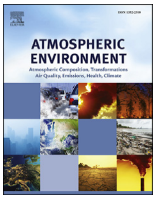
Atmospheric Environment 164 (2017) 71–84

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv



Influence of NH_3 on secondary organic aerosols from the ozonolysis and photooxidation of α-pinene in a flow reactor

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HIGHLIGHTS

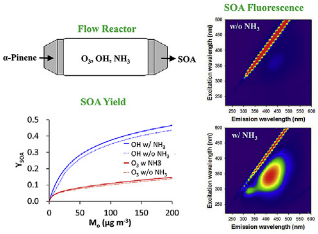
- A new flow reactor (ID 15 cm x L 70 cm) was developed for studying SOA.
- The reactor can simulate several days of photochemical aging in the atmosphere.
- NH_3 promoted the SOA yields and formed N-containing SOA species.
- N-containing species enhanced the UV-vis absorbance and fluorescence of SOA.

ARTICLE INFO

Article history:
Received 1 February 2017
Received in revised form
17 May 2017
Accepted 19 May 2017
Available online 25 May 2017

Keywords:
Secondary organic aerosol
α-Pinene
NH_3
Flow reactor
Optical properties
Brown carbon

GRAPHICAL ABSTRACT



ABSTRACT

This study presents detailed characterizations of a newly-developed flow reactor including (1) residence time distribution measurements, (2) relative humidity (RH) and temperature control, and (3) OH radical exposure range (i.e., atmospheric aging time). Hydroxyl (OH) radical exposures ranged from 8.20×10^{10} to 7.22×10^{11} molecules cm^{-3} s (0.5–4.9 d of atmospheric aging). In this study, the effects of NH_3 gas on the secondary organic aerosol (SOA) formation of α-pinene by dark ozonolysis and photooxidation were investigated using the newly-developed flow reactor. For both dark α-pinene ozonolysis and photooxidation, higher SOA yields were observed in the presence of NH_3 than in the absence of NH_3. At RH of ~50%, the SOA yield for ozonolysis and photooxidation in the presence of NH_3 increased by 23% and 15% relative to those in the absence of NH_3. Similar effects were observed at lower and higher RH conditions. Fourier transform infrared spectroscopy analysis confirmed the presence of nitrogen-containing functional groups in SOA formed in the presence of NH_3. The α-pinene SOA formed in the presence of NH_3 showed higher absorption and fluorescence for UV-visible radiation than those formed in the absence of NH_3.

1. Introduction

Atmospheric aerosols play a key role in air quality, climate change, and human health (Belalcazar et al., 2009; Davidson et al., 2005; Harrison and Yin, 2000; IPCC, 2013; US EPA, 2012). These fine particles are associated with mortality and serious health issues in humans such as cardiopulmonary and bronchial infections (Beelen et al., 2007; Brauer et al., 2012; Lall et al., 2004; WHO, 2013). They also influence the Earth's radiation budget by absorbing and scattering terrestrial and solar radiation; their physicochemical properties affect cloud formation processes (Khalizov et al., 2006). Therefore, understanding the formation mechanisms and key properties of aerosols is essential. Organic aerosols comprise a large

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http://dx.doi.org/10.1016/j.atmosenv.2017.05.034
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fraction of atmospheric aerosols (IPCC, 2001; Kanakidou et al., 2005; Putaud et al., 2010). Primary organic aerosols are directly emitted from sources such as vehicular exhaust, fossil fuel combustion, cooking, and biomass burning (Guzman-Morales et al., 2014; Ortega et al., 2013; Suarez-Bertoa et al., 2015). Gaseous organics emitted from biogenic and anthropogenic sources undergo atmospheric oxidation to form low-volatility compounds that partition into the aerosol-phase and form secondary organic aerosols (SOA) (de Gouw and Jimenez, 2009; Hallquist et al., 2009). A substantial fraction of fine organic particles consists of SOA (Hallquist et al., 2009).

Recently, brown carbon has received significant attention because it is more abundant than black carbon and has a strong effect on climate via direct light absorption (Andreae and Gelencsér, 2006; IPCC, 2013; Laskin et al., 2014). However, it is difficult to completely understand the origin of brown carbon and limited knowledge is available on the physicochemical properties of brown carbon. Reduced nitrogen species such as amino acids, amines, and ammonia react with carbonyl compounds to produce brown carbon (Galloway et al., 2008; Kampf et al., 2012; Nozière et al., 2009; Shapiro et al., 2009). For instance, NH_4^+ ion- or NH_3 gas-aging of SOA results in the formation of brown carbon through carbonyl-to-imine conversion (Bones et al., 2010; Lee et al., 2013; Nguyen et al., 2012; Updyke et al., 2012).

Over the last few decades, simplified laboratory techniques have substantially improved our understanding of the properties and atmospheric formation processes of SOA. Smog chambers have been successfully used as prime tools for physicochemical studies on SOA (Cocker III et al., 2001b; Hu et al., 2014; Paulsen et al., 2005; Platt et al., 2013; Presto et al., 2011; Wang et al., 2014). Smog chambers are batch reactors with sizes ranging from a few liters to 270 m^3 (Rohrer et al., 2004). They are typically operated at low oxidant levels comparable to the atmospheric levels, which means long reaction times to simulate atmospheric processes (Kang et al., 2007). Fast particle wall-loss prevents the extension of the reaction time for smog chambers to follow the lifetime aging processes of particles up to several days (Matsunaga and Ziemann, 2010; Ng et al., 2010).

Recently, flow reactors with compact sizes of 0.1 L–~1000 L and extremely high oxidant levels comparable to the lifetime of ambient aerosols have been developed as an alternative tool to smog chambers (Ezell et al., 2010; George et al., 2007; Kang et al., 2007; Lambe et al., 2011; Smith et al., 2009). The compact flow reactors have short residence times of several seconds to a few minutes. In the flow reactor, substantially high levels of OH radicals are produced by the UV photolysis of ozone at high concentrations and successive reactions in humid conditions. To produce high levels of OH radicals, UV source different from the solar spectrum is used. Despite using UV radiation with wavelengths shorter than the solar radiation for O_3 photolysis in OH radical formation, SOA yield and composition show similarities in smog chambers and flow tube reactors (Bruns et al., 2015; Kang et al., 2007; Lambe et al., 2015). This approach has been applied for simulating atmospheric photooxidation processes within a time scale of minutes and also for the SOA formation from various precursors, aging of primary aerosols, and inhalation toxicology (Hall IV et al., 2013; Kang et al., 2007; Keller and Burtscher, 2012; Lambe et al., 2011; Slowik et al., 2012).

In this study, a new Kyungpook National University (KNU) flow reactor has been developed and applied to the SOA formation. The reactor was used to examine the effect of NH_3 on the yield and composition of SOA. The formation of SOA from the dark ozonolysis and photooxidation of α-pinene in the presence and absence of NH_3 was investigated. The formation of nitrogen-containing species was examined by the presence of nitrogen-containing functional groups (e.g., amine, amino acid, and nitrate). The effect of NH_3 on the optical properties of SOA was also studied.

2. Materials and methods

2.1. Development and characterization of the KNU flow reactor

A schematic of the Kyungpook National University (KNU) flow reactor is shown in Fig. 1. It consists of a reaction tube, reactor enclosure, irradiation source, purified air supply, reactant injection system, O_3 and OH radical generation system, and analytical instruments. The frame of the reactor enclosure has the dimensions of 80 cm × 30 cm × 30 cm (L × W × H) and is constructed with aluminum profiles (2 cm × 2 cm). The frame is covered with 2-mm-thick stainless steel plates. The inner surfaces of the plates are covered with aluminum foil to enhance radiation reflection. The enclosure was sealed with 2-mm thick silicon foam attached between stainless steel plates and aluminum profiles. The inner enclosure space was purged with argon gas to maintain an inert atmosphere. Inside the enclosure, a 0.25 mm cylindrical FEP polymer tube (FHS113, Adtech Polymer Engineering, Stroud, Glos, England) with dimensions of 15.5 cm (I.D.) × 70 cm (L) was fixed to the cone-shaped stainless steel ends. The FEP tube was sealed by

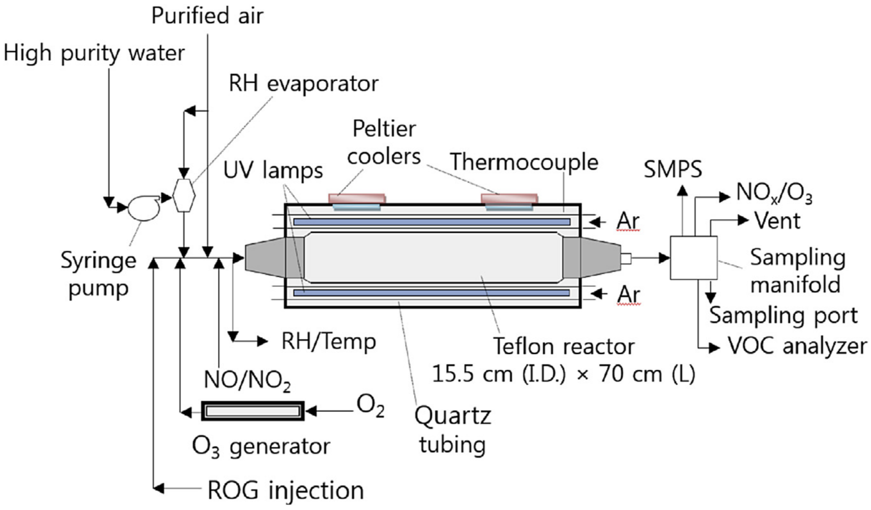

Fig. 1. A schematic of KNU flow reactor.