Effect of illumination intensity and light application time on secondary organic aerosol formation from the photooxidation of α-pinene

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Abstract

Secondary organic aerosol (SOA) formation from hydroxyl radical (OH·) initiated photooxidation of α-pinene was investigated in a home-made smog chamber. The size distribution of SOA particles was measured using aerodynamic particle sizer spectrometer. The effects of illumination intensity and light application time on SOA formation for α-pinene were evaluated. Experimental results show that the concentration of SOA particles increased significantly with an increasing of illumination intensity, and the light application time, the concentration, and the size of SOA particles were also increased. In addition, the factors influencing the formation of SOA were discussed. In addition, this article compared the effect of α-pinene with that of toluene, and discussed the contribution of α-pinene to SOA formation.

Introduction

Secondary organic aerosol (SOA) has diverse atmospheric influences, including causing visibility degradation, participating in radiation, damaging plant life, leading to the formation of photochemical smog, increasing ozone concentration, and causing cloud formation (Chung and Seinfeld, 2002; Seinfeld *et al*., 2003; Shilling *et al*., 2008). SOA is also harmful to human health, such as increased risk of cardiovascular disease and lung cancer (Dockery *et al*., 1993; Pope *et al*., 1995; Miller *et al*., 2007). Biogenic volatile organic compounds (BVOCs) contribute significantly to the formation of ozone and SOA. It is estimated that global SOA production from BVOCs ranges from 2.5 to 44.5 Tg (organic mass) per year, and the global SOA production from anthropogenic VOCs ranges from 0.05 to 2.62 Tg (organic mass) per year (Tsigaridis and Kanakidou, 2003). Monoterpenes give rise to SOA through the reactions of ozone, OH, and NO_3 radicals (Calogirou *et al*., 1999), and its annual global emission rate is about 127 Tg with α-pinene as the major terpene emitted (Guenther *et al*., 1995). China has a vast land with 12% of the surface covered by forest, and has almost all kinds of characteristic plants species of the northen hemisphere. Therefore, understanding formation mechanism and influence factors of SOA is needed.

Most previous studies on formation mechanism of SOA

from monoterpenes focused on the SOA ozonolysis products of α-pinene (Christoffersen *et al*., 1998; Hoffmann *et al*., 1997; Yu *et al*., 1999; Jang and Kamens, 1999; Glasius *et al*., 2000; Iinuma *et al*., 2004). In the present study, we focued on the effects of illumination intensity and light application time on SOA formation from the photooxidation of α-pinene. The home-made smog chamber was used to form SOA by hydroxyl radical (·OH) initiated photooxidation of α-pinene. TSI APS 3321 (TSI Model 3321) was employed in real-time detection of SOA particle size distribution. A series of α-pinene photooxidation experiments were performed. The results were compared with that of toluene photooxidation experiments.

1 Materials and methods

1.1 Materials

α-Pinene (> 99%) was obtained from Sigma-Aldrich Chemistry Corporation, Germany. Sodium nitrate (> 99%) and methanol (> 99%) were purchased from the Third Reagent Manufactory (Tianjin, China), and nitrogen oxide (99.9%) was obtained from Nanjing Special Gas Factory, China. They all were used without further purification.

Methyl nitrite (CH_3ONO) was synthesized by dropping sulfuric acid into a methanol solution of sodium nitrate. The reaction product was passed through a saturated sodium hydroxide trap to remove the trace sulfuric acid,

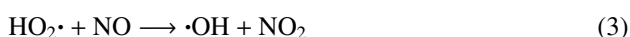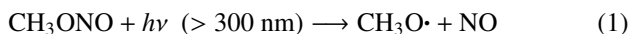* Corresponding author. E-mail: wjzhang@aiofm.ac.cn

dried using a calcium sulfate trap, and collected by a liquid nitrogen condenser at 77 K. The methyl nitrite was purified using a vacuum system.

1.2 Smog chamber experiments

The experimental apparatus consist of a sampling system, smog chamber system and detection system. The smog chamber was made of sealed collapsible polyethylene with a volume of 850 L. The ratio of surface to volume was 5.8 m^{-1}. The reactor is surrounded by 12 sets of 40 W fluorescent black lamps. The wavelength of UV radiation is in the range of 300–400 nm. The volume of the glass vacuum system is 0.84 L, and equipped with a vacuum gauge with a measuring range 10–5000 Pa. A schematic diagram of the experimental system is shown in Fig. 1.

Before performing experiment, the chamber was flushed continuously with dry purified laboratory compressed air for 40 min to remove hydrocarbon compounds, moisture, and the particles. The compressed air was processed through three consecutive packed-bed scrubbers, containing activated charcoal, silica gel, and a Balston DFU® filter (Grade BX), respectively. α-Pinene was sampled by a micro liter injector and directly transferred into the chamber. NO and methyl nitrate were expanded into the evacuated manifold to reach the desired pressure level through Teflon lines, and then were introduced into the smog chamber by a stream of purified air. The whole system was completely covered with a black polyethylene tarpaulin to avoid any light. Hydroxyl radicals were generated by the photolysis of methyl nitrite in air at wavelengths longer than 300 nm (Atkinson, 1981). The chemical reactions leading to the formation of the OH radical are as follows:

$$CH_3ONO + h\nu \ (> 300 \ nm) \longrightarrow CH_3O\cdot + NO \quad (1)$$

$$CH_3O\cdot + O_2 \longrightarrow HCHO + HO_2\cdot \quad (2)$$

$$HO_2\cdot + NO \longrightarrow \cdot OH + NO_2 \quad (3)$$

A series of experiments were carried out to investigate SOA from the OH-initiated α-pinene oxidation under different conditions. In all the experiments, the relative humidity was in the range of 50%–70%, and temperature was 295 ± 2 K, the concentrations of α-pinene, NO, and CH_3ONO are 2.7, 2, and 20 ppmv respectively. The size distribution, the number concentration and the mass concentration of SOA particles were detected by a TSI 3321 aerodynamic particle size spectrometer (TSI, model 3321, USA) in real time.

2 Results and discussion

2.1 Size distribution of the SOA particles

Figure 2 shows the size distribution of the SOA particles during the α-pinene 4 black lamps photooxidation experiment. The gas after cleaning contains a small amount of particles with the maximum concentration only 0.125 particles/cm^3. With the prolonging of reaction time, the number of SOA particles increases significantly, the aerodynamic diameter of SOA particles increases slowly, and the predominant particles change toward large diameter. But after about 45 min reaction period, the rate becomes slowly. The SOA particles created by the α-pinene photooxidation are predominant in the form of fine particle in diameter range 0.5 to 1.3 μm (less than 2.5 μm, i.e., PM$_{2.5}$). Scientific research have proved that these fine particles can deposit easily in lung, and are harmful to human health (Schwartz *et al.*, 1996).

Figure 3 shows the dependence of both number and mass concentration of SOA particles on the light application time in the α-pinene 4 black lamps photooxidation experiment. Both the number and mass concentrations are increase with the prolonging of the light application time, and reached the equilibrium 3000 particles/cm^3 and 1350 μg/cm^3, respectively, after 90 min.

The experimental results were compared with the results of toluene OH-initiated oxidation experiment (Hao *et al.*, 2005), which showed that the number of SOA particles increased slowly within the first 30 min and the amount
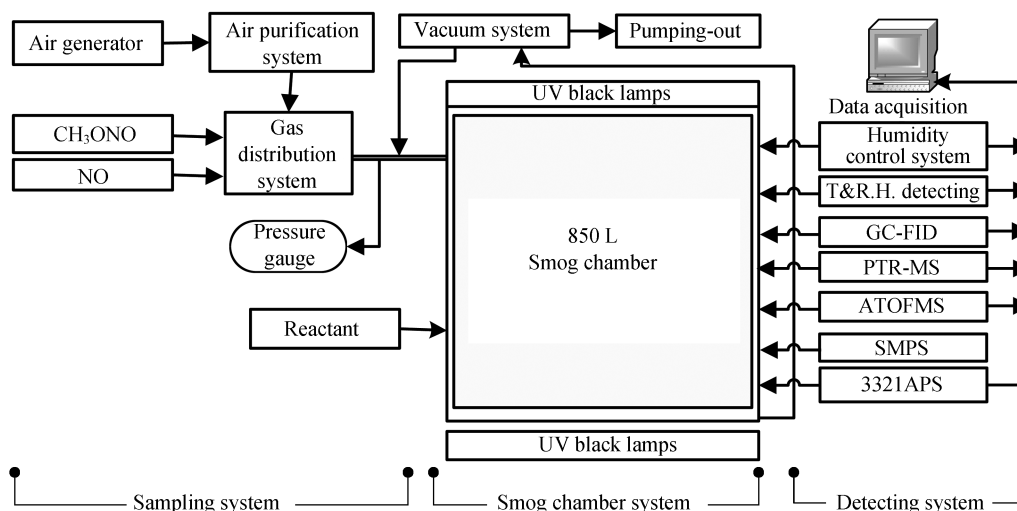

Fig. 1   Schematic of the experimental apparatus.
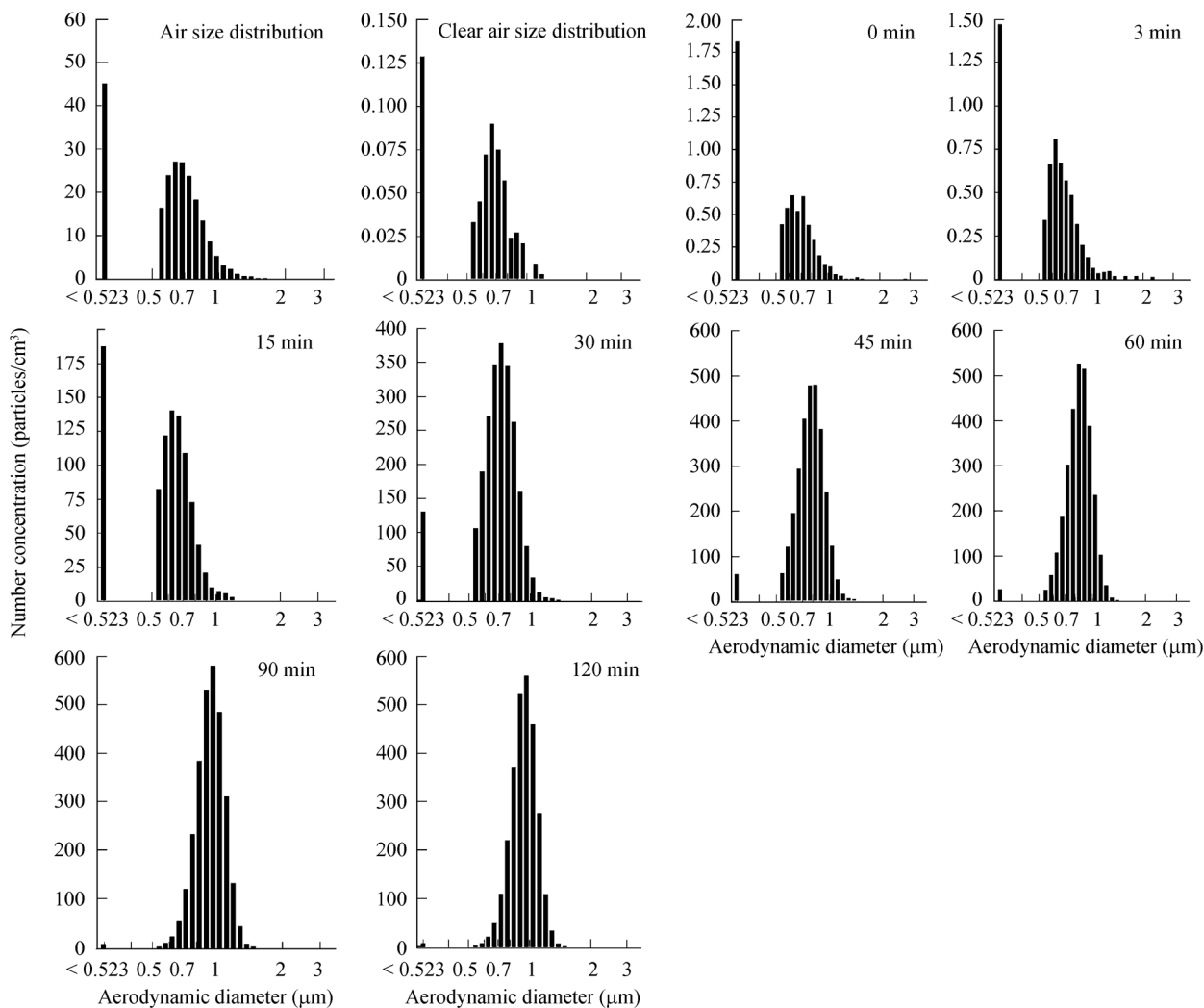
Fig. 2   Size distribution of SOA particles at different light application times.

of SOA particles increase slightly with the prolonged reaction time. After 30 min, the rate of the subsequent reaction becomes faster and the number of SOA particles increased. After 130 min, the number concentration of particles reaches 2300 particles/cm^3. It seemed that α-pinene is more easily to photolysis than toluene with the prolonged reaction time, and it has greater contribution to the formation of SOA than that of toluene.
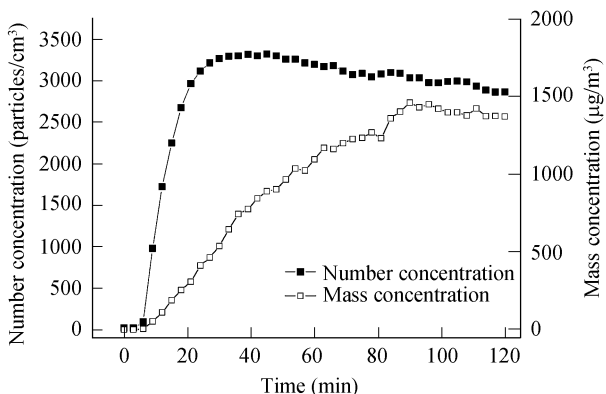

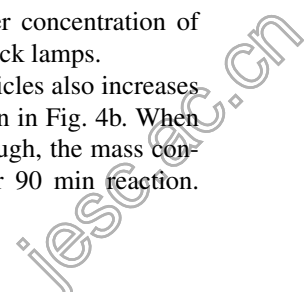**Fig. 3**   Number and mass concentrations as a function of light application time.

2.2 Effect of illumination intensity on the SOA formation

The dependence of SOA formation on the illumination intensity was investigated using 2, 4, and 8 black lamps, respectively (Fig. 4). Figure 4a shows the number concentration of SOA particles in α-pinene photooxidation experiments. The total number of SOA particles was 5000 particles/cm^3 at equilibrium under 8 black lamps radiation, which was much larger than that of 4 black lamps. While there is almost no particle formed with 2 black lamps. It could be concluded that the irradiative intensity has a great contribution to the formation of SOA particles. The conclusion can also be supported by Eq. (4) (Hao *et al.*, 2005):

$$Y = 153.11979 \times e^{\frac{x}{85.20773}} + 294.54746 \times e^{\frac{x}{277.74796}} - 385.05998 \tag{4}$$

where, Y (particles/cm^3) is the number concentration of SOA, x (W) represents the power of black lamps.

The mass concentration of SOA particles also increases with the illumination intensity as shown in Fig. 4b. When the illumination intensity is strong enough, the mass concentration will reach equilibrium after 90 min reaction.
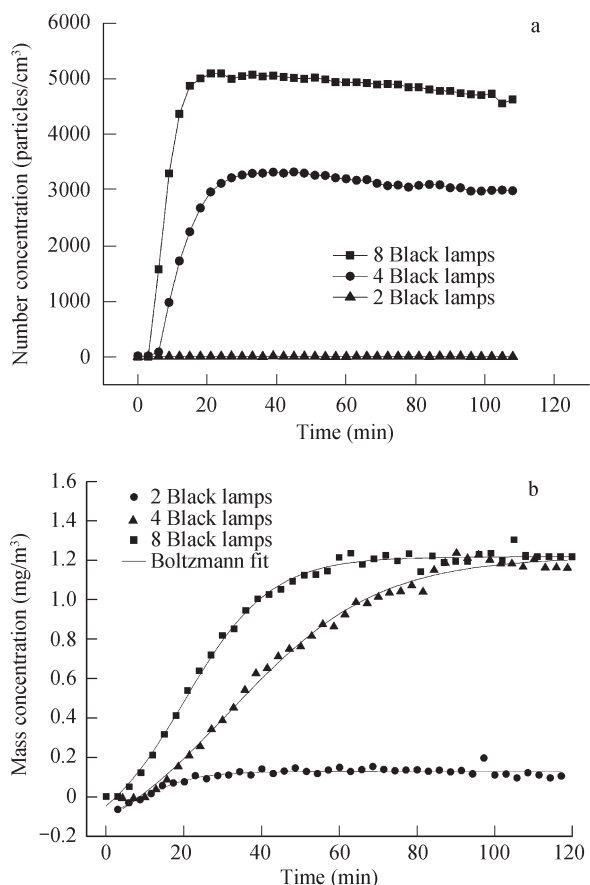
Fig. 4 Number concentration (a) and mass concentration (b) of SOA particles as a function of different illumination intensities.

The possible reason is that with the increment of reaction time, there are more products formed for the subsequent reaction, and the mass concentration of SOA particles will increase due to that the more semi-volatile organic compounds are partitioned between the gas phase and the particle phase. It will follow by that the fine particles become larger through a self-nucleation or condense in the pre-exiting aerosol process. The reaction will reach the equilibrium state as soon as the formation rate of fine particles equals to the formation rate of large particles condensed. However, when 2 black lamps were used, the mass concentration increases slowly, and there is a small amount of particles formed.

Comparing with the results of Hao *et al*. (2005), we can conclude that the illumination intensity of black lamps could significantly induce a high secondary organic aerosol particle concentration, and that the effect of illumination intensity on α-pinene photooxidation process follows the same rule as toluene.

3 Conclusions

The results clearly demonstrated that the number and mass concentrations of SOA particles were increased with the prolonged reaction time and enhanced illumination intensity. The irradiative intensity has a great contribution to the formation of SOA particles. The results also shown that α-pinene is more easily to photolysis than toluene, and

it has a greater contribution to the formation of SOA than toluene.

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