derived RO2. In this study the authors followed the arguments on that direction and delivered molecular explanations of the isoprene suppression effects on the NPF based on chamber (CLOUD) experiments and direct measurement of the RO2-HOMs through a nitrate CIMS. I think this paper is in general well written and fit the scope of ACP. It is definitely worth to be published in ACP.

I have the following comments for the authors to consider before publication.

1. It is important for the authors to have a better estimation (e.g. probably through a box model) of the OH and HO2 concentrations in the chamber. As pointed out by the authors, the addition of isoprene will change OH, HO2 and produce isoprene-RO2. It is important to answer whether the suppression of NPF by isoprene is due to the enhanced HO2 or additionally produced RO2. The H-shift of isoprene-RO2 also produce significant amount of HO2.

The referee raises the question whether the suppression of NPF is caused by enhanced HO2 or additionally produced RO2. We can address this question directly with our data, without the need to rely on a model, as HO2 termination has a different effect on the HOM distribution than RO2 termination.

If HO2 termination dominates, dimer formation (both C15 and C20) is unfavorable, while monomers formation is expected to be the only significant channel (C5 and C10). When we add isoprene to our α-pinene/ozone mixture, we see that C20 dimers decrease. This by itself could be caused by, either an HO2 or an RO2(isoprene) increase (see Figure S3); however, we also see a significant increase in C15 dimers, which rules out a HO2 dominated termination regime, as HO2 would terminate RO2(ap) to C10 monomers and RO2(isoprene) to C5 monomers. C15 dimers can only be formed by reactions between RO2(ap) and RO2(ip), which in turn only occurs in significant proportions, when HO2 termination does not dominate. So we can conclude that the suppression of NPF is indeed caused by RO2 and not HO2.

The referee points out that the H-shift of isoprene-RO2 can produce significant amounts of HO2. Crounse et al. (2011) studied the ratio of HO2 producing isomerization reactions of isoprene-RO2 to HO2 consuming ISOPOOH formation. They found that at 295 K both channels are approximately of same magnitude ($k_{isom}/k_{ISO2+HO2} = 1.18 \pm 0.18$). This temperature corresponds roughly to the 298 K used in
Our study. The importance of the isomerization channel (and thus HO₂ production) increases drastically at higher temperatures \( k_{\text{isom}}/k_{\text{ISO}_2+\text{HO}_2} = 10.7 \pm 1.1 \) at 318 K, but for the temperatures in our study (278 K and 298 K), we would not expect HO₂ to dominate. This agrees with our data, where we also see a RO₂ dominated termination regime, as shown above.

We agree however with the referee’s statement that a better estimation of the OH and HO₂ concentrations in the CLOUD chamber is important. As the best approach is always a direct measurement of those molecules, we are working to include this capability for upcoming campaigns to our experimental setup.

2. The figure 2 show the scheme of the isoprene impact on the C20 dimer clearly. Nevertheless, it is not clear that what is the branching ratio of the H-shift of isoprene-RO₂ proceed to C5H9O7,8,9 and the H-shift yield HAPLDs. In the observations (Figure S1), the observed C5H9O8,9 is presented. Have you also observed C5H9O3,5,7? I understand that the PTR3 can also detect RO₂-HOMs. Do the authors also analyzed the RO₂-HOMs from the PTR3 signal?

Below we provide a modified version of Fig S1, which includes additional traces from the CI-APITOF (panel b). We see that the dominant isoprene-RO₂S are C₅H₉H₇,₈,₉. We find smaller contributions from C₅H₉O₄,₅, but could not directly measure C₅H₉O₃ in the CI-APITOF.

The PTR3 can in principle measure RO₂ radicals, as well as HPALDs, however only when NH₄⁺ is used as reagent ion system. This was not the case for our experiments, as it would have reduced the sensitivity for precursor compounds. The H₃O⁺ mode is too hard for these molecules to survive ionization without fragmentation.

We do see a C₅H₉O₃ trace in the CI-APITOF (panel b, dark green dotted line), which could potentially originate from HPALDs. However, as only three oxygens are present in HPALDS, the ionization efficiency for these molecules with NO₃ reagent ions is already drastically below unity and thus a proper quantification remains challenging. (The given concentrations in panel b assume ionization efficiency of unity, so for low-oxygen molecules the given traces are a stark underrepresentation of actual concentrations. This is the reason why we have only given traces for molecules with five or more oxygens in the submitted manuscript).

So we cannot give an estimate for HPALDs as well as the branching ratio between HPALD and C₅H₉O₇,₈,₉. However, we would like to point out that this does not affect the conclusions of our manuscript.
This paper investigates the molecular mechanisms for the suppression of new particle formation from monoterpenes by isoprene. The authors found that isoprene significantly suppresses the nucleation and the growth of the smallest particles from α-pinene oxidation, and showed that this suppression is mainly a result of interference of isoprene oxidation on the production of α-pinene HOM dimers, which are the major ELVOCs driving particle nucleation and early growth. This paper is nicely written and provide important molecular constraints on new particle formation in isoprene-rich regions.

I recommend the publication of the paper in ACP after the authors address a few minor comments detailed below.

L101-102: The recent study by Berndt et al. (ES&T, 2018) that was cited in this paper reported the interactions between isoprene- and α-pinene-derived peroxy radicals in α-pinene/isoprene mixed systems. More recently, the Nature paper by McFiggans et al. (2019) that was also cited in the paper clearly showed that the concurrent isoprene oxidation largely scavenges α-pinene HOM dimers, in addition to scavenging OH radicals, leading to reduced SOA formation from α-pinene/isoprene mixtures. Therefore, the statement “the interaction of isoprene and monoterpene oxidation chemistry remains unclear” needs to be rephrased.

The statement was rephrased. It now reads:

“Recently, the interaction of isoprene and monoterpene oxidation chemistry was studied and it was found that isoprene derived RO₂ molecules can reduce the formation of monoterpene-derived dimers (Berndt et al., 2018; McFiggans et al., 2019). However, the effect of this interaction on nucleation and early growth of particles under atmospherically relevant conditions remains unclear so far.”

L270-280: A discussion of the relevant findings in McFiggans et al. (2019) should be included in this paragraph.

We have included the following discussion to the revised manuscript:

“McFiggans et al. (2019) showed that the same RO₂· mechanism that we describe here is also responsible for reduced SOA formation, together with an additional OH· scavenging effect. The oxidation chemistry in McFiggans et al. (2019) was dominated (> 90 %) by OH· for both monoterpenes and isoprene. In our experimental conditions, monoterpene oxidation was dominated by ozone, which is more common in the atmosphere, and we demonstrate the importance of the RO₂· mechanism directly in these conditions. Additionally, while the precursor concentrations in McFiggans et al. (2019) were much higher than typical atmospheric levels, the precursor levels in the current study resemble the atmosphere more closely. This is especially important as HOM formation is not a linear process and can thus not be scaled down to atmospheric levels in a straightforward manner.

All extrapolations of chamber experiments to atmospheric conditions must be treated with care; for example, it has been shown that isoprene OH· scavenging is stronger in common chamber conditions than in ambient conditions, where OH· recycling (e.g. by HPALD photolysis) counters the OH· consumption by isoprene (Taraborrelli et al., 2012).

McFiggans et al. (2019) also show that OH· scavenging by isoprene is important for reduced SOA formation. We also find a reduction in OH· levels due to isoprene addition in the CLOUD chamber. However, this is not the reason for the suppression of nucleation and early growth rates in our
experiments. Quite to the contrary, the dominant effect of increased OH· in our experiments is to increase RO2(ip) due to the fast reaction between isoprene and OH·. OH· thus suppresses C_{20} dimers and nucleation rates in our chemical system. Thus, while increased OH· levels restore SOA formation partially in the coupled monoterpenes/isoprene system, as shown by McFiggans et al. (2019), they suppress nucleation in our experiments. This further highlights the important differences between SOA formation with preexisting seed particles on the one hand and the nucleation of new particles on the other hand. SOA mass production and nucleation are not the same thing. SOA formation with preexisting particles can include molecules possessing comparatively high saturation vapor pressures; however, due to the Kelvin effect (Tröstl et al., 2016), nucleation depends critically on molecules with extremely low saturation vapor pressure. Most of the C_{20} and C_{15}, many of the C_{10} and some of the C_{5} products can form SOA mass, whereas nucleation under atmospheric conditions is driven largely by the C_{20} dimers. Even replacing C_{20} with C_{15} dimers suppresses nucleation, as shown in this study.”

L295: “α-pinene isoprene system” -> “α-pinene/isoprene system”.

Done

References:

List of relevant changes to the manuscript:

(All changes are marked in red in the manuscript)

l. 116-121: rephrased statement as required by referee #2

l. 325-355: added discussion as required by referee #2
Molecular understanding of the suppression of new-particle formation by isoprene

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Abstract

Nucleation of atmospheric vapors produces more than half of global cloud condensation nuclei and so has an important influence on climate. Recent studies show that monoterpenes (C_{10}H_{16}) oxidation yields highly-oxygenated products that can nucleate with or without sulfuric acid. Monoterpenes are emitted mainly by trees, frequently together with isoprene (C_{5}H_{8}), which has the highest global emission of all organic vapors. Previous studies have shown that isoprene suppresses new-particle formation from monoterpenes, but the cause of this suppression is under debate. Here, in experiments performed under atmospheric conditions in the CERN CLOUD chamber, we show that isoprene reduces the yield of highly-oxygenated dimers with 19 or 20 carbon atoms - which drive particle nucleation and early growth - while increasing the production of dimers with 14 or 15 carbon atoms. The dimers (termed C_{35} and C_{15}, respectively) are produced by termination reactions between pairs of peroxy radicals (RO_{2}·) arising from monoterpenes or isoprene. Compared with pure monoterpene conditions, isoprene reduces nucleation rates at 1.7 nm (depending on the isoprene/monoterpene ratio) and approximately halves particle growth rates between 1.3 and 3.2 nm. However, above 3.2 nm, C_{15} dimers contribute to secondary organic aerosol and the growth rates are unaffected by isoprene. We further show that increased hydroxyl radical (OH·) reduces particle formation in our chemical system rather than enhances it as previously proposed, since it increases isoprene derived RO_{2}· radicals that reduce C_{35} formation. RO_{2}· termination emerges as the critical step that determines the HOM distribution and the corresponding nucleation capability. Species that reduce the C_{35} yield, such as NO, HO_{2} and as we show isoprene, can thus effectively reduce biogenic nucleation and early growth. Therefore the formation rate of organic aerosol in a particular region of the atmosphere under study will vary according to the precise ambient conditions.

1. Introduction

Nucleation of aerosol particles is observed in many environments, ranging from boreal forests to urban and coastal areas, from polar to tropical regions and from the boundary layer to the free troposphere (Kerminen et al., 2018). Gaseous sulfuric acid, ammonia (Kirkby et al., 2011), amines (Almeida et al., 2013) and, in coastal regions, iodine (Sipilä et al., 2016), were shown to contribute to nucleation. Additionally, a small fraction of the large pool of organic molecules in the atmosphere, namely highly-oxygenated organic molecules (HOMs), some of which possess extremely low vapor pressures, nucleate together with other precursors as well as on their own (Riccobono et al., 2014; Kirkby et al., 2016; Tröstl et al., 2016). This means nature is nucleating particles on a large scale without pollution, and this may have been especially pervasive in the pre-industrial atmosphere (Gordon et al., 2016). HOMs can be formed with molar yields in the single-digit percent range from the oxidation of monoterpenes (C_{10}H_{16}) with endocyclic C=C double-bonds (Kirkby et al., 2016; Ehn et al., 2014). Monoterpenes are emitted by a variety of trees in regions ranging from the tropics to northern latitudes, often reaching mixing ratios of tens to hundreds of parts per trillion by volume (pptv) (Jardine et al., 2015; Guenther et al., 2012). Isoprene is a hemiterpene (C_{5}H_{8}) emitted by broad-leaf trees and has the highest emissions of any biogenic organic compound, with concentrations reaching several parts per billion by volume (ppbv) in the Amazon rainforest and the southeastern United States despite high reactivity (Guenther et al., 2012; Martin et al., 2010; Lee et al., 2016). Numerous studies report suppression of nucleation in isoprene-rich environments, even if sufficient monoterpenes are present (Lee et al., 2016; Kanawade et al., 2011; Yu et al., 2014; Kiendler-Scharr et al., 2009; Kiendler-Scharr et al., 2012; Varanda Rizzo et al., 2018; Wimmer et al., 2018). This isoprene suppression effect has been demonstrated in carefully controlled chamber studies (Kiendler-Scharr et al., 2009; Kiendler-Scharr et al., 2012) and observed in isoprene-rich ambient locations (Kanawade et al., 2011; Lee et al., 2016; Yu et al., 2014). A recent study reported also a suppression of secondary organic aerosol (SOA) formation due to isoprene in an OH· dominated chamber experiment (McFiggans et al., 2019). In addition to observing suppression of particle formation by isoprene, earlier studies have proposed mechanisms to explain it. One possibility is OH· depletion by isoprene, which would reduce the oxidation rate of monoterpenes and thus supersaturation driving nucleation (Kiendler-Scharr et al., 2009; Kiendler-Scharr et al., 2012; McFiggans et al., 2019). However, OH· is observed to remain high and undisturbed in isoprene-rich environments due to atmospheric OH· recycling mechanisms triggered by isoprene (Taraborrelli et al., 2012; Martinez et al., 2010; Fuchs et al., 2013). Further it was shown that ozonolysis is crucial for HOM formation (Ehn et al., 2014; Kirkby et al., 2016). Another proposed possibility for
Isoprene suppression of nucleation is the deactivation of sulfuric acid cluster growth due to addition of isoprene oxidation products (Lee et al., 2016). However, HOMs can nucleate without sulfuric acid (Kirkby et al., 2016) and suppression of nucleation by isoprene is observed in pristine environments such as the Amazon (Martin et al., 2010).

Isoprene oxidation by OH· triggers complex peroxy-radical chemistry with a variety of products such as hydroxy-hydroperoxides (ISOPOOH), hydroperoxy-aldehydes (HPALD) as well as second-generation low-volatility compounds (Teng et al., 2017; Berndt et al., 2016). Isoprene oxidation products with low volatility such as dihydroxyepoxides (IEPOX) contribute to secondary organic aerosol formation (Carlton et al., 2009; Krechmer et al., 2015; Paulot et al., 2009; Surratt et al., 2010; Lin et al., 2011; Budisulistiorini et al., 2013). However, the interaction of isoprene and monoterpene oxidation chemistry and the consequent effect on nucleation and growth of new particles remains unclear. Recently, the interaction of isoprene and monoterpene oxidation chemistry was studied and it was found that isoprene derived RO$_2$ molecules can reduce the formation of monoterpene derived dimers (Berndt et al., 2018b; McFiggans et al., 2019).

However, the effect of this interaction on nucleation and early growth of particles under atmospherically relevant conditions remains unclear so far. One consequence of this is an over-prediction of cloud condensation nuclei (CCN) in the Amazon by models that simulate pure biogenic nucleation, but neglect the role of isoprene in new-particle formation (Gordon et al., 2016).

Here, we present experiments performed under atmospherically relevant conditions at the CERN CLOUD chamber and show on a molecular level how isoprene affects the chemistry of monoterpene oxidation, thus reducing nucleation rates as well as early growth rates.

2. Methods

The Cosmics Leaving Outdoor Droplets (CLOUD) chamber at the European Center for Nuclear Research (CERN) is a 26.1 m$^3$ stainless steel aerosol chamber, in which a large variety of atmospheric conditions can be recreated under precisely controlled conditions (Kirkby et al., 2011; Kirkby et al., 2016; Duplissy et al., 2016). The chamber is thermally insulated and its temperature can be precisely controlled in the range from -65 °C to 100 °C. In order to reduce contaminations, air mixed from cryogenic nitrogen and oxygen is used. Trace gases like $\alpha$-pinene and isoprene can be added and controlled via a two stage dilution system at the parts per trillion by volume level. Mixing is ensured by two magnetically coupled fans. The chamber is equipped with a UV excimer laser and HgXe UV lamps in order to trigger photochemistry. Ion-free conditions can be generated by applying a high voltage electric field across the chamber that sweeps out naturally produced ions (neutral conditions). When this field is switched off, ions produced by galactic cosmic rays penetrating the chamber are allowed to stay inside the chamber and their effect on nucleation processes can be studied. Using the CERN $\pi^+$-beam increases the ion concentration artificially (see SI Appendix for more detail).

The air inside the chamber is continuously analyzed by a variety of instruments. Organic precursors ($\alpha$-pinene and isoprene) are measured by a PTR3 instrument (Breitenlechner et al., 2017). HOMs are measured by a nitrate CI-API-TOF (Kürten et al., 2011) that is connected to the chamber via a 1” core sampling probe, where only the inner part of the flow is sampled into the ion source of the instrument in order to minimize wall losses. Number concentration and size distribution of newly formed particles are measured with an array of butanol based condensation particle counters (CPCs), diethylene glycol based Particle Size Magnifiers (PSMs), as well as a DMA-train and a Scanning Mobility Particle Sizer (SMPS) (see SI Appendix for more detail).

A typical experiment starts with the injection of $\alpha$-pinene into the particle free chamber (see Fig. S1 and S2), while other parameters like temperature, humidity and ozone levels are already stabilized. Oxidation of $\alpha$-pinene by both O$_3$ and OH leads to the formation of HOMs, which subsequently lead to the formation of particles. The experiment is continued without intervention until a steady state in HOMs and nucleation rate has been established. Once the nucleation and growth rates have been determined, the next experiment is performed under slightly different conditions. Parameters that were varied are $\alpha$-pinene and isoprene levels, ion concentration, UV illumination, sulfuric acid concentration, temperature and relative humidity.
3. Results

We performed several experiments at +5 and +25 °C and relative humidity (RH) ranging from 20 to 80 % with most of the experiments being carried out at 38 % RH. Ozone levels ranged from 20 – 50 ppbv. We directly compare experiments performed with α-pinene as the sole biogenic vapor to experiments with a mixture of α-pinene and isoprene. α-Pinene levels ranged from 0.33 to 2.5 ppbv, while isoprene levels ranged from 2.5 to 10 ppbv. We thus could recreate conditions similar to Kirkby et al. (2016), as well as to regions like the Amazon (Martin et al., 2010; Yáñez-Serrano et al., 2018) and southeastern parts of the United States (Lee et al., 2016).

Ozone attack to the endocyclic α-pinene C=C double bond leads to the well-described formation of highly-oxygenated RO₂⁻ radicals via intramolecular H-shift and autoxidation (mainly C₁₀H₁₂O₅,6,8,10, from now on referred to as RO₂⁻(ap)) as well as a wide spectrum of closed-shell monomers (mainly C₁₀H₁₄,1₆O₅,7,9,11) and covalently bound dimers (mainly C₂₀H₃₀O₅,6,16 and C₁₉H₂₈O₇,1₁, see Fig. 1A) (Ehn et al., 2014; Kirkby et al., 2016; Rissanen et al., 2015; Berndt et al., 2018b; Molteni et al., 2019). These highly-oxygenated organic molecules (HOMs) nucleate at atmospherically relevant concentrations with the help of ions but without other species (e.g. sulfuric acid or bases) required (Kirkby et al., 2016). Here, we group the HOMs according to carbon atom number and define C₅, C₁₀, C₁₅ and C₂₀ classes as sum of all HOMs with 2-5, 6-10, 11-15 and 16-20 carbon atoms, respectively. This resembles the basic building block unit of a C₅ isoprenoid skeleton.

An isoprene/ozone mixture in the CLOUD chamber produces C₅H₈O₅,6,8 monomers and also some C₁₀H₁₄,1₆O₅,1₀ dimers under UV-illuminated conditions (see Fig. S5 A, B). The C₅H₈O₅,6,8 radicals originate presumably from OH-addition to isoprene and subsequent autoxidation. Under dark conditions, when the only source of OH- is isoprene ozonolysis at 26 % yield (Malkin et al., 2010), we observe only C₅ monomers. None of these molecules are able to nucleate under atmospherically relevant conditions despite having an oxygen to carbon ratio (O:C) ≥ 1, which agrees with earlier observations that products from isoprene ozonolysis do not drive significant new-particle formation (Kamens et al., 1982; Riva et al., 2017).

When isoprene is present together with α-pinene and ozone, the HOM chemistry of α-pinene is altered. We observe the appearance of C₁₅ and an increase in C₅ class molecules compared to α-pinene only conditions as well as a decrease in C₂₀ and C₁₀ class molecules (see Fig. 1 and S3). Without isoprene, RO₂⁻(ap) can terminate with another RO₂⁻(ap), thus forming either one C₂₀ dimer or two C₁₀ monomers. Monomers can also be formed by termination with HO₂ or unimolecular termination (Rissanen et al., 2015). The presence of RO₂⁻(ap) offers additional termination channels (Berndt et al., 2018a) (see Fig. 2) and acts as an additional loss term for RO₂⁻(ap). Reactions between RO₂⁻(ap) and RO₂⁻(ap) are expected to result in C₁₀ and C₁₅ monomers as well as C₁₅ dimers. Most importantly, the reduced RO₂⁻(ap) steady state concentrations lead to a reduction of C₂₀ class dimers by roughly 50 % (depending on detailed conditions) compared to their level in the absence of isoprene for all studied α-pinene concentrations (see Fig. S3). To our knowledge the only study that presented ambient measurements of HOMs for an isoprene-rich region is from the SOAS campaign (Southern Oxidant and Aerosol Study, Alabama, USA) (Massoli et al., 2018). When comparing our results with this study, we find good qualitative agreement for the distribution of HOMs with strong contributions in the C₅ and C₁₀ region and lesser contributions in the C₁₅ and C₂₀ region.

We have to caution however that the C₁₅ signal in the reported HOM distribution could also be caused by sesquiterpene products. Additionally, the presence of NO₃ affects HOM chemistry in Alabama, which also leads to C₂₀ reduction (Lehtipalo et al., 2018).

We measured the particle formation rate directly at a 1.7 nm cut-off diameter with a scanning Particle Size Magnifier (PSM) under neutral (high voltage field cage switched on, see SI Appendix for details) and ion conditions (high voltage field cage switched off, allowing for galactic cosmic ray (gcr) ionization in the chamber), further referred to as J_n and J_gcr (see SI Appendix for detail). Fig. 3A shows J_n and J_gcr plotted against the total HOM concentration (the sum of the C₅, C₁₀, C₁₅ and C₂₀ classes) for the α-pinene only case and α-pinene + isoprene. For +5 °C we find good agreement with Kirkby et al. (2016). However, the
The presence of isoprene and the consequent change in oxidation chemistry reduces $J_{\text{gcr}}$ by a factor of two to four and $J_n$ even more by around one order of magnitude at 5 °C. The suppression is stronger for lower α-pinene concentrations and thus higher values of $R$ (the ratio of isoprene to monoterpane carbon).

The larger gap between $J_{\text{gcr}}$ and $J_n$ with isoprene present compared to α-pinene only conditions is direct evidence that isoprene oxidation products destabilize the nucleating clusters, thus making cluster stabilization through the presence of charge more efficient. This also confirms that C$_{20}$ class molecules are mainly responsible for pure biogenic nucleation (Frege et al., 2018). C$_{15}$ class molecules, which tend to counteract the losses of the C$_{20}$ class, do not prevent a decrease in $J$. Earlier studies have already suggested that C$_{10}$ class molecules do not possess low enough vapor pressure to qualify as Extremely Low Volatility Organic Compounds (Kurtén et al., 2016; Tröstl et al., 2016) and thus do not drive nucleation, leaving C$_{20}$ class molecules as the most likely nucleator molecules. At +25 °C and UV light illumination, we find that nucleation rates of the pure α-pinene system are reduced by a factor of about 2-3 compared to +5 °C. This is a much smaller reduction in nucleation rate compared to e.g., the inorganic sulfuric acid water system, for which the same temperature increase reduces nucleation rates by around two orders of magnitude (Kirkby et al., 2011) due to an increase in vapor pressure at warmer temperatures. In our organic system, however, accelerated oxidation chemistry counters the effect of higher vapor pressures. This includes a higher rate of initial oxidation of α-pinene by ozone, as well as a faster autoxidation process, which leads to HOMs with generally higher oxygen content. When we add isoprene at +25 °C with a constant ratio of isoprene to monoterpane carbon (R = 2), we find a reduction in $J_{gcr}$ of around a factor of about 2. Similar to the data at +5 °C where R ranges from 1.6 to 6.5, we expect a stronger decrease for higher values of R. This can be understood as higher isoprene concentrations enhance $RO_2$(ip) formation, which in turn reduces C$_{20}$ production and subsequent nucleation. R can reach levels around 15 in the Amazon (Greenberg et al., 2004) and around 26 in Michigan (Kanawade et al., 2011), where we would thus expect an even stronger isoprene effect on nucleation.

Comparing HOM formation and nucleation for three different α-pinene/isoprene settings, we observe that the addition of 2.7 ppbv of isoprene to an α-pinene/ozone mixture (770 pptv and 49 ppbv, respectively) mitigates C$_{20}$ production and reduces $J_{1.7}$ from 3.2 cm$^{-3}$s$^{-1}$ to 0.81 cm$^{-3}$s$^{-1}$ (see Fig. S6). A rough doubling of both the α-pinene and isoprene levels to 1326 pptv and 4.87 ppbv, respectively, increases overall HOM production; however, C$_{20}$ levels and consequently $J_{1.7}$ remain lower than in the original pure α-pinene setting without isoprene. Thus even increasing monoterpane concentrations can lead to lower J values when isoprene is added as well. Additional evidence for the important role of C$_{20}$ is shown in Fig S9: Regressing each individual HOM peak with $J_{gcr}$ gives high coefficients of determination for C$_{20}$ class molecules.

It has been argued that OH· depletion by isoprene is responsible for the absence of nucleation in isoprene-rich environments (Kiendler-Scharr et al., 2009; Kiendler-Scharr et al., 2012); however, under atmospheric conditions, isoprene induced OH· recycling can lead to undisturbed high OH· levels, which might not be true in chamber experiments (Taraborrelli et al., 2012; Martinez et al., 2010; Fuchs et al., 2013). In our study we also see an OH· depletion effect due to isoprene addition (see Fig. S1 and SI Appendix for detailed discussion). However, if OH· depletion were the reason for suppression of nucleation, an increase of OH· would lead to an increase in the nucleation rate. When we increase OH· levels by switching on UV lights in the presence of isoprene, this reduces $RO_2$(ap) further, as well as the C$_{20}$ and C$_{10}$ class molecules, while enhancing the C$_5$ and C$_{15}$ classes (see Fig. S1, S4 and S5 C, D as well as SI Appendix for details). Accordingly, $J$ is also reduced slightly instead of being increased. In the atmosphere with considerable OH·-recycling, this effect, and therefore the suppression of new-particle formation, would be even stronger. We can understand this OH· effect by comparing the reactivity of α-pinene and isoprene towards OH· at our given concentrations. For 300 and 1200 pptv the reactivity of α-pinene towards OH· at +5 °C ($k_{\text{apOH}}$) is 25.1 and 6.3 times lower, respectively, than the reactivity of 4 ppbv isoprene towards OH· ($k_{\text{ipOH}}$). At +25 °C these numbers are similar (25.4 and 6.3, respectively). This implies that any additional OH· provided by e.g. UV illumination will favor the formation of additional $RO_2$(ip) instead of $RO_2$(ap), thus favoring the formation of C$_{15}$ over C$_{20}$ and consequently reducing nucleation rates. OH· does not enhance nucleation in this chemical system; it suppresses it.

We performed experiments at +25 °C with three different levels of relative humidity (20, 38 and 80 %) to probe the effect of water on new-particle formation. Changes in humidity do not significantly affect HOM
formation and \( J_{\text{ger}} \) (see Fig. S7). \( J_n \) increased slightly with humidity, showing an increased stabilization of nucleating clusters by water; however, in gcr conditions, this role is fulfilled more efficiently by ions.

We further studied the effect of sulfuric acid on nucleation of an \( \alpha \)-pinene/isoprene mixture (about 1300 pptv and 4.5 ppbv, respectively) in experiments with excess ammonia (0.4 - 2.5 ppbv) in order to reproduce typical conditions in the eastern parts of the United States (Lee et al., 2016). We find that sulfuric acid does not enhance biogenic nucleation up to a concentration of \( 5 \times 10^3 \) cm\(^{-3} \) (see Fig. S8). This decoupling of biogenic nucleation from low sulfuric acid levels is similar to the pure \( \alpha \)-pinene system reported in Kirkby et al. (2016). At sulfuric acid levels higher than \( 5 \times 10^3 \) cm\(^{-3} \), nucleation rates depend strongly on sulfuric acid levels, which agrees with a wide variety of atmospheric measurements (Kirkby et al., 2016). In the Amazon, sulfuric acid levels are typically in the range of \( 1 \times 10^3 \) cm\(^{-3} \) (Kanawade et al., 2011), well below the threshold value of \( 5 \times 10^3 \) cm\(^{-3} \). In Alabama this threshold was exceeded only three times in a 45-day measurement period due to transported sulfur plumes, which led to two events of particles growing to larger sizes (Lee et al., 2016). In Michigan, sulfuric acid concentrations are typically in the range of \( 1 \times 10^6 \) cm\(^{-3} \) (Kanawade et al., 2011). Sulfuric acid is thus not an important contributor to nucleation in the Amazon as well as different regions of the eastern United States.

We measured the growth rates of freshly nucleated particles from 1.3 nm onwards with a scanning Particle Size Magnifier, a DMA-train and a nanoSMPS (see SI Appendix for details). The change in HOM chemistry caused by concurrent isoprene oxidation reduces the growth rates of particles in the range of 1.3 – 1.9 nm and 1.8 – 3.2 nm roughly by a factor of two (Fig. 3B and 3C). This confirms that C\(_{15}\) class molecules have a higher saturation vapor pressure than C\(_{20}\) class molecules and are thus less efficient than C\(_{20}\) class molecules at causing growth of the smallest particles. Likewise, most C\(_{10}\) class molecules are too volatile to contribute significantly to the early stages of growth (Tröstl et al., 2016). For the size range from 3.2 – 8.0 nm and larger, we observed no suppression effect due to isoprene, indicating that molecules smaller than C\(_{20}\) are capable of condensing onto larger particles. We find a linear relationship of growth rate vs C\(_{20}\) for 1.3 - 1.9 and 1.8 - 3.2 nm, regardless of isoprene presence. For larger sizes the linear relationship is independent of isoprene presence, when plotted against C\(_{15}\) + C\(_{20}\); this again indicates that C\(_{15}\) contributes to growth at larger sizes (Fig. S10). Besides C\(_{15}\) and C\(_{20}\), however, even lighter and less oxygenated molecules can contribute to particle growth at larger sizes (Stolzenburg et al., 2018). Growth rates at +25 °C are typically halved compared to +5 °C due to higher saturation vapor pressure of the HOMs (Stolzenburg et al., 2018), which leads to a higher chance of particles being scavenged while growing, even more so in the presence of isoprene.

Fig. 4 shows the formation rate of particles measured at diameters of 1.7, 2.2, 2.5 and 6 nm for gcr conditions and six concentration values (low/mid/high \( \alpha \)-pinene mixing ratios with and without isoprene) at +25 °C. We find that due to the reduced growth rates in the presence of isoprene, a moderate reduction of formation rates at 1.7 nm becomes much more pronounced, while the particles grow to larger sizes. When we compare \( \alpha \)-pinene only data (771 pptv \( \alpha \)-pinene, 49 ppbv O\(_3\)) with a mixture (1320 pptv \( \alpha \)-pinene, 39 ppbv O\(_3\) and 4.9 ppbv isoprene, orange data points in Fig. 4), \( J_{1.7} \) is reduced by 45 %, while the corresponding formation rate at 6 nm is reduced by an order of magnitude. The corresponding precursor concentrations are similar to conditions found in e.g. Alabama (Lee et al., 2016). Isoprene can thus drastically reduce the formation of particles larger than 6 nm even at relatively warm temperatures like +25 °C. This growth-rate driven effect becomes stronger when \( \alpha \)-pinene concentrations are reduced. Our measurements agree with observations of small clusters that are unable to grow efficiently, as has been reported for Alabama (Lee et al., 2016) and the Amazon (Wimmer et al., 2018). Increased levels of preexisting aerosols (i.e. condensation sink) can scavenge freshly nucleated particles (Dada et al., 2017); however, due to the reduced initial growth rates, the likelihood for that process at a given condensation sink is increased when isoprene is present compared to \( \alpha \)-pinene only conditions.

4. Discussion

Pure biogenic nucleation was first described for \( \alpha \)-pinene oxidation in the CLOUD chamber (Kirkby et al., 2016). Global evaluation of this process with the help of atmospheric modeling found an over-prediction of CCN concentrations in the Amazon, leading to speculation about an as yet unaccounted chemical
suppression mechanism for new-particle formation involving isoprene (Gordon et al., 2016). With our findings, we provide the molecular understanding for such a mechanism and identify C_{20} class molecules as the main drivers of biogenic nucleation and early growth. This allows us to refine our understanding of biogenic nucleation for isoprene-rich regions, while at the same time large portions of the atmosphere where biogenic nucleation is very important, remain unaffected by our findings, especially boreal forests (Gordon et al., 2016).

Suppression of new-particle formation by isoprene was previously attributed to competition for OH-radicals during the initial oxidation of VOCs, which was then thought to be followed by independent oxidation pathways (Kiendler-Scharr et al., 2009). Instead we show that the suppression takes place via RO\textsubscript{2}· radical interactions that strongly couple the oxidation chains of monoterpene and isoprene.

McFiggans et al. (2019) showed that the same RO\textsubscript{2}· mechanism that we describe here is also responsible for reduced SOA formation, together with an additional OH· scavenging effect. The oxidation chemistry in McFiggans et al. (2019) was dominated (> 90 %) by OH· for both monoterpene and isoprene. In our experimental conditions, monoterpene oxidation was dominated by ozone, which is more common in the atmosphere, and we demonstrate the importance of the RO\textsubscript{2}· mechanism directly in these conditions. Additionally, while the precursor concentrations in McFiggans et al. (2019) were much higher than typical atmospheric levels, the precursor levels in the current study resemble the atmosphere more closely. This is especially important as HOM formation is not a linear process and can thus not be scaled down to atmospheric levels in a straightforward manner.

All extrapolations of chamber experiments to atmospheric conditions must be treated with care: for example, it has been shown that isoprene OH· scavenging is stronger in common chamber conditions than in ambient conditions, where OH· recycling (e.g. by HPALD photolysis) counters the OH· consumption by isoprene (Taraborrelli et al., 2012).

McFiggans et al. (2019) also show that OH· scavenging by isoprene is important for reduced SOA formation. We also find a reduction in OH· levels due to isoprene addition in the CLOUD chamber. However, this is not the reason for the suppression of nucleation and early growth rates in our experiments. Quite to the contrary, the dominant effect of increased OH· in our experiments is to increase RO\textsubscript{2}(ip) due to the fast reaction between isoprene and OH·. OH· thus suppresses C_{20} dimers and nucleation rates in our chemical system. Thus, while increased OH· levels restore SOA formation partially in the coupled monoterpene/isoprene system, as shown by McFiggans et al. (2019), they suppress nucleation in our experiments. This further highlights the important differences between SOA formation with preexisting seed particles on the one hand and the nucleation of new particles on the other hand. SOA mass production and nucleation are not the same thing. SOA formation with preexisting particles can include molecules possessing comparatively high saturation vapor pressures; however, due to the Kelvin effect (Tröstl et al., 2016), nucleation depends critically on molecules with extremely low saturation vapor pressure. Most of the C\textsubscript{20} and C\textsubscript{15} many of the C\textsubscript{16} and some of the C\textsubscript{15} products can form SOA mass, whereas nucleation under atmospheric conditions is driven largely by the C\textsubscript{20} dimers. Even replacing C\textsubscript{20} with C\textsubscript{15} dimers suppresses nucleation, as shown in this study.

This is Our findings are significant beyond the α-pinene/isoprene system, as they indicate the interaction of a variety of atmospheric VOCs with monoterpene-derived HOM formation and new-particle formation. Given that RO\textsubscript{2}(ap)-RO\textsubscript{2}(VOC) reaction rates are competitive (see SI Appendix for details), VOCs whose RO\textsubscript{2}· radicals lead to products that are smaller than C\textsubscript{20} when reacting with RO\textsubscript{2}(ap) (i.e. reduce the ELVOC (Extremely Low Volatility Organic Compounds) fraction in the HOM distribution) are expected to reduce biogenic nucleation and early growth. On the other hand, VOCs that lead to C\textsubscript{20} class or larger molecules are expected to accelerate both processes. RO\textsubscript{2}· termination emerges as the critical step in ELVOC formation and subsequently biogenic new-particle formation. The suppression of biogenic new-particle formation by isoprene and potentially other lighter VOCs, NO\textsubscript{x} (Lehtipalo et al., 2018) and elevated HO\textsubscript{2} concentrations all proceed along the same lines of RO\textsubscript{2}· termination and subsequent C\textsubscript{20} reduction, highlighting the importance of C\textsubscript{20} class molecules for biogenic new-particle formation.
In summary, we find that isoprene interferes with α-pinene HOM chemistry via RO₂· peroxy-radical termination. When isoprene is present, fewer C_{20} class molecules are formed, which directly reduces the nucleation rate. We show that C_{20} class molecules act as “nucleator” species. The reduction of nucleation rate becomes stronger with higher isoprene to monoterpenes carbon ratio (R), consistent with earlier observations (Kiendler-Scharr et al., 2009); however, in the monoterpane-isoprene chemical system, increased OH· does not enhance nucleation, but, on the contrary, reduces it due to C_{20} class reduction. Biogenic nucleation in the α-pinene isoprene system is not affected by typical concentrations of sulfuric acid found in the Amazon or in eastern parts of the United States. The change in monoterpane HOM chemistry due to isoprene reduces organic growth rates in the 1.3–3.2 nm range by around 50%, which strongly reduces the probability that the smallest, freshly-nucleated particles will survive scavenging as they grow to larger sizes. While other factors can also inhibit nucleation (e.g. NO₂ (Wildt et al., 2014) or a high condensation sink (Dada et al., 2017)), isoprene can make the difference between measurable new-particle formation events and their absence under a variety of atmospheric conditions.

Data Availability: Data are available by contacting the corresponding author.


Competing interests: The authors declare no competing interests.

Acknowledgments: We thank CERN for supporting CLOUD with technical and financial resources, and for providing a particle beam from the CERN Proton Synchrotron. We thank P. Carrie, L.-P. De Menezes, J. Dumollard, K. Ivanova, F. Josa, I. Krasin, R. Kristic, A. Laassiri, O. Marichy, H. Martini, S. V. Mizin, R. Sitals, A. Wasem and M. Wilhelmsson for their contributions to the experiment. This research has received funding from the EC Seventh Framework Programme and European Union’s Horizon 2020 programme (Marie Sklodowska Curie ITNs no. 316662 “CLOUD-TRAIN” and no. 764991 “CLOUD-MOTION”, MSCA-IF no. 656994 “nano-CAVa”, MC-COFUND grant no. 600377, ERC projects no. 692891 “DAMOCLES”, no. 638703 “COALA”, no. 616075 "NANODYNAMITE", no. 335478 “QAPPA”, no. 742206 “ATM-GP”, no. 714621 “GASPARCON”), the German Federal Ministry of Education and Research (projects no. 01LK0902A, 01LK1222A 01LK1601A), the Swiss National Science Foundation (projects no. 20020_152907, 200020_172602, 20F120_159851, 200020_172602, 20FI20_172622), the Academy of Finland (Center of Excellence no. 307331, projects 299574, 296628, 306853, 304013), the Finnish Funding Agency for Technology and Innovation, the Väisälä Foundation, the Nessling Foundation, the Austrian Science Fund (FWF; project no. J3951-N36, project no. P27295-N20), the Austrian research funding association (FFG, project no. 846050), the Portuguese Foundation for Science and Technology (project no. CERN/FP/116387/2010), the Swedish Research Council Formas (project number 2015-749), Vetenskapsrådet (grant 2011-5120), the Presidium of the Russian Academy of Sciences and Russian Foundation for Basic Research (grants 08-02-91006-CERN, 12-02-91522-CERN), the U.S. National Science Foundation (grants AGS1136479, AGS1447056, AGS1439551, CHE1012293, 12-04-00753, 13-02-00244, 12-04-00753, 13-02-00244).
AGS1649147, AGS1602086), the Wallace Research Foundation, the US Department of Energy (grant DE-SC0014469), the NERC GASSP project NE/J024252/1m, the Royal Society (Wolfson Merit Award), United Kingdom Natural Environment Research Council grant NE/K015966/1, Dreyfus Award EP-11-117, the French National Research Agency the Nord-Pas de Calais, European Funds for Regional Economic Development Labex-Cappa grant ANR-11-LABX-0005-01).
References


compounds in initial particle growth in the atmosphere, Nature, 533, 527, 10.1038/nature18271, 2016.


Figure 1. Mass defect plots of neutral HOM molecules measured with nitrate CI-API-TOF without isoprene (a) and with isoprene added (b) at +25 °C. α-Pinene levels were 771 and 1326 pptv, respectively. Ozone levels were 49 and 39 ppbv, respectively. Isoprene was 4.9 ppbv in (b). Relative humidity was 38 % in (a) and (b). The area of the marker points is linearly scaled with the intensity of the HOM signals. Color code shows the relative intensity change for each HOM peak due to isoprene addition, i.e. the percentage intensity change between (a) and (b). The color for each peak is thus the same in (a) and (b). HOM intensity in (a) was scaled up linearly by 38 % to match [α-pinene]-[O₃] levels present in (b) to calculate the intensity change.
Figure 2: Proposed mechanism for the interference of isoprene in α-pinene oxidation chemistry. The pathway of HOM formation of an α-pinene/ozone mixture alone is indicated by red arrows. When isoprene is present, the green arrows indicate the additional interference of isoprene in α-pinene oxidation chemistry via RO$_2^\cdot$ radicals. The oxidation of α-pinene at the conditions used in our experiments is dominated by ozonolysis. After the initial ozone attack a C$_{10}$H$_{15}$O$_4$ peroxy-radical forms via a vinylhydroperoxyde channel (VHP), which can undergo various intramolecular H-shifts and autodissociation steps. Thus the chain of RO$_2^\cdot$(αp) mostly consists of C$_{10}$H$_{15}$O$_{4,6,8,10}$. These radicals can terminate either via reaction with other RO$_2^\cdot$ radicals, via reaction with HO$_2$ or via unimolecular processes. The resulting closed shell products are then either covalently bound C$_{20}$ class dimers, which are mostly responsible for nucleation or C$_{10}$ class monomers. Possible fragmentation might also lead to a low amount of C$_5$ and C$_{15}$ class molecules being formed even without isoprene present. Isoprene oxidation is dominated by reactions with OH· in the CLOUD chamber, which produce a series of C$_5$ RO$_2^\cdot$ radicals (C$_5$H$_9$O$_{3,6,7,8,9}$). These RO$_2^\cdot$(ip) radicals can now interfere in the termination of RO$_2^\cdot$(αp). The reaction of RO$_2^\cdot$(ip) with RO$_2^\cdot$(αp) can lead to C$_{15}$ class dimers, C$_{10}$ class monomers or C$_5$ class monomers. The reaction of RO$_2^\cdot$(ip) with another RO$_2^\cdot$(ip) can lead to C$_{10}$ class dimers or C$_5$ class monomers. The presence of RO$_2^\cdot$(ip) reduces the steady state concentration of RO$_2^\cdot$(αp), as it acts as an additional sink for RO$_2^\cdot$(αp). This directly reduces the formation of C$_{20}$ class dimers, as two RO$_2^\cdot$(αp) radicals are needed to form one C$_{20}$ class dimer. We link this reduction of C$_{20}$ class dimers to the reduction of biogenic nucleation and early growth rates in the presence of isoprene.
Figure 3. Pure biogenic nucleation rates at 1.7 nm diameter (a) and growth rates (b, c) against total HOM concentration with and without isoprene added at +5 and +25 °C. HOM total is defined as the sum of C₅, C₁₀, C₁₅ and C₂₀ carbon classes. Relative humidity is 38 % for all data points. (a) Triangles represent $J_{\text{gcr}}$ and circles $J_{n}$. Small grey points were taken from Kirkby et al. (2016). Magenta edges indicate UV-illuminated conditions at +5 °C, at +25 °C all data points are with UV light on. Color shows isoprene to monoterpene carbon ratio (R). Black solid and dash-dotted lines are parametrizations of $J_{\text{gcr}}$ and $J_{n}$ from Kirkby et al (2016). Red solid and dash-dotted lines are power law fits to $J_{\text{gcr}}$ and $J_{n}$ in the presence of isoprene at +5 °C. Thick solid black and red line represent power law fits to +25 °C data for $\alpha$-pinene only and $\alpha$-pinene + isoprene systems. Bars indicate 1σ run-to-run uncertainty. The overall systematic scale uncertainty of HOMs of +78 %/−68 % and of $J$ for ±47 % is not shown. In (b) and (c), triangles represent $\alpha$-pinene only, circles $\alpha$-pinene + isoprene conditions. Marker color indicates the size range in which growth rate was measured: dark blue 1.3 – 1.9 nm (measured by scanning PSM), light blue 1.8 – 3.2 nm, orange 3.2 – 8.0 nm (both measured by DMA-train) and red 5.0 – 15 nm (measured by nanoSMPS). Bars indicate 1σ uncertainties in growth rate estimation. Dashed lines are linear fits to $\alpha$-pinene only data points; solid lines are linear fits to $\alpha$-pinene + isoprene conditions, respectively.
Figure 4: Formation rate (gcr) vs diameter of particles at +25 °C and 38 % RH. Triangles represent α-pinene only, circles α-pinene + isoprene conditions. α-Pinene levels were 456, 771 and 1442 pptv for triangles and 677, 1326 and 2636 pptv for circles. Ozone levels were 49 ppbv for triangles and 38 to 40 ppbv for circles. Isoprene levels ranged from 2.7 to 9.8 ppbv for circles. Color code represents HOM concentration. Bars indicate overall scale uncertainty for formation rates of ±47 %. The uncertainty in the diameters is ±0.3 nm. Dashed and solid lines are lines to guide the eye. The steeper slope at lower diameter values is caused by the Kelvin effect, i.e. a smaller growth rate at small sizes that leads to higher losses of newly formed particles. The formation rate measurements at 2.2 and 2.5 nm for the lowest α-pinene/isoprene setting (cyan circles) are upper limits.
Supplementary Information for

Molecular understanding of the suppression of new-particle formation by isoprene

**CLOUD Facility**

We conducted our measurements at the CLOUD (Cosmics Leaving OUtdoor Droplets) chamber at CERN (European Center for Nuclear Research), Geneva, Switzerland. The CLOUD chamber is a 26.1 m³ electro-polished stainless-steel tank used to recreate atmospheric condition in the laboratory (for more details on the chamber see Kirkby et al. (2011); Kirkby et al. (2016); Duplissy et al. (2016)). Data for this study are from the CLOUD 11 and 12 campaigns in autumn 2016 and 2017. Various measures are taken to reduce unwanted contaminants in the CLOUD chamber. The air in the chamber is mixed from cryogenic nitrogen and oxygen, all lines are made of stainless steel and intense cleaning cycles are performed prior to each campaign. Each cleaning cycle consists of at least 24 h of rinsing the chamber from the inside with ultrapure water, followed by a period of at least 24 h with the chamber at 100°C and high ozone levels (several parts per million by volume). These measures result in very low organic contamination below 150 pptv (Kirkby et al., 2016) in total.

Ultrapure water is used to humidify the air in the chamber. Ozone is produced by a UV ozone generator. Liquid α-pinene (Sigma Aldrich, purity >98 %) is stored in a temperature controlled water bath and evaporated into a dry nitrogen flow and fed into the chamber. Isoprene from a gas bottle (Carbagas AG, purity >99%) is additionally cleaned by a cryotrap. The cryotrap consists of a ~2 m long ¼” stainless steel tube spiral placed in a cryogenic liquid held at 233 K. By using this trap, non-negligible monoterpene-like contaminants in the isoprene gas bottle are effectively frozen out (Bernhammer et al., 2018). Isoprene and α-pinene are diluted by separate two stage dilution systems prior to being fed into the chamber. All gases are fed into the chamber from the bottom and are mixed by two magnetically driven fans.

A unique feature of the CLOUD chamber is its control of ion concentrations. A high voltage electric field cage (±30 kV) can sweep ions that are constantly produced by naturally occurring galactic cosmic rays out of the chamber in around 1 s. This enables us to study pure neutral nucleation. By switching the field cage off, the naturally formed ions are allowed to stay in the chamber and affect nucleation processes. To artificially enhance ion concentrations, CERN’s Proton Synchrotron provides a 3.5 GeV π⁺ beam that is diverged to >1 m² beam profile and crosses the center region of the chamber.

The CLOUD chamber is equipped with four HgXe UV lamps (LightningCure LC8, Hamamatsu Photonics K.K.) positioned at the top of the chamber and connected via fiber bundles. An additional UV source is provided by a KrF excimer laser (ATLEX-1000, ATL Lasertechnik GmbH) at 248 nm wavelength and also connected to the chamber via fiber bundles to enhance OH· production via photolysis of O₃ further.

**Typical Run sequence and conditions**

Our experiments were performed at +5 and +25 °C and mostly 38 % relative humidity. A typical run sequence can be seen in Fig. S1 and S2. First, α-pinene is present with ozone under both neutral and gcr conditions at three different atmospherically relevant concentrations. HOMs are forming as seen by the CI-API-TOF and new-particle formation is induced. The purpose of this experiment was also to ensure inter-campaign comparability to Kirkby et al. (2016). In the following run a stable isoprene concentration is established in the chamber and ozone is added shortly afterwards. As ozone and isoprene only react very slowly, effects on HOMs are minor. As UV light in the chamber is switched on, OH· production increases and thus formation of OH· induced isoprene HOMs. However, only the subsequent addition of α-pinene leads to formation of C₂₀ class HOMs and thus new-particle formation. UV effects were studied by switching on the Hamamatsu lamp, as well as the KrF-excimer laser.
Gas-phase measurements

Ozone was measured by a calibrated ozone monitor (Thermo Environmental Instruments TEI 49C). Isoprene and α-pinene were measured by the newly developed proton transfer reaction time-of-flight mass spectrometer (PTR3 (Breitenlechner et al., 2017)). The instrument was frequently calibrated for both gases and has a limit of detection of 2 pptv for isoprene and α-pinene for 1 s integration time. The accuracy of the instrument for both gases is mainly determined by the uncertainty of the calibration gas standard (5 %) and accuracies of mass flow controllers and is estimated to be 7 %.

The chemical ionization atmospheric pressure interface time-of-flight (CI-APi-TOF) mass spectrometer (Tofwerk AG) measured highly-oxygenated organic compounds with a limit of detection of ~5·10^4 cm^3. The instrument operates with a nitrate based ion source similar to the design in Eisele and Tanner (1993). However, a corona discharge was used instead of a radioactive source (Kürten et al., 2011). The instrument was calibrated for sulfuric acid (Kürten et al., 2012) and the data corrected for mass dependent transmission efficiency (Heinritzi et al., 2016). HOM quantification was performed as described in Kirkby et al. (2016).

The run-to-run uncertainty for HOMs is estimated to be 20 %. Due to technical reasons at the start of CLOUD 11 the CI-APi-TOF could only start measuring at 03 Oct 2016, 10:28 UTC (see Fig. S1). As HOMs depend linearly on the product [α-pinene][O_3] (Kirkby et al., 2016; Ehn et al., 2014), HOM concentrations measured during the mid α-pinene settings were used and scaled down according to this relation to obtain HOM concentrations for the low α-pinene settings for the appropriate times where J and growth rates were estimated. This also gave a higher uncertainty for this data point (28 %) as indicated in Fig. 3A. The overall uncertainty in HOM quantification consists of contributions from sulfuric acid calibration (+50 %/-33 %), charging efficiency of HOMs in the ion source (25 %), transmission correction (50 %) and sampling line loss correction (20 %). This results in an overall scale uncertainty for HOMs of +78 %/-68 %. There are however additional uncertainties in our HOM estimation that cannot be readily quantified. On the one hand nitrate ionization of HOMs shows a drop in charging efficiency for HOMs with six or less oxygen atoms (Hyttinen et al., 2017). This leads to an underestimation of these molecules. However, these molecules with comparably low oxygen content are not expected to contribute significantly to nucleation and early growth. Additionally, it was shown that nitrate ionization has a reduced charging efficiency towards HOMs formed by OH- oxidation compared to HOMs formed by ozonolysis (Berndt et al., 2015; Berndt et al., 2016). This could affect also C_{20} class molecules that show OH- dependence, like C_{20}H_{12}O_{7} (see Figure S1). The real increase of these C_{20} class HOMs due to UV light could be larger than the measured one, thus dampening the overall decrease of C_{20} when UV is switched on. The fact that J decreases when UV is switched on, however, confirms that the total nucleating molecules in the chamber decrease. That effect is thus not strong enough to lead to a real increase instead of a decrease in C_{20} class molecules.

We group all HOMs within the m/z range from 235 to 625 Th in four groups according to their carbon number. This m/z range was chosen to remain consistent with the definition of total HOM in Kirkby et al. (2016). We sum up HOMs with 2-5, 6-10, 11-15 and 16-20 carbon atoms to get C_3, C_{10}, C_{15} and C_{20} class HOMs, respectively. The sum of these four classes represents HOM total as shown e.g. in Fig. 3.

OH- estimation and comparison to ambient environments

We estimate OH- levels in our chamber via a steady state approach (see Fig. S1). OH- sources taken into account are ozonolysis of α-pinene and isoprene, with yields of 79 % (Tillmann et al., 2010) and 26 % (Malkin et al., 2010; Kroll Jesse et al., 2001), respectively, as well as photolysis of ozone with our UV laser. The OH- source strength of the UV laser was characterized with a separate experiment (SO_2 to sulfuric acid conversion) and depends on laser settings, ozone concentration and absolute water vapor concentration. Sink terms taken into account are reactions of OH- with α-pinene and isoprene. Secondary reactions of OH- with further oxidation products of α-pinene or isoprene are not taken into account, as their effect is expected to be minor (e.g. two orders of magnitude smaller than the former sink terms in case of
the pinonaldehyde-OH· reaction). OH· recycling in our chamber is expected to be weak, as we do not have NOx in the chamber and many runs are performed under dark conditions. The recycling mechanism due to photolysis of hydroperoxy-aldehydes (HPALDs) (Taraborrelli et al., 2012) can in principal take place during UV runs, however, HPALDs may also decompose on our stainless steel chamber walls without releasing OH· in a process similar to the one described in Bernhammer et al. (2017), thus further reducing recycling efficiency. However, the O3 recycling mechanisms (reaction of O3 and HO2 yielding OH·, as well as photolysis of H2O2 under UV conditions) might take place in our conditions (Lelieveld et al., 2016). All gas phase reaction rate constants are preferred values provided by IUPAC (International Union of Pure and Applied Chemistry) and were evaluated at +5 °C ($k_{ipOH} = 8.1 \cdot 10^{-17}$ cm$^3$s$^{-1}$, $k_{ipO3} = 5.8 \cdot 10^{-11}$ cm$^3$s$^{-1}$, $k_{ipO3} = 7.9 \cdot 10^{-18}$ cm$^3$s$^{-1}$ and $k_{ipOH} = 1.1 \cdot 10^{-10}$ cm$^3$s$^{-1}$) and +25 °C ($k_{ipO3} = 9.4 \cdot 10^{-17}$ cm$^3$s$^{-1}$, $k_{ipOH} = 5.2 \cdot 10^{-11}$ cm$^3$s$^{-1}$, $k_{ipO3} = 1.3 \cdot 10^{-17}$ cm$^3$s$^{-1}$ and $k_{ipOH} = 1.0 \cdot 10^{-10}$ cm$^3$s$^{-1}$).

We calculate OH· levels of around 1·10$^6$ cm$^{-3}$ during dark α-pinene ozonolysis, with roughly a doubling to 2·10$^6$ cm$^{-3}$ when the UV laser is switched on. When isoprene is present together with α-pinene it foremost acts as a sink for OH· and thus reduces its concentrations. The strength of this depletion depends on the main OH· source strength, i.e., the α-pinene ozonolysis rate. We find OH· levels 5 to 20 times lower when isoprene is present than under α-pinene only conditions. This depletion can also be recognized in the traces of HOMs that originate from OH· oxidation, like C$_{10}$H$_{18}$O$_6$ (see Fig. S1).

In the atmosphere, OH· levels of 10$^6$ cm$^{-3}$ and higher are reported even in the presence of isoprene, as several OH· recycling mechanisms take place (Lee et al., 2016; Martinez et al., 2010; Lelieveld et al., 2016). However, given the reduction in C$_{20}$ class molecules when OH· is increased from 2·10$^5$ cm$^{-3}$ to 4·10$^5$ cm$^{-3}$ by switching on UV light, it is a reasonable assumption that, if OH· would be fully replenished to 1·10$^6$ cm$^{-3}$, we would see a further decrease of total C$_{20}$ class molecules and subsequently a reduction in J and early growth rates. This assumption is also valid when the reduced charging efficiency of nitrate ionization towards OH· initiated HOMs is taken into account as outlined above. The decrease of C$_{20}$ class molecules and nucleation rate when OH· is increased is direct evidence that the suppression effect of isoprene on nucleation is not due to depletion of OH·.

### Particle Measurements

The total particle number concentration above 2.5 nm is measured by a TSI 3776 condensation particle counter (CPC) using butanol as working fluid. For smaller particles, an Airmodus A10 particle size magnifier (PSM), using diethylene glycol as working fluid, is used (Vanhanen et al., 2011) in combination with an Airmodus A20 CPC. This setup achieves detection of airborne particles down to 1 nm. By varying the supersaturation inside the PSM, particle size distributions between 1 – 3 nm can be inferred (Lehtipalo et al., 2014).

A DMA-train (Stolzenburg et al., 2017) is used to measure the particle size distribution and growth rates between 1.8 – 8.0 nm. It uses a parallel design of six sampling channels each equipped with a differential mobility analyser (DMA) together with an ultrafine condensation particle counter (uCPC). For detection of sub-2.5 nm particles, two of the channels are equipped with either an Airmodus A10 particle size magnifier (PSM) or a TSI 3777 nanoEnhancer as booster stage upstream of the CPC. The channels are operated at fixed sizes to increase time-resolution and counting-statistics leading to higher sensitivities for smaller sizes compared to standard scanning mobility devices.

The size distribution above 5 nm is measured with a TSI Scanning Mobility Particle Sizer (nanoSMPS, Model 3938) using a TSI 3082 nanoDMA and a water-based TSI 3788 CPC for detection of the size-selected particles. For particles larger than 65 nm a custom-built SMPS with a long column DMA was used.
Determination of nucleation rates

The nucleation rate \( J \) defines the number of particles formed within a volume per unit of time. It is calculated using the flux of the total concentration of particles growing past a specific diameter (here at 1.7, 2.2, 2.5 and 6 nm). In the following, the method for calculating \( J_{1.7} \) is presented; however the calculation for \( J_{2.2}, J_{2.5} \) and \( J_{6} \) follows the same procedure unless specified otherwise. The nucleation rate is the sum of the time derivative of the concentration of particles above a certain diameter, as well as correction terms accounting for aerosol losses due to dilution in the chamber, wall losses and coagulation.

\[
J_{1.7} = \frac{dN_{\geq 1.7 \text{ nm}}}{dt} + S_{\text{dil}} + S_{\text{wall}} + S_{\text{coag}}
\]  

\( N \) is the concentration of particles of diameter equal or larger than 1.7 nm. The term \( S_{\text{dil}} \) describes the size-independent losses of particles due to dilution of the gases in the chamber. The chamber is continuously flushed with a total flow of 230 liters per minute to replenish the sampling flow of the instruments. This results in the dilution factor \( k_{\text{dil}} = 1.47 \times 10^{-4} \text{ s}^{-1} \) and

\[
S_{\text{dil}} = N_{\geq 1.7 \text{ nm}} \cdot k_{\text{dil}}.
\]

The term \( S_{\text{wall}} \) describes the size-dependent particle losses to the chamber walls and was calculated based on the decay rate of sulfuric acid monomer (of mobility diameter = 0.85 nm (Kulmala et al., 2013)) in the chamber (at temperature = 278 K). The wall loss rate \( k_{\text{wall}} \) is a function of particle diameter and temperature.

\[
S_{\text{wall}}(T) = \sum_{d_{p,i}=1.7\text{nm}}^{d_{p,\text{max}}} N(d_{p,i}) \cdot k_{\text{wall}}(d_{p,i}, T)
\]

At 278 K

\[
k_{\text{wall}}(d_{p,i}) = 1.7 \times 10^{-3} \text{ nm s}^{-1} \cdot \frac{1}{d_{p,i}}
\]

The term \( S_{\text{coag}} \) represents the coagulation losses to the surface of pre-existing aerosol particles in the chamber and was calculated using the full number size distribution present in the chamber (Seinfeld and Pandis, 2016).

\[
S_{\text{coag}}(d_p = 1.7 \text{ nm}) = \sum_{d_{p,i}=d_p}^{d_{p,\text{max}}} \sum_{d_{p,j}=d_p}^{d_{p,\text{max}}} \delta_{ij} \cdot K(d_{p,i}, d_{p,j}) \cdot N_i \cdot N_j
\]

where \( K(d_{p,i}, d_{p,j}) \) is the coagulation coefficient for particles of the size \( d_{p,i} \) and \( d_{p,j} \). \( N_i \) and \( N_j \) are the number concentrations of particles in the size bins \( d_{p,i} \) and \( d_{p,j} \), and \( \delta_{ij} = 0.5 \), if \( i = j \), and \( \delta_{ij} = 1 \), if \( i \neq j \). \( d_{p,i} \) is the midpoint diameter for the size bin with index \( i \).

The number size distribution of particles used for the calculation of formation rates were obtained from the scanning PSM at cut-off diameters 1.7 nm and 2.2 nm for the determination of \( J_{1.7} \) and \( J_{2.2} \), and from a butanol CPC (model CPC3776, TSI Inc.) of fixed cut-off (2.5 nm) for determining the formation rate of 2.5 nm particles. For determining \( J_6 \), the integrated size bins from the nanoSMPS were used. A correction factor of +0.3 nm on the cut-off diameter of the PSM was included account for the poorer detection efficiency of neutral organic particles compared to calibration with tungsten oxide (Kangasluoma et al., 2014). The concentrations obtained were corrected for sampling line losses. During each run, the value of \( J \) was determined after reaching a steady state value. A median value of the formation rate was then obtained. The errors on the reported \( J \) rates were obtained by considering an inter-campaign reproducibility error of 30 % as well as a series of run-dependent systematic and statistical uncertainties which include errors on sampling (10 %), dilution (10 %), wall loss (20 %) and coagulation sink (20 %). The resulting overall scale uncertainty for \( J \) is 47 %. 


Determination of growth rates

Particle growth rates were derived from several instruments individually with the widely used appearance time method (Lehtipalo et al., 2014). For this method the signal rise in a single size channel is fitted with a sigmoidal function during the particle formation event. The fit determines the appearance time $t_{\text{app}}$ at which the signal intensity reaches 50% between a potential background and the final value reached at steady-state nucleation conditions. A linear fit of $t_{\text{app}}$ and the corresponding diameters of several size channels yields an average apparent growth rate of the size distribution for a diameter interval. To infer a size-dependence of the measured growth rates, several instruments and size-intervals were used. Growth rates between 1.3 – 1.9 nm were measured with the scanning PSM, the DMA-train size channels were split up into two intervals, one between 1.8 – 3.2 nm and one between 3.2 – 8.0 nm. For size-intervals above 8 nm the size channels of the nanoSMPS was used. Uncertainties in the sigmoidal fit result are promoted to the linear fit $k_2$ and so if [NO] is larger than these values the growth rates between 1.3 – 2 nm are interpreted as condensational growth rates.

Effect of lighter VOCs on RO$_2^·$ chemistry and HOM formation

Organic peroxy radical (RO$_2^·$) branching is critical to atmospheric chemistry. There are many thousands of different RO$_2^·$ radicals, but their chemistry can be simplified to the following basic reaction set:

$$
\begin{align*}
\text{RO}_2^· + \text{HO}_2 & \rightarrow \text{products} \quad (k_1 \sim 1 \cdot 10^{-11} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}, \text{independent of temperature (Atkinson, 1997)}) & (\text{R1}) \\
\text{RO}_2^· + \text{NO} & \rightarrow \text{products} \quad (k_2 \sim 1 \cdot 10^{-11} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}, \text{independent of temperature (Wallington et al., 1992; Atkinson, 1997)}) & (\text{R2}) \\
\text{RO}_2^· + \text{RO}_2^· & \rightarrow \text{products} \quad (k_3 \text{ highly variable (Madronich and Calvert, 1990; Atkinson, 1997)}) & (\text{R3})
\end{align*}
$$

This neglects important exceptions such as peroxy acyl radicals reacting with NO$_2$ to form PANs, but is sufficient to describe the essential features here and in the atmosphere (Finlayson-Pitts and Pitts Jr, 1999). The maximum rate constant (the collision constant) is roughly $3 \cdot 10^{-10} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}$, so R1 and R2 occur at slightly under one in ten collisions with only a very modest temperature dependence. Experimental kinetics show that the rate constants for these first two reactions depend only weakly on the organic substituent R (Finlayson-Pitts and Pitts Jr, 1999), and so here we consider two similar, temperature independent rate constants for all RO$_2^·$.

The ubiquity and similarity of the first two rate constants means that “high-NOx” chemistry is well defined. The ratio of NO to HO$_2$ is crucial. Data show that typical daytime HO$_2$ is around 2 – 30 pptv (Elshorbany et al., 2012; Stevens et al., 1997; Lelieveld et al., 2016; Finlayson-Pitts and Pitts Jr, 1999) (with photolysis of aldehydes, especially formaldehyde and oxidation of CO by OH being drivers of HO$_2$ concentrations (Finlayson-Pitts and Pitts Jr, 1999; Lelieveld et al., 2016)) and so if [NO] is larger than these values the reaction with NO will outcompete the reaction with HO$_2$ and the system becomes “high NOx”. However, even under “low NOx” conditions, high HO$_2$ levels can also reduce nucleation and early growth, as R1 only forms C$_{10}$ monomers and no C$_{20}$ dimers for monoterpene oxidation.

The total [RO$_2$] in the atmosphere rarely exceeds [HO$_2$] and is often significantly lower. Further, unlike the first two reactions, the RO$_2^·$ + RO$_2^·$ reactions depend strongly on the organic substituent, varying by over six orders of magnitude at room temperature (Madronich and Calvert, 1990). In general, electron donating substituents (i.e. t-butyl) make the reaction very slow, while electron withdrawing substituents (i.e. acetyl) can make the self-reaction fairly fast ($\text{CH}_3\text{C(O)O}_2^· + \text{CH}_3\text{C(O)O}_2^· \sim 1 \cdot 10^{-11} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}$) (Madronich and Calvert, 1990). Madronich and Calvert (1990) proposed a simplifying scheme to estimate cross reaction rate constants from self-reaction rate constants using the geometric mean ($k_{a,b,\text{cross}} = \sqrt{k_{a,\text{self}} \cdot k_{b,\text{self}}}$. Recently, it was shown (Berndt et al., 2018) that highly oxidized RO$_2^·$ produced from terpenes such as α-pinene can have $k_3 \sim 1 \cdot 10^{-10} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}$. 

25
These rapid $\text{RO}_2^\cdot + \text{RO}_2^\cdot$ reactions are extremely important for atmospheric chemistry and the analysis we present here. Only when $k_3 > 1 \cdot 10^{-11} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}$, can RO$_2^\cdot$ cross reactions have a significant effect in the atmosphere, but when this is true there are two consequences. First, the oxidation mechanisms of different hydrocarbons producing highly reactive RO$_2^\cdot$ become coupled, because they influence each other through their RO$_2^\cdot$. Second, the transition to “high NO,$_x$” is pushed to higher NO because of the faster self-reactions.

It is the first consequence that is most significant here. The RO$_2^\cdot$ from $\alpha$-pinene and isoprene both appear to be highly reactive and so will out compete HO$_2$ at low NO. Consequently, isoprene and monoterpenes become coupled by their RO$_2^\cdot$ interactions. RO$_2^\cdot$ radicals derived from smaller VOCs like CH$_4$ can have significantly lower self-reaction rates (e.g. for CH$_3$OO$^\cdot$: $k_{\text{self}} = 3.5 \cdot 10^{-13} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}$) (Madronich and Calvert, 1990). The resulting cross reaction would then be $1.2 \cdot 10^{-11} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1}$ and thus one order of magnitude smaller than the RO$_2(\alpha p)$ self-reaction rate. This would allow for at least some degree of coupling, depending on detailed atmospheric conditions.

However, if RO$_2^\cdot$ coupling of light VOCs or HO$_2$ would dominate atmospheric chemistry of RO$_2(\alpha p)$, it would not be possible to detect C20 signals there, as almost all RO$_2(\alpha p)$ radicals would be terminated to either C10 monomers or light dimers with e.g. 11 or 12 carbon atoms. There is however clear evidence of atmospheric C20 formation, i.e. RO$_2(\alpha p)$-RO$_2(\alpha p)$ reactions leading to dimers in the presence of relatively high levels of CO, CH$_4$, HO$_2$ and in some locations also NO$_x$ (Yan et al., 2016; Kürt et al., 2016; Massoli et al., 2018). The HOM spectrum reported for an isoprene-rich measurement site in Alabama during the SOAS campaign showed a qualitatively similar distribution of C5, C10, C15 and C20 classes as reported in our study (except for NO$_x$ effects) (Massoli et al., 2018). This is direct evidence for the atmospheric relevance of our findings.
Figure S1: Time series of a nucleation experiment with example HOM traces. (a) shows traces of α-pinene, isoprene and ozone. (b) and (c) show selected time traces of HOM monomers and dimers measured by the Cl-API-TOF, respectively. The temperature in the chamber was +5 °C and rel. humidity was 38 %. N, GCR and CLEAN indicate neutral (high voltage cleaning field on), galactic cosmic ray (high voltage cleaning field off) and cleaning (neutral periods to clean the chamber of particles) conditions, respectively.

In the first part until 04 Oct, 06:00 UTC, α-pinene was present in the chamber at three different concentrations to study pure biogenic nucleation under both neutral and gcr conditions with an additional UV stage at the end. Afterwards an isoprene/ozone mixture was studied under both dark and UV-illuminated conditions. Note that during the UV stage on 04 Oct the laser intensity deteriorated towards the end of the stage and thus corresponding HOM signals went down as well. At 04 Oct, starting at 18:40 UTC, α-pinene was added at three concentration levels similar to the first part of the experiment.
Figure S2: Time series of a nucleation experiment with particle counter data and nucleation rates. The temperature in the chamber was +5 °C and rel. humidity was 38 %. The time window shown is the same as in Figure S1. (a) shows traces of α-pinene, isoprene and ozone. N, GCR and CLEAN indicate neutral (high voltage cleaning field on), galactic cosmic ray (high voltage cleaning field off) and cleaning (neutral periods to clean the chamber of particles) conditions, respectively. (b) shows particle concentration above 1.7, 2.2 and 2.5 nm, measured with a scanning PSM (1.7 nm and 2.2 nm) and a butanol-based CPC (2.5 nm). (c) shows the nucleation rate $J$ determined at 1.7, 2.2 and 2.5 nm using the particle concentrations shown in (b). (d) shows a combined size distribution of aerosol particles in the CLOUD chamber. The DMA-train contributed the size range from 1.8 – 8 nm, the nanoSMPS from 8 – 65 nm and the long-SMPS for sizes >65 nm.
Figure S3: Effects of isoprene addition on RO$_2^·$ radical and HOM classes distribution. Chamber conditions were +25 °C and 38 % RH. α-Pinene levels were 456, 771 and 1442 pptv for α-pinene only and 677, 1326 and 2636 pptv for α-pinene + isoprene conditions. Ozone levels were 49 ppbv for α-pinene only and 38 to 40 ppbv for α-pinene + isoprene conditions. Isoprene levels were 2.7, 4.9 and 9.8 ppbv. All data from the α-pinene only runs was scaled up linearly (21, 38 and 45 % for low, mid and high α-pinene levels, respectively) to match the exact same [α-pinene]·[O$_3$] values as in the α-pinene + isoprene runs. (a) shows the distribution of the most prominent RO$_2^·$ radicals originating from isoprene and α-pinene oxidation. (b) shows the absolute and (c) the relative changes of the HOM class distribution due to isoprene addition.
Figure S4: Changes of RO$_2^\cdot$ radical and HOM classes distribution due to UV light in an α-pinene, isoprene and ozone mixture. Chamber conditions were +5 °C and 38 % RH. α-pinene levels were 1116 (dark) and 1096 pptv (UV illuminated). The ozone level was 48 ppbv, the isoprene level was 3.6 and 3.4 ppbv in dark and UV illuminated conditions, respectively. Data from the dark run was slightly scaled down linearly (1.2 %) to match exact same [α-pinene]×[O$_3$] values as in the UV run. (a) shows the distribution of the most prominent RO$_2^\cdot$ radicals originating from isoprene (green) and α-pinene (red) oxidation. (b) shows the absolute and (c) the relative changes of the HOM class distribution due to UV light.
Figure S5: Mass defect plots showing HOM production from isoprene alone (a, b) and the effect of UV light on an α-pinene/isoprene mixture (c, d). Chamber conditions were +5 °C and 38 % RH. HOM production from a mixture of isoprene (4.5 ppbv) and ozone (40 – 50 ppbv) under (a) dark conditions and (b) UV-illuminated conditions with higher OH· levels. The area of the marker points is linearly scaled to intensity of the HOM signals in all four panels. Color code represents oxygen-to-carbon ratio (O:C) of HOMs. UV light strongly enhances OH· and thus HOM production. This even leads to the formation of some C_{10} dimers resulting from the combination of two RO_{2}(ip). (c) and (d) show the mass defect plot of HOMs from a mixture of α-pinene, isoprene and ozone under (c) dark and (d) UV-illuminated conditions. α-pinene is 1116 and 1096 pptv, isoprene was 3.6 and 3.4 ppbv in (c), and (d), respectively. Ozone was 47 ppbv for both runs. Color code indicates the change in intensity for each HOM peak when switching from dark to UV light conditions, i.e. the percentage intensity change between (c) and (d). The color for each peak is thus the same in (c) and (d). Data from the dark run was slightly scaled down linearly (1.2 %) to match the same [α-pinene]-[O_{3}] values as in the UV run for calculating the intensity change.
Figure S6: Mass Defect plots showing the effect of increased isoprene and monoterpene concentrations on HOM formation and nucleation rate $J_{1,5}$. Chamber conditions were +25 °C and 38 % RH. (a) describes the base case without isoprene, (b) shows the effect of addition of isoprene. Color code in (b) and (c) shows the relative change in HOM intensity compared to (a). (c) shows HOM spectra after α-pinene and isoprene concentrations have been roughly doubled compared to (b).
Figure S7: Nucleation rate \( J_{1.7} \) vs relative humidity at +25 °C (a) and corresponding HOM spectra (b-d). All data shown was recorded with similar precursor concentrations (1.4 ppbv \( \alpha \)-pinene, 5.1-6.2 ppbv isoprene, however, ozone decreased slightly from 46 to 40 ppbv as humidity was increased). HOM levels were fairly constant ranging from \( 1.3 \times 10^8 \) to \( 1.6 \times 10^8 \) cm\(^{-3}\). Bars indicate 1σ run-to-run uncertainty. The overall systematic scale uncertainty of \( J \) for ±47 % is not shown. The mass defect plots (b, c and d) show the HOM distribution measured by the nitrate CI-APi-TOF under different humidity levels. The color code represents the relative change in HOM signal compared to the standard 38 % RH setting shown in (c). To calculate this change, HOM levels in (b) and (d) were scaled down by 11 % and scaled up by 10 %, respectively to match the same \([\alpha p] \cdot [O_3]\) levels as in (c). We attribute the strong increase of certain HOMs with low O:C ratios in (d) (red marker symbols) to a more efficient charging process with nitrate ions in our ion source due to assistance of water molecules rather than to an increased production inside the CLOUD chamber.
Figure S8: Nucleation rate $J_{1.7}$ (gcr) vs sulfuric acid at +25 °C. α-pinene and isoprene levels were kept constant for all data points (around 1300 pptv and 4.5 ppbv, respectively), ozone levels ranged from 35 to 39 ppbv. HOM levels were fairly constant for all data points, ranging from $1.2 \cdot 10^8$ to $1.5 \cdot 10^8$ cm$^{-3}$. All data was taken with excess ammonia (0.4 -2.5 ppbv), relative humidity was 38 % for all runs. Bars indicate 1σ run-to-run uncertainty. The overall systematic scale uncertainty of $J$ for ±47 % is not shown.
Figure S9: Correlation of individual HOMs with nucleation rate $J_{nuc}$. The data points displayed are taken from a run with 2.6 ppbv $\alpha$-pinene, 9.8 ppbv isoprene and 38 ppbv ozone under UV illuminated conditions. The area of the marker points is linearly scaled to the intensity of the HOM signals. The color code indicates coefficient of determination ($R^2$) of a power law fit of $J$ vs every individual HOM peak. The dataset used for the fit contains the six $J_{nuc}$ data points taken under low/medium/high $\alpha$-pinene levels with and without isoprene at +25 °C. High $R^2$ does not necessarily mean that the corresponding molecules contribute directly to nucleation, but that they are predominantly formed in a chemical setting that favors the production of nucleator molecules.
Figure S10: Growth rate vs (a) C_{20} class concentration and (b) C_{15} + C_{20} class concentration at +5 °C and 38 % RH. Growth rates were measured by scanning PSM (1.3 – 1.9 nm, dark blue), DMA-train (1.8 – 3.2 nm, light blue and 3.2 – 8.0 nm, orange) and nanoSMPS (5.0 – 15 nm, red). Triangles represent α-pinene only runs, circles represent α-pinene + isoprene runs. The growth rate between 1.8 nm and 3.2 nm can be parametrized by a linear fit when plotted against C_{20} class molecules, for the size range from 3.2 nm – 8.0 nm there is a linear relationship for growth rate when plotted against C_{15} + C_{20} class molecules.
SI References


Molecular understanding of the suppression of new-particle formation by isoprene

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Abstract

Nucleation of atmospheric vapors produces more than half of global cloud condensation nuclei and so has an important influence on climate. Recent studies show that monoterpene (C_{10}H_{16}) oxidation yields highly-oxygenated products that can nucleate with or without sulfuric acid. Monoterpenes are emitted mainly by trees, frequently together with isoprene (C_{5}H_{8}), which has the highest global emission of all organic vapors. Previous studies have shown that isoprene suppresses new-particle formation from monoterpenes, but the cause of this suppression is under debate. Here, in experiments performed under atmospheric conditions in the CERN CLOUD chamber, we show that isoprene reduces the yield of highly-oxygenated dimers with 19 or 20 carbon atoms - which drive particle nucleation and early growth - while increasing the production of dimers with 14 or 15 carbon atoms. The dimers (termed C_{30} and C_{15}, respectively) are produced by termination reactions between pairs of peroxy radicals (RO_{2} -) arising from monoterpenes or isoprene. Compared with pure monoterpene conditions, isoprene reduces nucleation rates at 1.7 nm (depending on the isoprene/monoterpene ratio) and approximately halves particle growth rates between 1.3 and 3.2 nm. However, above 3.2 nm, C_{15} dimers contribute to secondary organic aerosol and the growth rates are unaffected by isoprene. We further show that increased hydroxyl radical (OH·) reduces particle formation in our chemical system rather than enhances it as previously proposed, since it increases isoprene derived RO_{2} - radicals that reduce C_{30} formation. RO_{2} - termination emerges as the critical step that determines the HOM distribution and the corresponding nucleation capability. Species that reduce the C_{20} yield, such as NO, HO_{2} and as we show isoprene, can thus effectively reduce biogenic nucleation and early growth. Therefore the formation rate of organic aerosol in a particular region of the atmosphere under study will vary according to the precise ambient conditions.

1. Introduction

Nucleation of aerosol particles is observed in many environments, ranging from boreal forests to urban and coastal areas, from polar to tropical regions and from the boundary layer to the free troposphere (Kerminen et al., 2018). Gaseous sulfuric acid, ammonia (Kirkby et al., 2011), amines (Almeida et al., 2013) and, in coastal regions, iodine (Sipilä et al., 2016), were shown to contribute to nucleation. Additionally, a small fraction of the large pool of organic molecules in the atmosphere, namely highly-oxygenated organic molecules (HOMs), some of which possess extremely low vapor pressures, nucleate together with other precursors as well as on their own (Riccobono et al., 2014; Kirkby et al., 2016; Tröstl et al., 2016). This means nature is nucleating particles on a large scale without pollution, and this may have been especially pervasive in the pre-industrial atmosphere (Gordon et al., 2016). HOMs can be formed with molar yields in the single-digit percent range from the oxidation of monoterpenes (C_{10}H_{16}) with endocyclic C=C double-bonds (Kirkby et al., 2016; Ehn et al., 2014). Monoterpenes are emitted by a variety of trees in regions ranging from the tropics to northern latitudes, often reaching mixing ratios of tens to hundreds of parts per trillion by volume (pptv) (Jardine et al., 2015; Guenther et al., 2012). Isoprene is a hemiterpene (C_{5}H_{8}) emitted by broad-leaf trees and has the highest emissions of any biogenic organic compound, with concentrations reaching several parts per billion by volume (ppbv) in the Amazon rainforest and the southeastern United States despite high reactivity (Guenther et al., 2012; Martin et al., 2010; Lee et al., 2016). Numerous studies report suppression of nucleation in isoprene-rich environments, even if sufficient monoterpenes are present (Lee et al., 2016; Kanawade et al., 2011; Yu et al., 2014; Kiendler-Scharr et al., 2009; Kiendler-Scharr et al., 2012; Varanda Rizzo et al., 2018; Wimmer et al., 2018). This isoprene suppression effect has been demonstrated in carefully controlled chamber studies (Kiendler-Scharr et al., 2009; Kiendler-Scharr et al., 2012) and observed in isoprene-rich ambient locations (Kanawade et al., 2011; Lee et al., 2016; Yu et al., 2014). A recent study reported also a suppression of secondary organic aerosol (SOA) formation due to isoprene in an OH· dominated chamber experiment (McFiggans et al., 2019). In addition to observing suppression of particle formation by isoprene, earlier studies have proposed mechanisms to explain it. One possibility is OH· depletion by isoprene, which would reduce the oxidation rate of monoterpenes and thus supersaturation driving nucleation (Kiendler-Scharr et al., 2009; Kiendler-Scharr et al., 2012; McFiggans et al., 2019). However, OH· is observed to remain high and undisturbed in isoprene-rich environments due to atmospheric OH· recycling mechanisms triggered by isoprene (Taraborrelli et al., 2012; Martinez et al., 2010; Fuchs et al., 2013). Further it was shown that ozonolysis is crucial for HOM formation (Ehn et al., 2014; Kirkby et al., 2016). Another proposed possibility for
isoprene suppression of nucleation is the deactivation of sulfuric acid cluster growth due to addition of isoprene oxidation products (Lee et al., 2016). However, HOMs can nucleate without sulfuric acid (Kirkby et al., 2016) and suppression of nucleation by isoprene is observed in pristine environments such as the Amazon (Martin et al., 2010).

Isoprene oxidation by OH· triggers complex peroxy-radical chemistry with a variety of products such as hydroxy-hydroperoxides (ISOPOOH), hydroperoxy-aldehydes (HPALD) as well as second-generation low-volatility compounds (Teng et al., 2017; Berndt et al., 2016). Isoprene oxidation products with low volatility such as dihydroxyepoxides (IEPOX) contribute to secondary organic aerosol formation (Carlton et al., 2009; Krechmer et al., 2015; Paulot et al., 2009; Surratt et al., 2010; Lin et al., 2011; Budisulistiorini et al., 2013). However, the interaction of isoprene and monoterpene oxidation chemistry and the consequent effect on nucleation and growth of new particles remains unclear. Recently, the interaction of isoprene and monoterpene oxidation chemistry was studied and it was found that isoprene derived RO2 molecules can reduce the formation of monoterpene derived dimers (Berndt et al., 2018b; McFiggans et al., 2019). However, the effect of this interaction on nucleation and early growth of particles under atmospherically relevant conditions remains unclear so far. One consequence of this is an over-prediction of cloud condensation nuclei (CCN) in the Amazon by models that simulate pure biogenic nucleation, but neglect the role of isoprene in new-particle formation (Gordon et al., 2016).

Here, we present experiments performed under atmospherically relevant conditions at the CERN CLOUD chamber and show on a molecular level how isoprene affects the chemistry of monoterpene oxidation, thus reducing nucleation rates as well as early growth rates.

2. Methods

The Cosmics Leaving Outdoor Droplets (CLOUD) chamber at the European Center for Nuclear Research (CERN) is a 26.1 m3 stainless steel aerosol chamber, in which a large variety of atmospheric conditions can be recreated under precisely controlled conditions (Kirkby et al., 2011; Kirkby et al., 2016; Duplissy et al., 2016). The chamber is thermally insulated and its temperature can be precisely controlled in the range from -65 °C to 100 °C. In order to reduce contaminations, air mixed from cryogenic nitrogen and oxygen is used. Trace gases like α-pinene and isoprene can be added and controlled via a two stage dilution system at the parts per trillion by volume level. Mixing is ensured by two magnetically coupled fans. The chamber is equipped with a UV excimer laser and HgXe UV lamps in order to trigger photochemistry. Ion-free conditions can be generated by applying a high voltage electric field across the chamber that sweeps out naturally produced ions (neutral conditions). When this field is switched off, ions produced by galactic cosmic rays penetrating the chamber are allowed to stay inside the chamber and their effect on nucleation processes can be studied. Using the CERN π⁻-beam increases the ion concentration artificially (see SI Appendix for more detail).

The air inside the chamber is continuously analyzed by a variety of instruments. Organic precursors (α-pinene and isoprene) are measured by a PTR3 instrument (Breitenlechner et al., 2017). HOMs are measured by a nitrate CI-API-TOF (Kürtken et al., 2011) that is connected to the chamber via a 1” core sampling probe, where only the inner part of the flow is sampled into the ion source of the instrument in order to minimize wall losses. Number concentration and size distribution of newly formed particles are measured with an array of butanol based condensation particle counters (CPCs), diethylene glycol based Particle Size Magnifiers (PSMs), as well as a DMA-train and a Scanning Mobility Particle Sizer (SMPS) (see SI Appendix for more detail).

A typical experiment starts with the injection of α-pinene into the particle free chamber (see Fig. S1 and S2), while other parameters like temperature, humidity and ozone levels are already stabilized. Oxidation of α-pinene by both O3 and OH leads to the formation of HOMs, which subsequently lead to the formation of particles. The experiment is continued without intervention until a steady state in HOMs and nucleation rate has been established. Once the nucleation and growth rates have been determined, the next experiment is performed under slightly different conditions. Parameters that were varied are α-pinene and isoprene levels, ion concentration, UV illumination, sulfuric acid concentration, temperature and relative humidity.
3. Results

We performed several experiments at +5 and +25 °C and relative humidity (RH) ranging from 20 to 80 % with most of the experiments being carried out at 38 % RH. Ozone levels ranged from 30 – 50 ppbv. We directly compare experiments performed with α-pinene as the sole biogenic vapor to experiments with a mixture of α-pinene and isoprene. α-Pinene levels ranged from 0.33 to 2.5 ppbv, while isoprene levels ranged from 2.5 to 10 ppbv. We thus could recreate conditions similar to Kirkby et al. (2016), as well as to regions like the Amazon (Martin et al., 2010; Yáñez-Serrano et al., 2018) and southeastern parts of the United States (Lee et al., 2016).

Ozone attack to the endocyclic α-pinene C=C double bond leads to the well-described formation of highly-oxygenated RO$_2^\cdot$ radicals via intramolecular H-shift and autoxidation (mainly C$_{10}$H$_{15}$O$_{6,8,10}$, from now on referred to as RO$_2$(ap)) as well as a wide spectrum of closed-shell monomers (mainly C$_{10}$H$_{14,16}$O$_{5,7,9,11}$) and covalently bound dimers (mainly C$_{20}$H$_{30}$O$_{5,7}$ and C$_{19}$H$_{28}$O$_{5,11}$, see Fig. 1A) (Ehn et al., 2014; Kirkby et al., 2016; Rissanen et al., 2015; Berndt et al., 2018b; Molteni et al., 2019). These highly-oxygenated organic molecules (HOMs) nucleate at atmospherically relevant concentrations with the help of ions but without other species (e.g. sulfuric acid or bases) required (Kirkby et al., 2016). Here, we group the HOMs according to carbon atom number and define C$_5$, C$_{10}$, C$_{15}$ and C$_{20}$ classes as sum of all HOMs with 2-5, 6-10, 11-15 and 16-20 carbon atoms, respectively. This resembles the basic building block unit of a C$_5$ isoprenoid skeleton.

An isoprene/ozone mixture in the CLOUD chamber produces C$_5$H$_5$O$_5$ isoprene radicals (referred to as RO$_2$(ip)) which terminate to C$_5$H$_5$O$_{8,8}$ and C$_{10}$H$_{15}$O$_{5,9}$ monomers and also some C$_{10}$H$_{18}$O$_{10}$ dimers under UV-illuminated conditions (see Fig. S5 A, B). The C$_5$H$_5$O$_5$ radicals originate presumably from an OH-addition to isoprene and subsequent autoxidation. Under dark conditions, when the only source of OH- is isoprene ozonolysis at 26 % yield (Malkin et al., 2010), we observe only C$_5$ monomers. None of these molecules are able to nucleate under atmospherically relevant conditions despite having an oxygen to carbon ratio (O:C) ≥ 1, which agrees with earlier observations that products from isoprene ozonolysis do not drive significant new-particle formation (Kamens et al., 1982; Riva et al., 2017).

When isoprene is present together with α-pinene and ozone, the HOM chemistry of α-pinene is altered. We observe the appearance of C$_{15}$ and an increase in C$_5$ class molecules compared to α-pinene only conditions as well as a decrease in C$_{20}$ and C$_{10}$ class molecules (see Fig. 1 and S3). Without isoprene, RO$_2$(ap) can terminate with another RO$_2$(ap), thus forming either one C$_{20}$ dimer or two C$_{10}$ monomers. Monomers can also be formed by termination with HO$_2$ or unimolecular termination (Rissanen et al., 2015). The presence of RO$_2$(ip) offers additional termination channels (Berndt et al., 2018a) (see Fig. 2) and acts as an additional loss term for RO$_2$(ap). Reactions between RO$_2$(ip) and RO$_2$(ap) are expected to result in C$_5$ and C$_{10}$ monomers as well as C$_{15}$ dimers. Most importantly, the reduced RO$_2$(ap) steady state concentrations lead to a reduction of C$_{20}$ class dimers by roughly 50 % (depending on detailed conditions) compared to their level in the absence of isoprene for all studied α-pinene concentrations (see Fig. S3). To our knowledge the only study that presented ambient measurements of HOMs for an isoprene-rich region is from the SOAS campaign (Southern Oxidant and Aerosol Study, Alabama, USA) (Massoli et al., 2018). When comparing our results with this study, we find good qualitative agreement for the distribution of HOMs with strong contributions in the C$_5$ and C$_{10}$ region and lesser contributions in the C$_{15}$ and C$_{20}$ region.

We have to caution however that the C$_{15}$ signal in the reported HOM distribution could also be caused by sesquiterpene products. Additionally, the presence of NO$_x$ affects HOM chemistry in Alabama, which also leads to C$_{20}$ reduction (Lehtipalo et al., 2018).

We measured the particle formation rate directly at a 1.7 nm cut-off diameter with a scanning Particle Size Magnifier (PSM) under neutral (high voltage field cage switched on, see SI Appendix for details) and ion conditions (high voltage field cage switched off, allowing for galactic cosmic ray (gcr) ionization in the chamber), further referred to as $J_n$ and $J_{gcr}$ (see SI Appendix for detail). Fig. 3A shows $J_n$ and $J_{gcr}$ plotted against the total HOM concentration (the sum of the C$_5$, C$_{10}$, C$_{15}$ and C$_{20}$ classes) for the α-pinene only case and α-pinene + isoprene. For +5 °C we find good agreement with Kirkby et al. (2016). However, the
presence of isoprene and the consequent change in oxidation chemistry reduces $J_{gcr}$ by a factor of two to four and $J_n$ even more by around one order of magnitude at 5 °C. The suppression is stronger for lower α-pinene concentrations and thus higher values of R (the ratio of isoprene to monoterpene carbon).

The larger gap between $J_{gcr}$ and $J_n$ with isoprene present compared to α-pinene only conditions is direct evidence that isoprene oxidation products destabilize the nucleating clusters, thus making cluster stabilization through the presence of charge more efficient. This also confirms that C$_{20}$ class molecules are mainly responsible for pure biogenic nucleation (Frege et al., 2018). C$_{15}$ class molecules, which tend to counteract the losses of the C$_{20}$ class, do not prevent a decrease in $J_n$. Earlier studies have already suggested that C$_{10}$ class molecules do not possess low enough vapor pressure to qualify as Extremely Low Volatility Organic Compounds (Kurtén et al., 2016; Tröstl et al., 2016) and thus do not drive nucleation, leaving C$_{20}$ class molecules as the most likely nucleator molecules. At +25 °C and UV light illumination, we find that nucleation rates of the pure α-pinene system are reduced by a factor of about 2-3 compared to +5 °C. This is a much smaller reduction in nucleation rate compared to, e.g., the inorganic sulfuric acid water system, for which the same temperature increase reduces nucleation rates by around two orders of magnitude (Kirkby et al., 2011) due to an increase in vapor pressure at warmer temperatures. In our organic system, however, accelerated oxidation chemistry counters the effect of higher vapor pressures. This includes a higher rate of initial oxidation of α-pinene by ozone, as well as a faster autoxidation process, which leads to HOMs with generally higher oxygen content. When we add isoprene at +25 °C with a constant ratio of isoprene to monoterpene carbon (R = 2), we find a reduction in $J_{gcr}$ of around a factor of about 2. Similar to the data at +5 °C where R ranges from 1.6 to 6.5, we expect a stronger decrease for higher values of R. This can be understood as higher isoprene concentrations enhance RO$_2$(ip) formation, which in turn reduces C$_{20}$ production and subsequent nucleation. R can reach levels around 15 in the Amazon (Greenberg et al., 2004) and around 26 in Michigan (Kanawade et al., 2011), where we would thus expect an even stronger isoprene effect on nucleation.

Comparing HOM formation and nucleation for three different α-pinene/isoprene settings, we observe that the addition of 2.7 ppbv of isoprene to an α-pinene/ozone mixture (770 pptv and 49 ppbv, respectively) mitigates C$_{20}$ production and reduces $J_{1,7}$ from 3.2 cm$^{-3}$s$^{-1}$ to 0.81 cm$^{-3}$s$^{-1}$ (see Fig. S6). A rough doubling of both the α-pinene and isoprene levels to 1326 pptv and 4.87 ppbv, respectively, increases overall HOM production; however, C$_{20}$ levels and consequently $J_{1,7}$ remain lower than in the original pure α-pinene setting without isoprene. Thus even increasing monoterpene concentrations can lead to lower J values when isoprene is added as well. Additional evidence for the important role of C$_{20}$ is shown in Fig S9: Regressing each individual HOM peak with $J_{gcr}$ gives high coefficients of determination for C$_{20}$ class molecules.

It has been argued that OH· depletion by isoprene is responsible for the absence of nucleation in isoprene-rich environments (Kiendler-Scharr et al., 2009; Kiendler-Scharr et al., 2012); however, under atmospheric conditions, isoprene induced OH· recycling can lead to undisturbed high OH· levels, which might not be true in chamber experiments (Taraborrelli et al., 2012; Martinez et al., 2010; Fuchs et al., 2013). In our study we also see an OH· depletion effect due to isoprene addition (see Fig. S1 and SI Appendix for detailed discussion). However, if OH· depletion were the reason for suppression of nucleation, an increase of OH· would lead to an increase in the nucleation rate. When we increase OH· levels by switching on UV lights in the presence of isoprene, this reduces RO$_2$(ap) further, as well as the C$_{20}$ and C$_{10}$ class molecules, while enhancing the C$_5$ and C$_{15}$ classes (see Fig. S1, S4 and S5 C, D as well as SI Appendix for details). Accordingly, $J$ is also reduced slightly instead of being increased. In the atmosphere with considerable OH· recycling, this effect, and therefore the suppression of new-particle formation, would be even stronger. We can understand this OH· effect by comparing the reactivity of α-pinene and isoprene towards OH· at our given concentrations. For 300 and 1200 pptv the reactivity of α-pinene towards OH· at +5 °C ([$\alpha p$] $k_{a\rho \text{OH}}$) is 25.1 and 6.3 times lower, respectively, than the reactivity of 4 ppbv isoprene towards OH· ([$\text{ip}$] $k_{a\rho \text{OH}}$). At +25 °C these numbers are similar (25.4 and 6.3, respectively). This implies that any additional OH· provided by e.g. UV illumination will favor the formation of additional RO$_2$(ip) instead of RO$_2$(ap), thus favoring the formation of C$_{15}$ over C$_{20}$ and consequently reducing nucleation rates. OH· does not enhance nucleation in this chemical system; it suppresses it.

We performed experiments at +25 °C with three different levels of relative humidity (20, 38 and 80 %) to probe the effect of water on new-particle formation. Changes in humidity do not significantly affect HOM
formation and $J_{\text{ger}}$ (see Fig. S7). $J_n$ increased slightly with humidity, showing an increased stabilization of nucleating clusters by water; however, in gcr conditions, this role is fulfilled more efficiently by ions.

We further studied the effect of sulfuric acid on nucleation of an α-pinene/isoprene mixture (about 1300 pptv and 4.5 ppbv, respectively) in experiments with excess ammonia (0.4 - 2.5 ppbv) in order to reproduce typical conditions in the eastern parts of the United States (Lee et al., 2016). We find that sulfuric acid does not enhance biogenic nucleation up to a concentration of \(5 \times 10^6\) cm\(^{-3}\) (see Fig. S8). This decoupling of biogenic nucleation from low sulfuric acid levels is similar to the pure α-pinene system reported in Kirkby et al. (2016). At sulfuric acid levels higher than \(5 \times 10^6\) cm\(^{-3}\), nucleation rates depend strongly on sulfuric acid levels, which agrees with a wide variety of atmospheric measurements (Kirkby et al., 2016). In the Amazon, sulfuric acid levels are typically in the range of \(1 \times 10^5\) cm\(^{-3}\) (Kanawade et al., 2011), well below the threshold value of \(5 \times 10^6\) cm\(^{-3}\). In Alabama this threshold was exceeded only three times in a 45-day measurement period due to transported sulfur plumes, which led to two events of particles growing to larger sizes (Lee et al., 2016). In Michigan, sulfuric acid concentrations are typically in the range of \(1 \times 10^6\) cm\(^{-3}\) (Kanawade et al., 2011). Sulfuric acid is thus not an important contributor to nucleation in the Amazon as well as different regions of the eastern United States.

We measured the growth rates of freshly nucleated particles from 1.3 nm onwards with a scanning Particle Size Magnifier, a DMA-train and a nanoSMPS (see SI Appendix for details). The change in HOM chemistry caused by concurrent isoprene oxidation reduces the growth rates of particles in the range of 1.3 – 1.9 nm and 1.8 – 3.2 nm roughly by a factor of two (Fig. 3B and 3C). This confirms that C\(_{15}\) class molecules have a higher saturation vapor pressure than C\(_{20}\) class molecules and are thus less efficient than C\(_{20}\) class molecules at causing growth of the smallest particles. Likewise, most C\(_{10}\) class molecules are too volatile to contribute significantly to the early stages of growth (Tröstl et al., 2016). For the size range from 3.2 – 8.0 nm and larger, we observed no suppression effect due to isoprene, indicating that molecules smaller than C\(_{30}\) are capable of condensing onto larger particles. We find a linear relationship of growth rate vs C\(_{30}\) for 1.3 - 1.9 and 1.8 - 3.2 nm, regardless of isoprene presence. For larger sizes the linear relationship is independent of isoprene presence, when plotted against C\(_{15}\) + C\(_{20}\); this again indicates that C\(_{15}\) contributes to growth at larger sizes (Fig. S10). Besides C\(_{15}\) and C\(_{20}\), however, even lighter and less oxygenated molecules can contribute to particle growth at larger sizes (Stolzenburg et al., 2018). Growth rates at +25 °C are typically halved compared to +5 °C due to higher saturation vapor pressure of the HOMs (Stolzenburg et al., 2018), which leads to a higher chance of particles being scavenged while growing, even more so in the presence of isoprene.

Fig. 4 shows the formation rate of particles measured at diameters of 1.7, 2.2, 2.5 and 6 nm for gcr conditions and six concentration values (low/mid/high α-pinene mixing ratios with and without isoprene) at +25 °C. We find that due to the reduced growth rates in the presence of isoprene, a moderate reduction of formation rates at 1.7 nm becomes much more pronounced, while the particles grow to larger sizes. When we compare α-pinene only data (771 pptv α-pinene, 49 ppbv O\(_3\)) with a mixture (1320 pptv α-pinene, 39 ppbv O\(_3\) and 4.9 ppbv isoprene, orange data points in Fig. 4), $J_{1.7}$ is reduced by 45 %, while the corresponding formation rate at 6 nm is reduced by an order of magnitude. The corresponding precursor concentrations are similar to conditions found in e.g. Alabama (Lee et al., 2016). Isoprene can thus drastically reduce the formation of particles larger than 6 nm even at relatively warm temperatures like +25 °C. This growth-rate driven effect becomes stronger when α-pinene concentrations are reduced. Our measurements agree with observations of small clusters that are unable to grow efficiently, as has been reported for Alabama (Lee et al., 2016) and the Amazon (Wimmer et al., 2018). Increased levels of preexisting aerosols (i.e. condensation sink) can scavenge freshly nucleated particles (Dada et al., 2017); however, due to the reduced initial growth rates, the likelihood for that process at a given condensation sink is increased when isoprene is present compared to α-pinene only conditions.

4. Discussion

Pure biogenic nucleation was first described for α-pinene oxidation in the CLOUD chamber (Kirkby et al., 2016). Global evaluation of this process with the help of atmospheric modeling found an over-prediction of CCN concentrations in the Amazon, leading to speculation about an as yet unaccounted chemical
suppression mechanism for new-particle formation involving isoprene (Gordon et al., 2016). With our findings, we provide the molecular understanding for such a mechanism and identify C_{20} class molecules as the main drivers of biogenic nucleation and early growth. This allows us to refine our understanding of biogenic nucleation for isoprene-rich regions, while at the same time large portions of the atmosphere where biogenic nucleation is very important, remain unaffected by our findings, especially boreal forests (Gordon et al., 2016).

Suppression of new-particle formation by isoprene was previously attributed to competition for OH-radicals during the initial oxidation of VOCs, which was then thought to be followed by independent oxidation pathways (Kienel-Scharr et al., 2009). Instead we show that the suppression takes place via RO_2· radical interactions that strongly couple the oxidation chains of monoterpene and isoprene.

McFiggans et al. (2019) showed that the same RO_2· mechanism that we describe here is also responsible for reduced SOA formation, together with an additional OH· scavenging effect. The oxidation chemistry in McFiggans et al. (2019) was dominated (> 90 %) by OH· for both monoterpenes and isoprene. In our experimental conditions, monoterpene oxidation was dominated by ozone, which is more common in the atmosphere, and we demonstrate the importance of the RO_2· mechanism directly in these conditions. Additionally, while the precursor concentrations in McFiggans et al. (2019) were much higher than typical atmospheric levels, the precursor levels in the current study resemble the atmosphere more closely. This is especially important as HOM formation is not a linear process and cannot be scaled down to atmospheric levels in a straightforward manner.

All extrapolations of chamber experiments to atmospheric conditions must be treated with care; for example, it has been shown that isoprene OH· scavenging is stronger in common chamber conditions than in ambient conditions, where OH· recycling (e.g. by HPALD photolysis) counters the OH· consumption by isoprene (Taraborrelli et al., 2012).

McFiggans et al. (2019) also show that OH· scavenging by isoprene is important for reduced SOA formation. We also find a reduction in OH· levels due to isoprene addition in the CLOUD chamber. However, this is not the reason for the suppression of nucleation and early growth rates in our experiments. Quite to the contrary, the dominant effect of increased OH· in our experiments is to increase RO_2(ip) due to the fast reaction between isoprene and OH·. OH· thus suppresses C_{20} dimers and nucleation rates in our chemical system. Thus, while increased OH· levels restore SOA formation partially in the coupled monoterpene/isoprene system, as shown by McFiggans et al. (2019), they suppress nucleation in our experiments. This further highlights the important differences between SOA formation with preexisting seed particles on the one hand and the nucleation of new particles on the other hand. SOA mass production and nucleation are not the same thing. SOA formation with preexisting particles can include molecules possessing comparatively high saturation vapor pressures; however, due to the Kelvin effect (Tröstl et al., 2016), nucleation depends critically on molecules with extremely low saturation vapor pressure. Most of the C_{20} and C_{15}, many of the C_{16}, and some of the C_{15} products can form SOA mass, whereas nucleation under atmospheric conditions is driven largely by the C_{20} dimers. Even replacing C_{20} with C_{15} dimers suppresses nucleation, as shown in this study.

This is our findings are significant beyond the α-pinene/isoprene system, as they indicate the interaction of a variety of atmospheric VOCs with monoterpene-derived HOM formation and new-particle formation. Given that RO_2(ip)-RO_2(VOC) reaction rates are competitive (see SI Appendix for details), VOCs whose RO_2· radicals lead to products that are smaller than C_{20} when reacting with RO_2(ip) (i.e. reduce the ELVOC (Extremely Low Volatility Organic Compounds) fraction in the HOM distribution) are expected to reduce biogenic nucleation and early growth. On the other hand, VOCs that lead to C_{20} class or larger molecules are expected to accelerate both processes. RO_2· termination emerges as the critical step in ELVOC formation and subsequently biogenic new-particle formation. The suppression of biogenic new-particle formation by isoprene and potentially other lighter VOCs, NO_3 (Lehtipalo et al., 2018) and elevated HO_2 concentrations all proceed along the same lines of RO_2· termination and subsequent C_{20} reduction, highlighting the importance of C_{20} class molecules for biogenic new-particle formation.
In summary, we find that isoprene interferes with α-pinene HOM chemistry via RO₂· peroxy-radical termination. When isoprene is present, fewer C_{20} class molecules are formed, which directly reduces the nucleation rate. We show that C_{20} class molecules act as “nucleator” species. The reduction of nucleation rate becomes stronger with higher isoprene to monoterpenes carbon ratio (R), consistent with earlier observations (Kiendler-Scharr et al., 2009); however, in the monoterpen-e-isoprene chemical system, increased OH· does not enhance nucleation, but, on the contrary, reduces it due to C_{20} class reduction. Biogenic nucleation in the α-pinene isoprene system is not affected by typical concentrations of sulfuric acid found in the Amazon or in eastern parts of the United States. The change in monoterpenes HOM chemistry due to isoprene reduces organic growth rates in the 1.3 – 3.2 nm range by around 50 %, which strongly reduces the probability that the smallest, freshly-nucleated particles will survive scavenging as they grow to larger sizes. While other factors can also inhibit nucleation (e.g. NOx (Wildt et al., 2014) or a high condensation sink (Dada et al., 2017)), isoprene can make the difference between measurable new-particle formation events and their absence under a variety of atmospheric conditions.

Data Availability: Data are available by contacting the corresponding author.


Competing interests: The authors declare no competing interests.

Acknowledgments: We thank CERN for supporting CLOUD with technical and financial resources, and for providing a particle beam from the CERN Proton Synchrotron. We thank P. Carrie, L.-P. De Menezes, J. Dumollard, K. Ivanova, F. Josa, I. Krasin, R. Kristic, A. Laassiri, O. Marichy, H. Martinati, S. V. Mizin, R. Sitals, A. Wasem and M. Wilhelmsson for their contributions to the experiment. This research has received funding from the EC Seventh Framework Programme and European Union’s Horizon 2020 programme (Marie Skłodowska Curie ITNs no. 316662 “CLOUD-TRAIN” and no. 764991 “CLOUD-MOTION”, MSCA-IF no. 656994 “nano-CAVa”, MC-COFUND grant no. 600377, ERC projects no. 692891 “DAMOCLES”, no. 638703 “COALA”, no. 616075 "NANODYNAMITE", no. 335478 “QAPPA”, no. 742206 “ATM-GP”, no. 714621 “GASPARCH”), the German Federal Ministry of Education and Research (projects no. 01LK0902A, 01LK1222A 01LK1601A), the Swiss National Science Foundation (projects no. 20020_152907, 200202_172602, 20F120_159851, 200202_172602, 20F120_172622), the Academy of Finland (Center of Excellence no. 307331, projects 299574, 296628, 306853, 304013), the Finnish Funding Agency for Technology and Innovation, the Väisälä Foundation, the Nessling Foundation, the Austrian Science Fund (FWF; project no. J3951-N36, project no. P27295-N20), the Austrian research funding association (FFG, project no. 846050), the Portuguese Foundation for Science and Technology (project no. CERN/FP/116387/2010), the Swedish Research Council Formas (project number 2015-749), Vetenskapsrådet (grant 2011-5120), the Presidium of the Russian Academy of Sciences and Russian Foundation for Basic Research (grants 08-02-91006-CERN, 12-02-91522-CERN), the U.S. National Science Foundation (grants AGS1136479, AGS1447056, AGS1439551, CHE1012293,
AGS1649147, AGS1602086), the Wallace Research Foundation, the US Department of Energy (grant DE-SC0014469), the NERC GASSP project NE/J024252/1m, the Royal Society (Wolfson Merit Award), United Kingdom Natural Environment Research Council grant NE/K015966/1, Dreyfus Award EP-11-117, the French National Research Agency the Nord-Pas de Calais, European Funds for Regional Economic Development Labex-Cappa grant ANR-11-LABX-0005-01).
References


compounds in initial particle growth in the atmosphere, Nature, 533, 527, 10.1038/nature18271, 2016.
Figures

Figure 1. Mass defect plots of neutral HOM molecules measured with nitrate CI-API-TOF without isoprene (a) and with isoprene added (b) at +25 °C. α-Pinene levels were 771 and 1326 pptv, respectively. Ozone levels were 49 and 39 ppbv, respectively. Isoprene was 4.9 ppbv in (b). Relative humidity was 38 % in (a) and (b). The area of the marker points is linearly scaled with the intensity of the HOM signals. Color code shows the relative intensity change for each HOM peak due to isoprene addition, i.e. the percentage intensity change between (a) and (b). The color for each peak is thus the same in (a) and (b). HOM intensity in (a) was scaled up linearly by 38 % to match [α-pinene]-[O₃] levels present in (b) to calculate the intensity change.
Figure 2: Proposed mechanism for the interference of isoprene in α-pinene oxidation chemistry. The pathway of HOM formation of an α-pinene/ozone mixture alone is indicated by red arrows. When isoprene is present, the green arrows indicate the additional interference of isoprene in α-pinene oxidation chemistry via RO₂⁺ radicals. The oxidation of α-pinene at the conditions used in our experiments is dominated by ozonolysis. After the initial ozone attack a C₁₀H₁₅O₄ peroxy-radical forms via a vinylhydroperoxyde channel (VHP), which can undergo various intramolecular H-shifts and autoxidation steps. Thus the chain of RO₂⁺(αp) mostly consists of C₁₀H₁₅O₄,6,8,10. These radicals can terminate either via reaction with other RO₂⁺ radicals, via reaction with HO₂ or via unimolecular processes. The resulting closed shell products are then either covalently bound C₂₀ class dimers, which are mostly responsible for nucleation or C₁₀ class monomers. Possible fragmentation might also lead to a low amount of C₅ and C₁₅ class molecules being formed even without isoprene present. Isoprene oxidation is dominated by reactions with OH⁻ in the CLOUD chamber, which produce a series of C₅ RO₂⁺ radicals (C₅H₉O₃,6,7,8,9). These RO₂⁺(ip) radicals can now interfere in the termination of RO₂⁺(ap). The reaction of RO₂⁺(ip) with RO₂⁺(ap) can lead to C₁₅ class dimers, C₁₀ class monomers or C₅ class monomers. The reaction of RO₂⁺(ip) with another RO₂⁺(ip) can lead to C₁₀ class dimers or C₅ class monomers. The presence of RO₂⁺(ip) reduces the steady state concentration of RO₂⁺(ap), as it acts as an additional sink for RO₂⁺(ap). This directly reduces the formation of C₂₀ class dimers, as two RO₂⁺(ap) radicals are needed to form one C₂₀ class dimer. We link this reduction of C₂₀ class dimers to the reduction of biogenic nucleation and early growth rates in the presence of isoprene.
Figure 3. Pure biogenic nucleation rates at 1.7 nm diameter (a) and growth rates (b, c) against total HOM concentration with and without isoprene added at +5 and +25 °C. HOM total is defined as the sum of C₅, C₁₀, C₁₅ and C₂₀ carbon classes. Relative humidity is 38 % for all data points. (a) Triangles represent $J_{gcr}$ and circles $J_n$. Small grey points were taken from Kirkby et al. (2016). Magenta edges indicate UV-illuminated conditions at +5 °C, at +25 °C all data points are with UV light on. Color shows isoprene to monoterpene carbon ratio (R). Black solid and dash-dotted lines are parametrizations of $J_{gcr}$ and $J_n$ from Kirkby et al (2016). Red solid and dash-dotted lines are power law fits to $J_{gcr}$ and $J_n$ in the presence of isoprene at +5 °C. Thick solid black and red line represent power law fits to +25 °C data for $\alpha$-pinene only and $\alpha$-pinene + isoprene systems. Bars indicate 1σ run-to-run uncertainty. The overall systematic scale uncertainty of HOMs of +78%/−68 % and of $J$ for ±47 % is not shown. In (b) and (c), triangles represent $\alpha$-pinene only, circles $\alpha$-pinene + isoprene conditions. Marker color indicates the size range in which growth rate was measured: dark blue 1.3 – 1.9 nm (measured by scanning PSM), light blue 1.8 – 3.2 nm, orange 3.2 – 8.0 nm (both measured by DMA-train) and red 5.0 – 15 nm (measured by nanoSMPS). Bars indicate 1σ uncertainties in growth rate estimation. Dashed lines are linear fits to $\alpha$-pinene only data points; solid lines are linear fits to $\alpha$-pinene + isoprene conditions, respectively.
Figure 4: Formation rate (gcr) vs diameter of particles at +25 °C and 38 % RH. Triangles represent α-pinene only, circles α-pinene + isoprene conditions. α-Pinene levels were 456, 771 and 1442 pptv for triangles and 677, 1326 and 2636 pptv for circles. Ozone levels were 49 ppbv for triangles and 38 to 40 ppbv for circles. Isoprene levels ranged from 2.7 to 9.8 ppbv for circles. Color code represents HOM concentration. Bars indicate overall scale uncertainty for formation rates of ±47 %. The uncertainty in the diameters is ±0.3 nm. Dashed and solid lines are lines to guide the eye. The steeper slope at lower diameter values is caused by the Kelvin effect, i.e. a smaller growth rate at small sizes that leads to higher losses of newly formed particles. The formation rate measurements at 2.2 and 2.5 nm for the lowest α-pinene/isoprene setting (cyan circles) are upper limits.
Supplementary Information for
Molecular understanding of the suppression of new-particle formation by isoprene

**CLOUD Facility**

We conducted our measurements at the CLOUD (Cosmics Leaving OUtdoor Droplets) chamber at CERN (European Center for Nuclear Research), Geneva, Switzerland. The CLOUD chamber is a 26.1 m$^3$ electro-polished stainless-steel tank used to recreate atmospheric condition in the laboratory (for more details on the chamber see Kirkby et al. (2011); Kirkby et al. (2016); Duplissy et al. (2016)). Data for this study are from the CLOUD 11 and 12 campaigns in autumn 2016 and 2017. Various measures are taken to reduce unwanted contaminants in the CLOUD chamber. The air in the chamber is mixed from cryogenic nitrogen and oxygen, all lines are made of stainless steel and intense cleaning cycles are performed prior to each campaign. Each cleaning cycle consists of at least 24 h of rinsing the chamber from the inside with ultrapure water, followed by a period of at least 24 h with the chamber at 100°C and high ozone levels (several parts per million by volume). These measures result in very low organic contamination below 150 pptv (Kirkby et al., 2016) in total.

Ultrapure water is used to humidify the air in the chamber. Ozone is produced by a UV ozone generator. Liquid α-pinene (Sigma Aldrich, purity >98 %) is stored in a temperature controlled water bath and evaporated into a dry nitrogen flow and fed into the chamber. Isoprene from a gas bottle (Carbagas AG, purity >99%) is additionally cleaned by a cryotrap. The cryotrap consists of a ~2 m long ¼” stainless steel tube spiral placed in a cryogenic liquid held at 233 K. By using this trap, non-negligible monoterpane-like contaminants in the isoprene gas bottle are effectively frozen out (Bernhammer et al., 2018). Isoprene and α-pinene are diluted by separate two stage dilution systems prior to being fed into the chamber. All gases are fed into the chamber from the bottom and are mixed by two magnetically driven fans.

A unique feature of the CLOUD chamber is its control of ion concentrations. A high voltage electric field cage (±30 kV) can sweep ions that are constantly produced by naturally occurring galactic cosmic rays out of the chamber in around 1 s. This enables us to study pure neutral nucleation. By switching the field cage off, the naturally formed ions are allowed to stay in the chamber and affect nucleation processes. To artificially enhance ion concentrations, CERN’s Proton Synchrotron provides a 3.5 GeV π$^+$ beam that is diverged to >1 m$^2$ beam profile and crosses the center region of the chamber.

The CLOUD chamber is equipped with four HgXe UV lamps (LightningCure LC8, Hamamatsu Photonics K.K.) positioned at the top of the chamber and connected via fiber bundles. An additional UV source is provided by a KrF excimer laser (ATLEX-1000, ATL Lasertechnik GmbH) at 248 nm wavelength and also connected to the chamber via fiber bundles to enhance OH· production via photolysis of O$_3$ further.

**Typical Run sequence and conditions**

Our experiments were performed at +5 and +25 °C and mostly 38 % relative humidity. A typical run sequence can be seen in Fig. S1 and S2. First, α-pinene is present with ozone under both neutral and gcr conditions at three different atmospherically relevant concentrations. HOMs are forming as seen by the CI-APi-TOF and new-particle formation is induced. The purpose of this experiment was also to ensure inter-campaign comparability to Kirkby et al. (2016). In the following run a stable isoprene concentration is established in the chamber and ozone is added shortly afterwards. As ozone and isoprene only react very slowly, effects on HOMs are minor. As UV light in the chamber is switched on, OH· production increases and thus formation of OH· induced isoprene HOMs. However, only the subsequent addition of α-pinene leads to formation of C$_{20}$ class HOMs and thus new-particle formation. UV effects were studied by switching on the Hamamatsu lamp, as well as the KrF-excimer laser.
Gas-phase measurements

Ozone was measured by a calibrated ozone monitor (Thermo Environmental Instruments TEI 49C). Isoprene and α-pinene were measured by the newly developed proton transfer reaction time-of-flight mass spectrometer (PTR3 (Breitenlechner et al., 2017)). The instrument was frequently calibrated for both gases and has a limit of detection of 2 pptv for isoprene and α-pinene for 1 s integration time. The accuracy of the instrument for both gases is mainly determined by the uncertainty of the calibration gas standard (5 %) and accuracies of mass flow controllers and is estimated to be 7 %.

The chemical ionization atmospheric pressure interface time-of-flight (CI-APi-TOF) mass spectrometer (Tofwerk AG) measured highly-oxygenated organic compounds with a limit of detection of -5×10^4 cm^3. The instrument operates with a nitrate based ion source similar to the design in Eisele and Tanner (1993). However, a corona discharge was used instead of a radioactive source (Kürten et al., 2011). The instrument was calibrated for sulfuric acid (Kürten et al., 2012) and the data corrected for mass dependent transmission efficiency (Heinritzi et al., 2016). HOM quantification was performed as described in Kirkby et al. (2016).

The run-to-run uncertainty for HOMs is estimated to be 20 %. Due to technical reasons at the start of CLOUD 11 the CI-APi-TOF could only start measuring at 03 Oct 2016, 10:28 UTC (see Fig. S1). As HOMs depend linearly on the product [α-pinene] [O3] (Kirkby et al., 2016; Ehn et al., 2014), HOM concentrations measured during the mid α-pinene settings were used and scaled down according to this relation to obtain HOM concentrations for the low α-pinene settings for the appropriate times where J and growth rates were estimated. This also gave a higher uncertainty for this data point (28 %) as indicated in Fig. 3A. The overall uncertainty in HOM quantification consists of contributions from sulfuric acid calibration (+50%/-33 %), charging efficiency of HOMs in the ion source (25 %), transmission correction (50 %) and sampling line loss correction (20 %). This results in an overall scale uncertainty for HOMs of +78 %-68 %. There are however additional uncertainties in our HOM estimation that cannot be readily quantified. On the one hand nitrate ionization of HOMs shows a drop in charging efficiency for HOMs with six or less oxygen atoms (Hyttinen et al., 2017). This leads to an underestimation of these molecules. However, these molecules with comparably low oxygen content are not expected to contribute significantly to nucleation and early growth. Additionally, it was shown that nitrate ionization has a reduced charging efficiency towards HOMs formed by OH· oxidation compared to HOMs formed by ozonolysis (Berndt et al., 2015; Berndt et al., 2016). This could affect also C20 class molecules that show OH· dependence, like C20H2O2 (see Figure S1). The real increase of these C20 class HOMs due to UV light could be larger than the measured one, thus dampening the overall decrease of C20 when UV is switched on. The fact that J decreases when UV is switched on, however, confirms that the total nucleating molecules in the chamber decrease. That effect is thus not strong enough to lead to a real increase instead of a decrease in C20 class molecules.

We group all HOMs within the m/z range from 235 to 625 Th in four groups according to their carbon number. This m/z range was chosen to remain consistent with the definition of total HOM in Kirkby et al. (2016). We sum up HOMs with 2-5, 6-10, 11-15 and 16-20 carbon atoms to get C5, C10, C15 and C20 class HOMs, respectively. The sum of these four classes represents HOM total as shown e.g. in Fig. 3.

OH· estimation and comparison to ambient environments

We estimate OH· levels in our chamber via a steady state approach (see Fig. S1). OH· sources taken into account are ozonolysis of α-pinene and isoprene, with yields of 79 % (Tillmann et al., 2010) and 26 % (Malkin et al., 2010; Kroll Jesse et al., 2001), respectively, as well as photolysis of ozone with our UV laser. The OH· source strength of the UV laser was characterized with a separate experiment (SO2 to sulfuric acid conversion) and depends on laser settings, ozone concentration and absolute water vapor concentration. Sink terms taken into account are reactions of OH· with α-pinene and isoprene. Secondary reactions of OH· with further oxidation products of α-pinene or isoprene are not taken into account, as their effect is expected to be minor (e.g. two orders of magnitude smaller than the former sink terms in case of
the pinonaldehyde-OH- reaction). OH- recycling in our chamber is expected to be weak, as we do not have NOx in the chamber and many runs are performed under dark conditions. The recycling mechanism due to photolysis of hydroperoxy-aldehydes (HPALDs) (Taraborrelli et al., 2012) can in principal take place during UV runs, however, HPALDs may also decompose on our stainless steel chamber walls without releasing OH- in a process similar to the one described in Bernhammer et al. (2017), thus further reducing recycling efficiency. However, the O3 recycling mechanisms (reaction of O3 and HO2 yielding OH-, as well as photolysis of H2O2 under UV conditions) might take place in our conditions (Lelieveld et al., 2016). All gas phase reaction rate constants are preferred values provided by IUPAC (International Union of Pure and Applied Chemistry) and were evaluated at +5 °C \( k_{\text{ipO3}} = 8.1 \cdot 10^{-17} \text{ cm}^3 \text{s}^{-1} \), \( k_{\text{ipOH}} = 5.8 \cdot 10^{-11} \text{ cm}^3 \text{s}^{-1} \), \( k_{\text{ipOH}} = 7.9 \cdot 10^{-18} \text{ cm}^3 \text{s}^{-1} \) and \( k_{\text{ipOH}} = 1.1 \cdot 10^{-10} \text{ cm}^3 \text{s}^{-1} \) and +25 °C \( k_{\text{ipO3}} = 9.4 \cdot 10^{-17} \text{ cm}^3 \text{s}^{-1} \), \( k_{\text{ipOH}} = 5.2 \cdot 10^{-11} \text{ cm}^3 \text{s}^{-1} \), \( k_{\text{ipOH}} = 1.3 \cdot 10^{-17} \text{ cm}^3 \text{s}^{-1} \) and \( k_{\text{ipOH}} = 1.0 \cdot 10^{-10} \text{ cm}^3 \text{s}^{-1} \).

We calculate OH- levels of around 1 \( \cdot 10^6 \) cm\(^{-3} \) during dark α-pinene ozonolysis, with roughly a doubling to 2 \( \cdot 10^6 \) cm\(^{-3} \) when the UV laser is switched on. When isoprene is present together with α-pinene it foremost acts as a sink for OH- and thus reduces its concentrations. The strength of this depletion depends on the main OH- source strength, i.e., the α-pinene ozonolysis rate. We find OH- levels 5 to 20 times lower when isoprene is present than under α-pinene only conditions. This depletion can also be recognized in the traces of HOMs that originate from OH- oxidation, like C\(_{10}\)H\(_{18}\)O\(_6\) (see Fig. S1).

In the atmosphere, OH- levels of 10\(^6\) cm\(^{-3} \) and higher are reported even in the presence of isoprene, as several OH- recycling mechanisms take place (Lee et al., 2016; Martinez et al., 2010; Lelieveld et al., 2016). However, given the reduction in C\(_{20}\) class molecules when OH- is increased from 2 \( \cdot 10^5 \) cm\(^{-3} \) to 4 \( \cdot 10^5 \) cm\(^{-3} \) by switching on UV light, it is a reasonable assumption that, if OH- would be fully replenished to 1 \( \cdot 10^6 \) cm\(^{-3} \), we would see a further decrease of total C\(_{20}\) class molecules and subsequently a reduction in \( J \) and early growth rates. This assumption is also valid when the reduced charging efficiency of nitrate molecules when OH- is increased from 2 \( \cdot 10^8 \) cm\(^{-3} \) to \( \alpha(\text{class} + \text{higher}) \) molecules when OH- is set to \( \alpha(\text{class} + \text{higher}) \) at 1 \( \cdot 10^9 \) cm\(^{-3} \), \( \alpha(\text{class} + \text{higher}) \) at 1 \( \cdot 10^10 \) cm\(^{-3} \), \( \alpha(\text{class} + \text{higher}) \) at 1 \( \cdot 10^11 \) cm\(^{-3} \). We calculate OH- levels of around 1 \( \cdot 10^6 \) cm\(^{-3} \) during dark α-pinene ozonolysis, with roughly a doubling to 2 \( \cdot 10^6 \) cm\(^{-3} \) when the UV laser is switched on. When isoprene is present together with α-pinene it foremost acts as a sink for OH- and thus reduces its concentrations. The strength of this depletion depends on the main OH- source strength, i.e., the α-pinene ozonolysis rate. We find OH- levels 5 to 20 times lower when isoprene is present than under α-pinene only conditions. This depletion can also be recognized in the traces of HOMs that originate from OH- oxidation, like C\(_{10}\)H\(_{18}\)O\(_6\) (see Fig. S1).

### Particle Measurements

The total particle number concentration above 2.5 nm is measured by a TSI 3776 condensation particle counter (CPC) using butanol as working fluid. For smaller particles, an Airmodus A10 particle size magnifier (PSM), using diethylene glycol as working fluid, is used (Vanhanen et al., 2011) in combination with an Airmodus A20 CPC. This setup achieves detection of airborne particles down to 1 nm. By varying the supersaturation inside the PSM, particle size distributions between 1 – 3 nm can be inferred (Lehtipalo et al., 2014).

A DMA-train (Stolzenburg et al., 2017) is used to measure the particle size distribution and growth rates between 1.8 – 8.0 nm. It uses a parallel design of six sampling channels each equipped with a differential mobility analyser (DMA) together with an ultrafine condensation particle counter (uCPC). For detection of sub-2.5 nm particles, two of the channels are equipped with either an Airmodus A10 particle size magnifier (PSM) or a TSI 3777 nanoEnhancer as booster stage upstream of the CPC. The channels are operated at fixed sizes to increase time-resolution and counting-statistics leading to higher sensitivities for smaller sizes compared to standard scanning mobility devices.

The size distribution above 5 nm is measured with a TSI Scanning Mobility Particle Sizer (nanoSMPS, Model 3938) using a TSI 3082 nanoDMA and a water-based TSI 3788 CPC for detection of the size-selected particles. For particles larger than 65 nm a custom-built SMPS with a long column DMA was used.
Determination of nucleation rates

The nucleation rate $J$ defines the number of particles formed within a volume per unit of time. It is calculated using the flux of the total concentration of particles growing past a specific diameter (here at 1.7, 2.2, 2.5 and 6 nm). In the following, the method for calculating $J_{1.7}$ is presented, however the calculation for $J_{2.2}, J_{2.5}$ and $J_{6}$ follows the same procedure unless specified otherwise. The nucleation rate is the sum of the time derivative of the concentration of particles above a certain diameter, as well as correction terms accounting for aerosol losses due to dilution in the chamber, wall losses and coagulation.

$$J_{1.7} = \frac{dN_{\geq 1.7 \text{ nm}}}{dt} + S_{\text{dil}} + S_{\text{wall}} + S_{\text{coag}}$$

$N$ is the concentration of particles of diameter equal or larger than 1.7 nm. The term $S_{\text{dil}}$ describes the size-independent losses of particles due to dilution of the gases in the chamber. The chamber is continuously flushed with a total flow of 230 liters per minute to replenish the sampling flow of the instruments. This results in the dilution factor $k_{\text{dil}} = 1.47 \cdot 10^{-4} \text{ s}^{-1}$ and

$$S_{\text{dil}} = N_{\geq 1.7 \text{ nm}} \cdot k_{\text{dil}}.$$  

The term $S_{\text{wall}}$ describes the size-dependent particle losses to the chamber walls and was calculated based on the decay rate of sulfuric acid monomer (of mobility diameter = 0.85 nm (Kulmala et al., 2013)) in the chamber (at temperature = 278 K). The wall loss rate $k_{\text{wall}}$ is a function of particle diameter and temperature.

$$S_{\text{wall}}(T) = \sum_{d_{p,i}=1.7 \text{ nm}}^{d_{p,max}} N(d_{p,i}) \cdot k_{\text{wall}}(d_{p,i}, T)$$

At 278 K

$$k_{\text{wall}}(d_{p,i}) = 1.7 \cdot 10^{-3} \text{ nm s}^{-1} \cdot \frac{1}{d_{p,i}}$$

The term $S_{\text{coag}}$ represents the coagulation losses to the surface of pre-existing aerosol particles in the chamber and was calculated using the full number size distribution present in the chamber (Seinfeld and Pandis, 2016).

$$S_{\text{coag}}(d_p = 1.7 \text{ nm}) = \sum_{d_{p,i}=d_p}^{d_{p,max}} \sum_{d_{p,j}=d_p}^{d_{p,max}} \delta_{i,j} \cdot K(d_{p,i}, d_{p,j}) \cdot N_i \cdot N_j$$

where $K(d_{p,i}, d_{p,j})$ is the coagulation coefficient for particles of the size $d_{p,i}$ and $d_{p,j}$. $N_i$ and $N_j$ are the number concentrations of particles in the size bins $d_{p,i}$ and $d_{p,j}$, and $\delta_{i,j} = 0.5$, if $i = j$ and $\delta_{i,j} = 1$, if $i \neq j$. $d_{p,i}$ is the midpoint diameter for the size bin with index $i$.

The number size distribution of particles used for the calculation of formation rates were obtained from the scanning SMPS at cut-off diameters 1.7 nm and 2.2 nm for the determination of $J_{1.7}$ and $J_{2.2}$, and from a butanol CPC (model CPC3776, TSI Inc.) of fixed cut-off (2.5 nm) for determining the formation rate of 2.5 nm particles. For determining $J_{6}$, the integrated size bins from the nanoSMPS were used. A correction factor of +0.3 nm on the cut-off diameter of the PSM was included to account for the poorer detection efficiency of neutral organic particles compared to calibration with tungsten oxide (Kangasluoma et al., 2014). The concentrations obtained were corrected for sampling line losses. During each run, the value of $J$ was determined after reaching a steady state value. A median value of the formation rate was then obtained. The errors on the reported $J$ rates were obtained by considering an inter-campaign reproducibility error of 30 % as well as a series of run-dependent systematic and statistical uncertainties which include errors on sampling (10 %), dilution (10 %), wall loss (20 %) and coagulation sink (20 %). The resulting overall scale uncertainty for $J$ is 47 %. 


Determination of growth rates

Particle growth rates were derived from several instruments individually with the widely used appearance time method (Lehtipalo et al., 2014). For this method the signal rise in a single size channel is fitted with a sigmoidal function during the particle formation event. The fit determines the appearance time $t_{app}$ at which the signal intensity reaches 50% between a potential background and the final value reached at steady-state nucleation conditions. A linear fit of $t_{app}$ and the corresponding diameters of several size channels yields an average apparent growth rate of the size distribution for a diameter interval. To infer a size-dependence of the measured growth rates, several instruments and size-intervals were used. Growth rates between 1.3 – 1.9 nm were measured with the scanning PSM, the DMA-train size channels were split up into two intervals, one between 1.8 – 3.2 nm and one between 3.2 – 8.0 nm. For size-intervals above 8 nm the size channels of the nanoSMPS was used. Uncertainties in the sigmoidal fit result are promoted to the linear fit of the growth rate providing an estimate of the statistical uncertainties. However, at least a systematic uncertainty of approximately 50% has to be assumed if apparent growth rates are interpreted as condensational growth values.

Effect of lighter VOCs on RO$_2^*$ chemistry and HOM formation

Organic peroxy radical (RO$_2^*$) branching is critical to atmospheric chemistry. There are many thousands of different RO$_2^*$ radicals, but their chemistry can be simplified to the following basic reaction set:

1. $RO_2^* + HO_2 \rightarrow products$ \hspace{1cm} ($k_1 \sim 1 \cdot 10^{-11} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}$, independent of temperature (Atkinson, 1997)) (R1)
2. $RO_2^* + NO \rightarrow products$ \hspace{1cm} ($k_2 \sim 1 \cdot 10^{-11} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}$, independent of temperature (Wallington et al., 1992; Atkinson, 1997)) (R2)
3. $RO_2^* + RO_2^* \rightarrow products$ \hspace{1cm} ($k_3$ highly variable (Madronich and Calvert, 1990; Atkinson, 1997)) (R3)

This neglects important exceptions such as peroxy acyl radicals reacting with NO$_2$ to form PANs, but is sufficient to describe the essential features here and in the atmosphere (Finlayson-Pitts and Pitts Jr, 1999). The maximum rate constant (the collision constant) is roughly $3 \cdot 10^{-10} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}$, so R1 and R2 occur at slightly under one in ten collisions with only a very modest temperature dependence. Experimental kinetics show that the rate constants for these first two reactions depend only weakly on the organic substituent R (Finlayson-Pitts and Pitts Jr, 1999), and so here we consider two similar, temperature independent rate constants for all RO$_2^*$.

The ubiquity and similarity of the first two rate constants means that “high NOx” chemistry is well defined. The ratio of NO to HO$_2$ is crucial. Data show that typical daytime HO$_2$ is around 2 – 30 pptv (Elslobany et al., 2012; Stevens et al., 1997; Lelieveld et al., 2016; Finlayson-Pitts and Pitts Jr, 1999) (with photolysis of aldehydes, especially formaldehyde and oxidation of CO by OH being drivers of HO$_2$ concentrations (Finlayson-Pitts and Pitts Jr, 1999; Lelieveld et al., 2016)) and so if [NO] is larger than these values the reaction with NO will outcompete the reaction with HO$_2$ and the system becomes “high NOx”. However, even under “low NOx” conditions, high HO$_2$ levels can also reduce nucleation and early growth, as R1 only forms C$_{10}$ monomers and no C$_{20}$ dimers for monoterpane oxidation.

The total [RO$_2$] in the atmosphere rarely exceeds [HO$_2$] and is often significantly lower. Further, unlike the first two reactions, the RO$_2$ + RO$_2$ reactions depend strongly on the organic substituent, varying by over six orders of magnitude at room temperature (Madronich and Calvert, 1990). In general, electron donating substituents (i.e. t-butyl) make the reaction very slow, while electron withdrawing substituents (i.e. acetyl) can make the self-reaction fairly fast ($\text{CH}_3\text{C(}\text{O})\text{O}_2 + \text{CH}_3\text{C(}\text{O})\text{O}_2 \sim 1 \cdot 10^{-11} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}$) (Madronich and Calvert, 1990). Madronich and Calvert (1990) proposed a simplifying scheme to estimate cross reaction rate constants from self-reaction rate constants using the geometric mean ($k_{a,b,cross} = 2 \cdot \sqrt{k_{a,\text{self}} \cdot k_{b,\text{self}}}$). Recently, it was shown (Berndt et al., 2018) that highly oxidized RO$_2^*$ produced from terpenes such as α-pinene can have $k_3 \sim 1 \cdot 10^{-10} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}$.
These rapid RO₂⁺ + RO₂⁻ reactions are extremely important for atmospheric chemistry and the analysis we present here. Only when \( k_3 > \sim 1 \cdot 10^{-11} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1} \), can RO₂⁻ cross reactions have a significant effect in the atmosphere, but when this is true there are two consequences. First, the oxidation mechanisms of different hydrocarbons producing highly reactive RO₂⁻ become coupled, because they influence each other through their RO₂⁻. Second, the transition to “high NOₓ” is pushed to higher NO because of the faster self-reactions.

It is the first consequence that is most significant here. The RO₂⁻ from \( \alpha \)-pinene and isoprene both appear to be highly reactive and so will out compete HO₂ at low NO. Consequently, isoprene and monoterpenes become coupled by their RO₂⁻ interactions. RO₂⁻ radicals derived from smaller VOCs like CH₄ can have significantly lower self-reaction rates (e.g. for CH₃OO⁻ \( k_{\text{self}} = 3.5 \cdot 10^{-13} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1} \)) (Madronich and Calvert, 1990). The resulting cross reaction would then be \( 1.2 \cdot 10^{-11} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1} \) and thus one order of magnitude smaller than the RO₂(\( \alpha \pounds \)) self-reaction rate. This would allow for at least some degree of coupling, depending on detailed atmospheric conditions.

However, if RO₂⁻ coupling of light VOCs or HO₂ would dominate atmospheric chemistry of RO₂(\( \alpha \pounds \)), it would not be possible to detect C20 signals there, as almost all RO₂(\( \alpha \pounds \)) radicals would be terminated to either C10 monomers or light dimers with e.g. 11 or 12 carbon atoms. There is however clear evidence of atmospheric C20 formation, i.e. RO₂(\( \alpha \pounds \))-RO₂(\( \alpha \pounds \)) reactions leading to dimers in the presence of relatively high levels of CO, CH₄, HO₂ and in some locations also NOₓ (Yan et al., 2016; Kürten et al., 2016; Massoli et al., 2018). The HOM spectrum reported for an isoprene-rich measurement site in Alabama during the SOAS campaign showed a qualitatively similar distribution of C5, C10, C15 and C20 classes as reported in our study (except for NOₓ effects) (Massoli et al., 2018). This is direct evidence for the atmospheric relevance of our findings.
Figure S1: Time series of a nucleation experiment with example HOM traces. (a) shows traces of α-pinene, isoprene and ozone. (b) and (c) show selected time traces of HOM monomers and dimers measured by the CI-API-TOF, respectively. The temperature in the chamber was +5 °C and rel. humidity was 38 %. N, GCR and CLEAN indicate neutral (high voltage cleaning field on), galactic cosmic ray (high voltage cleaning field off) and cleaning (neutral periods to clean the chamber of particles) conditions, respectively. In the first part until 04 Oct, 06:00 UTC, α-pinene was present in the chamber at three different concentrations to study pure biogenic nucleation under both neutral and gcr conditions with an additional UV stage at the end. Afterwards an isoprene/ozone mixture was studied under both dark and UV-illuminated conditions. Note that during the UV stage on 04 Oct the laser intensity deteriorated towards the end of the stage and thus corresponding HOM signals went down as well. At 04 Oct, starting at 18:40 UTC, α-pinene was added at three concentration levels similar to the first part of the experiment.
Figure S2: Time series of a nucleation experiment with particle counter data and nucleation rates. The temperature in the chamber was +5 °C and rel. humidity was 38 %. The time window shown is the same as in Figure S1. (a) shows traces of α-pinene, isoprene and ozone. N, GCR and CLEAN indicate neutral (high voltage cleaning field on), galactic cosmic ray (high voltage cleaning field off) and cleaning (neutral periods to clean the chamber of particles) conditions, respectively. (b) shows particle concentration above 1.7, 2.2 and 2.5 nm, measured with a scanning PSM (1.7 nm and 2.2 nm) and a butanol-based CPC (2.5 nm). (c) shows the nucleation rate $J$ determined at 1.7, 2.2 and 2.5 nm using the particle concentrations shown in (b). (d) shows a combined size distribution of aerosol particles in the CLOUD chamber. The DMA-train contributed the size range from 1.8 – 8 nm, the nanoSMPS from 8 – 65 nm and the long-SMPS for sizes >65 nm.
Figure S3: Effects of isoprene addition on RO$_2$· radical and HOM classes distribution. Chamber conditions were +25 °C and 38 % RH. α-Pinene levels were 456, 771 and 1442 pptv for α-pinene only and 677, 1326 and 2636 pptv for α-pinene + isoprene conditions. Ozone levels were 49 ppbv for α-pinene only and 38 to 40 ppbv for α-pinene + isoprene conditions. Isoprene levels were 2.7, 4.9 and 9.8 ppbv. All data from the α-pinene only runs was scaled up linearly (21, 38 and 45 % for low, mid and high α-pinene levels, respectively) to match the exact same [α-pinene]·[O$_3$] values as in the α-pinene + isoprene runs. (a) shows the distribution of the most prominent RO$_2$· radicals originating from isoprene and α-pinene oxidation. (b) shows the absolute and (c) the relative changes of the HOM class distribution due to isoprene addition.
Figure S4: Changes of RO$_2^*$ radical and HOM classes distribution due to UV light in an α-pinene, isoprene and ozone mixture. Chamber conditions were +5 °C and 38 % RH. α-pinene levels were 1116 (dark) and 1096 pptv (UV illuminated). The ozone level was 48 ppbv, the isoprene level was 3.6 and 3.4 ppbv in dark and UV illuminated conditions, respectively. Data from the dark run was slightly scaled down linearly (1.2 %) to match exact same [α-pinene]·[O$_3$] values as in the UV run. (a) shows the distribution of the most prominent RO$_2^*$ radicals originating from isoprene (green) and α-pinene (red) oxidation. (b) shows the absolute and (c) the relative changes of the HOM class distribution due to UV light.
Figure S5: Mass defect plots showing HOM production from isoprene alone (a, b) and the effect of UV light on an α-pinene/isoprene mixture (c, d). Chamber conditions were +5 °C and 38 % RH. HOM production from a mixture of isoprene (4.5 ppbv) and ozone (40 – 50 ppbv) under (a) dark conditions and (b) UV-illuminated conditions with higher OH· levels. The area of the marker points is linearly scaled to intensity of the HOM signals in all four panels. Color code represents oxygen-to-carbon ratio (O:C) of HOMs. UV light strongly enhances OH· and thus HOM production. This even leads to the formation of some C₁₀ dimers resulting from the combination of two RO₂(ip). (c) and (d) show the mass defect plot of HOMs from a mixture of α-pinene, isoprene and ozone under (c) dark and (d) UV-illuminated conditions. α-pinene is 1116 and 1096 pptv, isoprene was 3.6 and 3.4 ppbv in (c), and (d), respectively. Ozone was 47 ppbv for both runs. Color code indicates the change in intensity for each HOM peak when switching from dark to UV light conditions, i.e. the percentage intensity change between (c) and (d). The color for each peak is thus the same in (c) and (d). Data from the dark run was slightly scaled down linearly (1.2 %) to match the same [α-pinene]-[O₃] values as in the UV run for calculating the intensity change.
Figure S6: Mass Defect plots showing the effect of increased isoprene and monoterpene concentrations on HOM formation and nucleation rate $J_{HOM}$. Chamber conditions were +25 °C and 38 % RH. (a) describes the base case without isoprene, (b) shows the effect of addition of isoprene. Color code in (b) and (c) shows the relative change in HOM intensity compared to (a). (c) shows HOM spectra after α-pinene and isoprene concentrations have been roughly doubled compared to (b).
Figure S7: Nucleation rate $J_{1.7}$ vs relative humidity at +25 °C (a) and corresponding HOM spectra (b-d). All data shown was recorded with similar precursor concentrations (1.4 ppbv α-pinene, 5.1-6.2 ppbv isoprene, however, ozone decreased slightly from 46 to 40 ppbv as humidity was increased). HOM levels were fairly constant ranging from $1.3 \cdot 10^8$ to $1.6 \cdot 10^8$ cm$^{-3}$. Bars indicate 1σ run-to-run uncertainty. The overall systematic scale uncertainty of $J$ for ±47 % is not shown. The mass defect plots (b, c and d) show the HOM distribution measured by the nitrate CI-API-TOF under different humidity levels. The color code represents the relative change in HOM signal compared to the standard 38 % RH setting shown in (c). To calculate this change, HOM levels in (b) and (d) were scaled down by 11 % and scaled up by 10 %, respectively to match the same [αp]·[O$_3$] levels as in (c). We attribute the strong increase of certain HOMs with low O:C ratios in (d) (red marker symbols) to a more efficient charging process with nitrate ions in our ion source due to assistance of water molecules rather than to an increased production inside the CLOUD chamber.
Figure S8: Nucleation rate $J_{1.7}$ (gcr) vs sulfuric acid at +25 °C. α-pinene and isoprene levels were kept constant for all data points (around 1300 pptv and 4.5 ppbv, respectively), ozone levels ranged from 35 to 39 ppbv. HOM levels were fairly constant for all data points, ranging from $1.2 \times 10^8$ to $1.5 \times 10^8$ cm$^{-3}$. All data was taken with excess ammonia (0.4 -2.5 ppbv), relative humidity was 38 % for all runs. Bars indicate 1σ run-to-run uncertainty. The overall systematic scale uncertainty of $J$ for ±47 % is not shown.
Figure S9: Correlation of individual HOMs with nucleation rate \( J \). The data points displayed are taken from a run with 2.6 ppbv \( \alpha \)-pinene, 9.8 ppbv isoprene and 38 ppbv ozone under UV illuminated conditions. The area of the marker points is linearly scaled to the intensity of the HOM signals. The color code indicates coefficient of determination \( (R^2) \) of a power law fit of \( J \) vs every individual HOM peak. The dataset used for the fit contains the six \( J_{\text{gcr}} \) data points taken under low/medium/high \( \alpha \)-pinene levels with and without isoprene at +25 °C. High \( R^2 \) does not necessarily mean that the corresponding molecules contribute directly to nucleation, but that they are predominantly formed in a chemical setting that favors the production of nucleator molecules.
Figure S10: Growth rate vs (a) C_{20} class concentration and (b) C_{15} + C_{20} class concentration at +5 °C and 38 % RH. Growth rates were measured by scanning PSM (1.3 – 1.9 nm, dark blue), DMA-train (1.8 – 3.2 nm, light blue and 3.2 – 8.0 nm, orange) and nanoSMPS (5.0 – 15 nm, red). Triangles represent α-pinene only runs, circles represent α-pinene + isoprene runs. The growth rate between 1.8 nm and 3.2 nm can be parametrized by a linear fit when plotted against C_{20} class molecules, for the size range from 3.2 nm – 8.0 nm there is a linear relationship for growth rate when plotted against C_{15} + C_{20} class molecules.
References


