Secondary reactions of aromatics-derived oxygenated organic molecules lead to plentiful highly oxygenated organic molecules within an intraday OH exposure

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ABSTRACT. Highly oxygenated organic molecules (HOMs) can participate in new particle formation (NPF) and enhance growth of newly formed particles partially because of their low volatility. Previous studies have shown formation of HOMs via autoxidation reactions of RO₂ intermediates generated by OH-initiated oxidation of anthropogenic volatile organic compounds (VOCs). It was also suggested that multi-generation OH oxidation could be an important source for aromatics-derived HOMs. However, our understanding on the generation of aromatics-derived HOMs are still insufficient, especially for their formation mechanisms, which determine molar yields of HOMs and are essential to the establishment of global chemical box models related to HOMs. In this study, with a potential aerosol formation oxidation flow reactor (PAM OFR), a series of OH-initiated oxidation experiments of 1,3,5-trimethylbenzene (1,3,5-TMB) were conducted to investigate the influences of the extent of OH exposure on the formation of aromatics-derived HOMs. The evolution of oxidation products of 1,3,5-TMB in an OH exposure range of (0.5 – 5.0)×10^10 molecules cm⁻³ s, equivalent to an OH exposure of 0.7 – 6.9 hours at an OH concentration of 2×10^9 molecules cm⁻³, was investigated by a nitrate-based chemical ionization mass spectrometer and a Vocus proton-transfer-reaction mass spectrometer, indicating significant secondary OH chemistry
during the ageing of stabilized first generation oxygenated products within an intraday OH exposure and formation of various HOMs with more oxygen content and thus lower volatility. In addition, organonitrates, formed after the introduction of NOx into the reaction systems, further confirmed the existence of such secondary reactions. Our study suggests an important role of secondary OH chemistry in the oxidation of aromatics and elucidates detailed formation mechanisms of certain HOM products.

1 Introduction

OH radicals can react with volatile organic compounds (VOCs) in the atmosphere, converting primary pollutants to secondary ones. Generated from oxidation of VOCs, oxygenated organic molecules (OOMs) are crucial in a variety of atmospheric chemical processes, contributing efficiently to the formation of secondary organic aerosols (SOAs) and ground-level O3 (Ng et al., 2010; Qu et al., 2021; Wang et al., 2022). Among the enormous number of oxygenated VOCs (OVOCs), highly oxygenated organic molecules (HOMs) have recently attracted significant attention (Bianchi et al., 2019). Most of HOMs are low volatile organic compounds (LVOCs) or extremely low volatile organic compounds (ELVOCs), and thus are able to drive the initial formation of nucleated particles under certain conditions and contribute to the subsequent growth of newly-formed particles, which finally enhance SOA formation (Lehtipalo et al., 2018; Mohr et al., 2019; Qiao et al., 2021; Stolzenburg et al., 2018; Tröstl et al., 2016).

Formation of HOMs is typically triggered by oxidation of VOCs in the gas phase. Peroxy radicals (RO2) are generated at the initial step and will undergo an intramolecular hydrogen atom shift forming a hydroperoxide functionality and an alkyl radical. A molecular oxygen will rapidly attach to this alkyl radical and form a new and more oxidized RO2. This reaction is called as autoxidation and the newly formed RO2 can go through another autoxidation or bimolecular termination reactions to form a stabilized product (Crounse et al., 2013). Autoxidation is suggested to be responsible for widely detected HOMs in the atmosphere, because it can form highly oxygenated RO2 in a short time scale. In terms of biomolecular reactions, RO2 reacts appreciable only with hydroperoxyl radical (HO2), NO, and another RO2. The RO2 reaction chain in polluted areas is largely terminated by NO, which prohibits generation of compounds with high oxidation levels and reduces yields of HOMs (Bianchi et al., 2019).

Nevertheless, autoxidation reactions alone are not enough to explain the large numbers of oxygen atoms in HOMs observed in laboratory experiments and ambient campaigns. Take alkylbenzenes as an example, previous studies suggest that the main products of OH oxidation
of alkylbenzenes (C\textsubscript{x}H\textsubscript{2x-6}, x=7, 8, or 9), i.e., bicyclic peroxy radicals (BPR, C\textsubscript{x}H\textsubscript{2x-6}O\textsubscript{5·}, x=7, 8, or 9), can undergo an autoxidation reaction and form a new peroxy radical, C\textsubscript{x}H\textsubscript{2x-6}O\textsubscript{5·} (x=7, 8, or 9) (Jenkin et al., 2003). The autoxidation reaction of BPR could be very fast because an allylic radical will be formed after the hydrogen shift (Wang et al., 2017). On the other hand, the structure of resulting C\textsubscript{x}H\textsubscript{2x-6}O\textsubscript{5·} is strongly different from that of BPR, whose autoxidation reaction rate can be as low as the order of 0.001 s\(^{-1}\), since it lacks enhancements from favorable transition state geometries and substitutes or resonance structures (Bianchi et al., 2019; Otkjær et al., 2018). Such a slow autoxidation reaction rate cannot explain the extensive existence of HOM monomers with more than 7 oxygen atoms and HOM dimers with more than 10 oxygen atoms, which are the maximum numbers of oxygen atoms in stabilized monomer and dimer products, respectively, formed from C\textsubscript{x}H\textsubscript{2x-6}O\textsubscript{5·} (Mentel et al., 2015; Molteni et al., 2018; Wang et al., 2020). Another possibility is the formation of a second oxygen bridge after the hydrogen shift of BPR (Molteni et al., 2018), but this reaction pathway would not allow a further oxygenation reaction without a breakage of the carbon ring, which is also unpromising.

Multigeneration reactions of VOCs complicate HOMs’ formation. Previous studies indicate that HOMs can also be formed by sequential oxidation of stabilized first-generation products of benzene and toluene (Cheng et al., 2021; Garmash et al., 2020). Garmash et al. (2020) conducted OH oxidation experiments of benzene and toluene with an OH exposure equivalent to atmospheric oxidation times of 10 hours – 15 days at OH concentrations of ~10\(^6\) molecules cm\(^{-3}\). Cheng et al. (2021) simulated oxidation of benzene and toluene with an OH exposure equivalent to 2.4 – 19.4 days of atmospheric photochemical ageing. Certainly, such extremely high OH exposures favor secondary OH chemistry and help to facilitate our understanding on product distributions, but such a long timescale limits atmospheric implications of their results, given the complex physical and chemical processes at night.

Compared to benzene and toluene, trimethylbenzene (TMB) is a precursor characterized with much larger HOM molar yields when reacted with OH, and the abundance of TMB in the atmosphere is unignorable (Molteni et al., 2018; Yuan et al., 2012). Previous laboratory experiments on TMB-derived HOMs mainly focused on the autoxidation reactions of BPR and the influences of NO\(_x\), while the quantity of experiments was finite with a limited range of OH exposure, bringing down the universality and applicability of conclusions (Tsiligiannis et al., 2019; Wang et al., 2020). From the mechanism perspective, a number of HOM monomers with more than 7 oxygen atoms detected in the OH-initiated oxidation of TMB were previously assumed to be generated via multiple autoxidation reactions (Molteni et al., 2018). Nevertheless, a subsequent OH oxidation of the first-generation oxygenated products might be more plausible for the formation of HOM monomers with more than 7 oxygen atoms from the present point of
Indeed, laboratory experiments show that RO$_2$ formed during the second-generation OH oxidation of the first-generation stabilized oxidation products can also undergo autoxidation reactions, which entangles reaction mechanisms potentially involved in the formation of those HOMs and justifies more investigations on the multigeneration OH oxidation of aromatics (Wang et al., 2020). High atmospheric concentrations of OH have been frequently observed in both urban and suburban environments in China (Lu et al., 2012; Tan et al., 2019), leading to a realistic implication of multigeneration OH oxidation. Therefore, it is imperative to study chemical characteristics of formation reactions of HOMs at different OH exposures, especially those fewer than or equivalent to one day of atmospheric oxidation.

In this study, a series of laboratory experiments were conducted on the OH-initiated oxidation of 1,3,5-TMB, selected as an example of anthropogenic VOCs with an OH exposure equivalent to atmospheric oxidation times of roughly 0.7 – 6.9 hours at an average daytime OH radical concentration of 2.0×10$^6$ molecules cm$^{-3}$. A nitrate-based chemical ionization mass spectrometer (nitrate CIMS) and a Vocus proton-transfer-reaction mass spectrometer (Vocus PTR) were deployed to measure the oxidation products and the precursor, respectively. From the evolution of oxygenated products, we explored secondary OH chemistry of stabilized first-generation oxygenated products generated by the oxidation of 1,3,5-TMB. Furthermore, the influence of NO on the formation of HOMs was investigated by introducing N$_2$O into the reaction system via formation of organonitrates.

2 Methods

OH-initiated oxidation of 1,3,5-TMB was investigated in a potential aerosol formation oxidation flow reactor (PAM OFR) system at $T = 298 \pm 1$ K and a pressure of 1 atm (Lambe et al., 2015). The experimental settings in this study differed slightly from what were used previously (Wang et al., 2020). Forty OH experiments (Exp. 1 – 40) and twenty-eight NO$_x$ experiments (Exp. 41 – 68) were performed, the experimental conditions of which are summarized in Table S1, including concentrations of the precursor, ozone, and NO and NO$_2$. The equivalent OH exposure in the OFR for each experiment was estimated according to the precursor consumption, also listed in Table S1. OH exposures in the OFR were in the range of (0.5 – 5.0)×10$^9$ molecules cm$^{-3}$ s, equivalent to atmospheric oxidation times of roughly 0.7 – 6.9 hours for 1,3,5-TMB at an average daytime OH radical concentration of 2.0×10$^6$ molecules cm$^{-3}$. In contrast, the OH oxidation lifetime for 1,3,5-TMB is around 2.4 hours at the aforementioned atmospheric average daytime OH concentrations.

A home-made 1,3,5-TMB/N$_2$ cylinder was used as a stable gaseous precursor source in the experiments, from which the flow rate of 1,3,5-TMB/N$_2$ varied between 1 – 3 sccm (standard
cubic centimeter per minute, standard to 0 °C, 1 atm), leading to 28.9 – 62.7 ppb of 1,3,5-TMB in the OH oxidation experiments (Table S1). A total flow of 15 slpm (standard liters per minute, standard to 0 °C, 1 atm) zero-gas generated by a zero-gas generator (model 737-13, Aadco Instruments Inc.), together with the 1,3,5-TMB/N₂ flow, was introduced into the OFR. The reaction time in this series of experiments was kept at around 53 s. The flow in the PAM OFR is laminar with a very low axial mixing, as characterized with a Taylor dispersion model in a previous study (Lambe et al., 2011). Among the 15 slpm zero-gas, 6 slpm was initially passed through a Nafion humidifier (Perma Pure Model FC100-80-6MSS) filled with ultra-pure water and finally converged with the main flow into the OFR to achieve and keep a desired RH of 20.0 ± 2.5 % in the OFR throughout all the experiments, and 2 slpm was initially passed through a separate ozone chamber, resulting in an initial ozone concentration of around 429 – 881 ppb in the OFR. The OFR was operated with only the 254 nm lights on, under which the primary oxidant production reactions in the OFR were \( O_3 + h\nu (254 \text{ nm}) \rightarrow O_2 + O(1D) \) and \( O(1D) + H_2O \rightarrow 2OH \). An ozone monitor (Model 106-M, 2B technologies) and a trace-gas analyzer for NO-NO₂-NOₓ (Thermo, 42i-TL) were placed at the exit of the OFR to measure concentrations of ozone and NOₓ, respectively.

For experiments with NOₓ, 350 sccm N₂O (99.999%, Air Liquid) was added into the OFR to produce and sustain NOₓ mixing ratios at levels that were sufficiently high to be a competitive sink for RO₂ radicals. NO and NO₂ were produced via the reaction \( N_2O + O(1D) \rightarrow 2NO \), followed by the reaction \( NO + O_3 \rightarrow NO_2 + O_2 \). Two sets of irradiance intensities were chosen for NOₓ experiments, generally resulting in two NOₓ levels, 1.8 ppb NO + 70 ppb NO₂ (Exp. 41 – 54) and 4.8 ppb NO + 120 ppb NO₂ (Exp. 55 – 68) at the exit of the OFR. With the aim to slightly modify OH exposure but keep NOₓ concentrations constant among each set of experiments, the initial concentrations of 1,3,5-TMB were adjusted in a large range (16.7 – 84.1 ppb), as an increase in the precursor concentration corresponds to a larger sink for OH, while RH and irradiances were not changed.

A nitrate CIMS (Ehn et al., 2014; Eisele and Tanner, 1993) and a Vocus PTR (Krechmer et al., 2018) were deployed at the exit of the OFR to measure the oxidation products of 1,3,5-TMB. These two mass spectrometers have been well characterized in a previous study (Wang et al., 2020).

In this study, the sample flow rate for the nitrate CIMS was 8 slpm through a Teflon tube with an outer diameter (OD) of 1/4 in. and a length of 70 cm. The sheath flow for the nitrate CIMS was supplied by a zero-gas generator at a flow rate of 15 slpm. Mass resolution was approximately 8000 for ions with m/z larger than 200 Th. HOMs generated from TMB oxidation were charged in the ambient pressure interface region by collisions with nitrate. 
clusters, (HNO₃)ₓ·NO₃⁻ (x = 0 – 2), and detected by nitrate CIMS as clusters with NO₃⁻, i.e.,
HOM-NO₃⁻ (Hytten et al., 2015). In addition, HOMs’ signals were corrected with relative
transmission efficiencies of our nitrate CIMS obtained via a method reported previously
(Heinritzi et al., 2016).

Vocus PTR was applied to quantify precursor concentrations and measure volatile and
intermediate volatility oxidation products. The focusing ion-molecule reactor (FIMR) was
heated up and its temperature was maintained at 100 °C during the experiments. The FIMR can
be operated under 2.0 mbar without a strong interference from corresponding water clusters
when ionizing the neutral compounds. The Vocus front and back voltages were 650 V and 15
V, respectively, forming an axial voltage of 635V and a reduced electrical field (E/N, where E
is the electric field strength and N is the number density of the buffer gas in FIMR) of 180 Td.

The radio frequency (RF) voltages and frequency were set to be 450 V and 1.3 MHz,
respectively. The sample flow was introduced to the Vocus PTR through a Teflon tube with an
OD of 1/4 in. and a length of 120 cm from the OFR. A total sample flow of 1.4 slpm was
maintained by a pump with an orifice to minimize the delay time of sampling, from which
approximately 125 sccm was sampled into the FIMR through a capillary tube.

We did not quantify HOMs’ concentrations. Since the inner diameters of PAM OFR,
sampling tube, and the nitrate CIMS inlet were different, and two reducing unions were used
during sampling, the estimation of the penetration efficiency and sampling efficiency of HOMs
are of a significant uncertainty. To precisely illustrate changes in the abundance of HOMs at
different OH exposures, a normalized signal was chosen to present the abundance of detected
HOMs, which is defined as the ratio of the signals of HOMs in the nitrate CIMS normalized by
the reagent ions and the initial signal of 1,3,5-TMB, i.e., \( S(\text{HOMs})/S(\text{TMB}) \). \( S(\text{HOMs}) \) is the
signal of HOM detected by the nitrate CIMS normalized with the signal of reagent ions,
whereas \( S(\text{TMB}) \) is the initial signal of 1,3,5-TMB detected by the Vocus PTR.

To further explore the secondary chemistry in the formation and evolution of HOMs, a
nominal relative molar yield of HOMs, defined as \( S(\text{HOMs})/k[\text{VOCs}][\text{OH}] \), was used as a
substitute of molar HOM yields to reveal their changes under different OH exposures, which is
similar to the definition from a previous study (Garmash et al., 2020). \( k \), [VOCs], and [OH]
stand for the loss coefficient of HOMs in the OFR timing the calibration factor of the nitrate
CIMS and then divided by the OH oxidation reaction coefficient of 1,3,5-TMB, 1,3,5-TMB
concentration detected at the exit of OFR, and calculated OH concentration in the OFR,
respectively. The detailed derivation processes and calculation methods are provided in
Supplementary Text S1.
3 Results and discussion

A total of 33 HOM monomers with formulae of C_{7-9}H_{24-30}O_{6-11} and 22 HOM dimers with formulae of C_{17-18}H_{24-30}O_{9-14} were observed in the gas phase OH-initiated oxidation of 1,3,5-TMB in the OFR, as listed in Table S2. The relative signal contributions of HOMs to the total signals of all HOMs at an OH exposure of 2.38×10^{10} molecules cm^{-3} s are listed as an example in Table S2. Figure 1 illustrates how OH exposures in the OFR are related to the total normalized signals of HOM monomers and HOM dimers measured at the OFR exit, which is superimposed by a gamma function \( f(x) = ax^m e^{-x} \) simulation line to guide the eyes. The sum of normalized HOM monomers’ abundance increased monotonically up to the highest OH exposure of 5×10^{10} molecule cm^{-3} s, whereas those of HOM dimers showed a non-monotonic dependence on OH exposure. The observed faster increase of accretion products than that of HOM monomers can be explained jointly by the fast second-order kinetics for accretion reactions of RO_{2} (Berndt et al., 2018b) and the high concentrations of relevant radicals in this work. On the other hand, most of the first-generation HOM dimers formed from accretion reactions contain at least one C=C bond and have more functionalities than HOM monomers, and thus should be more reactive to OH radicals, which, together with a faster deposition loss of dimers, results in a faster consumption of HOM dimers than monomers in the OFR. The faster production and consumption of HOM dimers allowed their concentrations to summit at middle levels of OH exposures.

3.1 HOM monomers in the absence of NOx

Previous studies indicate that oxidation products derived from the peroxide-bicyclic pathway represent a main fraction of HOMs (Wang et al., 2017; Zaytsev et al., 2019). For 1,3,5-TMB, this pathway, as recommended by Master Chemical Mechanism (MCM), starts from a BPR, C_{6}H_{10}O_{2}· (MCM name: TM135BPRO2) (Molteni et al., 2018). Scheme 1 has been proposed to provide a good understanding of this reaction system and the structures of oxidation products. Molteni et al. (2018) suggested that C_{6}H_{10}O_{2}·, i.e., peroxy radical formed from autooxidation of C_{6}H_{10}O_{2}· has two isomers, which are referred as C9H13O7A and C9H13O7B for clarity in this study. The structures of these two isomers have been provided in Scheme 1. Their termination products are nominated according to the name of these two isomers, respectively. A second-step of endo-cyclization is required in the formation of C9H13O7B, which is extremely slow and not competitive as shown in several previous studies using both experimental and theoretical approaches (Wang et al., 2017; Xu et al., 2020). Even if such a second O_{2} bridging to a double bond is assumed to be possible, the abundance of C9H13O7B should be significantly smaller than C9H13O7A, because of the much faster reaction rate of H-shift reaction in the reaction route for C9H13O7A. Therefore, the majority of HOM monomers
are generated from subsequent reactions of C₉H₁₁O₅· and C₉H₁₃O₇A, both of which contain one C=C bond in the carbon backbone and thus have a feasible site for OH addition. Meanwhile, the autoxidation reaction rate for C₉H₁₃O₇A should be significantly smaller than C₉H₁₁O₅·, as there is no hydrogen atom in C₉H₁₁O₂· that is able to undergo a hydrogen atom shift at an appreciable rate based on our current understanding. Therefore, the subsequent autoxidation reaction should not be able to generate large amounts of more oxidized RO₂.

The monomeric termination products of BPR, shown in Scheme 1, were not detected by nitrate CIMS because of their low oxygen content, whereas those of C₉H₁₁O₂· were all observed clearly, including C₉H₁₂O₆, C₉H₁₃O₆, and C₉H₁₅O₇. Especially, C₉H₁₄O₇ was the most abundant one among all of the HOM monomer products. As proved by a previous study, these three species should be typical first-generation stabilized products derived from autoxidation (Wang et al., 2020). Their nominal relative molar yields increased with the OH exposures in the OFR, as shown in Figure S1, which implies that the secondary OH reactions of stabilized products can also produce these HOM monomers otherwise the observed yields would remain constant or decline (, the latter of which is due to the consumption of the products). These HOM monomers thus should consist of several isomers bearing the same formula, because products from the secondary reactions cannot share the same structure as that of the one from the first-generation reaction.

In addition to these three ones, the nominal relative molar yields of other HOM monomers also showed an increase trend with more OH exposures. The next most prominent products to C₉H₁₁O₇ were C₉H₁₆O₈ and C₉H₁₆O₉ (Figure 2a), which are produced from multi-generation oxidation according to their hydrogen content (Cheng et al., 2021; Molteni et al., 2018). Based on the formulae of these three HOM monomers, they (C₉H₁₄O₇, C₉H₁₆O₈, and C₉H₁₆O₉) could be formed from the bimolecular termination reactions of C₉H₁₃O₅·, which can be generated by an OH attack to C₉H₁₂O₆, the hydroperoxyl termination product of the BPR C₉H₁₃O₅·. The other HOM monomers characterized with high signals were C₉H₁₃O₆ and C₉H₁₅O₇ (Fig. 2b). These two HOM monomers (C₉H₁₂O₆ and C₉H₁₄O₇), together with C₉H₁₆O₈, correspond to the monomeric termination products of C₉H₁₃O₅·, which is highly likely the proxy radical generated by an OH attack to C₉H₁₂O₆, i.e., the hydroxyl termination product of C₉H₁₃O₅·. As discussed earlier, C₉H₁₃O₇· is a typical autoxidation reaction product of the BPR of C₉H₁₃O₅·. Therefore, detected signals of C₉H₁₆O₈ should be the sum of two isomers’ signals at least. Other HOM monomers were generally observed at much lower signals and thus were not plotted individually.

We further examined the nominal relative molar yields of HOM products with 12, 14, and 16 hydrogen atoms, i.e., the common HOM monomers in our system. Based on the number of
hydrogen atoms, C_{9\mathrm{H}_{12\mathrm{O}_m}} (m \text{ refers to the oxygen atom number in a molecule}) are presumably derived from first generation radicals of C_{9\mathrm{H}_{15\mathrm{O}_m}}, and C_{9\mathrm{H}_{10\mathrm{O}_n}} are from second generation radicals of C_{9\mathrm{H}_{15\mathrm{O}_m}}\cdot, whereas C_{9\mathrm{H}_{14\mathrm{O}_n}} can be either products of the first-generation or second-generation OH oxidation (Molteni et al., 2018). Therefore, compounds with more hydrogen atoms are expected to increase more rapidly. However, the actual observation in our laboratory experiments conflicted with our preconceived expectations. The nominal relative molar yields of HOM monomers are shown in Figure 3. For clarity, only the 3 most abundant species with (a) 12, (b) 14, and (c) 16 hydrogen atoms, respectively are plotted. A prominent linear increase in the nominal molar yields of C_{9\mathrm{H}_{14\mathrm{O}_n}} with larger oxygen atom numbers and C_{9\mathrm{H}_{10\mathrm{O}_n}} was observed with the increase of OH exposure, whereas C_{9\mathrm{H}_{14\mathrm{O}_n}} with fewer oxygen atoms and C_{9\mathrm{H}_{12\mathrm{O}_n}} increased convexly. This is likely because the concentrations of RO_2 in the OFR increased with the increment of consumed precursors, which promoted the carbonyl and hydroxyl channels and favored formation of C_{9\mathrm{H}_{12\mathrm{O}_n}} and C_{9\mathrm{H}_{14\mathrm{O}_n}} with fewer oxygen atoms in the molecule.

It is worth noting that HOM monomers with 18 hydrogen atoms were never observed in our experiments, including a potential stabilized hydroperoxyl products formed from C_{9\mathrm{H}_{17\mathrm{O}_n}}\cdot. This is expected, since C_{9\mathrm{H}_{17\mathrm{O}_n}}\cdot should be in really low concentrations, if ever existed. As indicated by its hydrogen number, a C_{9\mathrm{H}_{17\mathrm{O}_n}}\cdot was formed by at least two OH additions to the C=C bond of a C_{9\mathrm{H}_{15\mathrm{O}_m}}\cdot, but the main BPR, C_{9\mathrm{H}_{15\mathrm{O}_m}}\cdot, and its autoxidation product (C_{9\mathrm{H}_{15\mathrm{O}_7}}\cdot), are characterized with one C=C bond on the ring, which makes this formation pathway impossible. Other ring-breakage pathways should not contribute to the formation of this radical (C_{9\mathrm{H}_{17\mathrm{O}_n}}\cdot) because of their low branching ratio as determined by recent studies (Xu et al., 2020; Zaytsev et al., 2019).

3.2 HOM dimers in the absence of NO_x

Accretion reaction RO_2 + RO_2' + O_2 \rightarrow ROOR' + O_2 is a source of gas-phase dimer compounds from highly oxidized, functional RO_2 radicals. (Berndt et al., 2018b, 2018a; Ehn et al., 2014; Zhao et al., 2018) C_{10\mathrm{H}_{26\mathrm{O}_8}} and C_{10\mathrm{H}_{26\mathrm{O}_{10}}} are two typical accretion reaction products in the 1,3,5-TMB + OH system, whose formation pathways have been elucidated. (Berndt et al., 2018b) C_{10\mathrm{H}_{26\mathrm{O}_8}} can only be formed via the accretion reaction of two C_{9\mathrm{H}_{13\mathrm{O}_7}}\cdot. In contrast, C_{10\mathrm{H}_{26\mathrm{O}_{10}}} can be formed either by the accretion reaction between C_{9\mathrm{H}_{13\mathrm{O}_7}}\cdot and C_{9\mathrm{H}_{13\mathrm{O}_7}}\cdot or via a second OH attack to C_{10\mathrm{H}_{26\mathrm{O}_8}}. These two HOM dimers are so far the only ones that are confirmed to be formed via the accretion reactions (Berndt et al., 2018b; Bianchi et al., 2019). There are currently no evidences supporting that C_{9\mathrm{H}_{15\mathrm{O}_m}}\cdot radicals can participate in the
formation of HOM dimers with 28 hydrogens. Therefore, it hints that one could attribute the
formation of C₁₈H₂₆O₁₁ to multi-generation OH oxidation of C₁₈H₂₆O₈.

C₁₈H₂₆O₁₀ was characterized with the highest dimer signals for experiments with OH
exposures under 3.5×10¹⁰ molecule cm⁻³ s. Nevertheless, C₁₈H₂₆O₁₁, together with C₁₈H₂₆O₁₂,
C₁₈H₂₆O₁₂, C₁₈H₂₆O₁₁, C₁₈H₂₆O₁₃, and C₁₈H₂₆O₁₀ contributed more than 50% of total HOM
dimer signals at any OH exposure levels (Fig. S2). These six most abundant HOM dimers
correspond exactly to the hydroperoxyl, hydroxyl, and carbonyl termination products of
C₁₈H₂₆O₁¹⁻ and C₁₈H₂₆O₁³⁻, respectively. These two RO₂ (C₁₈H₂₆O₁¹⁻ and C₁₈H₂₆O₁³⁻), on the
other hand, could be generated by OH attacks to C₁₈H₂₆O₈ and C₁₈H₂₆O₁₀, respectively, which
strongly suggests the significant role of secondary OH chemistry in the formation of HOMs in
our experiments. Figure 4 shows the normalized signals of these abundant HOM dimers at
different OH exposures. These HOM dimers increased under low OH exposure levels but
decreased with the increasing OH exposure that corresponds to 2.8 – 6.9 hours’ atmospheric
equivalent photochemical age.

The nominal relative molar yields of the abovementioned HOM dimers are shown in
Figure 5 as a function of OH exposure, except for C₁₈H₂₆O₁₁. The nominal relative molar yields
of C₁₈H₂₆O₁₁ are not plotted in the Figure 5, since they overlapped quite closely with those of
C₁₈H₂₆O₁₀, as can be deduced from Figure 4b. Compared with HOM monomers, variation
tendencies of the nominal relative molar yields of HOM dimers are more diverse. Especially,
the nominal relative molar yield of C₁₈H₂₆O₈ (Fig. S3) kept declination under growing OH
exposure conditions, whereas that of C₁₈H₂₆O₁₀ (Fig. 5) appeared to reduce after a slight growth
in the OH exposure range studied. The changes in the nominal relative molar yields of these
two HOM dimers along with the OH exposure confirm the combined influences of accretion
reactions and multi-generation OH oxidation reactions on their formation and evolution, i.e.,
further OH oxidation consumed C₁₈H₂₆O₈ and C₁₈H₂₆O₁₀, and produced C₁₈H₂₆O₁₆, C₁₈H₂₆O₁₂,
C₁₈H₂₆O₁₀, C₁₈H₂₆O₁₁, C₁₈H₂₆O₁₂ and C₁₈H₂₆O₁₃. These six HOM dimers contributed the
majority of the total HOM dimer signals as mentioned above, while most of them were HOM
dimers with 28 hydrogen atoms.

The nominal relative molar yields of dimer compounds with 28 hydrogen atoms tended to
increase with extended OH exposures, except that C₁₈H₂₆O₁₀ appeared to keep constant when
OH exposure was larger than 1×10¹⁰ molecules cm⁻³ s. This again indicates that these H28
products might be formed by an OH addition to a C=C bond in the accretion products, and then
the newly formed alkyl radical further reacted and would go through the typical RO₂
termination reactions.
It should be noted that the gas-phase chemistry in the PAM OFR cannot be exactly the same as that in the ambient. Reactions of OH with OVOCs often lead to HO$_2$ formation, resulting in a HO$_2$:RO$_2$ ratio larger than 1 in the real atmosphere (Bianchi et al., 2019). A recent campaign conducted at a rural site in the Yangtze River Delta estimated that the local ratio of HO$_2$:RO$_2$, the latter of which was presumably derived from longer chain alkanes (> C$_3$), alkenes, and aromatic compounds, was around 1.66 (Ma et al., 2022). Such a high OH:HO$_2$ ratio condition is typically difficult to be simulated in the laboratory experiments, as the precursors are usually hydrocarbons without any OVOCs (Peng and Jimenez, 2020). This is exactly the case for our experiments and the lower ratio of OH:HO$_2$ in our experiments than that in the ambient atmosphere was confirmed by a photochemical model in our previous study (Wang et al., 2020). In addition, high concentrations of radicals might also terminate the RO$_2$ chain earlier, which inhibits the autoxidation reactions in the PAM OFR. However, these could only influence the distribution of oxidation products at most, and would not affect the chemical behaviors of HOMs under different OH exposures.

Such an active secondary OH chemistry is consistent with the fast OH reaction rates of HOMs. We take C$_{18}$H$_{30}$O$_x$ as an example, which is the accretion product of two C$_9$H$_{15}$O$_x$·. Its OH reaction rate constant is estimated to be around $2.07 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ according to the structure-activity relationship (Jenkin et al., 2018b, 2018a), whose details are provided in Supplementary Text S2. This rate is several times larger than that of 1,3,5-TMB, which enables a very active secondary OH chemistry in the system. MCM recommended an OH reaction rate of $1.28 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for TM135BPOOH (C$_{18}$H$_{25}$O$_4$) and $1.00 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for TM135OBPOH (C$_{18}$H$_{26}$O$_3$) (Jenkin et al., 2003). The OH reaction rate for C$_{18}$H$_{30}$O$_x$ should be around twice of these values, as there are two C=C bonds in its structure. Our calculation result is consistent with this estimation.

3.3 Products in the presence of NO$_x$

Scheme 2 shows the NO termination pathways of the main BPR C$_4$H$_7$O$_2$· and its autoxidation product, C$_9$H$_{15}$O$_x$·. After introducing N$_2$O into PAM OFR, quantities of organonitrates were generated, including both C9 and C18 organonitrates. The averaged mass spectrometry of nitrate CIMS in the 1.8 ppb NO experiment and 4.8 ppb NO experiment is shown in Figure S4. Organonitrates were formed via the NO + RO$_2$ reaction, called as NO termination reactions. The distribution of oxidation products under these two NO settings were similar.

As discussed above, most of the first-generation HOMs should contain a C=C bond in the carbon backbone. The ubiquitous existence of organonitrates that contain two nitrogen atoms
exactly confirms the extensive secondary OH oxidation in the systems, because the NO termination reaction of RO$_2$ is the only pathway that can generate organonitrates and this pathway can only introduce one nitrogen atom at a time, as indicated in Scheme 2. Taking the most abundant organonitrates, C$_9$H$_{14}$N$_2$O$_{16}$, as an example, it was exactly the NO termination product of C$_9$H$_{14}$NO$_7$, which was generated from an OH attack and a subsequent O$_2$ addition to C$_9$H$_{13}$NO$_6$, the NO termination product of C$_9$H$_{14}$O$_7$. For other organonitrates, C$_{18}$H$_{13}$NO$_9$, the second most abundant organonitrates, could be either a NO termination product of C$_{18}$H$_{14}$O$_9$ or, together with other most abundant organonitrates, C$_{18}$H$_{15}$NO$_7$ and C$_{18}$H$_{16}$NO$_8$, classical termination products of C$_{18}$H$_{15}$NO$_9$.

The distributions of C18 organonitrates also verified the extensive secondary reactions. The most abundant C18 organonitrate, C$_{18}$H$_{27}$NO$_{12}$ was a NO termination product of radical C$_{18}$H$_{27}$O$_{11}$, which, as mentioned above, was the radical generated from the OH reaction with C$_{18}$H$_{26}$O$_6$. Other C18 organonitrates are believed to be formed in a similar pathway since no evidence supports that a nitrogen-containing monomeric RO$_2$ can go through accretion reactions. Hence, plenty of organonitrates have been formed via the multi-generation OH reactions of first-generation stabilized products.

4 Atmospheric Implications

This study highlights the influences of OH exposure on the distribution and evolution of 1,3,5-TMB-derived HOMs. Secondary OH reactions can influence HOMs’ composition by directly reacting with the stabilized first-generation oxidation products, leading to enhanced formation of HOMs. Organonitrates generated in the NO experiments further confirmed this. Due to the elevated abundance and the reduced volatility of HOMs, growth rates of newly formed nanoparticles in the presence of HOMs should be raised, especially in high-OH environments, which prevails in the summer noon. Substantially high concentrations of OH have been frequently observed in polluted environments during summer, e.g., megacities in China (Tan et al., 2019), and thus more active secondary OH reactions are expected compared to wintertime. As a plausible consequence, seasonal differences of HOMs and new particle formation (NPF) are resulted (Guo et al., 2022; Qiao et al., 2021; Yao et al., 2018). Furthermore, previous studies suggest that high concentrations of NO can suppress the formation of HOMs via the suppression of autoxidation (Pye et al., 2019), but the influences of such a suppression could have been overestimated, since secondary OH reactions can continue to oxidize the stabilized organonitrates. Our conclusions help to explain the existing gap between model prediction and ambient measurement on the HOMs concentrations (Qi et al., 2018), and to build a global HOMs simulation model.
Data availability. Data used in this work are available upon request from the corresponding authors.

Supplement. The supplement related to this article is available online.

Author contributions. LW and Yuwei Wang designed the experiments. Yuwei Wang conducted the laboratory experiments. Yuwei Wang analyzed the data. Yuwei Wang and LW wrote the paper. All co-authors discussed the results and commented on the manuscript.

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

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Figure Captions

Figure 1. Normalized signals of HOM monomers and HOM dimers measured at the exit of OFR in experiments without NOx as a function of OH exposure. The solid lines represent fitting results using a gamma function to guide the eye.

Figure 2. Normalized signals of (a) C9H14O7, C9H16O7, and C9H16O8 and (b) C9H14O8, C9H16O8, and C9H16O9 measured at the exit of OFR in experiments without NOx as a function of OH exposure. C9H16O8 are shown in both plots to better illustrate the chemical profiles of different compound groups.

Figure 3. The nominal relative molar yield of HOM monomers containing (a) 12, (b) 14, and (c) 16 hydrogen atoms as a function of OH exposure in the OH-initiated 1,3,5-TMB oxidation experiments.

Figure 4. Normalized signals of (a) C18H26O12, C18H28O12, and C18H28O13, and (b) C18H26O10, C18H28O10, and C18H28O11 measured at the exit of OFR in experiments without NOx as a function of OH exposure.

Figure 5. The nominal relative molar yield of (a) C18H26O10 and C18H26O12 and (b) C18H28O10, C18H28O12, and C18H28O13 as a function of OH exposure in the OH-initiated 1,3,5-TMB oxidation experiments.
Figure 1

- **HOM monomers in NO$_2$-free experiments**
- **HOM dimers in NO$_2$-free experiments**

**Normalized Signals**

**OH$_{exposure}$ (molecule cm$^{-3}$ s)**

Figure 1
Figure 2a

Figure 2b

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Figure 3a

Figure 3b
Figure 3c

Nominal relative molar yield vs. OH exposure (molecule cm$^{-3}$ s$^{-1}$) for different compounds: $C_9H_{16}O_7$, $C_9H_{16}O_8$, and $C_9H_{16}O_9$.
Figure 5a

Figure 5b
Scheme Captions

Scheme 1. Oxidation pathways of the bicyclic peroxy radical C\textsubscript{9}H\textsubscript{13}O\textsubscript{5}· (MCM name: TM135BPRO2) in the OH-initiated oxidation of 1,3,5-TMB. Green, blue, and black formulae denote alkyl peroxy radicals, alkoxy radicals and stabilized products, respectively. Red arrows denote the autoxidation pathway. MCM names for HO\textsubscript{2}· and RO\textsubscript{2}·-termination products of TM135BPRO2 are present, whereas MCM names for termination products of C\textsubscript{9}H\textsubscript{13}O\textsubscript{7}· are unavailable and thus named according to the autoxidation intermediates.

Scheme 2. NO termination reactions of the bicyclic peroxy radical C\textsubscript{9}H\textsubscript{13}O\textsubscript{5}· (MCM name: TM135BPRO2) and its autoxidation reaction products. Green, blue, and black formulae denote alkyl peroxy radicals, alkoxy radicals and stabilized products, respectively. Red arrows denote the autoxidation pathway. MCM names of NO-termination products of TM135BPRO2 are present, whereas MCM names for termination products of C\textsubscript{9}H\textsubscript{13}O\textsubscript{7}· are unavailable and thus named according to the autoxidation intermediates.
Scheme 1
Scheme 2