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Highly oxygenated organic molecules (HOM) formation in the isoprene oxidation by NO_3 radical

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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 O_3 and OH, HOM formation in the oxidation by NO_3 radical, an important oxidant at night-time and dawn, has received less attention. In this study, HOM formation in the reaction of isoprene with NO_3 was investigated in the SAPHIR chamber (Simulation of Atmospheric PHotochemistry In a large Reaction chamber). A large number of HOM including monomers (C_5), dimers (C_{10}), and trimers (C_{15}), 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 NO_3 addition to carbon double bond, forming peroxy radicals (RO_2), followed by autoxidation. 1N monomers were formed by both the direct reaction of NO_3 with isoprene and of NO_3 with first-generation products. 2N-monomers (e.g. $C_5H_8N_2O_{n\ (n=8\text{-}13)}$, $C_5H_{10}N_2O_{n\ (n=8\text{-}14)}$) were likely the termination products of $C_5H_9N_2O_n\bullet$, which was formed by the addition of NO_3 to C5-hydroxynitrate ($C_5H_9NO_4$), 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 isoprene+NO_3 under our reaction conditions. H-shift of alkoxy radicals to form peroxy radicals and subsequent autoxidation ("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 RO_2 and via the termination reactions of dimer RO_2 formed by further reaction of closed-shell dimers with NO_3 and possibly by the reaction of C5-RO_2 with isoprene. HOM trimers were likely formed by the accretion reaction of dimer RO_2 with monomer RO_2. 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 $C_5H_9NO_6$ as the lower limit. This yield suggests that HOM may contribute a significant fraction to SOA yield in the reaction of isoprene with NO_3.

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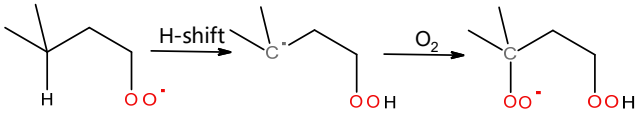
1 Introduction

Highly oxygenated organic molecules (HOM) are an important class of compounds formed in the oxidation of volatile of organic compounds (VOC) including biogenic VOC 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; Quelever et al., 2019). A number of recent studies have demonstrated that HOM play a pivotal role in both nucleation and growth of 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 intermolecular H-shift forming alky radicals, followed by O_2 addition leading to formation of new RO_2 as shown in R1 (Vereecken et al., 2007; Crounse et al., 2013; Ehn et al., 2017; Bianchi et al., 2019; Moller et al., 2019; Vereecken and Noziere, 2020).



(R1)

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.

$$RO_2+R'O_2 \rightarrow ROH+R=O \quad (R1)$$

$$RO_2+R'O_2 \rightarrow R=O+R'OH \quad (R2)$$

$$RO_2+HO_2 \rightarrow ROOH \quad (R3)$$

$$RO_2+R'O_2 \rightarrow RO+R'O+O_2 \quad (R4)$$

$$RO_2+NO_3 \rightarrow RO+NO_2+O_2 \quad (R5)$$

$$RO_2+R'O_2 \rightarrow ROOR'+O_2 \quad (R6)$$

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 studies of HOM formation focus on the VOC oxidation by OH and O_3 (Crounse et al., 2013; Ehn et al., 2014; Jokinen et al., 2014; Rissanen et al., 2014; Jokinen et al., 2015; Krechmer et al., 2015;

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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; Quelever et al., 2019). HOM formation in the oxidation of VOC with NO_3 has received much less attention. NO_3 is another important oxidant of VOC mainly operating during nighttime. Particularly, NO_3 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 may also be formed. Despite the potential importance, studies of HOM formation in the oxidation of BVOC by NO_3 are still limited compared with the HOM formation via oxidation by O_3 and OH. Although a number of studies have investigated the reaction of NO_3 with BVOC (Fry et al., 2009; Fry et al., 2011; Fry et al., 2014; Boyd et al., 2015; Nah et al., 2016; Boyd et al., 2017; Claflin and Ziemann, 2018; Faxon et al., 2018; Draper et al., 2019; Takeuchi and Ng, 2019), 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 NO_3 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, and its chemical lifetime with respect to its reaction with OH is typically only a few hours, its concentration can remain high after sunset. A substantial fraction of isoprene can then be oxidized by NO_3 (Brown et al., 2009). Regarding the budget of NO_3, the reaction of isoprene with NO_3 contributes to a significant fraction of NO_3 loss at night, and in some circumstances even during the day, especially in the afternoon and afterwards (Ayres et al., 2015). The reaction of isoprene with NO_3 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). These studies focus on the oxidation mechanism and "traditional" oxidation products, as well as SOA yields. The initials step is the NO_3 addition to one of the C=C double bounds, preferentially to the carbon C1 (Schwantes et al., 2015), followed by O_2 addition forming a nitrooxyalkyl peroxy radical (RO_2). This RO_2 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 NO_2 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 C_{10} 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 NO_3 functional groups), were

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detected in the gas phase. The detailed mechanism of HOM formation and their yields in the reaction of BVOC+NO_3 are still unclear.

In this study, we investigated the HOM formation in the oxidation of isoprene by NO_3. 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 isoprene+NO_3 and assess their roles in SOA formation.

2 Experimental

2.1 Chamber setup and experiments

Experiments investigating the reaction of isoprene with NO_3 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 m^3. 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 O_3 concentrations were measured using a chemiluminescence NO_x analyzer (ECO PHYSICS TR480) and an UV photometer O_3 analyzer (ANSYCO, model O341M), respectively. OH, HO_2 and RO_2 concentrations were measured using a laser induced fluorescence system (LIF) (Fuchs et al., 2012). NO_3 and N_2O_5 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). NO_3 was directly detected in one cavity by its absorption at 662 nm and the sum of NO_3 and N_2O_5 in a second, heated cavity, which had a heated inlet to thermally decompose N_2O_5 to NO_3. 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 switch 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 NO_3 was measured every 20 s by chemically removing NO_3 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 NO_3 and N_2O_5. In the case of N_2O_5 a transmission of (85±10) % was achieved and in the case of NO_3 of (50±30) %.

Before an experiment, the chamber was flushed with high purity synthetic air (purity>99.9999% O_2 and N_2). Experiments were conducted under dry condition. NO_2 and O_3 were added to the chamber first to form N_2O_5 and NO_3, reaching concentrations of ~60 ppb for NO_2 and ~100 ppb for O_3. After around half an hour, isoprene

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was sequentially added into the chamber for three times at intervals of ~1 h. Around 40 min after the third isoprene injection, NO_2 was added to compensate the loss of NO_3 and N_2O_5. Afterwards, three isoprene additions were repeated in the same way as before. O_3 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 NO_3 and the reaction of isoprene with O_3 did not play a major role. Figure S2 shows the relative contributions of the reaction of O_3 and NO_3 with isoprene to the total chemical loss of isoprene using the NO_3 and O_3 concentrations measured. The reaction with NO_3 accounted for >95% of the isoprene consumption at all time.

2.2 Characterization of HOM

HOM were detected using a Chemical Ionization time-of-flight Mass Spectrometer (Aerodyne Research Inc., USA) with nitrate as the reagent ion (CIMS). ^{15}N nitric acid was used to produce $^{15}NO_3^-$ in order to distinguish the NO_3 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). HOM concentrations were estimated using the calibration coefficient of H_2SO_4 as described by Pullinen et al. (2020) because the charge efficiency of HOM and H_2SO_4 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 H_2SO_4 are provided in the supplement S1. 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 loss of HOM to the chamber was corrected using a wall loss rate of 6×10^{-4} 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 ~1×10^{-6} s^{-1}) (Zhao et al., 2015b). The influence of wall loss correction and dilution correction on HOM yield was ~12% and <1%, 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. The reaction products can be roughly divided into three classes: monomers (C5, ~200-400 Th), dimers (C10, ~400-600 Th), and trimers (C15, ~>600 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

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increasing oxygenation were found, such as $C_5H_9NO_n$, $C_5H_7NO_n$, $C_5H_8N_2O_n$, $C_5H_{10}N_2O_n$ (Table 1, Table S1-2 and Fig. 2). These monomers included both stable closed-shell molecules and open-shell radicals, such as $C_5H_8NO_n$• and $C_5H_9N_2O_n$•. 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.

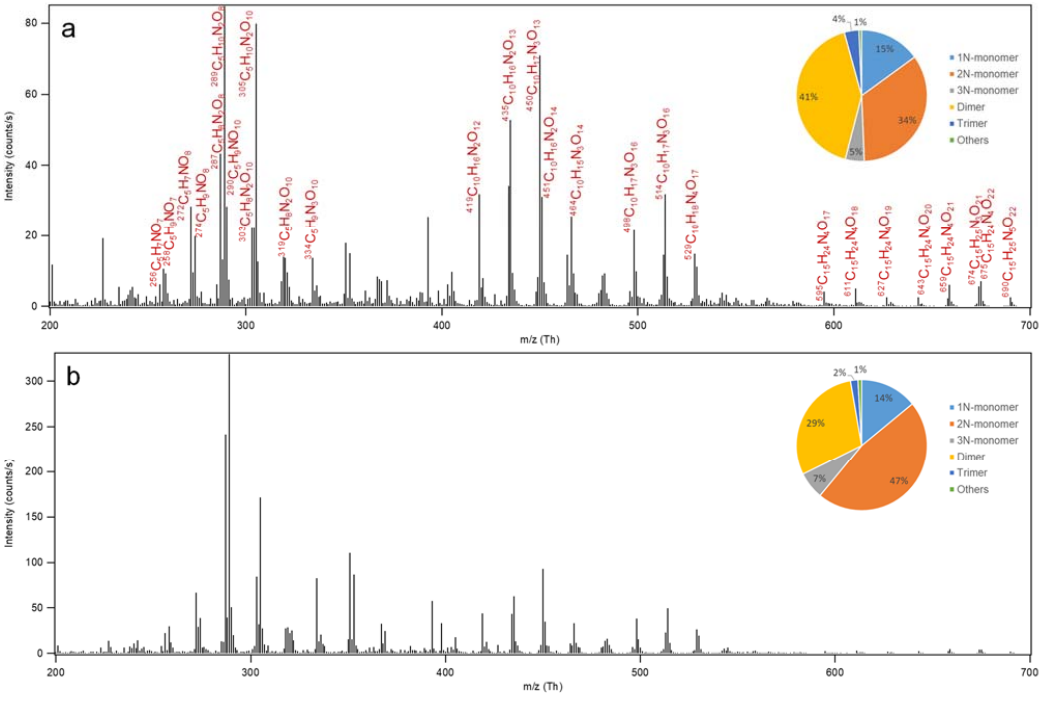

Figure 1. Mass spectrum of the HOM formed in the oxidation of isoprene by NO_3. Panel a and b show the average spectrum during the first isoprene addition period (P1) and for the whole period of six isoprene additions (P1-6), respectively. The insets show the contributions of different classes of HOM. 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. The contribution of 2N-monomers such as $C_5H_{10}N_2O_n$ and $C_5H_8N_2O_n$ 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 $C_5H_{10}N_2O_8$, $C_5H_{10}N_2O_9$, and $C_5H_8N_2O_8$. The termination products of $C_5H_9NO_8$, $C_5H_9NO_9$, and $C_5H_7NO_8$ 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

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addition periods (Fig. 1b), where the abundance of $C_5H_{10}N_2O_n$ and $C_5H_8N_2O_n$ 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.

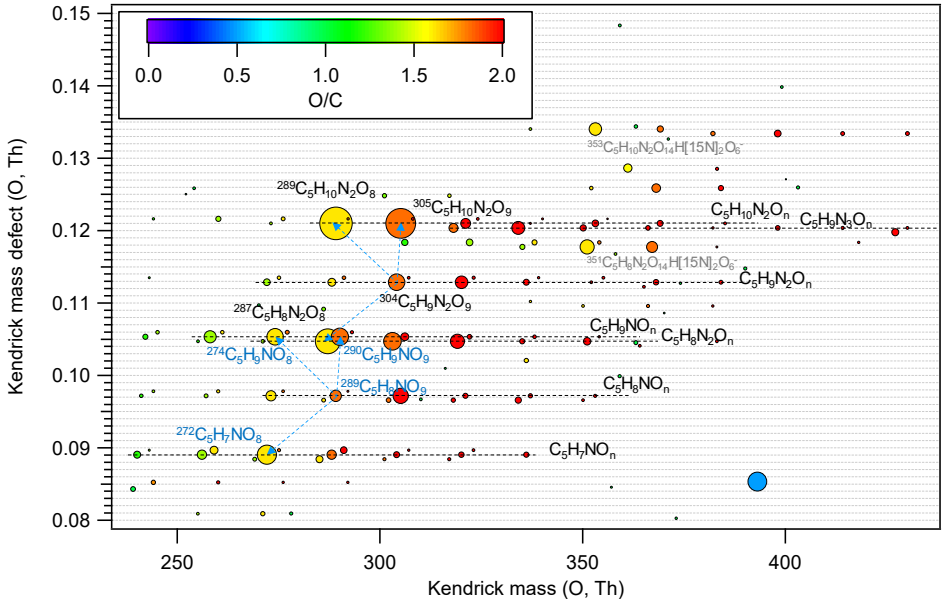

Figure 2. Kendrick mass defect plot for O of HOM monomers. The size (area) of circles is set to be proportional to the average peak intensity of each molecular formula during the first isoprene addition period (P1). The species at m/z 351 and 353 (labelled in grey) are the adducts of $C_5H_8N_2O_8$ and $C_5H_8N_2O_8$ with $H[15N]_2O_6^-$, 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 $C_5H_8NO_n$• (n=7-12) series (series M1), as well as its corresponding termination products $C_5H_7NO_{n-1}$, $C_5H_9NO_{n-1}$, and $C_5H_9NO_n$ via the reactions with RO_2 and HO_2, which contain carbonyl, hydroxyl, and hydroperoxy group, respectively. Overall, the peak intensities of $C_5H_9NO_n$ and $C_5H_7NO_n$ series first increased and then decreased as oxygen number increased (Fig. 2), with the peak intensity of $C_5H_9NO_8$ and $C_5H_7NO_8$ 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	$C_5H_8NO_{n\ (n=7\text{-}12)}$	RO_2	Isoprene+NO_3 Isoprene+NO_3+NO_3
	$C_5H_9NO_n$	ROOH	
	$C_5H_9NO_{n-1}$	ROH	
	$C_5H_7NO_{n-1}$	R=O	

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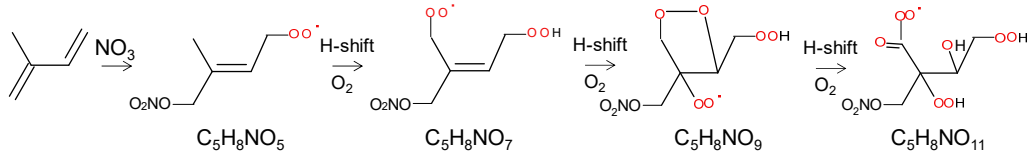
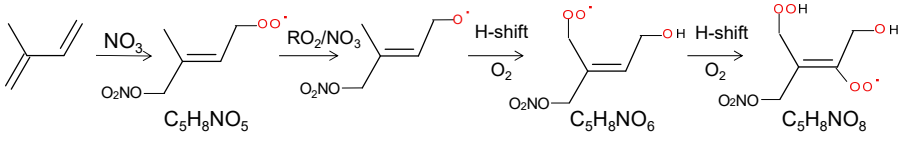
M2a/b	$C_5H_9N_2O_{n\ (n=9-14)}$	RO_2	Isoprene +NO_3+NO_3
	$C_5H_{10}N_2O_n$	ROOH	
	$C_5H_{10}N_2O_{n-1}$	ROH	
	$C_5H_8N_2O_{n-1}$	R=O	
	$C_5H_9N_3O_{n+2}$	PN	
M3	$C_5H_7N_2O_{n\ (n=9)}$	RO_2	Isoprene +NO_3+NO_3
	$C_5H_8N_2O_n$	ROOH	
	$C_5H_8N_2O_{n-1}$	ROH	
	$C_5H_6N_2O_{n-1}$	R=O	
M4	$C_5H_{10}NO_{n\ (n=8-9)}$	RO_2	Isoprene +NO_3+OH
	$C_5H_{11}NO_n$	ROOH	
	$C_5H_{11}NO_{n-1}$	ROH	
	$C_5H_9NO_{n-1}$	R=O	

[a]: RO_2 denotes peroxy radical and ROOH, ROH, and R=O donote the termination products containing hydroperoxy, hydroxyl, and carbonyl group, respectively.



(a)



(b)

Scheme 1. The pathway to form HOM RO_2 $C_5H_8NO_n$• (n=7, 9, 11) series (a) and $C_5H_8NO_n$• (n=8, 10, 12) series (b) in the reaction of isoprene with NO_3.

$C_5H_8NO_n$• 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, 12) (series M1b in Table 1) were possibly formed after H-shift of an alkoxy radical formed in reaction R5 or R6 and subsequent O_2 addition ("alkoxy-peroxy" channel) (Scheme 1b). The RO_2 can undergo further autoxidation adding two oxygen atoms after each H-shift.

Some HOM monomers may contain multiple isomers and be formed via different pathways. For example, $C_5H_9NO_n$ can contain alcohols ($C_5H_9NO_n$) corresponding to RO_2 $C_5H_8NO_{n+1}$•, hydroperoxides ($C_5H_9NO_n$) corresponding to RO_2 $C_5H_8NO_n$• or the ketones from RO_2 $C_5H_{10}NO_{n+1}$•. Some RO_2 $C_5H_8NO_n$• may be formed via the reaction of first-generation products with NO_3 in addition to direct reaction of isoprene with NO_3. For example, $C_5H_8NO_7$• can be formed by the reaction of NO_3 with $C_5H_8O_2$, which is a first-generation product observed previously

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in in the reaction of isoprene with NO_3 or OH (Scheme S1b) (Kwan et al., 2012). Moreover, RO_2 $C_5H_8NO_n$• can be formed from C5-carbonylnitrate, a first-generation product, with OH (Scheme S1a). Trace amount of OH can be produced in the reaction isoprene with NO_3 (Kwan et al., 2012; Wennberg et al., 2018). OH can also be formed via Criegee intermediates formed in isoprene+O_3 (Nguyen et al., 2016), but this OH source was likely minor because the contribution of isoprene+O_3 to total isoprene loss was negligible (<5%, Fig. S2). $C_5H_8NO_8$• may also be formed by the reaction of NO_3 with $C_5H_8O_3$, which is a first-generation product observed in the reaction of isoprene with OH (Kwan et al., 2012). The $C_5H_8NO_n$• formed via direct reaction of isoprene with NO_3 is a first-generation RO_2 while that formed via other indirect pathways is a second-generation RO_2. The time profile of the isomers from these two pathways, however, are expected to be different as will be discussed below.

Time series of HOM can shed light on their formation mechanisms. It is expected that first-generation products increase fast with isoprene addition and reach a maximum earlier in the presence of wall loss of organic vapour, while second-generation products reach a maximum in the later stage or increase continuously if the production rate is higher than the loss rate. As a reference to analyze the time profiles of HOM, the times profile of isoprene, NO_3, and N_2O_5 are also shown (Fig. S3). After isoprene was added in each period, NO_3 and N_2O_5 dropped dramatically and then gradually increased. We found that termination products within the same M1 series showed different time profiles. For example, in $C_5H_9NO_n$ series, $C_5H_9NO_8$ clearly increased instantaneously with isoprene addition, and decreased fast afterwards (Fig. 3a), indicating that it was a first-generation product, which was expected according to the mechanism Scheme 1. $C_5H_9NO_6$ and $C_5H_9NO_{10}$ had a general increasing trend with time. While $C_5H_9NO_6$ increased continuously with time, $C_5H_9NO_{10}$ reached maximum intensity in the late phase of each isoprene addition period and then decreased naturally or after isoprene addition. The faster loss of $C_5H_9NO_{10}$ may result from the faster wall loss due to its lower volatility. $C_5H_9NO_7$ and $C_5H_9NO_9$ showed a mixing time profile with features of the former two kinds of time profiles, increasing almost instantaneously with isoprene additions especially in the first two periods while increasing continuously or decreasing first with isoprene additions and then increasing later in each periods. This kind of time series indicates that there were significant contributions from both first- and second-generation products.

The second-generation products may be different isomers formed in pathways other than Scheme 1. Second-generation $C_5H_9NO_6$ can be formed via $C_5H_8NO_7$•, which can also be formed by the reaction 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 series of $C_5H_8NO_7$• did show the contribution of both the first- and second-generation processes, which generally increased with time while also responding to isoprene addition (Fig. S4). The time profiles of $C_5H_8NO_8$• showed 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. For the RO_2 in $C_5H_8NO_n$• series, the peak of $C_5H_8NO_n$• 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 sensitively detect all isomers of $C_5H_9NO_6$ due to the sensitivity limitation. Therefore, we cannot exclude the possibility that the

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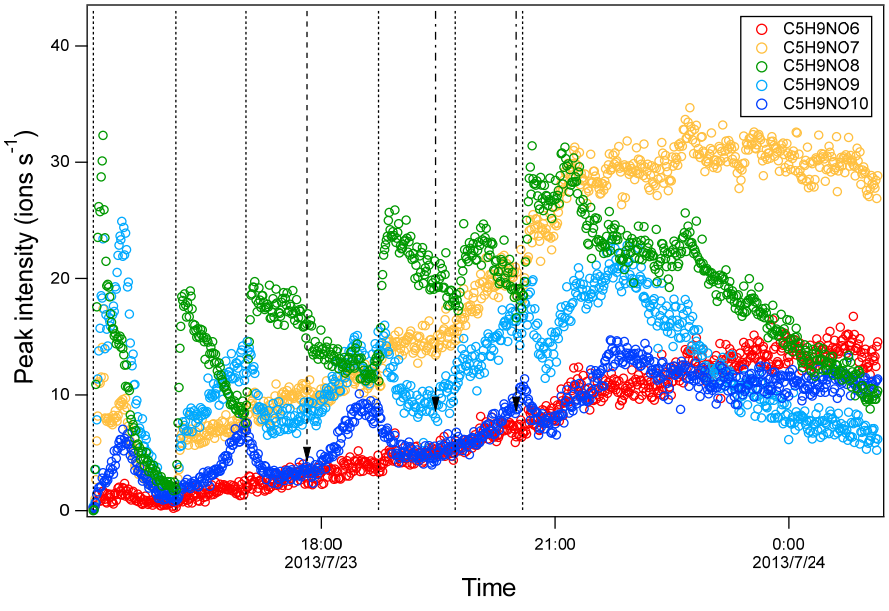
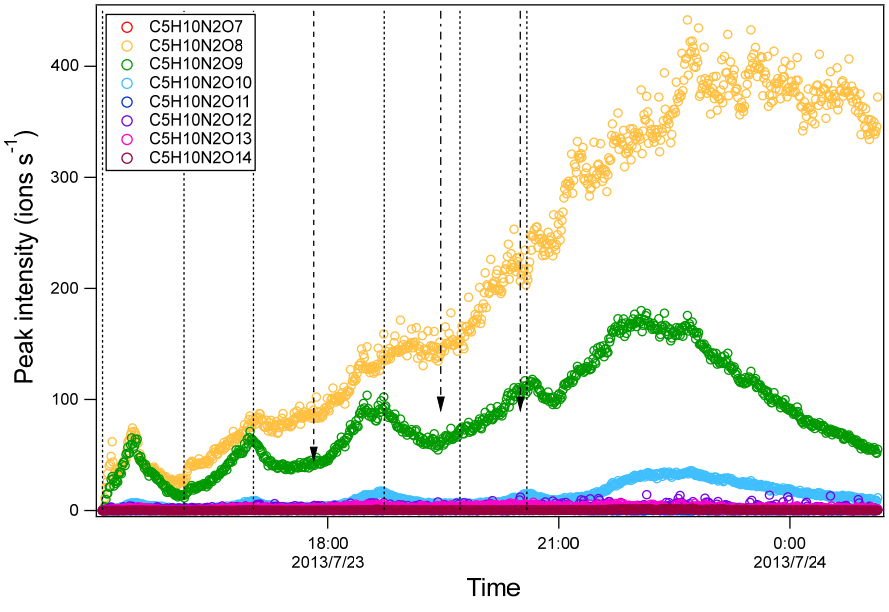
absence of some first-generation isomers of $C_5H_9NO_6$ was due to the low sensitivity of these isomers. Similar to $C_5H_9NO_6$, the second-generation pathway for $C_5H_9NO_7$, $C_5H_9NO_9$, and $C_5H_9NO_{10}$ are shown in Scheme S1, S3, S4.



(a)



(b)

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 $C_5H_8NO_n$• and $C_5H_9N_2O_n$•, respectively. The dashed lines

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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 $C_5H_8NO_n$• with odd and even number of oxygen atom in general, although the most abundant termination product of $C_5H_8NO_n$• , i.e. $C_5H_7NO_8$, was likely formed from $C_5H_8NO_9$• in series M1a. This fact indicates that both the peroxy pathway and alkoxy-peroxy pathway were important for the HOM formation in isoprene+NO_3 under our conditions.

In addition to the termination products of RO_2 M1, minor peaks of the RO_2 series $C_5H_{10}NO_n$• (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 $C_5H_{10}NO_n$•. In addition, a few very minor but noticeable peaks of $C_5H_9O_n$• and their corresponding termination products $C_5H_{10}O_n$ and $C_5H_8O_n$ 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, $C_5H_9NO_7$ 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, $C_5H_{7\text{-}11}NO_{4\text{-}9}$ have been observed in aerosol particles during the Southern Oxidant and Aerosol Study in rural Alabama, US, where isoprene is abundant. 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).

3.2.3 2N-mononmers

2N-monomer RO_2, $C_5H_9N_2O_n$•(n=9-14) series, were observed, as well as its likely termination products, $C_5H_8N_2O_n$ and $C_5H_{10}N_2O_n$, which contain a carbonyl and hydroxyl or hydroperoxide functional group, respectively. The RO_2 series $C_5H_9N_2O_n$• with even number of oxygen atoms (n=9, 11) (M2a in Table 1) were likely formed from the first-generation product $C_5H_9NO_4$ (C5-hydroxynitrate) by adding NO_3 to the remaining double bond, forming $C_5H_9N_2O_9$•, 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. $C_5H_9NO_5$, C5-nitrooxyhydroperoxide) and subsequent alkoxy-peroxy step (Scheme 2b). $C_5H_9N_2O_n$• 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

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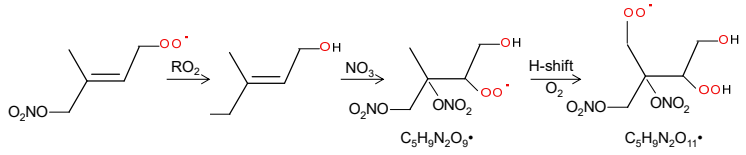
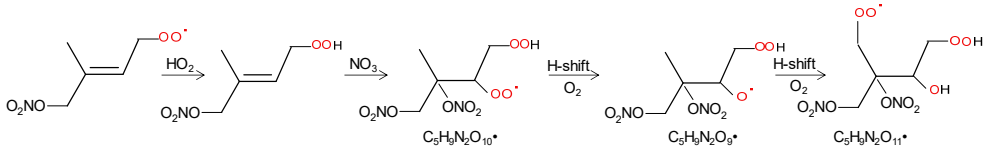
316 $C_5H_9NO_5$ followed by autoxidation (Scheme. 3a), or of $C_5H_9NO_4$ followed by alkoxy-peroxy step (Scheme. 3b).
317 The formation pathways of $C_5H_9N_2O_{13/14}$• cannot be well explained, as they contain too many oxygen atoms to
318 be formed via the pathways in Scheme 2 or 3.

319 Formation through either Scheme 2 or 3 means that $C_5H_8N_2O_n$ and $C_5H_{10}N_2O_n$ were second-generation
320 products. The time series of $C_5H_{10}N_2O_n$ species clearly indicates that they were indeed second-generation
321 products. $C_5H_{10}N_2O_n$ species generally did not increase immediately with isoprene addition (Fig. 3b), but
322 increased gradually with time and reached its maximum in the later stage of each period before decreasing with
323 time (in the period 1 and 6), or decreasing after the next isoprene addition (periods 2-5). This time profile can
324 be explained by the time series of the precursor of $C_5H_{10}N_2O_n$, $C_5H_9N_2O_n$• (RO_2) (Fig. S5). The changing rate
325 (production rate minus destruction rate) of $C_5H_{10}N_2O_n$ concentration was dictated by the concentration of
326 $C_5H_9N_2O_n$• and the wall loss rate. During periods 2 to 5, $C_5H_9N_2O_n$• gradually increased but decreased sharply
327 after the isoprene additions, resulted from chemical reactions of $C_5H_9N_2O_n$• and additionally from wall loss.
328 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
329 with time. After isoprene additions, the rate of change of the $C_5H_{10}N_2O_n$ concentration decreased dramatically
330 to even negative, leading to decreasing concentrations. Similar to $C_5H_{10}N_2O_n$, the $C_5H_8N_2O_n$ series did not
331 respond immediately to isoprene additions (Fig. S6), which is expected for second-generation products
332 according to the mechanism discussed above (Scheme 2-3). Particularly, the continuing increase of $C_5H_8N_2O_n$
333 after isoprene was completely depleted (~ at 21:40, Fig. S6) clearly indicates that these compounds were second-
334 generation products, although in the end they decreased due to wall loss.

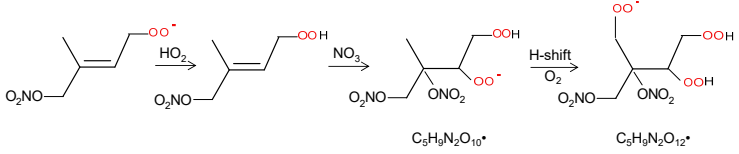


335
336 (a)



337
338 (b)

339 Scheme 2. The pathway to form $C_5H_9N_2O_n$ (n=9, 11) HOM RO_2 series by RO_2 channel (a) and alkoxy-
340 peroxy channel.



341
342 (a)

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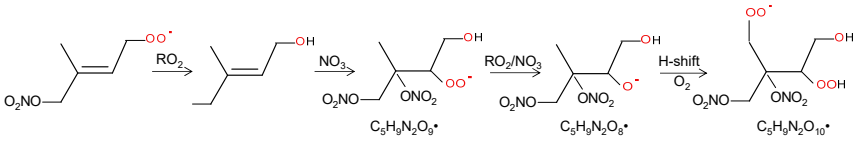

(b)

Scheme 3. The pathway to form $C_5H_9N_2O_n$ (n=8, 10, 12) HOM RO_2 series by RO_2 channel (a) and alkoxy-peroxy channel (b).

According to the finding of Ng et al. (2008), C5-hydroxynitrate decays much faster than C5-nitrooxyhydroperoxides. Therefore, it is likely that $C_5H_9N_2O_n$• M2a series was mainly formed from $C_5H_9NO_4$ instead of $C_5H_9NO_5$, while $C_5H_9N_2O_n$• M2b were formed from $C_5H_9NO_4$ followed by an alkoxy-peroxy step. That is, Scheme 2 was more likely.

Similar to $C_5H_8NO_n$•, the intensity of carbonyl species from $C_5H_9N_2O_n$• was also comparable with that of hydroxyl/hydroperoxide species, suggesting that RO_2+RO_2 reaction forming ketone and alcohol was likely an important pathway of HOM formation in isoprene+NO_3. In general, the intensity of the termination products from $C_5H_9N_2O_n$• 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 isoprene+NO_3. The intensity of $C_5H_{10}N_2O_n$ and $C_5H_8N_2O_n$ decreased with oxygen number with the $C_5H_{10}N_2O_8$ and $C_5H_8N_2O_8$ 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. $C_5H_{10}N_2O_8$ has been detected in the particle phase by Ng et al. (2008) and $C_5H_8N_2O_7$ was detected in the gas phase by Kwan et al. (2012). $C_5H_9N_2O_9$• 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. $C_5H_8N_2O_7$ 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 $C_5H_9N_2O_8$•. Admittedly, $C_5H_8N_2O_7$ may contain both isomers. In addition, Ng et al. (2008) detected $C_5H_8N_2O_6$ in the gas phase, which was not detected in this study likely due to the selectivity of NO_3^--CIMS.

One could suppose that $C_5H_7N_2O_n$• should also be formed since C5-nitrooxycarbonyl ($C_5H_7NO_4$) also contains one double bond that can be attacked by NO_3 in a second oxidation step. However, concentrations of $C_5H_7N_2O_n$ were too low to assign molecular formulas with confidence except for $C_5H_7N_2O_9$•, clearly showing that $C_5H_7N_2O_n$• was not important. This fact is consistent with the finding of Ng et al. (2008) that C5-nitrooxycarbonyls react slowly with NO_3. In addition, 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 VOCs with more than one double bond, NO_3 can add to all the double bonds as for isoprene and limonene.

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3.2.4 3N-monomers

HOM containing three nitrogen atoms, $C_5H_9N_3O_n$ (n=9-16), were observed. These compounds were possibly peroxynitrates formed by the reaction of RO_2 ($C_5H_9N_2O_n$•) with NO_2. The time series of $C_5H_9N_3O_n$ was examined to check whether they match such a mechanism. If $C_5H_9N_3O_n$ were formed by the reaction of $C_5H_9N_2O_{n-2}$• with NO_2, the concentration would be a function of the concentrations of $C_5H_9N_2O_{n-2}$• and NO_2 as follows:

$$\frac{d[C_5H_9N_3O_n]}{dt} = k[C_5H_9N_2O_{n-2}\bullet][NO_2] - k_{wl}[C_5H_9N_3O_n]$$

where $[C_5H_9N_3O_n]$, $[C_5H_9N_2O_{n-2}\bullet]$, and $[NO_2]$ are the concentration of these species, k is the rate constant and k_{wl} is the wall loss rate. Because the products of $C_5H_9N_2O_{n-2}$• and NO_2 were at their maximum at the end of each period and decreased rapidly after isoprene addition (Fig. S7), the concentration should have the maximum increasing rate at the end of each isoprene addition period. However, we found that only $C_5H_9N_3O_{12,\,15,\,16}$ showed such a time profile (Fig. S8), while $C_5H_9N_3O_{9,\,10,\,11,\,13,\,14}$ generally increased with time, different from what one would expect based on the proposed pathway. Therefore, it is likely that $C_5H_9N_3O_{12,\,15,\,16}$ were mainly formed via the reaction of $C_5H_9N_2O_n$• with NO_2, whereas $C_5H_9N_3O_{9,10,11,13,14}$ were not. Moreover, $C_5H_9N_3O_9$ cannot be explained by the reaction $C_5H_9N_2O_n$• (n≥9) with NO_2 or NO_3, because these reactions would add at least one more oxygen atom. One possible pathway to form $C_5H_9N_3O_9$ was the direct addition of N_2O_5 to the carbon double bond of C5-hydroxynitrate, forming a nitronitrate. Such an mechanism has been proposed previously in the heterogeneous reaction of N_2O_5 with 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) because -NO_2 and -NO_3 groups were detected (Lai and Finlayson-Pitts, 1991). This pathway generally matched the time series of $C_5H_9N_3O_{9,10,11,13,14}$ typical of second-generation products since C5-hydroxynitrate was a first-generation product. It is possible that the main pathway of $C_5H_9N_3O_{9,10,11,13,14}$ was the reaction of $C_5H_9NO_{4,5,6}$ with N_2O_5, although the reaction of N_2O_5 with C=C double bonds in common alkenes and unsaturated alcohols are believed to be not important (Japar and Niki, 1975; Pfrang et al., 2006).

3N-monomers, $C_5H_9N_3O_{10}$, has been observed in the particles formed in isoprene+NO_3 by Ng et al. (2008). Here a complete series of $C_5H_9N_3O_n$ were observed. $C_5H_9N_3O_{10}$ was previously proposed to be formed by another pathway, i.e. the reaction of RO_2 ($C_5H_9N_2O_9$•) and NO_3 (Ng et al., 2008). We further examined the possibility of such a pathway in our study. Similar to NO_2, if $C_5H_9N_3O_n$ were formed by the reaction of $C_5H_9N_2O_{n-2}$• with NO_3, the concentration would have the maximum increasing rate at the end of each isoprene addition period. Among $C_5H_9N_2O_n$•, the precursors of $C_5H_9N_3O_n$, $C_5H_9N_2O_{9,\,10,\,13,\,14}$• showed a maximum increasing rate and a subsequent decrease after isoprene addition. The difference in oxygen number between $C_5H_9N_3O_{12,\,15,\,16}$, the termination products, and $C_5H_9N_2O_{9,\,10,\,13,\,14}$•, the corresponding RO_2 with the consistent time profile is mostly two. Since the reaction of $C_5H_9N_2O_n$ with NO_2 and NO_3 result an increased oxygen number by two and by one, respectively, we infer that it is more likely that $C_5H_9N_3O_{12,\,15,\,16}$ were formed by the reaction of $C_5H_9N_2O_{10,\,13,\,14}$• with NO_2 rather than NO_3, and thus they were likely peroxynitrates rather than nitrates

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formed by the reaction of RO_2 with NO_3. Since alkyl peroxynitrates decompose rapidly (Finlayson-Pitts and Pitts, 2000; Ziemann and Atkinson, 2012), it is possible that these compounds contained peroxyacylnitrates.

Little attention has been paid to the RO_2+NO_2 pathway in nighttime chemistry of isoprene in the literature (Wennberg et al., 2018), which is likely due to the stability of the products. According to this pathway, $C_5H_8N_2O_n$, which was proposed to be a ketone formed via $C_5H_9N_2O_9$• in the M2 series (Table 1) as discussed above, can also comprise peroxynitrate formed by the reaction of $C_5H_8NO_n$• (M1a RO_2) with NO_2.

3.3 HOM dimers and their formation

Table 2. HOM dimers and trimers formed in the oxidation of isoprene by NO_3.

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	$C_{10}H_{14}N_2O_{n\ (n=11-12)}$	ROOR	Unknown
Dimer 8	$C_{10}H_{15}NO_{n\ (n=9-12)}$	ROOR	$C_{10}H_{16}NO_n$
Dimer 9	$C_{10}H_{17}NO_{n\ (n=11-19)}$	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	$C_{10}H_{16}NO_{n\ (n=10-16)}$	RO_2	M1+C_5H_8
Trimer 1	$C_{15}H_{24}N_4O_{n\ (n=17-23)}$	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	$C_{15}H_{25}N_3O_{n\ (n=12-20)}$	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=14-17), 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 RO_2 of M1a/b (Reaction R7).

$$C_5H_8NO_{n1}\bullet + C_5H_8NO_{n2}\bullet \rightarrow C_{10}H_{16}N_2O_{n1+n2-2}+O_2 \quad \text{R7}$$

Similarly, $C_{10}H_{18}N_4O_n$ series (dimer 2, Table 2) were likely formed by the accretion reaction of two monomer RO_2 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.

$$C_5H_9N_2O_{n1}\bullet + C_5H_9N_2O_{n2}\bullet \rightarrow C_{10}H_{18}N_4O_{n1+n2-2}+O_2 \quad \text{R8}$$

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$C_{10}H_{17}N_3O_n$ series (dimer 3, Table 2) were likely formed by the cross accretion reaction of one M1 RO_2 and one M2 RO_2 (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.

$$C_5H_8NO_{n1}\bullet + C_5H_9N_2O_{n2}\bullet \rightarrow C_{10}H_{17}N_3O_{n1+n2-2} + O_2 \quad \text{R9}$$

Similarly, $C_{10}H_{18}N_2O_{n\ (n=10-16)}$ and $C_{10}H_{15}N_3O_{n\ (n=14-17)}$ series (dimer 4, dimer 5, Table 2) were likely formed from the accretion reaction of one M1 RO_2 and one M4 RO_2, and of one M1 RO_2 and one M3 RO_2 ($C_5H_7N_2O_9\bullet$). Other dimer series than dimer 1-5 were also present. However, they had quite low intensity (Fig. 4), which was consistent with the low abundance of their parent monomer RO_2. They can be formed from various accretion reactions of monomer RO_2. For example, $C_{10}H_{19}N_3O_n$ can be formed by the accretion reaction of $C_5H_9N_2O_n\bullet$ and $C_5H_{10}NO_n\bullet$ (Table 2).

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

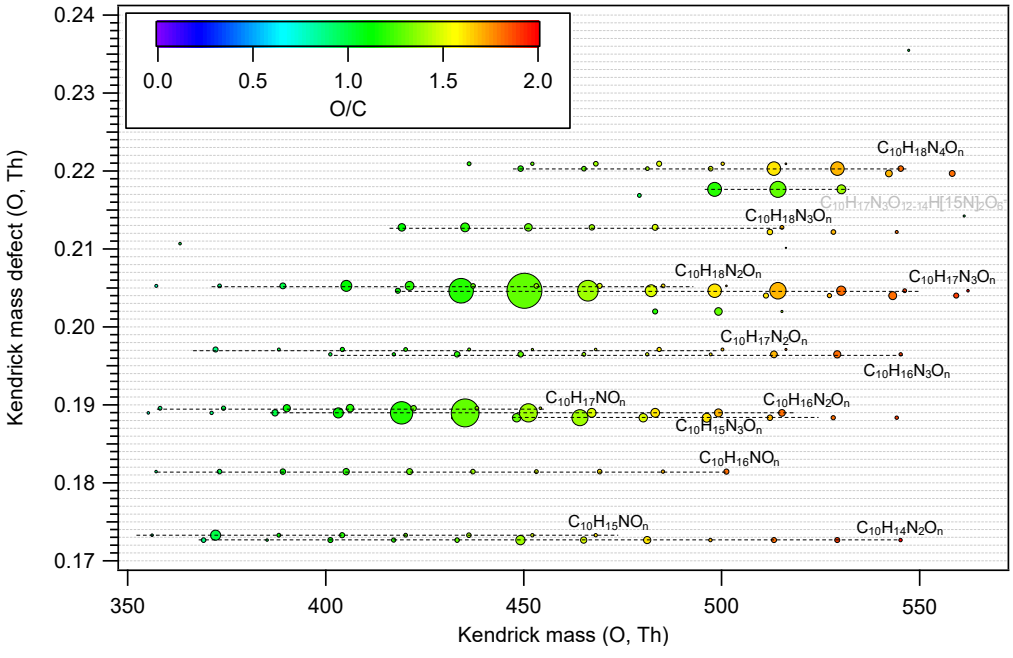

Figure 4. Kendrick mass defect plot for O of HOM dimers formed in isoprene+NO_3. The size (area) of circles is set to be proportional to the average peak intensity of each molecular formula during the first isoprene addition period (P1).

According to the mechanism above (R7-9), we attempt to explain the relative intensities of the dimers using the signal intensities of monomer RO_2. Assuming that the rate constant for each of HOM-RO_2+ HOM-RO_2 reaction forming dimers is the same considering that all HOM-RO_2 are highly oxygenated with a number of functional groups,

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it is expected that the dimer formed by the recombination between the most abundant RO_2 has the highest intensity. The most abundant monomer RO_2 were $C_5H_9N_2O_9$• and $C_5H_9N_2O_{10}$• and thus the most abundant dimers are expected 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 that the most abundant dimers were $C_{10}H_{17}N_3O_{12\text{-}14}$ and $C_{10}H_{16}N_2O_{12\text{-}14}$ (Fig. 4). The discrepancy is possibly attributed to the presence of less oxygenated RO_2 (with O≤5) that have a low detection sensitivity in the NO_3-CIMS (Riva et al., 2019) due to their lower oxygenation compared with other HOM RO_2 shown above. These RO_2 may react with $C_5H_9N_2O_9$• and $C_5H_9N_2O_{10}$•. For example, $C_5H_8NO_5$• (RO_2) is proposed to be an important first-generation RO_2 in the oxidation of isoprene by NO_3 (Ng et al., 2008; Rollins et al., 2009; Kwan et al., 2012; Schwantes et al., 2015). Although $C_5H_8NO_5$• showed very low signal in our mass spectra, it was likely to have high abundance since it was the first RO_2 formed in the reaction of isoprene with NO_3. Indeed we found that the termination products of $C_5H_8NO_5$• such as $C_5H_9NO_5$, $C_5H_7NO_4$, and $C_5H_9NO_4$ had high abundance in another study (Wu et al., 2020), indicating the high abundance of $C_5H_8NO_5$•. The accretion reaction of $C_5H_8NO_5$• with $C_5H_8N_2O_{9\text{-}10}$• and $C_5H_8NO_{9\text{-}10}$• can explain the high abundance of $C_{10}H_{17}N_3O_{12\text{-}14}$ and $C_{10}H_{16}N_2O_{12\text{-}14}$ among all dimers.

Provided that $C_5H_8NO_5$• is abundant, we still cannot explain the relative intensity of $C_{10}H_{17}N_3O_{12}$, $C_{10}H_{17}N_3O_{13}$, and $C_{10}H_{17}N_3O_{14}$ that were all formed by the accretion reaction with $C_5H_8NO_5$•. $C_{10}H_{17}N_3O_{12}$ should have the highest intensity among $C_{10}H_{17}N_3O_{12\text{-}14}$ as its precursor RO_2, $C_5H_9N_2O_9$•, is the most abundant. This suggests that accretion reactions other than those of $C_5H_8NO_5$• with $C_5H_8N_2O_{9\text{-}10}$• also contributed to $C_{10}H_{17}N_3O_{12\text{-}14}$.

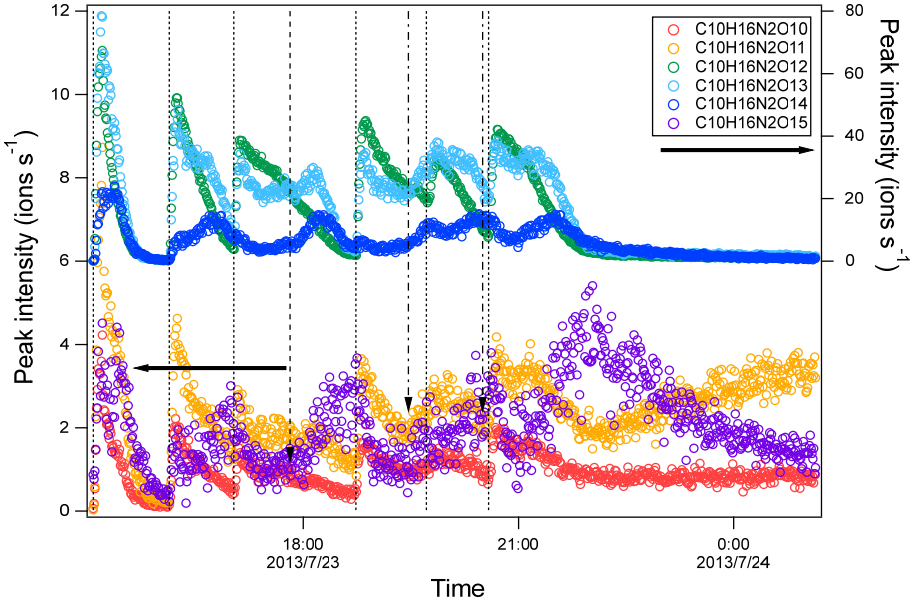

Figure 5. Time series of peak intensity of several HOM dimers of $C_{10}H_{16}N_2O_n$ series. The dashed lines indicate the time of isoprene additions. The long-dashed arrow indicates the time of NO_2 addition. The dash-dotted arrows indicate the time of O_3 additions. The horizontal arrows indicate y-axis scales for different markers.

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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 $C_5H_8NO_5$• as discussed above, the instantaneous increase may result from the increase of $C_5H_8NO_5$• as well as other first-generation RO_2. After the initial increase, $C_{10}H_{16}N_2O_{10\text{-}12}$ then decayed with time (Fig. 5) while $C_{10}H_{16}N_2O_{13\text{-}15}$ increased again in the later phase of a period besides when NO_2 and O_3 were added. The second increase indicated that $C_{10}H_{16}N_2O_{13\text{-}15}$ may contain more than one isomers, which had different production pathways. As discussed above, $C_5H_8NO_n$• 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 $C_{10}H_{16}N_2O_{13\text{-}15}$ 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 $C_{10}H_{16}N_2O_{14\text{-}15}$ after isoprene addition was not obvious, 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 $C_5H_9N_2O_n$• (RO_2), the time profile of $C_{10}H_{18}N_4O_n$ was as expected since $C_5H_9N_2O_n$• 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 $C_5H_9N_2O_n$•. 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 $C_5H_9N_2O_9$• 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 $C_5H_9N_2O_9$• 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. S9), 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 $C_5H_8NO_n$• (M1 RO_2) and $C_5H_9N_2O_n$• (M2 RO_2), which were first- or second-generation, and second-generation RO_2, respectively,

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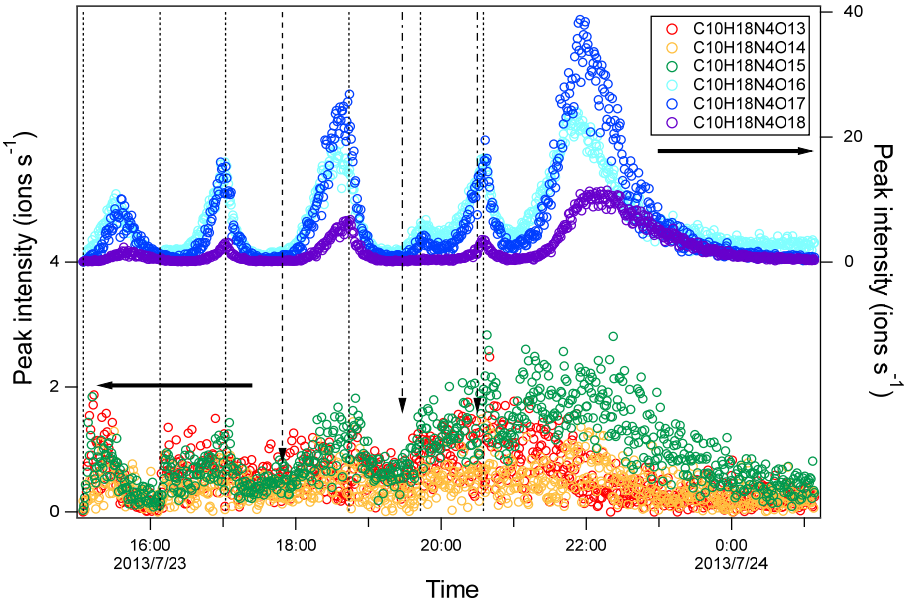

Figure 6. Time series of peak intensity of several HOM dimers of $C_{10}H_{18}N_4O_n$ series. The dashed lines indicate the time of isoprene additions. The long-dashed arrow indicates the time of NO_2 addition. The dash-dotted arrows indicate the time of O_3 additions. The horizontal arrows indicate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

Some dimers that cannot be explained by accretion reactions such as $C_{10}H_{16}N_3O_{n\ (n=12\text{-}15)}$•, $C_{10}H_{17}N_2O_n$•, $C_{10}H_{16}NO_{n\ (n=10\text{-}16)}$•, $C_{10}H_{15}NO_{n\ (n=9\text{-}12)}$, $C_{10}H_{17}NO_{n\ (n=11\text{-}19)}$ were also observed. These dimers had low abundance. Since $C_{10}H_{16}NO_{n\ (n=10\text{-}16)}$•, $C_{10}H_{16}N_3O_{n\ (n=12\text{-}15)}$•, and $C_{10}H_{17}N_2O_n$• contain unpaired electrons, they cannot be formed via the direct accretion reaction of two RO_2. $C_{10}H_{16}N_3O_{n\ (n=12\text{-}15)}$ • (dimer R1) and $C_{10}H_{17}N_2O_n$• (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.

$$C_{10}H_{16}N_2O_n+NO_3+O_2 \rightarrow C_{10}H_{16}N_3O_n\bullet \quad \text{R10}$$

$$C_{10}H_{16}N_2O_n+OH+O_2 \rightarrow C_{10}H_{17}N_2O_n\bullet \quad \text{R11}$$

The corresponding termination products of $C_{10}H_{16}N_3O_n$• 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 $C_{10}H_{17}N_2O_n$• 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 $C_{10}H_{17}N_4O_n$• with another RO_2 wherein $C_{10}H_{17}N_4O_n$• can be formed as follows:

$$C_{10}H_{17}N_3O_n+NO_3+O_2 \rightarrow C_{10}H_{17}N_4O_n\bullet \quad \text{R12}$$

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

$$C_5H_8NO_n\bullet+C_5H_8+O_2 \rightarrow C_{10}H_{16}NO_n\bullet \quad \text{R13}$$

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It seems that only $C_5H_8NO_n$• with more than eight oxygen atoms reacted with isoprene, because only $C_{10}H_{16}NO_n$ with n>8 were detected. Such a reaction of RO_2 with isoprene has been proposed by Ng et al. (2008) and Kwan et al. (2012). The corresponding termination products of $C_{10}H_{16}NO_n$• are $C_{10}H_{15}NO_n$ (ketone) and $C_{10}H_{17}NO_n$ species (hydroperoxide/alcohol). $C_{10}H_{17}NO_n$ species showed a time profile of typical first-generation products (Fig. S10), 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 RO_2 is likely low due to the high activation energy (Stark, 1997, 2000). It is worth noting that to our knowledge no kinetic data on the addition of RO_2 to alkenes in the gas phase in atmospheric relevant conditions are available, though fast, low-barrier ring closure reactions in unsaturated RO_2 radicals have been reported (Vereecken and Peeters, 2004, 2012; Kaminski et al., 2017; Richters et al., 2017).

Some of the dimers discussed above have been observed in previous studies. Ng et al. (2008) found $C_{10}H_{16}N_2O_8$ and $C_{10}H_{16}N_2O_9$ in the gas phase and $C_{10}H_{17}N_3O_{12}$, $C_{10}H_{17}N_3O_{13}$, $C_{10}H_{18}N_4O_{16}$, and $C_{10}H_{17}N_5O_{18}$ in the particle phase. $C_{10}H_{16}N_2O_8$ and $C_{10}H_{16}N_2O_9$ 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 $C_{10}H_{16}N_2O_{8,9}$ in NO_3^--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 $C_{10}H_{16}N_2O_8$ and $C_{10}H_{16}N_2O_9$ have no and only one H-bond donor function groups, respectively, they are expected to have low sensitivity in NO_3^--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 $C_{10}H_{16}N_2O_8$ and $C_{10}H_{16}N_2O_9$ (Ng et al., 2008). $C_{10}H_{17}N_3O_{12}$, $C_{10}H_{17}N_3O_{13}$, $C_{10}H_{18}N_4O_{16}$, and $C_{10}H_{17}N_5O_{18}$ were all observed in the gas phase in this study, wherein the concentration of $C_{10}H_{17}N_5O_{18}$ was very low. The formation pathways of $C_{10}H_{17}N_3O_{12}$, $C_{10}H_{17}N_3O_{13}$, and $C_{10}H_{18}N_4O_{16}$ (R8) were generally similar to those proposed by Ng et al. (2008) except that the products from H-shift of RO_2 were involved in the formation of $C_{10}H_{17}N_3O_{13}$. Among the two pathways of $C_{10}H_{18}N_4O_{16}$ formation (R8 and via R12), our results indicate that R8 was the main pathway, based on the low concentrations of $C_{10}H_{17}N_4O_{16/17}$• and other termination product of them, $C_{10}H_{16}N_4O_{15/16}$. That the time profile of $C_{10}H_{18}N_4O_{16}$ 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 $C_{15}H_{24}N_4O_{n\ (n=17\text{-}23)}$, $C_{15}H_{25}N_5O_{n\ (n=20\text{-}22)}$, $C_{15}H_{25}N_3O_{n\ (n=12\text{-}20)}$, $C_{15}H_{26}N_4O_{n\ (n=17\text{-}21)}$, and $C_{15}H_{24}N_2O_{n\ (n=12\text{-}16)}$. Among trimers, $C_{15}H_{24}N_4O_{n\ (n=17\text{-}23)}$ was the most abundant series (Fig. S11). The $C_{15}H_{24}N_4O_n$ series can be explained by the accretion reaction of one monomer HOM RO_2 and one dimer HOM RO_2.

$$C_{10}H_{16}N_3O_{n1}\bullet + C_5H_8NO_{n2}\bullet \rightarrow C_{15}H_{24}N_4O_{n1+n2-2}+O_2 \quad \text{R14}$$

The formation pathways of dimer RO_2 $C_{10}H_{16}N_3O_n$ (n=14-20) and $C_{10}H_{17}N_2O_n$ are shown above (reaction R14).

The other trimers were likely formed via similar pathways (Table 2 and Supplement S2). Since NO_3^--CIMS cannot provide the structural information of these HOM trimers, we cannot elucidate the major pathways. However, in all these pathways, dimer-RO_2 is necessary to form a trimer, and most of the dimer-RO_2 formation pathways

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require at least one double bond in the dimer molecule except for the reaction of RO_2 with isoprene. Since one double bond has already reacted in the monomer-RO_2 formation, we anticipate that in the reaction with NO_3 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 RO_2 radicals from these dimers by attack on the remaining double bond(s).

The time profile of $C_{15}H_{24}N_4O_n$ showed the mixed behavior of first- and second-generation products (Fig. S12), consistent with the mechanism discussed above since $C_5H_8NO_n$• and $C_{10}H_{16}N_3O_n$• 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, $C_{15}H_{25}N_3O_n$ showed instantaneous increase with isoprene addition (Fig. S13), which was typical for time profiles of first-generation products. Both the formation pathways of $C_{15}H_{25}N_3O_n$ (RS6 and RS7) contained a second-generation RO_2, 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 $C_{10}H_{17}N_2O_n$• were formed very fast or there were other formation pathways of $C_{15}H_{25}N_3O_n$ that have not been 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-momomers. Overall, the relative contribution of total HOM monomers decreased immediately after isoprene addition while the contribution of HOM dimers increased rapidly (Fig. S14), 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 NO_3 was estimated to be $1.2\%^{+1.3\%}_{-0.7\%}$ using the sensitivity of H_2SO_4 (Pullinen et al., 2020). The uncertainty was estimated as shown in the Supplement S1. Despite the uncertainty, the HOM yield here was much higher than the 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.

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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. The formation mechanisms of 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 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. 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 C5-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 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 mixture of both. Additionally, some dimers were formed by the reaction of dimer with NO_3 forming dimer RO_2. HOM trimers were proposed to be formed by accretion reactions between the monomer RO_2 and dimer RO_2, the latter formed by the reaction of NO_3 with dimers containing a C=C double bond.

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 $C_5H_8N_2O_n$, $C_5H_{10}N_2O_n$, $C_{10}H_{17}N_3O_n$, and $C_{10}H_{16}N_2O_n$ series. 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 isoprene+NO_3. 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 $1.3\%^{+1.3\%}_{-0.7\%}$ 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. 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 NO_3 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 ($C_5H_9NO_6$), 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 isoprene+NO_3 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 isoprene+NO_3. Comparing the potential SOA yield produced by HOM with SOA yield in the literature suggests that HOM may play an important role in the SOA formation in isoprene+NO_3.

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Data availability

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

Competing interests

The authors declare that they have no conflict of interest.

Author contribution

TFM, HF, SS, DZ, IP, AW, and AKS designed the experiments. Instrument deployment and operation were carried 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, TFM, RW, JW, SK, and LV interpreted the compiled data set. DZ and TFM wrote the paper. All co-authors discussed the results and commented on the paper.

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