Highly oxygenated organic molecule (HOM) formation in the isoprene oxidation by NO₃ 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 ozone (O₃) and hydroxyl radical (OH), HOM formation in the oxidation by nitrate radical (NO₃), an important oxidant at nighttime and dawn, has received less attention in the oxidation by nitrate radical (NO₃), 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 oxidation under our experimental 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 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, 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%, which corresponded to a SOA yield of ~3.6%.
assuming the molecular weight of C_{3}H_{9}NO_{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}.

1 Introduction

Highly oxygenated organic molecules (HOM) are an important class of compound 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., 2020; McFiggans et al., 2019; Molteni et al., 2019; Quéléver 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 clarifying HOM definition. Currently, most laboratory 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; Mentel et al., 2015; Rissanen et al., 2015; Kirky 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 alkyl 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; Mößler 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 (Reactions R1–3), including organic hydroperoxide, alcohol, and carbonyl, or forming alkoxy radicals (RO, Reactions R4–5) via the following reactions.

\[
\begin{align*}
\text{RO}_{2} + \text{R}^\prime \text{O}^\prime & \rightarrow \text{ROH} + \text{R} = \text{O} \\
\text{RO} & \rightarrow \text{RO} + \text{O} + \text{R}^\prime \text{OH} \\
\text{RO}_{2} + \text{HO}_{2} & \rightarrow \text{ROOH} \\
\text{RO}_{2} + \text{R}^\prime \text{O}^\prime & \rightarrow \text{RO} + \text{R}^\prime \text{O} + \text{O}_{2} \\
\text{RO}_{2} + \text{NO}_{3} & \rightarrow \text{RO} + \text{NO}_{2} + \text{O}_{2} \\
\text{RO}_{2} + \text{R}^\prime \text{O}^\prime & \rightarrow \text{ROOR}^\prime + \text{O}_{2}
\end{align*}
\]

The termination products are detected in the mass spectra at masses \( M + 1, M - 15, \text{ and } M - 17 \), respectively, with \( M \) being the molecular mass of the parent \( \text{RO}_{2} \) (Ehn et al., 2014; Mentel et al., 2015). In case \( \text{RO}_{2} \) is an acyl peroxy radical, percarboxylic acids and carboxylic acids are formed instead of hydroperoxides and alcohols in Reactions (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}: Reaction (R6) (Berndt et al., 2018a, b; Valiev et al., 2019). Additionally, HOM can be formed via H shift in RO followed by O_{2} addition (referred to as the “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.

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 is 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 NO_{3} (Brown et al., 2009) 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; Kirky et al., 2016; Tröstl et al., 2016; Kenseth et al., 2018; Molteni et al., 2018; Garmash et al., 2020; McFiggans et al., 2019; Molteni et al., 2019; Quéléver et al., 2019; Wang et al., 2020; Yan et al., 2020). 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, 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 on 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 NO_{3} are still limited compared with the HOM formation via oxidation by O_{3} and OH. Although a number of laboratory studies have investigated the reaction of NO_{3} 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; Claffin 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 a few oxidation steps.
Under some circumstances, the reaction of isoprene with NO$_3$ can contribute a significant fraction during the afternoon and afterwards (Ayres et al., 2015; Hamilton et al., 2021). 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; 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 NO$_3$ addition to one of the C=C double bonds, preferentially to the carbon C1 (Schwantes et al., 2015), followed by O$_2$ addition forming a nitroxyalkyl peroxy radical (RO$_2$). This RO$_2$ can undergo the reactions described above, forming a series of products such as C$_5$-nitrooxyhydroperoxide, C$_5$-nitrooxy carbonyl, and C$_5$-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 into 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 $\leq 2$ in addition to NO$_3$ functional groups), were 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 the 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 + NO$_3$ reaction 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 the Forschungszentrum Jülich, Germany. The details of the chamber have been described before (Rohrer et al., 2005; Zhao et al., 2015a, b, 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 a 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$_2$ and N$_2$O$_5$ 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$_2$O$_5$ in a second, heated cavity, which had a heated inlet to thermally decompose N$_2$O$_5$ to NO$_3$. The sampling flow rate was 3 to 4 L/min. 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 1 s. 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$_2$O$_5$. In the case of N$_2$O$_5$ a transmission of (85 ± 10) % was achieved and, in the case of NO$_3$, (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 conditions (RH < 2 %), and temperature was at 302 ± 3 K. NO$_2$ and O$_3$ were added to the chamber first to form N$_2$O$_5$ and NO$_3$, reaching concentrations of ~60 ppb for NO$_2$ and ~100 ppb for O$_3$. 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, NO$_2$ was added to compensate for the loss of NO$_3$ and N$_2$O$_5$. Afterwards, three isoprene additions were repeated in the same way as before. O$_3$ was added before the fifth and sixth isoprene additions 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 (<3 % of the isoprene consumption). 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$_3$ con-

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centrations measured. The reaction with NO$_3$ accounted for >95% of the isoprene consumption for the whole experiment periods. The contribution of the reaction of isoprene with a trace amount of OH, mainly produced in the reaction of isoprene + O$_3$ 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 + O$_3$. This is consistent with the contribution determined using measured OH concentration, despite some uncertainty in measured OH concentration due to the interference from NO$_3$. In these experiments, RO$_2$ fate is estimated to be dominated by its reaction with NO$_3$ according to the measured NO$_3$, RO$_2$, and HO$_2$ concentrations and their rate constants for the reactions with RO$_2$ (MCM v3.2; Jenkin et al., 1997, 2003; Saunders et al., 2003; Jenkin et al., 2015, via the website: http://mcm.leeds.ac.uk/MCM, last access: 1 November 2020) despite uncertainties in the measured RO$_2$ and HO$_2$ concentration due to interference from NO$_3$. As a large portion of RO$_2$ is not measured by LIF (Vereecken et al., 2021) and thus RO$_2$ is underestimated, we expected the reaction of RO$_2$ + RO$_2$ to also be important. Overall, we estimate that the RO$_2$ fate is dominated by the reaction RO$_2$ + NO$_3$ with a significant contribution of RO$_2$ + RO$_2$.

### 2.2 Characterization of HOM

In this study we refer to a 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). $^{15}$N nitric acid was used to produce $^{15}$NO$_3^-$ in order to distinguish the NO$_3$ group into 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 H$_2$SO$_4$ as described by Pullinen et al. (2020) because the charge efficiency of HOM and H$_2$SO$_4$ 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$_2$SO$_4$ are provided in Supplement Sect. 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$_2$SO$_4$, 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 out 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 $6 \times 10^{-4}$ 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 $\sim 1 \times 10^{-6}$ 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 photooxidation experiments (Zhao et al., 2018), HOM yield is not sensitive to the vapor wall loss rate. An increase in 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 C$_5$H$_{10}$O and C$_5$H$_8$O$_{11}$ with very minor peaks ($<1\%$ of the maximum peak). The reaction products can be roughly divided into three classes: monomers (C$_5$, $\sim 200$–$400$ Th), dimers (C$_{10}$, $\sim 400$–$600$ Th), and trimers (C$_{15}$, $\geq 600$ 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 increasing oxygenation mass of oxygen) (Fig. 1a). Here a number of series of HOM monomers with continuously increasing oxygenation
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. Panels (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 one to three nitrogen atoms in the molecular formula.

Table 1. HOM monomers formed in the oxidation of isoprene by NO$_3$.

<table>
<thead>
<tr>
<th>Series number</th>
<th>Product</th>
<th>Type$^a$</th>
<th>Pathway of RO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1a/b</td>
<td>C$_5$H$_8$NO$_n$ ($n=7$–11)</td>
<td>RO$_2$</td>
<td>Isoprene+NO$_3$</td>
</tr>
<tr>
<td></td>
<td>C$_5$H$_9$NO$_n$ ($n=6$–11)</td>
<td>ROOH/ROH</td>
<td>Isoprene+NO$_3$+NO$_3$</td>
</tr>
<tr>
<td></td>
<td>C$_5$H$_7$NO$_n$ ($n=6$–10)</td>
<td>R=O</td>
<td></td>
</tr>
<tr>
<td>M2a/b</td>
<td>C$_5$H$_9$N$_2$O$_n$ ($n=8$–11, 13, 14) $^b$</td>
<td>RO$_2$</td>
<td>Isoprene+NO$_3$+NO$_3$</td>
</tr>
<tr>
<td></td>
<td>C$_5$H$_9$N$_2$O$_n$ ($n=8$–11, 13, 14) $^b$</td>
<td>ROOH/ROH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C$_5$H$_8$N$_2$O$_n$ ($n=7$–11)</td>
<td>R=O</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C$_5$H$_9$N$_2$O$_n$ ($n=9$–16) $^b$</td>
<td>RO$_2$NO$_2$</td>
<td></td>
</tr>
<tr>
<td>M3</td>
<td>C$_5$H$_7$N$_2$O$_n$ ($n=9$)</td>
<td>RO$_2$</td>
<td>Isoprene+NO$_3$+NO$_3$</td>
</tr>
<tr>
<td></td>
<td>C$_5$H$_9$N$_2$O$_n$ ($n=8$)</td>
<td>ROOH/ROH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C$_5$H$_9$N$_2$O$_n$ ($n=8$)</td>
<td>R=O</td>
<td></td>
</tr>
<tr>
<td>M4</td>
<td>C$_5$H$_9$NO$_n$ ($n=8$–9)</td>
<td>RO$_2$</td>
<td>Isoprene+NO$_3$+OH</td>
</tr>
<tr>
<td></td>
<td>C$_5$H$_9$NO$_n$ ($n=7$–9)</td>
<td>ROOH/ROH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C$_5$H$_9$NO$_n$ ($n=7$–8)</td>
<td>R=O</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ RO$_2$ denotes peroxy radical, and ROOH, ROH, R=O, and RO$_2$NO$_2$ denote the termination products containing hydroperoxy, hydroxyl, carbonyl group, and peroxynitrate, respectively.

$^b$ Peak assignment of compounds with $n=13, 14$ may be subject to uncertainties.
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 (≤1% of the maximum peak) possibly assigned to C_{5}H_{10}O_{8} and C_{5}H_{8}O_{11}. The contribution of 2N-monomers such as C_{5}H_{10}N_{2}O_{8} and C_{5}H_{8}N_{2}O_{6} was higher than that of the 1N-HOM monomers, and that of 3N-monomers was the lowest (Fig. 1, inset). The most abundant monomers were C_{5}H_{10}N_{2}O_{8}, C_{5}H_{10}N_{2}O_{8}, and C_{5}H_{8}N_{2}O_{6}. The termination products of C_{5}H_{9}NO_{8}, C_{5}H_{9}NO_{9}, and C_{5}H_{9}NO_{10} also showed relatively high abundance. These limited numbers 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 abundances of C_{5}H_{10}N_{2}O_{8} and C_{5}H_{8}N_{2}O_{6} 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 C_{5}H_{9}NO_{4/5} and C_{5}H_{9}NO_{5} may have high abundance but are not detected by NO_{3}-CIMS and are not HOM and thus not included in HOM 1N-monomers.

### 3.2.2 1N-monomers

In our experiments we observed a C_{5}H_{9}NO_{n} • (n = 7–12) series (series M1) as well as its corresponding termination products C_{5}H_{7}NO_{n−1}, C_{5}H_{7}NO_{n−1}, and C_{5}H_{9}NO_{n} via the reactions with RO_{2} and HO_{2}, which contain carbonyl, hydroxyl, and hydroperoxy group, respectively. Overall, the peak intensities of C_{5}H_{7}NO_{n} and C_{5}H_{7}NO_{n} series first increased and then decreased as oxygen number increased (Fig. 2), with the peak intensity of C_{5}H_{7}NO_{5} and C_{5}H_{7}NO_{8} being the highest within their respective series when averaged over the whole experiment period. C_{5}H_{9}NO_{n} • with odd numbers of 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_{5}H_{8}NO_{5} • with even numbers of oxygen atoms (n = 8, 10, series M1b in Table 1) were possibly formed after H shift of an alkoxy radical formed in Reactions (R4) or (R5) and subsequent O_{2} addition (“alkoxy–peroxy” chan-
nel) (Scheme 1b), where the alkoxy radicals can be formed from both the RO₂ + NO₃ and RO₂ + RO₂ reactions. The hydroxy RO₂ 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 molecules. It is likely that many of the reactions occurring are not the dominant channels as otherwise there would be much higher HOM yield as discussed below.

Some HOM monomers may contain multiple isomers and be formed via different pathways. For example, C₅H₆NO₂ can contain alcohols derived from RO₂ C₅H₆NO₃₊1*, hydroperoxides derived from RO₂ C₅H₆NO₄*, or the ketones from RO₂C₅H₁₀NO₅₊1*. Some RO₂ C₅H₆NO₃* may be formed via the reaction of first-generation products with NO₃ in addition to direct reaction of isoprene with NO₃. For example, C₅H₆NO₂* can be formed by the reaction of NO₃ with C₅H₆O₂, which is a first-generation product observed previously in the reaction of isoprene with NO₃ or OH (Scheme S1b) (Kwan et al., 2012). Moreover, RO₂ C₅H₆NO₄* can be formed from C₅-carbonylnitrate, a first-generation product, with OH (Scheme S1a). Trace amount of OH can be produced in the reaction of isoprene with NO₃ (Kwan et al., 2012; Wennberg et al., 2018). OH can also be formed via Criegee intermediates formed in the isoprene + O₃ reaction (Nguyen et al., 2016), but this OH source was likely minor because the contribution of the isoprene + O₃ reaction to total isoprene loss was negligible (<5%, Fig. S2). In addition, C₅H₆NO₅* may also be formed by the reaction of NO₃ with C₅H₆O₃, which is a first-generation product observed in the reaction of isoprene with OH (Kwan et al., 2012). The C₅H₆NO₄* formed via direct reaction of isoprene with NO₃ is a first-generation RO₂, while that formed via other indirect pathways is a second-generation RO₂. The time profiles 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 will increase quickly with isoprene addition and reach a maximum earlier in the presence of wall loss of organic vapor, while second-generation products will 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 time profiles of isoprene, NO₃, and N₂O₅ are also shown (Fig. S4). After isoprene was added in each period, NO₃ and N₂O₅ dropped dramatically and then gradually increased. We found that termination products within the same M₁ series showed different time profiles. For example, in C₅H₆NO₅₉ series, C₅H₆NO₅₉ clearly increased instantaneously with isoprene addition and decreased quickly afterwards (Fig. 3a), indicating that it was a first-generation product, which was expected according to mechanism Scheme 1. C₅H₆NO₉ and C₅H₆NO₁₀ had a general increasing trend with time. While C₅H₆NO₅ increased continuously with time, C₅H₆NO₁₀ reached maximum intensity in the late phase of each isoprene addition period and then decreased naturally or after isoprene addition. The faster loss of C₅H₆NO₁₀ than C₅H₆NO₅ may result from the faster wall loss due to its lower volatility. C₅H₆NO₁₇ and C₅H₆NOₙ 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 period. 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 shown in Scheme 1. Second-generation C₅H₆NO₂ can be formed via C₅H₆NO₇*, which can also be formed by the reaction of NO₃ and O₂ with C₅H₆O₂ as mentioned above (Scheme S2b) or by the reaction of OH with C₅H₇NO₄ (Scheme S2a). The time profiles of C₅H₆NO₇* did show more contribution of second-generation processes because C₅H₆NO₇* continuously increased with time in general. If the pathways via the reaction of NO₃ and O₂ with C₅H₆O₂ and the reaction of OH with C₅H₇NO₄ contribute more to C₅H₆NO₆, C₅H₆NO₅ would show mostly a time profile of second-generation products. Similarly, second-generation C₅H₆NO₁ can be formed via C₅H₆NO₉* or C₅H₆NO₇*. The time series of C₅H₆NO₆* 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). Similarly to C₅H₆NO₆, the second-generation pathways for C₅H₆NO₇*, C₅H₆NO₉*, and C₅H₆NO₁₀ are shown in Schemes S1, S3, and S4. For the RO₂ in C₅H₆NO₇* series other than C₅H₆NO₇/₈*, the peak of C₅H₆NO₇* overlaps with C₅H₁₀N₂O₆ in the mass spectra, which is a much larger peak and thus cannot be differentiated from C₅H₆NO₇/₈O₆. 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 C₅H₆NO₆ due to the sensitivity limitation. Therefore, we cannot exclude the possibility that the absence of some first-generation isomers of C₅H₆NO₆ was due to the low sensitivity of these isomers.

Among the termination products of the 1N-monomer RO₂, carbonyl and hydroxyl/hydroperoxide species had comparable abundance in general (Table S1), suggesting that disproportionation reactions between RO₂ and RO₂ forming hydroxy and carbonyl species (R1–2) were likely an important RO₂ termination pathway. However, dependence of the exact ratio of carbonyl species to hydroxy/hydroperoxide species on the number of oxygen atoms did not show a clear trend (Table S1), suggesting that the reactions of HOM RO₂ depended on their specific structure. There was no clear difference in the abundance between the termination products from C₅H₆NO₇* with odd and even numbers of oxygen atoms in general, although the most abundant termination prod-

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served in field studies. For example, C5H5NO3, where isoprene is abundant. Xu et al. (2021) observed a number of C5H5NO3 in series M1a, respectively, in a rural area of the southeastern US, while others have not been observed in previous laboratory studies of the reaction of isoprene with NO3. In addition to the termination products of RO2 M1, minor peaks of the RO2 series C5H10NOx (n = 8–9) (M4, Table 1) and their corresponding termination products including hydroperoxide, alcohol, and carbonyl species were detected (Table S3). C5H10NOx were likely formed by sequential addition of NO3 and OH to two double bonds of isoprene (Scheme S5). OH can react quickly with isoprene or with the first-generation products of the reaction of isoprene with NO3, thus forming C5H10NOx. In addition, a few very minor but noticeable peaks of C5H9Ox and their corresponding termination products C5H10Ox and C5H5Ox were also observed. These HOM may be formed by the reactions of isoprene with trace amounts of OH and with O3, although their contributions to reacted isoprene were negligible. These HOM may be formed by the reactions of alkoxyl radicals from the reaction of RO2 with trace amounts of OH and with O3 (Jokinen et al., 2015). Among 1N-monomer HOM, C5H5NO7 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 NO3, to our knowledge. A number of C5 organic nitrates have been observed in field studies. For example, C5H7–11NO6–8 and C5H11–11NO4–9 have been observed in the gas phase (Massoli et al., 2018) and the particle phase (Lee et al., 2016; Chen et al., 2020), respectively, in a rural area of the southeastern US, where isoprene is abundant. Xu et al. (2021) observed a number of C5 1N-HOM such as C5H7,9,11NO6,7 in the polluted megacities of Nanjing and Shanghai of eastern China during summer. While many of these HOM have daytime sources and are attributed to photooxidation in the presence of NO3, nighttime oxidation with NO3 also contributed to their formation (Lee et al., 2016; Chen et al., 2020; Xu et al., 2021). C5H7–11NO4–9 were also observed in chamber experiments of the reaction of isoprene with OH in the presence of NO3 (Lee et al., 2016). C5H8NO4–9 and C5H9NO4–10 have also been observed in the gas phase and particle phase, respectively, in a monoterpenedominating rural area in southwestern Germany (Huang et al., 2019).

### 3.2.3 2N-monomers

The 2N-monomer RO2 series C5H9NO2n (n = 8–14) were observed, as well as its likely termination products, C5H8NO2n and C5H10NO2n, which contain a carbonyl and hydroxyl or hydroperoxide functional group, respectively. The RO2 series C5H9NO2n with an odd number of oxygen atoms (n = 9, 11) (M2a in Table 1) were likely formed from the first-generation product C5H9NO2, followed by autoxidation (Scheme 2a). This RO2 series can also be formed by the addition of NO3 to the double bond of first-generation products (e.g., C5H9NO5, C5-nitroxyhydroperoxide) and a subsequent alkoxyl–peroxy step (Scheme 2b). C5H9NO2n with an even number of oxygen atoms (n = 8, 10, 12) (M2b in Table 1) can be formed by the addition of NO3 to the double bond of C5H9NO3 followed by autoxidation (Scheme 3a) or of C5H9NO4 followed by an alkoxyl–peroxy step (Scheme 3b). The formation pathways of C5H9NO2nO13/14* and C5H9NO2O8* 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 Schemes 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 C$_5$H$_9$N$_2$O$_n$ and C$_5$H$_{10}$N$_2$O$_n$ were second-generation products. The time series of C$_5$H$_{10}$N$_2$O$_n$ species clearly indicates that they were indeed second-generation products. C$_5$H$_9$N$_2$O$_n$ species generally did not increase immediately

Figure 3. Time series of peak intensity of several HOM monomers of C$_5$H$_9$NO$_n$ series (a) and of C$_5$H$_{10}$N$_2$O$_n$ series (b). They are likely the termination products of RO$_2$ C$_5$H$_9$NO$_n$ and C$_5$H$_{10}$N$_2$O$_n$, 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.
Scheme 2. The example pathways to form C$_5$H$_9$N$_2$O$_n$ ($n = 9, 11$) HOM RO$_2$ series by RO$_2$ channel (a) and alkoxy–peroxy channel. The detected products are in bold.

Scheme 3. The example pathways to form C$_5$H$_9$N$_2$O$_n$ ($n = 10, 12$) HOM RO$_2$ series by RO$_2$ channel (a) and alkoxy–peroxy channel (b). The detected products are in bold.

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 periods 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 C$_5$H$_{10}$N$_2$O$_n$, C$_5$H$_9$N$_2$O$_n$$^*$ (RO$_2$) (Fig. S6). The changing rate (production rate minus destruction rate) of C$_5$H$_{10}$N$_2$O$_n$ concentration was dictated by the concentration of C$_5$H$_9$N$_2$O$_n$$^*$ and the wall loss rate. During periods 2 to 5, C$_5$H$_9$N$_2$O$_n$$^*$ gradually increased but decreased sharply after the isoprene additions, resulting from chemical reactions of C$_5$H$_9$N$_2$O$_n$$^*$ and additionally from wall loss. When the rate of change of the C$_5$H$_{10}$N$_2$O$_n$ concentration was positive, the concentration of C$_5$H$_{10}$N$_2$O$_n$ increased with time. After isoprene additions, the rate of change of the C$_5$H$_{10}$N$_2$O$_n$ concentration decreased dramatically to even negative, leading to decreasing concentrations. Similarly to C$_5$H$_{10}$N$_2$O$_n$$^*$, the C$_5$H$_8$N$_2$O$_n$ series did not respond immediately to isoprene additions (Fig. S7), which is expected for second-generation products according to the mechanism discussed above (Schemes 2–3). Particularly, the continuing increase in C$_5$H$_8$N$_2$O$_n$ even after isoprene was completely depleted (at $\sim$ 21:40, Fig. S7) clearly indicates that these compounds were second-generation products, although in the end they decreased due to wall loss.

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

Similarly to C$_5$H$_8$NO$_n$$^*$, the intensity of carbonyl species from C$_5$H$_9$N$_2$O$_n$$^*$ was also comparable with that of hydroxyl/hydroperoxide species, suggesting that RO$_2^+$ + RO$_2$ reaction forming ketone and alcohol was likely an impor-
tant pathway of HOM formation in the isoprene + NO$_3$ reaction. In general, the intensities of the termination products from C$_5$H$_{10}$N$_2$O$_4$• 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 C$_5$H$_8$N$_2$O$_5$ first increased and then decreased with oxygen number, while C$_5$H$_{10}$N$_2$O$_6$ decreased with oxygen number, with C$_5$H$_8$N$_2$O$_5$ and C$_5$H$_8$N$_2$O$_7$ 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$_5$H$_{10}$N$_2$O$_8$ was detected in the particle phase by Ng et al. (2008), and C$_5$H$_8$N$_2$O$_7$ was detected in the gas phase by Kwan et al. (2012). C$_5$H$_8$N$_2$O$_7$• 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$_5$H$_8$N$_2$O$_7$ species has been proposed as a dinitrooxy epoxide formed by the oxidation of nitroxyhydroperoxide (Kwan et al., 2012) instead of being a dinitrooxy ketone proposed in our study, a termination product of C$_5$H$_8$N$_2$O$_7$•. Admittedly, C$_5$H$_8$N$_2$O$_7$• may contain both isomers. In addition, Ng et al. (2008) detected C$_5$H$_8$N$_2$O$_6$ in the gas phase, which was not detected in this study, likely due to the selectivity of NO$_3$-CIMS. 2N-monomers have also been observed in previous field studies.

For example, Massoli et al. (2018) observed C$_5$H$_{10}$N$_2$O$_{10}$– in rural Alabama, US, during the SOAS campaign. Xu et al. (2021) observed C$_5$H$_{8.10}$N$_2$O$_8$ and C$_5$H$_{10.10}$N$_2$O$_8$ in the polluted megacities of Nanjing and Shanghai during summer.

One could suppose that C$_5$H$_7$N$_2$O$_{9.9}$• should also be formed since C$_5$-nitrooxycarbonyl (C$_5$H$_3$NO$_4$) also contains one double bond that can be attacked by NO$_3$ in a second oxidation step. However, concentrations of C$_5$H$_7$N$_2$O$_9$ were too low to assign molecular formulas with confidence except for C$_5$H$_7$N$_2$O$_{9.9}$•, clearly showing that C$_5$H$_7$N$_2$O$_{9.9}$• was not important. This fact is consistent with the finding by Ng et al. (2008) that C$_5$-nitrooxycarbonyls react slowly with NO$_3$. Additionally, the peroxy radical formed in the reaction of C$_5$-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 C$_5$H$_7$N$_2$O$_9$. 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, C$_5$H$_8$N$_3$O$_n$ ($n = 9–16$), were observed. These compounds were possibly peroxyxinitrates formed by the reaction of RO$_2$ (C$_5$H$_8$N$_2$O$_7$•) with NO$_2$. The time series of C$_5$H$_8$N$_3$O$_n$ was examined to check whether they match such a mechanism. If C$_5$H$_8$N$_3$O$_n$ were formed by the reaction of C$_5$H$_8$N$_2$O$_{n-2}$• with NO$_2$, the concentration would be a function of the concentrations of C$_5$H$_8$N$_2$O$_{n-2}$• and NO$_2$ as follows:

$$\frac{d[C_5H_8N_3O_n]}{dr} = k[C_5H_8N_2O_{n-2}][NO_2] - k_{wall}[C_5H_8N_3O_n],$$

where [C$_5$H$_8$N$_3$O$_n$], [C$_5$H$_8$N$_2$O$_{n-2}$•], and [NO$_2$] are the concentrations of these species, $k$ is the rate constant, and $k_{wall}$ is the wall loss rate. Because the products of C$_5$H$_8$N$_2$O$_{n-2}$• and NO$_2$ were at their maximum at the end of each period and decreased rapidly after isoprene addition (Fig. S8), the concentration should have its maximum increasing rate at the end of each isoprene addition period. However, we found that only C$_5$H$_8$N$_2$O$_{12.15}$ showed such a time profile (Fig. S9), while C$_5$H$_8$N$_2$O$_{9.10,11,13,14}$ generally increased with time, different from what one would expect based on the proposed pathway. Therefore, it is likely that C$_5$H$_8$N$_3$O$_{12.15}$ were mainly formed via the reaction of C$_5$H$_8$N$_2$O$_{n-2}$• with NO$_2$, whereas C$_5$H$_8$N$_2$O$_{9,10,11,13,14}$ were not. Moreover, C$_5$H$_8$N$_2$O$_9$ cannot be explained by the reaction C$_5$H$_8$N$_2$O$_{n-2}$• ($n \geq 9$) with NO$_2$ or NO$_3$, because these reactions would add at least one more oxygen atom. One possible pathway to form C$_5$H$_8$N$_2$O$_9$ was the direct addition of N$_2$O$_5$ to the carbon double bond of C$_5$-hydroxynitrile, forming a nitronitrile. Such a mechanism was proposed previously in the heterogeneous reaction of N$_2$O$_3$ 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$_5$H$_8$N$_3$O$_{9,10,11,13,14}$ typical of second-generation products since C$_5$-hydroxynitrile was a first-generation product. It is possible that the main pathway of C$_5$H$_8$N$_3$O$_{9,10,11,13,14}$ was the reaction of C$_5$H$_8$NO$_{4.5.6}$ with N$_2$O$_5$, although the reaction of N$_2$O$_5$ with C=C double bonds in common alkenes and unsaturated alcohols is believed to be unimportant (Japar and Niki, 1975; Pfaffner et al., 2006).

3N-monomer, C$_5$H$_8$N$_2$O$_{10}$, has been observed in the particles formed in the isoprene + NO$_3$ reaction by Ng et al. (2008). Here a complete series of C$_5$H$_8$N$_2$O$_n$ was observed. C$_5$H$_8$N$_2$O$_{10}$ was previously proposed to be formed by another pathway, i.e., the reaction of RO$_2$ (C$_5$H$_8$N$_2$O$_7$•) and NO$_3$ (Ng et al., 2008). We further examined the possibility of such a pathway in our study. Similarly to NO$_2$, if C$_5$H$_8$N$_2$O$_n$ were formed by the reaction of C$_5$H$_8$N$_2$O$_{n-2}$• with NO$_3$, the concentration would have its maximum increasing rate at the end of each isoprene addition period. Among C$_5$H$_8$N$_2$O$_n$•, the precursors of C$_5$H$_8$N$_3$O$_n$, C$_5$H$_8$N$_2$O$_{9,10,13,14}$ showed a maximum increasing rate and a subsequent decrease after isoprene addition. The difference in oxygen number between C$_5$H$_8$N$_2$O$_{12.15,16}$, the termination products, and C$_5$H$_8$N$_2$O$_{9,10,13,14}$•, the corresponding RO$_2$ with the consistent time profile, is mostly two. Since

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the reaction of C$_5$H$_3$NO$_2$ with NO$_2$ and NO$_3$ results in increased oxygen numbers by two and by one, respectively, we infer that it is more likely that C$_5$H$_3$NO$_3$O$_{2,15,16}$ were formed by the reaction of C$_5$H$_3$NO$_2$O$_{10,13,14}$ with NO$_2$ rather than NO$_3$, and thus they were likely peroxyxinitrates rather than nitrates formed by the reaction of RO$_2$ with NO$_3$. Since alkyl peroxyxinitrates decompose rapidly (Finlayson-Pitts and Pitts, 2000; Ziemann and Atkinson, 2012), it is possible that these compounds contained peroxyxinitrates.

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 instability of the products. According to this pathway, C$_5$H$_3$NO$_3$, which was proposed as a ketone formed via C$_5$H$_3$NO$_2$O$_*$ in the M2 series (Table 1) as discussed above, can also comprise peroxyxinitrate formed by the reaction of C$_5$H$_3$NO$_2$O$^*$ (M1a RO$_2$) with NO$_3$. 3N dimers such as C$_5$H$_3$NO$_3$O$_{10}$ have been observed in a recent field study in polluted cities in eastern China (Xu et al., 2021).

### 3.3 HOM dimers and their formation

A number of HOM dimer series were observed, including C$_{10}$H$_{18}$N$_2$O$_n$ ($n = 10–17$), C$_{10}$H$_{17}$N$_3$O$_n$ ($n = 11–19$), and C$_{10}$H$_{18}$N$_2$O$_n$ ($n = 15–18$), C$_{10}$H$_{19}$N$_2$O$_n$ ($n = 10–16$), C$_{10}$H$_{15}$N$_3$O$_n$ ($n = 13–17$), and C$_{10}$H$_{19}$N$_2$O$_n$ ($n = 14–15$) series (Tables 2, S3). C$_{10}$H$_{16}$N$_2$O$_n$ series (dimer 1, Table 2) was likely formed by the accretion reaction of two monomer RO$_2$ of M1a/b (Reaction R7).

C$_5$H$_3$NO$_{n_1}$ + C$_5$H$_3$NO$_{n_2}$ → C$_{10}$H$_{16}$N$_2$O$_{n_1+n_2-2}$ + O$_2$ (R7)

Similarly, C$_{10}$H$_{18}$N$_4$O$_n$ series (dimer 2, Table 2) were likely formed by the accretion reaction of two monomer RO$_2$ of M2 (Reaction R8). As $n_1$ and $n_2$ are $\geq 9$, the number of oxygen in C$_{10}$H$_{18}$N$_4$O$_n$ is expected to be $\geq 16$. This is consistent with our observation that only C$_{10}$H$_{18}$N$_4$O$_n$ with $n \geq 16$ had significant concentrations.

C$_5$H$_3$NO$_{n_1}$ + C$_5$H$_3$NO$_{n_2}$ → C$_{10}$H$_{18}$N$_4$O$_{n_1+n_2-2}$ + O$_2$ (R8)

C$_{10}$H$_{17}$N$_3$O$_n$ 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 $n_1$ is $\geq 5$ and $n_2$ is $\geq 9$, the number of oxygen atoms in C$_{10}$H$_{17}$N$_3$O$_n$ is expected to be $\geq 12$, which is also roughly consistent with our observation that only C$_{10}$H$_{17}$N$_3$O$_n$ with $n \geq 11$ were detected.

C$_5$H$_3$NO$_{n_1}$ + C$_5$H$_3$NO$_{n_2}$ → C$_{10}$H$_{17}$N$_3$O$_{n_1+n_2-2}$ + O$_2$ (R9)

Similarly, C$_{10}$H$_{18}$N$_2$O$_n$ ($n = 10–16$) and C$_{10}$H$_{15}$N$_3$O$_n$ ($n = 13–17$) series (dimer 4, dimer 5, Table 2) were likely formed from the accretion reaction between one M1 RO$_2$ and one M4 RO$_2$ and between one M1 RO$_2$ and one M3 RO$_2$ (C$_5$H$_7$N$_2$O$_9$). Other dimer series than dimers 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$_3$O$_n$ can be formed by the accretion reaction of C$_5$H$_3$NO$_2$O$^*$ and C$_3$H$_{10}$NO$_4$O$^*$ (Table 2).

Similarly to monomers, a few species dominated in the HOM dimer spectrum. The dominant dimer series were C$_{10}$H$_{17}$N$_3$O$_n$, and C$_{10}$H$_{16}$N$_2$O$_n$ series, with C$_{10}$H$_{17}$N$_3$O$_{12–14}$ and C$_{10}$H$_{16}$N$_2$O$_{12–14}$ showing the highest intensity among each series (Fig. 4). In addition, the O/C ratio or oxidation state of HOM dimers was generally lower than that of monomers (Figs. 2, 4), which resulted from the loss of two oxygen atoms in the accretion reaction of two monomer RO$_2$.

According to the mechanism above (Reactions R7–R9), 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 the HOM-RO$_2$ + HOM-RO$_2$ reactions forming dimers is the same considering that all HOM-RO$_2$ are highly oxygenated with a number of functional groups, it is expected that the dimer formed by the recombination between the most abundant RO$_2$ has the highest intensity. The most abundant monomers RO$_2$ were C$_5$H$_3$NO$_2$O$^*$ and C$_5$H$_3$NO$_2$O$_{10}$, and thus the most abundant dimers are expected to be C$_{10}$H$_{16}$N$_4$O$_{16}$, C$_{10}$H$_{16}$N$_4$O$_{17}$, and C$_{10}$H$_{16}$N$_4$O$_{18}$. This expected result is in contrast with our observation showing that the most abundant dimers were C$_{10}$H$_{17}$N$_3$O$_{12–14}$ and C$_{10}$H$_{16}$N$_2$O$_{12–14}$ (Fig. 4). The discrepancy is possibly attributed to the presence of less oxygenated RO$_2$ (with O $\leq 5$) 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$_5$H$_3$N$_2$O$^*$ and C$_5$H$_3$N$_2$O$_{10}$, for example, C$_5$H$_8$NO$_4$O$^*$ (RO$_2$) is proposed as 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$_5$H$_8$NO$_4$ showed a 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$_5$H$_8$NO$_4$ such as C$_5$H$_8$NO$_5$, C$_5$H$_7$NO$_4$, and C$_5$H$_8$NO$_4$ had high abundance in another study, indicating the high abundance of C$_5$H$_8$NO$_4$. The accretion reaction of C$_5$H$_8$NO$_4$O$^*$ with C$_5$H$_3$NO$_2$O$_{9–10}$ and C$_5$H$_8$NO$_4$O$_{9–10}$ can explain the high abundance of C$_{10}$H$_{17}$N$_3$O$_{12–14}$ and C$_{10}$H$_{16}$N$_2$O$_{12–14}$ among all dimers.

Provided that C$_5$H$_8$NO$_4$ is abundant, we still cannot explain the relative intensities of C$_{10}$H$_{17}$N$_3$O$_{12}$, C$_{10}$H$_{17}$N$_3$O$_{13}$, and C$_{10}$H$_{17}$N$_3$O$_{14}$ that were all formed by the accretion reaction with C$_5$H$_8$NO$_4$. C$_{10}$H$_{17}$N$_3$O$_{12}$ should have the highest intensity among C$_{10}$H$_{17}$N$_3$O$_{12–14}$ as its precursor RO$_2$, C$_5$H$_3$N$_2$O$_9$, is the most abundant. This suggests that accretion reactions other than those of C$_5$H$_8$NO$_4$O$^*$ with C$_5$H$_3$NO$_2$O$_{9–10}$ also contributed to C$_{10}$H$_{17}$N$_3$O$_{12–14}$. Admittedly, the assumption of different RO$_2$ having similar rate constants in accretion reactions may not be valid. For exam-
Table 2. HOM dimers and trimers formed in the oxidation of isoprene by NO3.

<table>
<thead>
<tr>
<th>Series number</th>
<th>Formula</th>
<th>Type</th>
<th>Pathway of RO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimer 1</td>
<td>C10H16N2O_n(n=10–17)</td>
<td>ROOR</td>
<td>M1b + M1</td>
</tr>
<tr>
<td>Dimer 2</td>
<td>C10H17N3O_n(n=11–19)</td>
<td>ROOR</td>
<td>M1 + M2/M3 + M4</td>
</tr>
<tr>
<td>Dimer 3</td>
<td>C10H18N4O_n(n=15–18)</td>
<td>ROOR</td>
<td>M2 + M2</td>
</tr>
<tr>
<td>Dimer 4</td>
<td>C10H18N2O_n(n=10–16)</td>
<td>ROOR</td>
<td>M1 + M4</td>
</tr>
<tr>
<td>Dimer 5</td>
<td>C10H15N3O_n(n=13–17)</td>
<td>ROOR</td>
<td>M1 + M3</td>
</tr>
<tr>
<td>Dimer 6</td>
<td>C10H19N3O_n(n=14–15)</td>
<td>ROOR</td>
<td>M2 + M4</td>
</tr>
<tr>
<td>Dimer 7</td>
<td>C10H14N2O_n(n=10–16)</td>
<td>ROOR</td>
<td>Unknown</td>
</tr>
<tr>
<td>Dimer 8</td>
<td>C10H15NO_n(n=9–12)</td>
<td>ROOR</td>
<td>C10H16NO_n</td>
</tr>
<tr>
<td>Dimer 9</td>
<td>C10H17NO_n(n=9–15)</td>
<td>ROOR</td>
<td>C10H16NO_n</td>
</tr>
<tr>
<td>Dimer R1</td>
<td>C10H16N3O_n(n=12–15)</td>
<td>RO2</td>
<td>Dimer 1 + NO3</td>
</tr>
<tr>
<td>Dimer R2</td>
<td>C10H17N2O_n(n=11–12)</td>
<td>RO2</td>
<td>Dimer 1 + OH</td>
</tr>
<tr>
<td>Dimer R3</td>
<td>C10H17N4O_n(n=16–18)</td>
<td>RO2</td>
<td>Dimer 2 + NO3</td>
</tr>
<tr>
<td>Dimer R4</td>
<td>C10H16NO_n(n=10–14)</td>
<td>RO2</td>
<td>M1 + C5H8</td>
</tr>
<tr>
<td>Trimer 1</td>
<td>C15H24N4O_n(n=17–22)</td>
<td>ROOR</td>
<td>Dimer R1 + M1</td>
</tr>
<tr>
<td>Trimer 2</td>
<td>C15H23N5O_n(n=20–22)</td>
<td>ROOR</td>
<td>Dimer R3 + M1; dimer R1 + M2</td>
</tr>
<tr>
<td>Trimer 3</td>
<td>C15H25N3O_n(n=13–20)</td>
<td>ROOR</td>
<td>Dimer R2 + M1; dimer R4 + M2</td>
</tr>
<tr>
<td>Trimer 4</td>
<td>C15H26N4O_n(n=17–21)</td>
<td>ROOR</td>
<td>Dimer R2 + M2</td>
</tr>
</tbody>
</table>

a ROOR denotes organic peroxide. b The numbering refers to Table 1.

Figure 4. Kendrick mass defect plot for O of HOM dimers formed in the isoprene + NO3 reaction. 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 molecular formula includes the reagent ion 15NO3−, which is not shown for simplicity. The species labeled in grey (C10H17N3O12–14 H[15N]2O6) are the adducts of C10H17N3O12–14 with H[15N]2O6.

Discussion: self-reaction of tertiary RO2 is slower than secondary and primary RO2 (Jenkin et al., 1998; Finlayson-Pitts and Pitts, 2000). Different rate constants may also lead to the observation that the most abundant dimers could not be explained by the most abundant RO2.

The time profiles of C10H16N2O_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 C10H16N2O_n compounds increased instantaneously after isoprene additions, indicating significant contributions of first-generation products. Since the formation of C10H16N2O_n likely involved C5H8NO4, as discussed above, the instantaneous increase may result from the increase in C5H8NO4 as well as other first-generation RO2. After the initial increase, C10H16N2O_{10–12} then decayed with time (Fig. 5), while C10H16N2O_{13–15}

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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$_2$O$_{13-15}$ may contain more than one isomer, which had different production pathways. As discussed above, C$_5$H$_8$NO$_4^+$ can be either a first-generation RO$_2$ formed directly via the reaction of isoprene with NO$_3$ and autodissociation or a second-generation RO$_2$, e.g., formed via the reaction of C$_3$H$_6$O$_2$ with NO$_3$. Therefore, the second increase in C$_{10}$H$_{16}$N$_2$O$_{13-15}$ 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 in C$_{10}$H$_{16}$N$_2$O$_{14-15}$ after isoprene addition was not large, indicating the larger contributions from second-generation products compared with other C$_{10}$H$_{16}$N$_2$O$_n$.

Overall, as the number of oxygen increased, the contribution of second-generation products to C$_{10}$H$_{16}$N$_2$O$_n$ increased.

In contrast to C$_{10}$H$_{16}$N$_2$O$_n$ series, C$_{10}$H$_{16}$N$_2$O$_n$ 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$_4$O$_4$ was likely formed by the accretion reaction of C$_5$H$_8$NO$_2^+$ (RO$_2$), the time profile of C$_{10}$H$_{18}$N$_4$O$_n$ was as expected since C$_5$H$_8$NO$_2^+$ was formed via the reaction of NO$_3$ with first-generation products C$_3$H$_6$NO$_2$. The C$_{10}$H$_{18}$N$_4$O$_n$ concentration depended on the product of the concentrations of two C$_5$H$_8$NO$_2^+$. Taking C$_{10}$H$_{18}$N$_4$O$_{16}$ as an example, its concentration can be expressed as follows:

$$
\frac{d[C_{10}H_{18}N_4O_{16}]}{dt} = k[C_5H_8N_2O_2][C_5H_8N_2O_2] - k_{de}[C_{10}H_{18}N_4O_{16}].
$$

When the concentration of C$_5$H$_8$NO$_2^+$ increased, the changing rate of C$_{10}$H$_{18}$N$_4$O$_{16}$ was positive and increased, and thus the concentration of C$_{10}$H$_{18}$N$_4$O$_{16}$ increased. When the concentration of C$_5$H$_8$NO$_2^+$ decreased sharply after isoprene additions, the changing rate of C$_{10}$H$_{18}$N$_4$O$_{16}$ decreased and even became negative values, and thus the concentration of C$_{10}$H$_{18}$N$_4$O$_{16}$ decreased after isoprene addition.

Similarly to the C$_{10}$H$_{16}$N$_2$O$_n$ series, while C$_{10}$H$_{17}$N$_3$O$_n$ 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$_3$O$_n$ was as expected in general because C$_{10}$H$_{17}$N$_3$O$_n$ was likely formed via the accretion reaction of C$_5$H$_8$NO$_4^+$ (M1 RO$_2$) and C$_5$H$_8$N$_2$O$_n^+$ (M2 RO$_2$), which were first- or second-generation, and second-generation RO$_2$, respectively.

Some dimers that cannot be explained by accretion reactions, such as C$_{10}$H$_{16}$N$_3$O$_n(n=12-15)$*, C$_{10}$H$_{17}$N$_2$O$_n(n=11-12)$*, C$_{10}$H$_{16}$N$_3$O$_n(n=10-14)$*, C$_{10}$H$_{15}$N$_2$O$_n(n=9-12)$, and C$_{10}$H$_{17}$N$_2$O$_n(n=9-15)$, 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$_n(n=10-16)$*, C$_{10}$H$_{16}$N$_3$O$_n(n=12-15)$*, and C$_{10}$H$_{17}$N$_2$O$_n^*$ contain unpaired electrons, they cannot be formed via the direct accretion reaction of two RO$_2$. Instead, C$_{10}$H$_{16}$N$_3$O$_n(n=12-15)$ (dimer R1) and C$_{10}$H$_{17}$N$_2$O$_n^*$ (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$_2$.

$$
C_{10}H_{16}N_2O_n + NO_3 + O_2 \rightarrow C_{10}H_{16}N_3O_n^* \quad (R10)
$$
$$
C_{10}H_{16}N_2O_n + OH + O_2 \rightarrow C_{10}H_{17}N_2O_n. \quad (R11)
$$

The corresponding termination products of C$_{10}$H$_{16}$N$_3$O$_n^*$ RO$_2$ series such as C$_{10}$H$_{15}$N$_3$O$_n$ (ketone) and C$_{10}$H$_{17}$N$_3$O$_n$ (hydroperoxide/alcohol) were also observed, although these compounds can also be formed via reactions between two RO$_2$ radicals (Reaction R9 and Table 1). Among the termination products, C$_{10}$H$_{15}$N$_3$O$_n$ had low intensity. Reaction (R13) and the termination reaction of C$_{10}$H$_{17}$N$_3$O$_n^*$ with HO$_2$ provided an additional pathway to C$_{10}$H$_{17}$N$_3$O$_n$ besides the Reaction (R9) pathway discussed above. Similarly, other dimers may also be formed by the termination reactions of dimer RO$_2$ with RO$_2$ or HO$_2$. For example, C$_{10}$H$_{18}$N$_4$O$_n$ can be formed via termination reaction of C$_{10}$H$_{17}$N$_4$O$_n^*$ with another RO$_2$ wherein C$_{10}$H$_{17}$N$_4$O$_n$ can be formed as follows.

$$
C_{10}H_{17}N_4O_n + NO_3 + O_2 \rightarrow C_{10}H_{17}N_4O_n^* \quad (R12)
$$
$$
C_{10}H_{16}NO_n(n=10-14)^* \text{ could be explained by the reaction of monomer RO}_2 \text{ with isoprene.}
$$
$$
C_5H_8N_2O_n^* + C_5H_8 + O_2 \rightarrow C_{10}H_{16}NO_n^*. \quad (R13)
$$

Only C$_{10}$H$_{16}$NO$_n^*$ with $n \geq 10$ were detected, while according to the mechanism of self-reaction between C$_5$H$_8$NO$_2^+$, the $n$ range of C$_{10}$H$_{16}$NO$_n^*$ is expected to be 7–14. The absence of C$_{10}$H$_{16}$NO$_{n(n<10)}$ 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 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$_{15}$N$_3$O$_n$ (ketone) and C$_{10}$H$_{17}$N$_2$O$_n$ species (hydroperoxide/alcohol). C$_{10}$H$_{17}$N$_2$O$_n$ 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 behavior 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 experimental 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; Chen et al., 2021). We would like
to note that there is unlikely interference to C$_{10}$-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 $\sim$ 50 ppt (3$\sigma$).

Some of the dimers discussed above have been observed in previous laboratory studies. Ng et al. (2008) found C$_{10}$H$_{16}$N$_2$O$_8$ and C$_{10}$H$_{16}$N$_2$O$_9$ in the gas phase and C$_{10}$H$_{17}$N$_3$O$_{12}$, C$_{10}$H$_{17}$N$_3$O$_{13}$, C$_{10}$H$_{18}$N$_4$O$_{16}$, and C$_{10}$H$_{17}$N$_3$O$_{18}$ in the particle phase. C$_{10}$H$_{16}$N$_2$O$_8$ and C$_{10}$H$_{16}$N$_2$O$_9$ 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$_2$O$_{8,9}$ in NO$_3^-$-CIMS. Accord-
ing to modeling 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_{2}O_{8} and C_{10}H_{16}N_{2}O_{9} have no and only one H-bond donor functional 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_{2}O_{8} and C_{10}H_{16}N_{2}O_{9} (Ng et al., 2008). C_{10}H_{17}N_{2}O_{12}, C_{10}H_{17}N_{2}O_{13}, C_{10}H_{18}N_{4}O_{16}, and C_{10}H_{17}N_{2}O_{18} were all observed in the gas phase in this study, wherein the concentration of C_{10}H_{17}N_{2}O_{18} was very low. The formation pathways of C_{10}H_{17}N_{2}O_{12}, C_{10}H_{17}N_{2}O_{13}, and C_{10}H_{18}N_{4}O_{16} (Reaction 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_{2}O_{13}. Among the two pathways of C_{10}H_{18}N_{4}O_{16} formation (Reaction R8 and via Reaction R12), our results indicate that Reaction (R8) was the main pathway, based on the low concentrations of C_{10}H_{17}N_{2}O_{16}/17∗ and other termination products of them, C_{10}H_{16}N_{2}O_{15}/16. The time profile of C_{10}H_{18}N_{4}O_{16} was consistent with what is expected from Reaction (R8) as discussed above offers additional evidence for that conclusion.

Few field studies have reported HOM dimers formed via the reaction of NO_{3} with isoprene. This might be because NO_{3} + isoprene-HOM dimers can have the identical molecular formula to the HOM monomers from monoterpene oxidation. Possible contribution of dimer formation in the isoprene oxidation to C6–10 HOM in the particle phase observed at a rural site, Yorkville, US, is reported by Chen et al. (2020), although these HOM are thought to be more likely from monoterpene oxidation.

### 3.4 HOM trimers and their formation

A series of HOM trimers were observed, such as C_{15}H_{24}N_{4}O_{n}(n=17−22), C_{15}H_{25}N_{5}O_{n}(n=20−22), C_{15}H_{25}N_{5}O_{n}(n=13−20), C_{15}H_{26}N_{6}O_{n}(n=17−21), and C_{15}H_{24}N_{2}O_{n}(n=12−16). Among the trimers, C_{15}H_{24}N_{4}O_{n} was the most abundant series (Fig. S12). The C_{15}H_{24}N_{4}O_{n} series can be explained by the accretion reaction of one monomer HOM RO_{2} and one dimer HOM RO_{2}.

\[
C_{10}H_{16}N_{3}O_{n}^\cdot + C_{3}H_{8}NO_{2}^\cdot 
\rightarrow C_{15}H_{24}N_{4}O_{n+1} + n \cdot H_{2}O
\]  

(R14)

The formation pathways of dimer RO_{2} C_{10}H_{16}N_{3}O_{n} (n = 12−15) and C_{10}H_{17}N_{2}O_{n} are shown above (Reactions R10 and R11).

The other trimers were likely formed via similar pathways (Table 2 and Supplement Sect. 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 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 will be more favorable for precursors (VOC) containing more than one double bond 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_{4}O_{n} showed the mixed behavior of first- and second-generation products (Fig. S13), consistent with the mechanism discussed above since C_{3}H_{8}NO_{2}^\cdot and C_{10}H_{16}N_{3}O_{n}^\cdot 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_{5}O_{n} showed instantaneous increase with isoprene addition (Fig. S14), which was typical for time profiles of first-generation products. Both proposed formation pathways of C_{15}H_{25}N_{5}O_{n} (Reactions 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_{2}O_{n}^\cdot were formed very, very quickly or that there were other formation pathways of C_{15}H_{25}N_{5}O_{n} not accounted for here.

We are not aware of field studies reporting NO_{3} + isoprene-HOM trimers, which is likely for the same reason as dimers discussed above. It is challenging to distinguish HOM trimers formed in the reaction NO_{3} with isoprene from the dimers formed by cross-reaction of the RO_{2} from monoterpene oxidation (C10-RO_{2}) with that from isoprene oxidation (C5-RO_{2}), as their molecular formulas can be identical.

### 3.5 Contributions of monomers, dimers, and trimers to HOM

The concentration (represented by peak intensity) of monomers was higher than that of dimers, but overall their concentrations remained on 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.

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rapidly (Fig. S15), which was attributed to the faster increase in dimer 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 using the sensitivity of H$_2$SO$_4$. 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 the literature, thus denoted as primary HOM yield (Pullinen et al., 2020), and was estimated to be $1.2 \pm 1.3 \%$. The uncertainty was estimated as shown in Supplement Sect. 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 ozonolysis and photooxidation of isoprene (Jokinen et al., 2018). The difference may be attributed to the more efficient ozonolysis and photooxidation of isoprene (Jokinen et al., 2018). The difference may be attributed to the more efficient ozonolysis and photooxidation of isoprene (Jokinen et al., 2018). The difference may be attributed to the more efficient ozonolysis and photooxidation of isoprene (Jokinen et al., 2018).

Compared with the reaction with O$_3$ or OH, the initial peroxy radicals contain five oxygen atoms when isoprene reacts with NO$_3$, while the initial peroxy radicals contain only three oxygen atoms when reacting with OH, and the ozonide contains three 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 provided additional constraints on their formation mechanism besides 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$_5$-hydroxynitrates with NO$_3$ and are thus second-generation products. 3N-monomers likely comprised peroxy/peroxyacyl nitrates formed by the reaction of 2N-monomer RO$_2$ with NO$_3$ and possibly nitronitrates formed via the direct addition of N$_2$O$_5$ to the first-generation products. HOM dimers were mostly formed by the accretion reactions between various HOM monomers 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, second-generation products, or a combination of both. Additionally, some dimer peroxy radicals (dimer RO$_2$) were formed by the reaction of NO$_3$ with dimers containing a C=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 C$_5$H$_8$N$_2$O$_n$, C$_5$H$_{10}$N$_2$O$_n$, C$_{10}$H$_{17}$N$_3$O$_n$, and C$_{10}$H$_{16}$N$_2$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 $1.3 \pm 0.7 \%$ 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 (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 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$_5$H$_8$NO$_6$), 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 the isoprene + NO$_3$ reaction of 4.3 %–23.8 %. Rollins et al. (2009) reported a SOA yield of 2 % at low organic aerosol loading ($\sim 0.52 \mu g m^{-3}$) and 14 % if the further oxidation of the first-generation products is considered in the isoprene + NO$_3$ 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 + NO$_3$ reaction.

The RO$_2$ lifetime is approximately 20–50 s in our experiments, which is generally comparable to or shorter than the lifetime of RO$_2$ in the ambient atmosphere at night, varying from several tens to several hundreds of seconds (Fry et al., 2018), depending on the NO$_3$, HO$_2$, and RO$_2$ concentrations. Assuming a HO$_2$, RO$_2$, and NO$_3$ concentration of 5 ppt, 5 ppt (Tan et al., 2019), and 300 ppt (Brown and Stutz, 2012), respectively, the RO$_2$ lifetime in our study is

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comparable to the nighttime RO\(_2\) lifetime (50 s) found in urban locations and areas influenced by urban plume. In areas with longer RO\(_2\) lifetime such as remote areas, the autoxidation 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 RO\(_2\) concentration and thus longer RO\(_2\) lifetime, reduced rates of RO\(_2\) + RO\(_2\) reactions producing low-volatility dimers can reduce the SOA yield by reducing dimer yield (McFiggans et al., 2019; Pullinen et al., 2020). The RO\(_2\) fate in our experiments is dominated the reaction RO\(_2\) + NO\(_3\) with significant contribution of RO\(_2\) + RO\(_2\), which can also represent the RO\(_2\) fate in the urban areas and areas influenced by urban plume. Our experiment condition cannot represent the chemistry in HO\(_2\)-dominated regions such as clean forest environments (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 NO\(_3\) (Wennberg et al., 2018), are ∼5 and ∼1.3–4 h, respectively, with respect to the reaction with OH and NO\(_3\) assuming a typical OH concentration of 2 × 10\(^{6}\) molec. cm\(^{-3}\) (Lu et al., 2014; Tan et al., 2019) and a NO\(_3\) concentration of 100–300 ppt in urban areas (Brown and Stutz, 2012). Therefore, they have the chance to react further with OH and NO\(_3\) at dawn. In our experiments, the lifetimes of these first-generation nitrates with respect to OH and NO\(_3\) are comparable to the aforementioned lifetime due to comparable OH and NO\(_3\) 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 C\(_x\)H\(_{8,16}\)N\(_2\)O\(_8\) and multi-generation nitrooxyorganosulfates have been observed in recent field studies in polluted megacities in eastern 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).

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/acp-21-1-2021-supplement.

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

Competing interests. The authors declare that they have no conflict of interest.

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