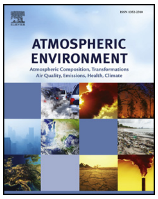
Atmospheric Environment 191 (2018) 116–125

Contents lists available at ScienceDirect

Atmospheric Environment

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



The influence of UV-light irradiation and stable Criegee intermediate scavengers on secondary organic aerosol formation from isoprene ozonolysis

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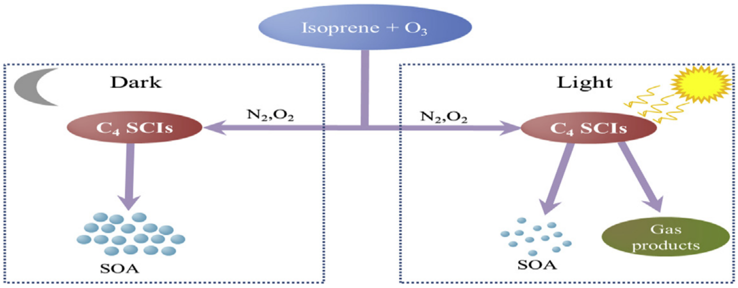
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Isoprene ozonolysis
SOA formation
Stable Criegee Intermediate FTICR-MS
Oligomers

ABSTRACT

The formation of secondary organic aerosol (SOA) from isoprene ozonolysis was investigated using a FEP Teflon reactor with and without the presence of H_2O, CO, SO_2 and UV-light irradiation (365 nm) to reveal their possible influence on SOA formation. Compared with the base experiment (isoprene + O_3) under dark condition, the presence of 2000 ppm H_2O and 1000 ppm CO could remarkably suppress SOA formation from isoprene ozonolysis, with SOA yields reduced from 2.96% to 1.47% and 2.08%, respectively. The evident reduction of SOA yields from isoprene ozonolysis with the presence of H_2O and CO was mainly ascribed to the suppression of Stable Criegee Intermediates (SCIs). In contrast, the particle yield from isoprene ozonolysis with the presence of SO_2 pronouncedly increased from 2.96% to 57.9%, suggesting that the oxidation of SO_2 by SCIs made great contribution to the particle formation. The SOA or particle yields from all the reaction systems with and without presence of H_2O, CO and SO_2 reduced more than 27% under the UV-light irradiation with respect to dark condition, which were mainly attributed to the SCIs photolysis. The contribution of OH channel to SOA formation from isoprene ozonolysis was estimated to be less than 30%. Considering the 50% reduction of SOA yield from isoprene ozonolysis under light irradiation, the disappearance of the component with low O:C and H:C and high molecule weight in the SOA sample collected under light irradiation indicated the polymerization of

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https://doi.org/10.1016/j.atmosenv.2018.08.014
Received 23 April 2018; Received in revised form 16 July 2018; Accepted 2 August 2018
Available online 07 August 2018
1352-2310/

unsaturated SCIs might be an important SOA formation channel besides the oligomerization of SCIs, HCHO, and MACR from isoprene ozonolysis under dark condition.

1. Introduction

Atmospheric isoprene is mainly from the emission of vegetation, with the global annual emission strength of 500-700 Tg (Guenther et al., 2006; Sindelarova et al., 2014). It can react with O_3 (Kamens et al., 1982; Kleindienst et al., 2007; Riva et al., 2016; Sato et al., 2013), OH radicals (Atkinson, 1997; Claeys et al., 2004; Edney et al., 2005; Kroll et al., 2006; Nguyen et al., 2010; Zhang et al., 2011), leading to formation of secondary pollutants to affect regional air quality (Carlton et al., 2009; Pacifico et al., 2009; Shen et al., 2015).

The contribution of isoprene to atmospheric secondary organic aerosol (SOA) has aroused great attention since 2004 when 2-methyltetrols (with the same carbon skeleton as isoprene) were first identified in the aerosol samples of Amazon forest (Claeys et al., 2004). Thereafter, 2-methyltetrols, 2-methylglyceric acid and C5 alkene triols were further detected in the aerosol samples of many areas (Edney et al., 2005; Ion et al., 2005; Kourtchev et al., 2005, 2008) and verified to be from OH initiated photooxidation of isoprene in smog chamber experiments (Edney et al., 2005; Surratt et al., 2006; Liu et al., 2009). Besides the OH reactions, isoprene ozonolysis has also been found to form SOA in smog chamber studies. A series of low volatility compounds of oligomeric compounds (with chain units of CH_2OO, H_2CO and MACR) have been identified in the filter samples from isoprene ozonolysis (Inomata et al., 2014; Nguyen et al., 2010; Sakamoto et al., 2013). At least 14% of the organic sulfates measured at two rural locations of the USA were ascribed to isoprene ozonolysis based on the results of chamber simulation with the presence of OH scavenger and sulfate aerosol seed (Riva et al., 2016). SOA yield from isoprene ozonolysis has also been investigated by several studies (Clark et al., 2016; Czoschke et al., 2003; Jang et al., 2002; Kamens et al., 1982; Kleindienst et al., 2007; Ren et al., 2017; Sato et al., 2013), ranging from 0.12 to 9%. The large range of SOA yields could be ascribed to various factors, such as temperature, relative humidity (RH), the presence and absence of seeds and the OH scavengers.

Because atmospheric isoprene is dominated by emission of vegetation under sunlight irradiation and its lifetime is usually less than 2 h (Pacifico et al., 2009), the reaction of isoprene ozonolysis mainly occurs during the daytime (Wang et al., 2013; Zhang et al., 2000). However, the possible influence of light irradiation on SOA formation from isoprene ozonolysis has not been investigated in previous studies. Although the oligomerization of CH_2OO has been identified as a SOA formation channel (Jia and Xu, 2018; Wang et al., 2016; Yao et al., 2014; Zhao et al., 2015a, 2015b), the role of unsaturated Stable Criegee Intermediate (SCI) from isoprene ozonolysis in SOA formation remains unclear. Here, we present the results about isoprene ozonolysis through comparison investigations to reveal the possible influence of light irradiation as well as the role of unsaturated SCIs in SOA formation.

2. Materials and methods

The experiments were carried out in a 3-m^3 collapsible FEP Teflon reactor. The reactor was suspended in a heat-insulated room of 14.4 m^3, and the temperature in the room was exactly controlled at 25 ± 1 °C by an air conditioner (refrigerating capacity of 5 KW) placed on the inside wall of the room. Sixty-three black light lamps (Philips, 30 W) with central light emission of 365 nm are uniformly equipped on the wall of the room to provide the light sources needed. The nearest linear distance between the reactor and the lamps is 40 cm when the reactor is filled with 3 m^3 synthetic air. The intensity of irradiation in the bag was estimated by the Leighton relationship (Leighton, 1961) among NO, NO_2 and O_3, with the photolysis rate constant of NO_2 (J_{NO2}) of $2.6 \times 10^{-3}\ s^{-1}$. The air temperature in the room was measured by a thermocouple thermometer which was placed on the top and in the middle of the room. The variation of the air temperature was not observed when the sixty-three lamps were turned on. The wall loss rates for SO_2, and O_3 were measured to be $7.3 \times 10^{-8} s^{-1}$ and $2.31 \times 10^{-6} s^{-1}$, respectively. The variation of isoprene concentration in the synthetic air was within the measurement uncertainty (1.5%) of the GC-PID during 2-h period. The wall loss of particles was estimated to be $0.23\ h^{-1}$ based on the first-order decay of the particles after reaching their peak values.

The synthetic air (≥99.999%, Haike Ltd, Beijing) was used as buffer gas and the H_2O concentration in it was less than 2 ppm which is equal to a relative humidity (RH) of 0.9% at 25 °C. The experiments 8–9 were conducted with the presence of 2000 ppm H_2O (RH ≈ 8.1%), and the remaining experiments were carried out without the presence of H2O (RH < 0.9%). Isoprene (generated from liquid isoprene (99.9%, Sigma-Aldich)), O_3 (generated using an electrical discharge generator (ZA-XF-1, ZhengAo Ltd, China)), CO (99.995%, Linggas Ltd, Beijing), and SO_2 (464 ppm in N_2, HuaYuan Ltd, Beijing) were injected to the reactor using glass syringes to reach the target concentrations. H_2O was introduced through N_2 bubbling with a 60 °C water bath. Gas-phase isoprene was analyzed using a gas chromatography with photoionization detector (GC-PID) method conducted in the previous study (Zhang et al., 2000). SO_2 and O_3 were monitored using a SO_2 analyzer and O_3 analyzer (Model 47i, Model 49i, Thermofisher Scientific Inc, USA), respectively. Before the start of each experiment, all gas-phase instruments were checked with a calibration standard. The size (15–495 nm), number, and volume distribution of the SOA were measured through a scanning mobility particle sizer (SMPS, TSI 3760). SOA yield is given by $Y = M_0/\Delta isoprene$, where M_0 and Δisoprene represent the SOA mass concentration and the reacted isoprene at corresponding time. SOA density of a 1.4 g/cm^3 is used to convert the volume concentration to the mass concentration (Carlton et al., 2009). Each experiment lasted for 2 h.

Aerosol samples were collected for the experiments of 2 ppm isoprene +1 ppm O_3 under both dark and light condition by pulling chamber air through a Teflon-coated filter (Millipore, 0.2 μm) at a flow rate of 16.7 standard liters per minute (SLM) for 1 h after the mixture reacted for 1 h. The filters were extracted in 5 mL methanol (HPLC grade, Sigma-Aldrich) with 10 min sonication. The extracts were directly analyzed using a solariX XR FT-ICR MS (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 9.4 T refrigerated actively shielded superconducting magnet (Bruker Biospin, Wissembourg, France) and the Paracell analyzer cell. The extracts were ionized in negative ion mode using the ESI ion source (Bruker Daltonik GmbH, Bremen, Germany). The detection mass range was set to *m/z* 150–1200. Ion accumulation time was set to 0.6 s. A total of 200 continuous 4 M data FT-ICR transients were co-added to enhance the signal-to-noise ratio and dynamic range. A blank filter was processed and analyzed following the same procedure to detect possible contamination. The mass spectra were calibrated externally with arginine clusters in negative ion mode using a linear calibration. The final spectrum was internally recalibrated with typical O_2 class species peaks using quadratic calibration in DataAnalysis 4.4 (Bruker Daltonics). A typical mass-resolving power (m/Δm50%, in which Δm50% is the magnitude of the mass spectral peak full width at half-maximum peak height) > 450 000 at m/z 319 with < 0.3 ppm absolute mass error was achieved". Under the above operation condition of the ESI-FTICR-MS, polar compounds such as organic acid and alcohol, which are the