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The influence of OH concentration on SOA formation from isoprene photooxidation

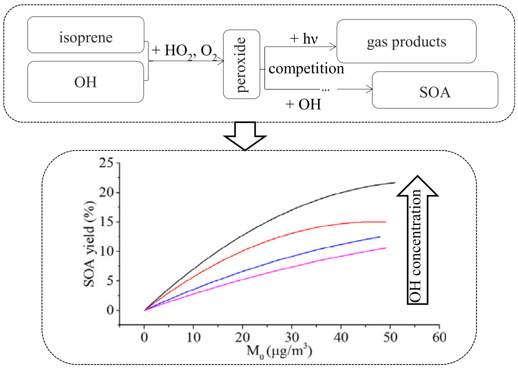
Min Song [a,d], Chenglong Zhang [a,b,d,**], Hai Wu [e], Yujing Mu [a,b,c,d,*], Zhuobiao Ma [a,d], Yuanyuan Zhang [a,b,d], Junfeng Liu [a,b,d], Xuran Li [a,d]

[a] *Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China*
[b] *Center for Excellence in Urban Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China*
[c] *National Engineering Laboratory for VOCs Pollution Control Material & Technology, University of Chinese Academy of Sciences, Beijing 100049, China*
[d] *University of Chinese Academy of Sciences, Beijing 100049, China*
[e] *National Institute of Metrology, Beijing 100029, China*

HIGHLIGHTS

- SOA could be detected under less isoprene consumption with increasing OH concentration.
- SOA yield under atmospheric relevant conditions was greater than those of previous studies.
- OH concentration played important role in SOA formation from isoprene photooxidation.

GRAPHICAL ABSTRACT



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ABSTRACT

The formation of secondary organic aerosol (SOA) from isoprene photooxidation was investigated to reveal the influence of OH concentration on SOA formation through varying the concentrations of isoprene and H_2O_2 in a smog chamber. The results indicated that the higher the OH concentration was, the less the isoprene consumed for the detectable SOA mass concentration, for example, the lowest isoprene consumption for the detectable SOA was about 14.4 ppb under the OH concentration of about 1.65×10^7 molecules cm^{-3}, whereas tens ppb of isoprene consumption were needed under the OH concentrations $<1.0 \times 10^7$ molecules cm^{-3}, and even no detectable SOA was observed with isoprene consumption of 75.1 ppb under OH concentration of 7.2×10^5 molecules cm^{-3}. SOA yield was also found to increase with increasing OH concentration for a given aerosol loading (M_0) at atmospherically relevant conditions, confirming that OH concentration played important role in SOA formation from isoprene photooxidation. The maximal SOA yields (5.8–42.8%) obtained by this study were a factor of 1.5–3.1 greater than those reported by previous study for the almost the same initial reactant concentrations of isoprene and H_2O_2, and the difference was mainly ascribed to the higher OH concentrations in the reaction systems of this study than those of previous study. The OH concentrations adopted in this study closed to those in the real atmosphere around noontime, and hence the SOA yield obtained from the isoprene photooxidation might be representative.

** Correspondence to: C. Zhang, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China.
* Correspondence to: Y. Mu, National Engineering Laboratory for VOCs Pollution Control Material & Technology, University of Chinese Academy of Sciences, Beijing 100049, China.
E-mail addresses: clzhang@rcees.ac.cn (C. Zhang), yjmu@rcees.ac.cn (Y. Mu).

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1. Introduction

Isoprene (2-methyl-1,3-butadiene, C_5H_8) is the most abundant non-methane volatile organic compound (VOC) emitted into the atmosphere, with its global atmospheric emission of about 600 $Tg\cdot yr^{-1}$ (Guenther et al., 2006; Kroll et al., 2006). It can be readily oxidized by OH (Atkinson, 1997; Claeys et al., 2004; Edney et al., 2005; Kroll et al., 2005, 2006; Nguyen et al., 2011), O_3 (Kamens et al., 1982; Kleindienst et al., 2007b; Ren et al., 2017; Sato et al., 2013) and NO_3 (Ng et al., 2008) to form secondary organic aerosol (SOA), influencing regional air quality (Schell et al., 2001), human health (Carlton et al., 2009), global radiation balance (Shen et al., 2015), and climate change (Pacifico et al., 2009).

The contribution of atmospheric isoprene to SOA has received increasing attention since the detection of 2-methyltetrols, the tracer compounds of isoprene photooxidation, in the aerosol samples from Amazon forest (Claeys et al., 2004). Thereafter, several additional compounds (such as 2-methylglyceric acid, C5 alkene triols) of isoprene SOA were further identified in the samples from field and laboratory studies (Edney et al., 2005; Ion et al., 2005). To quantify the contribution of isoprene to atmospheric SOA, SOA yields from isoprene photooxidation have been investigated through smog chamber experiments, but the values reported largely varied from 0% to 41% (Clark et al., 2016; Dommen et al., 2006; Edney et al., 2005; Jia and Xu, 2018; Kleindienst et al., 2006; Kroll et al., 2005, 2006; Lambe et al., 2015; Nguyen et al., 2011; Pandis et al., 1991; Sato et al., 2011; Zhang et al., 2011). The large variation of SOA yield was ascribed to many influencing factors (Carlton et al.), such as temperature, relative humidity (RH), and NOx level, aerosol loading (M_0) et al., but the extent of the influence factors on SOA yields still remained unclear. For example, Nguyen et al. (2011) and Dommen et al. (2006) found that RH had little effect on SOA yields from isoprene photooxidation with presence of NOx, while Zhang et al. (2011) and Jia and Xu (2018) found SOA yield evidently decreased under humid condition in comparison with dry condition. Although SOA yield has been found to depend on aerosol loading (M_0), the measured yields spanned over an order of magnitude for a given value of M_0 (Carlton et al., 2009). SOA yields from isoprene photooxidation may also be strongly affected by the OH concentration (Carlton et al., 2009) because the SOA formation from isoprene photooxidation is involved in multiple-step OH reactions and there may be possible competition reactions (such as photolysis of peroxides) versus OH reactions to affect SOA formation. To our best knowledge, however, there has been no study concerning the effect of OH concentration on SOA formation from isoprene photooxidation under atmospherically relevant conditions.

In this study, the influence of OH concentrations on SOA formation from isoprene photooxidation was investigated by using H_2O_2 as the OH precursor in a smog chamber. The finding of this study will help to improve the understanding of the contribution of isoprene to atmospheric SOA.

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 5KW). Sixty-three lamp holders are equipped on the wall of the room to install different ultraviolet lamps. The nearest linear distance between the reactor and the lamps is 40 cm when the reactor is filled with 3 m^3 synthetic air. There are nine outlets evenly distributed at the bottom of the reactor for introducing synthetic air and gas-phase reagents as well as for sampling gas-phase and particulate compounds. The Teflon reactor was flushed at least 3 times with high purity nitrogen before each experiment to ensure that there were no interfering substances in the reactor.

H_2O_2 was introduced into the reactor by 3 L/min N_2 passing through a bubbler containing 30% H_2O_2 solution (Sigma-Aldrich) and a filter (avoiding introduction of droplets) to the target concentrations. Liquid isoprene (99.9%, Sigma-Aldrich) of 50 μL was firstly injected into a FEP Teflon bag containing 5 L N_2 for preparing a gas mixture of high concentration isoprene, and then the gas mixture was transferred into the reactor through a 100 mL glass syringe to achieve target concentrations. Synthetic air was introduced into the reactor at a flow rate of 70 L/min through a flow totalizer (NAURA Technology Group Co., Ltd., Beijing) to achieve a total volume of 3 m^3 for each experiment. The concentrations of isoprene in the chamber were measured every 5 min by using a gas chromatograph with a photoionization detector (GC-PID) (Zhang et al., 2000) which was calibrated by diluted isoprene standard gas (10 ppm in N_2, Center of Standard Reference Materials, China). Particle volume and number concentrations within the size distribution between 14.7 and 495.8 nm were monitored every 3 min through a scanning mobility particle sizer (SMPS, TSI 3760). H_2O_2 concentrations were indirectly measured by the O_3 monitor (Model 49i, Thermo-Fisher Scientific Inc., USA) based on the difference of the extinction coefficients between O_3 and H_2O_2 at 253.7 nm (Kleindienst et al., 2009). The concentrations of isoprene and H_2O_2 in the reactor under dark conditions were measured to be stable after the gas mixture mixed for 30 min, indicating that no dark reaction occurred in the reaction system of isoprene + H_2O_2 + air. And the variation of isoprene concentration in the synthetic air was within the measurement uncertainty (±1.5%) of the GC-PID during four-hour period. Each experiment was conducted by turning on the lights after the mixture well-mixed in 30 min and lasted for 240 min. Two low-pressure mercury lamps (Philips, 30 W, O_3 free) with central light emission of 253.7 nm were used as the light source for Runs 2–10 and sixty-three black-light lamps (Philips, 30 W) with central light emission of 365 nm were used for Run 1 (Table 1). All the experiments were conducted under dry condition (relative humidity <10%).

SOA yield is given by the relationship of $Y = M_0 / \Delta\text{isoprene}$, where M_0 and Δisoprene represent the SOA mass concentration and the reacted isoprene at a given time, respectively. The SOA density of 1.25 g/cm^3 was used to convert the volume concentration to the mass concentration according to the previous study (Kroll et al., 2006). It should be mentioned that the maximal SOA yield around the reaction time of 1 h when isoprene was almost consumed was adopted in this study for each reaction system. Considering the SOA wall loss rate (calculated based on the first-order decay of the SOA mass concentration after reaching the peak value) of around 0.38 h^{-1}, the amount of SOA consumption due to the wall loss around the reaction time of 1 h only accounted for <19% of the total SOA mass concentration, and thus the maximal SOA yields obtained in this study was not corrected didn't correct for the wall loss.

3. Results and discussion

3.1. SOA formation from isoprene photooxidation

Isoprene photooxidation was firstly investigated by using sixty-three black-light lamps (which emits a Gaussian shaped spectrum between 300 and 500 nm, with the maximum intensity of 365 nm) for irradiating H_2O_2 as the OH source in this study, but no SOA formation was detected during a period of 6 h (Table 1, Run 1). In contrast, Kroll et al. (2006) found evident SOA formation at the reaction time of 1 h with similar initial concentrations of H_2O_2 and isoprene under black-light irradiation. The distinct difference between their results and ours might be ascribed to the fact that the OH concentration for the study of Kroll et al. (2006) was higher than this study, e.g. 50% isoprene consumption within 1 h for their study, whereas only 22% for our study. Considering the variation of isoprene concentration in the synthetic air in this study was within the measurement uncertainty (±1.5%) of the GC-PID during four-hour period, the consumption of isoprene was mainly ascribed to