Formation mechanism of secondary organic aerosol from ozonolysis of gasoline vehicle exhaust[☆]

Bo Yang [a, *], Pengkun Ma [a, b], Jinian Shu [a, b], Peng Zhang [a, b], Jingyun Huang [a, b], Haixu Zhang [a, b]

[a] State Key Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] National Engineering Laboratory for VOCs Pollution Control Material & Technology, University of Chinese Academy of Sciences, Beijing 100049, China

ABSTRACT

Gasoline vehicles are a major source of anthropogenic secondary organic aerosols (SOAs). However, current models based on known precursors fail to explain the substantial SOAs from vehicle emissions due to the inadequate understanding of the formation mechanism. To provide more information on this issue, the formation of SOAs from ozonolysis of four light-duty gasoline vehicle exhaust systems was investigated with a vacuum ultraviolet photoionization mass spectrometer (VUV-PIMS). Remarkable SOAs formation was observed and the SOAs were primarily aliphatic alkenes. PI mass spectra of the SOAs from all vehicles exhibited similar spectral patterns (a regular mass group with m/z at 98, 112, 126 …). Interestingly, most carbonyl products of aliphatic alkenes observed as major gaseous products have specific molecular weights, and the main formation pathway of SOAs can be explained well using aldol condensation reactions of these carbonyls. This is a direct observation of the aldol condensation as a dominated pathway for SOAs formation, and the first report on the composition and formation mechanism of the SOAs from the ozonolysis of gasoline vehicle exhaust is given. The study reveals that low molecular weight alkenes may play a more significant role in vehicle-induced SOAs formation than previously believed. More importantly, the PI mass spectra of SOAs from vehicles show similarities to the field aerosol sample mass spectra, suggesting the possible significance of the aldol condensation reactions in ambient aerosol formation. Since carbonyls are a major degradation product of biogenic and anthropogenic VOCs through atmospheric oxidation processes, the mechanism proposed in this study can be applied more generally to explain aerosol formation from the oxidation of atmospheric hydrocarbons.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Secondary organic aerosols (SOAs) are the largest component of the ambient organic aerosol budget, accounting for approximately two-thirds of the total organic aerosols in urban areas (Jimenez et al., 2009; Zhang et al., 2010; Stone et al., 2009). The use of petroleum-derived fuels is an important source of nonmethane organic gases (NMOG) that react to form SOAs in the atmosphere (Borbon et al., 2013; Liu et al., 2012). In some recent studies, gasoline emissions were predicted to contribute far more SOAs mass than diesel emissions (Bahreini et al., 2012; Jathar et al., 2017). The investigation of the chemical composition and formation mechanism of SOAs induced by gasoline exhaust is crucial to evaluate its effects on human health and the climate.

SOAs formation from the photooxidation of dilute gasoline vehicle emissions or simulated automobile exhaust has been investigated extensively using smog chambers (Kleindienst et al., 2002; Liu et al., 2015; Nordin et al., 2013; Platt et al., 2013; Presto et al., 2014; Tkacik et al., 2014). Traditionally, SOAs formation from vehicle emissions was mainly attributed to light aromatic hydrocarbons (Odum et al., 1997). The contribution of aromatic or light aromatic precursors to SOAs was variously estimated to be 60%, 50–90%, and 75–85%, respectively, from three investigations using different exhaust sources (Kleindienst et al., 2002; Liu et al., 2015; Nordin et al., 2013). However, Platt et al. suggested that

light aromatics and naphthalene only account for <20% of observed SOAs production (Platt et al., 2013). Similarly, some recent investigations highlighted that speciated SOAs precursors (single-ring aromatics, polycyclic aromatic hydrocarbons (PAHs), and alkanes) only explain a small fraction of the SOAs formed from vehicle emissions, while unspeciated SOAs precursors, which were assigned as certain semi-volatile and intermediate-volatility organic compounds (SVOCs and IVOCs), contribute the largest proportion of predicted SOAs (Robinson et al., 2007; Gordon et al., 2013; Platt et al., 2013; Tkacik et al., 2014; Zhao et al., 2014). Using a source-specific parameterization model, Jathar et al., 2014 predicted that more than 80% of the SOAs from combustion emissions was from unspeciated organics. Zhao et al., 2017 investigated SOAs formation by oxidizing gasoline vehicle exhaust and revealed that IVOCs and SVOCs contributed only ~5% of the NMOG emissions but 45—76% of the predicted SOAs. After investigating SOAs formation from fifteen light-duty gasoline vehicles ranging from 1987 to 2011, Gordon et al., 2014 concluded that traditional precursors could explain the SOAs from older vehicles, while unspeciated organics were responsible for the majority of SOAs from newer vehicles. To better understand SOAs formation from gasoline vehicle exhaust and its potential contribution to atmospheric organic aerosols, more mechanistic information is needed.

Alkenes, as a reactive species, constitute from 8 to 25% (vol %) or 6—33% (wt %) of gasoline vehicle exhaust, which varies among different vehicle models and driving conditions (Gentner et al., 2013; Guo et al., 2011; Huang et al., 2015; Liu et al., 2008; Wang et al., 2013). These alkenes accounted for only approximately 15% in the mixing ratio of VOCs but provided nearly 75% of the reactivity of ambient VOCs in Beijing, and these alkenes were mainly from vehicle exhaust and gasoline evaporation (Shao et al., 2005). Previous studies have shown that the ozonolysis of some small or biogenic alkenes could form low-volatile organic compounds (LVOCs) and oligomers that play an important role in SOAs formation (Gao et al., 2004; Heaton et al., 2007; Hall and Johnston, 2011; Sadezky et al., 2008; Sakamoto et al., 2013; Tolocka et al., 2004; Walser et al., 2008). We can expect that the ozonolysis of alkenes in vehicle exhaust may also produce substantial LVOCs and oligomers that contribute to SOAs formation. Since O_3 is a ubiquitous oxidant also generated in the photooxidation of vehicle exhaust, it is necessary to investigate SOAs from the ozonolysis of alkenes in vehicle exhaust. However, little research has been performed on this subject.

In this study, SOAs formation from the ozonolysis of exhaust from four idling light-duty gasoline vehicles was investigated in a smog chamber. The composition of the reactive gaseous organics and generated SOAs was analyzed with a sensitive vacuum ultraviolet photoionization mass spectrometer (VUV-PIMS), which can provide additional information compared to commonly used commercial instruments. The results of this study improve the understanding of the composition and formation mechanism of SOAs from vehicle emissions, both of which are linked to the explanation of anthropogenic pollution in the urban environment.

2. Materials and methods

2.1. Vehicles and instruments

Four light-duty gasoline vehicles with brands originating from America, Germany, Korea, and Japan were used, which are represented as Vehicles I, II, III, and IV in this study. Details of the individual vehicles are listed in Table 1.

A UV lamp O_3 generator (NBF30/W) was employed to produce O_3 by passing a flow (0.3 L min^{-1}) of oxygen/argon gas mixture through a UV lamp. An O_3 monitor (model 205, 2B Technologies)

was used to measure the O_3 concentration. A scanning mobility particle sizer (SMPS; TSI Inc., classifier model 3081, CPC model 3010) was used to measure the size distribution and particle mass concentration of the SOAs. A laboratory-built VUV-PIMS was used on-line to monitor the gas-phase organic species and off-line to characterize SOA components (Sun et al., 2015). In the VUV-PIMS, organic vapor was photoionized with VUV light radiated from a radio frequency (RF) powered krypton lamp. The photon flux was ~5 × 10^{14} photon s^{-1}, and the photon energies were 10.0 eV (~80%) and 10.6 eV (~20%). The mass resolution of the PIMS is ~300. The PIMS is a quantitative instrument; however, it needs calibration with the standard sample. The sensitivity of the PIMS to an analyte depends on the photoionization efficiency of the analyte. The detection limits of the VUV-PIMS to chain alkenes, cycloalkanes, and light aromatics were estimated to be approximately 0.7, 0.4, and 0.1 ppbv, respectively, by using isoprene, 1,3-cyclohexadiene, and benzene as reference compounds.

2.2. Experiment procedure

Experiments were conducted under ambient pressure and room temperature (297 ± 2 K). The reaction chamber consisted of an open head stainless steel drum (50 cm diameter × 60 cm height) covered by a Teflon film bag (50 cm diameter × 50 cm length) with a total volume of 200 L. A small fan placed at the bottom of the chamber was used to rapidly mix reactants. Before each experiment, the reaction chamber was cleaned several times with filtered air produced by a zero air generator (XYA-100LGZ, Shanghai XiYou Analytical Instrument Co., Ltd.). The residual total hydrocarbon and airborne particles in the chamber were reduced to less than 10 ppbv and 0.5 μg m^{-3}, respectively. Gasoline vehicle exhaust was generated from the vehicle running under idling conditions. The entire raw exhaust was directly injected into the reaction chamber through a stainless-steel tube after the engine had been running for ~3 min. The injection process took 10—20 s when the chamber was filled to half of its volume. Subsequently, the chamber was diluted with filtered air to its maximum volume. The temperature of the exhaust within the chamber is decreased to room temperature (~297 K) before the ozonolysis experiments. The relative humidity in the chamber was estimated to be >50%.

The gas-phase organics and particle mass concentrations were monitored by the VUV-PIMS and SMPS directly with stainless-steel and conductive tubing, respectively, throughout the experiment. To minimize vapor loss, the sampling tube used to determine the gaseous species was heated to ~60 °C. The mass spectrum of the gas-phase organics was recorded at 11 s intervals (10 s for acquisition and 1 s for data file storage). The particles measured by SMPS ranged in size from 15 to 673 nm and were at the given density of 1.4 g cm^{-3}. The particle wall loss in ~30 min was measured to be ~10% and the vapor loss during the same period was negligible. The particle and vapor wall losses were ignored in this study. After the concentrations of the gas-phase organics and primary particle masses stabilized (0.5—1.7 μg m^{-3}), O_3 was introduced to the chamber with a mixing concentration of ~500 ppbv. The total consumed alkenes concentration was estimated by monitoring the decay of individual species, which were 50—1200 ppbv varying between different vehicles. The sensitivity of the VUV-PIMS towards alkenes is ~15 counts ppbv^{-1} in 10 s of sampling. The particle formation was observed in each experiment with maximal mass concentrations of 5—2000 μg m^{-3}. Fig. S1 shows the mass concentrations of primary aerosols and the increase of secondary aerosols in an ozonolysis experiment. When the mass concentration of particles reached its maximum, the particles in the chamber were collected with a pre-cleaned quartz filter (47 mm, PALL Corporation) using a metallic membrane support coupled with a