

Molecular Composition of Anthropogenic Oxygenated Organic Molecules and Their Contribution to Organic Aerosol in a Coastal City

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ABSTRACT: Organic aerosols (OA) have gained attention as a substantial component of atmospheric aerosols owing to their impact on atmospheric visibility, climate, and human health. Although oxygenated organic molecules (OOMs) are essential contributors to OA formation, the sources, transformations, and fates of the OOMs are not fully understood. Herein, anthropogenic OOMs (AOOMs), anthropogenic volatile organic compounds (AVOCs), and OA were concurrently measured in Xiamen, a coastal city in southeastern China. Our results show that the AOOMs exhibited a high nitrogen content (76%) and a low oxidation degree. Strong photochemical processes of aromatic VOCs were the predominant sources of AOOMs. Also, NOx concentrations and the occurrence of multigeneration OH radical



oxidations were the critical factors that might influence the formation of AOOMs. Finally, the newly developed aerosol dynamic model's results show that more than 35% of the OA mass growth rate is attributed to the gas-particle partitioning of AOOMs. Further sensitivity testing demonstrates that the contribution of AOOMs to OA growth is significantly enhanced during high-particulate-concentration periods, especially under low-temperature conditions. This study emphasizes the vital role of photochemically produced AOOMs derived from AVOCs in OA growth in a coastal urban atmosphere.

KEYWORDS: oxygenated organic molecules (OOMs), gas-particle partitioning, multigeneration oxidation, aerosol dynamic model, coastal city

1. INTRODUCTION

Atmospheric aerosols have emerged as an important concern due to their ability to reduce atmospheric visibility, influence local and global climates, and pose health risks to humans.¹⁻⁴ Among these, organic aerosols (OA), comprising both primary OA and secondary OA (SOA), make up a substantial fraction (20-90%) of fine particulate matter $(PM_{2.5})$.⁵⁻⁷ In Chinese megacities, SOA, formed through gas-to-particle conversion or heterogeneous reactions, constitute 44-71% of OA during haze events.⁸ Recent case studies in megacities of southern China have demonstrated a considerable contribution of oxygenated organic molecules (OOMs) to SOA formation. Specifically, OOMs accounted for 70% of SOA formation in Nanjing, whereas in Shanghai and Hong Kong, the contributions reached 71 and 68% respectively.⁹ The OOMs were defined as the gas-phase oxygen-containing organic molecules formed during the atmospheric oxidation of volatile organic compounds (VOCs) or evaporation process from aerosols.^{10–13}

A comprehensive understanding of atmospheric OOMs is necessary to elucidate their sources, transformations, and fates. The Nitrate Chemical Ionization Atmosphere-Pressure-interface long-Time-of-Flight mass spectrometer (Nitrate-CI-APi-TOF) has facilitated the detection of OOMs and provided chemical composition information at the molecular level.¹⁴ Laboratory studies have explored the formation mechanisms of OOMs in various oxidation systems using precursors such as sesquiterpenes, isoprenes, monoterpenes, and aromatics.^{15–24} In addition to the traditional VOCs-to-OOMs mechanism, applying novel theories such as autoxidation and multigeneration oxidation has improved our understanding of the OOMs oxidation process.^{13,22} Recent studies on OOMs in

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Figure 1. (a) Time series of meteorological parameters, gaseous pollutants, VOCs, gaseous AOOMs, and OA (in PM₁) in the sampling period. (b) AOOMs concentrations dependent on temperature from 24 to 42 °C during the sampling period. The spots are colored by $j(O^{1}D)$, measured in units of 10^{-5} s^{-1} . The concentration of AOOMs at different temperature ranges is presented by using box plots additionally. In a box plot, the central line represents the median and the box represents the interquartile range (IQR), with the upper and lower limits indicating the upper and lower quartiles, respectively. As the temperature increases, the concentration of AOOMs rises, and high concentrations of AOOMs tend to occur at times of high radiation intensity. (c) AOOMs concentrations depend on the temperature at various lower tropospheric sites. Square and circle markers represent urban and suburban areas, respectively.

urban areas have found that anthropogenic OOMs (AOOMs), generated by the oxidation of anthropogenic VOCs, contribute dominantly to the growth of urban OA rather than OOMs derived from biogenic VOCs.^{9,25} AOOMs consist of aromatic and aliphatic OOMs, which are formed by the oxidation of aromatic and aliphatic VOCs, respectively.

Despite their important role in the urban atmosphere, the current knowledge of AOOMs remains limited. For instance, previous studies have not adequately investigated the precursors of AOOMs. Although laboratory experiments have explored the atmospheric transformation of AVOCs into AOOMs, the actual atmospheric conditions are often far more complex. Moreover, research has indicated that the high levels of radiation and temperature, which are characteristic of coastal areas, may facilitate the formation of OOMs.²⁵ Therefore, further investigations are necessary to fully understand this phenomenon in the coastal urban atmosphere.

This study comprehensively investigated the molecular composition of AOOMs, their potential precursors, and partitioning to OA in urban Xiamen by deploying a set of novel online instruments. The AOOMs were categorized into aliphatic and aromatic OOMs, and the chemical characteristics of each, as well as the factors influencing their formation, were investigated. Furthermore, the connection between aromatic OOMs and their precursors was depicted, and the source of the precursors was identified. Finally, the contribution of AOOMs to OA mass growth rate was modeled with a newly developed Atmospherically Relevant Chemistry and Aerosol box model (ARCA Box), which applies the analytical predictor of the condensation method to simulate the dynamic condensation/evaporation processes.^{26,27} Sensitivity tests of the parameters affecting the contribution were also performed.

2. MATERIALS AND METHODS

2.1. Field Measurement and Instrumentation. The field measurements were conducted at the Institute of Urban Environment (IUE, 24.61°N, 118.06°E, Figure S1), Chinese Academy of Sciences, in Xiamen City, Southeast China. The atmospheric environment observation supersite, located at this institute and approximately 80 m above ground level, was selected as the sampling site. This site is close to major traffic arteries with high traffic volumes, commercial properties, and residential areas, making it representative of a typical urban environment.²⁸

The Nitrate-CI-APi-TOF (Aerodyne Research Inc., USA, and Tofwerk AG, Switzerland) was deployed to detect the OOMs.¹⁴ The calibration of OOMs is based on the calibration coefficients of sulfuric acid after mass transmission correction, which is the preferred method in the current study of OOMs.^{28,29} Details of instrument setup, calibration, and



Figure 2. (a) Fractional profiles of each aliphatic OOM during the sampling period. The fraction of aliphatic OOM is calculated as the average concentration of each OOM divided by the total aliphatic OOMs during the sampling period. The mass-to-charge ratio (m/z) denotes OOM clustered with NO₃⁻. The red, blue, and green bars represent CHO-OOMs, CHON-OOMs, and CHON2-OOMs, respectively. (b) Fractional profiles of each aromatic OOM during the sampling period. (c) The number of carbon (nC), effective oxygen (nO_{eff}), nitrogen (nN), and double bond equivalence (DBE) distribution of aliphatic OOMs. (d) The nC, nO_{eff} nN, and DBE distribution of aromatic OOMs.

uncertainty analysis of OOMs concentrations are given in Text S1. On the basis of the current knowledge of VOCs oxidation, a recently developed workflow was utilized to attribute these OOMs to their likely VOCs precursor classes, including aliphatics, aromatics, isoprenes, and monoterpenes.⁹ The details of the workflow and uncertainty analysis for the classification of the sources of the OOMs are introduced in Text S2. Text S3 presents the details of measurements on $PM_{2.5}$, gaseous pollutants, particle size distribution, and VOCs, whereas Text S4 describes the details of OA measurement by the Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Research Inc., USA).

2.2. Volatility Distribution of OOM. The saturation concentrations of OOMs are predominantly influenced by their functional groups.³⁰ The functional groups of aliphatic OOMs and aromatic OOMs are mainly hydroxyl, nitrate, and carbonyl groups, whereas hydroperoxide groups are minimal.²⁴ The method employed to compute the saturation concentrations of these OOMs was based on the approach described by Donahue et al. (2012).³¹ These OOMs were categorized into volatility bins using a volatility basis set (VBS). The method used for estimating the volatility with temperature adjustment and bin classification is outlined in Text S5.

2.3. ARCA Box Model. The Atmospherically Relevant Chemistry and Aerosol box model (ARCA Box) was applied to evaluate the contribution of AOOMs to the mass growth rate of OA during the measurement period from September 2 to October 11, 2021.²⁷ The measured concentrations and estimated volatility values of each compound (Tables S1 and S2) were incorporated into the model. Additionally, the particle size distributions within the diameter range of 7.5 nm

to 15.2 μ m were measured and fed into the model at 5 min intervals. Between the two input time points, the particle size distributions were calculated according to the condensation/ evaporation of the input OOMs as well as the coagulation process. The updated particle size distribution modified only the particle number concentration but kept the single particle composition for each size bin. On the basis of the input information mentioned above, the model can first output the concentration of a specific q-OOM in the particle phase at each time point. The modeled mass flux (Φ) of an OOM compound q from the gas to particle phase within each 5 min slot was then calculated by

$$\Phi = [m_{q(04:50)} - m_{q(04:00)}]/50$$

here, m_q is the mass concentration of OOM q in the particle phase in the unit of $\mu g \cdot m^{-3}$ and 50 is the time difference (in seconds) between 04:50 and 04:00. The mean mass growth rate within 1 h was calculated by averaging all the 5 min slot values within this hour.

The periods with an increasing trend in measured OA mass concentration were chosen to investigate the contribution of AOOMs to the OA mass growth rate. The calculation method mentioned here was similar to that of Wang et al.³²

3. RESULTS AND DISCUSSION

3.1. AOOMs Observation. Figure 1a depicts the temporal variation of AOOMs, related precursor VOCs, meteorological parameters, and gaseous pollutants during the sampling period. For further details regarding the parameters mentioned above, please refer to Table S3, whereas comprehensive observations are presented in Text S6. AOOMs exhibited an evident daily

variation pattern driven by photochemistry (Figure S2), consistent with the daily variation pattern of the ultraviolet radiation (UV) intensity. From October 4 to 12, a relatively pristine air mass transported from the ocean (Figure S3), resulting in reduced concentrations of VOCs, gaseous inorganic vapors, and OAs. However, because of the sustained high temperature and UV intensity levels, the concentration of AOOMs remained relatively high. This serves as evidence that AOOMs were formed via photochemical reaction with locally sourced precursors in this coastal city. Figure 1b shows the concentration of AOOMs as a function of temperature and ozone photolysis frequency $[i(O^{1}D)]$, which indicates that high temperature and intense radiation have a robust positive effect on the generation of AOOMs.²⁸ Furthermore, as shown in Figure 1c and Table S7, the AOOM concentration in Xiamen and other sampling sites exhibited a temperature dependence.

3.2. Molecular Composition of AOOMs. The molecular information on AOOMs provided in Figure 2 reveals two main categories of predominant species, as detailed in Table S7. The mass spectrometry analyses were conducted on aliphatic and aromatic OOMs, which displayed certain similarities in their chemical formulas, such a difference of "CH2". However, distinct differences were also observed. C6 products were found to be the most abundant in aliphatic AOOMs, whereas C7 and C8 products were predominant in aromatic AOOMs. In addition, compared to aromatic OOMs, aliphatic OOMs showed a higher nitrogen content, and CHON2 groups contributed more (Figure 2a,b). The relatively low nitrogen content of aromatic OOMs compared to aliphatic VOCs has also been documented in various urban centers across China.^{9,25,29} Nevertheless, the precise underlying mechanisms remain contingent on chamber experiments and theoretical calculations.

 $C_6H_9O_7N_7$, one of the dominant species in aliphatic OOMs during this investigation, substantially correlated with UV intensity and the concentration of OH radicals as shown in Figure S4. In comparison, C₆H₉O₆N was found to be the most abundant aliphatic OOMs during autumn in Beijing, with one less effective oxygen atom than C₆H₉O₇N.²⁵ These differences may arise from variations in the types and concentrations of aliphatic VOC precursors, as well as in atmospheric oxidant concentrations and other species participating in the oxidation reactions, such as HO₂ radicals, RO₂ radicals, and NO. The most prevalent C7 aromatic OOMs identified in this investigation was C7H10O5, which was also observed in the OH-initiated oxidation experiments of toluene.¹⁸ C₇H₁₀O₅ may be a product of the reaction between C₇H₉O₅ radicals and HO₂ radicals, whereas C₇H₁₀O₇ and C₇H₁₀O₉ may be products of multistep autoxidation reactions of C7H9O5 radicals followed by reaction with HO₂ radicals. In a chamber experiment, the signal intensities of $C_7H_{10}O_7$ and $C_7H_{10}O_9$ were observed to be much higher than that of $C_7H_{10}O_{51}$ indicating that the autoxidation reaction of C7H9O5 radicals takes priority over the termination reaction with HO₂ radicals. This suggests that, under the conditions of the chamber study, the termination reaction of RO₂ radicals with HO₂ radicals may be less important than the multistep autoxidation reaction.^{20,33} However, contrary to the previous findings in chamber experiments, during this study, the signal intensity of C₇H₁₀O₅ was significantly higher than that of the product produced after further oxidation reactions (see Table S2). This observation may be due to the remarkably lower concentration

of OH radicals, as well as the presence of NO, which acts as an inhibitor to autoxidation reactions, in the actual atmospheric environment compared to the experimental conditions (see Table S8).²²

The molecular characteristics of AOOMs were analyzed and visualized by using a mass defect (MD) plot (Figure S5). Two novel modifications of AOOMs were identified, marked with arrows in Figure S5. One modification is manifested by the addition of a "CH2" due to the coemissions of homologous compounds and carbon chain fragmentation.³⁴ The other trajectory can be attributed to various emission sources and atmospheric oxidation processes, adding an oxygen atom and removing "CH2". To further characterize aliphatic OOMs and aromatic OOMs, the distributions of carbon number (nC), nitrogen number (nN), effective oxygen number (nO_{eff} , nO_{eff} = $nO - 2 \times nN$), and double bond equivalence (DBE) of both of them were analyzed (Figure 2c,d). For AOOMs with $4 \leq$ nC \leq 10, C7 products were the most abundant, and a decreasing trend can be seen along with an increasing nC. Most AOOMs contained nO_{eff} between 4 and 6, accounting for 73-81% of the total AOOMs. Regarding nitrogen content, all AOOMs contained 0 to 2 nitrogen atoms, with CHON-AOOMs comprising the predominant fraction (50%). Furthermore, AOOMs primarily consisted of 1 to 4 DBE values, among which the ones with DBE = 3 contributed the most (35%).

3.3. Nitrogen Content of AOOMs. The study revealed that aliphatic OOMs contained a higher proportion of nitrogen-containing compounds (91%) in comparison to aromatic ones (49%) (Figure 2c,d). The higher nitrogen content in aliphatic OOMs is supported by aliphatic VOCs having a higher branching rate to nitrogenous compounds than aromatic VOCs.²⁹ However, the fraction of nitrogen-containing compounds was higher than any known branching ratio for the reaction between RO₂ and NO, which forms organonitrates.^{35–37} Both aliphatic OOMs (34%) and aromatic OOMs (9%) comprised a considerable fraction of dinitrate OOMs (Figure 2c,d). These findings unveil the influential role of multistep bimolecular oxidation on AOOMs formation.

It is suggested that two pathways add N atoms to AOOMs: RO₂ radicals terminated by NO and oxidation initiated by NO₃ radicals.³⁸ To investigate the pathways for the incorporation of N atoms into AOOMs during the daytime and nighttime, the observation-based model (OBM, seeText S7) was employed to simulate the oxidation processes of selected aliphatic VOCs and aromatic VOCs by three oxidants (OH radicals, NO₃ radicals, and O₃). The loss rate of AVOCs (see Text S8) was used as an indicator to show the proportion of AVOCs oxidized by the three oxidants throughout the sampling period, during daytime, and at nighttime, respectively (Figure S6).³⁵ The results indicate that NO₃ radicals may dominate the oxidation reactions of AVOCs during the nighttime periods. However, considering the overall contribution throughout the day, NO3 radicals account for only 5.9%. Referring to the diurnal variations of AOOMs shown in Figure S2, it can be observed that for aliphatic OOMs, the concentration of CHON is much higher than that of CHO. For aromatic OOMs, the concentration of CHON is slightly higher than that of CHO. This finding also confirms the vital role of NO₃ radicals during nighttime. During daytime, OH radicals play an overwhelmingly dominant role, and the OOMs generated by the oxidation of AVOCs by OH radicals are non-nitrogenous. However, both types of AOOMs exhibit high peaks of CHON



Figure 3. (a) Simplified oxidation mechanism for alkanes attacked by primary OH radicals under NO_{x} -controlled conditions. Black fonts represent precursors, green fonts represent intermediate radicals, and red fonts represent primary OH radical oxidation products. (b) Molecular formula changes for the first- to third-generation products of alkanes based on the basic reaction scheme in panel a. The brown fonts represent secondary OH radical oxidation products, and the purple fonts represent third OH radical oxidation products. (c) Fraction of the potential alkane-derived compounds in aliphatic OOMs. The compounds listed in panel c are grouped according to the molecular formulas in panel b. The bars are colored with nO_{auto} .

around noon, indicating that the termination reactions of RO₂ radicals and NO dominate the addition of N atoms to AOOMs during daytime.

Further, the impact of NOx on formation of AOOMs containing zero, one, and two nitrogen atoms was investigated (Figure S7). The results indicate that the impacts of the NOxconcentration on the two types of AOOMs are complex, likely due to differences in the reaction mechanisms of the two AVOCs. For aromatic OOMs, an increase in NOxconcentration leads to a decrease in the proportion of CHO-OOMs and an increase in the proportion of CHON-OOMs, whereas there is no evident change in the proportion of CHON2-OOMs. Besides, an increase in the NOx concentration results in a decrease in the proportion of CHON-OOMs, an increase in the proportion of CHON2-OOMs, and no salient change in the proportion of CHO-OOMs for aliphatic OOMs. Overall, increasing the NOx concentration changed the composition of AOOMs and promoted the increase in the nitrogen content of AOOMs.

3.4. Oxidation Mechanisms of AOOMs. The OSc_{eff} is a modified version of average carbon oxidation states (OSc), with the formula $OSc_{eff} = 2 \times nO_{eff}/nC - nH/nC$ used to describe the oxidation degree of carbon atoms of AOOM molecules.⁴⁰ The overall OSc_{eff} value of AOOMs in this study (-0.58) was lower than forested sites (0-0.50) but slightly higher than Shanghai (-0.68).^{41,42} This discrepancy may be attributed to the observed NOx level, which was higher than that in the forested atmosphere but lower than that in highly polluted megacities. NOx can terminate peroxy radicals (RO₂), outcompeting autoxidation propagation reactions and other bimolecular reactions (RO₂ + RO₂, RO₂ + HO₂) and resulting in a reduced degree of oxidation in the products.⁴² An alternative explanation could be the varying dominant VOC types in different research areas, resulting in differences in the

structures of dominant VOCs in different fields of study. The structure of VOCs largely determines the fate of RO₂ radicals, which in turn influences the oxidation degree of AOOMs.²⁹

The species with $nO_{eff} = 4$ contributed most to the aliphatic OOMs (55%). Recent research suggests that aliphatic compounds are more susceptible to undergo autoxidation than previously recognized.²⁴ The number of oxygen atoms involved in autoxidation (nO_{auto}) was calculated via nO_{auto} = $nO_{eff} - nN - DBE$, where the specific derivation details can be found in Text S9. As shown in Figure S8, the nO_{auto} mainly ranges from 1 to 3, indicating that autoxidation occurred in one to three steps. Figure 3a shows the photochemical oxidation process of aliphatic compounds in the presence of NOx using alkanes as an example. In this case, the termination of RO₂ occurs entirely via NO. Without carbon chain breakage, the products of this process include $C_nH_{2n}O$ (with one more carbonyl group than the precursor) and C_nH_{2n+1}O₃N (with one more nitrate group than the precursor). The reoxidation process of the products is a repetition of the basic oxidation reaction scheme (Figure 3a).⁴¹ To investigate mechanisms that differ from this basic scheme, reference chemical formulas from first- to third-generation products generated from alkanes are listed in Figure 3b. Specifically, this comparison was conducted between aliphatic OOMs having the same number of carbon, nitrogen, and hydrogen atoms as the reference compounds but different numbers of oxygen atoms. The majority of observed aliphatic OOMs were third-generation products followed by second-generation products (Figure 3c). Only a small percentage of first-generation products were observed. Most of the second-generation products underwent two autoxidation reactions, whereas the majority of the third-generation products underwent only one. Above all, these results underscore the discernible prevalence of multigeneration OH radical reactions and autoxidation reactions of aliphatic OOMs.



Figure 4. Diurnal variation of selected aromatic OOMs, corresponding precursor VOCs, UV intensity, and OH radical concentration. The selected OOMs are the two most abundant in aromatic OOMs with different carbon numbers: panel a includes $C_6H_8O_5$ and $C_6H_8O_6$, panel b includes $C_7H_{10}O_5$ and $C_6H_9O_7N$, and panel c includes $C_8H_{12}O_{10}N_2$. There is only one precursor VOC for C6 and C7 aromatic OOMs, i.e., benzene and toluene, respectively. The precursors for C8 aromatic OOMs include ethylbenzene, oxylene, p/m-xylene, and styrene.

Species dominated aromatic OOMs with nO_{eff} values of 4-6 (57%), which contained more effective oxygen atoms than aliphatic OOMs. The primary OH radical addition of monomeric aromatic compounds (C_xH_y) in the presence of NOx may generate termination products with a total number of hydrogen and nitrogen atoms equal to y or y + 2 (Figure S9).²² Secondary OH radical attacks occurred through either OH radical addition or H-abstraction reaction, and the products of secondary OH radical attacks are listed in Table S9. It was observed that products with total hydrogen and nitrogen atoms less than y or greater than y + 2 were produced only when a secondary OH radical attack occurred. For example, C₇H₆O₄ was formed from toluene via two OH radical reactions, where the secondary OH radical attack involves Habstraction. C₇H₁₂O₄ was also the product of toluene undergoing two OH radical additions, where the secondary OH radical attack involves OH-addition.^{19,20} Products with total hydrogen and nitrogen atoms less than y or greater than y + 2 contributed substantially to this study (Table S2), highlighting the importance of multigeneration OH radical reactions in the formation of aromatic OOMs.

3.5. Potential Sources of Aromatic OOMs. High NO*x* chamber experiments on benzene and toluene oxidation by OH radicals indicated that over 90% of the products maintained the same carbon number as their precursors.²² These findings suggest that there is almost no carbon chain fragmentation during the oxidation of aromatic VOCs to form aromatic OOMs as detected by Nitrate-CI-APi-TOF. How-

ever, there is limited evidence on the oxidation of aliphatic VOCs to OOMs in the laboratory experiment; it is challenging to infer the precursors of aliphatic OOMs. Therefore, this section focuses solely on the discussion of aromatic OOMs.

Figure 4 summarizes the diurnal variations in the concentrations of selected aromatic OOMs, corresponding VOCs, UV intensity, and estimated OH radical concentration (see Text S10 for the calculation method). Concentrations of aromatic VOCs peaked at 6:00 am and decreased throughout the day, whereas aromatic OOMs gradually increased from 6:00 am and reached a maximum at 2:00 pm before decreasing after sunset. The OH radical concentration increased along with UV intensity in the morning, which led to an increase in AOOM concentration. During nighttime hours, the emission rate of aromatic VOCs exceeded the atmospheric oxidation rate. Combined with a shallow and stable boundary layer, this resulted in an accumulation of VOC concentrations. However, despite the high concentrations of precursors, the concentration of AOOMs at night was an order of magnitude lower than during the day due to the lack of photolytic driving forces.

Figure S10 presents potential mechanisms for forming representative aromatic OOMs with varying carbon numbers, which are shown in Figure 4. These mechanisms are based on the latest understanding of aromatic oxidation.^{19,20,22,23,43} When monomeric aromatic compounds react with OH radicals and O₂, they form $C_xH_yO_{2z+1}$ radicals ($6 \le x \le 8$, y = 2x - 6, $z \ge 0$), which undergo further autoxidation reactions or chain propagation, eventually leading to the formation of closed-shell



Figure 5. (a) The proportions of ELVOCs, LVOCs, and SVOCs to the total mass flux of AOOMs for different PM_1 levels. Note that the contribution of IVOCs is too small (lower than 1%) and not drawn in the figure. (b) The contribution of total AOOM mass flux to OA mass growth rate during the daytime, night, and the entire day (box line diagram). The bar chart indicates the percentage contribution of aliphatic (green) and aromatic (blue) AOOMs to the total AOOMs mass flux. (c) The mass flux of AOOMs decreases with increasing temperature. (d) The mass flux of AOOMs increases with increasing particle number concentration. The value of the *x*-axis coordinate is a multiple of the average particle number concentration compared to the present study, which is 0.5, 1, 2, 10, 20, 30, 40, and 50, respectively.

OOMs. $C_6H_8O_5$, $C_7H_{10}O_5$, and $C_8H_{12}O_5$ are plausible bicyclic organic hydroperoxides, which could be the termination products of the $C_xH_yO_5$ radical with the HO₂ radicals.^{18,21} $C_6H_8O_6$ may be an alcohol product generated by the direct reaction of the $C_6H_7O_7$ radical with the other RO₂ radicals (Figure S10a). Additionally, the formation of $C_7H_{10}O_5$ and $C_7H_9O_7N$ could potentially occur via the termination reaction of the $C_7H_9O_6$ radical (Figure S10b). However, autoxidation reactions alone cannot generate organic radicals containing an even number of oxygen atoms by the OH-addition oxidation pathway. The pathway of $C_7H_9O_6$ radical generation may involve the following steps:

$$C_7H_9O_5$$
 + NO $\rightarrow C_7H_9O_4$
 $C_7H_9O_4$ + $O_2 \rightarrow C_7H_9O_4$

Furthermore, the $C_7H_9O_6$ radical has the potential to either react with another RO_2 radical, leading to the formation of $C_7H_{10}O_5$, or be terminated by NO to generate $C_7H_9O_7N$. The formation of the most abundant dinitrates of $C_8H_{12}O_{10}N_2$ necessitates an OH radical attack on a nitrated compound known as $C_8H_{11}O_6N$, along with the termination of the RO_2 radical chain with NO (Figure S10c).²¹ The precursor for the reaction described above, $C_8H_{11}NO_6$, could be derived from a termination reaction of the $C_8H_{11}O_5$ radical with NO.

A positive matrix factorization analysis (see details in Text S11) on the VOC data set identified five sources: solvents, industry, oil and gas volatilization, motor vehicle exhaust, and combustion (Figure S11). The contribution proportions of the five sources to aromatic VOCs are summarized in Table S10. C7 aromatic VOCs and C7 aromatic OOMs, having the highest concentrations, were of particular interest. The solvent sources contributed 80% of toluene, consistent with the previous VOC research conducted in Xiamen City.^{44,45} Figure S12 identifies the prominent VOC-emitting enterprises, mainly related to the production of paints and plastics (Table S11). This underscores the significant contribution of solvent-related industries in Xiamen City to the precursors of AOOMs, particularly those regarding C7 aromatics.

3.6. Contribution of AOOMs to OA. Figure S13 provides an overview of the volatility characteristics associated with AOOMs based on the average temperature (32 °C) during the sampling period. Semivolatile organic compounds (SVOCs) had a higher contribution to aliphatic OOMs (64%), whereas low-volatility organic compounds (LVOCs) contributed the most to aromatic OOMs (62%).³² LVOCs and extremely low

volatility organic compounds (ELVOCs), which are representative of condensable vapors, make substantial contributions to particulate matter.⁴⁶ In particular, LVOCs and ELVOCs accounted for 36% and a striking 76% of aliphatic and aromatic OOMs, respectively. This result suggests that aromatic OOMs may play a dominant role in contributing to OA growth. Another piece of evidence is that 9 out of the top 10 condensable vapors with the highest concentrations were aromatic OOMs, as shown in Figure S14.

This assertion is further substantiated by the contributions of two types of AOOMs to the OA mass growth rate in particles with an aerodynamic diameter equal to or less than 1 μm (PM₁), calculated based on the ARCA Box model. Figure 5a provides evidence that, out of all measured AOOMs, the largest contribution to the OA mass growth rate was from LVOCs and ELVOCs. Our simulation also revealed that SVOCs, despite their typically minimal impact on aerosol growth, contributed approximately 14% to the mass growth rate of OA. The mass flux of AOOMs contributed remarkably to the OA mass growth rate, with more than 35% attributed to AOOMs as a whole, around 26% attributed to aromatic AOOMs, and 9% attributed to aliphatic AOOMs (Figure 5b). These results suggest that the gas-particle partitioning of AOOMs generated from AVOCs can explain a considerable portion of the OA growth observed in this study, with aromatic VOCs playing a dominant role as precursors. The higher AOOMs mass flux during the day compared to at night is likely due to the higher AOOMs concentrations at the daytime. During the night, the contribution of aliphatic OOMs to total AOOMs mass flux was slightly elevated. This is due to the larger reaction rate constants of aliphatic VOCs and NO3 radicals compared to aromatic VOCs, resulting in a higher concentration of aliphatic OOMs at night.

Because only the gas-particle partitioning of AOOMs was considered in this study, the measured OA mass growth rate needs to be fully explained in the future. The additional OA growth may arise from a combination of aqueous condensedphase chemistry and the equilibrium partitioning of unmeasured L/SVOCs. In addition, the contribution of biogenic OOMs to the OA growth may not be negligible. The results showed that isoprene OOMs and monoterpene OOMs contributed up to 7 and 12% to the OA mass growth rate, respectively, as discussed in detail in Text S12. Table S12 highlights the top six species that contributed the most to the total AOOMs mass flux, namely, C₈H₁₁O₇N, C₈H₁₂O₅, $C_7H_{10}O_5$, $C_8H_{12}O_{10}N_2$, $C_8H_{11}O_8N$, and $C_7H_8O_5$, all of which belong to aromatic OOMs. This suggests that the majority of mass fluxes were driven by products associated with aromatic precursors, particularly C7 and C8 aromatic VOCs.

In addition, sensitivity tests were conducted using the ARCA Box to investigate the impact of the temperature and particle number concentration on the mass flux of AOOMs. The results showed that as the temperature decreased from +42 to +12 °C, the total mass flux of AOOMs increased by 54% (Figure 5c). This indicates that the mass flux at lower temperatures is higher due to the reduced volatilities of the AOOMs at lower temperatures. The observed temperature effect suggests a potentially more crucial role for AOOMs in colder regions in essential processes, such as the growth of newly formed particles. In addition to temperature, an exponential empirical relationship was observed between mass flux and condensation sink (CS) in Figure S15, implying that the concentration of atmospheric aerosols remarkably influenced the mass flux of AOOMs. The impact of particle size distributions on the mass flux of AOOMs has been evaluated, which showed that increasing the particle number concentration in each size bin by 10 or 50 times led to an 8-and a 25-fold increase in mass flux (Figure 5d), respectively. These results have confirmed a positive feedback loop between the condensation of AOOMs and particulate matter pollution: the condensation of AOOMs promotes the accumulation of particulate pollution, and the increase in particulate number concentration and size in turn facilitates the condensation of AOOMs.^{9,32}

China has made substantial improvements in mitigating fine particulate matter pollution. However, the control of fine particulate matter has mainly achieved good results in inorganic components, such as sulfate, nitrate, and ammonium. The lack of understanding of the molecular-level formation mechanism of OA has limited scientific control of organic components in fine particulate matter. This study partially explains the OA mass growth rate observed in field observations and quantifies the contribution of AOOMs to the OA growth. The findings can contribute to advancing the scientific understanding of the critical gaps among VOCs, organic vapors, and OA in coastal urban areas, which is essential for implementing effective particulate matter control measures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.3c03244.

Detailed information about the OOM measurement and classification (Text S1 and S2; Tables S1, S2, S13, and S14; and Figures S16 and 17), auxiliary measurements (Text S3 and Tables S3-S5), OA measurement (Text S4), estimation of OOM volatility (Text S5), general overview of the campaign (Text S6), OBM model (Text S7), calculation of loss rate of VOCs (Text S8), calculation and distribution of nO_{auto} (Text S9, Figure S8), estimation of OH radical concentration (Text S10), PMF model (Text S11), biogenic OOMs (Text S12, Figure S18), study site location (Figure S1), diurnal patterns of OOMs (Figure S2), wind rose plot (Figure S3), diurnal patterns of typical AOOM (Figure S4), mass defect plots (Figure S5), contributions of three oxidants to the VOC loss rates (Figure S6), fraction of nitrogen OOMs (Figure S7), simplified oxidation mechanism for aromatics (Figure S9), proposed formation mechanism for the selected species (Figure S10), PMF analysis (Figure S11 and Table S10), industrial distribution of Xiamen (Figure S12 and Table S11), volatility distribution of OOMs (Figure S13), fractional profiles of each AOOM (Figure S14), mass fluxes as a function of CS (Figure S15), AOOM concentration comparison (Table S6), predominant AOOM category classification (Table S7), condition comparison of this study and chamber experiment (Table S8), aromatic VOC oxidation product by a second OH radical attack (Table S9), and contribution of 10 selected AOOMs to the mass flux of total AOOMs (Table S12) (PDF)

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Notes

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ABBREVIATIONS

OA organic aerosol SOA secondary organic aerosol VOCs volatile organic compounds OOMs oxygenated organic molecules NPF new particle formation Nitrate-CI-APi-TOF nitrate chemical ionization atmosphere-pressure-interface long-time-of-flight mass spectrometer AOOMs anthropogenic oxygenated organic molecules AVOCs anthropogenic volatile organic compounds ARCA Box atmospherically relevant chemistry and aerosol box model VBS volatility basis set PMF positive matrix factorization SVOCs semivolatile organic compounds LVOCs low-volatility organic compounds IVOCs intermediate-volatility organic compounds ELVOCs extremely low volatility organic compounds ACSM aerosol chemical speciation monitor CS condensation sink

REFERENCES

(1) Nozière, B.; Kalberer, M.; Claeys, M.; Allan, J.; D'Anna, B.; Decesari, S.; Finessi, E.; Glasius, M.; Grgić, I.; Hamilton, J. F.; Hoffmann, T.; Iinuma, Y.; Jaoui, M.; Kahnt, A.; Kampf, C. J.; Kourtchev, I.; Maenhaut, W.; Marsden, N.; Saarikoski, S.; Schnelle-Kreis, J.; Surratt, J. D.; Szidat, S.; Szmigielski, R.; Wisthaler, A. The Molecular Identification of Organic Compounds in the Atmosphere: State of the Art and Challenges. *Chem. Rev.* **2015**, *115* (10), 3919–3983.

(2) Makkonen, R.; Asmi, A.; Kerminen, V. M.; Boy, M.; Arneth, A.; Hari, P.; Kulmala, M. Air pollution control and decreasing new particle formation lead to strong climate warming. *Atmos. Chem. Phys.* **2012**, *12* (3), 1515–1524.

(3) Valari, M.; Martinelli, L.; Chatignoux, E.; Crooks, J.; Garcia, V. Time scale effects in acute association between air-pollution and mortality. *Geophys. Res. Lett.* **2011**, *38* (10), L10806.

(4) Lin, Z.; Wang, Y.; Zheng, F.; Zhou, Y.; Guo, Y.; Feng, Z.; Li, C.; Zhang, Y.; Hakala, S.; Chan, T.; Yan, C.; Daellenbach, K. R.; Chu, B.; Dada, L.; Kangasluoma, J.; Yao, L.; Fan, X.; Du, W.; Cai, J.; Cai, R.; Kokkonen, T. V.; Zhou, P.; Wang, L.; Petäjä, T.; Bianchi, F.; Kerminen, V. M.; Liu, Y.; Kulmala, M. Rapid mass growth and enhanced light extinction of atmospheric aerosols during the heating season haze episodes in Beijing revealed by aerosol-chemistry-radiation-boundary layer interaction. *Atmos. Chem. Phys.* **2021**, *21* (16), 12173–12187.

(5) Jimenez, J. L.; Canagaratna, M. R.; Donahue, N. M.; Prevot, A. S. H.; Zhang, Q.; Kroll, J. H.; DeCarlo, P. F.; Allan, J. D.; Coe, H.; Ng, N. L.; Aiken, A. C.; Docherty, K. S.; Ulbrich, I. M.; Grieshop, A. P.; Robinson, A. L.; Duplissy, J.; Smith, J. D.; Wilson, K. R.; Lanz, V. A.; Hueglin, C.; Sun, Y.; Tian, J.; Laaksonen, A.; Raatikainen, T.; Rautiainen, J.; Vaattovaara, P.; Ehn, M.; Kulmala, M.; Tomlinson, J. M.; Collins, D. R.; Cubison, M. J.; Dunlea, J.; Huffman, J. A.; Onasch, T. B.; Alfarra, M. R.; Williams, P. I.; Bower, K.; Kondo, Y.; Schneider, J.; Drewnick, F.; Borrmann, S.; Weimer, S.; Demerjian, K.; Salcedo, D.; Cottrell, L.; Griffin, R.; Takami, A.; Miyoshi, T.; Hatakeyama, S.; Shimono, A.; Sun, J.; Zhang, Y.; Dzepina, K.; Kimmel, J. R.; Sueper, D.; Jayne, J. T.; Herndon, S. C.; Trimborn, A. M.; Williams, L. R.; Wood, E. C.; Middlebrook, A. M.; Kolb, C. E.; Baltensperger, U.; Worsnop, D. R. Evolution of organic aerosols in the atmosphere. *Science* **2009**, *326* (5959), 1525–1529.

(6) Kanakidou, M.; Seinfeld, J. H.; Pandis, S. N.; Barnes, I.; Dentener, F. J.; Facchini, M. C.; Van Dingenen, R.; Ervens, B.; Nenes, A.; Nielsen, C. J.; Swietlicki, E.; Putaud, J. P.; Balkanski, Y.; Fuzzi, S.; Horth, J.; Moortgat, G. K.; Winterhalter, R.; Myhre, C. E. L.; Tsigaridis, K.; Vignati, E.; Stephanou, E. G.; Wilson, J. Organic aerosol and global climate modelling: a review. *Atmos. Chem. Phys.* **2005**, 5 (4), 1053–1123.

(7) Zhang, Q.; Jimenez, J. L.; Canagaratna, M. R.; Allan, J. D.; Coe, H.; Ulbrich, I.; Alfarra, M. R.; Takami, A.; Middlebrook, A. M.; Sun, Y. L.; Dzepina, K.; Dunlea, E.; Docherty, K.; DeCarlo, P. F.; Salcedo, D.; Onasch, T.; Jayne, J. T.; Miyoshi, T.; Shimono, A.; Hatakeyama, S.; Takegawa, N.; Kondo, Y.; Schneider, J.; Drewnick, F.; Borrmann, S.; Weimer, S.; Demerjian, K.; Williams, P.; Bower, K.; Bahreini, R.; Cottrell, L.; Griffin, R. J.; Rautiainen, J.; Sun, J. Y.; Zhang, Y. M.; Worsnop, D. R. Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes. *Geophys. Res. Lett.* **2007**, *34* (13), L13801.

(8) Huang, R.; Zhang, Y.; Bozzetti, C.; Ho, K.; Cao, J.; Han, Y.; Daellenbach, K. R.; Slowik, J. G.; Platt, S. M.; Canonaco, F.; Zotter, P.; Wolf, R.; Pieber, S. M.; Bruns, E. A.; Crippa, M.; Ciarelli, G.; Piazzalunga, A.; Schwikowski, M.; Abbaszade, G.; Schnelle-Kreis, J.; Zimmermann, R.; An, Z.; Szidat, S.; Baltensperger, U.; Haddad, I. E.; Prévôt, A. S. H. High secondary aerosol contribution to particulate pollution during haze events in China. *Nature* **2014**, *514* (7521), 218–222.

(9) Nie, W.; Yan, C.; Huang, D. D.; Wang, Z.; Liu, Y.; Qiao, X.; Guo, Y.; Tian, L.; Zheng, P.; Xu, Z.; Li, Y.; Xu, Z.; Qi, X.; Sun, P.; Wang, J.; Zheng, F.; Li, X.; Yin, R.; Dallenbach, K. R.; Bianchi, F.; Petäjä, T.; Zhang, Y.; Wang, M.; Schervish, M.; Wang, S.; Qiao, L.; Wang, Q.; Zhou, M.; Wang, H.; Yu, C.; Yao, D.; Guo, H.; Ye, P.; Lee, S.; Li, Y. J.; Liu, Y.; Chi, X.; Kerminen, V. M.; Ehn, M.; Donahue, N. M.; Wang, T.; Huang, C.; Kulmala, M.; Worsnop, D.; Jiang, J.; Ding, A. Secondary organic aerosol formed by condensing anthropogenic vapours over China's megacities. *Nat. Geosci.* **2022**, *15* (4), 255–261. (10) Rissanen, M. P.; Kurten, T.; Sipila, M.; Thornton, J. A.; Kausiala, O.; Garmash, O.; Kjaergaard, H. G.; Petäjä, T.; Worsnop, D. R.; Ehn, M.; Kulmala, M. Effects of chemical complexity on the autoxidation mechanisms of endocyclic alkene ozonolysis products: From methylcyclohexenes toward understanding α -pinene. J. Phys. Chem. A **2015**, 119 (19), 4633–4650.

(11) Rissanen, M. P.; Kurtén, T.; Sipilä, M.; Thornton, J. A.; Kangasluoma, J.; Sarnela, N.; Junninen, H.; Jørgensen, S.; Schallhart, S.; Kajos, M. K.; Taipale, R.; Springer, M.; Mentel, T. F.; Ruuskanen, T.; Petäjä, T.; Worsnop, D. R.; Kjaergaard, H. G.; Ehn, M. The formation of highly oxidized multifunctional products in the ozonolysis of cyclohexene. *J. Am. Chem. Soc.* **2014**, *136* (44), 15596–15606.

(12) Berndt, T.; Richters, S.; Kaethner, R.; Voigtländer, J.; Stratmann, F.; Sipilä, M.; Kulmala, M.; Herrmann, H. Gas-phase ozonolysis of cycloalkenes: formation of highly oxidized RO2 radicals and their reactions with NO, NO2, SO2, and other RO2 radicals. *J. Phys. Chem. A* **2015**, *119* (41), 10336–10348.

(13) Jokinen, T.; Sipilä, M.; Richters, S.; Kerminen, V. M.; Paasonen, P.; Stratmann, F.; Worsnop, D. R.; Kulmala, M.; Ehn, M.; Herrmann, H.; Berndt, T. Rapid autoxidation forms highly oxidized RO2 radicals in the atmosphere. *Angew. Chem., Int. Ed.* **2014**, *53* (52), 14596–14600.

(14) Jokinen, T.; Sipilä, M.; Junninen, H.; Ehn, M.; Lönn, G.; Hakala, J.; Petäjä, T.; Mauldin Iii, R. L.; Kulmala, M.; Worsnop, D. R. Atmospheric sulphuric acid and neutral cluster measurements using CI-APi-TOF. *Atmos. Chem. Phys.* **2012**, *12* (9), 4117–4125.

(15) Kirkby, J.; Duplissy, J.; Sengupta, K.; Frege, C.; Gordon, H.; Williamson, C.; Heinritzi, M.; Simon, M.; Yan, C.; Almeida, J.; Tröstl, J.; Nieminen, T.; Ortega, I. K.; Wagner, R.; Adamov, A.; Amorim, A.; Bernhammer, A. K.; Bianchi, F.; Breitenlechner, M.; Brilke, S.; Chen, X.; Craven, J.; Dias, A.; Ehrhart, S.; Flagan, R. C.; Franchin, A.; Fuchs, C.; Guida, R.; Hakala, J.; Hoyle, C. R.; Jokinen, T.; Junninen, H.; Kangasluoma, J.; Kim, J.; Krapf, M.; Kürten, A.; Laaksonen, A.; Lehtipalo, K.; Makhmutov, V.; Mathot, S.; Molteni, U.; Onnela, A.; Peräkylä, O.; Piel, F.; Petäjä, T.; Praplan, A. P.; Pringle, K.; Rap, A.; Richards, N. A. D.; Riipinen, I.; Rissanen, M. P.; Rondo, L.; Sarnela, N.; Schobesberger, S.; Scott, C. E.; Seinfeld, J. H.; Sipilä, M.; Steiner, G.; Stozhkov, Y.; Stratmann, F.; Tomé, A.; Virtanen, A.; Vogel, A. L.; Wagner, A. C.; Wagner, P. E.; Weingartner, E.; Wimmer, D.; Winkler, P. M.; Ye, P.; Zhang, X.; Hansel, A.; Dommen, J.; Donahue, N. M.; Worsnop, D. R.; Baltensperger, U.; Kulmala, M.; Carslaw, K. S.; Curtius, J. Ion-induced nucleation of pure biogenic particles. Nature 2016, 533 (7604), 521-526.

(16) Ehn, M.; Thornton, J. A.; Kleist, E.; Sipilä, M.; Junninen, H.; Pullinen, I.; Springer, M.; Rubach, F.; Tillmann, R.; Lee, B.; Lopez-Hilfiker, F.; Andres, S.; Acir, I. H.; Rissanen, M.; Jokinen, T.; Schobesberger, S.; Kangasluoma, J.; Kontkanen, J.; Nieminen, T.; Kurtén, T.; Nielsen, L. B.; Jørgensen, S.; Kjaergaard, H. G.; Canagaratna, M.; Maso, M. D.; Berndt, T.; Petäjä, T.; Wahner, A.; Kerminen, V. M.; Kulmala, M.; Worsnop, D. R.; Wildt, J.; Mentel, T. F. A large source of low-volatility secondary organic aerosol. *Nature* **2014**, 506 (7489), 476–479.

(17) Jokinen, T.; Berndt, T.; Makkonen, R.; Kerminen, V.; Junninen, H.; Paasonen, P.; Stratmann, F.; Herrmann, H.; Guenther, A. B.; Worsnop, D. R.; Kulmala, M.; Ehn, M.; Sipilä, M. Production of extremely low volatile organic compounds from biogenic emissions: Measured yields and atmospheric implications. *Proc. Natl. Acad. Sci. U.S.A.* **2015**, *112* (23), 7123–7128.

(18) Richters, S.; Herrmann, H.; Berndt, T. Highly oxidized RO2 radicals and consecutive products from the ozonolysis of three sesquiterpenes. *Environ. Sci. Technol.* **2016**, *50* (5), 2354–2362.

(19) Molteni, U.; Bianchi, F.; Klein, F.; El Haddad, I.; Frege, C.; Rossi, M. J.; Dommen, J.; Wahner, A.; Baltensperger, U. Formation of highly oxygenated organic molecules from aromatic compounds. *Atmos. Chem. Phys.* **2018**, *18* (3), 1909–1921.

(20) Garmash, O.; Rissanen, M. P.; Pullinen, I.; Schmitt, S.; Kausiala, O.; Tillmann, R.; Zhao, D.; Percival, C.; Bannan, T. J.; Priestley, M.; Hallquist, Å. M.; Kleist, E.; Kiendler-Scharr, A.;

Hallquist, M.; Berndt, T.; McFiggans, G.; Wildt, J.; Mentel, T. F.; Ehn, M. Multi-generation OH oxidation as a source for highly oxygenated organic molecules from aromatics. *Atmos. Chem. Phys.* **2020**, 20 (1), 515–537.

(21) Tsiligiannis, E.; Hammes, J.; Salvador, C. M.; Mentel, T. F.; Hallquist, M. Effect of NOx on 1,3,5-trimethylbenzene (TMB) oxidation product distribution and particle formation. *Atmos. Chem. Phys.* **2019**, *19* (23), 15073–15086.

(22) Cheng, X.; Chen, Q.; Jie Li, Y.; Zheng, Y.; Liao, K.; Huang, G. Highly oxygenated organic molecules produced by the oxidation of benzene and toluene in a wide range of OH exposure and NOx conditions. *Atmos. Chem. Phys.* **2021**, *21* (15), 12005–12019.

(23) Wang, Y.; Mehra, A.; Krechmer, J. E.; Yang, G.; Hu, X.; Lu, Y.; Lambe, A.; Canagaratna, M.; Chen, J.; Worsnop, D.; Coe, H.; Wang, L. Oxygenated products formed from OH-initiated reactions of trimethylbenzene: autoxidation and accretion. *Atmos. Chem. Phys.* **2020**, 20 (15), 9563–9579.

(24) Wang, Z.; Ehn, M.; Rissanen, M. P.; Garmash, O.; Quéléver, L.; Xing, L.; Monge-Palacios, M.; Rantala, P.; Donahue, N. M.; Berndt, T.; Sarathy, S. M. Efficient alkane oxidation under combustion engine and atmospheric conditions. *Commun. Chem.* **2021**, *4*, 18.

(25) Guo, Y.; Yan, C.; Liu, Y.; Qiao, X.; Zheng, F.; Zhang, Y.; Zhou, Y.; Li, C.; Fan, X.; Lin, Z.; Feng, Z.; Zhang, Y.; Zheng, P.; Tian, L.; Nie, W.; Wang, Z.; Huang, D.; Daellenbach, K. R.; Yao, L.; Dada, L.; Bianchi, F.; Jiang, J.; Liu, Y.; Kerminen, V. M.; Kulmala, M. Seasonal variation in oxygenated organic molecules in urban Beijing and their contribution to secondary organic aerosol. *Atmos. Chem. Phys.* **2022**, 22 (15), 10077–10097.

(26) Jacobson, M. Z. Numerical Techniques to Solve Condensational and Dissolutional Growth Equations When Growth is Coupled to Reversible Reactions. *Aerosol Sci. Technol.* **1997**, *27* (4), 491–498. (27) Clusius, P.; Xavier, C.; Pichelstorfer, L.; Zhou, P.; Olenius, T.; Roldin, P.; Boy, M. Atmospherically Relevant Chemistry and Aerosol box model – ARCA box (version 1.2). *Geosci. Model Dev.* **2022**, *15* (18), 7257–7286.

(28) Zheng, P.; Chen, Y.; Wang, Z.; Liu, Y.; Pu, W.; Yu, C.; Xia, M.; Xu, Y.; Guo, J.; Guo, Y.; Tian, L.; Qiao, X.; Huang, D. D.; Yan, C.; Nie, W.; Worsnop, D. R.; Lee, S.; Wang, T. Molecular Characterization of Oxygenated Organic Molecules and Their Dominating Roles in Particle Growth in Hong Kong. *Environ. Sci. Technol.* **2023**, *57* (20), 7764–7776.

(29) Tian, L.; Huang, D.; Li, Y.; Yan, C.; Nie, W.; Wang, Z.; Wang, Q.; Qiao, L.; Zhou, M.; Zhu, S.; Liu, Y.; Guo, Y.; Qiao, X.; Zheng, P.; Jing, S.; Lou, S.; Wang, H.; Huang, C. Enigma of Urban Gaseous Oxygenated Organic Molecules: Precursor Type, Role of NOx, and Degree of Oxygenation. *Environ. Sci. Technol.* 2023, *57* (1), 64–75. (30) Schervish, M.; Donahue, N. M. Peroxy radical chemistry and the volatility basis set. *Atmos. Chem. Phys.* 2020, *20* (2), 1183–1199. (31) Donahue, N. M.; Kroll, J. H.; Pandis, S. N.; Robinson, A. L. A

two-dimensional volatility basis set-Part 2: Diagnostics of organicaerosol evolution. Atmos. Chem. Phys. 2012, 12 (2), 615-634.

(32) Wang, Y.; Clusius, P.; Yan, C.; Dallenbach, K.; Yin, R.; Wang, M.; He, X. C.; Chu, B.; Lu, Y.; Dada, L.; Kangasluoma, J.; Rantala, P.; Deng, C.; Lin, Z.; Wang, W.; Yao, L.; Fan, X.; Du, W.; Cai, J.; Heikkinen, L.; Tham, Y. J.; Zha, Q.; Ling, Z.; Junninen, H.; Petaja, T.; Ge, M.; Wang, Y.; He, H.; Worsnop, D. R.; Kerminen, V. M.; Bianchi, F.; Wang, L.; Jiang, J.; Liu, Y.; Boy, M.; Ehn, M.; Donahue, N. M.; Kulmala, M. Molecular Composition of Oxygenated Organic Molecules and Their Contributions to Organic Aerosol in Beijing. *Environ. Sci. Technol.* **2022**, *S6* (2), 770–778.

(33) Schwantes, R. H.; Schilling, K. A.; McVay, R. C.; Lignell, H.; Coggon, M. M.; Zhang, X.; Wennberg, P. O.; Seinfeld, J. H. Formation of highly oxygenated low-volatility products from cresol oxidation. *Atmos. Chem. Phys.* **2017**, *17* (5), 3453–3474.

(34) Xu, Z. N.; Nie, W.; Liu, Y. L.; Sun, P.; Huang, D. D.; Yan, C.; Krechmer, J.; Ye, P. L.; Xu, Z.; Qi, X. M.; Zhu, C. J.; Li, Y. Y.; Wang, T. Y.; Wang, L.; Huang, X.; Tang, R. Z.; Guo, S.; Xiu, G. L.; Fu, Q. Y.; Worsnop, D.; Chi, X. G.; Ding, A. J. Multifunctional Products of

Isoprene Oxidation in Polluted Atmosphere and Their Contribution to SOA. *Geophys. Res. Lett.* **2021**, 48 (1), e2020GL089276.

(35) Praske, E.; Crounse, J. D.; Bates, K. H.; Kurtén, T.; Kjaergaard, H. G.; Wennberg, P. O. Atmospheric fate of methyl vinyl ketone: Peroxy radical reactions with NO and HO2. *J. Phys. Chem. A* **2015**, *119* (19), 4562–4572.

(36) Jenkin, M. E.; Valorso, R.; Aumont, B.; Rickard, A. R. Estimation of rate coefficients and branching ratios for reactions of organic peroxy radicals for use in automated mechanism construction. *Atmospheric Chemistry and Physics* **2019**, *19* (11), 7691–7717.

(37) Jenkin, M. E.; Saunders, S. M.; Wagner, V.; Pilling, M. J. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds. *Atmos. Chem. Phys.* **2003**, 3 (1), 181–193.

(38) Ng, N. L.; Kroll, J. H.; Chan, A. W. H.; Chhabra, P. S.; Flagan, R. C.; Seinfeld, J. H. Secondary organic aerosol formation from mxylene, toluene, and benzene. *Atmos. Chem. Phys.* **2007**, *7* (14), 3909–3922.

(39) Mermet, K.; Perraudin, E.; Dusanter, S.; Sauvage, S.; Léonardis, T.; Flaud, P.-M.; Bsaibes, S.; Kammer, J.; Michoud, V.; Gratien, A.; Cirtog, M.; Al Ajami, M.; Truong, F.; Batut, S.; Hecquet, C.; Doussin, J.-F.; Schoemaecker, C.; Gros, V.; Locoge, N.; Villenave, E. Atmospheric reactivity of biogenic volatile organic compounds in a maritime pine forest during the LANDEX episode 1 field campaign. *Sci. Total Environ.* **2021**, *756*, No. 144129.

(40) Kroll, J. H.; Donahue, N. M.; Jimenez, J. L.; Kessler, S. H.; Canagaratna, M. R.; Wilson, K. R.; Altieri, K. E.; Mazzoleni, L. R.; Wozniak, A. S.; Bluhm, H.; Mysak, E. R.; Smith, J. D.; Kolb, C. E.; Worsnop, D. R. Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol. *Nat. Chem.* **2011**, 3 (2), 133–139.

(41) Liu, Y.; Nie, W.; Li, Y.; Ge, D.; Liu, C.; Xu, Z.; Chen, L.; Wang, T.; Wang, L.; Sun, P.; Qi, X.; Wang, J.; Xu, Z.; Yuan, J.; Yan, C.; Zhang, Y.; Huang, D.; Wang, Z.; Donahue, N. M.; Worsnop, D.; Chi, X.; Ehn, M.; Ding, A. Formation of condensable organic vapors from anthropogenic and biogenic volatile organic compounds (VOCs) is strongly perturbed by NOx in eastern China. *Atmos. Chem. Phys.* **2021**, *21* (19), 14789–14814.

(42) Yan, C.; Nie, W.; Vogel, A. L.; Dada, L.; Lehtipalo, K.; Stolzenburg, D.; Wagner, R.; Rissanen, M. P.; Xiao, M.; Ahonen, L.; Fischer, L.; Rose, C.; Bianchi, F.; Gordon, H.; Simon, M.; Heinritzi, M.; Garmash, O.; Roldin, P.; Dias, A.; Ye, P.; Hofbauer, V.; Amorim, A.; Bauer, P. S.; Bergen, A.; Bernhammer, A. K.; Breitenlechner, M.; Brilke, S.; Buchholz, A.; Mazon, S. B.; Canagaratna, M. R.; Chen, X.; Ding, A.; Dommen, J.; Draper, D. C.; Duplissy, J.; Frege, C.; Heyn, C.; Guida, R.; Hakala, J.; Heikkinen, L.; Hoyle, C. R.; Jokinen, T.; Kangasluoma, J.; Kirkby, J.; Kontkanen, J.; Kürten, A.; Lawler, M. J.; Mai, H.; Mathot, S.; Mauldin, R. L.; Molteni, U.; Nichman, L.; Nieminen, T.; Nowak, J.; Ojdanic, A.; Onnela, A.; Pajunoja, A.; Petäjä, T.; Piel, F.; Quéléver, L. L. J.; Sarnela, N.; Schallhart, S.; Sengupta, K.; Sipilä, M.; Tomé, A.; Tröstl, J.; Väisänen, O.; Wagner, A. C.; Ylisirniö, A.; Zha, Q.; Baltensperger, U.; Carslaw, K. S.; Curtius, J.; Flagan, R. C.; Hansel, A.; Riipinen, I.; Smith, J. N.; Virtanen, A.; Winkler, P. M.; Donahue, N. M.; Kerminen, V. M.; Kulmala, M.; Ehn, M.; Worsnop, D. R. Size-dependent influence of NOx on the growth rates of organic aerosol particles. Sci. Adv. 2020, 6 (22), No. eaay4945. (43) Mentel, T.; Springer, M.; Ehn, M.; Kleist, E.; Pullinen, I.;

Kurtén, T.; Rissanen, M.; Wahner, A.; Wildt, J. Formation of highly oxidized multifunctional compounds: autoxidation of peroxy radicals formed in the ozonolysis of alkenes-deduced from structure-product relationships. *Atmos. Chem. Phys.* **2015**, *15* (12), 6745–6765.

(44) Zhuang, Y.; Cheng, C.; Weng, X.; Chen, J.; Lv, X.; Li, M.; Zhou, Z. Characteristics and Source Apportionment of Atmospheric Volatile Organic Compounds During Emission Control Period in Xiamen. *Chin. J. Anal. Chem.* **2019**, *47*, 890–898.

(45) Niu, Z.; Zhang, H.; Xu, Y.; Liao, X.; Xu, L.; Chen, J. Pollution characteristics of volatile organic compounds in the atmosphere of Haicang District in Xiamen City, Southeast China. *J. Environ. Monit.* **2012**, *14* (4), 1144–1151.

(46) Boy, M.; Hellmuth, O.; Korhonen, H.; Nilsson, E. D.; ReVelle, D.; Turnipseed, A.; Arnold, F.; Kulmala, M. MALTE-model to predict new aerosol formation in the lower troposphere. *Atmos. Chem. Phys.* **2006**, *6* (12), 4499–4517.