Contribution of Methyl Group to Secondary Organic Aerosol Formation from Aromatic Hydrocarbon Photooxidation

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Abstract

The complete atmospheric oxidation pathways leading to secondary organic aerosol remain elusive for aromatic compounds including the role of methyl substituents on oxidation. This study investigates the contribution of methyl group to Secondary Organic Aerosol (SOA) formation during the photooxidation of aromatic hydrocarbon under low NO_x condition by applying methyl carbon labeled aromatic hydrocarbons (¹³C₂) *m*-xylene and (¹³C₂) *p*-xylene. Particle and gas phase oxidation products are analyzed by a series of mass spectrometers (HR-TOF-AMS, PTR-MS and SIFT-MS). The methyl group carbon containing oxidation products partition to the particle-phase at a lower rate than the carbons originating from the aromatic ring as a result of ring opening reactions. Further, the methyl carbon in the original aromatic structure is at least 7 times less likely to be oxidized when forming products that partition to SOA than the aromatic ring carbon. Therefore, oxidation of the methyl group in xylenes exerts little impact on SOA formation in current study. This study provides supporting evidence for a recent finding -- a similarity in the SOA formation and composition from aromatic hydrocarbons regardless of the alkyl substituents.

26 **Key Word**

27 Aromatic hydrocarbon; Methyl substitute; Isotope; Photooxidation; Secondary organic
28 aerosol; HR-ToF-AMS

29 **1. Introduction**

30 Aromatic hydrocarbons are major anthropogenic SOA precursors (Kanakidou et al., 2005;
31 Henze et al., 2008). It is considered that OH-initiated reaction results in ~10% H-abstraction
32 from one methyl group to form a methylbenzyl radical and ~90% OH addition to the aromatic
33 ring to form hydroxycyclohexadienyl radical in methylated aromatic hydrocarbon (Calvert, et
34 al., 2002). However, the mechanism of SOA formation from aromatic hydrocarbons remains
35 uncertain (Hallquist et al., 2009). Identified aromatic photooxidation products include
36 benzaldehyde, nitrophenol, benzoquinone, phthalic acid, unsaturated anhydride, epoxide,
37 carbonyl and carboxylic acid(Forstner et al., 1997; Yu et al., 1997; Smith et al., 1999; Sato et
38 al., 2007; Borrás and Tortajada-Genaro2012; McDonald et al., 2012; Lund et al., 2013).
39 However, summation of identified compounds accounts for less than 50% of the reacted
40 carbon(Forstner et al., 1997; White et al., 2014).The identified products are mostly formed
41 under non-atmospherically relevant high-NO_x conditions (Yu et al., 1997; Forstner et al.,
42 1997; Smith et al., 1999; Kleindienst et al., 1999; Cocker et al., 2001; Jang and Kamens 2001;
43 Fisseha et al., 2004;Sato et al., 2007; Müller et al., 2012; Praplan et al., 2014), based on
44 offline filter sample analysis (Hamilton et al., 2005; Borrás and Tortajada-Genaro2012) or
45 only focused on gas phase products (Wyche et al., 2009).It is noticed that recent studies also
46 suggest that oligomerization attributes to a large portion of SOA componentsduring the
47 photooxidation aromatics photooxidation (Kalberer et al., 2004; Gross et al., 2006;Li et al.,
48 2016a). The combination of isotope labeled SOA precursors with state-of-art instruments
49 enhances the analysis of SOA formation pathways. White et al. (2014) used toluene with all H
50 labeled (Toluene-d₈) or all carbon labeled with ¹³C (Toluene-¹³C₇) to interpret products
51 measured by GC-MS (Gas Chromatography–Mass Spectrometry) and to exclude pretreatment
52 interference in offline filter analysis. Recent studies used isotopically labeled precursors to

study the mixing state of SOA (Hildebrandt et al., 2011; Robinson et al., 2013; Ye, et al., 2016).

Molecular structure exerts a significant impact on SOA formation mechanism and therefore determine SOA yield. Aromatic isomer study indicates that aromatic with alkyl substitutes in *para*- position suppress SOA formation compared with those in *meta* or *ortho* position (Izumi and Fukuyama, 1990; Songet al., 2007; Liet al., 2016b). Exploring the differences in the photooxidation products among different aromatic isomers facilitates the understanding of alkyl substitutelocation impact on SOA formation from aromatics, which is essential to elucidate SOA formation mechanisms from aromatic hydrocarbons.

Xylenes (*m*-, *p*-, and *o*-xylene) are the second most important ambient aromatic hydrocarbons after toluene (Zhou et al., 2011). Xylenes compose fundamental position structures that could be extended to more complicated aromatic structures. SOA formation results from a combination of functionalization, fragmentation and oligomerization (Jimenez et al., 2009; Kroll et al., 2009). It is important to distinguish the role of different functional groups, such as aromatic ring and methyl substitute, during photooxidation. In this study, SOA formation from *m*-xylene and *p*-xylene with methyl group labeled with ^{13}C is investigated to demonstrate the methyl group contribution to SOA formation from aromatics in low NO_x condition. Also, the nitric oxide (NO) contribution to organic nitrate and SOA formation is studied by using isotope labeled ^{15}NO . Real time gas phase and particle phase mass spectrometers (SIFT-MS, PTR-MS and HR-TOF-AMS) are applied to illustrate the distribution of methyl-carbon during xylene photooxidation. This study aims to shed lights on the mechanism of SOA formation from aromatic hydrocarbons.

2. Methods

2.1 Environmental chamber

The UC Riverside/CE-CERT indoor dual 90 m³ environmental chambers were used in this study and are described in detail elsewhere (Carter et al., 2005). Experiments were all conducted at dry conditions ($\text{RH} < 0.1\%$), in the absence of inorganic seed aerosol and with

temperature controlled to 27 ± 1 °C. Two movable top frames were slowly lowered during each experiment to maintain a slight positive differential pressure (~ 0.02 "H₂O) between the reactors and enclosure to minimize dilution and/or contamination of the reactors. 276 pieces of 115 W Sylvania 350BL blacklights are used as light sources for photooxidation. A known volume of high purity liquid hydrocarbon precursor (¹³C₂) *m*-xylene: Sigma-Aldrich, 99% atom ¹³C, (¹²C₂) *m*-xylene: Sigma-Aldrich, $\geq 99.5\%$, (¹³C₂), *p*-xylene: Sigma-Aldrich, 99% atom ¹³C, (¹²C₂) *p*-xylene: Sigma-Aldrich, $\geq 99\%$) was injected through a heated glass injection manifold system and flushed into the chamber with pure N₂. NO or ¹⁵NO (Sigma-Aldrich, 98 atom % ¹⁵N) was introduced by flushing pure N₂ through a calibrated glass bulb filled to a predetermined partial pressure of pure NO. All initial experimental conditions are listed in Table 1.

2.2 Particle and Gas Measurement

Particle phase chemical composition evolution was obtained with a High Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS; Aerodyne Research Inc.) (Canagaratna et al., 2007; DeCarlo et al., 2006). The sample is vaporized by a 600 °C oven followed by 70 eV electron impact ionization. The AMS was switched between a high resolution "W-mode" and a high sensitivity "V-mode". The high resolution "W-mode" allowed for identification of different elemental compositions from each unit mass using the PIKA toolbox (DeCarlo et al., 2006). Isotopic fragment concentrations are analyzed by using peak fitting without the constraint of corresponding parent species. f_x in this study is calculated as the fraction of the organic signal at certain fragments or *m/z*. For example, $f_{\text{CO}_2^+}$ and $f_{\text{C}_2\text{H}_3\text{O}^+}$ are the ratios of the organic signal at CO₂⁺ and C₂H₃O⁺, respectively, to the total organic signal and f_{44} and f_{43} are the percentage of organic fragments at *m/z* 44 and *m/z* 43.

Gas phase composition was determined with a Proton Transfer Reaction Mass Spectrometer (PTR-MS, standard PTR-QMS series, Ionicon Analytik, Austria) (Lindinger et al., 1998) or Selected Ion Flow Tube-Mass Spectrometer (SIFT-MS; Syft Technologies) (Prince et al., 2010). NO_x was monitored by a Thermo Environmental Instruments model 42C chemiluminescence NO_x analyzer.

3. Result

3.1 Contribution of methyl group to significant organic fragments in particle phase products

The m/z 43 ($C_2H_3O^+$) and m/z 44 (CO_2^+) are prominent fragment peaks observed by the AMS during the photooxidation of non-isotopic xylene precursors (Table S1: *m*-xylene 931A $f_{C_2H_3O^+}=14.95\%$ and $f_{CO_2^+}=9.63\%$; *p*-xylene 2087A $f_{C_2H_3O^+}=12.03\%$ and $f_{CO_2^+}=6.72\%$). A significant increase in f_{44} and a decrease in f_{43} are observed in SOA formed from the photooxidation of ^{13}C labeled xylenes (929A *m*-xylene and 2088A *p*-xylene) when comparing those from non-isotopic xylenes (Table 1, Fig. 1) due to the formation of $^{13}CCH_3O^+$ peaks at m/z 44 (Fig. S1 & Fig. S2). The contribution of methyl carbon to each fragment is quantified as

$$P_{^{13}CC_{x-1}H_yO_z} = \frac{[^{13}CC_{x-1}H_yO_z]}{[C_xH_yO_z] + [^{13}CC_{x-1}H_yO_z] + [^{13}C_2C_{x-2}H_yO_z]} \quad (x > 1) \text{ Eq-1a}$$

$$P_{^{13}CH_yO_z} = \frac{[^{13}CH_yO_z]}{[C_xH_yO_z] + [^{13}CH_yO_z]} \quad (x=1) \quad \text{Eq-1b}$$

$$P_{^{13}C_2C_{x-2}H_yO_z} = \frac{[^{13}C_2C_{x-2}H_yO_z]}{[C_xH_yO_z] + [^{13}CC_{x-1}H_yO_z] + [^{13}C_2C_{x-2}H_yO_z]} \quad (x > 1) \text{ Eq-2}$$

where $P_{^{13}CC_{x-1}H_yO_z}$ and $P_{^{13}C_2C_{x-2}H_yO_z}$ are the percentages of isotope containing fragment in fragments with same number of elements; $^{13}CC_{x-1}H_yO_z$ and $^{13}C_2C_{x-2}H_yO_z$ are fragments containing one and two isotope labeled carbons, correspondingly; $[C_xH_yO_z]$, $[^{13}CC_{x-1}H_yO_z]$ and $[^{13}C_2C_{x-2}H_yO_z]$ are fragment intensities of the parent fragment and the isotopic fragments containing one or two isotope carbons, respectively. Large $P_{^{13}CCH_3O}$ is found during the photooxidation of isotope labeled xylenes (Table 2, *m*-xylene, $P_{^{13}CCH_3O} = 71.9\%$; *p*-xylene, $P_{^{13}CCH_3O} = 77.6\%$) indicating a large contribution of methyl carbon to non-acid oxygenates fragments (Ng, et al., 2011). A small fraction (~20-30%) of non-isotope labeled $C_2H_3O^+$ may associate with the fragments containing two ring carbons attached to $-OH$ or oxygen function group with 1 hydrogen shift (e.g. hydroperoxide bicyclic compound or formylmethyl structure). The importance of methyl group to $C_2H_3O^+$ fragments in SOA

agrees with previously observed increases in $f_{C_2H_3O^+}$ with increasing number of methyl groups attached to aromatic ring precursor (Li, et al., 2016a; Sato et al., 2010). One isotope containing $C_2H_3O^+$ or $^{13}CCH_3O^+$ usually composes a carbonyl functional group (-C(O)-) and a methyl group (-CH₃). It is less likely that the isotopic labeled methyl is oxidized to -C(O)- since it is impossible for an aromatic ring carbon with high double bond equivalent (DBE=2) to gain enough hydrogen to form -CH₃. Therefore, the high $P_{^{13}CCH_3O}$ suggests that products contributing to SOA formation are less likely to associate with the oxidation of methyl groups during the photooxidation of aromatic hydrocarbons, especially under the low NO_x conditions studied herein.

The fractions of isotope labeled fragments in highly oxidized components (e.g. CO₂⁺) are further investigated to study the potential of the oxidation in methyl groups. $P_{^{13}CO_2}$ (Eq-1) is calculated by using an isotopic xylene experiment. A slight amount (Table 2, $P_{^{13}CO_2}$ = 11.5%) of $^{13}CO_2$ is observed during the photooxidation of *m*-xylene and little $^{13}CO_2$ (Table 2, $P_{^{13}CO_2}$ = 4.70 %) is detected during the photooxidation of *p*-xylene.

The location of methyl group on aromatic ring may affect the oxidation potential of methyl group as demonstrated in below. However, the low $P_{^{13}CO_2}$ and low $f_{CO_2^+}$ indicate that the oxidation of methyl substitute is of minor importance to SOA bulk composition during xylene oxidation. Therefore, insignificant (within the O/C standard deviation reported) differences are observed in O/C and H/C in SOA formed from *m*-xylene and *p*-xylene (Li et al, 2016b). The higher $P_{^{13}CO_2}$ in SOA formed from *m*-xylene than *p*-xylene suggests that methyl substitute in *m*-xylene is more oxidized compared with that in *p*-xylene during photooxidation. The oxidation of methyl substitute may lead to aromatic ring containing products such as *m*-toluic acid and thereby contributes to the higher $P_{^{13}CO_2}$ in *m*-xylene than *p*-xylene. This agrees with the observation by Forstner et al (1997) of greater amounts of *m*-toluic acid than *p*-toluic acid. It is noted that the higher oxidation of methyl group in *m*-xylene may lead to the formation of less volatile products compared with *p*-xylene,

however, the oxidation of methyl group contributes little to the overall SOA yield due to its small percentage to overall oxidation. On the other hand, it is possible that the hindrance effect of methyl group on further oxidation of ring opening products leads to the SOA yield difference between *m*-xylene and *p*-xylene. Different fractions of methyl substitute may remain in particle phase during the photooxidation of different isomers since aging is a combination of functionalization, fragmentation and oligomerization (see also Sections 3.2 and 4).

CO^+ (m/z 28), which represents carbonyl fraction, is also an important organic fragment in addition to CO_2^+ and $\text{C}_2\text{H}_3\text{O}^+$. It is difficult to separate CO^+ peak from N_2 peak. However, $^{13}\text{CO}^+$ (m/z 29) is potentially available to be separated from other peaks (especially, CHO^+ ; $^{15}\text{NN}=0.0070874*\text{N}_2$). Nevertheless, no significant $f_{^{13}\text{CO}}$ is observed. This suggests methyl carbon in xylenes are rarely oxidized into carbonyl carbon. The lack of observed $f_{^{13}\text{CO}}$ relative to $f_{^{13}\text{CO}_2}$, especially during the photooxidation of *m*-xylene, contradicts the traditionally assumed m/z 28 = m/z 44 (Zhang et al., 2005) used for elemental analysis within the AMS. This implies that the m/z 28 = m/z 44 assumption may need adjustment depending on the SOA precursors used in chamber studies. This finding agrees with recent work by Canagaratna et al (2015).

Only two shifts from m/z 46 (NO_2^+) to m/z 47 ($^{15}\text{NO}_2^+$) and from m/z 30 (NO^+) to m/z 31 ($^{15}\text{NO}^+$), respectively, are observed in the mass spectra obtained from SOA during the photooxidation of *m*-xylene with ^{15}NO compared with non-isotopic experiments. This confirms that all organic nitrates formed during the oxidation of *m*-xylene appear at m/z 46 (NO_2^+) and m/z 30 (NO^+). The less than 10% organic nitrate fragment observed under low NO_x conditions in this study indicates a low contribution of organic nitrate to SOA formation from aromatic precursors in the urban atmosphere. It is noted that the underestimation of organic nitrate by AMS suggested by Farmer et al (2010) is minimized in this work since inorganic nitrate is excluded and ^{15}NO is used to confirm important nitrate fragments.

3.2 Evolution of bulk SOA $^{13}\text{C}/^{12}\text{C}$ during the photooxidation of ^{13}C containing xylenes

The evolution of $^{13}\text{C}/^{12}\text{C}$ in SOA during the photooxidation of $^{13}\text{CH}_3$ -containing xylenes can be used as an indicator of the extent of methyl carbon participation in SOA formation during the photooxidation of xylenes and further suggests aromatic hydrocarbon reaction pathways. A mole ratio of $^{13}\text{C}/^{12}\text{C}$ in particle phase is calculated by using high resolution fragments in HR-TOF-AMS with all significant ($\text{Diff} > 0.05 \text{ Hz}$) peaks included (Fig. 2). It is assumed that $^{12}\text{CO} = ^{12}\text{CO}_2$ and $^{13}\text{C}/^{12}\text{C}$ is nearly constant during photooxidation after initial nucleation (happened around 120 min to 150 min) for all xylenes and conditions studied. The major reaction that impacts $^{13}\text{C}/^{12}\text{C}$ should be fragmentation (aromatic ring opening), which is largely influenced by NO concentration (Jang et al., 2001; Song et al., 2005). The influence of NO on aromatic ring decomposition mostly occurs before nucleation when NO concentration is sufficiently high to dominate NO+RO₂ reaction (Ng et al., 2007; Li et al., 2015). Therefore, it is reasonable to assume a steady $^{13}\text{C}/^{12}\text{C}$ after nucleation.

$^{13}\text{C}/^{12}\text{C}$ under the higher NO_x condition (929A) is larger than that in lower NO_x (928A) condition. It is possible that the higher NO concentration might serve as an impetus for certain methyl-rich ring opening products (e.g., 3,5-dimethyl-2(5H)-furanone ($^{13}\text{C}/^{12}\text{C}=0.4$) instead of 5-methyl-2(5H)-furanone ($^{13}\text{C}/^{12}\text{C}=0.25$)). *p*-Xylene has a higher average $^{13}\text{C}/^{12}\text{C}$ compared with *m*-xylene assuming NO_x impact on *m*-xylene can be extended to *p*-xylene. It is possible that methyl-rich ring retaining products (e.g. bicyclic hydroperoxide and xylenol derivatives with two methyl, $^{13}\text{C}/^{12}\text{C}=0.33$) contribute more to SOA formation from *p*-xylene than that from *m*-xylene and ring opening products from *p*-xylene photooxidation are less likely to further react into low volatility products than that from *m*-xylene (Section 4.1).

3.3 Contribution of methyl group to gas-phase products

A series of gas-phase products are identified during the photooxidation of xylenes under low NO_x conditions (Table 3). Gas-phase mass spectrum shifts during the photooxidation of ^{13}C labeled xylenes compared with that of non-isotope xylenes demonstrate the contribution of

methyl group carbon to corresponding gas-phase products. The difference between the mass spectrum from ^{13}C labeled xylenes and that from non-isotope labeled xylenes represents the number of methyl carbon in each gas-phase products. The carbon composition (number of ^{13}C and ^{12}C) and sources (methyl carbon or aromatic ring carbon) in gas-phase products are identified according to the agreement in the intensities of those gas-phase products between the isotopic runs and non-isotopic runs (Fig. S3 and Fig. S4). Isotope carbons mostly remain as methyl group carbon in gas-phase products. However, the identification of two isotope carbon containing products at MW=120 (MW=122 in isotope experiment) indicating the formation of 4-methylbenzaldehyde, in which one methyl carbon is oxidized into carbonyl carbon. It is also found that carbon in formaldehyde can originate from both methyl and aromatic ring carbons. The contribution of methyl carbon to gas-phase products are calculated as

$$P_{^{13}\text{C},j} = \frac{[j_{^{13}\text{C}}]}{[(j-n)_{^{12}\text{C}}]} \text{Eq-3}$$

where $P_{^{13}\text{C},j}$ is the percentage of isotope containing products in the identified products; $[j_{^{13}\text{C}}]$ is the signal intensity in PTR-MS or SIFT-MS at $m/z=j$ in the isotope containing experiment; $[(j-n)_{^{12}\text{C}}]$ is the signal intensity in PTR-MS or SIFT-MS at $m/z=j-n$ in a parallel non-isotope containing experiment and $n=1$ or 2 depending on the number of isotope carbon at j . ^{13}C contributes to 42.28% and 46.02% of formaldehyde formation during the photooxidation of *m*-xylene and *p*-xylene under the low NO_x condition studied according to Eq-3. The high ^{13}C percentage in volatile oxidized products such as formaldehyde compared with the low ^{13}C percentage in oxidized products in aerosol phase demonstrates that the oxidation of methyl substitute is more likely to happen in gas phase after the aromatic ring opening reaction. Most identified products observed in this study are consistent with previous studies and agree with the mechanisms proposed therein (Yu et al., 1997a; Yu et al., 1997b; Smith et al., 1999; Jang and Kames 2001; Jenkin et al, 2003; Bloss et al 2005; Borrás and Tortajada-Genaro 2012; Müller et al, 2012). The current study also verifies that the formation of several gas phase products depends on methyl group location on aromatic ring including

2,4-dimethylfuran (meta only), maleic anhydride (meta only), 3,5-Dimethyl-2(5H)-furanone (meta only) and 4-methylbenzaldehyde (para only). The formation of nitric acid is also identified by using ^{15}N labeled NO.

4. Discussion

4.1 The extent of oxidation in methyl carbon and aromatic ring carbon

The contribution of methyl carbon and ring carbon to overall oxygen content is quantified as

$$O: ^{12}C = \sum_i [(1 - P_i)\alpha_i(O: ^{12}C)_{i,1} + P_i\alpha_i(O: ^{12}C)_{i,2}] \text{Eq-4}$$

$$O: ^{13}C = \sum_i P_i\alpha_i(O: ^{13}C)_i \text{Eq-5}$$

where $O: ^{12}C$ and $O: ^{13}C$ are the adjusted $O:C$ associated with non-isotope and isotope carbon, respectively; i is a specific organic fragment; P_i is the percentage of isotope containing fragments at i and is already defined in Eq-1 and Eq-2; α_i is the mass to mole adjusting coefficient, which is calculated as reciprocal of molecular weight of i ; $(O: ^{12}C)_{i,2}$ and $(O: ^{12}C)_{i,1}$ are mole ratios of $O:C$ assigned to ^{12}C at identified fragments i containing ^{13}C or not, respectively; and $(O: ^{13}C)_i$ is the mole ratio of $O:C$ assigned to ^{13}C at identified fragments i . The ratio of $O: ^{12}C$ and $O: ^{13}C$ ($R_{O,12/13}$) suggests the relative importance of aromatic ring carbon and methyl carbon to overall oxidation. Three major oxygenated fragments ($\text{C}_2\text{H}_3\text{O}^+$, CO_2^+ and CO^+) are included in the oxygen contribution calculation and corresponding P_i and $(O:C)_i$ are listed in Table 2 and Table S1. It is found that $R_{O,12/13}$ is ~21 and ~74 in the photooxidation of methyl carbon labeled *m*-xylene and *p*-xylene, respectively. This suggests that oxidized ring carbon contributes to at least 20 times more to overall oxygen than methyl carbon in SOA during the photooxidation of xylene under low NO_x condition despite only being three times higher in the parent xylene. Therefore, the potential of oxidation of each ring carbon is 7 and 24 times higher than methyl carbon for *m*-xylene and *p*-xylene, respectively. Our recently published work observed that the aromatic ring obtains a near constant amount of oxygen (~4) during photooxidation under low NO_x conditions, regardless of the number or size of alkyl substitute number (Li et al., 2016c). This work further confirms

that the aromatic ring is a driving force to form low volatility products during the photooxidation of aromatic hydrocarbon and therefore aromatic ring is much critical to SOA formation than alkyl substitute. ^{13}C labeled methyl carbons mostly coexistent with high H:C fragments in HR-TOF-AMS supporting its high contribution to overall H:C in SOA components and therefore consistent with a recent study demonstrating that alkyl substitute number determines H/C ratio (Li et al., 2016c).

4.2 Molecular structure impact on photooxidation pathways

A lower $^{13}\text{C}/^{12}\text{C}$ is observed in SOA formed from the photooxidation of methyl labeled *m*-xylene than *p*-xylene. A lower $^{13}\text{C}/^{12}\text{C}$ indicates a lower content or contribution of methyl substitutes in SOA. Previous studies found that SOA yield from *m*-xylene is higher than that from *p*-xylene (Song et al., 2007; Li et al., 2016b). This indicates that the lack of methyl groups, possibly by ring opening pathways, further enhances select reactions (e.g. oligomerization (Kalberer et al., 2004; Li et al., 2016a)) to produce low volatility products. A possible explanation for the differences in $^{13}\text{C}/^{12}\text{C}$ and SOA yield between *m*-xylene and *p*-xylene is that oligomerization from ring opening products (e.g. maleic anhydride and 5-methyl-2(5H)-furanone, which lowers $^{13}\text{C}/^{12}\text{C}$ compared with ring-retaining products), is favored in SOA formation from *m*-xylene while ring-retaining products are favored in that from *p*-xylene. According to a higher single SOA fragment $^{13}\text{CO}_2^+$ but lower bulk $^{13}\text{C}/^{12}\text{C}$ from isotope labeled *m*-xylene compared with *p*-xylene (section 3.2), the contribution of methyl oxidation products such as toluic acid to SOA formation is considered to be substantially lower than that from the oligomerization of ring opening products.

5. Atmospheric Implication

The alkyl substitute on aromatic hydrocarbon may increase the complexity of SOA precursor and estimation of aromatic hydrocarbon photooxidation. However, this study confirms that aromatic ring is a driving force to form low volatility products during the photooxidation of aromatic hydrocarbon and alkyl substitute contributing less oxidized low volatility products compared with aromatic ring carbon. The methyl carbon contributes less to the particle phase

products than gas phase products according to the decrease in $^{13}\text{C}/^{12}\text{C}$ from SOA precursor formula to SOA composition and corresponding gas phase and particle phase mass spectrum. SOA formation depends on the gas-particle partitioning of the oxidation products. Precursor functional groups, which are oxidized to form low volatility products, exerts dominating impact on SOA formation. However, alkyl substitute is either not significantly oxidized in particle phase or oxidized into high volatility gas phase products. Therefore, the alkyl substitute exerts minimum impact on SOA formation. This study serves as a powerful proof for the recent finding that aromatic hydrocarbon obtains ~4 oxygen per aromatic ring regardless of alkyl substitute number (Li et al., 2016c). Besides, the impact of molecular structure on the photooxidation of aromatic hydrocarbon is confirmed by isotope experiments. Oligomerization in addition to retaining product formation is proposed to explain differences in the SOA formation from *m*-xylene and *p*-xylene. In addition, the application of isotope SOA precursor in chamber studies is an innovative method to explore the role of different functional group during atmospheric aging, which can be applied to future SOA formation studies.

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Table 1 Experimental Conditions

Run ID	Compounds ^a	HC _i ^b ppb	NO _{x,i} ^b ppb
928A	(¹³ C ₂) <i>m</i> -xylene/NO	80.5	9.9
929A	(¹³ C ₂) <i>m</i> -xylene/NO	85.2	43.8
931A	<i>m</i> -xylene/NO	75.4	43.6
932A	<i>m</i> -xylene/ ¹⁵ NO	86.2	50.0*
2087A	<i>p</i> -xylene/NO	69.4	16.4
2088A	(¹³ C ₂) <i>p</i> -xylene/NO	66.1	18.7

Note: a) Compounds are none isotope containing unless they are labeled; b) Initial concentration; *Target concentration

Table 2 Contribution of methyl substitute (¹³C) to major particle phase products during aromatic hydrocarbon photooxidation

m/z	Fragments	Isotope fragments	Isotope m/z	Average P _{13C} ^a	
				<i>m</i> -xylene	<i>p</i> -xylene
43	C ₂ H ₃ O	¹³ CCH ₃ O	44	71.9%	77.6%
44	CO ₂	¹³ CO ₂	45	11.5%	4.70% ^b
28	CO	¹³ CO	29	0% ^c	0% ^c

Note: a) Average P_{13C} is calculated according to time series isotope containing fragment percentage value (Eq-1), starting from peak suspended particle concentration (HR-TOF-AMS Org > 2μg·m⁻³ for *m*-xylene and Org > 0.5μg·m⁻³ for *p*-xylene); b) Data is noisy and is difficult to find a trend; c) Assume ¹²CO = ¹²CO₂, average ¹³C /(¹²C+¹³C) < 1e⁻¹⁵

Table 3 Contribution of methyl substitute (¹³C) to significant gas phase products during xylene photooxidation

MW ^a	# ¹³ C ^b	meta	para	Proposed Formula	Proposed product
30	0 or 1	✓	✓	CH ₂ O	formaldehyde
43	1	✓	✓	C ₂ H ₃ O ⁺	CH ₃ C(O)-(O)R ¹
44	0	✓		C ₂ H ₄ O	ethylene oxide or ethenol ^c
	1	✓		C ₂ H ₄ O	acetaldehyde
45	0	✓		HNO ₃	nitic acid ² or nitrate fragments ³
46	0	✓	✓	CH ₂ O ₂	formic acid
58	0	✓		C ₂ H ₂ O ₂	glyoxal
60	0	✓		C ₂ H ₄ O ₂	glycolaldehyde ⁴
	1	✓	✓	C ₂ H ₄ O ₂	acetic acid
72	1	✓	✓	C ₃ H ₄ O ₂	methyl glyoxal
74	1		✓	C ₃ H ₆ O ₂	acetol ⁴
86	0	✓		C ₃ H ₂ O ₃	oxomalonaldehyde
	1		✓	C ₄ H ₆ O ₂	2R,3S)-3-methyl-2-oxiranecarbaldehyde ⁴
	2	✓		C ₅ H ₁₀ O	Not sure
96	2	✓		C ₆ H ₈ O	2,4-dimethylfuran
98	0	✓		C ₄ H ₂ O ₃	maleic anhydride
98	1	✓	✓	C ₅ H ₆ O ₂	α-angelic lactone; 3-methyl-2(5H)-furanone; 4-keto-2-pentenal
112	0	✓		C ₅ H ₄ O ₃	Not sure
	1	✓	✓	C ₅ H ₄ O ₃	citraconic anhydride
	2	✓		C ₆ H ₈ O ₂	3,5-dimethyl-2(5H)-furanone
120	2		✓	C ₈ H ₈ O	4-methylbenzaldehyde

Note: a) Molecular weight of gas phase products or fragments identified in non-isotopic experiment; b) Number of ¹³C in a specific formula according to the shift in mass spectrum, 0-no shift, no ¹³C, 1- one m/z shift, one ¹³C, 2- two m/z shift, two ¹³C; c) Not confirmed; 1) Spanel, et al 1997; 2) Grieshop, et al., 2009; 3) Müller, et al., 2012; 4) Yu, et al., 1997

Fig. 1 Comparison of organic mass spectrum in SOA formed from the photooxidation of xylenes: a) ^{12}C (931A) and ^{13}C (929A) *m*-xylene; b) ^{12}C (2087A) and ^{13}C (2088A) *p*-xylene under low NO_x Conditions (Underline m/z number indicates abundant ^{13}C containing fragment); Note: the intensity of $^{12}\text{CO}^+$ (m/z 28) is assumed equal to that of $^{12}\text{CO}_2^+$ (m/z 44) due to the high intensity of N_2^+ signal at $m/z=28$.

Fig. 2 Average $^{13}\text{C}/^{12}\text{C}$ of SOA formed during the photooxidation of ^{13}C *m*-xylene (928A and 929A) and ^{13}C *p*-xylene (2088A) under low NO_x Conditions