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影响异戊二烯大气光解形成二次有机气溶胶的环境因素研究

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摘要:通过自制的烟雾腔系统研究羟基启动的异戊二烯光解形成二次有机气溶胶(SOA)过程中环境因素的影响.使用气溶胶粒径光谱仪测量了 SOA 的粒径分布,通过光解实验研究了光照时间、反应物浓度以及 CH₃ONO 浓度对异戊二烯光解形成 SOA 的影响.结果表明,异戊二烯光解形成的 SOA 空气动力学直径在 0.4 μm~1.4 μm 之间,这些粒子的直径小于 2.5 μm 的微细粒子很容易沉积在人体肺泡内,对人体健康产生很大危害;不管是 SOA 粒子的粒子数浓度还是质量数浓度都随着反应时间的增长、光照强度的增强和反应物浓度的增加而增加.该研究为大气颗粒物排放源的外场测量提供了非常有用的信息.

关键词:光谱探测;异戊二烯;羟基自由基;二次有机气溶胶;粒径分布

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Effects of Environmental Factors on Secondary Organic Aerosol Formed from Isoprene Atmospheric Photo-oxidation Reactions

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Abstract: The effect of environmental factors on Secondary Organic Aerosol (SOA) formed from hydroxyl radical (OH·) initiated photooxidation of isoprene were investigated by using a home-made smog chamber. The size distribution of SOA particles from the above reaction were measured using Aerodynamic Particle Sizer spectrometer (APS). The effect of radiation time, reactant concentration, and CH₃ONO concentration on SOA formation from isoprene were evaluated by performing photooxidation experiments under varying conditions. Experimental results showed that aerodynamic diameter for SOA detected in isoprene photo-oxidation experiments was predominantly in 0.4 μm~1.4 μm, which were in the form of fine particles with diameters less than 2.5 μm. These fine particulate matters are more easily deposit in the lung of the human being, and do great harm to the health. This paper also highlighted that both the number and mass concentration of SOA particles were increasing with the prolonging of the radiation time, the increasing of light intensity, and the increasing of the reactant concentrations. The results could provide useful information to infer possible emission sources of

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atmospheric particles in future field measurement.

Key words: Spectrum detection; Isoprene; hydroxyl radical; Secondary organic aerosol; Size distribution

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0 Introduction

Large quantities of non-methane organic compounds are emitted into the atmosphere from biogenic sources, mainly from forest and vegetation. Most Biogenic Volatile Organic Compounds (BVOCs) are structured with isoprene-like units. The dominating species of natural emitted VOCs are isoprene and terpenes. BVOCs play an important role in the chemistry of the lower troposphere, and in the troposphere these organic compounds react with hydroxyl (OH) radicals, nitrate (NO_3) radicals, and ozone (O_3). These reactions may contribute to the formation of Secondary Organic Aerosols (SOA). SOA can cause visibility degradation, participate in radiation forcing, damage to plant life, lead to the formation of photochemical smog, increase of ozone concentration, and cloud formation^[1-3]. SOA is also harmful to human health, such as increased risk of cardiovascular disease and lung cancer^[4-6]. It is estimated that global SOA production from BVOCs ranges from 2.5 to 44.5 Tg (organic mass) per year, whereas the global SOA production from anthropogenic VOCs ranges from 0.05 to 2.62 Tg (organic mass) per year^[7]. Isoprene is the largest source of nonmethane hydrocarbons to the atmosphere (about 500 Tg C/year)^[8-10], and forms SOA through photooxidation with OH radicals, NO_3 radicals, and O_3 , with the daytime OH radical reaction dominating^[11].

To reduce the impacts of SOA, understanding formation mechanism of SOA is needed, and obtaining the influence factors on the formation of SOA is important. Most laboratory studies have been made to study the formation mechanism of SOA particles formed from the photooxidation of isoprene^[10,12-20]. In the present work, we focused on the effect of radiation time, reactant concentration and CH_3ONO concentration on SOA formation from isoprene by using a home-made smog chamber to form SOA, TSI Aerodynamic Particle Sizer spectrometer (APS) (TSI Model 3321) was employed in real-time detection of size distribution of SOA particles, a series of isoprene photooxidation experiments were performed. The results were compared with that of α -pinene and toluene photooxidation experiments.

1 Materials and methods

1.1 Materials

Isoprene (2-methyl-1, 3-butadiene) (99%) (CAS # 78-79-5) was obtained from Alfa Aesar, a Johnson Matthey company, United States, without additional purification in our experimental study. Sodium nitrate (> 99%) and methanol (> 99%) were purchased from Tianjin (The third Reagent Manufactory), and nitrogen oxide (99.9%) from Nanjing Special Gas Factory, which were used without further purification.

Methyl nitrite was synthesized by dropping sulfuric acid into a methanol solution of sodium nitrate. The reaction products passed through saturated sodium hydroxide trap to remove the traces of sulfuric acid, dried by passing through a calcium sulfate trap, and collected using a condenser of liquid nitrogen at 77 K. The methyl nitrite was purified using a vacuum system of glass.

1.2 Smog chamber experiment

The experimental system consists of sampling system, smog chamber system and detecting system. The experimental apparatus was described previously elsewhere^[21]. In brief, the smog chamber was made of sealed collapsible polyethylene with a volume of 850 L, and the ratio of surface to volume was 5.8 m^{-1} . The reactor is surrounded by 12 sets of 40 W fluorescent black lamps with the wavelength of UV radiation in the range of 300~400 nm. The volume of the glass vacuum system is 0.84 L, which equipped with a vacuum gauge whose measuring range is 10~5 000 Pa.

Before each experiment, the chamber was flushed continuously with dry purified laboratory compressed air for about 40 min. In order to remove the trace of hydrocarbon compounds, moisture and 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. Isoprene was sampled

by a micro liter injector and injected directly into the chamber. NO and methyl nitrate were expanded into the evacuated manifold to the desired pressure through Teflon lines, and introduced into the smog chamber by a stream of purified air. The whole sampling system was completely shrouded from light with a black polyethylene tarpaulin. Hydroxyl radicals were generated by the photolysis of methyl nitrite in air at wavelengths longer than 300 nm^[22].

A series of experiments were conducted to investigate SOA generated from the OH-initiated oxidation of isoprene under different experimental conditions. Experimental results were compared with the results of α -pinene OH-initiated oxidation experiment^[21]. 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 SOA particles and the effect of radiation time on SOA formation

In order to examine the size distribution of SOA particles, a series of experiments were carried out. In the experiments, kept the relative humidity about 53%, and the temperature about 31 °C the concentration of isoprene, NO, and CH₃ONO were 1.5 ppm, 2 ppm, and 20 ppm respectively, with 8 black lamps continuously radiation for 9 hours.

Fig. 1 showed the size distribution of SOA particles during the isoprene photooxidation experiment measured by the TSI APS 3321 aerodynamic particle size spectrometer (particles/cm³) in real time. As shown in Fig. 1, the SOA particles created by isoprene photooxidation experiment are predominant in the form of fine particles, which have diameter (0.5-1.3 μ m), being less than 2.5 μ m (i.e., PM_{2.5}). Scientific research works have proved that these fine particles are easily deposit in the lung, and do great harm to human health^[23].

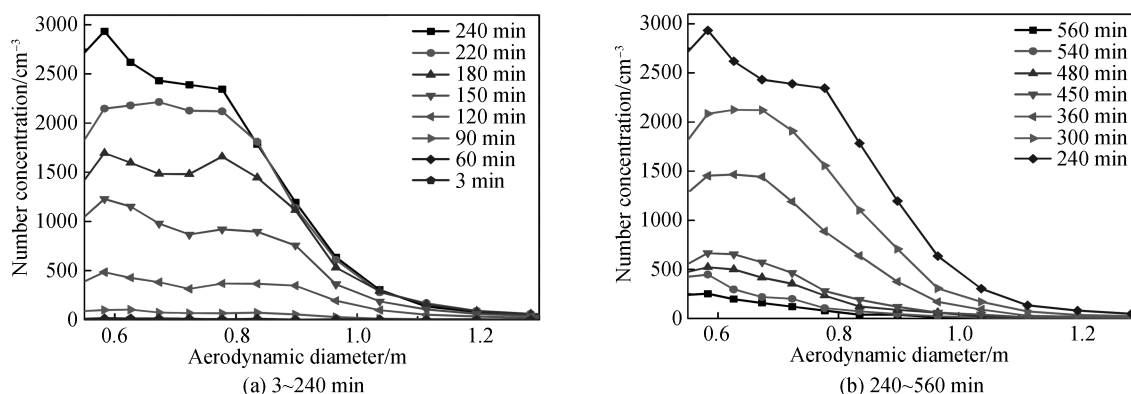


Fig.1 Size distribution of SOA particles formed from isoprene photooxidation reactions at different radiation time

Fig. 1 also showed that both the number of SOA particles and the aerodynamic diameter of SOA particles increased slowly at the first stage. After 60 min' reaction, the number of particles increased significantly, and the predominant particles changed toward large diameter. After 4 hours' radiation, the generated SOA particles reach maximum. After then, with the increasing of the radiation time, the SOA particles decreased slowly, after 9 hours reaction, the generated SOA particles reached equilibrium. This was different from the α -pinene photooxidation experiment^[21], in which, with the prolonging of the reaction time, the number of SOA particles increased significantly at first, and aerodynamic diameter of SOA particles also increased slowly, and the predominant particles change toward large diameter. But after about 45 min' reaction, the rate became slowly. By comparison, we found that with the prolonging of the reaction time, isoprene was easier to photolysis than α -pinene.

Fig. 2 showed the dependence of both number and mass concentration of SOA particles on the light radiation time during the isoprene 8 black lamps photooxidation experiment. It could be seen from Fig. 2 that, at first, both number and mass concentrations had no change, which means no particles generated in the first stage, but after 60min' light radiation both the number and mass concentrations were increase with the prolonging of the radiation time. The concentrations increased continuously to the maximum of

3 300 particles/cm³. After that, number and mass concentrations decreased slowly, this was because the short photooxidation 'age' of isoprene.

While the results of α -pinene photooxidation experiment^[21] showed that both the number and mass concentration reached equilibrium after about 90 min of reaction time, and kept at a level of 3 000 particles/cm³. It seemed that with the prolonging of the reaction time, isoprene was more easily to photolysis than α -pinene, and it has large contribution to the formation of SOA than that of α -pinene.

2.2 The effect of reactant concentration on SOA formation

To investigate the dependence of SOA formation on the reactant concentration, we carried out a series of experiment by change the concentration of isoprene samples. In the isoprene photooxidation experiments, we kept NO and CH₃ONO at 2 ppm, and 20 ppm respectively, with 8 black lamps continuously radiation for 9 hours, and then detected the number and mass concentration of SOA particles in real time by changing the isoprene concentration.

Fig.3 showed the effect of reactant concentrations on SOA formation. It can be seen from Fig.3 that both the SOA number concentration and mass concentration increased with increasing of isoprene concentration. As seen from Fig. 3(a) the total number of SOA particles was in about 3 300 particles/cm³ reached peak radiated with the isoprene concentration of 2 mg/L, which was much larger than that of 1.5 mg/L isoprene radiation experiment. It seemed that the increase was more obvious at higher isoprene concentration.

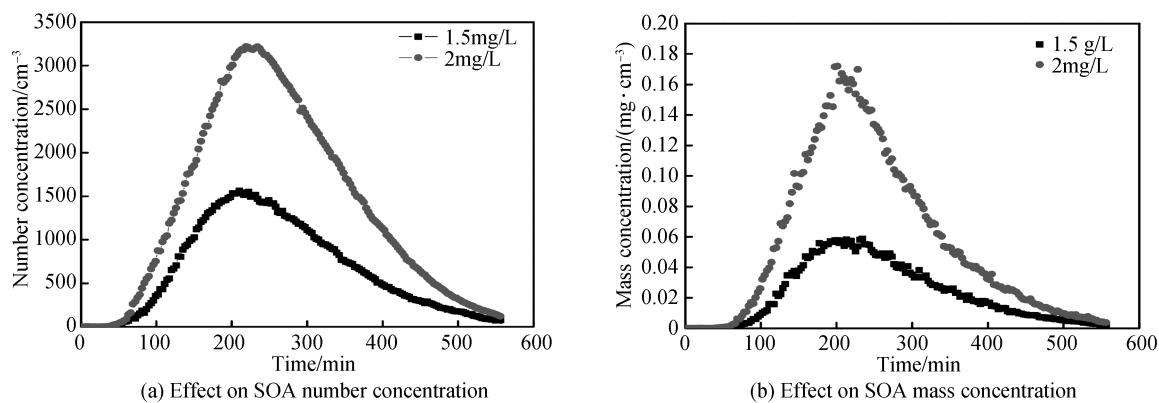


Fig.3 Effect of reactant concentrations on SOA formation

The mass concentration of SOA particles also increases with the reactant concentration as shown in Fig.3(b). It seemed because with the increment of the reaction time, there were more products formed for the subsequent reaction, and the mass concentration of SOA particles would increase due to more semi-volatile organic compounds partitioned between gas phase and particle phase, it would follow that the fine particles became larger through a self-nucleation or condense on the pre-existing aerosol process. Total reaction will be in equilibrium state as soon as the formation rate of fine particles was equal to that of large particles condensed. For lower concentration of toluene, the amount of SOA particles would be increased slightly with increasing concentration of isoprene. At higher concentration of isoprene, the yield of SOA particles would increase rapidly with increasing isoprene.

Compared with the results of toluene^[24], we could get the conclusion that the effect of reactant concentration on isoprene photooxidation followed the same pattern as toluene.

2.3 The effect of CH₃ONO concentration on SOA formation

Hydroxyl radical (OH) concentration plays an important role in the formation of SOA compounds, as in our experiment the hydroxyl radical was generated using the photolysis of methyl nitrite^[22]:

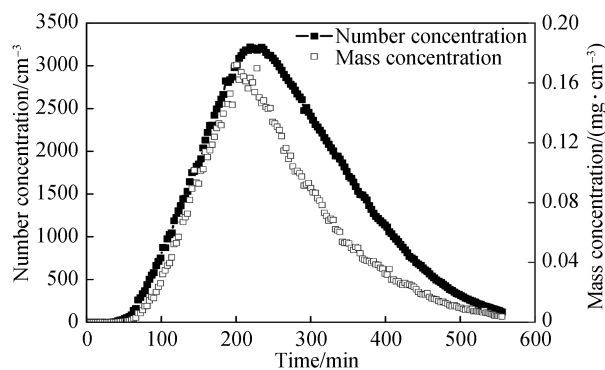
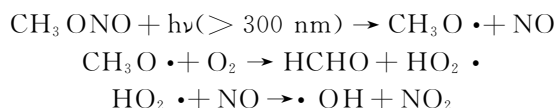


Fig.2 Dependence of number and mass concentration on the radiation time



OH is the initiator of the photooxidation reaction of isoprene. So we investigated the effect of CH₃ONO concentration on SOA formation.

A mixture of 2 mg/L isoprene, 2 mg/L NO and CH₃ONO were illuminated by eight black lamps for 9 h, the effect of concentration of CH₃ONO on the formation of SOA could be studied through the concentration change of CH₃ONO. The experimental results were shown in Fig.4, as can be seen from the figures that both the number and mass concentrations of SOA particles were increased with increasing concentration of methyl nitrate.

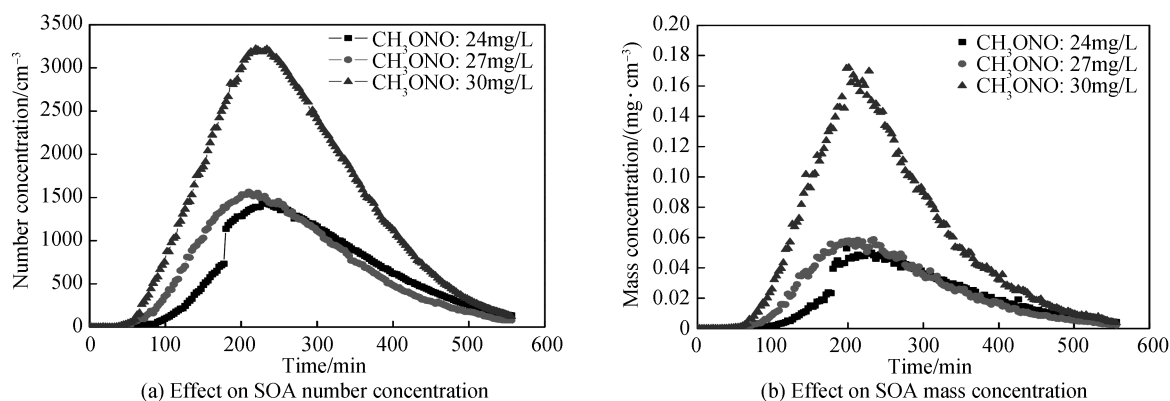


Fig.4 Effect of CH₃ONO concentrations on SOA formation

3 Conclusion

To investigate the effect of radiation time, reactant concentration, and CH₃ONO concentration on SOA formation from the photooxidation of isoprene, a series of chamber experiment were carried out by real time detection of products with *aerodynamic particle sizer spectrometer*. Results showed that, the size distribution of isoprene generated SOA particles was in the range of fine particles and that isoprene was more easily to photolysis, it had large contribution to the formation of SOA. This study clearly demonstrated that the number and mass concentration of SOA particles were increasing with the prolonging of the radiation time and the isoprene concentration, and that the concentration of CH₃ONO had a great contribution to the formation of SOA particles.

References

- [1] CHUNG S H, SEINFELD J H. Global distribution and climate forcing of carbonaceous aerosols[J]. *Journal of Geophysical Research*, 2002, **107**(D19): 4407.
- [2] SEINFELD J H, KLEINDIENST T E, EDNEY E O, *et al.* Aerosol growth in a steady-state, continuous flow chamber: Application to studies of secondary aerosol formation[J]. *Aerosol Science and Technology*, 2003, **37**(9): 728-734.
- [3] SHILLING J E, CHEN Q, KING S M, *et al.* Particle mass yield in secondary organic aerosol formed by the dark ozonolysis of α -pinene[J]. *Atmospheric Chemistry and Physics*, 2008, **8**(7): 17927-17965.
- [4] NAH T, MCVAY R C, ZHANG X, *et al.* Influence of seed aerosol surface area and oxidation rate on vapor wall deposition and SOA mass yields: a case study with α -pinene ozonolysis[J]. *Atmospheric Chemistry and Physics*, 2016, **16**(14): 9361-9379.
- [5] ROMIEU I, GOUVEIA N, CIFUENTES L A, *et al.* Multicity study of air pollution and mortality in Latin America (the ESCALA study)[J]. *Research Report (Health Effects Institute)*, 2012, **24**(171): 5-86.
- [6] MILLER K A, SISCOVICK D S, SHEPPARD L, *et al.* Long-term exposure to air pollution and incidence of cardiovascular events in women[J]. *The New England Journal of Medicine*, **356**(5): 447(2007).
- [7] TSIGARIDIS K, KANAKIDOU M. Global modeling of secondary organic aerosol in the troposphere: a sensitivity analysis[J]. *Atmospheric Chemistry and Physics*, 2003, **3**(5): 2879 -2929.
- [8] SQUIRE O J, ARCHIBALD A, ABRAHAM N L, *et al.* Influence of future climate and cropland expansion on isoprene emissions and tropospheric ozone[J]. *Atmospheric Chemistry and Physics*, 2014, **14**(2): 1011-1024.
- [9] HENZE D K, SEINFELD J H, NG N L, *et al.* Global modeling of secondary organic aerosol formation from aromatic hydrocarbons: high vs. low yield pathways[J]. *Atmospheric Chemistry and Physics*, 2008, **8**(9): 2405-2420.

- [10] PAULOT F, WENBERG P O. Unexpected epoxide formation in the gas-phase photooxidation of isoprene[J]. *Science*, 2009, **325**(5941): 730-733.
- [11] THOMAS D S, AMY E W, AUTUMN R D. Isoprene emission from plants; why and how? [J]. *Annals of Botany*, 2008, **101**(1): 5-18.
- [12] BRÉGONZIO-ROZIER L, DOUSSIN J F, PANGUI E, *et al.* Secondary organic aerosols formation from isoprene photooxidation[J]. *European Aerosol Conference*, 2012, **16**(24): 1869-77.
- [13] SURRATT J D, MURPHY S M, KROLL J H, *et al.* Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene[J]. *Journal of Physical Chemistry A*, 2006, **110**(31): 9665-9690.
- [14] WONG J P S, LEE A K Y, ABBATT J P D. Impacts of sulfate seed acidity and water content on isoprene secondary organic aerosol formation[J]. *Environmental Science and Technology*, 2015, **49**(22): 13215-13221.
- [15] KROLL J H, NG N L, MURPHY S M, *et al.* Secondary organic aerosol formation from isoprene photooxidation[J]. *Environmental Science and Technology*, 2006, **40**(6): 1869-1877.
- [16] KWOK E S, ATKINSON R, AREY J. Observation of hydroxycarbonyls from the OH radical-initiated reaction of isoprene[J]. *Environmental Science and Technology*, 1995, **29**(9): 2467-2469.
- [17] WANG S, WU D, WANG X M, *et al.* Relative contributions of secondary organic aerosol formation from toluene, xylenes, isoprene, and monoterpenes in Hong Kong and Guangzhou in the Pearl River Delta, China: an emission-based box modeling study[J]. *Journal of Geophysical Research: Atmospheres*, 2013, **118**(2): 507-519.
- [18] SZMIGIELSKI R, SURRATT J D, VERMEYLEN R, *et al.* Characterization of 2-methylglyceric acid oligomers in secondary organic aerosol formed from the photooxidation of isoprene using gas chromatography/ion trap mass spectrometry[J]. *Journal of Mass Spectrometry*, 2007, **42**(1): 101-116.
- [19] RUPPERT L, BECKER K H. A product study of the OH radical-initiated oxidation of isoprene: formation of C5-unsaturated diols[J]. *Atmospheric Environment*, 2007, **34**(10): 1529-1542.
- [20] JANG M, CZOSCHKE N M, LEE S, KAMENS R M. Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reaction[J]. *Science*, 2002, **298**(5594): 814-817.
- [21] LIU X, ZHANG W, HUANG M, *et al.* Effect of illumination intensity and light application time on secondary organic aerosol (SOA) formation from the photooxidation of α -pinene[J]. *Journal of Environmental Sciences*, 2009, **21**(4): 447-451.
- [22] ATKINSON R, CARTER W P L, WINER A M, *et al.* An experimental protocol for the determination of OH radical rate constants with organics using methyl nitrite photolysis as an OH \cdot radical source[J]. *Air Pollution Control Association*, 1981, **31**(10): 1090-1092.
- [23] SCHWARTZ J, DOCKERY D W, NEAS L M J. Is daily mortality associated specifically with fine particles? [J]. *Journal of Air and Waste Management Association*, 1996, **46**(10): 927-939 (1996).
- [24] HAO L, WANG Z, HUANG M, *et al.* Size distribution of the secondary organic aerosol particles from the photooxidation of toluene[J]. *Journal of Environmental Sciences*, 2005, **17**(6): 912-916.