



Contribution of methyl group to secondary organic aerosol formation from aromatic hydrocarbon photooxidation



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HIGHLIGHTS

- Isotope labeled precursors facilitate the understanding of SOA formation.
- Majority of aromatic methyl carbons oxidized to form volatile products.
- Aromatic ring is the driving force for SOA formation from xylenes.

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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 substitutes on oxidation. This study investigates the contribution of methyl group to Secondary Organic Aerosol (SOA) formation during the photooxidation of aromatic hydrocarbons 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 substitutes.

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1. Introduction

Aromatic hydrocarbons are major anthropogenic SOA precursors (Kanakidou et al., 2005; Henze et al., 2008). It is considered that OH-initiated reaction results in ~10% H-abstraction from one methyl group to form a methylbenzyl radical and ~90% OH addition to the aromatic ring to form hydroxycyclohexadienyl radical in methylated aromatic hydrocarbon (Calvert et al., 2002). However, the mechanism of SOA formation from aromatic hydrocarbons

remains uncertain (Hallquist et al., 2009). Identified aromatic photooxidation products include benzaldehyde, nitrophenol, benzoquinone, phthalic acid, unsaturated anhydride, epoxide, carbonyl and carboxylic acid (Forstner et al., 1997; Yu et al., 1997; Yu and Jeffries, 1997; Smith et al., 1999; Sato et al., 2007; Borrás and Tortajada-Genaro, 2012; McDonald et al., 2012; Lund et al., 2013). However, summation of identified compounds accounts for less than 50% of the reacted carbons (Forstner et al., 1997; White et al., 2014). The identified products are mostly formed under non-atmospherically relevant high-NO_x conditions (Yu and Jeffries, 1997; Forstner et al., 1997; Smith et al., 1999; Kleindienst et al., 1999; Cocker et al., 2001; Jang and Kamens, 2001; Fisseha et al., 2004; Sato et al., 2007; Müller et al., 2012; Praplan et al., 2014), based on offline filter sample analysis (Hamilton et al., 2005; Borrás and Tortajada-Genaro, 2012) or only focused on gas phase products

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(Wyche et al., 2009). It is noticed that recent studies also suggest that oligomerization attributes to a large portion of SOA components during the photooxidation aromatics photooxidation (Kalberer et al., 2004; Gross et al., 2006; Li et al., 2016a). The combination of isotope labeled SOA precursors with state-of-art instruments enhances the analysis of SOA formation pathways. White et al. (2014) used toluene with all H labeled (Toluene- d_8) or all carbon labeled with ^{13}C (Toluene- $^{13}C_7$) to interpret products measured by GC-MS (Gas Chromatography–Mass Spectrometry) and to exclude pretreatment 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; Song et al., 2007; Li et al., 2016b). Exploring the differences in the photooxidation products among different aromatic isomers facilitates the understanding of alkyl substitute location 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 (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 ($^{13}C_2$) *m*-xylene: Sigma-Aldrich, 99% atom ^{13}C , ($^{12}C_2$) *m*-xylene: Sigma-Aldrich, ≥99.5%, ($^{13}C_2$), *p*-xylene: Sigma-Aldrich, 99% atom ^{13}C , ($^{12}C_2$) *p*-xylene: Sigma-Aldrich, ≥99%) was injected through a heated glass injection manifold system and flushed into the chamber with pure N₂. NO or ^{15}NO (Sigma-Aldrich, 98 atom % ^{15}N) 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

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 ^c
2087A	<i>p</i> -xylene/NO	69.4	16.4
2088A	($^{13}C_2$) <i>p</i> -xylene/NO	66.1	18.7

^a Note: Compounds are none isotope containing unless they are labeled.

^b Initial concentration.

^c Target concentration.

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, $f_{CO_2^+}$ and $f_{C_2H_3O^+}$ are the ratios of the organic signal at CO_2^+ and $C_2H_3O^+$, 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

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

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