

Highly oxygenated organic molecules (HOM) formation in the isoprene oxidation by NO₃ radical

Defeng Zhao^{1, 2, 3}, Iida Pullinen^{2, a}, Hendrik Fuchs², Stephanie Schrade², Rongrong Wu², Ismail-Hakki Acir^{2, b}, Ralf Tillmann², Franz Rohrer², Jürgen Wildt², Yindong Guo¹, Astrid Kiendler-Scharr², Andreas Wahner², Sungah Kang², Luc Vereecken², Thomas F. Mentel²

¹Department of Atmospheric and Oceanic Sciences & Institute of Atmospheric Sciences, Fudan University, Shanghai, 200438, China;

²Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich, 52425, Jülich, Germany

³Big Data Institute for Carbon Emission and Environmental Pollution, Fudan University, Shanghai, 200438, China

^aNow at: Department of Applied Physics, University of Eastern Finland, Kuopio, 7021, Finland.

^bNow at: Institute of Nutrition and Food Sciences, University of Bonn, Bonn, 53115, Germany;

Correspondence to: Thomas F. Mentel (t.mentel@fz-juelich.de), Defeng Zhao (dfzhao@fudan.edu.cn)

Abstract

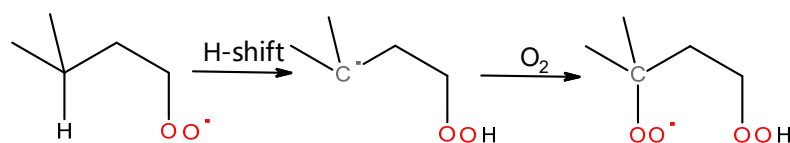
Highly oxygenated organic molecules (HOM) are found to play an important role in the formation and growth of secondary organic aerosol (SOA). SOA is an important type of aerosol with significant impact on air quality and climate. Compared with the oxidation of volatile organic compounds by O₃ and OH, HOM formation in the oxidation by NO₃ radical, an important oxidant at night-time and dawn, has received less attention. In this study, HOM formation in the reaction of isoprene with NO₃ was investigated in the SAPHIR chamber (Simulation of Atmospheric PHotochemistry In a large Reaction chamber). A large number of HOM including monomers (C₅), dimers (C₁₀), and trimers (C₁₅), both closed-shell compounds and open-shell peroxy radicals, were identified and were classified into various series according to their formula. Their formation pathways were proposed based on the peroxy radicals observed and known mechanisms in the literature, which were further constrained by the time profiles of HOM after sequential isoprene addition to differentiate first- and second-generation products. HOM monomers containing one to three N atoms (1-3N monomers) were formed, starting with NO₃ addition to carbon double bond, forming peroxy radicals (RO₂), followed by autooxidation. 1N monomers were formed by both the direct reaction of NO₃ with isoprene and of NO₃ with first-generation products. 2N-monomers (e.g. C₅H₈N₂O_n (n=7-13), C₅H₁₀N₂O_n (n=8-14)) were likely the termination products of C₅H₉N₂O_n•, which was formed by the addition of NO₃ to C5-hydroxynitrate (C₅H₉NO₄), a first-generation product containing one carbon double bond. 2N-monomers, which were second-generation products, dominated in monomers and accounted for ~34% of all HOM, indicating the important role of second-generation oxidation in HOM formation in the isoprene+NO₃ reaction under our experimental conditions. H-shift of alkoxy radicals to form peroxy radicals and subsequent autooxidation (“alkoxy-peroxy” pathway) was found to be an important pathway of HOM formation. HOM dimers were mostly formed by the accretion reaction of various HOM monomer RO₂ and via the termination reactions of dimer RO₂ formed by further reaction of closed-shell dimers with NO₃ and possibly by the reaction of C5-RO₂ with isoprene. HOM trimers were likely formed by the accretion reaction of dimer RO₂ with monomer RO₂. The concentrations of different HOM showed distinct time profiles during the reaction, which was linked to their formation pathway. HOM concentrations either showed a typical time profile of first-generation products, or of second-generation products, or a combination of both, indicating multiple formation pathways and/or multiple isomers. Total HOM molar yield was estimated to be 1.2%^{+1.3%}_{-0.7%}, which corresponded to a SOA yield of ~3.6% assuming the molecular weight of C₅H₉NO₆ as the lower limit.

40 This yield suggests that HOM may contribute a significant fraction to SOA yield in the reaction of isoprene with
41 NO_3 .

1 Introduction

Highly oxygenated organic molecules (HOM) are an important class of compounds formed in the oxidation of volatile organic compounds (VOC) including biogenic VOC (BVOC) and anthropogenic VOC (Crounse et al., 2013; Ehn et al., 2014; Jokinen et al., 2014; Rissanen et al., 2014; Jokinen et al., 2015; Krechmer et al., 2015; Mentel et al., 2015; Rissanen et al., 2015; Kenseth et al., 2018; Molteni et al., 2018; Garmash et al., 2019; McFiggans et al., 2019; Molteni et al., 2019; Quelevar et al., 2019). A number of recent studies have demonstrated that HOM play a pivotal role in both nucleation and also particle growth of pre-existing particles, thus contributing to secondary organic aerosol (SOA) (Ehn et al., 2014; Kirkby et al., 2016; Tröstl et al., 2016). Particularly, in the early stage of aerosol growth, HOM may contribute a significant fraction of SOA mass (Tröstl et al., 2016).

HOM are formed by the autoxidation of peroxy radicals (RO_2), which means they undergo intramolecular H-shift forming alkoxy radicals, followed by O_2 addition leading to formation of new RO_2 as shown below (Vereecken et al., 2007; Crounse et al., 2013; Ehn et al., 2017; Bianchi et al., 2019; Møller et al., 2019; Nozière and Vereecken, 2019; Vereecken and Nozière, 2020).



Besides autoxidation, the RO_2 can also react with HO_2 , RO_2 and NO_3 , either forming a series of termination products (R1-3), including organic hydroxyperoxide, alcohol, and carbonyl, or forming alkoxy radicals (RO , R4-5) via the following reactions.



The termination products are detected in the mass spectra at masses $M+1$, $M-15$, $M-17$ respectively with M being the molecular mass of the parent RO_2 (Ehn et al., 2014; Mentel et al., 2015). In case that RO_2 is an acyl peroxy radical, percarboxylic acids and carboxylic acids are formed instead of hydroperoxides and alcohols in R3 and R1, respectively (Atkinson et al., 2006; Mentel et al., 2015). RO_2 can also form HOM dimers by the accretion reaction of two RO_2 (R6) (Berndt et al., 2018a; Berndt et al., 2018b; Valiev et al., 2019). Additionally, HOM can be formed via H-shift in RO followed by O_2 addition (referred to as “alkoxy-proxy” pathway) (Finlayson-Pitts and Pitts, 2000; Vereecken and Peeters, 2010; Vereecken and Francisco, 2012; Mentel et al., 2015). These pathways are summarized in a recent comprehensive review (Bianchi et al., 2019), which also further clarifies HOM definition.

Currently, most laboratory studies of HOM formation focus on the VOC oxidation by OH and O₃ (Crounse et al., 2013; Ehn et al., 2014; Jokinen et al., 2014; Rissanen et al., 2014; Jokinen et al., 2015; Krechmer et al., 2015; Mentel et al., 2015; Rissanen et al., 2015; Kirkby et al., 2016; Tröstl et al., 2016; Kenseth et al., 2018; Molteni et al., 2018; Garmash et al., 2019; McFiggans et al., 2019; Molteni et al., 2019; Quelever et al., 2019; Wang et al., 2020; Yan et al., 2020). HOM formation in the oxidation of VOC with NO₃ has received much less attention. NO₃ is another important oxidant of VOC mainly operating during nighttime. Particularly, NO₃ has high reactivity with unsaturated BVOC such as monoterpene and isoprene. It is often the dominant oxidant of these compounds at night, especially in regions where biogenic and anthropogenic emissions mix (Geyer et al., 2001; Brown et al., 2009; Brown et al., 2011). The reaction products contribute to SOA formation (Xu et al., 2015; Lee et al., 2016). Also, the organic nitrates produced in these reactions play an important role in nitrogen chemistry by altering NO_x concentration, which further influences photochemical recycling and ozone formation in the next day. Among these reaction products, HOM can also be formed (Xu et al., 2015; Lee et al., 2016; Yan et al., 2016). Despite the potential importance, studies of HOM formation in the oxidation of BVOC by NO₃ are still limited compared with the HOM formation via oxidation by O₃ and OH. Although a number of laboratory studies have investigated the reaction of NO₃ with BVOC (Ng et al., 2008; Fry et al., 2009; Rollins et al., 2009; Fry et al., 2011; Kwan et al., 2012; Fry et al., 2014; Boyd et al., 2015; Schwantes et al., 2015; Nah et al., 2016; Boyd et al., 2017; Clafin and Ziemann, 2018; Faxon et al., 2018; Draper et al., 2019; Takeuchi and Ng, 2019; Novelli et al., 2021; Vereecken et al., 2021), these studies mostly focus on either SOA yield and composition, or on the gas-phase chemistry mechanism mainly for “traditional” oxidation products that stem from few oxidation steps.

Importantly, HOM formation in the reaction of NO₃ with isoprene, the most abundant BVOC accounting for more than half of the global BVOC emissions, has not been explicitly addressed yet, to the best of our knowledge. Although isoprene from plants are mainly emitted under light conditions, i.e., in the daytime, isoprene can remain high after sunset in significant concentrations (Starn et al., 1998; Stroud et al., 2002; Brown et al., 2009) because of the reduced consumption by OH and is found to decay rapidly. A substantial fraction of isoprene can then be oxidized by NO₃ (Brown et al., 2009). Regarding the budget of NO₃, the reaction of isoprene with NO₃ can contribute to a significant or even dominant fraction of NO₃ loss at night in regions where VOC is dominated by isoprene such as Northeast US (Brown et al., 2009). Under some circumstances, the reaction of isoprene with NO₃ can contribute to a significant fraction during the afternoon and afterwards (Ayres et al., 2015; Hamilton et al., 2021). The reaction of isoprene with NO₃ is the subject of a number of studies (Ng et al., 2008; Perring et al., 2009; Rollins et al., 2009; Kwan et al., 2012; Schwantes et al., 2015; Vereecken et al., 2021). These studies focus on the oxidation mechanism and “traditional” oxidation products, as well as SOA yields. The initial step is the NO₃ addition to one of the C=C double bonds, preferentially to the carbon C1 (Schwantes et al., 2015), followed by O₂ addition forming a nitrooxyalkyl peroxy radical (RO₂). This RO₂ can undergo the reactions described above, forming a series of products such as C5-nitrooxyhydroperoxide, C5-nitrooxycarbonyl, and C5-hydroxynitrate (Ng et al., 2008; Kwan et al., 2012), as well as methyl vinyl ketone (MVK), potentially methacrolein (MACR), formaldehyde, OH radical, and NO₂ as minor products (Schwantes et al., 2015). A high

nitrate yield (57-95%) was found (Perring et al., 2009; Rollins et al., 2009; Kwan et al., 2012; Schwantes et al., 2015). Products in the particle phase such as C₁₀ dimers were also detected (Ng et al., 2008; Kwan et al., 2012; Schwantes et al., 2015). The SOA yield varies from 2% to 23.8% depending on the organic aerosol concentration (Ng et al., 2008; Rollins et al., 2009). These studies have provided valuable insights in oxidation mechanism, particle yield and composition. However, because HOM formation was not the focus of these studies, only a limited number of products, mainly moderately oxygenated ones (oxygen number ≤ 2 in addition to NO₃ functional groups), were detected in the gas phase. The detailed mechanism of HOM formation and their yields in the reaction of BVOC+NO₃ are still unclear.

In this study, we investigated the HOM formation in the oxidation of isoprene by NO₃. We report the identification of HOM, including HOM monomers, dimers, and trimers. According to the reaction products and literature, we discuss the formation mechanism of these HOM. The formation mechanism of various HOM is further constrained with time series of HOM upon repeated isoprene additions. We also provide an estimate of HOM yield in the isoprene+NO₃ reaction and assess their roles in SOA formation.

2 Experimental

2.1 Chamber setup and experiments

Experiments investigating the reaction of isoprene with NO₃ were conducted in the SAPHIR chamber (Simulation of Atmospheric PHotochemistry In a large Reaction chamber) at Forschungszentrum Jülich, Germany. The details of the chamber have been described before (Rohrer et al., 2005; Zhao et al., 2015a; Zhao et al., 2015b; Zhao et al., 2018). Briefly, SAPHIR is a Teflon chamber with a volume of 270 m³. It can utilize natural sunlight for illumination and is equipped with a louvre system to switch between light and dark conditions. In this study, the experiments were conducted in the dark with the louvres closed.

Temperature and relative humidity were continuously measured. Gas and particle phase species were characterized using a comprehensive set of instruments with the details described before (Zhao et al., 2015b). VOC were characterized using a Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS, Ionicon Analytik, Austria). NO_x and O₃ concentrations were measured using a chemiluminescence NO_x analyzer (ECO PHYSICS TR480) and an UV photometer O₃ analyzer (ANSYCO, model O341M), respectively. OH, HO₂ and RO₂ concentrations were measured using a laser induced fluorescence system (LIF) (Fuchs et al., 2012). NO₃ and N₂O₅ were detected by a custom-built instrument based on cavity ring-down spectroscopy. The design of the instrument is similar to that described by Wagner et al. (2011). NO₃ was directly detected in one cavity by its absorption at 662 nm and the sum of NO₃ and N₂O₅ in a second, heated cavity, which had a heated inlet to thermally decompose N₂O₅ to NO₃. The sampling flow rate was 3 to 4 liters per minute. The detection by cavity ring-down spectroscopy was achieved by a diode laser that was periodically switched on and off with a repetition rate of 200 Hz. Ring-down events were observed by a digital oscilloscope PC card during the time when the laser was switched off and were averaged over 1s. The zero-decay time that is needed to calculate the concentration of NO₃ was measured every 20 s by chemically removing NO₃ in the reaction with excess nitric

oxide (NO) in the inlet system. The accuracy of measurements was limited by the uncertainty in the correction for inlet losses of NO₃ and N₂O₅. In the case of N₂O₅ a transmission of (85±10) % was achieved and in the case of NO₃ of (50±30) %.

Before an experiment, the chamber was flushed with high purity synthetic air (purity>99.9999% O₂ and N₂). Experiments were conducted under dry condition (RH<2 %) and temperature was at 302±3 K. NO₂ and O₃ were added to the chamber first to form N₂O₅ and NO₃, reaching concentrations of ~60 ppb for NO₂ and ~100 ppb for O₃. After around half an hour, isoprene was sequentially added into the chamber for three times at intervals of ~1 h. Around 40 min after the third isoprene injection, NO₂ was added to compensate the loss of NO₃ and N₂O₅. Afterwards, three isoprene additions were repeated in the same way as before. O₃ was added before the fifth and the sixth isoprene addition to compensate for its loss by reaction. The schematic for the experimental procedure is shown in Fig. S1. Experiments were designed such that the chemical system was dominated by the reaction of isoprene with NO₃ and the reaction of isoprene with O₃ did not play a major role (<3% of the isoprene consumption). Figure S2 shows the relative contributions of the reaction of O₃ and NO₃ with isoprene to the total chemical loss of isoprene using the NO₃ and O₃ concentrations measured. The reaction with NO₃ accounted for >95% of the isoprene consumption for the whole experiments. The contribution of the reaction of isoprene with trace amount of OH, mainly produced in the reaction of isoprene+O₃ via Criegee intermediates (Nguyen et al., 2016), is negligible as the OH yield is less than one (Malkin et al., 2010) and thus its contribution is less than that of isoprene+O₃. This is consistent with the contribution determined using measured OH concentration, despite some uncertainty in measured OH concentration due to the interference from NO₃. In these experiments, RO₂ fate is estimated to be dominated by its reaction with NO₃ according to the measured NO₃, RO₂, and HO₂ concentration and their rate constants for the reactions with RO₂ (MCM v3.2(Jenkin et al., 1997; Jenkin et al., 2003; Saunders et al., 2003; Jenkin et al., 2015), via website: <http://mcm.leeds.ac.uk/MCM>) despite uncertainties of the measured RO₂ and HO₂ concentration due to interference from NO₃. As a large portion of RO₂ is not measured by LIF (Vereecken et al., 2021) and thus RO₂ is underestimated, we expected the reaction of RO₂+RO₂ to be also important. Overall, we estimate that the RO₂ fate is dominated the reaction RO₂+NO₃ with significant contribution of RO₂+RO₂.

2.2 Characterization of HOM

In this study we refer to similar definition for HOM by Bianchi et al. (2019), i.e., HOM typically contain six or more oxygen atoms formed via autoxidation and related chemistry of peroxy radicals. HOM were detected using a Chemical Ionization time-of-flight Mass Spectrometer (Aerodyne Research Inc., USA) with nitrate as the reagent ion (CIMS) (Eisele and Tanner, 1993; Jokinen et al., 2012). ¹⁵N nitric acid was used to produce ¹⁵NO₃⁻ in order to distinguish the NO₃ group in target molecules formed in the reaction from the reagent ion. The details of the instrument are described in our previous publications (Ehn et al., 2014; Mentel et al., 2015; Pullinen et al., 2020). The CIMS has a mass resolution of ~4000 (m/dm). Examples of peak fitting are shown in Fig. S3. HOM concentrations were estimated using the calibration coefficient of H₂SO₄ as described by Pullinen et al. (2020) because the charge efficiency of HOM and H₂SO₄ can be assumed to be equal and close to the collision limit (Ehn et al., 2014; Pullinen et al., 2020). The details of the calibration with H₂SO₄ are provided in the supplement S1. Since HOM contain more than six oxygen atoms and their clusters with nitrate ions are quite stable (Ehn et al., 2014), the

charge efficiency of HOM is thus assumed to be equal to that of H_2SO_4 , which is close to the collision limit (Viggiano et al., 1997). If HOM do not charge with nitrate ions at their collision limit or the clusters formed break during the short residence time in the charger, its concentration would be underestimated as pointed by Ehn et al. (2014). Thus, our assumption provides a lower limit of the HOM concentration. The HOM yield was derived using the concentration of the HOM produced, divided by the concentration of isoprene that was consumed by NO_3 . The uncertainty of HOM yield was estimated to -55%/+103%. The loss of HOM to the chamber was corrected using a wall loss rate of $6 \times 10^{-4} \text{ s}^{-1}$ as quantified previously (Zhao et al., 2018). HOM concentrations were also corrected for dilution due to the replenishment flow needed to maintain a constant overpressure of the chamber (loss rate $\sim 1 \times 10^{-6} \text{ s}^{-1}$) (Zhao et al., 2015b). The influence of wall loss correction and dilution correction on HOM yield was $\sim 12\%$ and $<1\%$, respectively. Although the wall loss rate of vapors in this study might not be exactly the same as in our previous photo-oxidation experiments (Zhao et al., 2018), HOM yield is not sensitive to the vapor wall loss rate. An increase of wall loss rate by 100% or a decrease by 50% only changes the HOM yield by 11% and -6%, respectively.

3 Results and discussion

3.1 Overview of HOM

The mass spectra of HOM in the gas phase formed in the oxidation of isoprene by NO_3 are shown in Fig. 1. A large number of HOM were detected. Almost all peaks are assigned HOM containing nitrogen atoms with possibly few exceptions such as $\text{C}_5\text{H}_{10}\text{O}_8$ and $\text{C}_5\text{H}_8\text{O}_{11}$ with very minor peaks ($< \sim 1\%$ of the maximum peak). The reaction products can be roughly divided into three classes: monomers (C_5 , $\sim 200\text{-}400 \text{ Th}$), dimers (C_{10} , $\sim 400\text{-}600 \text{ Th}$), and trimers (C_{15} , $\sim >600 \text{ Th}$), according to their mass to charge ratio (m/z). The detailed peak assignment of monomers, dimers, and trimers is discussed in the following sections.

3.2 HOM monomers and their formation

3.2.1 Overview of HOM monomers

HOM monomers showed a roughly repeating pattern in the mass spectrum at every 16 Th (corresponding to the mass of oxygen) (Fig. 1a). Here a number of series of HOM monomers with continuously increasing oxygenation were found, such as $\text{C}_5\text{H}_9\text{NO}_n$, $\text{C}_5\text{H}_7\text{NO}_n$, $\text{C}_5\text{H}_8\text{N}_2\text{O}_n$, $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_n$ (Table 1, Table S1-2 and Fig. 2). These monomers included both stable closed-shell molecules and open-shell radicals, such as $\text{C}_5\text{H}_8\text{NO}_n\cdot$ and $\text{C}_5\text{H}_9\text{N}_2\text{O}_n\cdot$. The open-shell molecules were likely RO_2 radicals because of their much longer life time and hence higher concentrations compared with alkoxy radicals (RO) and alkyl radicals (R). Since the observed stable products were mostly termination products of RO_2 reactions, we describe the stable products in a RO_2 -oriented approach. It is worth noting that some of the termination products may contain multiple isomers formed from different pathways.

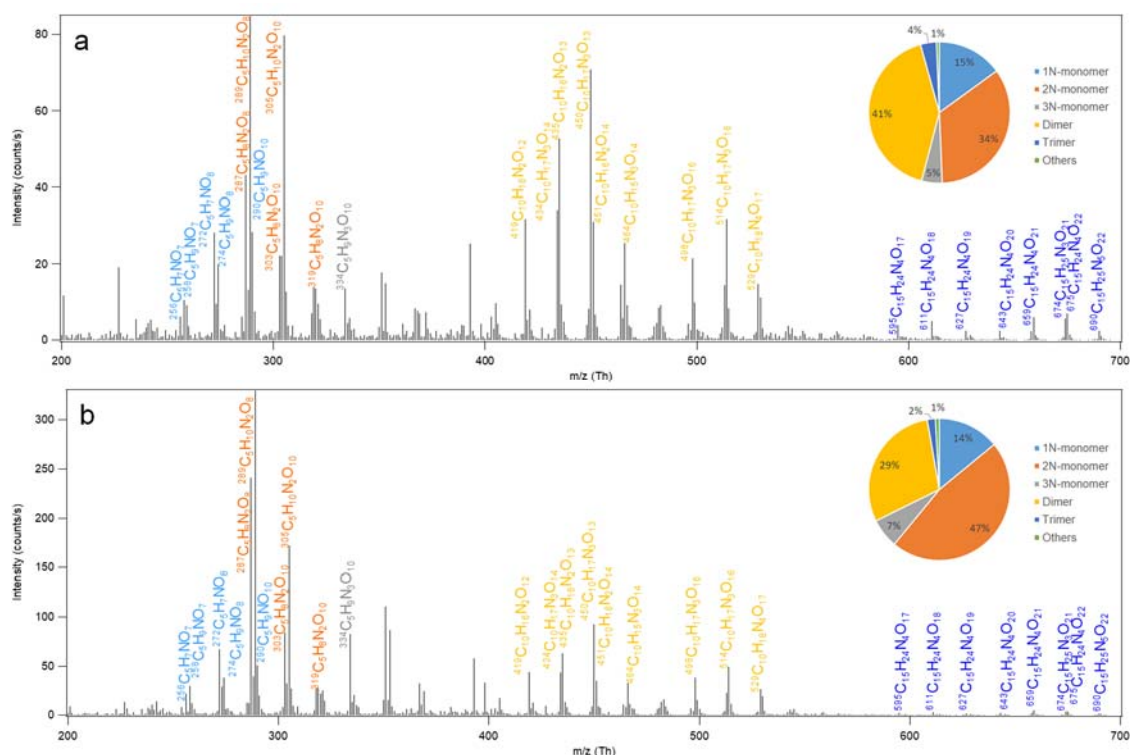


Figure 1. Mass spectrum of the HOM formed in the oxidation of isoprene by NO_3 . HOM are detected as clusters with the reagent ion $^{15}\text{NO}_3^-$, which is not shown in the molecular formula in the figure for simplicity. Panel a and b show the average spectrum during the first isoprene addition period (P1) and for the whole period of six isoprene additions (P1-6), respectively. The insets show the contributions of different classes of HOM. 1-3N-monomer refers to the monomers containing 1-3 nitrogen atoms in the molecular formula.

HOM monomers were classified into 1N-, 2N-, and 3N-monomers according to the number of nitrogen atoms that they contain. HOM without nitrogen atoms were barely observed except for very minor peaks ($< \sim 1\%$ of the maximum peak) possibly assigned to $\text{C}_5\text{H}_{10}\text{O}_8$ and $\text{C}_5\text{H}_8\text{O}_{11}$. The contribution of 2N-monomers such as $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_n$ and $\text{C}_5\text{H}_8\text{N}_2\text{O}_n$ was higher than that of the 1N-HOM monomers, and that of 3N-monomers was the least (Fig. 1, inset). The most abundant monomers were $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_8$, $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_9$, and $\text{C}_5\text{H}_8\text{N}_2\text{O}_8$. The termination products of $\text{C}_5\text{H}_9\text{NO}_8$, $\text{C}_5\text{H}_9\text{NO}_9$, and $\text{C}_5\text{H}_7\text{NO}_8$ also showed relatively high abundance. These limited number of compounds dominated the HOM monomers. Since 2N-monomers were second-generation products as discussed below, the higher abundance 2N- monomers indicate that the second-generation HOM play an important role in the reaction of NO_3 with isoprene in the reaction conditions of our study, as also seen by Wu et al. (2020). This is more evident for the mass spectrum averaged over six isoprene addition periods (Fig. 1b), where the abundance of $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_n$ and $\text{C}_5\text{H}_8\text{N}_2\text{O}_n$ were more dominant. This observation is in contrast with the finding for the reaction of O_3 with BVOC which contains only one double bond such as α -pinene (Ehn et al., 2014), where HOM are mainly first-generation products formed via autoxidation. The higher abundance of HOM 2N-monomers than 1N-monomers is likely because HOM production rate via the autoxidation of 1N-monomer RO_2 following the reaction of isoprene with NO_3 may be slower than that of the reaction of 1N-monomers (including both HOM and non-HOM monomers) with NO_3 . We would like to note that some less oxygenated 1N-monomers such as $\text{C}_5\text{H}_9\text{NO}_{4/5}$ and $\text{C}_5\text{H}_7\text{NO}_4$ may have high abundance but are not detected by NO_3^- -CIMS and are not HOM and thus not included in HOM 1N-monomers.

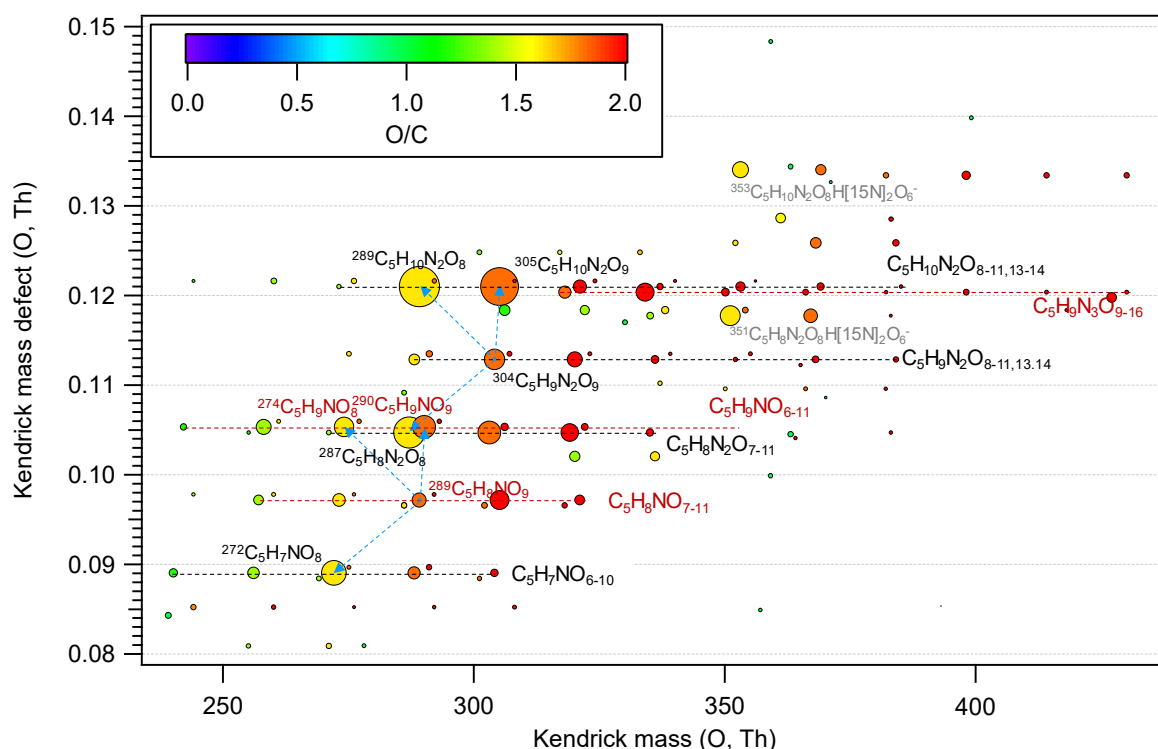


Figure 2. Kendrick mass defect plot for O of HOM monomers. The m/z in the molecular formula include the reagent ion $^{15}\text{NO}_3^-$, which is not shown for simplicity. The size (area) of circles is set to be proportional to the average peak intensity of each molecular formula during the first isoprene addition period (P1). The species at m/z 351 and 353 (labelled in grey) are the adducts of $\text{C}_5\text{H}_8\text{N}_2\text{O}_8$ and $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_8$ with $\text{H}[^{15}\text{N}]_2\text{O}_6^-$, respectively. The blue dashed lines with arrows indicate the termination product hydroperoxide (M+H), alcohol (M-O+H), and ketone (M-O-H) with M the molecular formula of a HOM RO_2 .

3.2.2 1N-monomers

In our experiments we observed a $\text{C}_5\text{H}_8\text{NO}_n$ ($n=7-12$) series (series M1), as well as its corresponding termination products $\text{C}_5\text{H}_7\text{NO}_{n-1}$, $\text{C}_5\text{H}_9\text{NO}_{n-1}$, and $\text{C}_5\text{H}_9\text{NO}_n$ via the reactions with RO_2 and HO_2 , which contain carbonyl, hydroxyl, and hydroperoxy group, respectively. Overall, the peak intensities of $\text{C}_5\text{H}_9\text{NO}_n$ and $\text{C}_5\text{H}_7\text{NO}_n$ series first increased and then decreased as oxygen number increased (Fig. 2), with the peak intensity of $\text{C}_5\text{H}_9\text{NO}_8$ and $\text{C}_5\text{H}_7\text{NO}_8$ being the highest within their respective series when averaged over the whole experiment period.

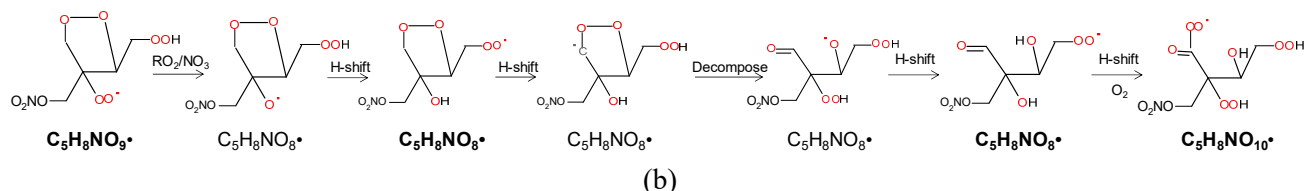
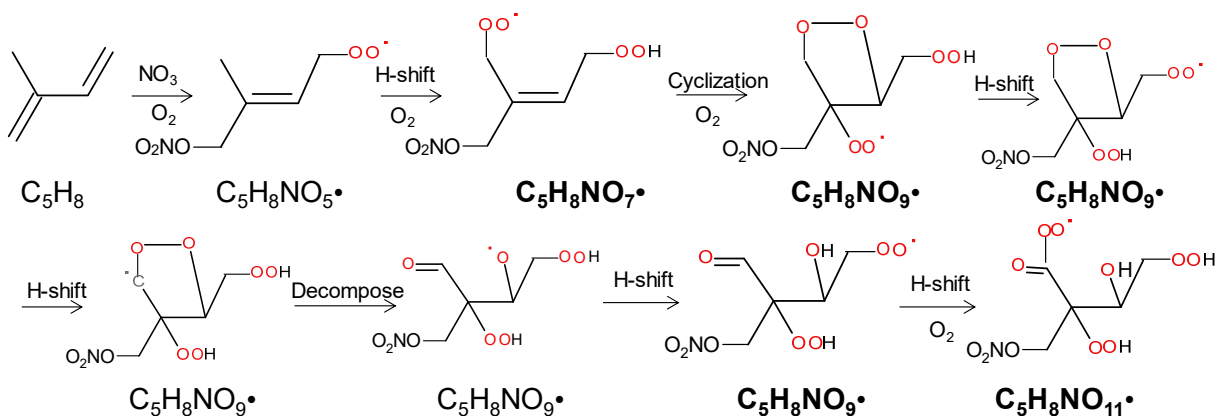
Table 1. HOM monomers formed in the oxidation of isoprene by NO_3 .

Series Number	Product	Type ^a	Pathway of RO_2
M1a/b	$\text{C}_5\text{H}_8\text{NO}_n$ ($n=7-11$)	RO_2	Isoprene+ NO_3 Isoprene+ NO_3 + NO_3
	$\text{C}_5\text{H}_9\text{NO}_n$ ($n=6-11$)	ROOH/ROH	
	$\text{C}_5\text{H}_7\text{NO}_n$ ($n=6-10$)	R=O	
M2a/b	$\text{C}_5\text{H}_9\text{N}_2\text{O}_n$ ($n=8-11,13,14$) ^b	RO_2	Isoprene + NO_3 + NO_3
	$\text{C}_5\text{H}_{10}\text{N}_2\text{O}_n$ ($n=8-11,13,14$) ^b	ROOH/ROH	
	$\text{C}_5\text{H}_8\text{N}_2\text{O}_n$ ($n=7-11$)	R=O	

	$C_5H_9N_3O_n$ (n=9-16) ^b	RO_2NO_2	
M3	$C_5H_7N_2O_n$ (n=9)	RO_2	Isoprene + NO_3 + NO_3
	$C_5H_8N_2O_n$ (n=8, 9)	$ROOH$	
	$C_5H_6N_2O_n$ (n=8)	$R=O$	
M4	$C_5H_{10}NO_n$ (n=8-9)	RO_2	Isoprene + NO_3 + OH
	$C_5H_{11}NO_n$ (n=7-9)	$ROOH/ROH$	
	$C_5H_9NO_n$ (n=7-8)	$R=O$	

^a: RO_2 denotes peroxy radical and $ROOH$, ROH , $R=O$, and RO_2NO_2 denote the termination products containing hydroperoxy, hydroxyl, carbonyl group, and peroxyxynitrate, respectively.

^b: Peak assignment of compounds with n=13,14 may be subject to uncertainties.



Scheme 1. The example pathways to form HOM RO_2 $C_5H_8NO_n$ • (n=7, 9, 11) series (a) and $C_5H_8NO_n$ • (n=8, 10) series (b) in the reaction of isoprene with NO_3 . The detected products are in bold.

$C_5H_8NO_n$ • with odd number oxygen atoms (n=7, 9, 11, series M1a) were possibly formed by the attack of NO_3 to one double bond (preferentially to C1 according to previous studies (Skov et al., 1992; Berndt and Böge, 1997; Schwantes et al., 2015) and followed by autoxidation (Scheme 1a). We would like to note that NO_3^- -CIMS only observed HOM with oxygen numbers ≥ 6 in this study due to its selectivity of detection. $C_5H_8NO_n$ • with even number oxygen atoms (n=8, 10, series M1b in Table 1) were possibly formed after H-shift of an alkoxy radical formed in reaction R4 or R5 and subsequent O_2 addition (“alkoxy-peroxy” channel) (Scheme 1b), where the alkoxy radicals can be formed both from the RO_2+NO_3 and RO_2+RO_2 reactions. The hydroxy RO_2 formed can undergo further autoxidation adding two oxygen atoms after each H-shift. We would like to note that the scheme and other schemes in this study only show example isomers and pathways to form these

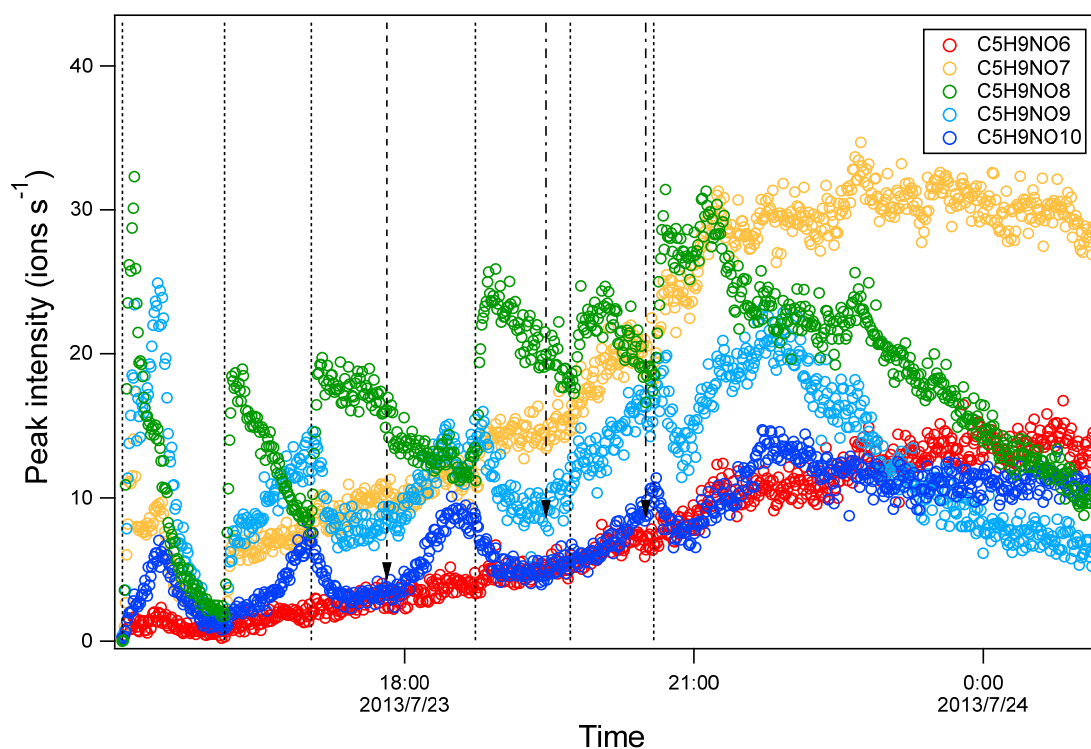
272 molecules. It is likely that many of the reactions occurring are not the dominant channels as otherwise there would
273 be much higher HOM yield as discussed below.

274 Some HOM monomers may contain multiple isomers and be formed via different pathways. For
275 example, $C_5H_9NO_n$ can contain alcohols derived from RO_2 $C_5H_8NO_{n+1}\bullet$, hydroperoxides derived from RO_2
276 $C_5H_8NO_n\bullet$ or the ketones from RO_2 $C_5H_{10}NO_{n+1}\bullet$. Some RO_2 $C_5H_8NO_n\bullet$ may be formed via the reaction of first-
277 generation products with NO_3 in addition to direct reaction of isoprene with NO_3 . For example, $C_5H_8NO_7\bullet$ can
278 be formed by the reaction of NO_3 with $C_5H_8O_2$, which is a first-generation product observed previously in the
279 reaction of isoprene with NO_3 or OH (Scheme S1b) (Kwan et al., 2012). Moreover, RO_2 $C_5H_8NO_n\bullet$ can be
280 formed from C5-carbonylnitrate, a first-generation product, with OH (Scheme S1a). Trace amount of OH can
281 be produced in the reaction of isoprene with NO_3 (Kwan et al., 2012; Wennberg et al., 2018). OH can also be
282 formed via Criegee intermediates formed in the isoprene+ O_3 reaction (Nguyen et al., 2016), but this OH source
283 was likely minor because the contribution of the isoprene+ O_3 reaction to total isoprene loss was negligible (<5%,
284 Fig. S2). In addition, $C_5H_8NO_8\bullet$ may also be formed by the reaction of NO_3 with $C_5H_8O_3$, which is a first-
285 generation product observed in the reaction of isoprene with OH (Kwan et al., 2012). The $C_5H_8NO_n\bullet$ formed
286 via direct reaction of isoprene with NO_3 is a first-generation RO_2 while that formed via other indirect pathways
287 is a second-generation RO_2 . The time profile of the isomers from these two pathways, however, are expected to
288 be different as will be discussed below.

289 Time series of HOM can shed light on their formation mechanisms. It is expected that first-generation
290 products increase fast with isoprene addition and reach a maximum earlier in the presence of wall loss of organic
291 vapour, while second-generation products reach a maximum in the later stage or increase continuously if the
292 production rate is higher than the loss rate. As a reference to analyze the time profiles of HOM, the times profile
293 of isoprene, NO_3 , and N_2O_5 are also shown (Fig. S4). After isoprene was added in each period, NO_3 and N_2O_5
294 dropped dramatically and then gradually increased. We found that termination products within the same M1
295 series showed different time profiles. For example, in $C_5H_9NO_n$ series, $C_5H_9NO_8$ clearly increased
296 instantaneously with isoprene addition, and decreased fast afterwards (Fig. 3a), indicating that it was a first-
297 generation product, which was expected according to the mechanism Scheme 1. $C_5H_9NO_6$ and $C_5H_9NO_{10}$ had a
298 general increasing trend with time. While $C_5H_9NO_6$ increased continuously with time, $C_5H_9NO_{10}$ reached
299 maximum intensity in the late phase of each isoprene addition period and then decreased naturally or after
300 isoprene addition. The faster loss of $C_5H_9NO_{10}$ than $C_5H_9NO_6$ may result from the faster wall loss due to its
301 lower volatility. $C_5H_9NO_7$ and $C_5H_9NO_9$ showed a mixing time profile with features of the former two kinds of
302 time profiles, increasing almost instantaneously with isoprene additions, especially in the first two periods,
303 while increasing continuously or decreasing first with isoprene additions and then increasing later in each period.
304 This kind of time series indicates that there were significant contributions from both first- and second-generation
305 products.

306 The second-generation products may be different isomers formed in pathways other than shown in
307 Scheme 1. Second-generation $C_5H_9NO_6$ can be formed via $C_5H_8NO_7\bullet$, which can also be formed by the reaction
308 of NO_3 and O_2 with $C_5H_8O_2$ as mentioned above (Scheme S2b), or by the reaction of OH with $C_5H_7NO_4$ (Scheme

S2a). The time profiles of $C_5H_8NO_7\bullet$ did show more contribution of second-generation processes because it continuously increased with time in general. If the pathways via the reaction of NO_3 and O_2 with $C_5H_8O_2$ and the reaction of OH with $C_5H_7NO_4$ contribute most to $C_5H_9NO_6$, $C_5H_9NO_6$ would show mostly a time profile of second-generation products. Similarly, second-generation $C_5H_9NO_7$ can be formed via $C_5H_8NO_7\bullet$ or $C_5H_8NO_8\bullet$. The time series of $C_5H_8NO_8\bullet$ did show the contribution of both the first- and second-generation processes, which generally increased with time while also responding to isoprene addition (Fig. S5). Similar to $C_5H_9NO_6$, the second-generation pathway for $C_5H_9NO_7$, $C_5H_9NO_9$, and $C_5H_9NO_{10}$ are shown in Scheme S1, S3, S4. For the RO_2 in $C_5H_8NO_n\bullet$ series other than $C_5H_8NO_{7/8}\bullet$, the peak of $C_5H_8NO_n\bullet$ overlaps with $C_5H_{10}N_2O_n$ in the mass spectra, which is a much larger peak, and thus cannot be differentiated from $C_5H_{10}N_2O_n$. Therefore, it is not possible to obtain reliable separate time profiles in order to differentiate their major sources. It is worth noting that nitrate CIMS may not be able to detect all isomers of $C_5H_9NO_6$ due to the sensitivity limitation. Therefore, we cannot exclude the possibility that the absence of some first-generation isomers of $C_5H_9NO_6$ was due to the low sensitivity of these isomers.



(a)

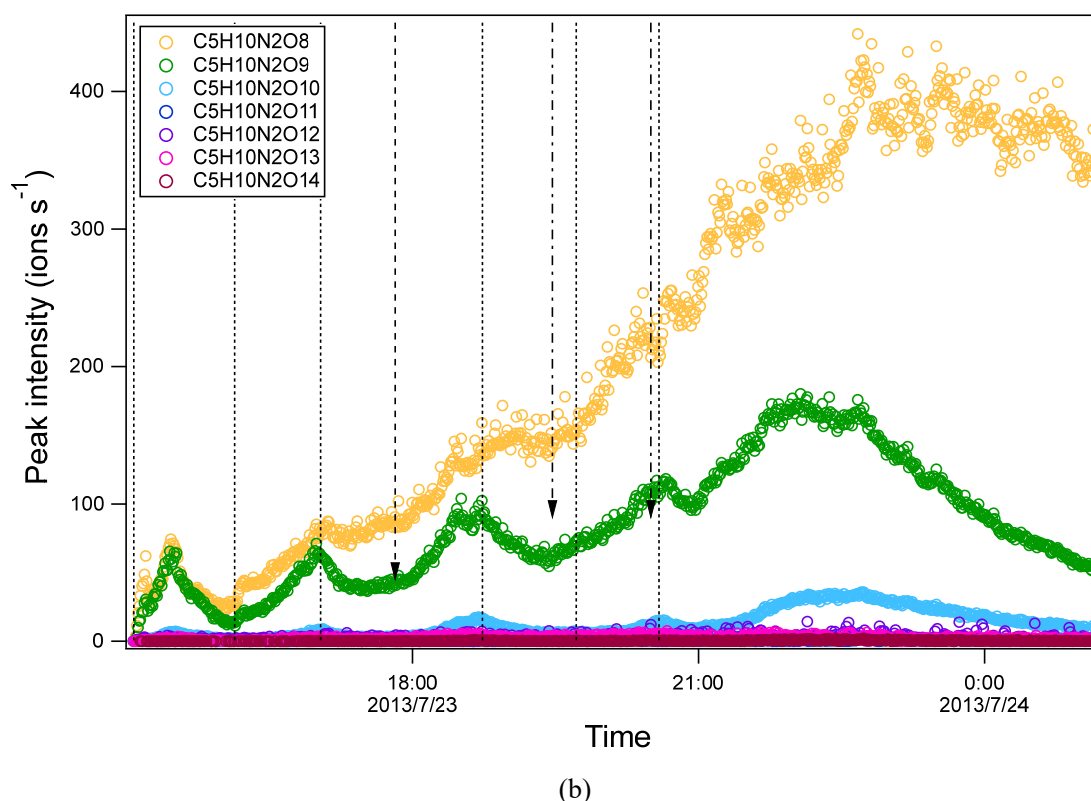


Figure 3. Time series of peak intensity of several HOM monomers of $C_5H_9NO_n$ series (a) and of $C_5H_{10}N_2O_n$ series (b). They are likely the termination products of RO_2 $C_5H_8NO_n\bullet$ and $C_5H_9N_2O_n\bullet$, respectively. The dashed lines indicate the time of isoprene additions. The long-dashed arrow indicates the time of NO_2 addition. The dash-dotted arrows indicate the time of O_3 additions.

Among the termination products of the 1N-monomer RO_2 , carbonyl and hydroxyl/hydroperoxide species had comparable abundance in general (Table S1), suggesting that disproportionation reactions between RO_2 and RO_2 forming hydroxy and carbonyl species (R1-2) was likely an important RO_2 termination pathway. However, dependence of the exact ratio of carbonyl species to hydroxyl/hydroperoxide species on the number of oxygen atoms did not show a clear trend (Table S1), suggesting that the reactions of HOM RO_2 depended on their specific structure. There was no clear difference in the abundance between the termination products from $C_5H_8NO_n\bullet$ with odd and even number of oxygen atom in general, although the most abundant termination product of $C_5H_8NO_n\bullet$, i.e. $C_5H_7NO_8$, was likely formed from $C_5H_8NO_9\bullet$ in series M1a. This fact indicates that both the peroxy pathway and alkoxy-peroxy pathway were important for the HOM formation in the isoprene+ NO_3 reaction under our conditions, in agreement with the significant formation of alkoxy radicals from the reaction of RO_2 with NO_3 and RO_2 .

In addition to the termination products of RO_2 M1, minor peaks of the RO_2 series $C_5H_{10}NO_n\bullet$ ($n=8-9$) (M4, Table 1) and their corresponding termination products including hydroperoxide, alcohol and carbonyl species were detected (Table S3). $C_5H_{10}NO_n$ were likely formed by sequential addition of NO_3 and OH to two double bonds of isoprene (Scheme S5). OH can react fast with isoprene or with the first-generation products of the reaction of isoprene

with NO_3 , thus forming $\text{C}_5\text{H}_{10}\text{NO}_n^\bullet$. In addition, a few very minor but noticeable peaks of $\text{C}_5\text{H}_9\text{O}_n^\bullet$ and their corresponding termination products $\text{C}_5\text{H}_{10}\text{O}_n$ and $\text{C}_5\text{H}_8\text{O}_n$ were also observed. These HOM may be formed by the reactions of isoprene with trace amount of OH and with O_3 , although their contributions to reacted isoprene were negligible. These HOM were also observed in the reaction of isoprene with O_3 with and without OH scavengers (Jokinen et al., 2015).

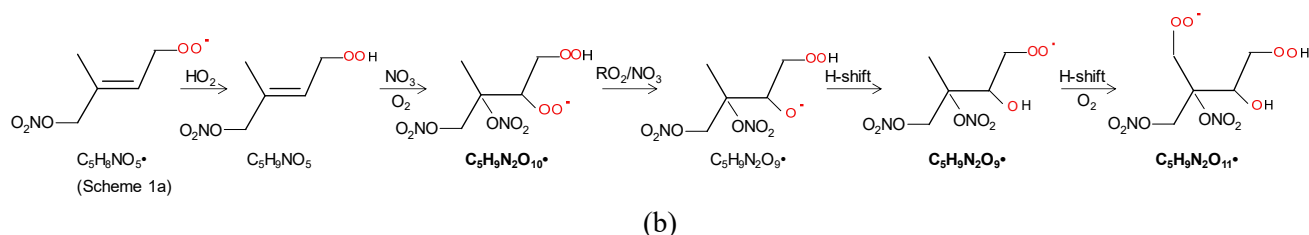
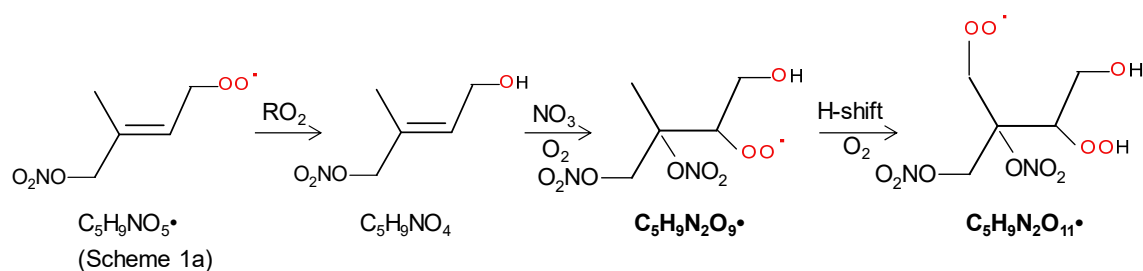
Among 1N-monomer HOM, $\text{C}_5\text{H}_9\text{NO}_7$ has been observed in the particle phase using ESI-TOFMS by Ng et al. (2008) while others have not been observed in previous laboratory studies of the reaction of isoprene with NO_3 , to our knowledge. A number of C_5 organic nitrates have been observed in field studies. For example, $\text{C}_5\text{H}_{7-11}\text{NO}_{4-9}$ have been observed in aerosol particles during the Southern Oxidant and Aerosol Study in rural Alabama, US, where isoprene is abundant (Lee et al., 2016). Those compounds were also observed in chamber experiments of the reaction of isoprene with OH in the presence of NO_x (Lee et al., 2016). $\text{C}_5\text{H}_x\text{NO}_{4-9}$ and $\text{C}_5\text{H}_x\text{NO}_{4-10}$ have been observed in the gas phase and particle, respectively, in a rural area in southwest Germany (Huang et al., 2019).

3.2.3 2N-monomers

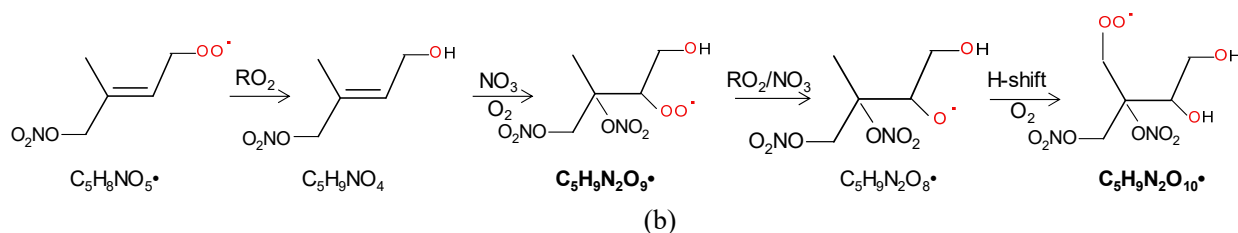
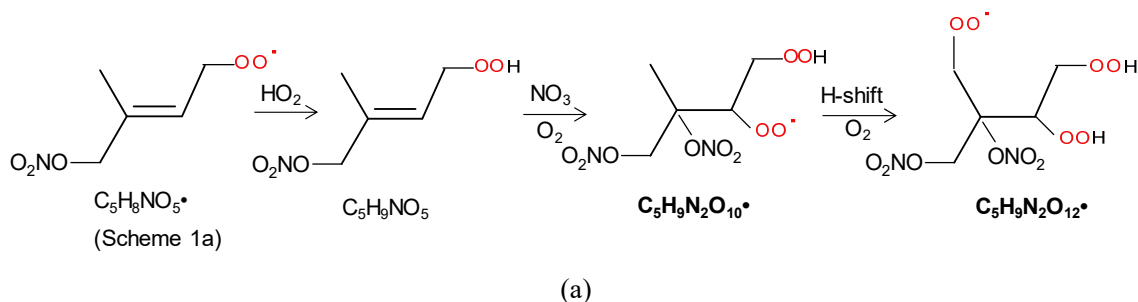
The 2N-monomer RO_2 series $\text{C}_5\text{H}_9\text{N}_2\text{O}_n^\bullet$ ($n=8-14$), were observed, as well as its likely termination products, $\text{C}_5\text{H}_8\text{N}_2\text{O}_n$ and $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_n$, which contain a carbonyl and hydroxyl or hydroperoxide functional group, respectively. The RO_2 series $\text{C}_5\text{H}_9\text{N}_2\text{O}_n^\bullet$ with odd number of oxygen atoms ($n=9, 11$) (M2a in Table 1) were likely formed from the first-generation product $\text{C}_5\text{H}_9\text{NO}_4$ (C5-hydroxynitrate) by adding NO_3 to the remaining double bond, forming $\text{C}_5\text{H}_9\text{N}_2\text{O}_9^\bullet$, followed by autoxidation (Scheme 2a). This RO_2 series can also be formed by the addition of NO_3 to the double bond of first-generation products (e.g. $\text{C}_5\text{H}_9\text{NO}_5$, C5-nitrooxyhydroperoxide) and a subsequent alkoxy-peroxy step (Scheme 2b). $\text{C}_5\text{H}_9\text{N}_2\text{O}_n^\bullet$ with even number of oxygen atoms ($n=8, 10, 12$) (M2b in Table 1), can be formed by the addition of NO_3 to the double bond of $\text{C}_5\text{H}_9\text{NO}_5$ followed by autoxidation (Scheme. 3a), or of $\text{C}_5\text{H}_9\text{NO}_4$ followed by an alkoxy-peroxy step (Scheme. 3b). The formation pathways of $\text{C}_5\text{H}_9\text{N}_2\text{O}_{13/14}^\bullet$ and $\text{C}_5\text{H}_9\text{N}_2\text{O}_8^\bullet$ cannot be well explained, as they contain too many or too few oxygen atoms to be formed via the pathways in Scheme 2 or 3. In Scheme 2 and 3, we show the reactions starting from 1- NO_3 -isoprene-4-OO as an example. In the supplement, we have also shown the pathways starting from 1- NO_3 -isoprene-2-OO peroxy radicals, which is indicated in a recent study by Vereecken et al. (2021) to be the dominant RO_2 in the reaction of isoprene with NO_3 .

Formation through either Scheme 2 or 3 means that $\text{C}_5\text{H}_8\text{N}_2\text{O}_n$ and $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_n$ were second-generation products. The time series of $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_n$ species clearly indicates that they were indeed second-generation products. $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_n$ species generally did not increase immediately with isoprene addition (Fig. 3b), but increased gradually with time and reached its maximum in the later stage of each period before decreasing with time (in the period 1 and 6), or decreasing after the next isoprene addition (periods 2-5). This time profile can be explained by the time series of the precursor of $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_n$, $\text{C}_5\text{H}_9\text{N}_2\text{O}_n^\bullet$ (RO_2) (Fig. S6). The changing rate (production rate minus destruction rate) of $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_n$ concentration was dictated by the concentration of $\text{C}_5\text{H}_9\text{N}_2\text{O}_n^\bullet$ and the wall loss rate. During periods 2 to 5, $\text{C}_5\text{H}_9\text{N}_2\text{O}_n^\bullet$ gradually increased but decreased sharply

after the isoprene additions, resulted from chemical reactions of $C_5H_9N_2O_n\cdot$ and additionally from wall loss. When the rate of change of the $C_5H_{10}N_2O_n$ concentration was positive, the concentration of $C_5H_{10}N_2O_n$ increased with time. After isoprene additions, the rate of change of the $C_5H_{10}N_2O_n$ concentration decreased dramatically to even negative, leading to decreasing concentrations. Similar to $C_5H_{10}N_2O_n$, the $C_5H_8N_2O_n$ series did not respond immediately to isoprene additions (Fig. S7), which is expected for second-generation products according to the mechanism discussed above (Scheme 2-3). Particularly, the continuing increase of $C_5H_8N_2O_n$ even after isoprene was completely depleted (at ~21:40, Fig. S7) clearly indicates that these compounds were second-generation products, although in the end they decreased due to wall loss.



Scheme 2. The example pathways to form $C_5H_9N_2O_n$ ($n=9, 11$) HOM RO₂ series by RO₂ channel (a) and alkoxy-peroxy channel. The detected products are in bold.



Scheme 3. The example pathways to form $C_5H_9N_2O_n$ ($n=10, 12$) HOM RO₂ series by RO₂ channel (a) and alkoxy-peroxy channel (b). The detected products are in bold.

According to the finding of Ng et al. (2008), C5-hydroxynitrate decays much faster than C5-nitrooxyhydroperoxides. Additionally, C5-hydroxynitrate concentration is expected to be higher than that of nitrooxyhydroperoxides because $\text{RO}_2 + \text{RO}_2$ forming alcohol is likely more important than $\text{RO}_2 + \text{HO}_2$ forming hydroperoxide in this study. Therefore, it is likely that $\text{C}_5\text{H}_9\text{N}_2\text{O}_n$ • M2a series was mainly formed from $\text{C}_5\text{H}_9\text{NO}_4$ instead of $\text{C}_5\text{H}_9\text{NO}_5$, while $\text{C}_5\text{H}_9\text{N}_2\text{O}_n$ • M2b were formed from $\text{C}_5\text{H}_9\text{NO}_4$ followed by an alkoxy-peroxy step. That is, Scheme 2a and 3b appear more likely.

Similar to $\text{C}_5\text{H}_8\text{NO}_n$ •, the intensity of carbonyl species from $\text{C}_5\text{H}_9\text{N}_2\text{O}_n$ • was also comparable with that of hydroxyl/hydroperoxide species, suggesting that $\text{RO}_2 + \text{RO}_2$ reaction forming ketone and alcohol was likely an important pathway of HOM formation in the isoprene+ NO_3 reaction. In general, the intensity of the termination products from $\text{C}_5\text{H}_9\text{N}_2\text{O}_n$ • with both even and odd oxygen numbers were comparable. This again suggests that both peroxy and alkoxy-peroxy pathways were important for HOM formation in the isoprene+ NO_3 reaction. The intensity of $\text{C}_5\text{H}_8\text{N}_2\text{O}_n$ first increased and then decreased with oxygen number while $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_n$ decreased with oxygen number, with $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_8$ and $\text{C}_5\text{H}_8\text{N}_2\text{O}_8$ being the most abundant within their respective series.

Some 2N-monomers have been detected in previous studies of the reaction of isoprene with NO_3 . $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_8$ has been detected in the particle phase by Ng et al. (2008) and $\text{C}_5\text{H}_8\text{N}_2\text{O}_7$ was detected in the gas phase by Kwan et al. (2012). $\text{C}_5\text{H}_9\text{N}_2\text{O}_9$ • has been proposed to be formed via the pathway as in Scheme 2a (Ng et al., 2008), and it was directly detected in our study. $\text{C}_5\text{H}_8\text{N}_2\text{O}_7$ species has been proposed to be a dinitrooxy epoxide formed by the oxidation of nitrooxyhydroperoxide (Kwan et al., 2012), instead of being a dinitrooxy ketone proposed in our study, a termination product of $\text{C}_5\text{H}_9\text{N}_2\text{O}_8$ •. Admittedly, $\text{C}_5\text{H}_8\text{N}_2\text{O}_7$ may contain both isomers. In addition, Ng et al. (2008) detected $\text{C}_5\text{H}_8\text{N}_2\text{O}_6$ in the gas phase, which was not detected in this study likely due to the selectivity of NO_3^- -CIMS.

One could suppose that $\text{C}_5\text{H}_7\text{N}_2\text{O}_n$ • should also be formed since C5-nitrooxycarbonyl ($\text{C}_5\text{H}_7\text{NO}_4$) also contains one double bond that can be attacked by NO_3 in a second oxidation step. However, concentrations of $\text{C}_5\text{H}_7\text{N}_2\text{O}_n$ were too low to assign molecular formulas with confidence except for $\text{C}_5\text{H}_7\text{N}_2\text{O}_9$ •, clearly showing that $\text{C}_5\text{H}_7\text{N}_2\text{O}_n$ • was not important. This fact is consistent with the finding of Ng et al. (2008) that C5-nitrooxycarbonyls react slowly with NO_3 . Additionally, the peroxy radical formed in the reaction of C5-nitrooxycarbonyls with NO_3 likely leads to more fragmentation in H-shift as found in the OH oxidation of methacrolein (Crounse et al., 2012), which may also contribute to the low abundance of $\text{C}_5\text{H}_7\text{N}_2\text{O}_n$. The presence of HOM containing two N atoms is in line with the finding by Faxon et al. (2018) who detected products containing two N atoms in the reaction of NO_3 with limonene, which also contain two carbon double bonds. It is anticipated that for VOC with more than one double bond, NO_3 can add to all the double bonds as for isoprene and limonene.

3.2.4 3N-monomers

HOM containing three nitrogen atoms, $\text{C}_5\text{H}_9\text{N}_3\text{O}_n$ ($n=9-16$), were observed. These compounds were possibly peroxy nitrates formed by the reaction of RO_2 ($\text{C}_5\text{H}_9\text{N}_2\text{O}_n$ •) with NO_2 . The time series of $\text{C}_5\text{H}_9\text{N}_3\text{O}_n$ was examined to check whether they match such a mechanism. If $\text{C}_5\text{H}_9\text{N}_3\text{O}_n$ were formed by the reaction of

438 C₅H₉N₂O_{n-2}• with NO₂, the concentration would be a function of the concentrations of C₅H₉N₂O_{n-2}• and NO₂ as
 439 follows:

$$440 \quad \frac{d[C_5H_9N_3O_n]}{dt} = k[C_5H_9N_2O_{n-2}•][NO_2] - k_{wall}[C_5H_9N_3O_n]$$

441 where [C₅H₉N₃O_n], [C₅H₉N₂O_{n-2}•], and [NO₂] are the concentration of these species, k is the rate
 442 constant and k_{wall} is the wall loss rate. Because the products of C₅H₉N₂O_{n-2}• and NO₂ were at their maximum at
 443 the end of each period and decreased rapidly after isoprene addition (Fig. S8), the concentration should have its
 444 maximum increasing rate at the end of each isoprene addition period. However, we found that only C₅H₉N₃O₁₂,
 445 _{15, 16} showed such a time profile (Fig. S9), while C₅H₉N₃O_{9, 10, 11, 13, 14} generally increased with time, different
 446 from what one would expect based on the proposed pathway. Therefore, it is likely that C₅H₉N₃O_{12, 15, 16} were
 447 mainly formed via the reaction of C₅H₉N₂O_n• with NO₂, whereas C₅H₉N₃O_{9,10,11,13,14} were not. Moreover,
 448 C₅H₉N₃O₉ cannot be explained by the reaction C₅H₉N₂O_n• (n≥9) with NO₂ or NO₃, because these reactions
 449 would add at least one more oxygen atom. One possible pathway to form C₅H₉N₃O₉ was the direct addition of
 450 N₂O₅ to the carbon double bond of C5-hydroxynitrate, forming a nitronitrate. Such a mechanism has been
 451 proposed previously in the heterogeneous reaction of N₂O₅ with 1-palmitoyl-2-oleoyl-sn-glycero-3-
 452 phosphocholine (POPC) because -NO₂ and -NO₃ groups were detected (Lai and Finlayson-Pitts, 1991). This
 453 pathway generally matched the time series of C₅H₉N₃O_{9,10,11,13,14} typical of second-generation products since
 454 C5-hydroxynitrate was a first-generation product. It is possible that the main pathway of C₅H₉N₃O_{9,10,11,13,14} was
 455 the reaction of C₅H₉NO_{4,5,6} with N₂O₅, although the reaction of N₂O₅ with C=C double bonds in common alkenes
 456 and unsaturated alcohols are believed to be not important (Japar and Niki, 1975; Pfrang et al., 2006).

457 3N-monomers, C₅H₉N₃O₁₀, has been observed in the particles formed in the isoprene+NO₃ reaction by
 458 Ng et al. (2008). Here a complete series of C₅H₉N₃O_n were observed. C₅H₉N₃O₁₀ was previously proposed to
 459 be formed by another pathway, i.e. the reaction of RO₂ (C₅H₉N₂O₉•) and NO₃ (Ng et al., 2008). We further
 460 examined the possibility of such a pathway in our study. Similar to NO₂, if C₅H₉N₃O_n were formed by the
 461 reaction of C₅H₉N₂O_{n-2}• with NO₃, the concentration would have its maximum increasing rate at the end of each
 462 isoprene addition period. Among C₅H₉N₂O_n•, the precursors of C₅H₉N₃O_n, C₅H₉N₂O_{9, 10, 13, 14}• showed a
 463 maximum increasing rate and a subsequent decrease after isoprene addition. The difference in oxygen number
 464 between C₅H₉N₃O_{12, 15, 16}, the termination products, and C₅H₉N₂O_{9, 10, 13, 14}•, the corresponding RO₂ with the
 465 consistent time profile is mostly two. Since the reaction of C₅H₉N₂O_n with NO₂ and NO₃ result an increased
 466 oxygen number by two and by one, respectively, we infer that it is more likely that C₅H₉N₃O_{12, 15, 16} were formed
 467 by the reaction of C₅H₉N₂O_{10, 13, 14}• with NO₂ rather than NO₃, and thus they were likely peroxy nitrates rather
 468 than nitrates formed by the reaction of RO₂ with NO₃. Since alkyl peroxy nitrates decompose rapidly (Finlayson-
 469 Pitts and Pitts, 2000; Ziemann and Atkinson, 2012), it is possible that these compounds contained
 470 peroxyacyl nitrates.

471 Little attention has been paid to the RO₂+NO₂ pathway in nighttime chemistry of isoprene in the
 472 literature (Wennberg et al., 2018), which is likely due to the instability of the products. According to this
 473 pathway, C₅H₈N₂O_n, which was proposed to be a ketone formed via C₅H₉N₂O₉• in the M2 series (Table 1) as

discussed above, can also comprise peroxyxynitrate formed by the reaction of $C_5H_8NO_n\bullet$ (M1a RO₂) with NO₂. 3N dimer such as $C_5H_9N_3O_{10}$ as well as 2N-monomers such as $C_5H_8N_2O_8$ and $C_5H_8N_2O_{10}$ have been observed in a recent field study in polluted cities in east China (Xu et al., 2021).

3.3 HOM dimers and their formation

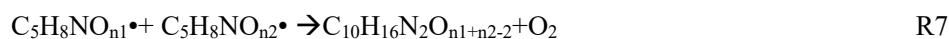
Table 2. HOM dimers and trimers formed in the oxidation of isoprene by NO₃.

Series Number	Formula	Type	Pathway of RO ₂
Dimer 1	$C_{10}H_{16}N_2O_n$ (n=10-17)	ROOR ^a	M1 ^b +M1
Dimer 2	$C_{10}H_{17}N_3O_n$ (n=11-19)	ROOR	M1+M2/M3+M4
Dimer 3	$C_{10}H_{18}N_4O_n$ (n=15-18)	ROOR	M2+M2
Dimer 4	$C_{10}H_{18}N_2O_n$ (n=10-16)	ROOR	M1+M4
Dimer 5	$C_{10}H_{15}N_3O_n$ (n=13-17)	ROOR	M1+M3
Dimer 6	$C_{10}H_{19}N_3O_n$ (n=14-15)	ROOR	M2+M4
Dimer 7	$C_{10}H_{14}N_2O_n$ (n=10-16)	ROOR	Unknown
Dimer 8	$C_{10}H_{15}NO_n$ (n=9-12)	ROOR	$C_{10}H_{16}NO_n$
Dimer 9	$C_{10}H_{17}NO_n$ (n=9-15)	ROOR	$C_{10}H_{16}NO_n$
Dimer R1	$C_{10}H_{16}N_3O_n$ (n=12-15)	RO ₂	Dimer 1+NO ₃
Dimer R2	$C_{10}H_{17}N_2O_n$ (n=11-12)	RO ₂	Dimer 1+OH
Dimer R3	$C_{10}H_{17}N_4O_n$ (n=16-18)	RO ₂	Dimer 2+NO ₃
Dimer R4	$C_{10}H_{16}NO_n$ (n=10-14)	RO ₂	M1+C ₅ H ₈
Trimer 1	$C_{15}H_{24}N_4O_n$ (n=17-22)	ROOR	Dimer R1+M1
Trimer 2	$C_{15}H_{25}N_5O_n$ (n=20-22)	ROOR	Dimer R3+M1; Dimer R1+M2
Trimer 3	$C_{15}H_{25}N_3O_n$ (n=13-20)	ROOR	Dimer R2+M1; Dimer R4+M2
Trimer 4	$C_{15}H_{26}N_4O_n$ (n=17-21)	ROOR	Dimer R2+M2

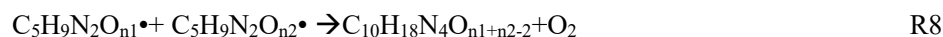
^a: ROOR denotes for organic peroxide.

^b: The numbering is referred to Table 1.

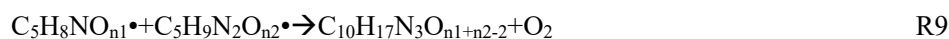
A number of HOM dimer series were observed, including $C_{10}H_{16}N_2O_n$ (n=10-17), $C_{10}H_{17}N_3O_n$ (n=11-19), and $C_{10}H_{18}N_4O_n$ (n=15-18), $C_{10}H_{18}N_2O_n$ (n=10-16), $C_{10}H_{15}N_3O_n$ (n=13-17), and $C_{10}H_{19}N_3O_n$ (n=14-15) series (Table 2, Table S3). $C_{10}H_{16}N_2O_n$ series (dimer 1, Table 2) was likely formed by the accretion reaction of two monomer RO₂ of M1a/b (Reaction R7).



Similarly, $C_{10}H_{18}N_4O_n$ series (dimer 2, Table 2) were likely formed by the accretion reaction of two monomer RO₂ of M2 (Reaction R8). As n₁ and n₂ are ≥ 9, the number of oxygen in $C_{10}H_{18}N_4O_n$ is expected to be ≥ 16. This is consistent with our observation that only $C_{10}H_{18}N_4O_n$ with n ≥ 16 had significant concentrations.

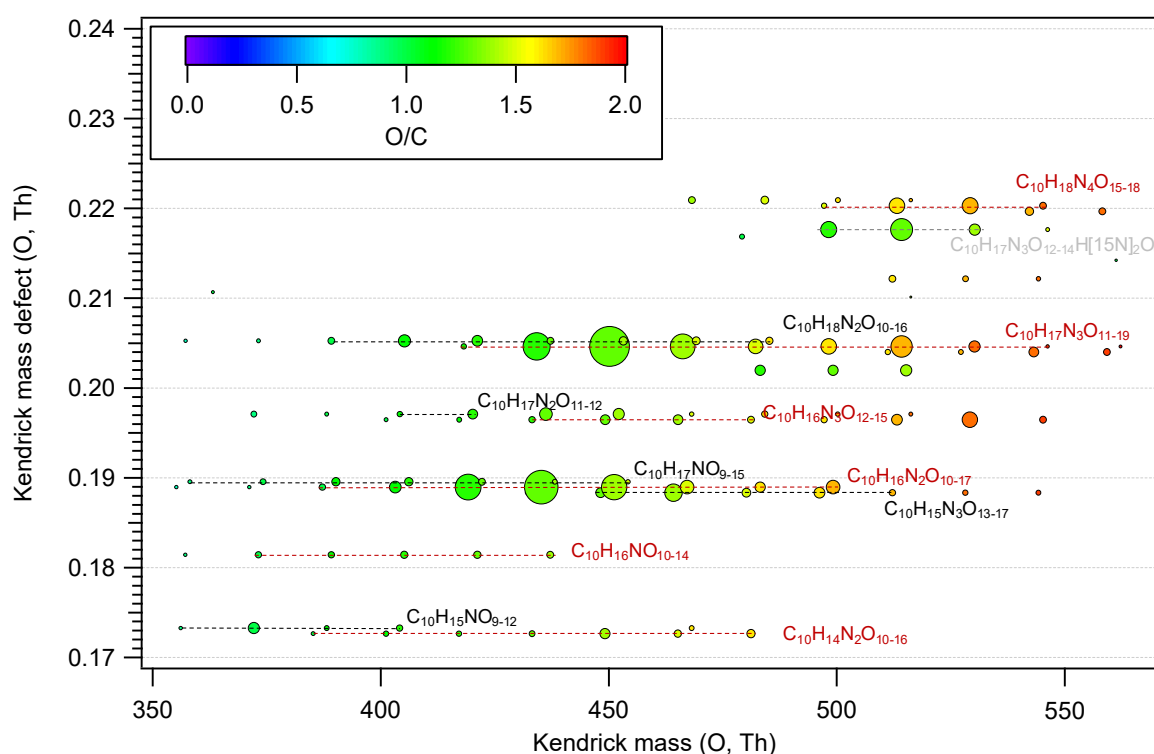


$C_{10}H_{17}N_3O_n$ series (dimer 3, Table 2) were likely formed by the cross accretion reaction of one M1 RO₂ and one M2 RO₂ (reaction R9). Since n₁ is ≥ 5 and n₂ is ≥ 9, the number of oxygen atoms in $C_{10}H_{17}N_3O_n$ is expected to be ≥ 12, which is also roughly consistent with our observation that only $C_{10}H_{17}N_3O_n$ with n ≥ 11 were detected.



494 Similarly, $C_{10}H_{18}N_2O_n$ ($n=10-16$) and $C_{10}H_{15}N_3O_n$ ($n=13-17$) series (dimer 4, dimer 5, Table 2) were likely formed
 495 from the accretion reaction between one M1 RO_2 and one M4 RO_2 , and between one M1 RO_2 and one M3 RO_2
 496 ($C_5H_7N_2O_9\bullet$). Other dimer series than dimer 1-5 were also present. However, they had quite low intensity (Fig. 4),
 497 which was consistent with the low abundance of their parent monomer RO_2 . They can be formed from various
 498 accretion reactions of monomer RO_2 . For example, $C_{10}H_{19}N_3O_n$ can be formed by the accretion reaction of
 499 $C_5H_9N_2O_n\bullet$ and $C_5H_{10}NO_n\bullet$ (Table 2).

500 Similar to monomers, a few species dominated in HOM dimers spectrum. The dominant dimer series were
 501 $C_{10}H_{17}N_3O_x$ and $C_{10}H_{16}N_2O_x$ series, with $C_{10}H_{17}N_3O_{12-14}$ and $C_{10}H_{16}N_2O_{12-14}$ showing highest intensity among each
 502 series (Fig. 4). In addition, the O/C ratio or oxidation state of HOM dimers were generally lower than that of
 503 monomers (Fig. 2, Fig. 4), which resulted from the loss of two oxygen atoms in the accretion reaction of two
 504 monomer RO_2 .



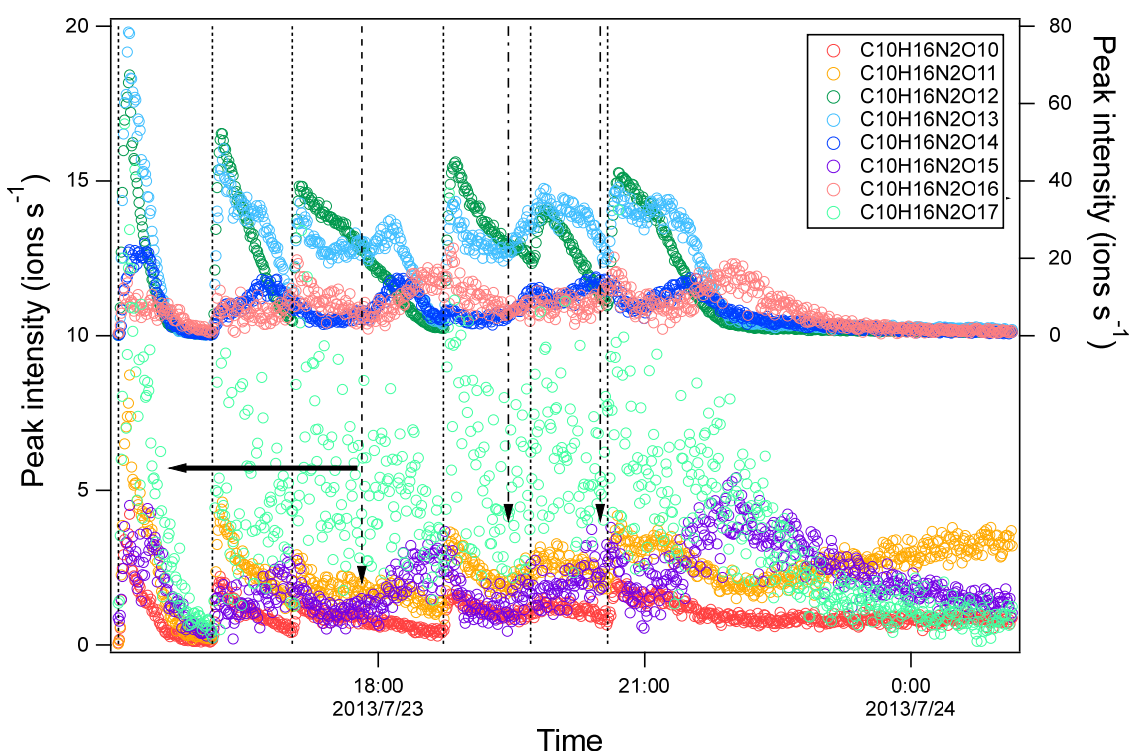
505
 506 Figure 4. Kendrick mass defect plot for O of HOM dimers formed in the isoprene+ NO_3 reaction. The size (area)
 507 of circles is set to be proportional to the average peak intensity of each molecular formula during the first isoprene addition
 508 period (P1). The molecular formula include the reagent ion $^{15}NO_3^-$, which is not shown for simplicity. The species
 509 labelled in grey ($C_{10}H_{17}N_3O_{12-14} H[^{15}N]_2O_6^-$) are the adducts of $C_{10}H_{17}N_3O_{12-14}$ with $H[^{15}N]_2O_6^-$.

510 According to the mechanism above (R7-9), we attempt to explain the relative intensities of the dimers using
 511 the signal intensities of monomer RO_2 . Assuming that the rate constant for each of HOM- RO_2 + HOM- RO_2 reaction
 512 forming dimers is the same considering that all HOM- RO_2 are highly oxygenated with a number of functional groups,
 513 it is expected that the dimer formed by the recombination between the most abundant RO_2 has the highest intensity.
 514 The most abundant monomer RO_2 were $C_5H_9N_2O_9\bullet$ and $C_5H_9N_2O_{10}\bullet$ and thus the most abundant dimers are expected
 515 to be $C_{10}H_{16}N_4O_{16}$, $C_{10}H_{16}N_4O_{17}$, and $C_{10}H_{16}N_4O_{18}$. This expected result is in contrast with our observation showing
 516 that the most abundant dimers were $C_{10}H_{17}N_3O_{12-14}$ and $C_{10}H_{16}N_2O_{12-14}$ (Fig. 4). The discrepancy is possibly

517 attributed to the presence of less oxygenated RO₂ (with O₂≤5) that have a low detection sensitivity in the NO₃-CIMS
 518 (Riva et al., 2019) due to their lower oxygenation compared with other HOM RO₂ shown above. These RO₂ may
 519 react with C₅H₉N₂O₉• and C₅H₉N₂O₁₀•. For example, C₅H₈NO₅• (RO₂) is proposed to be an important first-
 520 generation RO₂ in the oxidation of isoprene by NO₃ (Ng et al., 2008; Rollins et al., 2009; Kwan et al., 2012;
 521 Schwantes et al., 2015). Although C₅H₈NO₅• showed very low signal in our mass spectra, it was likely to have high
 522 abundance since it was the first RO₂ formed in the reaction of isoprene with NO₃. Indeed, we found that the
 523 termination products of C₅H₈NO₅• such as C₅H₉NO₅, C₅H₇NO₄, and C₅H₉NO₄ had high abundance in another study,
 524 indicating the high abundance of C₅H₈NO₅•. The accretion reaction of C₅H₈NO₅• with C₅H₉N₂O₉₋₁₀• and C₅H₈NO₉₋₁₀•
 525 can explain the high abundance of C₁₀H₁₇N₃O₁₂₋₁₄ and C₁₀H₁₆N₂O₁₂₋₁₄ among all dimers.

526 Provided that C₅H₈NO₅• is abundant, we still cannot explain the relative intensity of C₁₀H₁₇N₃O₁₂,
 527 C₁₀H₁₇N₃O₁₃, and C₁₀H₁₇N₃O₁₄ that were all formed by the accretion reaction with C₅H₈NO₅•. C₁₀H₁₇N₃O₁₂ should
 528 have the highest intensity among C₁₀H₁₇N₃O₁₂₋₁₄ as its precursor RO₂, C₅H₉N₂O₉•, is the most abundant. This
 529 suggests that accretion reactions other than those of C₅H₈NO₅• with C₅H₉N₂O₉₋₁₀• also contributed to C₁₀H₁₇N₃O₁₂₋₁₄.
 530 Admittedly, the assumption of different RO₂ having similar rate constants in accretion reactions may not be valid.
 531 For example, self-reaction of tertiary RO₂ is slower than secondary and primary RO₂ (Jenkin et al., 1998; Finlayson-
 532 Pitts and Pitts, 2000). Different rate constants may also lead to the observation that the most abundant dimers could
 533 not be explained the most abundant RO₂.

534



535

536 Figure 5. Time series of peak intensity of several HOM dimers of C₁₀H₁₆N₂O_n series. The dashed lines
 537 indicate the time of isoprene additions. The long-dashed arrow indicates the time of NO₂ addition. The dash-dotted
 538 arrows indicate the time of O₃ additions. The horizontal arrows indicate y-axis scales for different markers.

The time profiles of $C_{10}H_{16}N_2O_n$ indicate contributions of both the first- and second-generation products. The dominance of the first- or second-generation products depended on the specific compounds. Most $C_{10}H_{16}N_2O_n$ compounds increased instantaneously after isoprene additions, indicating significant contributions of first-generation products. Since the formation of $C_{10}H_{16}N_2O_n$ likely involved $C_5H_8NO_5^\bullet$ as discussed above, the instantaneous increase may result from the increase of $C_5H_8NO_5^\bullet$ as well as other first-generation RO_2 . After the initial increase, $C_{10}H_{16}N_2O_{10-12}$ then decayed with time (Fig. 5) while $C_{10}H_{16}N_2O_{13-15}$ increased again in the later phase of a period and when NO_2 and O_3 were added. The second increase indicated that $C_{10}H_{16}N_2O_{13-15}$ may contain more than one isomer, which had different production pathways. As discussed above, $C_5H_8NO_n^\bullet$ can be either a first-generation RO_2 formed directly via the reaction of isoprene with NO_3 and autoxidation, or a second-generation RO_2 , e.g. formed via the reaction of with $C_5H_8O_2$ with NO_3 . Therefore the second increase of $C_{10}H_{16}N_2O_{13-15}$ may result from the reaction of two first-generation RO_2 and of two second-generation RO_2 or between one first-generation and one second-generation RO_2 . The increase of $C_{10}H_{16}N_2O_{14-15}$ after isoprene addition was not large, indicating the larger contributions from second-generation products compared with other $C_{10}H_{16}N_2O_n$. Overall, as the number of oxygen increased, the contribution of second-generation products to $C_{10}H_{16}N_2O_n$ increased.

In contrast to $C_{10}H_{16}N_2O_n$ series, $C_{10}H_{18}N_4O_n$ increased gradually after each isoprene addition and then decreased afterward (Fig. 6), either naturally or after isoprene additions, which is typical for second-generation products. Since $C_{10}H_{18}N_4O_n$ was likely formed by the accretion reaction of $C_5H_9N_2O_n^\bullet$ (RO_2), the time profile of $C_{10}H_{18}N_4O_n$ was as expected since $C_5H_9N_2O_n^\bullet$ was formed via the reaction of NO_3 with first-generation products $C_5H_9NO_n$. The $C_{10}H_{18}N_4O_n$ concentration depended on the product of the concentrations of two $C_5H_9N_2O_n^\bullet$. Taking $C_{10}H_{18}N_4O_{16}$ as an example, its concentration can be expressed as follows:

$$\frac{d[C_{10}H_{18}N_4O_{16}]}{dt} = k[C_5H_9N_2O_9][C_5H_9N_2O_9] - k_{wl}[C_{10}H_{18}N_4O_{16}]$$

When the concentration of $C_5H_9N_2O_9^\bullet$ increased, the changing rate of $C_{10}H_{18}N_4O_{16}$ was positive and increased and thus the concentration of $C_{10}H_{18}N_4O_{16}$ increased. When the concentration $C_5H_9N_2O_9^\bullet$ decreased sharply after isoprene additions, the changing rate of $C_{10}H_{18}N_4O_{16}$ decreased and even became negative values, and thus the concentration of $C_{10}H_{18}N_4O_{16}$ decreased after isoprene addition.

Similar to the $C_{10}H_{16}N_2O_n$ series, while $C_{10}H_{17}N_3O_n$ first increased instantaneously with isoprene addition, it increased again during the later stage of each period (Fig. S10), showing a mixed behavior of the first-generation products and second-generation products. The time series of $C_{10}H_{17}N_3O_n$ was as expected in general because $C_{10}H_{17}N_3O_n$ was likely formed via the accretion reaction of $C_5H_8NO_n^\bullet$ (M1 RO_2) and $C_5H_9N_2O_n^\bullet$ (M2 RO_2), which were first- or second-generation, and second-generation RO_2 , respectively,

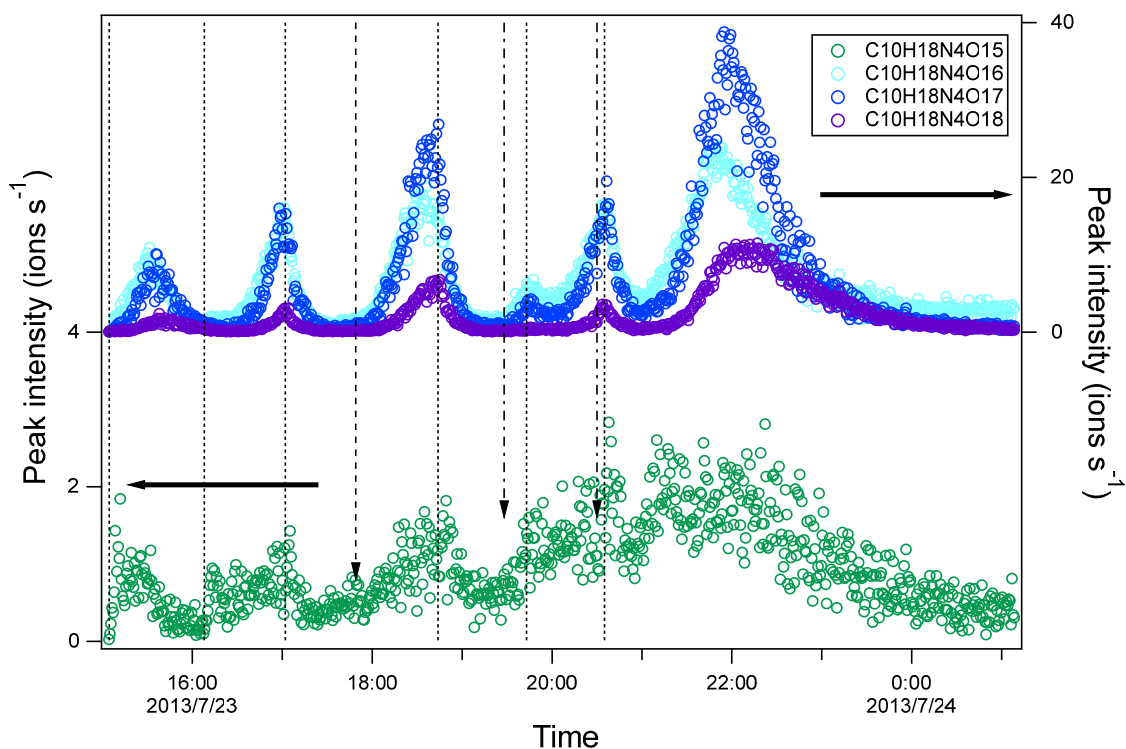
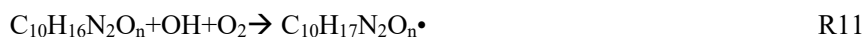
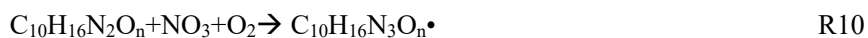


Figure 6. Time series of peak intensity of several HOM dimers of $C_{10}H_{18}N_4O_n$ series. The dashed lines indicate the time of isoprene additions. The long-dashed arrow indicates the time of NO_2 addition. The dash-dotted arrows indicate the time of O_3 additions. The horizontal arrows indicate y-axis scales for different markers.

Some dimers that cannot be explained by accretion reactions such as $C_{10}H_{16}N_3O_n$ ($n=12-15$) $\bullet$, $C_{10}H_{17}N_2O_n$ ($n=11-12$) $\bullet$, $C_{10}H_{16}NO_n$ ($n=10-14$) $\bullet$, $C_{10}H_{15}NO_n$ ($n=9-12$), $C_{10}H_{17}NO_n$ ($n=9-15$) were also observed. These dimers had low abundance. We note that due to their low signals in the mass spectra, their assignment and thus range of n may be subject to uncertainties. Since $C_{10}H_{16}NO_n$ ($n=10-16$) $\bullet$, $C_{10}H_{16}N_3O_n$ ($n=12-15$) $\bullet$, and $C_{10}H_{17}N_2O_n$ $\bullet$ contain unpaired electrons, they cannot be formed via the direct accretion reaction of two RO_2 . Instead, $C_{10}H_{16}N_3O_n$ ($n=12-15$) $\bullet$ (dimer R1) and $C_{10}H_{17}N_2O_n$ $\bullet$ (dimer R2) were likely RO_2 formed by the reaction of HOM dimers containing a double bond (dimer 1) with NO_3 and with OH , respectively, followed by the reaction with O_2 .



The corresponding termination products of $C_{10}H_{16}N_3O_n$ $\bullet$ RO_2 series such as $C_{10}H_{15}N_3O_n$ (ketone), $C_{10}H_{17}N_3O_n$ (hydroperoxide/alcohol) were also observed, although these compounds can also be formed via reactions between two RO_2 radicals (R9 and R11). Among the termination products, $C_{10}H_{15}N_3O_n$ had low intensity. Reaction R13 and the termination reaction of $C_{10}H_{17}N_2O_n$ $\bullet$ with HO_2 provided an additional pathway to $C_{10}H_{17}N_3O_n$ besides the R9 pathway discussed above. Similarly, other dimers may also be formed by the termination reactions of dimer RO_2 with RO_2 or HO_2 . E.g., $C_{10}H_{18}N_4O_n$ can be formed via termination reaction of $C_{10}H_{17}N_4O_n$ $\bullet$ with another RO_2 wherein $C_{10}H_{17}N_4O_n$ $\bullet$ can be formed as follows:



$C_{10}H_{16}NO_n$ ($n=10-14$) $\bullet$ could be explained by the reaction of monomer RO_2 with isoprene.

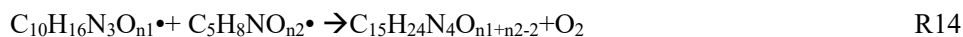


Only C₁₀H₁₆NO_n• with n ≥ 10 were detected, while according to the mechanism of self-reaction between C₅H₈NO_n•, the n range of C₁₀H₁₆NO_n• is expected to be 7-14. The absence of C₁₀H₁₆NO_{n(n<10)}• is likely attributed to their low abundance, which might result from low precursor concentrations, low reaction rates with isoprene, and/or faster reactive losses with other radicals. Such a reaction of RO₂ with isoprene has been proposed by Ng et al. (2008) and Kwan et al. (2012). The corresponding termination products of C₁₀H₁₆NO_n• are C₁₀H₁₅NO_n (ketone) and C₁₀H₁₇NO_n species (hydroperoxide/alcohol). C₁₀H₁₇NO_n species showed a time profile of typical first-generation products (Fig. S11), i.e. increasing immediately with isoprene addition and then decaying with time. This behaviour further supports the possibility of reaction R13. Yet, the reaction rate of alkene with RO₂ is likely low due to the high activation energy (Stark, 1997, 2000). It is worth noting that to our knowledge no experimental kinetic data on the addition of RO₂ to alkenes in the gas phase in atmospheric relevant conditions are available, though fast, low-barrier ring closure reactions in unsaturated RO₂ radicals have been reported (Vereecken and Peeters, 2004, 2012; Kaminski et al., 2017; Richters et al., 2017; Chen et al., 2021). We would like to note that there is unlikely interference to C₁₀-HOM from monoterpenes, which has been reported previously (Bernhammer et al., 2018), as the concentration of monoterpenes in the chamber during this study was below the limit of detection, which was ~50 ppt (3σ).

Some of the dimers discussed above have been observed in previous studies. Ng et al. (2008) found C₁₀H₁₆N₂O₈ and C₁₀H₁₆N₂O₉ in the gas phase and C₁₀H₁₇N₃O₁₂, C₁₀H₁₇N₃O₁₃, C₁₀H₁₈N₄O₁₆, and C₁₀H₁₇N₅O₁₈ in the particle phase. C₁₀H₁₆N₂O₈ and C₁₀H₁₆N₂O₉ were also observed in our study, but their intensity in the MS was too low to assign molecular formulas with high confidence. The low intensity may be due to the low sensitivity of C₁₀H₁₆N₂O_{8,9} in NO₃⁻-CIMS. According to modelling results of the products formed in cyclohexene ozonolysis by Hyttinen et al. (2015), at least two hydrogen bond donor functional groups are needed for a compound to be detected in a nitrate CIMS. As C₁₀H₁₆N₂O₈ and C₁₀H₁₆N₂O₉ have no and only one H-bond donor function groups, respectively, they are expected to have low sensitivity in NO₃⁻-CIMS. Moreover, the low intensity can be partly attributed to the much lower isoprene concentrations used in this study compared to previous studies, leading to the low concentration of C₁₀H₁₆N₂O₈ and C₁₀H₁₆N₂O₉ (Ng et al., 2008). C₁₀H₁₇N₃O₁₂, C₁₀H₁₇N₃O₁₃, C₁₀H₁₈N₄O₁₆, and C₁₀H₁₇N₅O₁₈ were all observed in the gas phase in this study, wherein the concentration of C₁₀H₁₇N₅O₁₈ was very low. The formation pathways of C₁₀H₁₇N₃O₁₂, C₁₀H₁₇N₃O₁₃, and C₁₀H₁₈N₄O₁₆ (R8) were generally similar to those proposed by Ng et al. (2008) except that the products from H-shift of RO₂ were involved in the formation of C₁₀H₁₇N₃O₁₃. Among the two pathways of C₁₀H₁₈N₄O₁₆ formation (R8 and via R12), our results indicate that R8 was the main pathway, based on the low concentrations of C₁₀H₁₇N₄O_{16/17}• and other termination product of them, C₁₀H₁₆N₄O_{15/16}. That the time profile of C₁₀H₁₈N₄O₁₆ was consistent with what is expected from R8 as discussed above offers additional evidence to that conclusion.

3.4 HOM trimers and their formation

A series of HOM trimers were observed, such as C₁₅H₂₄N₄O_n (n=17-22), C₁₅H₂₅N₅O_n (n=20-22), C₁₅H₂₅N₃O_n (n=13-20), C₁₅H₂₆N₄O_n (n=17-21), and C₁₅H₂₄N₂O_n (n=12-16). Among the trimers, C₁₅H₂₄N₄O_n was the most abundant series (Fig. S12). The C₁₅H₂₄N₄O_n series can be explained by the accretion reaction of one monomer HOM RO₂ and one dimer HOM RO₂.



The formation pathways of dimer RO₂ C₁₀H₁₆N₃O_n (n=12-15) and C₁₀H₁₇N₂O_n are shown above (reaction R10 and R11).

The other trimers were likely formed via similar pathways (Table 2 and Supplement S2). Since NO₃⁻-CIMS cannot provide the structural information of these HOM trimers, we cannot elucidate the major pathways. However, in all these pathways, dimer-RO₂ is necessary to form a trimer, and most of the dimer-RO₂ formation pathways require at least one double bond in the dimer molecule except for the reaction of RO₂ with isoprene. Since one double bond has already reacted in the monomer-RO₂ formation, we anticipate that in the reaction with NO₃ it is more favourable for precursors (VOC) containing more than one double bonds to form trimer molecules than precursors containing only one double bond, as it is easier to generate new RO₂ radicals from these dimers by attack on the remaining double bond(s).

The time profile of C₁₅H₂₄N₄O_n showed the mixed behavior of first- and second-generation products (Fig. S13), consistent with the mechanism discussed above since C₅H₈NO_n[•] and C₁₀H₁₆N₃O_n[•] were of first- or second-generation and second-generation, respectively. The contributions of the second-generation products became larger as the number of oxygen atoms increased. In contrast, C₁₅H₂₅N₃O_n showed instantaneous increase with isoprene addition (Fig. S14), which was typical for time profiles of first-generation products. Both proposed formation pathways of C₁₅H₂₅N₃O_n (RS6 and RS7) contained a second-generation RO₂, which was not in line with the time profile observed. The observation cannot be well explained, unless we assume molecular adducts of a dimer with one monomer. It is also possible that some C₁₀H₁₇N₂O_n[•] were formed very fast or that there were other formation pathways of C₁₅H₂₅N₃O_n not accounted for here.

3.5 Contributions of monomers, dimer, and trimers to HOM

The concentration (represented by peak intensity) of monomers was higher than that of dimers, but overall their concentrations remained of the same order of magnitude (Fig 1a, inset). The concentration of trimers was much lower than that of monomers and dimers. The relative contributions of monomers, dimers, and trimers evolved in time due to the changing concentration of each HOM species. Comparing the contributions of various classes of HOM in period 1 with those in periods 1-6 reveals that the relative contribution of monomers increased with time, especially that of 2N-monomers, while the contribution of dimers decreased. This trend is attributed to the larger wall loss of dimers compared to monomers because of their lower volatility and also to the continuous formation of second-generation monomers, mostly 2N-monomers. Overall, the relative contribution of total HOM monomers decreased immediately after isoprene addition while the contribution of HOM dimers increased rapidly (Fig. S15), which was attributed to the faster increase of dimers intensity due to their rapid formation. Afterwards, the contribution of monomers to total HOM gradually increased and that of dimers decreased, which was partly due to the faster wall loss rate of dimers and to the continuous formation of second-generation monomers.

3.6 Yield of HOM

The HOM yield in the oxidation of isoprene by NO₃ was estimated using the sensitivity of H₂SO₄. It was derived for the first isoprene addition period to minimize the contribution of multi-generation products and to better compare with the data in literature, thus denoted as primary HOM yield (Pullinen et al., 2020) and was estimated to

be $1.2\%_{-0.7\%}^{+1.3\%}$. The uncertainty was estimated as shown in the Supplement S1. Despite the uncertainty, the primary HOM yield here was much higher than the HOM yield from the ozonolysis and photooxidation of isoprene (Jokinen et al., 2015). The difference may be attributed to the more efficient oxygenation in the addition of NO_3 to carbon double bonds. Compared with the reaction with O_3 or OH , the initial peroxy radicals contains 5 oxygen atoms when isoprene reacts with NO_3 , while the initial peroxy radicals contains only 3 oxygen atoms when reacting with OH , and the ozonide contains 3 oxygen atoms in the case of O_3 .

4 Conclusion and implications

HOM formation in the reaction of isoprene with NO_3 was investigated in the SAPHIR chamber. A number of HOM monomers, dimers, and trimers containing one to five nitrogen atoms were detected, and their time-dependent concentration profiles were tracked throughout the experiment. Some formation mechanisms for various HOM were proposed according to the molecular formula identified, and the available literature. HOM showed a variety of time profiles with multiple isoprene additions during the reaction. First-generation HOM increased instantaneously after isoprene addition and then decreased while second-generation HOM increased gradually and then decreased with time, reaching a maximum concentration at the later stage of each period. The time profiles provide additional constraints on their formation mechanism beside the molecular formula, suggesting whether they were first-generation products or second-generation products or a combination of both. 1N-monomers (mostly C_5) were likely formed by NO_3 addition to a double bond of isoprene, forming monomer RO_2 , followed by autoxidation and termination via the reaction with HO_2 , RO_2 , and NO_3 . Time series suggest that some 1N-monomer could also be formed by the reaction of first-generation products with NO_3 , and thus be of second-generation. 2N-monomers were likely formed via the reaction of first-generation products such as C_5 -hydroxynitrate with NO_3 and thus second-generation products. 3N-monomers likely comprised peroxy/peroxyacyl nitrates formed by the reaction of 2N-monomer RO_2 with NO_2 , and possibly nitronitrates formed via the direct addition of N_2O_5 to the first-generation products. HOM dimers were mostly formed by the accretion reactions between various HOM monomer RO_2 , either first-generation or second-generation or with the contributions of both, and thus showed time profiles typical of either first-generation products, or second-generation products, or a combination of both. Additionally, some dimers peroxy radicals (dimer RO_2) were formed by the reaction of NO_3 with dimers containing a $\text{C}=\text{C}$ double bond. HOM trimers were proposed to be formed by accretion reactions between the monomer RO_2 and dimer RO_2 .

Overall, both HOM monomers and dimers contribute significantly to total HOM while trimers only contributed a minor fraction. Within both the monomer and dimer compounds, a limited set of compounds dominated the abundance, such as $\text{C}_5\text{H}_8\text{N}_2\text{O}_n$, $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_n$, $\text{C}_{10}\text{H}_{17}\text{N}_3\text{O}_n$, and $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_n$ series. 2N-monomers, which were second-generation products, dominated in monomers and accounted for $\sim 34\%$ of all HOM, indicating the important role of second-generation oxidation in HOM formation in the isoprene+ NO_3 reaction. Both RO_2 autoxidation and “alkoxy-peroxy” pathways were found to be important for 1N- and 2N-HOM formation. In total, the yield of HOM monomers, dimers, and trimers accounted for $1.3\%_{-0.7\%}^{+1.3\%}$ of the isoprene reacted, which was much higher than the HOM yield in the oxidation of isoprene by OH and O_3 reported in the literature (Jokinen et al., 2015). This means that the reaction of isoprene with NO_3 is a competitive pathway of HOM formation from isoprene.

The HOM in the reaction of isoprene with NO₃ may account for a significant fraction of SOA. If all the HOM condense on particles, using the molecular weight of the HOM with the least molecular weight observed in this study (C₅H₉NO₆), the HOM yield corresponds to a SOA yield of 3.6%. Although SOA concentrations were not measured in this study, Ng et al. (2008) reported a SOA yield of the isoprene+NO₃ reaction of 4.3%-23.8%. Rollins et al. (2009) reported a SOA yield of 2% at low organic aerosol loading (~0.52 μg m⁻³) and 14% if the further oxidation of the first-generation products are considered in the isoprene+NO₃ reaction. Comparing the potential SOA yield produced by HOM with SOA yields in the literature suggests that HOM may play an important role in the SOA formation in the isoprene+NO₃ reaction.

The RO₂ lifetime is approximately 20-50 s in our experiments, which is generally comparable or shorter than the lifetime of RO₂ in the ambient atmosphere at night, varying from several 10 s to several 100 s (Fry et al., 2018), depending on the NO₃, HO₂, and RO₂ concentrations. Assuming a HO₂, RO₂, and NO₃ concentration of 5 ppt, 5 ppt (Tan et al., 2019), and 300 ppt (Brown and Stutz, 2012) respectively, the RO₂ lifetime in our study is comparable to the nighttime RO₂ lifetime (50 s) found in urban locations and areas influenced by urban plume. In areas with longer RO₂ lifetime such as remote areas, the autooxidation is expected to be more important relative to bimolecular reactions. This may enhance HOM yield and thus enhance SOA yield. However, on the other hand, at lower RO₂ concentration and thus longer RO₂ lifetime, reduced rates of RO₂+RO₂ reactions producing low-volatility dimers can reduce the SOA yield via reducing dimer yield (McFiggans et al., 2019; Pullinen et al., 2020). The RO₂ fate in our experiments is dominated the reaction RO₂+NO₃ with significant contribution of RO₂+RO₂, which can also represent the RO₂ fate in the urban areas and areas influenced by urban plume. Our experiment condition cannot represent the chemistry in HO₂-dominated regions such as clean forest environment (Schwantes et al., 2015).

We observed the second-generation products formed by the reaction of first-generation products. The lifetime of first-generation nitrates in the ambient atmosphere, according their rate constants with OH and NO₃ (Wennberg et al., 2018), are ~5 h and ~1.3-4 h, respectively, with respect to the reaction with OH and NO₃ assuming a typical OH concentration of 2×10⁶ molecules cm⁻³ (Lu et al., 2014; Tan et al., 2019) and NO₃ concentration of 100-300 ppt in urban areas (Brown and Stutz, 2012). Therefore, they have the chance to react further with OH and NO₃ at dawn. In our experiments, the lifetimes of these first-generation nitrates with respect to OH and NO₃ are comparable to the aforementioned lifetime due to comparable OH and NO₃ concentrations with these ambient conditions. Therefore, our findings on the second-generation products are relevant to the ambient urban atmosphere and areas influenced by urban plumes. Some of these products such as C₅H₈10N₂O₈ and multi-generation nitrooxyorganosulfates have been observed in recent field studies in polluted megacities in east China (Hamilton et al., 2021; Xu et al., 2021).

Data availability

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

736 **Competing interests**

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

738 **Author contribution**

739 TFM, HF, SS, DZ, IP, AW, and AKS designed the experiments. Instrument deployment and operation were carried
740 out by IP, HF, SS, IA, RT, FR, DZ, and RW. Data analysis was done by DZ, HF, SS, RW, IA, RT, FR, YG, SK. DZ,
741 TFM, RW, JW, SK, and LV interpreted the compiled data set. DZ and TFM wrote the paper. All co-authors discussed
742 the results and commented on the paper.

743 **Acknowledgements**

744 We thank the SAPHIR team for supporting our measurements and providing helpful data. D. Zhao and Y. Guo would
745 like to thank the support of National Natural Science Foundation of China (41875145). We would like to thank three
746 anonymous reviewers and Kristian Møller for their helpful comments.

References

- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - gas phase reactions of organic species, *Atmos. Chem. Phys.*, 6, 3625-4055, 2006.
- Ayres, B. R., Allen, H. M., Draper, D. C., Brown, S. S., Wild, R. J., Jimenez, J. L., Day, D. A., Campuzano-Jost, P., Hu, W., de Gouw, J., Koss, A., Cohen, R. C., Duffey, K. C., Romer, P., Baumann, K., Edgerton, E., Takahama, S., Thornton, J. A., Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Wennberg, P. O., Nguyen, T. B., Teng, A., Goldstein, A. H., Olson, K., and Fry, J. L.: Organic nitrate aerosol formation via NO_3 + biogenic volatile organic compounds in the southeastern United States, *Atmos. Chem. Phys.*, 15, 13377-13392, 10.5194/acp-15-13377-2015, 2015.
- Berndt, T., and Böge, O.: Gas-phase reaction of NO_3 radicals with isoprene: a kinetic and mechanistic study, *Int. J. Chem. Kinet.*, 29, 755-765, 10.1002/(sici)1097-4601(1997)29:10<755::Aid-kin4>3.0.Co;2-I, 1997.
- Berndt, T., Mender, B., Scholz, W., Fischer, L., Herrmann, H., Kulmala, M., and Hansel, A.: Accretion Product Formation from Ozonolysis and OH Radical Reaction of α -Pinene: Mechanistic Insight and the Influence of Isoprene and Ethylene, *Environ. Sci. Technol.*, 52, 11069-11077, 10.1021/acs.est.8b02210, 2018a.
- Berndt, T., Scholz, W., Mentler, B., Fischer, L., Herrmann, H., Kulmala, M., and Hansel, A.: Accretion Product Formation from Self- and Cross-Reactions of RO_2 Radicals in the Atmosphere, *Angew. Chem.-Int. Edit.*, 57, 3820-3824, 10.1002/anie.201710989, 2018b.
- Bernhammer, A. K., Fischer, L., Mentler, B., Heinritzi, M., Simon, M., and Hansel, A.: Production of highly oxygenated organic molecules (HOMs) from trace contaminants during isoprene oxidation, *Atmos. Meas. Tech.*, 11, 4763-4773, 10.5194/amt-11-4763-2018, 2018.
- Bianchi, F., Kurten, T., Riva, M., Mohr, C., Rissanen, M. P., Roldin, P., Berndt, T., Crounse, J. D., Wennberg, P. O., Mentel, T. F., Wildt, J., Junninen, H., Jokinen, T., Kulmala, M., Worsnop, D. R., Thornton, J. A., Donahue, N., Kjaergaard, H. G., and Ehn, M.: Highly Oxygenated Organic Molecules (HOM) from Gas-Phase Autoxidation Involving Peroxy Radicals: A Key Contributor to Atmospheric Aerosol, *Chem. Rev.*, 119, 3472-3509, 10.1021/acs.chemrev.8b00395, 2019.
- Boyd, C. M., Sanchez, J., Xu, L., Eugene, A. J., Nah, T., Tuet, W. Y., Guzman, M. I., and Ng, N. L.: Secondary organic aerosol formation from the β -pinene+ NO_3 system: effect of humidity and peroxy radical fate, *Atmos. Chem. Phys.*, 15, 7497-7522, 10.5194/acp-15-7497-2015, 2015.
- Boyd, C. M., Nah, T., Xu, L., Berkemeier, T., and Ng, N. L.: Secondary Organic Aerosol (SOA) from Nitrate Radical Oxidation of Monoterpenes: Effects of Temperature, Dilution, and Humidity on Aerosol Formation, Mixing, and Evaporation, *Environ. Sci. Technol.*, 51, 7831-7841, 10.1021/acs.est.7b01460, 2017.
- Brown, S. S., deGouw, J. A., Warneke, C., Ryerson, T. B., Dube, W. P., Atlas, E., Weber, R. J., Peltier, R. E., Neuman, J. A., Roberts, J. M., Swanson, A., Flocke, F., McKeen, S. A., Brioude, J., Sommariva, R., Trainer, M., Fehsenfeld, F. C., and Ravishankara, A. R.: Nocturnal isoprene oxidation over the Northeast United States in summer and its impact on reactive nitrogen partitioning and secondary organic aerosol, *Atmos. Chem. Phys.*, 9, 3027-3042, 10.5194/acp-9-3027-2009, 2009.
- Brown, S. S., Dube, W. P., Peischl, J., Ryerson, T. B., Atlas, E., Warneke, C., de Gouw, J. A., Hekkert, S. t. L., Brock, C. A., Flocke, F., Trainer, M., Parrish, D. D., Fehsenfeld, F. C., and Ravishankara, A. R.: Budgets for nocturnal VOC oxidation by nitrate radicals aloft during the 2006 Texas Air Quality Study, *J. Geophys. Res.-Atmos.*, 116, 10.1029/2011jd016544, 2011.

- Brown, S. S., and Stutz, J.: Nighttime radical observations and chemistry, *Chem. Soc. Rev.*, 41, 6405-6447, 10.1039/c2cs35181a, 2012.
- Chen, J., Möller, K. H., Wennberg, P. O., and Kjaergaard, H. G.: Unimolecular Reactions Following Indoor and Outdoor Limonene Ozonolysis, *J. Phys. Chem. A* 125, 669-680, 10.1021/acs.jpca.0c09882, 2021.
- Claffin, M. S., and Ziemann, P. J.: Identification and Quantitation of Aerosol Products of the Reaction of β -Pinene with NO_3 Radicals and Implications for Gas- and Particle-Phase Reaction Mechanisms, *The Journal of Physical Chemistry A*, 122, 3640-3652, 10.1021/acs.jpca.8b00692, 2018.
- Crounse, J. D., Knap, H. C., Ørnsø, K. B., Jørgensen, S., Paulot, F., Kjaergaard, H. G., and Wennberg, P. O.: Atmospheric Fate of Methacrolein. 1. Peroxy Radical Isomerization Following Addition of OH and O_2 , *The Journal of Physical Chemistry A*, 116, 5756-5762, 10.1021/jp211560u, 2012.
- Crounse, J. D., Nielsen, L. B., Jørgensen, S., Kjaergaard, H. G., and Wennberg, P. O.: Autoxidation of Organic Compounds in the Atmosphere, *J. Phys. Chem. Lett.*, 4, 3513-3520, 10.1021/jz4019207, 2013.
- Draper, D. C., Myllys, N., Hyttinen, N., Möller, K. H., Kjaergaard, H. G., Fry, J. L., Smith, J. N., and Kurten, T.: Formation of Highly Oxidized Molecules from NO_3 Radical Initiated Oxidation of Delta-3-Carene: A Mechanistic Study, *Acs Earth and Space Chemistry*, 3, 1460-1470, 10.1021/acsearthspacechem.9b00143, 2019.
- Ehn, M., Thornton, J. A., Kleist, E., Sipila, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I. H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurten, T., Nielsen, L. B., Jørgensen, S., Kjaergaard, H. G., Canagaratna, M., Dal Maso, M., Berndt, T., Petaja, T., Wahner, A., Kerminen, V. M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-volatility secondary organic aerosol, *Nature*, 506, 476-479, 10.1038/nature13032, 2014.
- Ehn, M., Berndt, T., Wildt, J., and Mentel, T.: Highly Oxygenated Molecules from Atmospheric Autoxidation of Hydrocarbons: A Prominent Challenge for Chemical Kinetics Studies, *Int. J. Chem. Kinet.*, 49, 821-831, 10.1002/kin.21130, 2017.
- Eisele, F. L., and Tanner, D. J.: Measurement of the gas phase concentration of H_2SO_4 and methane sulfonic acid and estimates of H_2SO_4 production and loss in the atmosphere, 98, 9001-9010, 10.1029/93jd00031, 1993.
- Faxon, C., Hammes, J., Le Breton, M., Pathak, R. K., and Hallquist, M.: Characterization of organic nitrate constituents of secondary organic aerosol (SOA) from nitrate-radical-initiated oxidation of limonene using high-resolution chemical ionization mass spectrometry, *Atmos. Chem. Phys.*, 18, 5467-5481, 10.5194/acp-18-5467-2018, 2018.
- Finlayson-Pitts, B., and Pitts, J.: *Chemistry of the upper and lower atmosphere*, Academic Press, San Diego, 2000.
- Fry, J. L., Kiendler-Scharr, A., Rollins, A. W., Wooldridge, P. J., Brown, S. S., Fuchs, H., Dube, W., Mensah, A., dal Maso, M., Tillmann, R., Dorn, H. P., Brauers, T., and Cohen, R. C.: Organic nitrate and secondary organic aerosol yield from NO_3 oxidation of beta-pinene evaluated using a gas-phase kinetics/aerosol partitioning model, *Atmos. Chem. Phys.*, 9, 1431-1449, 2009.
- Fry, J. L., Kiendler-Scharr, A., Rollins, A. W., Brauers, T., Brown, S. S., Dorn, H. P., Dube, W. P., Fuchs, H., Mensah, A., Rohrer, F., Tillmann, R., Wahner, A., Wooldridge, P. J., and Cohen, R. C.: SOA from limonene: role of NO_3 in its generation and degradation, *Atmos. Chem. Phys.*, 11, 3879-3894, 10.5194/acp-11-3879-2011, 2011.
- Fry, J. L., Draper, D. C., Barsanti, K. C., Smith, J. N., Ortega, J., Winkle, P. M., Lawler, M. J., Brown, S. S., Edwards, P. M., Cohen, R. C., and Lee, L.: Secondary Organic Aerosol Formation and Organic Nitrate Yield from NO_3 Oxidation of Biogenic Hydrocarbons, *Environ. Sci. Technol.*, 48, 11944-11953, 10.1021/es502204x, 2014.

- Fry, J. L., Brown, S. S., Middlebrook, A. M., Edwards, P. M., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Allen, H. M., Ryerson, T. B., Pollack, I., Graus, M., Warneke, C., de Gouw, J. A., Brock, C. A., Gilman, J., Lerner, B. M., Dube, W. P., Liao, J., and Welti, A.: Secondary organic aerosol (SOA) yields from NO₃ radical + isoprene based on nighttime aircraft power plant plume transects, *Atmos. Chem. Phys.*, 18, 11663-11682, 10.5194/acp-18-11663-2018, 2018.
- Fuchs, H., Dorn, H. P., Bachner, M., Bohn, B., Brauers, T., Gomm, S., Hofzumahaus, A., Holland, F., Nehr, S., Rohrer, F., Tillmann, R., and Wahner, A.: Comparison of OH concentration measurements by DOAS and LIF during SAPHIR chamber experiments at high OH reactivity and low NO concentration, *Atmos. Meas. Tech.*, 5, 1611-1626, 10.5194/amt-5-1611-2012, 2012.
- Garmash, O., Rissanen, M. P., Pullinen, I., Schmitt, S., Kausiala, O., Tillmann, R., Percival, C., Bannan, T. J., Priestley, M., Hallquist, Å. M., Kleist, E., Kiendler-Scharr, A., Hallquist, M., Berndt, T., McFiggans, G., Wildt, J., Mentel, T., and Ehn, M.: Multi-generation OH oxidation as a source for highly oxygenated organic molecules from aromatics, *Atmos. Chem. Phys. Discuss.*, 2019, 1-33, 10.5194/acp-2019-582, 2019.
- Geyer, A., Alicke, B., Konrad, S., Schmitz, T., Stutz, J., and Platt, U.: Chemistry and oxidation capacity of the nitrate radical in the continental boundary layer near Berlin, *J. Geophys. Res.-Atmos.*, 106, 8013-8025, 10.1029/2000jd900681, 2001.
- Hamilton, J. F., Bryant, D. J., Edwards, P. M., Ouyang, B., Bannan, T. J., Mehra, A., Mayhew, A. W., Hopkins, J. R., Dunmore, R. E., Squires, F. A., Lee, J. D., Newland, M. J., Worrall, S. D., Bacak, A., Coe, H., Percival, C., Whalley, L. K., Heard, D. E., Slater, E. J., Jones, R. L., Cui, T., Surratt, J. D., Reeves, C. E., Mills, G. P., Grimmond, S., Sun, Y., Xu, W., Shi, Z., and Rickard, A. R.: Key Role of NO₃ Radicals in the Production of Isoprene Nitrates and Nitrooxyorganosulfates in Beijing, *Environ. Sci. Technol.*, 55, 842-853, 10.1021/acs.est.0c05689, 2021.
- Huang, W., Saathoff, H., Shen, X. L., Ramisetty, R., Leisner, T., and Mohr, C.: Chemical Characterization of Highly Functionalized Organonitrates Contributing to Night-Time Organic Aerosol Mass Loadings and Particle Growth, *Environ. Sci. Technol.*, 53, 1165-1174, 10.1021/acs.est.8b05826, 2019.
- Hyttinen, N., Kupiainen-Määttä, O., Rissanen, M. P., Muuronen, M., Ehn, M., and Kurtén, T.: Modeling the Charging of Highly Oxidized Cyclohexene Ozonolysis Products Using Nitrate-Based Chemical Ionization, *The Journal of Physical Chemistry A*, 119, 6339-6345, 10.1021/acs.jpca.5b01818, 2015.
- Japar, S. M., and Niki, H.: Gas-phase reactions of the nitrate radical with olefins, *The Journal of Physical Chemistry*, 79, 1629-1632, 10.1021/j100583a002, 1975.
- Jenkin, M. E., Saunders, S. M., and Pilling, M. J.: The tropospheric degradation of volatile organic compounds: A protocol for mechanism development, *Atmos. Environ.*, 31, 81-104, 10.1016/s1352-2310(96)00105-7, 1997.
- Jenkin, M. E., Boyd, A. A., and Lesclaux, R.: Peroxy Radical Kinetics Resulting from the OH-Initiated Oxidation of 1,3-Butadiene, 2,3-Dimethyl-1,3-Butadiene and Isoprene, *J. Atmos. Chem.*, 29, 267-298, 10.1023/A:1005940332441, 1998.
- Jenkin, M. E., Saunders, S. M., Wagner, V., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds, *Atmos. Chem. Phys.*, 3, 181-193, 2003.
- Jenkin, M. E., Young, J. C., and Rickard, A. R.: The MCM v3.3.1 degradation scheme for isoprene, *Atmos. Chem. Phys.*, 15, 11433-11459, 10.5194/acp-15-11433-2015, 2015.

- Jokinen, T., Sipila, M., Junninen, H., Ehn, M., Lonn, G., Hakala, J., Petaja, T., Mauldin, R. L., III, Kulmala, M., and Worsnop, D. R.: Atmospheric sulphuric acid and neutral cluster measurements using CI-API-TOF, *Atmos. Chem. Phys.*, 12, 4117-4125, 10.5194/acp-12-4117-2012, 2012.
- Jokinen, T., Sipila, M., Richters, S., Kerminen, V. M., Paasonen, P., Stratmann, F., Worsnop, D., Kulmala, M., Ehn, M., Herrmann, H., and Berndt, T.: Rapid Autoxidation Forms Highly Oxidized RO₂ Radicals in the Atmosphere, *Angew. Chem.-Int. Edit.*, 53, 14596-14600, 10.1002/anie.201408566, 2014.
- Jokinen, T., Berndt, T., Makkonen, R., Kerminen, V. M., Junninen, H., Paasonen, P., Stratmann, F., Herrmann, H., Guenther, A. B., Worsnop, D. R., Kulmala, M., Ehn, M., and Sipila, M.: Production of extremely low volatile organic compounds from biogenic emissions: Measured yields and atmospheric implications, *Proc. Nat. Acad. Sci. U.S.A.*, 112, 7123-7128, 10.1073/pnas.1423977112, 2015.
- Kaminski, M., Fuchs, H., Acir, I.-H., Bohn, B., Brauers, T., Dorn, H.-P., Haeseler, R., Hofzumahaus, A., Li, X., Lutz, A., Nehr, S., Rohrer, F., Tillmann, R., Vereecken, L., Wegener, R., and Wahner, A.: Investigation of the beta-pinene photooxidation by OH in the atmosphere simulation chamber SAPHIR, *Atmos. Chem. Phys.*, 17, 6631-6650, 10.5194/acp-17-6631-2017, 2017.
- Kenseth, C. M., Huang, Y. L., Zhao, R., Dalleska, N. F., Hethcox, C., Stoltz, B. M., and Seinfeld, J. H.: Synergistic O₃ + OH oxidation pathway to extremely low-volatility dimers revealed in beta-pinene secondary organic aerosol, *Proc. Nat. Acad. Sci. U.S.A.*, 115, 8301-8306, 10.1073/pnas.1804671115, 2018.
- Kirkby, J., Duplissy, J., Sengupta, K., Frege, C., Gordon, H., Williamson, C., Heinritzi, M., Simon, M., Yan, C., Almeida, J., Tröstl, J., Nieminen, T., Ortega, I. K., Wagner, R., Adamov, A., Amorim, A., Bernhammer, A.-K., Bianchi, F., Breitenlechner, M., Brilke, S., Chen, X., Craven, J., Dias, A., Ehrhart, S., Flagan, R. C., Franchin, A., Fuchs, C., Guida, R., Hakala, J., Hoyle, C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Kim, J., Krapf, M., Kürten, A., Laaksonen, A., Lehtipalo, K., Makhmutov, V., Mathot, S., Molteni, U., Onnela, A., Peräkylä, O., Piel, F., Petäjä, T., Praplan, A. P., Pringle, K., Rap, A., Richards, N. A. D., Riipinen, I., Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger, S., Scott, C. E., Seinfeld, J. H., Sipilä, M., Steiner, G., Stozhkov, Y., Stratmann, F., Tomé, A., Virtanen, A., Vogel, A. L., Wagner, A. C., Wagner, P. E., Weingartner, E., Wimmer, D., Winkler, P. M., Ye, P., Zhang, X., Hansel, A., Dommen, J., Donahue, N. M., Worsnop, D. R., Baltensperger, U., Kulmala, M., Carslaw, K. S., and Curtius, J.: Ion-induced nucleation of pure biogenic particles, *Nature*, 533, 521-526, 10.1038/nature17953, 2016.
- Krechmer, J. E., Coggon, M. M., Massoli, P., Nguyen, T. B., Crounse, J. D., Hu, W. W., Day, D. A., Tyndall, G. S., Henze, D. K., Rivera-Rios, J. C., Nowak, J. B., Kimmel, J. R., Mauldin, R. L., Stark, H., Jayne, J. T., Sipila, M., Junninen, H., St Clair, J. M., Zhang, X., Feiner, P. A., Zhang, L., Miller, D. O., Brune, W. H., Keutsch, F. N., Wennberg, P. O., Seinfeld, J. H., Worsnop, D. R., Jimenez, J. L., and Canagaratna, M. R.: Formation of Low Volatility Organic Compounds and Secondary Organic Aerosol from Isoprene Hydroxyhydroperoxide Low-NO Oxidation, *Environ. Sci. Technol.*, 49, 10330-10339, 10.1021/acs.est.5b02031, 2015.
- Kwan, A. J., Chan, A. W. H., Ng, N. L., Kjaergaard, H. G., Seinfeld, J. H., and Wennberg, P. O.: Peroxy radical chemistry and OH radical production during the NO₃-initiated oxidation of isoprene, *Atmos. Chem. Phys.*, 12, 7499-7515, 10.5194/acp-12-7499-2012, 2012.
- Lai, C. C., and Finlayson-Pitts, B. J.: Reactions of dinitrogen pentoxide and nitrogen-dioxide with 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine, *Lipids*, 26, 306-314, 10.1007/bf02537142, 1991.
- Lee, B. H., Mohr, C., Lopez-Hilfiker, F. D., Lutz, A., Hallquist, M., Lee, L., Romer, P., Cohen, R. C., Iyer, S., Kurten, T., Hu, W., Day, D. A., Campuzano-Jost, P., Jimenez, J. L., Xu, L., Ng, N. L., Guo, H., Weber, R. J., Wild, R. J., Brown, S. S., Koss, A., de Gouw, J., Olson, K., Goldstein, A. H., Seco, R., Kim, S., McAvey, K., Shepson, P. B.,

Starn, T., Baumann, K., Edgerton, E. S., Liu, J., Shilling, J. E., Miller, D. O., Brune, W., Schobesberger, S., D'Ambro, E. L., and Thornton, J. A.: Highly functionalized organic nitrates in the southeast United States: Contribution to secondary organic aerosol and reactive nitrogen budgets, *Proc. Nat. Acad. Sci. U.S.A.*, 113, 1516-1521, 10.1073/pnas.1508108113, 2016.

Lu, K. D., Rohrer, F., Holland, F., Fuchs, H., Brauers, T., Oebel, A., Dlugi, R., Hu, M., Li, X., Lou, S. R., Shao, M., Zhu, T., Wahner, A., Zhang, Y. H., and Hofzumahaus, A.: Nighttime observation and chemistry of HO_x in the Pearl River Delta and Beijing in summer 2006, *Atmos. Chem. Phys.*, 14, 4979-4999, 10.5194/acp-14-4979-2014, 2014.

Malkin, T. L., Goddard, A., Heard, D. E., and Seakins, P. W.: Measurements of OH and HO₂ yields from the gas phase ozonolysis of isoprene, *Atmos. Chem. Phys.*, 10, 1441-1459, 10.5194/acp-10-1441-2010, 2010.

McFiggans, G., Mentel, T. F., Wildt, J., Pullinen, I., Kang, S., Kleist, E., Schmitt, S., Springer, M., Tillmann, R., Wu, C., Zhao, D., Hallquist, M., Faxon, C., Le Breton, M., Hallquist, Å. M., Simpson, D., Bergström, R., Jenkin, M. E., Ehn, M., Thornton, J. A., Alfarra, M. R., Bannan, T. J., Percival, C. J., Priestley, M., Topping, D., and Kiendler-Scharr, A.: Secondary organic aerosol reduced by mixture of atmospheric vapours, *Nature*, 565, 587-593, 10.1038/s41586-018-0871-y, 2019.

Mentel, T. F., Springer, M., Ehn, M., Kleist, E., Pullinen, I., Kurten, T., Rissanen, M., Wahner, A., and Wildt, J.: Formation of highly oxidized multifunctional compounds: autoxidation of peroxy radicals formed in the ozonolysis of alkenes - deduced from structure-product relationships, *Atmos. Chem. Phys.*, 15, 6745-6765, 10.5194/acp-15-6745-2015, 2015.

Møller, K. H., Bates, K. H., and Kjaergaard, H. G.: The Importance of Peroxy Radical Hydrogen-Shift Reactions in Atmospheric Isoprene Oxidation, *J. Phys. Chem. A* 123, 920-932, 10.1021/acs.jpca.8b10432, 2019.

Molteni, U., Bianchi, F., Klein, F., El Haddad, I., Frege, C., Rossi, M. J., Dommen, J., and Baltensperger, U.: Formation of highly oxygenated organic molecules from aromatic compounds, *Atmos. Chem. Phys.*, 18, 1909-1921, 10.5194/acp-18-1909-2018, 2018.

Molteni, U., Simon, M., Heinritzi, M., Hoyle, C. R., Bernhammer, A. K., Bianchi, F., Breitenlechner, M., Brilke, S., Dias, A., Duplissy, J., Frege, C., Gordon, H., Heyn, C., Jokinen, T., Kurten, A., Lehtipalo, K., Makhmutov, V., Petaja, T., Pieber, S. M., Praplan, A. P., Schobesberger, S., Steiner, G., Stozhkov, Y., Tome, A., Trostl, J., Wagner, A. C., Wagner, R., Williamson, C., Yan, C., Baltensperger, U., Curtius, J., Donahue, N. M., Hansel, A., Kirkby, J., Kulmala, M., Worsnop, D. R., and Dommen, J.: Formation of Highly Oxygenated Organic Molecules from alpha-Pinene Ozonolysis: Chemical Characteristics, Mechanism, and Kinetic Model Development, *Acs Earth and Space Chemistry*, 3, 873-883, 10.1021/acsearthspacechem.9b00035, 2019.

Nah, T., Sanchez, J., Boyd, C. M., and Ng, N. L.: Photochemical Aging of alpha-pinene and beta-pinene Secondary Organic Aerosol formed from Nitrate Radical Oxidation, *Environ. Sci. Technol.*, 50, 222-231, 10.1021/acs.est.5b04594, 2016.

Ng, N. L., Kwan, A. J., Surratt, J. D., Chan, A. W. H., Chhabra, P. S., Sorooshian, A., Pye, H. O. T., Crounse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO₃), *Atmos. Chem. Phys.*, 8, 4117-4140, 10.5194/acp-8-4117-2008, 2008.

Nguyen, T. B., Tyndall, G. S., Crounse, J. D., Teng, A. P., Bates, K. H., Schwantes, R. H., Coggon, M. M., Zhang, L., Feiner, P., Milller, D. O., Skog, K. M., Rivera-Rios, J. C., Dorris, M., Olson, K. F., Koss, A., Wild, R. J., Brown, S. S., Goldstein, A. H., de Gouw, J. A., Brune, W. H., Keutsch, F. N., Seinfeld, J. H., and Wennberg, P. O.: Atmospheric fates of Criegee intermediates in the ozonolysis of isoprene, *Phys. Chem. Chem. Phys.*, 18, 10241-10254, 10.1039/c6cp00053c, 2016.

Novelli, A., Cho, C., Fuchs, H., Hofzumahaus, A., Rohrer, F., Tillmann, R., Kiendler-Scharr, A., Wahner, A., and Vereecken, L.: Experimental and theoretical study on the impact of a nitrate group on the chemistry of alkoxy radicals, *Phys. Chem. Chem. Phys.*, 23, 5474-5495, 10.1039/D0CP05555G, 2021.

Nozière, B., and Vereecken, L.: Direct Observation of Aliphatic Peroxy Radical Autoxidation and Water Effects: An Experimental and Theoretical Study, *Angew. Chem.-Int. Edit.*, 58, 13976-13982, 10.1002/anie.201907981, 2019.

Perring, A. E., Wisthaler, A., Graus, M., Wooldridge, P. J., Lockwood, A. L., Mielke, L. H., Shepson, P. B., Hansel, A., and Cohen, R. C.: A product study of the isoprene+NO₃ reaction, *Atmos. Chem. Phys.*, 9, 4945-4956, 10.5194/acp-9-4945-2009, 2009.

Pfrang, C., Martin, R. S., Canosa-Mas, C. E., and Wayne, R. P.: Gas-phase reactions of NO₃ and N₂O₅ with (Z)-hex-4-en-1-ol, (Z)-hex-3-en-1-ol ('leaf alcohol'), (E)-hex-3-en-1-ol, (Z)-hex-2-en-1-ol and (E)-hex-2-en-1-ol, *Phys. Chem. Chem. Phys.*, 8, 354-363, 10.1039/b510835g, 2006.

Pullinen, I., Schmitt, S., Kang, S., Sarrafzadeh, M., Schlag, P., Andres, S., Kleist, E., Mentel, T. F., Rohrer, F., Springer, M., Tillmann, R., Wildt, J., Wu, C., Zhao, D., Wahner, A., and Kiendler-Scharr, A.: Impact of NO_x on secondary organic aerosol (SOA) formation from α -pinene and β -pinene photooxidation: the role of highly oxygenated organic nitrates, *Atmos. Chem. Phys.*, 20, 10125-10147, 10.5194/acp-20-10125-2020, 2020.

Quelever, L. L. J., Kristensen, K., Jensen, L. N., Rosati, B., Teiwes, R., Daellenbach, K. R., Perakyla, O., Roldin, P., Bossi, R., Pedersen, H. B., Glasius, M., Bilde, M., and Ehn, M.: Effect of temperature on the formation of highly oxygenated organic molecules (HOMs) from alpha-pinene ozonolysis, *Atmos. Chem. Phys.*, 19, 7609-7625, 10.5194/acp-19-7609-2019, 2019.

Richters, S., Pfeifle, M., Olzmann, M., and Berndt, T.: endo-Cyclization of unsaturated RO₂ radicals from the gas-phase ozonolysis of cyclohexadienes, *Chem. Commun.*, 53, 4132-4135, 10.1039/c7cc01350g, 2017.

Rissanen, M. P., Kurten, T., Sipila, M., Thornton, J. A., Kangasluoma, J., Sarnela, N., Junninen, H., Jørgensen, S., Schallhart, S., Kajos, M. K., Taipale, R., Springer, M., Mentel, T. F., Ruuskanen, T., Petaja, T., Worsnop, D. R., Kjaergaard, H. G., and Ehn, M.: The Formation of Highly Oxidized Multifunctional Products in the Ozonolysis of Cyclohexene, *J. Am. Chem. Soc.*, 136, 15596-15606, 10.1021/ja507146s, 2014.

Rissanen, M. P., Kurten, T., Sipila, M., Thornton, J. A., Kausiala, O., Garmash, O., Kjaergaard, H. G., Petaja, T., Worsnop, D. R., Ehn, M., and Kulmala, M.: Effects of Chemical Complexity on the Autoxidation Mechanisms of Endocyclic Alkene Ozonolysis Products: From Methylcyclohexenes toward Understanding alpha-Pinene, *J. Phys. Chem. A* 119, 4633-4650, 10.1021/jp510966g, 2015.

Riva, M., Rantala, P., Krechmer, J. E., Perakyla, O., Zhang, Y. J., Heikkinen, L., Garmash, O., Yan, C., Kulmala, M., Worsnop, D., and Ehn, M.: Evaluating the performance of five different chemical ionization techniques for detecting gaseous oxygenated organic species, *Atmos. Meas. Tech.*, 12, 2403-2421, 10.5194/amt-12-2403-2019, 2019.

Rohrer, F., Bohn, B., Brauers, T., Bruning, D., Johnen, F. J., Wahner, A., and Kleffmann, J.: Characterisation of the photolytic HONO-source in the atmosphere simulation chamber SAPHIR, *Atmos. Chem. Phys.*, 5, 2189-2201, 2005.

Rollins, A. W., Kiendler-Scharr, A., Fry, J. L., Brauers, T., Brown, S. S., Dorn, H. P., Dube, W. P., Fuchs, H., Mensah, A., Mentel, T. F., Rohrer, F., Tillmann, R., Wegener, R., Wooldridge, P. J., and Cohen, R. C.: Isoprene oxidation by nitrate radical: alkyl nitrate and secondary organic aerosol yields, *Atmos. Chem. Phys.*, 9, 6685-6703, 2009.

Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, *Atmos. Chem. Phys.*, 3, 161-180, 2003.

Schwantes, R. H., Teng, A. P., Nguyen, T. B., Coggon, M. M., Crounse, J. D., St Clair, J. M., Zhang, X., Schilling, K. A., Seinfeld, J. H., and Wennberg, P. O.: Isoprene NO₃ Oxidation Products from the RO₂ + HO₂ Pathway, *J. Phys. Chem. A* 119, 10158-10171, 10.1021/acs.jpca.5b06355, 2015.

Skov, H., Hjorth, J., Lohse, C., Jensen, N. R., and Restelli, G.: Products and mechanisms of the reactions of the nitrate radical (NO₃) with isoprene, 1,3-butadiene and 2,3-dimethyl-1,3-butadiene in air, *Atmospheric Environment. Part A. General Topics*, 26, 2771-2783, [https://doi.org/10.1016/0960-1686\(92\)90015-D](https://doi.org/10.1016/0960-1686(92)90015-D), 1992.

Stark, M. S.: Epoxidation of Alkenes by Peroxyl Radicals in the Gas Phase: Structure–Activity Relationships, *The Journal of Physical Chemistry A*, 101, 8296-8301, 10.1021/jp972054+, 1997.

Stark, M. S.: Addition of Peroxyl Radicals to Alkenes and the Reaction of Oxygen with Alkyl Radicals, *J. Am. Chem. Soc.*, 122, 4162-4170, 10.1021/ja993760m, 2000.

Starn, T. K., Shepson, P. B., Bertman, S. B., Riemer, D. D., Zika, R. G., and Olszyna, K.: Nighttime isoprene chemistry at an urban-impacted forest site, 103, 22437-22447, <https://doi.org/10.1029/98JD01201>, 1998.

Stroud, C. A., Roberts, J. M., Williams, E. J., Hereid, D., Angevine, W. M., Fehsenfeld, F. C., Wisthaler, A., Hansel, A., Martinez-Harder, M., Harder, H., Brune, W. H., Hoenninger, G., Stutz, J., and White, A. B.: Nighttime isoprene trends at an urban forested site during the 1999 Southern Oxidant Study, 107, ACH 7-1-ACH 7-14, <https://doi.org/10.1029/2001JD000959>, 2002.

Takeuchi, M., and Ng, N. L.: Chemical composition and hydrolysis of organic nitrate aerosol formed from hydroxyl and nitrate radical oxidation of alpha-pinene and beta-pinene, *Atmos. Chem. Phys.*, 19, 12749-12766, 10.5194/acp-19-12749-2019, 2019.

Tan, Z. F., Lu, K. D., Hofzumahaus, A., Fuchs, H., Bohn, B., Holland, F., Liu, Y. H., Rohrer, F., Shao, M., Sun, K., Wu, Y. S., Zeng, L. M., Zhang, Y. S., Zou, Q., Kiendler-Scharr, A., Wahner, A., and Zhang, Y. H.: Experimental budgets of OH, HO₂, and RO₂ radicals and implications for ozone formation in the Pearl River Delta in China 2014, *Atmos. Chem. Phys.*, 19, 7129-7150, 10.5194/acp-19-7129-2019, 2019.

Tröstl, J., Chuang, W. K., Gordon, H., Heinritzi, M., Yan, C., Molteni, U., Ahlm, L., Frege, C., Bianchi, F., Wagner, R., Simon, M., Lehtipalo, K., Williamson, C., Craven, J. S., Duplissy, J., Adamov, A., Almeida, J., Bernhammer, A.-K., Breitenlechner, M., Brilke, S., Dias, A., Ehrhart, S., Flagan, R. C., Franchin, A., Fuchs, C., Guida, R., Gysel, M., Hansel, A., Hoyle, C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Keskinen, H., Kim, J., Krapf, M., Kürten, A., Laaksonen, A., Lawler, M., Leiminger, M., Mathot, S., Möhler, O., Nieminen, T., Onnela, A., Petäjä, T., Piel, F. M., Miettinen, P., Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger, S., Sengupta, K., Sipilä, M., Smith, J. N., Steiner, G., Tomè, A., Virtanen, A., Wagner, A. C., Weingartner, E., Wimmer, D., Winkler, P. M., Ye, P., Carslaw, K. S., Curtius, J., Dommen, J., Kirkby, J., Kulmala, M., Riipinen, I., Worsnop, D. R., Donahue, N. M., and Baltensperger, U.: The role of low-volatility organic compounds in initial particle growth in the atmosphere, *Nature*, 533, 527-531, 10.1038/nature18271, 2016.

Valiev, R. R., Hasan, G., Salo, V.-T., Kubecka, J., and Kurten, T.: Intersystem Crossings Drive Atmospheric Gas-Phase Dimer Formation, *The journal of physical chemistry. A*, 123, 6596-6604, 10.1021/acs.jpca.9b02559, 2019.

Vereecken, L., and Peeters, J.: Nontraditional (per)oxy ring-closure paths in the atmospheric oxidation of isoprene and monoterpenes, *J. Phys. Chem. A* 108, 5197-5204, 10.1021/jp049219g, 2004.

Vereecken, L., Mueller, J. F., and Peeters, J.: Low-volatility poly-oxygenates in the OH-initiated atmospheric oxidation of alpha-pinene: impact of non-traditional peroxyl radical chemistry, *Phys. Chem. Chem. Phys.*, 9, 5241-5248, 10.1039/b708023a, 2007.

- Vereecken, L., and Peeters, J.: A structure-activity relationship for the rate coefficient of H-migration in substituted alkoxy radicals, *Phys. Chem. Chem. Phys.*, 12, 12608-12620, 10.1039/c0cp00387e, 2010.
- Vereecken, L., and Francisco, J. S.: Theoretical studies of atmospheric reaction mechanisms in the troposphere, *Chem. Soc. Rev.*, 41, 6259-6293, 10.1039/c2cs35070j, 2012.
- Vereecken, L., and Peeters, J.: A theoretical study of the OH-initiated gas-phase oxidation mechanism of beta-pinene (C₁₀H₁₆): first generation products, *Phys. Chem. Chem. Phys.*, 14, 3802-3815, 10.1039/c2cp23711c, 2012.
- Vereecken, L., and Nozière, B.: H migration in peroxy radicals under atmospheric conditions, *Atmos. Chem. Phys.*, 20, 7429-7458, 10.5194/acp-20-7429-2020, 2020.
- Vereecken, L., Carlsson, P. T. M., Novelli, A., Bernard, F., Brown, S. S., Cho, C., Crowley, J. N., Fuchs, H., Mellouki, W., Reimer, D., Shenolikar, J., Tillmann, R., Zhou, L., Kiendler-Scharr, A., and Wahner, A.: Theoretical and experimental study of peroxy and alkoxy radicals in the NO₃-initiated oxidation of isoprene, *Phys. Chem. Chem. Phys.*, 23, 5496-5515, 10.1039/d0cp06267g, 2021.
- Viggiano, A. A., Seeley, J. V., Mundis, P. L., Williamson, J. S., and Morris, R. A.: Rate Constants for the Reactions of XO₃-(H₂O)_n (X = C, HC, and N) and NO₃-(HNO₃)_n with H₂SO₄: Implications for Atmospheric Detection of H₂SO₄, *The Journal of Physical Chemistry A*, 101, 8275-8278, 10.1021/jp971768h, 1997.
- Wagner, N. L., Dubé, W. P., Washenfelder, R. A., Young, C. J., Pollack, I. B., Ryerson, T. B., and Brown, S. S.: Diode laser-based cavity ring-down instrument for NO₃, N₂O₅, NO₂ and O₃ from aircraft, *Atmos. Meas. Tech.*, 4, 1227-1240, 10.5194/amt-4-1227-2011, 2011.
- Wang, Y., Mehra, A., Krechmer, J. E., Yang, G., Hu, X., Lu, Y., Lambe, A., Canagaratna, M., Chen, J., Worsnop, D., Coe, H., and Wang, L.: Oxygenated products formed from OH-initiated reactions of trimethylbenzene: autoxidation and accretion, *Atmos. Chem. Phys.*, 20, 9563-9579, 10.5194/acp-20-9563-2020, 2020.
- Wennberg, P. O., Bates, K. H., Crounse, J. D., Dodson, L. G., McVay, R. C., Mertens, L. A., Nguyen, T. B., Praske, E., Schwantes, R. H., Smarte, M. D., St Clair, J. M., Teng, A. P., Zhang, X., and Seinfeld, J. H.: Gas-Phase Reactions of Isoprene and Its Major Oxidation Products, *Chem. Rev.*, 118, 3337-3390, 10.1021/acs.chemrev.7b00439, 2018.
- Wu, R., Vereecken, L., Tsiligiannis, E., Kang, S., Albrecht, S. R., Hantschke, L., Zhao, D., Novelli, A., Fuchs, H., Tillmann, R., Hohaus, T., Carlsson, P. T. M., Shenolikar, J., Bernard, F., Crowley, J. N., Fry, J. L., Brownwood, B., Thornton, J. A., Brown, S. S., Kiendler-Scharr, A., Wahner, A., Hallquist, M., and Mentel, T. F.: Molecular composition and volatility of multi-generation products formed from isoprene oxidation by nitrate radical, *Atmos. Chem. Phys. Discuss.*, 2020, 1-37, 10.5194/acp-2020-1180, 2020.
- Xu, L., Guo, H. Y., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., de Gouw, J., Baumann, K., Lee, S. H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, *Proc. Nat. Acad. Sci. U.S.A.*, 112, 37-42, 10.1073/pnas.1417609112, 2015.
- Xu, Z. N., Nie, W., Liu, Y. L., Sun, P., Huang, D. D., Yan, C., Krechmer, J., Ye, P. L., Xu, Z., Qi, X. M., Zhu, C. J., Li, Y. Y., Wang, T. Y., Wang, L., Huang, X., Tang, R. Z., Guo, S., Xiu, G. L., Fu, Q. Y., Worsnop, D., Chi, X. G., and Ding, A. J.: Multifunctional Products of Isoprene Oxidation in Polluted Atmosphere and Their Contribution to SOA, 48, e2020GL089276, <https://doi.org/10.1029/2020GL089276>, 2021.
- Yan, C., Nie, W., Aijala, M., Rissanen, M. P., Canagaratna, M. R., Massoli, P., Junninen, H., Jokinen, T., Sarnela, N., Hame, S. A. K., Schobesberger, S., Canonaco, F., Yao, L., Prevot, A. S. H., Petaja, T., Kulmala, M., Sipila, M.,

Worsnop, D. R., and Ehn, M.: Source characterization of highly oxidized multifunctional compounds in a boreal forest environment using positive matrix factorization, *Atmos. Chem. Phys.*, 16, 12715-12731, 10.5194/acp-16-12715-2016, 2016.

Yan, C., Nie, W., Vogel, A. L., Dada, L., Lehtipalo, K., Stolzenburg, D., Wagner, R., Rissanen, M. P., Xiao, M., Ahonen, L., Fischer, L., Rose, C., Bianchi, F., Gordon, H., Simon, M., Heinritzi, M., Garmash, O., Roldin, P., Dias, A., Ye, P., Hofbauer, V., Amorim, A., Bauer, P. S., Bergen, A., Bernhammer, A. K., Breitenlechner, M., Brilke, S., Buchholz, A., Mazon, S. B., Canagaratna, M. R., Chen, X., Ding, A., Dommen, J., Draper, D. C., Duplissy, J., Frege, C., Heyn, C., Guida, R., Hakala, J., Heikkinen, L., Hoyle, C. R., Jokinen, T., Kangasluoma, J., Kirkby, J., Kontkanen, J., Kurten, A., Lawler, M. J., Mai, H., Mathot, S., Mauldin, R. L., Molteni, U., Nichman, L., Nieminen, T., Nowak, J., Ojdanic, A., Onnela, A., Pajunoja, A., Petaja, T., Piel, F., Quelever, L. L. J., Sarnela, N., Schallhart, S., Sengupta, K., Sipila, M., Tome, A., Trostl, J., Vaisanen, O., Wagner, A. C., Ylisirnio, A., Zha, Q., Baltensperger, U., Carslaw, K. S., Curtius, J., Flagan, R. C., Hansel, A., Riipinen, I., Smith, J. N., Virtanen, A., Winkler, P. M., Donahue, N. M., Kerminen, V. M., Kulmala, M., Ehn, M., and Worsnop, D. R.: Size-dependent influence of NO_x on the growth rates of organic aerosol particles, *Science Advances*, 6, 9, 10.1126/sciadv.aay4945, 2020.

Zhao, D. F., Buchholz, A., Kortner, B., Schlag, P., Rubach, F., Kiendler-Scharr, A., Tillmann, R., Wahner, A., Flores, J. M., Rudich, Y., Watne, Å. K., Hallquist, M., Wildt, J., and Mentel, T. F.: Size-dependent hygroscopicity parameter (κ) and chemical composition of secondary organic cloud condensation nuclei, *Geophys. Res. Lett.*, 42, 10920-10928, 10.1002/2015gl066497, 2015a.

Zhao, D. F., Kaminski, M., Schlag, P., Fuchs, H., Acir, I. H., Bohn, B., Häseler, R., Kiendler-Scharr, A., Rohrer, F., Tillmann, R., Wang, M. J., Wegener, R., Wildt, J., Wahner, A., and Mentel, T. F.: Secondary organic aerosol formation from hydroxyl radical oxidation and ozonolysis of monoterpenes, *Atmos. Chem. Phys.*, 15, 991-1012, 10.5194/acp-15-991-2015, 2015b.

Zhao, D. F., Schmitt, S. H., Wang, M. J., Acir, I. H., Tillmann, R., Tan, Z. F., Novelli, A., Fuchs, H., Pullinen, I., Wegener, R., Rohrer, F., Wildt, J., Kiendler-Scharr, A., Wahner, A., and Mentel, T. F.: Effects of NO_x and SO₂ on the secondary organic aerosol formation from photooxidation of alpha-pinene and limonene, *Atmos. Chem. Phys.*, 18, 1611-1628, 10.5194/acp-18-1611-2018, 2018.

Ziemann, P. J., and Atkinson, R.: Kinetics, products, and mechanisms of secondary organic aerosol formation, *Chem. Soc. Rev.*, 41, 6582-6605, 10.1039/c2cs35122f, 2012.