



Identification of highly oxygenated organic molecules and their role in aerosol formation in the reaction of limonene with nitrate radical

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Abstract. Nighttime NO₃-initiated oxidation of biogenic volatile organic compounds (BVOCs) such as monoterpenes is important for the atmospheric formation and growth of secondary organic aerosol (SOA), which has significant impact on climate, air quality, and human health. In such SOA formation and growth, highly oxygenated organic molecules (HOM) may be crucial, but their formation pathways and role in aerosol formation have yet to be clarified. Among monoterpenes, limonene is of particular interest for its high emission globally and high SOA yield. In this work, HOM formation in the reaction of limonene with nitrate radical (NO₃) was investigated in the SAPHIR chamber (Simulation of Atmospheric PHotochemistry In a large Reaction chamber). About 280 HOM products were identified, grouped into 19 monomer families, 11 dimer families, and 3 trimer families. Both closed-shell products and open-shell peroxy radicals (RO₂^{*}) were observed, and many of them have not been reported previously. Monomers and dimers accounted for 47 % and 47 % of HOM concentrations, respectively, with trimers making up the remaining 6 %. In the most abundant monomer families, C₁₀H_{15–17}NO_{6–14}, carbonyl products outnumbered hydroxyl products, indicating the importance of RO₂^{*} termination by unimolecular dissociation. Both RO₂^{*} autoxidation and alkoxy–peroxy pathways were found to be important processes leading to HOM. Time-dependent concentration profiles of monomer products containing nitrogen showed mainly second-generation formation patterns. Dimers were likely formed via the accretion reaction of two monomer RO₂^{*}, and HOM-trimers via the accretion reaction between monomer RO₂^{*} and dimer RO₂^{*}. Trimers are suggested to play an important role in new particle formation (NPF) observed in our experiment. A HOM yield of 1.5 %^{+1.7 %}_{–0.7 %} was estimated considering only first-generation products. SOA mass growth could be reasonably explained by HOM condensation on particles assuming irreversible uptake of ultra-low volatility organic compounds (ULVOCs), extremely low volatility organic compounds (ELVOCs), and low volatility organic compounds (LVOCs). This

work provides evidence for the important role of HOM formed via the limonene + NO₃ reaction in NPF and growth of SOA particles.

1 Introduction

The nitrate radical (NO₃) is an important nighttime oxidant in tropospheric chemistry, and can reach mixing ratios of several hundred pptv during nighttime (Seinfeld and Pandis, 2006). It can react with volatile organic compounds (VOCs) and is especially reactive to alkenes, where the nitrate radical can undergo an addition reaction to the C=C double bond (Finlayson-Pitts and Pitts, 1997; Seinfeld and Pandis, 2006). Biogenic monoterpenes (C₁₀H₁₆) are a large contribution to the alkenes in the atmosphere (Klinger et al., 2002; Guenther et al., 2012), and their major nighttime loss pathway is reaction with NO₃ (Beaver et al., 2012; Rollins et al., 2012; Ayres et al., 2015; Fry et al., 2013). The chemistry of monoterpenes with NO₃ has implications on the cycle of reactive nitrogen and thus on ozone formation (Brown and Stutz, 2012). Furthermore, since the NO₃ radical is formed through the reaction of NO₂ with O₃, it is considered to be of anthropogenic origin, and reactions of NO₃ with biogenic VOC (BVOC) thus represent an important interaction between biogenic emissions and anthropogenic emissions.

The reaction of NO₃ with monoterpenes can form secondary organic aerosols (SOAs), which can have a large impact on global climate, air quality, and human health (Hallquist et al., 2009; Shrivastava et al., 2017). Laboratory studies showed that monoterpenes have high SOA yields in the reaction with NO₃ due to the low volatility of oxidation products (Ng et al., 2008; Rollins et al., 2009; Fry et al., 2013, 2014; Ayres et al., 2015; Jokinen et al., 2015; Zhou et al., 2015; Boyd et al., 2015; Nah et al., 2016; Boyd et al., 2017; Slade et al., 2017; Clafflin and Ziemann, 2018; Bates et al., 2022; Dam et al., 2022). Field studies also showed that nighttime NO₃-initiated oxidation of monoterpenes contributes significantly to SOA in forested regions influenced by anthropogenic emissions (Pye et al., 2010; Rollins et al., 2012; Fry et al., 2013; Ayres et al., 2015; Zhou et al., 2015; Xu et al., 2015; Lee et al., 2016; Zhang et al., 2018; Chen et al., 2020) and potentially in urban areas due to the extensive usage of so-called volatile chemical products (VCPs) (Nazaroff and Weschler, 2004; McDonald et al., 2018). For example, the Southern Oxidant and Aerosol Study (SOAS) showed that the BVOC + NO₃ reactions were a substantial source of SOA (Ayres et al., 2015; Xu et al., 2015; Lee et al., 2016; Massoli et al., 2018). Therefore, accurate predictions and evaluations of SOA concentration and thus its climate and environmental effects require a comprehensive understanding of the reactions of monoterpenes with NO₃.

Recently, a class of organic compounds named highly oxygenated molecules (HOM) have been shown to be critical substances in the SOA formation from BVOC oxidation, particularly monoterpenes, featuring high O/C ratio and low to extremely low volatility (Ehn et al., 2014; Tröstl et al., 2016; Kirkby et al., 2016; Bianchi et al., 2019). HOM here refers to compounds formed in the gas phase via autooxidation which contain at least six oxygen atoms (Bianchi et al., 2019). Most HOM are classified as ULVOC/ELVOC or LVOC (Bianchi et al., 2019) according to the classification of atmospheric organics based on their volatility (saturation concentration, C*) by Donahue et al. (2012) (extremely low volatility organic compounds, ELVOCs; low volatility organic compounds, LVOCs; semi-volatile organic compounds, SVOCs; intermediate volatility organic compounds, IVOCs; volatile organic compounds, VOCs), and a recent update by Schervish and Donahue (2020) (ultra-low volatility organic compounds, ULVOCs). Thus, HOM can be a substantial contribution to growth of SOA particles through gas–particle partitioning.

A better description of the HOM formation chemistry in the oxidation of monoterpenes by NO₃ will improve our understanding of the role of HOM in SOA formation, and the relationship between oxidation products, SOA formation, and reaction systems. Field observation campaigns and laboratory experiments have proven the important contribution of HOM in monoterpene + NO₃ SOA (Lee et al., 2016; Faxon et al., 2018). In the SOAS campaign, HOM-ON (organic nitrates) were identified in both gas and particle phase using a NO₃[−]-chemical ionization time-of-flight mass spectrometer (CI-API-TOF) and a high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS) coupled to a Filter Inlet for Gases and AEROSOLS (FIGAERO). Species with the sum formula C₁₀H_{15,17,19}NO_{4–11} were observed, which are formed through the oxidation of monoterpenes by NO₃ (Lee et al., 2016; Massoli et al., 2018). In a campaign in a boreal forest in Hyytiälä, measurement using a NO₃[−]-CI-API-TOF and positive matrix factor (PMF) analysis showed a nighttime factor of HOM-ON formed via NO₃ oxidation of monoterpenes (Yan et al., 2016). Besides the observations at forested regions, monoterpene-derived HOM via NO₃ oxidation also contribute to organic aerosols in urban regions. For example, Liu et al. (2021) and Nie et al. (2022) have found that HOM derived from monoterpene nighttime chemistry are important in megacities in China, especially during summertime. A number of laboratory studies have reported HOM formation by the oxidation of monoterpenes with NO₃. Boyd et al. (2015) observed C₁₀H₁₇NO_{4/5} and C₁₀H₁₅NO_{5/6} in the gas phase in β-pinene + NO₃ experiments using a quadrupole chemical ionization mass spectrometer with I[−] as the reagent

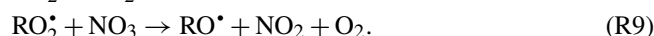
ion (I[−]-CIMS). They proposed possible formation schemes of these ONs. Nah et al. (2016) further detected 5 and 41 HOM-ON in the NO₃ oxidation of α -pinene and β -pinene, respectively, such as C₁₀H_{15/17/19}NO_{4–9} in the gas- and particle-phase using I[−]-FIGAERO HR-ToF-CIMS. Claffin and Ziemann (2018) provided formation mechanisms for HOM-ON via gas-phase and particle-phase reactions in the β -pinene + NO₃ reaction system, where particle-phase products were analyzed using reversed-phase high-performance liquid chromatography equipped with a UV-vis photodiode array detector (HPLC-UV), electron-ionization thermal desorption particle beam mass spectrometer (EI-TDPBMS), chemical ionization Finnigan PolarisQ ion trap mass spectrometer (CI-ITMS), and electrospray-ionization mass spectrometer (ESI-MS). Recently, Shen et al. (2021) found a large number of HOM (> 150 species) in the β -pinene + NO₃ reaction using NO₃[−]-CI-API-TOF. HOM formed in the reaction of four monoterpenes (α -pinene, β -pinene, Δ -3-carene, and α -thujene) with NO₃ were also detected using NO₃[−]-CI-API-TOF by Dam et al. (2022). Bell et al. (2021) found that dimer dinitrates (C₂₀H₃₂N₂O_{8–13}) contribute a large portion to SOA from α -pinene + NO₃, and also detected monomer ON such as C₁₀H₁₅NO_{5–10} and C₁₀H_{14,16}N₂O_{7–11}) using FIGAERO-CIMS and an extractive electrospray ionization time-of-flight mass spectrometer (EESI-ToF-MS). However, the detailed speciation depends on analytical method to some extent. Moreover, the HOM composition in the particle-phase was found to depend on aging time and reaction conditions such as dark versus light (Bell et al., 2021; C. Wu et al., 2021).

Among the monoterpenes, understanding the reaction system of limonene with NO₃ is of specific importance. The emission of limonene makes the fourth largest contribution with an estimated global emission of 11.4 Tg annually, preceded only by α -pinene, trans- β -ocimene, and β -pinene (Guenther et al., 2012). Besides its biogenic origin, limonene is also a common additive in cleaning products (Nazaroff and Weschler, 2004) and can even be used as a tracer for fragrances in some places (Gkatzelis et al., 2021). Several studies have shown adverse health effects due to indoor pollution caused by the ozonolysis of limonene (Clausen et al., 2001; Fan et al., 2003; Carslaw et al., 2012; Pagonis et al., 2019). Moreover, limonene stands out with its high reactivity towards the NO₃ radical (with a lifetime of 3 min at 298 K at 20 pptv NO₃) (Ziemann and Atkinson, 2012), and NO₃ oxidation of limonene has high SOA yield (SOA mass yield 15 % to 231 %) (Hallquist et al., 1999; Spittler et al., 2006; Fry et al., 2011, 2014; Boyd et al., 2017; Berke-meier et al., 2020; Mutzel et al., 2021). A number of earlier studies have provided valuable insights into the reaction of limonene with NO₃ regarding its main products and their formation pathways, the SOA yield, and the SOA physicochemical properties. For example, Hallquist et al. (1999) measured the SOA mass yield and revealed the dominance of organic nitrates (ONs) and carbonyl compounds in the products. Fry

et al. (2011) determined the organic nitrate yield and proposed a reaction scheme leading to the formation of ON and carbonyls, and Fry et al. (2014) compared the SOA and ON yields from the NO₃ oxidation of α -pinene, β -pinene, and limonene, and demonstrated why limonene + NO₃ leads to more SOA and ON than α -pinene from a structural perspective. Boyd et al. (2017) found a higher N : C ratio for limonene + NO₃ SOA than for β -pinene + NO₃ SOA. Finally, Peng et al. (2018) studied the optical properties of the limonene + NO₃ SOA.

Regarding the HOM formation in the reaction of limonene with NO₃, Faxon et al. (2018) reported a series of HOM in the particle phase, including C_{7–10} monomers with 3–11 oxygen atoms and C_{11–20} dimers with 5–19 oxygen atoms using I[−]-FIGAERO HR-ToF-CIMS. However, identification of gas-phase HOM products in the limonene + NO₃ reaction is still lacking and their formation mechanisms remain unclear. Theoretical investigations have revealed that NO₃ addition on the endocyclic C=C double bond is more favorable than the exocyclic one due to a lower energy barrier (Jiang et al., 2009), and this endocyclic double bond of limonene thus tends to be attacked by NO₃ and leads to products including hydroxy-substituted ON or diketone products. The remaining exocyclic double bond can also be attacked by NO₃ in secondary chemistry, leading to more functionalized products (Fry et al., 2011).

The formation of HOM via autoxidation involves a sequence of multiple intramolecular H-shift and O₂ addition reactions, and results in highly oxygenated peroxy radicals (HOM-RO₂[•]) (Ehn et al., 2014). These HOM-RO₂[•] can react similarly to traditional RO₂[•] (Bianchi et al., 2019). The bimolecular reactions of HOM-RO₂[•] with RO₂[•], HO₂[•], and NO lead to highly oxidized closed shell products including carbonyls, hydroperoxides, alcohols, or organic nitrates as termination groups (Reactions R1 to R3), or form accretion products (Reaction R4) (Ehn et al., 2014; Mentel et al., 2015). Unimolecular termination reactions of HOM-RO₂[•] lead to carbonyls or epoxides (reactions R5 to R6) (Crounse et al., 2013). On the other hand, reactions of HOM-RO₂[•] with NO, RO₂[•], NO₃ at nighttime can lead to alkoxy radicals as chain propagating steps (reactions R7 to R9):



If the reactive HOM-RO[•] products undergo an H-migration reaction, they will again form HOM-RO₂ radicals (“alkoxy-

peroxy” pathway) (Mentel et al., 2015), continuing the autoxidation chain. Finally, the HOM-RO[•] may also fragment leading to small RO₂ radicals, isomerize leading to carbonyls (Bianchi et al., 2019), or react with O₂ to form carbonyls (Ziemann and Atkinson, 2012).

In this study, HOM formation in the NO₃ oxidation of limonene was investigated. We report the identification of gas-phase HOM products, including monomers, dimers, and trimers. The formation pathways of dominant products in each category are proposed based on their time profiles in response to multiple additions of limonene in the experiment and on the information in literature. Based on this analysis, we estimated HOM yields, and discuss the role of HOM in nucleation and growth of SOA particles.

2 Experiment and methods

2.1 Experiment setup

The limonene + NO₃ experiment was performed in the atmospheric simulation chamber SAPHIR (Simulation of Atmospheric PHotochemistry In a large Reaction chamber) at the Forschungszentrum Jülich, Germany. SAPHIR is a 270 m³ double-wall cylindrical Teflon chamber with a surface-to-volume ratio of ∼ 1 m² m⁻³. Details of SAPHIR have been described before (Rohrer et al., 2005; Zhao et al., 2015a, b; Zhao et al., 2018) and are only summarized here. Detailed experimental procedures can be found in Fig. 1a. Before each experiment, SAPHIR was flushed for about 4 h at a flow rate of 370 m³ h⁻¹ with high-purity synthetic air (purity > 99.9999 % O₂ and N₂) in order to clean the chamber. To simulate nighttime conditions for the NO₃ chemistry, the chamber roof remained closed throughout the experiment. The experiment was performed under dry conditions (RH < 2 %) at a temperature of 302 ± 3 K. No seed aerosols were used in the experiments. A fan was used for active mixing in the chamber, leading to a typical mixing time of ∼ 1 min (Fuchs et al., 2013).

NO₃ radicals were generated via the reaction of ozone with nitrogen dioxide:



Therefore, O₃ and NO₂ were first added to the chamber to form N₂O₅ and NO₃ with mixing ratios of ∼ 2 and ∼ 0.15 ppbv, respectively. About 20 min later, 5 ppbv of limonene was added to start the organic chemistry. Five more additions of limonene followed, with added concentrations of about 3, 3, 2, 2, and finally 8 ppbv, which divided the experiment into six periods (P1 to P6) (Fig. 1a). For period P3 and P5, NO₂ and O₃ were also added to compensate for the loss of NO₃ and N₂O₅ (Fig. 1a). The concentrations of NO₂ and O₃ were maintained around 20 to 70 ppbv throughout the experiment, ensuring the major loss of limonene was

by reaction with NO₃ rather than with O₃ (Figs. S1). In the first 10 min of reaction (named period P1a hereafter, Fig. 1a), NO₃ accounted for 86 % of the chemical loss of limonene.

2.2 Instrumentation

Gas-phase HOM were detected by a chemical ionization time-of-flight mass spectrometer (CI-API-TOF, Aerodyne Research Inc., USA) with a resolution (m/z)/($\Delta m/z$) of ∼ 3800 using ¹⁵NO₃⁻ as the reagent ion, which is capable of detecting organic molecules with high oxygen content (Eisele and Tanner, 1993; Jokinen et al., 2012). The mass spectra were analyzed using the software Tofware (Tofwerk/Aerodyne) in Igor Pro (WaveMetrics, Inc.). Peak identification was conducted by a high-resolution analysis (examples shown in Fig. S2). We observed several peaks which were obviously products from the isoprene + NO₃ reaction, such as C₅H₁₀N₂O₈⁺ · ¹⁵NO₃⁻ at m/z 289. Such peaks were present before the limonene oxidation reaction started, suggesting that these compounds preexisted in the chamber. These isoprene oxidation products were likely formed in an isoprene + NO₃ experiment performed 2 d before (Zhao et al., 2021) and released slowly from chamber walls due to their semi-volatile character. Their total concentration is less than 1 ppt. All the isoprene-HOM observed (C₅H₉NO_{7,10}, C₅H₈N₂O_{8–10}, C₅H₁₀N₂O₈, C₅H₉N₃O_{9,10}) are saturated and do not contain C=C double bond. The isoprene-HOM will not influence the reaction of limonene with NO₃ in this study. Therefore, they are not discussed as products from the limonene oxidation in our experiment. (However, we cannot exclude that they were partly generated from fragmentation in the limonene + NO₃ reaction.)

A set of instruments were used to measure other gas-phase species, including VOC, NO_x, O₃, NO₃, and N₂O₅ (Shen et al., 2021). Concentrations of NO₃ and N₂O₅ were measured in situ using a home-built diode laser-based, cavity ring-down spectrometer similar to the instrument described in the work by Wagner et al. (2011). The concentrations of limonene were measured using a proton transfer reaction time-of-flight mass spectrometer (PTR-TOF-MS, Ionicon Analytik, Austria). The SOA number concentration, surface concentration, and size distribution were detected by a scanning mobility particle sizer (SMPS, TSI DMA3081/TSI CPC3786) and a condensation particle counter (CPC, TSI3785). Temperature and relative humidity were continuously monitored throughout the experiment.

2.3 Determination of HOM concentration and “primary” HOM yield

HOM concentrations were obtained from the normalized signals to the total signals of the mass spectra (nc, normalized counts) by applying a calibration coefficient (C) of 2.5×10^{10} molecule cm⁻³ nc⁻¹. C was determined using H₂SO₄ as the charging efficiency of HOM and H₂SO₄ are consid-

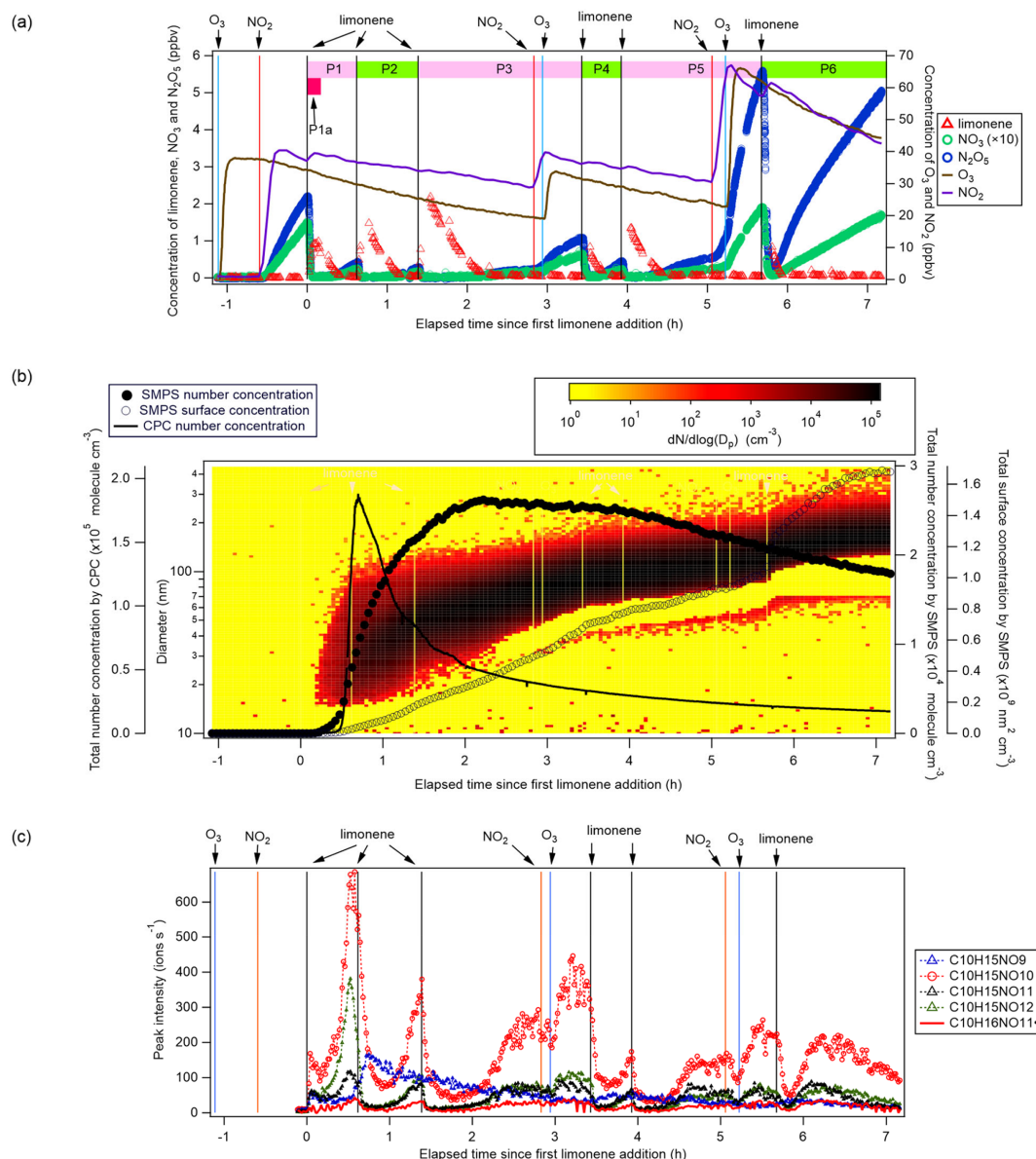


Figure 1. (a) Time series of the concentrations of limonene, NO₃, and N₂O₅ (left panel, the concentrations of NO₃ are magnified by a factor of 10 for clarity), and O₃ and NO₂ (right panel). The time periods P1 to P6 and P1a are also marked. (b) Total particle concentration and its size distribution during the whole period of experiment detected by SMPS and CPC. The solid and hollow black circles refer to total number concentration and total surface concentration detected by SMPS, respectively. Colors represent particle number concentration distribution based on log(*D_p*). The solid black line refers to total number concentration detected by CPC. (c) Time series of peak intensity of typical products of the C₁₀H₁₅NO_{*x*} family and C₁₀H₁₆NO_{*x*} family as a representative of the C₁₀H₁₆NO_{*x*} family. Vertical lines indicate the time of O₃ and NO₂ additions, and six limonene injections.

ered to be equal (Ehn et al., 2014; Pullinen et al., 2020; Shen et al., 2021). The details of determination of the calibration coefficient are shown in Sect. S1 in the Supplement. A mass-independent transmission efficiency was used according to our previous study, which causes an additional uncertainty of 14 % (Pullinen et al., 2020). In this previous study, the transmission efficiency curve of nitrate CI-API-TOF was determined and found to monotonously decrease with increas-

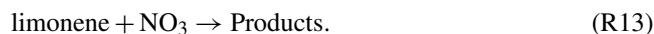
ing mass of ions but only slightly depend on the mass range (14 % change). As we used the same setting as our previous study, we have included the slight dependence of transmission on *m/z* in the uncertainties. The concentrations of HOM were corrected for chamber wall losses, which were determined for a number of HOM similar to our previous study (Zhao et al., 2018), with details described in the Supplement. When the chamber is actively mixed, the wall loss was deter-

mined to be $(2.2 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$. As the HOM yield was determined during the first 3 min of the experiment, we considered the wall loss rate to be constant ($2.2 \times 10^{-3} \text{ s}^{-1}$) during this period. Sensitivity analysis showed that the HOM yield in this study is not very sensitive to the wall loss rate and is changing by only +0.88 % and −0.44 % if the wall loss rate is varied by +100 % or −50 %.

The HOM yield was calculated as

$$Y = \frac{[HOM]}{[VOC]_r} = \frac{I(HOM) \cdot C}{[N_2O_5]_r}, \quad (1)$$

where $[HOM]$ is the concentration of HOM, $I(HOM)$ is the total signal intensity of HOM, C is the calibration factor, and $[VOC]_r$ and $[N_2O_5]_r$ stand for the concentrations of limonene and N₂O₅ reacted, respectively. We used the reacted concentration of N₂O₅ rather than the measured reacted limonene concentration as a large fraction of limonene was already reacting away during the VOC injection before it was homogeneously mixed in the chamber. During this part of the experiment, the high limonene concentration resulted in a rapid loss of NO₃, such that every NO₃ formed from the decomposition of N₂O₅ reacted with limonene:



The initial NO₃ concentration before the limonene injection was small compared to the time-integrated loss of N₂O₅, and other NO₃ loss processes were negligible right after the limonene injection, so that the observed decrease in the N₂O₅ concentration equals indeed the consumption of limonene. The wall loss rate constant of N₂O₅ in the SAPHIR chamber is $7.2 \times 10^{-5} \text{ s}^{-1}$ (Fry et al., 2009). As the HOM yield determination is based on the first 3 min, the wall loss of N₂O₅ can be ignored compared to the loss via the reaction of NO₃ with limonene.

The uncertainty of the HOM yield was estimated to be −55 %/+117 % based on the combined uncertainties of the HOM-ON peak intensities (~10 %), the limonene concentration (~15 %), the transmission efficiency (−0 %/+14 %), and the calibration factor (−52 %/+101 %) using error propagation (Zhao et al., 2021). The first 3 min after the injection of limonene were used to calculate the HOM yield, when most of the first-generation oxidation products were produced and negligible particles were formed. The HOM yield thus reflects the “primary” HOM yield.

2.4 Determination of HOM condensation on SOA

The SOA mass from the condensation of HOM was calculated to evaluate the role of HOM for the SOA mass growth. Detailed estimation methods are described in the Supplement, including the determination of particle wall loss and dilution loss rate (Sect. S2). In brief, the growth rate of SOA through HOM vapor condensation is based on the collision

rate of vapor molecules with aerosols in the kinetic regime. The Fuchs–Sutugin approach is applied to describe the correction for transition from the kinetic to the diffusion regime (Fuchs and Sutugin, 1971; Ehn et al., 2014). Based on the volatility of HOM, we considered two scenarios for HOM condensation. In scenario 1, all HOM were assumed to irreversibly condense on the surface of particles leading to particle mass growth. In scenario 2, only the irreversible uptake of LVOC and ULVOC/ELVOC compounds were considered to contribute to the growth of SOA particles in order to examine the role of LVOC and ELVOC while IVOC and SVOC were not included, although they may also contribute to SOA. The calculation of saturation concentration C^* (in $\mu\text{g m}^{-3}$) of each HOM was done based on their molecular compositions using two different parameterizations considering the uncertainties in estimating volatility (R. Wu et al., 2021):

1. an updated version of the parameterization of Donahue et al. (2011) by Mohr et al. (2019) (scenario 2a):

$$\log_{10}(C) = (25 - n_C) \times 0.475 - (n_O - 3n_N) \times 0.2 - 2 \frac{(n_O - 3n_N)n_C}{(n_C + n_O - 3n_N)} \times 0.9 - n_N \times 2.5, \quad (2)$$

where n_C , n_O , n_N , and n_H are the number of carbon, oxygen, nitrogen, and hydrogen atoms of the compound, respectively.

2. a parameterization based on HOM from α -pinene ozonolysis by Peräkylä et al. (2020) (scenario 2b):

$$\log_{10}(C) = n_C \times 0.18 - n_H \times 0.14 - n_O \times 0.38 + n_N \times 0.80 + 3.1, \quad (3)$$

with similar parameter notation.

2.5 Simulations of the RO₂^{*} loss pathway based on the Master Chemical Mechanism (MCM)

The RO₂^{*} loss pathways were estimated based on MCM simulations (<http://mcm.york.ac.uk/>, last access: 14 November 2021). The gas-phase reactions of limonene + NO₃ under dark condition were simulated using iChamber, an open-source program (<https://sites.google.com/view/wangsiyuan/models?authuser=0>, last access: 14 November 2021) (Wang and Pratt, 2017). The default chemistry of limonene + NO₃ in the MCM was applied in this study (Saunders et al., 2003). Photolysis reactions were excluded by setting the zenith angle to 90°. Concentrations of O₃, NO₃, NO₂ and N₂O₅, and temperature and relative humidity were constrained to the experimental data with a time resolution of 1 min. The chamber dilution rate of $1.5 \times 10^{-5} \text{ s}^{-1}$ was applied to all species. The P1 period was simulated using the above conditions, and the initial concentrations of limonene were added in the model according to the experimental procedures. The sum of all 140 RO₂^{*} in the limonene subset of MCM v3.3.1 were used

in the usual way to estimate the loss rates of RO₂[•] bimolecular reactions. The reaction rate constants are provided in Table S3 in the Supplement, and calculated loss rates are shown in Fig. S3. We note that the MCM reaction schemes do not include the accretion reactions between HOM-RO₂[•]. Berndt et al. (2018a) determined the rate constant of accretion reaction of C₁₀H₁₅O₄[•] formed via α -pinene ozonolysis to be $\sim 1 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, which is of the same order as the upper limit for RO₂[•] + RO₂[•] reactions used in the MCM schemes for functionalized peroxy radicals such as acyl peroxy radicals (Jenkin et al., 1997; Saunders et al., 2003). However, currently we do not see a reliable updated set of rate coefficients that are applicable to the reaction system in this study. If the rate constants of some RO₂[•] + RO₂[•] reactions were higher than those used in MCM, the concentrations of RO₂[•] would be lower and relative importance of RO₂[•] + RO₂[•] in RO₂[•] fate would increase. Several simulation results are shown in Fig. S4, including NO₃, N₂O₅, limonene, RO₂[•], reaction rate of limonene with NO₃ ($k \times \text{limonene} \times \text{NO}_3$), and examples of first- and second-generation RO₂[•].

In the early stage of each period, RO₂[•] mainly reacted with RO₂[•] and NO₃, although in the later stage the reaction with NO₂ also contributed to a significant fraction of RO₂[•] loss (Fig. S3, showing period P1 as an example). During the period P1a which our peak assignment was based on, the RO₂[•] loss was dominated by RO₂[•] + RO₂[•] and RO₂[•] + NO₃.

3 Results and discussion

3.1 Experiment overview and observed HOM

After each limonene addition, the concentration of limonene rose first and then rapidly declined, while the concentrations of NO₃ and N₂O₅ rapidly decreased due to the fast reaction between limonene and NO₃, and gradually increased when limonene had been consumed (Fig. 1a). About 10 min after the first limonene addition, new particles had already formed and quickly grew in size (Fig. 1b). Therefore, we used the first 10 min reaction time (period P1a) to identify gas-phase HOM products, and the whole experiment to examine the contribution of HOM to SOA.

During period P1, HOM were quickly formed. We identified about 280 HOM compounds, including monomers (C₇–C₁₀, ~ 280 –460 Th), dimers (C₁₇–C₂₀, ~ 490 –700 Th), and trimers (C₂₆–C₃₀, ~ 720 –960 Th) (Fig. 2a). Their detailed formulas can be found in Table S1. HOM on the horizontal lines of the Kendrick mass defect plot (O-based) (Figs. 3, S5, and S6) share the same number of C, N, and H atoms, with the number of oxygen atoms increasing from left to right. Such HOM compounds are defined as a family. We notice that most monomer peroxy radical families are each related to two monomer closed-shell product families, with one H atom more or one H atom less, which are the expected termination products of RO₂[•] + RO₂[•] reactions, or if HO₂[•] is present, RO₂[•] + HO₂[•] termination

products. These three related families are defined as a “series”, with the same number of C and N number, such as C₁₀H_{15–17}NO_{6–14}. In total, we identified 6 monomer series (C₁₀H_{15–17}NO_{6–14}, C₁₀H_{14–16}N₂O_{9–15}, C₁₀H_{14–16}O_{7–12}, C₉H_{13–15}NO_{7–14}, C₈H_{11–13}NO_{6–13}, and C₇H_{9–11}NO_{7–11}) and 1 monomer family (C₁₀H₁₇N₃O_{12–16}), 11 dimer families (C₂₀H₃₁NO_{10–15}, C₂₀H₃₃NO_{12–16}, C₂₀H₃₂N₂O_{9–20}, C₂₀H₃₁N₃O_{14–20}, C₂₀H₃₃N₃O_{12–20}, C₂₀H₃₄N₄O_{15–20}, C₂₀H₃₂O_{13–16}, C₁₉H₂₉NO_{10–13}, C₁₉H₃₁NO_{10–15}, C₁₉H₃₀N₂O_{10–18}, and C₁₉H₃₁N₃O_{15–19}), and 3 trimer families (C₃₀H₄₇N₃O_{18–24}, C₃₀H₄₈N₄O_{16–24}, and C₂₉H₄₆N₄O_{19–24}). The monomer family C₁₀H₁₇N₃O_{12–16} is not classified as series because the supposedly relevant families are not clearly identified. Compounds containing at least one nitrogen atom accounted for more than 90 % of the identified HOM products. We assume that compounds containing nitrogen atoms are organic nitrates, because other N-containing species such as amines or nitro compounds are very unlikely to be formed from the reaction of limonene with NO₃. Organic nitrates formed in this study could be alkyl nitrates, or (acyl)peroxynitrates formed via the reaction of RO₂[•] with NO₂.

During period P1a, in the absence of particles, both HOM monomers and oligomers were observed, including monomers (47 %), dimers (47 %), and trimers (6 %) (Fig. 2a). Concentrations of gas-phase dimers and trimers decreased evidently after particle formation (Figs. 2b, 5, 6), indicating a fast gas–particle condensation and strong tendency of oligomers to condense on particles.

Based on their typical time series (Fig. 1c), products can be classified as first-generation or second-generation products. Generally, the concentrations of first-generation products, which result from the direct reaction of limonene with NO₃, are expected to quickly increase after the limonene addition, followed by a steady decline due to wall loss or chemical reactions. Concentrations of typical second-generation products, which result from further reactions of first-generation products, are expected to show a gradually increasing concentration pattern after a limonene addition and reach their maximum concentration later than first-generation products. These general expectations are modified in our case, since the particle concentration increased in our experiment (Fig. 1b) and the condensational sink of HOM products became stronger over time. Thus, an increase in concentration suggests that the increasing condensational sink was exceeded by increasing production with time, i.e., from second-generation pathways.

To sum up, gas-phase HOM formed in the limonene + NO₃ system were dominated by HOM monomers and dimers. Time series patterns of the products indicate multiple generations of reaction pathways.

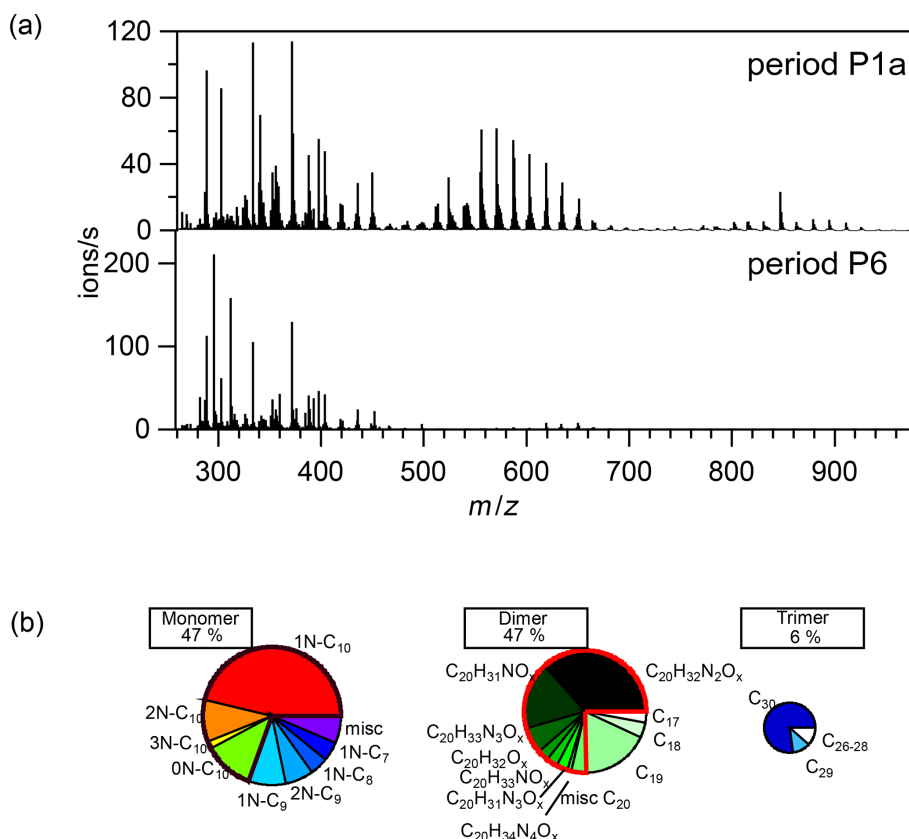
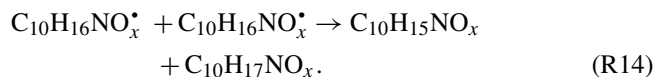


Figure 2. (a) Average mass spectra of the first 10 min reaction time after the first addition of limonene (period P1a, upper panel) and the last limonene addition period till particles reached maximum mass concentration (period P6, lower panel). (b) Pie charts (from left to right: rainbow, green, and blue colors) representing the relative contributions of identified families to HOM monomers, dimers, and trimers, respectively, during the P1a period. The area of each pie is in proportion to their concentrations during the P1a period.

3.2 Monomers and their formation pathways

3.2.1 Overview of HOM monomers

A number of HOM monomer families were detected with an increasing oxygenation pattern at 16 Th intervals (Fig. 3). Such a pattern is attributed to autoxidation of RO₂[•] (with 32 Th interval for each O₂ addition) plus the alkoxy–peroxy pathway (shifted by 16 Th compared with exclusive autoxidation) as discussed below. During period P1a, the most abundant HOM monomers are C₁₀ compounds (64 %), such as peroxy radicals C₁₀H₁₆NO_x[•] and closed-shell products C₁₀H₁₅NO_x and C₁₀H₁₇NO_x, which are carbonyl compounds and hydroxyl or hydroperoxy compounds from the termination reactions of C₁₀H₁₆NO_x[•], respectively. Reaction (R14):



According to the nitrogen atoms contained, C₁₀-HOM monomers can be classified into 1N-, 2N-, 3N-monomers, and monomers without nitrogen atoms. While 1N-C₁₀ HOM monomers were likely formed by direct NO₃ addition to

limonene, C₁₀ HOM monomers containing multiple N atoms were likely formed via multiple reaction steps. Besides C₁₀ HOM monomers, C_{6–9} HOM monomers were also observed. These C_{6–10} families are discussed below in the order of their contributions to HOM monomers.

3.2.2 1N-C₁₀ monomers

Among C₁₀ HOM monomers, the 1N-C₁₀ families were most abundant and included stable closed-shell products C₁₀H₁₅NO_x ($x = 7–13$) and C₁₀H₁₇NO_x ($x = 9–14$) and peroxy radicals C₁₀H₁₆NO_x[•] ($x = 6–14$). The concentration of C₁₀H₁₆NO₁₁[•] increased in the later phase of each limonene addition period (Fig. 1c), showing mostly a time profile of a second-generation product, similar as most of the other radicals in the C₁₀H₁₆NO_x[•] family (Fig. S7). However, the time series of C₁₀H₁₅NO_x compounds showed an overlaying pattern of first- and second-generation products dominated by a second-generation time profile with the exception of C₁₀H₁₅NO₉ (Fig. 1c). Due to sensitivity restrictions of CIMS, the primary peroxy radical C₁₀H₁₆NO₅[•] was not detected, which was supposed to show first-generation pattern.

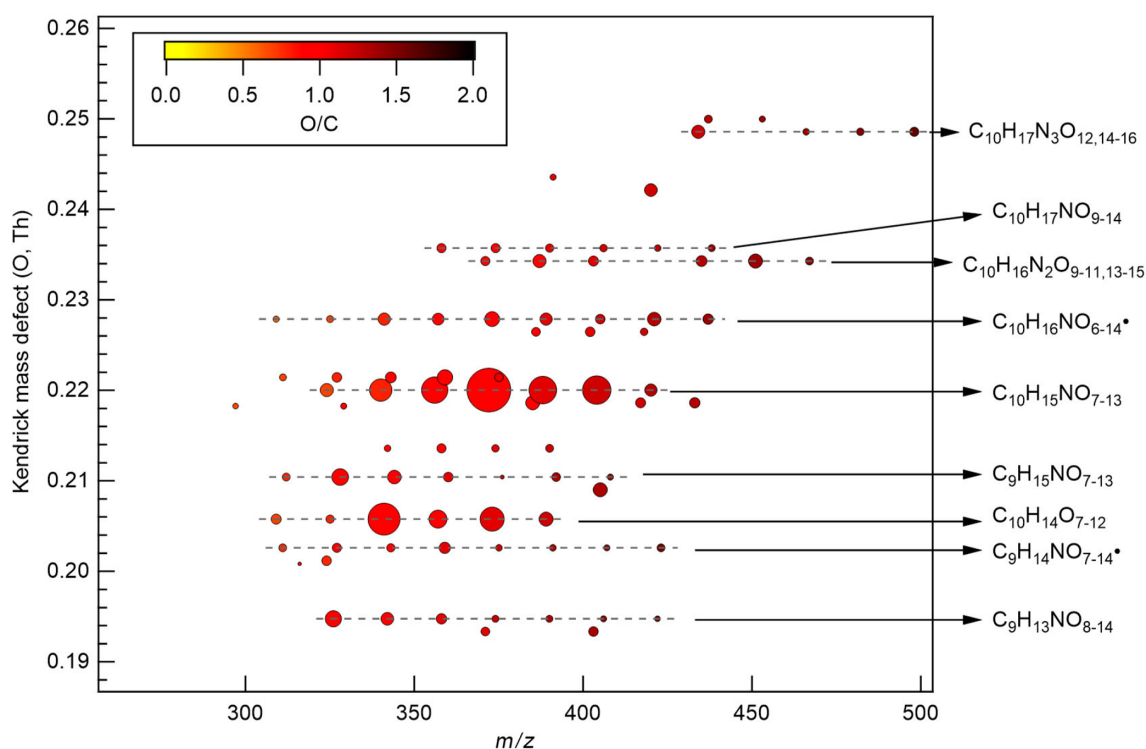


Figure 3. Kendrick mass defect plot (O-atom-based) of major monomer products. The area of the circles is proportional to the average intensity of each compound during the P1a period with the largest circle representing C₁₀H₁₅NO₁₀. The color denotes O/C ratios. Dashed lines indicate major product families. For clarity, the reagent ions ¹⁵NO₃[−] are omitted from molecular formula. The calculation of O-atom-based Kendrick mass defect includes two steps. First, the IUPAC mass scale (based on the ¹²C atomic mass as exactly 12 Da) is rescaled to Kendrick mass: Kendrick mass = IUPAC mass × (16/15.9949), which converts the mass of O from 15.9949 to exactly 16. Then, Kendrick mass defect is given by Kendrick mass defect = nominal Kendrick mass − exact Kendrick mass. Thus, compounds with the same number of each kind of atom except for O have equal O-atom-based Kendrick mass defect, and are shown in a horizontal line in the O-atom-based Kendrick mass defect plot.

The absence of first-generation characteristics of the time profile of most HOM peroxy radicals C₁₀H₁₆NO_{*x*}[•] (*x* ≥ 6) may be attributed to two possible reasons. They either did not undergo efficient autoxidation, or they underwent immediate conversion including autoxidation and/or bimolecular reactions with other RO₂[•] or NO₃ forming closed-shell products such as dimers or continuing the radical chain forming RO[•]. The instantaneous increase of 2N-dimers and trimers after the first limonene addition shown below suggests that C₁₀H₁₆NO_{*x*}[•] (*x* ≥ 6) were indeed formed efficiently via autoxidation. Therefore, the latter reason is more likely. At this time, we do not have a reasonable explanation for the trend of C₁₀H₁₅NO₉, though we should consider that there are many isomers at play, which may have very different chemical pathways (un)available.

Since the C₁₀H₁₅NO_{*x*} family showed an overlaying pattern of the first-generation and second-generation products, they likely contained multiple isobaric substances produced through different pathways. Based on the literature, possible formation pathways of these products were tentatively proposed (Seinfeld and Pandis, 2006; Vereecken and Peeters,

2010; Mentel et al., 2015; Vereecken and Nozière, 2020). As an example of the pathways to form first-generation products, C₁₀H₁₆NO_{*2x*−1}[•] (with an odd number of oxygen atom) and their corresponding termination products can be formed via autoxidation of the first peroxy radical C₁₀H₁₆NO₅[•] (R1OO), showing C₁₀H₁₆NO₉[•] (R3OO) as an example (scheme 1a, first-generation products). C₁₀H₁₆NO_{*2x*}[•] (with an even number of oxygen atom) can be formed via alkoxy–peroxy channels. For example, the ring-opening of the alkoxy radical C₁₀H₁₆NO₄[•] (R1O), which was formed via the reaction of C₁₀H₁₆NO₅[•] (R1OO) with another RO₂[•] or NO₃ radical (scheme 1a, first-generation products). Ring-opening of R1O leads to C₁₀H₁₆NO₆[•] (R4OO), which can undergo autoxidation forming C₁₀H₁₆NO_{*2x*}[•]. In addition, the alkoxy radical C₁₀H₁₆NO₄[•] (R1O) is susceptible to ring-opening reactions (Novelli et al., 2021), which can lead to a first-generation stable product 3-isopropenyl-6-oxoheptanal (endolim, TP1) after C–C bond cleavage followed by the elimination of a NO₂ fragment (scheme 1b, second-generation products). Endolim (TP1) has been detected as a major product in previ-

ous limonene + NO₃ studies (Hallquist et al., 1999; Spittler et al., 2006).

As an example of second-generation chemistry, the remaining double bond of endolim could react with NO₃ to form RO₂[•], followed by the autoxidation to form second-generation C₁₀H₁₆NO_{*x*}[•] (with odd number of oxygen atoms). Similar to first-generation pathways, second-generation C₁₀H₁₆NO_{*x*}[•] with even number of oxygen atoms can be formed via alkoxy–peroxy channel. From the time profile of C₁₀H₁₅NO_{*x*}, the second-generation pathway (scheme 1b) was expected to play a more important role, in agreement with the theoretical result by Kurtén et al. (2017), in which the two bond–cleavage pathways of limonene-derived RO[•] radical were considered. It is worth mentioning that the reaction products of limonene with O₃ may also react with NO₃, forming C₁₀H₁₆NO_{*x*}[•] (scheme S1). However, as shown above, this was a minor pathway in our experiment (Sect. 2.1). We would like to note that to simplify the scheme, only the reaction of NO₃ with the endocyclic double bond is presented, since this reaction is faster than that with the exocyclic double bond (Jiang et al., 2009; Fry et al., 2011).

C₁₀H₁₆NO_{*x*}[•] with both even and odd number of oxygen atoms and their termination products had comparable abundance, which suggests that the alkoxy–peroxy pathway was important for RO₂[•] formation in this reaction. This finding is analogous to the findings in the reaction of a number of alkenes with O₃ and in the reaction of isoprene and β-pinene with NO₃ (Mentel et al., 2015; Zhao et al., 2021; Shen et al., 2021).

Among 1N-C₁₀ monomers, concentrations of carbonyl compounds were much higher than the sum of hydroxy- and hydroperoxy-substituted compounds (Table 1). According to Hyttinen et al. (2015), for nitrate CI-API-TOF, HOM containing two hydrogen bond donors (such as -OOH and -OH group) have strong binding energy with NO₃⁻. Additional hydrogen bond donors only enhance the binding energy marginally. If we compare HOM carbonyl product (such as C₁₀H₁₅NO₁₀) with the corresponding hydroxy product (C₁₀H₁₇NO₁₀), they only differ in one functional group. As both are highly functionalized, it is likely that HOM carbonyl have a quite similar sensitivity with HOM alcohol. If the sensitivity of carbonyl HOM were lower, this would result in even more dominance of carbonyl HOM over hydroxyl HOM. Thus, we conclude that carbonylnitrates are more abundant than hydroxynitrates or hydroperoxynitrates. This finding is likely attributed to unimolecular termination reactions of RO₂[•], although reaction paths via RO[•] also cannot be excluded. Smaller unbranched RO[•] tend to react with O₂ forming carbonyl compounds, while for larger or branched RO[•], isomerization can also form carbonyl compounds and is a more energetically favorable and thus faster pathway compared with the reaction with O₂ (Ziemann and Atkinson, 2012). The importance of unimolecular termination reactions of HOM-RO₂[•] and the resulting high ratio of carbonyl compounds to hydroxyl/hydroperoxyl com-

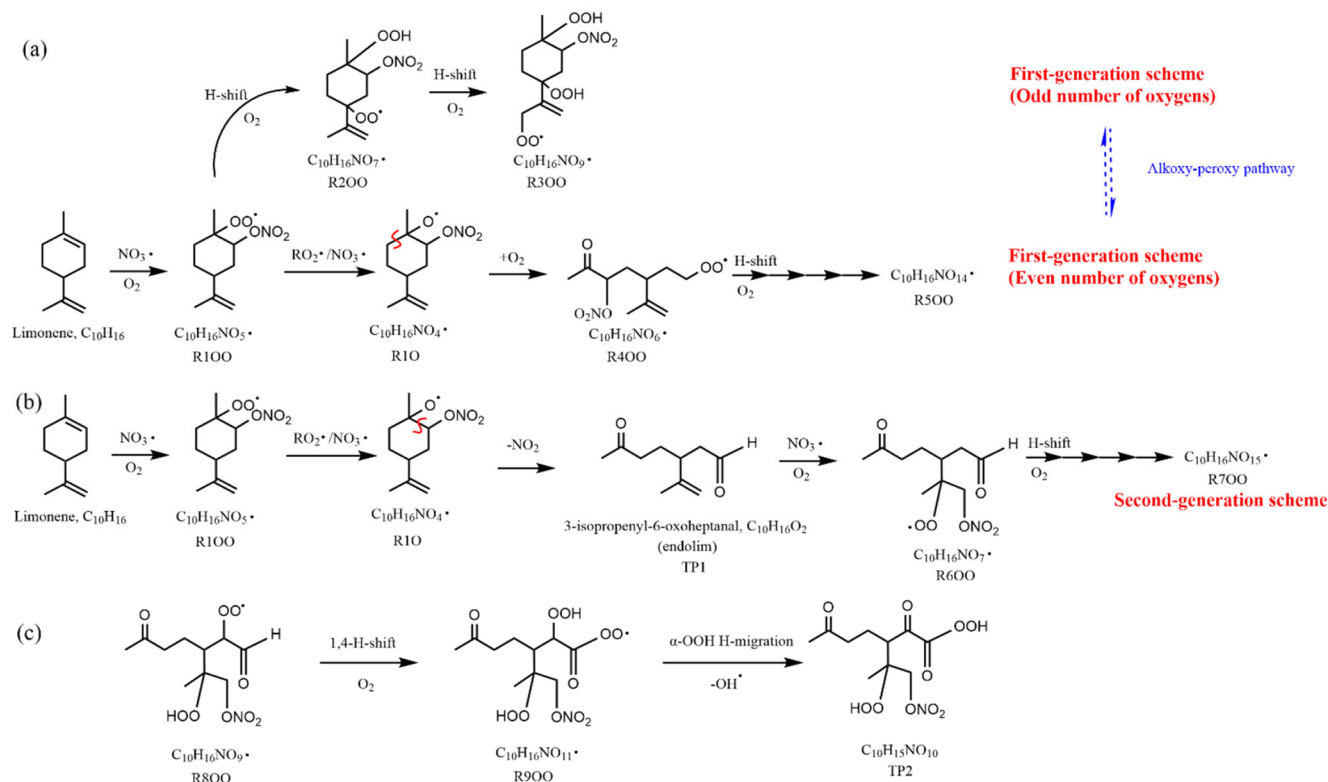
pounds has also been found in the reaction system of β-pinene + NO₃ (Shen et al., 2021; Dam et al., 2022). This high ratio is also consistent with findings in the ozonolysis of alkenes (Mentel et al., 2015), where unimolecular termination reactions were also proposed to be the likely explanation (Crounse et al., 2013; Rissanen et al., 2014). As discussed in our previous study by Shen et al. (2021), this higher abundance of carbonylnitrates is not likely to be explained by the reaction of alkoxy RO[•] + O₂ forming carbonyls and HO₂[•], decomposition of β-nitrooxyperoxynitrate, or self-reactions of RO₂[•] via the Bennett and Summers mechanism forming carbonyls and H₂O₂. Reactions between RO₂[•] in general should produce overall equal amounts of carbonyl and hydroxyl compounds. The decomposition of β-nitrooxyperoxynitrate is slow in the gas-phase. The reaction of alkoxy RO[•] with O₂ for large RO[•] is generally slower than isomerization and decomposition (Vereecken and Peeters, 2009, 2010). Thus, the higher abundance of carbonylnitrates compared to hydroxynitrates may be attributed to unimolecular termination of HOM-RO₂[•]. In addition, isomerization of RO[•] forming carbonyl compounds may also contribute to this finding. Our result thus further emphasizes that unimolecular termination reactions of RO₂ radicals are important pathways in the formation of HOM monomers derived from the reactions of monoterpenes with NO₃ (Shen et al., 2021). Scheme 1c shows this unimolecular termination process using a C₁₀H₁₆NO₉[•] radical as an example. C₁₀H₁₆NO₉[•] undergoes a 1,4-H-shift, and O₂ addition to form a C₁₀H₁₆NO₁₁[•] radical. The C₁₀H₁₆NO₁₁[•] radical further undergoes an H-shift of the α-OOH H-atom, which produces a carbonyl closed-shell product and an OH[•] radical.

For 1N-C₁₀ HOM monomers, the products detected in this study generally agree with previous laboratory and field studies on the reaction of limonene and other monoterpenes. Faxon et al. (2018) also observed C₁₀H₁₅NO_{*x*} as the most prevalent products in the particle phase from limonene + NO₃. In the SOAS campaign, both C₁₀H₁₅NO_{*x*} and C₁₀H₁₇NO_{*x*} products were detected and were believed to be products of nighttime chemistry (Lee et al., 2016). The high abundance of 1N-C₁₀ HOM monomers is consistent with the finding that C₁₀H₁₅NO_{*x*} and C₁₀H₁₇NO_{*x*} dominate the chemical composition of SOA formed via NO₃ oxidation of α-pinene and β-pinene, as shown in previous chamber studies (Takeuchi and Ng, 2019).

In summary, 1N-C₁₀ HOM monomers are mainly formed via second-generation pathways, and unimolecular termination of RO₂[•] likely plays an important role leading to higher abundance of carbonyl HOM-ON (C₁₀H₁₅NO_{*x*}) than hydroxy/hydroperoxy HOM-ON (C₁₀H₁₇NO_{*x*}).

3.2.3 2N and 3N-C₁₀ monomers

C₁₀ monomers with 2 and 3 nitrogen atoms accounted for 27 % and 1 % of HOM monomers, respectively. They were likely formed via the reaction of a second attack



Scheme 1. Illustrative scheme for HOM formation in the limonene + NO₃ reaction. **(a)** Example formation pathways leading to first-generation 1N-C₁₀ HOM-RO₂ radicals (C₁₀H₁₆NO_x[•] with even or odd numbers of O-atoms). **(b)** Second-generation scheme involving the formation of endolim. **(c)** Scheme of intramolecular termination of RO₂[•] radicals forming carbonyl products taking the C₁₀H₁₆NO₉[•] radical as an example. Note that the depicted reactions may not be the dominant pathways.

of NO₃ to the first-generation products as the 1N-C₁₀ closed-shell products formed via the reactions shown in scheme 1a should contain a remaining limonene C=C double bond. Typical 2N- and 3N-HOM showed a second-generation time profile (Fig. 4). For clarity, only periods P1 to P3 are shown. This time profile is consistent with the pathways with multiple NO₃ attacks. Scheme 2 shows possible formation pathways of 2N- and 3N-C₁₀ monomers. 2N-C₁₀ HOM were likely to be formed from NO₃ oxidation of 1N-C₁₀ monomers (C₁₀H₁₅NO_x and C₁₀H₁₇NO_x), resulting in C₁₀H₁₅N₂O_x[•] and C₁₀H₁₇N₂O_x[•] (scheme 2a, b). While C₁₀H₁₅N₂O_x[•] ($x = 9-12$) were observed, C₁₀H₁₇N₂O_x[•] could not be uniquely identified because the peaks of the C₁₀H₁₇N₂O_x[•] and C₁₀H₁₅NO_x families are too close in the mass spectra to be separated based on the resolution of our mass spectrometer. 3N-C₁₀ monomers, C₁₀H₁₇N₃O_x, were expected to be formed from limonene via two steps of NO₃ oxidation to the double bonds and an addition of NO₂ to an RO₂ radical, leading to a peroxyxynitrate or peroxyacylnitrate. NO₂ addition reactions may also contribute to the formation of 2N-C₁₀ monomers. The addition of NO₂ to RO₂ radicals could occur either before (scheme 2d) or after (scheme 2c) the second NO₃ attack.

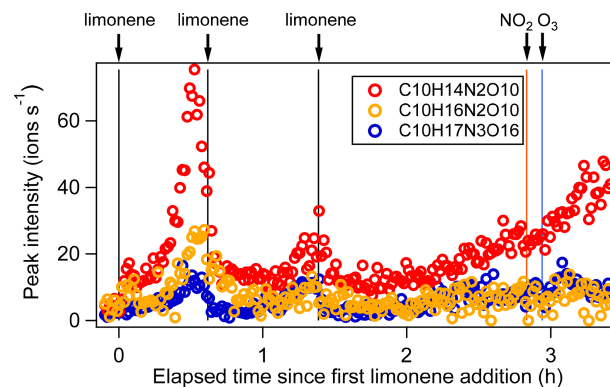


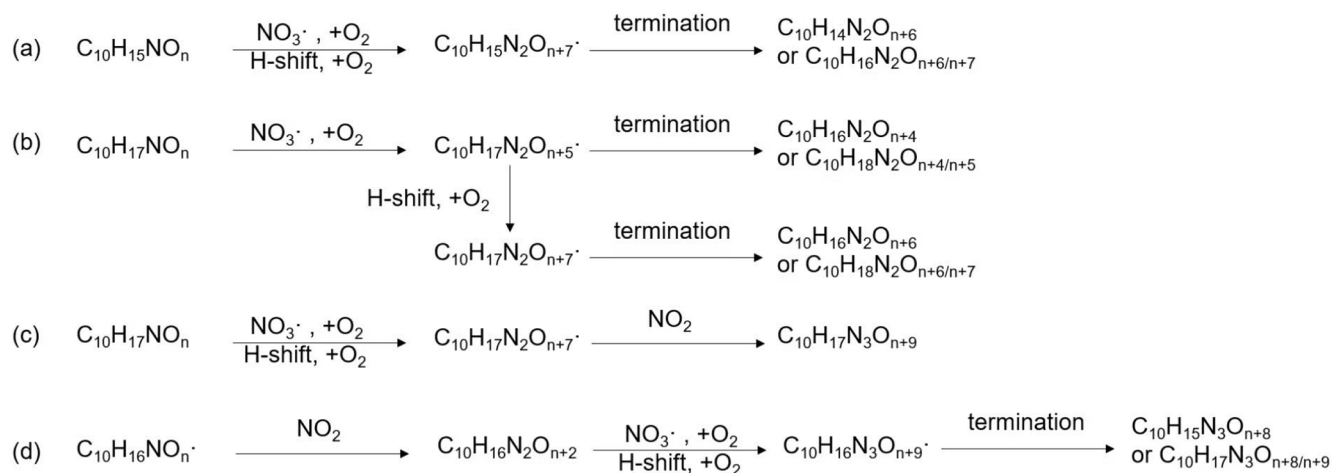
Figure 4. Time series of peak intensity of several monomers C₁₀H₁₄N₂O₁₀, C₁₀H₁₆N₂O₁₀, and C₁₀H₁₇N₃O₁₆ as the representatives of multiple N monomers during the periods P1 to P3.

3.2.4 Formation pathways of C₁₀ monomers without N-atoms and monomers with less than 10 C-atoms

Besides C₁₀ products containing nitrogen atoms, HOM monomers without nitrogen atoms were also identified. Among these products, C₁₀H₁₄O_x ($x = 7-12$) were the most

Table 1. Observed C₁₀H₁₆NO_x[•] radicals (m) and their termination products, including carbonyl compounds (m−17), hydroxyl compounds (m−15), and hydroperoxy compounds (m+1). Their concentrations during period P1a are normalized to that of C₁₀H₁₅NO₁₀, which had the highest concentration among the families of 1N-C₁₀ monomers. Their relative signal intensities during the P1a period are shown in the second line of each cell.

Peroxy radical m	Carbonyl m−17	Hydroxy m−15	Hydroperoxy m+1
C ₁₀ H ₁₆ NO ₆ [•] 1.5 %			
C ₁₀ H ₁₆ NO ₇ [•] 2.0 %			
C ₁₀ H ₁₆ NO ₈ [•] 6.7 %	C ₁₀ H ₁₅ NO ₇ 8.0 %		
C ₁₀ H ₁₆ NO ₉ [•] 6.0 %	C ₁₀ H ₁₅ NO ₈ 25.2 %		C ₁₀ H ₁₇ NO ₉ 3.7 %
C ₁₀ H ₁₆ NO ₁₀ [•] 10.2 %	C ₁₀ H ₁₅ NO ₉ 34.6 %	C ₁₀ H ₁₇ NO ₉ 3.7 %	C ₁₀ H ₁₇ NO ₁₀ 3.6 %
C ₁₀ H ₁₆ NO ₁₁ [•] 6.6 %	C ₁₀ H ₁₅ NO ₁₀ 100.0 %	C ₁₀ H ₁₇ NO ₁₀ 3.6 %	C ₁₀ H ₁₇ NO ₁₁ 3.0 %
C ₁₀ H ₁₆ NO ₁₂ [•] 4.1 %	C ₁₀ H ₁₅ NO ₁₁ 39.0 %	C ₁₀ H ₁₇ NO ₁₁ 3.0 %	C ₁₀ H ₁₇ NO ₁₂ 2.3 %
	C ₁₀ H ₁₅ NO ₁₂ 41.2 %	C ₁₀ H ₁₇ NO ₁₂ 2.3 %	C ₁₀ H ₁₇ NO ₁₃ 1.5 %
C ₁₀ H ₁₆ NO ₁₄ [•] 4.7 %	C ₁₀ H ₁₅ NO ₁₃ 6.7 %	C ₁₀ H ₁₇ NO ₁₃ 1.5 %	C ₁₀ H ₁₇ NO ₁₄ 1.8 %
		C ₁₀ H ₁₇ NO ₁₄ 1.8 %	



Scheme 2. Possible formation pathways of C₁₀-monomers containing 2 nitrogen atoms (**a**, **b**) and 3 nitrogen atoms (**c**, **d**). Termination denotes reactions of RO₂[•] with other RO₂[•] or HO₂, or unimolecular reactions, leading to closed-shell products.

prevalent family, which were also detected in limonene ozonolysis (Jokinen et al., 2015). The C₁₀H₁₄O_x family showed a time series typical of first-generation products (Fig. S8). C₁₀H₁₄O_x and C₁₀H₁₆O_x could be formed from limonene + NO₃ with C₁₀H₁₆NO_x[•] terminating their autoxidation by migration of the α-NO₃ H-atom, eliminating an NO₂ fragment (scheme S2) (Novelli et al., 2021). Alternatively, these products could be formed via the reaction of O₃ with limonene (scheme S2). Either way, C₁₀H₁₄O_x and C₁₀H₁₆O_x were formed via first-generation pathways.

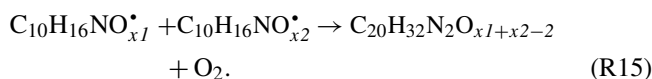
We also observed monomers with carbon atom number less than 10. During the P1a period, C₉ monomer families were the most abundant contributors to C < 10 HOM monomers, followed by C₈ families. The majority of C₉ monomers were C₉H₁₅NO_x (x = 7–13) (time series shown in Fig. S9) and C₉H₁₃NO_x (x = 8–14). The loss of one carbon atom may follow the mechanism shown in scheme S3 (Fry et al., 2011; Bianchi et al., 2019). The major product family in C₈ monomers is C₈H₁₁NO_x (x = 6, 7, 9–13). While during period P1a C₈H₁₁NO_x compounds could be hardly observed, their concentrations increased considerably in the later periods (Fig. S10). The gas-phase concentration of C₈H₁₁NO₇ was even the highest among all compounds in later periods (highest intensity signal in Fig. 2b). This is partly attributed to the relatively high volatility of C₈ compounds compared with C₁₀ HOM species and accretion products, which tend to condense on particles. The major family in C₇ monomers, C₇H₉NO_x (x = 6–13), showed a time series pattern similar to C₈H₁₁NO_x compounds (Fig. S11). Such a time profile indicates that C₇ and C₈ products were likely a result of multi-generation gas-phase reactions.

3.3 Dimers and their formation

Among dimers, C₂₀ products were the most abundant, followed by C₁₉ products. Among C₂₀ and C₁₉ dimers, the most prevalent families included C₂₀H₃₂N₂O_x (x = 9–20), C₂₀H₃₃N₃O_x (x = 12–20), C₂₀H₃₁NO_x (x = 10–15), C₂₀H₃₁N₃O_x (x = 14–20), C₂₀H₃₄N₄O_x (x = 15–20), and C₁₉H₃₀N₂O_x (x = 10–18) (Fig. S5). The O/C ratio of dimers did not exceed one, while that of monomers was as high as two. This could be due to oxygen atom loss and participation of less oxygenated RO₂[•] in the dimer formation as discussed below. Time series of dimers also showed different behavior compared to monomers. For example, compounds of the C₂₀H₃₂N₂O_x family only reached a considerable peak intensity in period P1 and decreased rapidly thereafter, while the signal intensity in periods P2 to P6 were low (Fig. 5). Generally, other dimers showed similar patterns (Figs. S12–S14), though the difference of their concentration between P2–P6 and P1 were not as large as for the C₂₀H₃₂N₂O_x family. The time when signals of several dimers (e.g., C₂₀H₃₂N₂O_x, C₂₀H₃₃N₃O_x, C₂₀H₃₄N₄O_x) dropped substantially matched the time of new particle formation (NPF) and the onset of particle growth, indicating that

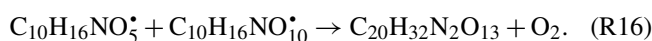
some dimers were likely involved in the early growth of particles. Such a behavior is expected since dimers have a much lower volatility than monomers. This observation is consistent with the limonene + NO₃ laboratory study by Faxon et al. (2018) that found a significant fraction of HOM dimer derived in the particle phase.

In general, C₂₀H₃₂N₂O_x showed an overlaying time profile of first- and second-generation products (Fig. 5). C₂₀H₃₂N₂O_x were likely formed via the accretion reaction between two monomer RO₂[•] (C₁₀H₁₆NO_x[•]):

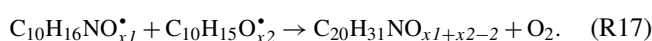


Since C₁₀H₁₆NO_x[•] can be first- or second-generation products, the resulting dimers C₂₀H₃₂N₂O_x can also be first- or second-generation products. The time series shows that C₂₀H₃₂N₂O_x with lower O number presented more of a first-generation product time profile (Fig. 5), while the relative contribution of second-generation formation was observed to increase with oxygen number.

We compared the observed dimer formula with those expected based on accretion reactions of HOM-RO₂[•]. x in the C₂₀H₃₂N₂O_x observed was ≥ 9; however, according to the accretion mechanism and the observed C₁₀H₁₆NO_x[•] (x ≥ 6), x in C₂₀H₃₂N₂O_x should be ≥ 10 (6 + 6 – 2 = 10). Moreover, as the most abundant RO₂[•] within the C₁₀H₁₆NO_x[•] family was C₁₀H₁₆NO₁₀[•] (Table 1), the most abundant C₂₀H₃₂N₂O_x would have an oxygen number of 18 if they were exclusively formed by the accretion reaction of HOM RO₂[•]. This contradicted the fact that the most abundant molecule among the C₂₀H₃₂N₂O_x family was C₂₀H₃₂N₂O₁₃. The findings above could only be explained by the participation of less oxygenated RO₂[•] such as C₁₀H₁₆NO_{5,6}[•] in the accretion reaction (Berndt et al., 2018a, b; McFiggans et al., 2019). C₁₀H₁₆NO₅[•] was not detected by our CI-API-TOF, which is attributed to the lower detection sensitivity of molecules with O number ≤ 5 in the NO₃[−]-CIMS (Riva et al., 2019). Still, C₁₀H₁₆NO₅[•] is the first RO₂ radical formed in the limonene + NO₃ reaction (scheme 1a) so a high mass flux has to pass through this RO₂[•]. If we assume that the abundance of C₁₀H₁₆NO₅[•] was high, and considering that the concentration of C₁₀H₁₆NO₁₀[•] was the highest in the C₁₀H₁₆NO_x[•] family, their accretion reaction (R16) could form C₂₀H₃₂N₂O₁₃ and support that C₂₀H₃₂N₂O₁₃ was the most abundant C₂₀ dimer product:



Time series of dimers with different numbers of N atoms were different, indicating different formation pathways. For example, the C₂₀H₃₁NO_x family were mainly first-generation products (Fig. S12), which may be formed via the following reaction:



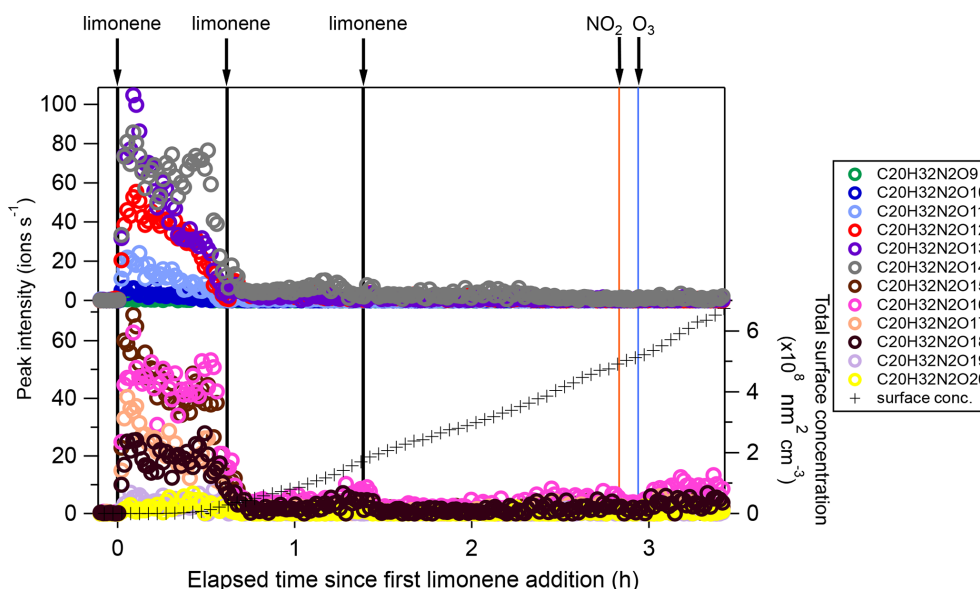


Figure 5. Time series of peak intensity of the C₂₀H₃₂N₂O_x family compounds during the periods P1 to P3. The cross markers (lower right y axis) indicate total particle surface concentration.

C₁₀H₁₅O_x[•] were first-generation radicals (Sect. 3.2.4), while C₁₀H₁₆NO_x[•] were mainly second-generation radicals. C₁₀H₁₆NO_x[•] could also be formed via first-generation pathway as discussed above (scheme 1a), but that was not borne out by the time profile, suggesting a fast termination of first-generation C₁₀H₁₆NO_x[•] radicals. Reaction (R17) could be one of the termination pathways of first-generation C₁₀H₁₆NO_x[•] based on the first-generation time profile of C₂₀H₃₁NO_x. In the study by Faxon et al. (2018), the formation of 1N-C₂₀ dimers was explained by a mechanism involving two 1N-RO₂ radicals which produced HNO₃ as a by-product. However, C₁₀ RO₂ radicals without nitrogen atoms were identified in our study, which provided a direct formation pathway of 1N-C₂₀ dimers through reaction (R17).

On the other hand, C₂₀H₃₃N₃O_x and C₂₀H₃₄N₄O_x were mainly second-generation products (Figs. S13, S14). C₂₀H₃₃N₃O_x and C₂₀H₃₄N₄O_x were likely to be formed via NO₃ oxidation of dimers containing less nitrogen atoms, and were thus second-generation products. The related radicals were also detected, such as C₂₀H₃₂N₃O_x[•] ($x = 16$ – 19) and C₂₀H₃₁N₂O_x[•] ($x = 13$ – 16). Possible formation pathways of dominant oligomer families are displayed in Table 2. We cannot exclude that the formation pathway of C₂₀H₃₃NO_x, C₂₀H₃₄N₄O_x, and C₁₉H₃₁NO_x may also involve limonene oxidation by OH[•] (Table 2), which can be formed in the ozonolysis of limonene as a minor pathway. In addition, the high abundance of C₂₀H₃₁NO_x ($x = 10$ – 15) among the dimers may be partly attributed to a contribution of the reaction of limonene with O₃.

The initial drop of the products (dimers and monomers) in Figs. 1, S8, and S12 during P1 (the characteristic time of the fastest decay was 15, 10, and 13 min, respectively)

is attributed to the balance of their sources via the reaction of limonene with NO₃, their wall loss, and their potential loss by the reaction with NO₃. The characteristic time of the fastest decay of the HOM over the second limonene addition in Figs. 1, 4, 5, S12, and S13 are 4–8 min. These decays can be explained by the wall loss rate (characteristic time $\sim$ 8 min) and condensation sink of vapor loss to particles according to the study of Kulmala et al. (2012) (characteristic time $\sim$ 13 min). The characteristic times of the fastest decay of the HOM at the end of P2 in Figs. S12 and S13 are 1.4–3.4 min, which can also be well explained by the updated wall loss rate and condensation sink of vapor loss to particles at the end of P2 (characteristic time $\sim$ 1.4 min). In addition, for some HOM (e.g., C₁₀H₁₅NO₁₀, Fig. 1; C₁₀H₁₄N₂O₁₀, Fig. 4; C₂₀H₃₃N₃O₁₇, Fig. S13; C₂₀H₃₄N₄O₁₇, Fig. S14), the times of limonene additions (except for the first time) matched the time when HOM signals dropped rapidly. This phenomenon implies a sudden decrease of the source of these HOM at limonene additions as sinks including the losses to walls and particles were largely invariant in such a short time. The decrease of the source may be attributed to the rapid depletion of NO₃ at limonene injections (Fig. 1). As many of these HOM are second-generation products, i.e., formed via the reactions of first-generation products with NO₃, the depletion of NO₃ could lead to sudden decreases of the source of the second-generation HOM, which accounted for most HOM in the study.

In summary, HOM dimers are likely to be formed via accretion reactions of monomer RO₂[•], and some dimers can undergo secondary oxidation by NO₃. Some dimers were likely involved in the early growth of SOA particles.

Table 2. Major dimer and trimer families and their possible formation pathways.

Dimer/trimer family	Possible formation pathways
C ₂₀ H ₃₂ N ₂ O _x	C ₁₀ H ₁₆ NO _x [•] + C ₁₀ H ₁₆ NO _x [•]
C ₂₀ H ₃₃ N ₃ O _x /C ₂₀ H ₃₁ N ₃ O _x	C ₂₀ H ₃₂ N ₂ O _x + NO ₃ + HO ₂ [•] /RO ₂ [•]
C ₂₀ H ₃₁ NO _x	C ₁₀ H ₁₆ NO _x [•] + C ₁₀ H ₁₅ O _x [•]
C ₂₀ H ₃₃ NO _x	C ₁₀ H ₁₆ + OH [•] + C ₁₀ H ₁₆ NO _x [•]
C ₂₀ H ₃₄ N ₄ O _x	(C ₁₀ H ₁₆ N ₂ O _x + OH [•]) + (C ₁₀ H ₁₆ N ₂ O _x + OH [•])
C ₁₉ H ₃₀ N ₂ O _x	C ₁₀ H ₁₆ NO _x [•] + C ₉ H ₁₄ NO _x [•]
C ₁₉ H ₃₁ N ₃ O _x	C ₁₉ H ₃₀ N ₂ O _x + NO ₃ + HO ₂ [•] /RO ₂ [•]
C ₁₉ H ₂₉ NO _x	C ₉ H ₁₄ NO _x [•] + C ₁₀ H ₁₅ O _x [•]
C ₁₉ H ₃₁ NO _x	C ₁₀ H ₁₆ + OH [•] + C ₉ H ₁₄ NO _x [•]
C ₃₀ H ₄₈ N ₄ O _x	C ₂₀ H ₃₂ N ₃ O _x [•] + C ₁₀ H ₁₆ NO _x [•]
C ₃₀ H ₄₇ N ₃ O _x	C ₂₀ H ₃₁ N ₂ O _x [•] + C ₁₀ H ₁₆ NO _x [•]

3.4 Trimers and their formation

Trimers (C_{26–30}) were dominated by C₃₀ compounds (Fig. S6, Table S1). To the best of our knowledge, this is the first study that identified gas-phase trimers in the limonene + NO₃ reaction. The O/C ratio of trimers was lower than that of monomers and dimers, suggesting possible multiple accretion reactions in their formation pathways, which lose 2 oxygen atoms in each reaction. As each accretion reaction terminates the peroxy radical chain, the observation of trimers also implies that some dimers could further react with NO₃, creating dimer RO₂[•]. The most prevalent product families were C₃₀H₄₈N₄O_x ($x = 16–24$) and C₃₀H₄₇N₃O_x ($x = 18, 19, 21, 23, 24$), which were likely formed via the most abundant monomer RO₂[•] radicals – C₁₀H₁₆NO_x[•] and the most abundant dimer RO₂[•] radicals – C₂₀H₃₂N₃O_x[•] and C₂₀H₃₁N₂O_x[•]. Trimers from other monoterpenes + NO₃ have been observed in previous laboratory studies. For example, C₃₀H₄₈N₄O₁₆ and C₃₀H₄₇N₃O₁₆ were observed in the mass spectra of α -pinene + NO₃ SOA by C. Wu et al. (2021), and C₃₀H₄₇N₃O₁₃ was identified in β -pinene + NO₃ SOA by Clafin and Ziemann (2018).

Similar to their precursors C₂₀H₃₂N₂O_x, C₃₀H₄₈N₄O_x showed negligible signal except in period P1, and presented an overlaying time profile of first- and second-generation product pattern (Fig. 6). For comparison, gas-phase trimer products were not observed in the β -pinene + NO₃ reaction (Shen et al., 2021), and the trimers observed in SOA from β -pinene + NO₃ are likely formed via particle phase reactions (Clafin and Ziemann, 2018). An efficient gas-phase trimer production via subsequent accretion reactions between peroxy radicals requires that the precursor dimer has a high enough reactivity to create a dimer RO₂[•], e.g., via NO₃ reaction to a double bond. This suggests that the VOC containing at least two double bonds are likely more favorable to form trimers, which is consistent with our previous findings that trimers were formed in the NO₃ reaction with isoprene which also contains two double bonds (Zhao et al., 2021), while they were not observed in the reaction of NO₃ with

β -pinene which contains only one double bond (Shen et al., 2021).

3.5 “Primary” incremental HOM yields

We chose period P1 for the calculation of HOM yields in order to minimize the influence of the condensational sink on HOM concentration. However, both first-generation and second-generation products existed in this period, as discussed in Sect. 3.2 through Sect. 3.4 and supported by the time-behavior of the total HOM concentration (Fig. S15). Period P1 can be roughly divided into three phases based on the trends in HOM concentration. Shortly after the limonene injection, large quantities of HOM were produced (first-production phase) followed by a balanced intermediate phase when HOM concentrations stopped increasing. After the intermediate phase, HOM concentrations began to increase again (second-production phase). The first-production phase overlapped with the time span where limonene, NO₃, and N₂O₅ concentrations decreased, implying the dominance of first-generation HOM production process. During the second production period, wall loss was compensated by second-generation HOM formation, leading to another rise of the total HOM concentrations. Therefore, we use the first-production phase to estimate primary HOM production, determined over the first 3 min of the experiment. The calculated “primary” HOM molar yield is 1.5 %^{+1.7%}_{–0.7%}. This value is significantly lower than the HOM yield of 5 % to 17 % in earlier limonene ozonolysis experiments (Ehn et al., 2014; Jokinen et al., 2015; Pagonis et al., 2019). It should be emphasized that second-generation HOM, which contributed greatly to the limonene + NO₃ reaction system, is not included in this primary HOM yield.

3.6 Contribution of HOM to particle formation and growth

We observed nucleation and growth of SOA particles in the limonene + NO₃ reaction. We calculated the contribution

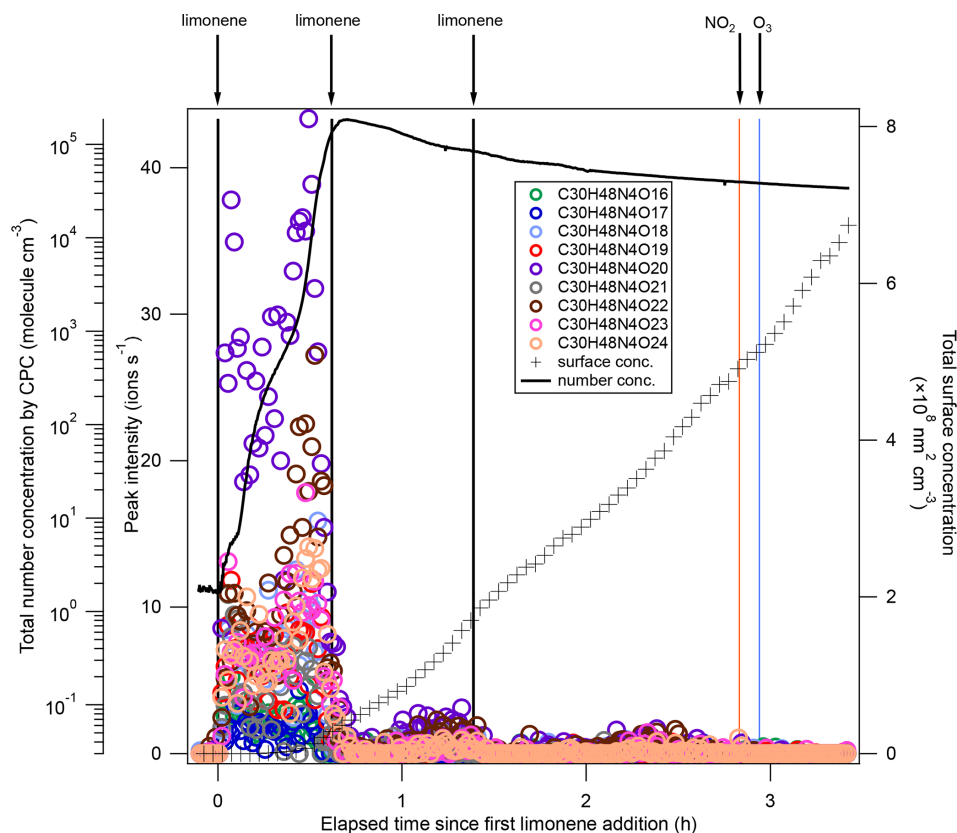


Figure 6. Time series of peak intensity of the C₃₀H₄₈N₄O_x family compounds during the periods P1 to P3. The solid black line refers to total number concentrations detected by CPC. The cross markers (right y axis) indicate total particle surface concentration.

of HOM to SOA formation and particle growth, and compared it to the measured particle growth (Fig. 7a). We assumed different scenarios of HOM uptake on aerosol particles, using the calculation methods described in the literature (Ehn et al., 2014; Seinfeld and Pandis, 2006; Nieminen et al., 2010). The assumption that all HOM irreversibly condense on the particles (scenario 1) resulted in a strong overestimation of particle mass growth (red markers in Fig. 7a). Applying the parameterizations of Mohr et al. (2019) (scenario 2a) or Peräkylä et al. (2020) (scenario 2b) for classification and accounting only LVOC- and ULVOC/ELVOC-HOM for irreversible uptake framed the observed values (blue and yellow markers in Fig. 7a). While scenario 2a agreed quite well with the observations and only slightly overestimated SOA concentrations after 7 h by +11 %, scenario 2b underestimated the SOA concentration at the end by −53 %. The agreement between the modeled and observed SOA concentration suggests that HOM, and particularly LVOC- and ULVOC/ELVOC-HOM, play a major role in growth of SOA particles in this study. This is consistent with the work by Faxon et al. (2018) who found that many of the dimers are ELVOC, which is also supported by our calculation result based on the method of Mohr et al. (2019).

Since neither SO₂ nor H₂SO₄ was added in our experiment, new particle formation (NPF) could be attributed to the nucleation initiated by HOM of low volatility. HOM trimers with as many as 30 carbon atoms were identified in the early stage of this study, and their sudden loss matched the onset of rapid formation of SOA. Trimers identified in our experiment are classified as ULVOC/ELVOC, with much lower volatility than monomers and dimers (Fig. 7b). Therefore, NPF in the current study can more likely be attributed to HOM trimers since they have the strongest potential of initiating nucleation, although we cannot rule out some contributions of dimers in the NPF. In contrast, in an earlier experiment investigating the NO₃-initiated oxidation of β-pinene also conducted in the SAPHIR chamber under similar conditions, new particles were barely formed (< 20 cm⁻³) (Shen et al., 2021). As already mentioned above, no trimer HOM products were observed in that study, and only molecules with C ≤ 20 were detected (Sect. 3.4). Extremely low volatile organic vapors formed in α-pinene ozonolysis have been shown to induce nucleation and drive initial particle growth in the atmosphere (Tröstl et al., 2016; Kirkby et al., 2016). Since our experiment of NO₃ oxidation of limonene was performed under near atmospheric conditions, such NPF events induced by the oxidation of limonene by NO₃ could

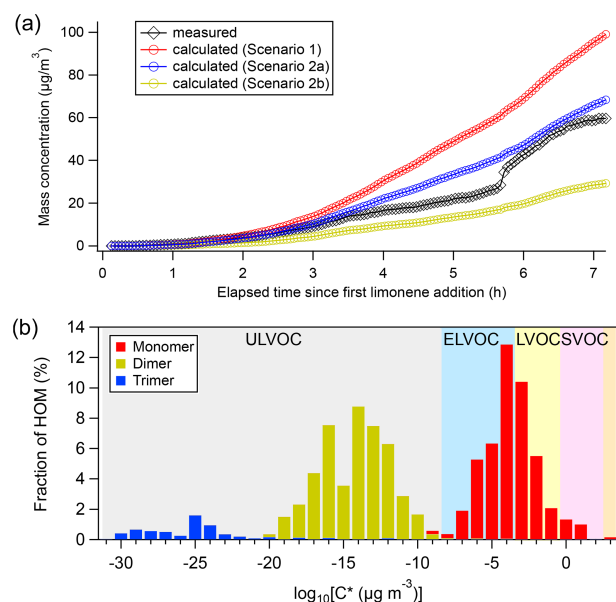


Figure 7. (a) Comparison of measured particle concentrations (black) against those predicted from condensation of measured HOM on aerosol particles, where red markers were calculated under scenario 1, and blue and yellow markers were calculated under scenario 2 (only considering the condensation of ULVOC, ELVOC, and LVOC), with the volatility calculated using the method by Mohr et al. (2019) scenario 2a) and Peräkylä et al. (2020) (scenario 2b) respectively. (b) HOM volatility distribution using formula provided by Mohr et al. (2019). Average concentrations of HOM in the P1 period were used to calculate the fraction of HOM.

also occur in the ambient atmosphere. Although monoterpene concentrations in this study (0–0.92 ppbv) are higher than in most ambient regions, they are still in the range of ambient concentrations (~ 0.01 –1 ppbv) (e.g., Coggon et al., 2021; Wang et al., 2022), especially for forested regions (e.g., Xu et al., 2015; Kontkanen et al., 2016; Janson, 1992). Assuming that dimers react with NO₃ at a rate similar to limonene, and that they have a condensation sink similar to H₂SO₄ (10^{-3} – 10^{-1} s⁻¹) (Dada et al., 2020), the lifetime with respect to NO₃ at an NO₃ concentration of 5–300 ppt and to condensation on particles are ~ 0.1 –10 and ~ 0.1 –20 min, respectively. Therefore, although aerosols may scavenge HOM dimers in the ambient atmosphere, dimers can still react with NO₃ at nighttime, forming trimers. Such reactions are particularly important when the ambient aerosol concentration is low. Several field observations have shown NPF events taking place at nighttime where biogenic emissions dominate (Kammer et al., 2018; Huang et al., 2019). The work by Ortega et al. (2012) demonstrated an important role of monoterpene ozonolysis products in nocturnal NPF events in chamber experiments. In a previous laboratory study, limonene + NO₃ appears more effective at initiating nucleation than the limonene + O₃ reaction (Fry et al., 2014), which supports that limonene + NO₃ can play a significant

role in nighttime nucleation. Our study suggests that NO₃ oxidation of limonene could contribute to the nighttime NPF via HOM trimer formation. In contrast, we infer that NO₃ reactions with other monoterpenes containing only one double bond such as α -pinene and β -pinene are less likely candidates for nighttime NPF, because gas-phase trimers are not observed.

4 Conclusion and implications

HOM formation in the reaction of limonene with NO₃ was investigated in the SAPHIR chamber. About 280 gas-phase HOM products were identified, including monomers (C₆–10, O₆–16, N₀–3), dimers (C₁₇–20, O₇–20, N₀–4), and trimers (C₂₇–30, O₁₆–25, N₁–6). Nitrogen-containing products dominated the HOM, with compounds of the C₁₀H₁₅–17NO₆–14 series being the most prevalent. Dimers contributed 47 % in the early stage of the experiment when particle surface concentration was rather low ($< 6 \times 10^4$ nm² cm⁻³), which was similar to monomers (47 %). Tentative formation pathways of major families were proposed in this work based on their time-dependent concentration profiles.

In HOM monomers, the abundance of carbonyl compounds significantly exceeded that of hydroxy or hydroperoxy compounds, indicating the significance of unimolecular termination of HOM-RO₂ radicals. Both RO₂ autoxidation and alkoxy-peroxy pathways were found to be important in the formation of HOM monomers. Monomers with 1 nitrogen atom (1N-monomers) contained both first- and second-generation products, which could be formed via NO₃ oxidation of limonene and its first-generation products, with the latter being more important. Monomers with 2 nitrogen atoms were classified as second-generation products, which could be formed via NO₃ oxidation of the remaining C=C double bond of 1N-monomers.

Dimers showed both first- and second-generation time pattern. Dimers were mostly formed via accretion reactions between monomer RO₂ radicals, resulting in a decrease in O/C ratio compared to monomers. The initial less oxygenated RO₂, including the C₁₀H₁₆NO₅ radical that cannot be observed in our instrument, likely played an important role in dimer formation, based on the comparison of measured dimers against expected dimer identity and concentrations according to accretion monomer RO₂ reactions. Trimers were likely formed via accretion reactions between monomer RO₂ and dimer RO₂ radicals formed from secondary reactions of dimers with NO₃. Trimer formation is thus linked to the presence of two double bonds in limonene, of which the first reacts with NO₃ leading to dimer products while the remaining C=C double bond provides a reactive site for further oxidation of the dimers by NO₃, forming dimer RO₂ radicals.

A “primary” HOM molar yield of $1.5\%_{-0.7}^{+1.7}$ in the limonene + NO₃ reaction was estimated, including only the

first-generation HOM. Second-generation HOM contributed greatly to monomers, dimers, and trimers, and hence the HOM yield we obtained is a lower limit of the total HOM yield, and is likewise much lower than the total HOM yield in the reaction of limonene with ozone (5 % to 17 %) (Ehn et al., 2014; Jokinen et al., 2015; Pagonis et al., 2019).

NPF observed in this work was likely related to the trimer formation due to much lower volatility of trimers compared to monomers and dimers. The SOA concentration in the limonene + NO₃ reaction could be explained by the condensation of the HOM belonging to LVOC and ULVOC/ELVOC classes assuming irreversible uptake, indicating an important role of HOM for growth of SOA particles in this reaction system. To our knowledge, this work is the first identifying trimer products from the limonene + NO₃ reaction system, suggesting that limonene + NO₃ is a possible crucial source of new particles formed in nighttime biogenic emission-dominated areas (Kammer et al., 2018; Huang et al., 2019). Our work highlights the need to consider the role of limonene + NO₃ in NPF in models simulating nighttime aerosols formation in biogenic-emission dominated areas, especially with large limonene emissions. In addition, comparison with the reactions of NO₃ with isoprene (Zhao et al., 2021) and other monoterpenes (Shen et al., 2021) reveals a strong dependence of HOM products on the molecular structure of the VOC species in NO₃-initiated chemistry.

The concentration of limonene and NO₃ in this study was on the order of few ppb and a few to 100 ppt, respectively, which are similar to the ambient levels in rural and forest regions affected by anthropogenic emissions (Brown and Stutz, 2012). The chemical lifetime of RO₂[•] was of the order of 50 to 500 s, which is also similar to ambient conditions at nighttime (Fry et al., 2018). The RO₂[•] loss pathway in our study was dominated by the reactions RO₂[•] + NO₃ and RO₂[•] + RO₂[•], which is relevant for the RO₂[•] fate in urban areas and forested areas influenced by an urban plume at nighttime. However, in more pristine forested regions, the RO₂[•] fate is mostly determined by RO₂[•] + HO₂ and RO₂[•] + RO₂[•], as shown by Bates et al. (2022) for the example of a Southeast US forest. As NO₃ concentration is generally enhanced with increased anthropogenic emissions, RO₂[•] + NO₃ will become more important going from remote to urban areas. Therefore, the HOM products and their formation process in our study are relevant for rural and forested regions influenced by anthropogenic plumes and ambient urban regions with high volatile commercial products emissions, as limonene is a typical component of volatile chemical products (VCPs) (Nazaroff and Weschler, 2004). In these regions, HOM from monoterpene + NO₃ reactions can be major components of nighttime SOA. As nitrooxy-RO₂ fate can strongly affect the oxidation product distribution and SOA yield as shown for the reaction of α -pinene with NO₃ (Bates et al., 2022), more studies of HOM formation by NO₃ at various RO₂[•] fates are needed to be representative of various environments, including (remote) forested regions.

This study also highlights the important role of second-generation chemistry in HOM formation, which needs to be further investigated and should be included in chemical mechanisms used in numerical models. Additional work is also needed to investigate the role of different HOM formed via NO₃-initiated BVOC oxidation reactions in NPF and growth of SOA particles in order to better constrain the climatic and environmental effects of BVOC + NO₃ chemistry.

Data availability. All the data in the figures and tables of this study are available upon request to the corresponding author (t.mentel@fz-juelich.de or dfzhao@fudan.edu.cn).

Supplement. The supplement related to this article is available online at: <https://doi.org/10.5194/acp-22-11323-2022-supplement>.

Author contributions. DZ, TFM, and HF designed the study. IP, HF, IHA, RT, FR, and DZ carried out instrument deployment and operation. YG analyzed the MS data and did the MCM simulation with the aid of DZ, HS, and HL. YG, DZ, TFM, and LV interpreted the compiled data set. LV examined the reaction schemes. YG, DZ, TFM, and LV wrote the paper and HS, IP, HL, SK, LV, HF edited the paper. All the co-authors discussed the results and commented on the paper.

Competing interests. The contact author has declared that none of the authors has any competing interests.

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