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Characterization of secondary organic aerosol from photo-oxidation of gasoline exhaust and specific sources of major components[☆]

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ABSTRACT

To further explore the composition and distribution of secondary organic aerosol (SOA) components from the photo-oxidation of light aromatic precursors (toluene, *m*-xylene, and 1,3,5-trimethylbenzene (1,3,5-TMB)) and idling gasoline exhaust, a vacuum ultraviolet photoionization mass spectrometer (VUV-PIMS) was employed. Peaks of the molecular ions of the SOA components with minimum molecular fragmentation were clearly observed from the mass spectra of SOA, through the application of soft ionization methods in VUV-PIMS. The experiments comparing the exhaust-SOA and light aromatic mixture-SOA showed that the observed distributions of almost all the predominant cluster ions in the exhaust-SOA were similar to that of the mixture-SOA. Based on the characterization experiments of SOA formed from individual light aromatic precursors, the SOA components with molecular weights of 98 and 110 amu observed in the exhaust-SOA resulted from the photo-oxidation of toluene and *m*-xylene; the components with a molecular weight of 124 amu were derived mainly from *m*-xylene; and the components with molecular weights of 100, 112, 128, 138, and 156 amu were mainly derived from 1,3,5-TMB. These results suggest that C₇–C₉ light aromatic hydrocarbons are significant SOA precursors and that major SOA components originate from gasoline exhaust. Additionally, some new light aromatic hydrocarbon-SOA components were observed for the first time using VUV-PIMS. The corresponding reaction mechanisms were also proposed in this study to enrich the knowledge base of the formation mechanisms of light aromatic hydrocarbon-SOA compounds.

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1. Introduction

Heavy haze pollution episodes in megacities have serious negative impacts on human health, climate, and visibility (Carmichael et al., 2009; Davidson et al., 2005; Wang et al., 2014). A significant fraction of the total ambient aerosol mass in megacities is secondary organic aerosol (SOA) (Baltensperger et al., 2005; Cao et al., 2003; Duan et al., 2007; Hagler et al., 2006; Hallquist et al., 2009; He et al., 2001). Light aromatic hydrocarbons (C₆–C₉) from vehicle exhaust, a vital class of SOA precursors, have recently been estimated to be responsible for 60–85% of the SOA formation in idling emissions (Kleindienst et al., 2002; Nordin et al., 2013). Thus,

the rapid increase in the number of vehicles is a growing concern because vehicle exhaust emissions are important sources of anthropogenic SOA in megacities, greatly affecting haze pollution (Zhang et al., 2017).

The photo-oxidation of light aromatic hydrocarbons under high/low-NO_x conditions (benzene, toluene, xylenes, and trimethylbenzene (TMB)) have been conducted through smog chamber experiments (Hildebrandt et al., 2009; Ng et al., 2007b; Sato et al., 2007; Song et al., 2007; Wyche et al., 2009). In order to understand the mechanisms of one-component aromatic SOA formation, the composition and molecular structure of SOA have been identified and proposed, respectively, in recent studies (Huang et al., 2014; Jang and Kamens, 2001; Loza et al., 2012; Pan and Wang, 2014; Praplan et al., 2014). However, it is still unclear whether some unknown SOA components could be formed and observed only in mixture precursors-SOA compounds due to interactions between different SOA components. Therefore, it will be very necessary to investigate the SOA composition of mixture precursor to further

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understand the formation mechanism of exhaust-SOA.

To further understand the contribution of these aromatic precursors in the formation of exhaust-SOA, numerous laboratory chamber experiments have recently been conducted in an attempt to mimic the SOA formation from the photochemical aging of gasoline/diesel vehicle exhaust with different vehicle types, models, and operating conditions. Nordin et al. investigated SOA formation in the gasoline exhaust of three idling passenger vehicles (Euro 2–Euro 4) and found that C₆–C₉ light aromatics contributed up to 60% of the formed SOA (Nordin et al., 2013). Liu et al. suggested that traditional single-ring aromatic precursors and naphthalene could explain 51–90% of the formed SOA of the two idling light-duty gasoline vehicles (LDGVs) (Euro 1 and Euro 4) (Liu et al., 2015). Based on assuming equivalence in SOA precursors between the fuel and exhaust, Gentner et al. suggested that diesel exhaust was responsible for 65%–90% of vehicular-derived SOA, with substantial contributions from aromatic and aliphatic hydrocarbons (Gentner et al., 2012). However, Gordon et al. suggested that only a small fraction of SOA, formed during the photo-oxidation of dilute LDGV exhaust, was explained by single-ring aromatic compounds, and they hypothesized that the unexplained SOA production may come from intermediate volatility organic compounds (IVOCs) (Gordon et al., 2014a, 2014b). Zhao et al. also proposed that IVOCs are estimated to produce as much or more SOA than single-ring aromatics, about 5 times that produced from single-ring aromatics (Zhao et al., 2014). Therefore, these experimental results were not always consistent with each other. Moreover, current models based on known precursors also fail to explain the substantial SOA from vehicle emissions due to a large proportion of unspiciated SOA precursors. This could be attributed to highly complex SOA compounds and the corresponding formation mechanisms. For example, some studies have shown that the SOA yield and the SOA formation process were influenced by NO_x concentrations and suggest the importance of the reactions of HO₂ and RO₂ radicals under low-NO_x conditions in SOA formation of aromatics (Camredon et al., 2007; Kessler et al., 2011; Ng et al., 2007a, 2007b; Song et al., 2005; Wyche et al., 2009; Ziemann and Atkinson, 2012). Therefore, the characterization and distribution of SOA composition formed via the reactions of HO₂ and RO₂ radicals under low-NO_x conditions are very necessary to understand the complex formation mechanism of SOA.

Over the past few years, some chamber experiments have focused on identifying the molecular composition of exhaust-SOA, using real-time high-resolution time-of-flight aerosol mass spectrometry (HR-TOF-AMS) (Liu et al., 2015; Nordin et al., 2013). A direct comparison of key organic signals at $m/z = 43$ (C₂H₃O⁺) and $m/z = 44$ (CO₂⁺) in HR-TOF-AMS measurements, along with the O:C ratio and the overall mass spectrum, were employed to investigate the oxidation process of SOA (Aiken et al., 2008; Lanz et al., 2007). However, the shortcomings of the extensive fragmentation of molecules, which is caused by using traditional electron ionization (EI), make distinguishing the organic constituents of SOA extremely difficult. Thus, this online aerosol mass spectrometry is not suitable for investigating the relative distribution of SOA composition of different SOA precursors in vehicle exhaust nor the contribution of important SOA formed from the photo-oxidation of light aromatic hydrocarbons to exhaust-SOA.

In this study, we selected toluene (>99%, Sigma Aldrich), *m*-xylene (>99%, Sigma Aldrich), and 1,3,5-trimethylbenzene (1,3,5-TMB) (>99%, Sigma Aldrich) in gasoline exhaust as SOA precursors for the analysis of SOA formed in photo-oxidation chamber experiments under low-NO_x conditions using vacuum ultraviolet photoionization mass spectrometer (VUV-PIMS). The aim of this study was to investigate: (1) the similarities between the chemical composition of SOA from gasoline vehicle exhaust and C₇–C₉ light

aromatic hydrocarbons and (2) the relative distribution of SOA composition from C₇–C₉ light aromatic hydrocarbons.

2. Materials and methods

2.1. Experimental setup

The photochemical aging experiments were carried out in a 1.2-m³ smog chamber at 25 °C. Eight 254-nm UV lamps (1.2-m long, 60 W Philips/10R BL, Royal Dutch Philips Electronics Ltd, the Netherlands) surrounded the Teflon bag and were used as a light source. One stainless steel fan was installed inside the reactor to guarantee a well-mixed mixture of the introduced gas species and the oxidants within 60 s. Prior to each experiment, the reaction chamber was cleaned several times and filtered with air produced by a zero-air generator (XYA-100LGZ, Shanghai Xi You Analytical Instrument Co., Ltd.), which guaranteed that the residual total hydrocarbon and SOA particles in the chamber were less than 5 ppbv and 0.5 μg m⁻³, respectively. Given that the distribution of light aromatics in the exhaust from a motorcycle (HONDA, WH11OT-A engine) was quite similar to that in the exhaust from the Beijing taxi (see Fig. S1 in the Supporting Information; SI hereafter), a motorcycle running under idling conditions was used to generate gasoline vehicle exhaust. The motorcycle was fuelled with gasoline (Chinese Grade 95#), which complies with the Euro IV gasoline fuel standard.

2.2. Experimental procedure

Prior to each experiment, the reactor chamber was flushed with filtered air at least five times until no residual hydrocarbons, NO_x, O₃, or particles were detected in the reactor. For the photo-oxidation of gasoline exhaust, the motor engine was allowed to run for approximately 3 min before the introduction of exhaust. Gasoline exhaust was injected into the reactor for 10 s through stainless steel bellows after half of the volume of the chamber had been filled with filtered air. Subsequently, the chamber was diluted with filtered air to its maximum volume. After introducing the exhaust, the relative humidity in the chamber was observed to be ~19% in the exhaust experiments. Next, 10 μL of hydrogen peroxide (30% by weight in water, Sigma Aldrich) was injected into the chamber, with a stream of air serving as a hydroxyl radical (OH) source. After allowing several minutes for equilibration, the lights were turned on. The mass concentration of exhaust-SOA became stable after 35 min of irradiation. SOA particles were collected immediately with the pre-cleaned quartz filter when the mass concentration of SOA was observed to be stable.

In the photo-oxidation experiments, toluene, *m*-xylene, 1,3,5-TMB, and their mixture were introduced into the chamber using a 10-μL microsyringe. For better comparison with the experiments results of exhaust-SOA and light aromatic-SOA, SOA in these experiments were also collected after 35 min of irradiation. The relative humidity in aromatic mixture experiments were also controlled at 19% to ensure parallel experiments. Three repetitive experiments were conducted for each type of experiment. The initial experimental conditions are shown in Table 1.

2.3. Characterization of gas- and particle-phase chemical compositions and particle sizes

A newly built vacuum ultraviolet photoionization mass spectrometer (VUV-PIMS) was used to monitor the gas-phase organic species in exhaust online and characterize SOA components offline. The VUV radiation, one of the soft ionization methods that can minimize molecular fragmentation, was used in VUV-PIMS. The

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