Size distribution of the secondary organic aerosol particles from the photooxidation of toluene

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Abstract: In a smog chamber, the photooxidation of toluene was initiated by hydroxyl radical (OH ·) under different experimental conditions. The size distribution of secondary organic aerosol(SOA) particles from the above reaction was measured using aerodynamic particle sizer spectrometer. It was found from our experimental results that the number of SOA particles increased with increasing the concentration of toluene. As the reaction time prolonged, the sum of SOA particles was also increased. After a reaction time of 130 min, the concentration of secondary organic aerosol particles would be kept constant at 2300 particles/cm^3. Increasing illumination power of blacklamps could significantly induce a higher concentration of secondary organic aerosol particle. The density of SOA particles would also be increased with increasing concentration of CH$_3$ONO, however, it would be decreased as soon as the concentration of CH$_3$ONO was larger than 225.2 ppm. Nitrogen oxide with initial concentration higher than 30.1 ppm was also found to have little effect on the formation of secondary organic aerosol.

Keywords: toluene; hydroxyl radical; secondary organic aerosol; smog chamber

Introduction

Aerosol is the solid and liquid phase particles suspending in the atmosphere, and it has possible impact on the ecologic environment and our health. It can be divided into two kinds: organic aerosol and inorganic aerosol. Secondary organic aerosol (SOA) is one kind of organic aerosol. The formation of SOA in the atmosphere has renewed our interest. The terpene system emitted from terrestrial vegetation, and aromatic hydrocarbon from anthropogenic source, might be the main sources to form SOA particles. These molecules can easily be attacked by a reactive species, such as hydroxyl radical (OH ·), ozone (O$_3$) and nitrate radical (NO$_3$), generating large number of primary and secondary compounds. The situation is further complicated by the formation of semivolatile products which can result in SOA formation through either a self-nucleation process or the gas/particle partitioning on preexisting particulate matter (Myoseon, 2001).

Volatile aromatics are very important constituents in urban and regional atmosphere. It comprises up to 44% of the urban volatile hydrocarbon mixture in various parts of the world. Of the aromatics, benzene, toluene, xylene, ethylbenzene and 1,2,4-trimethylbenzene make up 60%—75% of this load, with toluene being one of the most significant compounds. They have been identified as aerosol precursors (Jang, 2001). Over the last two decades, laboratory studies on the formation mechanism of SOA from photooxidation of toluene (Suh, 2003; Myoseon, 2001; Forstner, 1997; Odum, 1996), and on the identification of their oxidation products (Kleindienst, 2004; Jaoui, 2004; Myoseon, 2001; Forstner, 1997) have been conducted in some laboratories over the world. Some studies involving the effects of environmental factors on the formation of SOA were also performed at times, for example, Sewon *et al*. thought of that existing atmospheric aerosols in atmosphere should be favorable for the formation of SOA(Sewon, 2000); Edney *et al*. (Edney, 2000) pointed out that SOA yields from the oxidation products of toluene may not be obviously affected by

the presence of aerosol liquid water, while Takekawa (Takekawa, 2003) told us according to his experimental study that the temperature is one of the most important factors in the formation of SOA. However, the influence of other factors on the formation of SOA, such as the initial concentration of toluene, NOx, and OH radical, intensity of illumination and the irradiative reaction time, has not been clarified. Under such situations, a series of toluene photo-oxidation experiments have been performed using a static smog chamber in this paper. The sum and distribution of SOA particles were detected using an aerodynamic particle sizer spectrometer. The factors impacting the formation of SOA were also discussed.

1 Experimental section

1.1 Materials

Toluene (> 99%) was obtained from Sigma-Aldrich Chemistry Corporation, Germany. Sodium nitrate(> 99%) and methanol(> 99%) were purchased from the Tianjin(The Third Reagent Manufactory, China), and nitrogen oxide (99.9%) from Nanjing Special Gas Factory, China.

Methyl nitrite was synthesized by the dropping sulfuric acid into a methanol solution of sodium nitrate. Their reaction products passed through saturated sodium hydroxide trap to remove the traces of sulfuric acid, and were dried by passing through a calcium sulfate trap and was collected using a condenser of liquid nitrogen at 196 K. The methyl nitrite was purified using a vacuum system of glass.

1.2 Smog chamber experiments

The experimental setup consists of a smog chamber and manifold vacuum system. The smog chamber was made of quartz tube, and its volume and the ratio of surface to volume were 23.3 L and 22.4 m^{-1} respectively. The reactor is surrounded by 16 fluorescent blacklamps used to initiate the reactions. The output power of each black lamp is 20 W and its wavelength of UV radiation is in the range of 300—400 nm. The volume of glass vacuum system is 0.84 L, equipped with a vacuum gauge whose measuring range is 10—5000 Pa. A schematic diagram of the experimental system is shown in
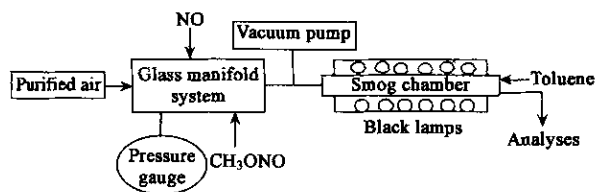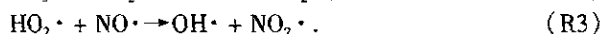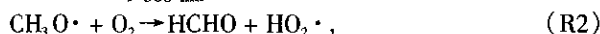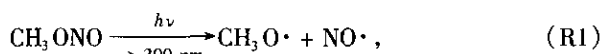
Fig.1   Schematic of experimental apparatus

Fig.1.

Prior to start each experiment, the chamber was continuously flushed with purified laboratory compressed air for 20 min, and evaluated to a vacuum of 10^{-1} Pa by a mechanical pump. The compressed air was processed through three consecutive packed-bed scrubbers containing, in order, activated charcoal, silica gel and a Balston DFU* filter (Grade BX) respectively, to remove the trace of hydrocarbon compounds, moisture and particles. Toluene 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 steam of purified air. The whole system was completely shrouded from sunlight with a black polyethylene tarpaulin. 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

$$CH_3ONO \xrightarrow[> 300\ nm]{h\nu} CH_3O \cdot + NO \cdot ,$$ (R1)

$$CH_3O \cdot + O_2 \rightarrow HCHO + HO_2 \cdot ,$$ (R2)

$$HO_2 \cdot + NO \cdot \rightarrow OH \cdot + NO_2 \cdot .$$ (R3)

After injection of the reactant gases into the smog chamber, the purified air got into it again until the pressure within it became 10^5 Pa. Then, turn on two blacklamps to begin the photooxidation experiment for 10 min. In all the experiments, the relative humidity was controlled in a range from 50% to 70% , and temperature was in the range of 295 ±2 K.

1.3 Product characterization

At the end of reaction, the resulting aerosol mixtures were drawn into the sampling head of the TSI 3321 aerodynamic particle sizer spectrometer (TSI Corporation, USA) through a Teflon line. The numbers, size and mass concentration of SOA particles can be measured directly with this spectrometer with a classified aerosol flow rate of 1.0 L/min. The sampling time was 20 s. This instrument can detect particles with aerodynamic size range of 0.5—20 μm, and with high resolution of 0.02 μm at 1.0 μm diameter and 0.03 μm at 10 μm diameter.

2 Results and discussion

2.1 Effect of toluene concentration on the SOA formation

A series of experiments were conducted to examine the effect of toluene concentration on SOA formation. At the first, the primary concentrations of methyl nitrate and NO were maintained at 90.2 ppm and 60.1 ppm respectively, and the irradiating time is fixed as 10 min, and then, seven individual experiments with selected toluene concentration of 0, 4.9, 9.8, 19.6, 29.5, 39.7 and 49.1 ppm were

performed. Fig.2 and Fig.3 show the size distribution of SOA particles in these experiments. It is found that the particles size distribution was in a range of 0.5—1.0 μm (Fig.2). The number and size of particles are increased obviously with increasing the concentration of toluene. The concentration of particles increased from 8 molecules/cm^3 for [toluene]$_0$ = 1.0 ppm to 1926 molecules/cm^3 for [toluene]$_0$ = 49.1 ppm, here [toluene]$_0$ represents the initial concentration of toluene(Fig.3). It appears that the increase is more obvious at higher toluene concentration. The relationship between number density of particles and concentration of toluene is shown in Fig.3. These seven datum can be fitted well using Eq.(1):

$$Y = 112.16414 \times e^{\frac{x}{17.1447}} - 75.98583.$$ (1)

Where Y and x are the number density of SOA particles (molecules/cm^3) and the concentration of toluene (ppm). Using the curve from Fig.3, the number density of SOA particles increased with the concentration of toluene. For lower concentration of toluene, the amount of SOA particles will be increased slightly with increasing concentration of toluene. At higher concentration of toluene, the yield of SOA particles will increase rapidly with increasing [toluene]$_0$.
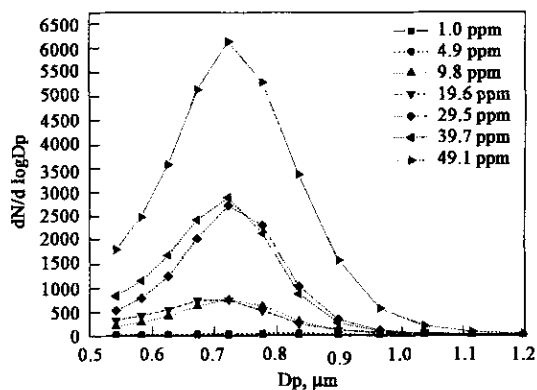
Fig.2   Size distribution of SOA particles(Dp) with $\varphi > 0.523$ μm with a series of toluene concentrations
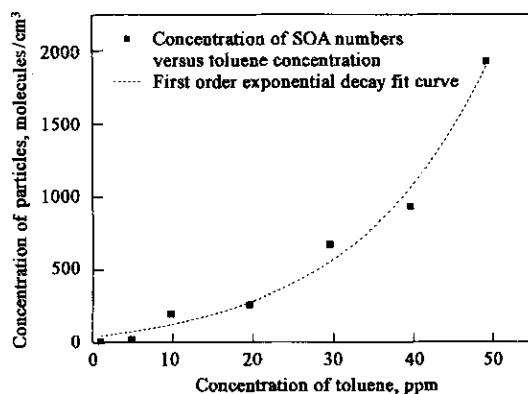
Fig.3   Number density of SOA particle as a function of [toluene]$_0$. The dot profile was fit to the datum by the first order exponential decay

2.2 Dependence of SOA formation on reaction time

In order to study the dependence of SOA formation on reaction time, the concentrations of toluene, methyl nitrate, and NO were fixed at 4.9 ppm, 90.2 ppm and 60.1 ppm, respectively, and the reaction times were changed in the

range of 5—180 min. The results are shown in Fig.4, 5 and
6. The size of the SOA particles might be distributed in the
range of 0.523—20.0 μm (Fig. 4 and Fig. 5), while the
relation of the total numbers of the SOA particles(diameter <
0.523 μm) to reaction times is shown in Fig.6. The number
of SOA particles will be increased slowly within the first 30
min of the reaction time and the amount of SOA particles will
increase slightly with prolonging the reaction time. Perhaps
there exists an induction process in OH · initiated
photooxidation of toluene. After the reaction time of 30 min,
the rate of its subsequent reaction becames quicker than
before and the number of SOA particles also increased. After
130 min, the concentration of particles is kept at a level of
2300 molecules/cm^3. Although the number of particles(size
> 0.523 μm) will be increased with the reaction time after
130 min in Fig.5, the number of particles(size < 0.523 μm)
decreased with the reaction time (Fig. 6), and the whole
concentration of particles will be kept as shown in Fig.7. The
size of SOA particles was not changed although the total
number of SOA increased within 180 min reaction. Under the
experimental conditions mentioned above, the longer the
reaction time was, the higher the concentration of the
subsequent reaction products was. Therefore, the number of
SOA particles will be increased due to that more semi-volatile
organic compounds are partitioned between gas phase and
particle phases. It was followed that the fine particles matter
became larger through a self-nucleation or condense on the
pre-exiting aerosol process. Total reaction system would be in
equilibrium state as soon as the formation rate of fine particles
was equal to that of large particles condensed, and the
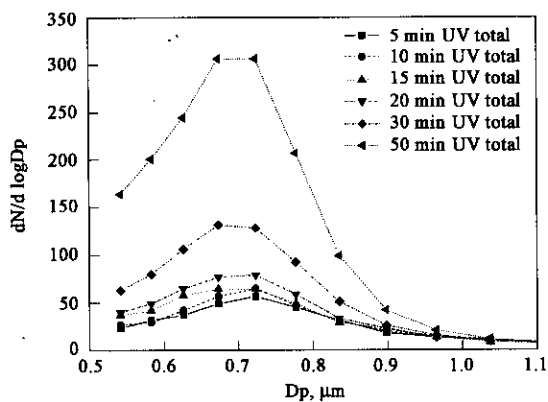number density of SOA will be kept constantly.

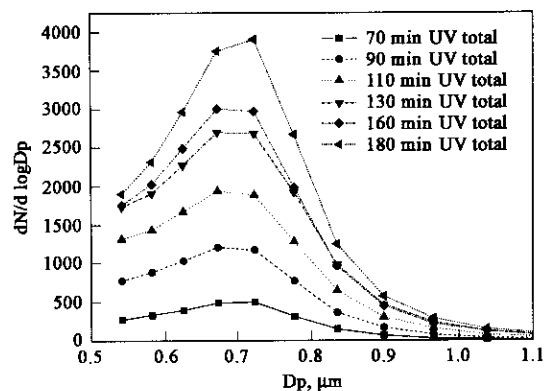Fig.5   Size distribution of SOA particles with $\varphi > 0.523$ μm after 70—180
min irradiation time
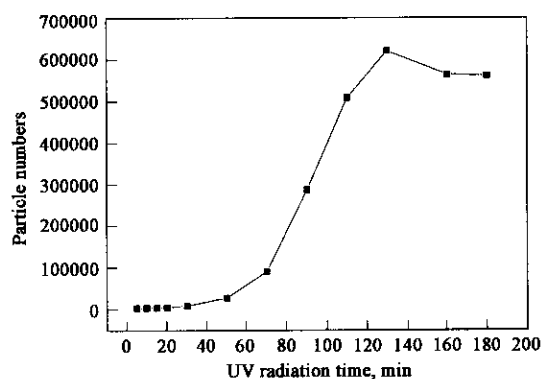
Fig.6   SOA particle numbers with $\varphi < 0.523$ μm vs different irradiation times

Fig.4   Size distribution of SOA particles with $\varphi > 0.523$ μm after 5—50 min
irradiation time
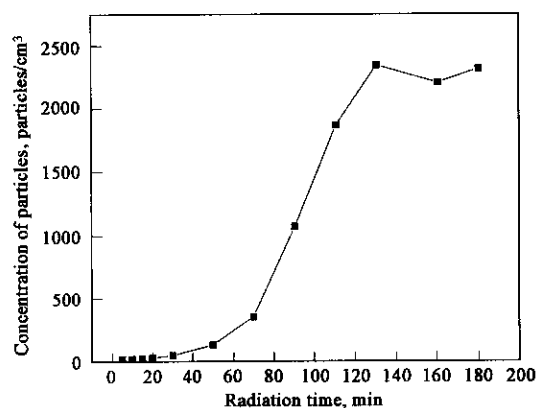

Fig.7   Number density of SOA particles with diameter of 0—20 μm vs
different irradiation times(5—180 min)

2.3   Effect of illumination intensity on SOA formation

When the concentrations of toluene, methyl nitrate, and
NO were fixed at 4.9, 90.2 and 60.1 ppm, the effects of
illumination intensity on SOA formation can be investigated
through the change of intensity of illumination of blacklamps.
Within the same reaction time for 10 min, if the irradiating
intensity of blacklamps was increased properly, for example,
40, 80, 120, 160, 200 and 280 W, the photodissociation
rate of methyl nitrate would increase, photooxidation reaction
rate of toluene increased, and more particles of SOA were
formed as shown in Fig.8 and Fig.9. The total number of
SOA particles was 2127 particles/cm^3 radiated by 280 W
black lamps, much higher than 19 particles/cm^3 by 40 W.

However, the diameter of their particles at the peak of their
plot was always kept around 0.72 μm. A function form of the
total amount of SOA (molecules/cm^3) in terms of power of
blacklamps(W) is presented as Eq.(2):

$$Y = 153.11979 \times e^{\frac{x}{85.20773}} + 294.54746 \times$$
$$e^{\frac{x}{277.74796}} - 385.05998.   \qquad (2)$$

Where Y is the concentration of SOA(molecules/cm^3),
and x represents the power of blacklamps(W). As suggested
by Eq. (2), the number of SOA can be prominently
increased with irradiative intensity. The irradiative intensity
has a great contribution to the formation of SOA particles.

2.4   Effect of NO concentration on SOA formation

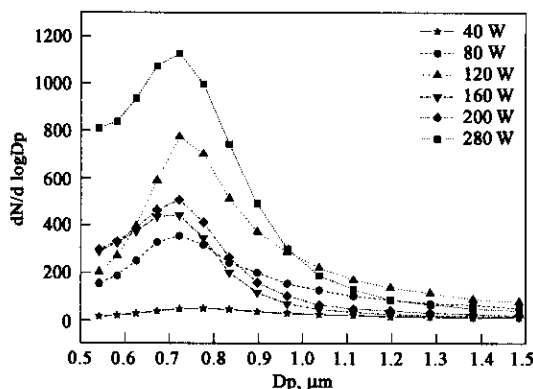When the primary concentration of toluene and methyl

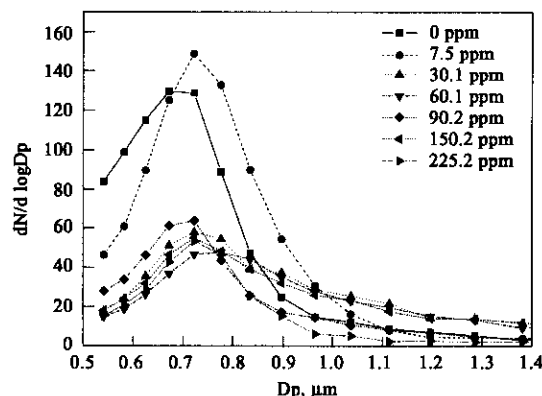Fig.8   Size distribution of SOA particles with φ > 0.523 μm using different illumination intensity

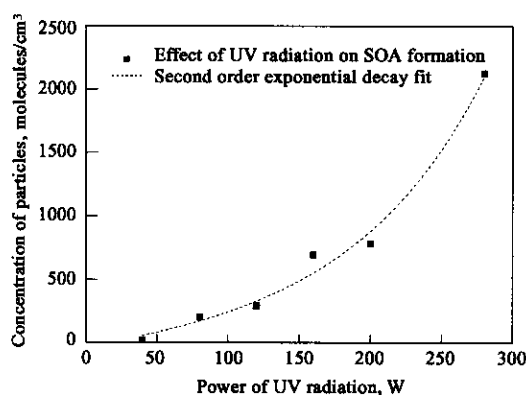Fig.10   Size distribution of SOA particles at different concentration of NO

Fig.9   Numbers density of SOA particles with diameter of 0—20 μm vs illumination intensity.
Curve was fit to the datum using secondary order exponential decay fitting

Fig.11   SOA particle numbers vs the concentration of NO

nitrate were kept as 4.9 ppm and 90.2 ppm, and the time of photochemical reaction was kept for 10 min, the effect of NO concentration on SOA formation can be studied through changing the concentration of NO in the range of 0—225.2 ppm. As shown in Fig.10 and Fig.11, the number of SOA particles was 160 molecule/cm^3 when [NO]$_o$ was 0.0 ppm, and then, the sum of particles decreased with increasing NO concentration. When [NO]$_0$ was higher than 30.1 ppm, the concentration of particles was fixed at 22 molecule/cm^3. It appears that [NO]$_0$ has a negligible effect on the aerosol yield when the value was higher than 30.1 ppm. Hall(Hall, 1997) pointed out that it is favorable to the formation of SOA particles in case of ratios of hydrocarbon to NOx at least 25. According to Hall's theory, the optimal concentration of NO should be lower than 0.2 ppm. However, the experimental study using this optimal parameter of NO was not done due to the limitation of our experimental conditions.

2.5   Effect of CH$_3$ONO concentration on SOA formation

Hydroxyl radical was generated using the photolysis of methyl nitrite, and initiator of the photooxidation reaction of toluene. A mixture of 4.9 ppm toluene, 60.1 ppm NO and CH$_3$ONO was illuminated by two blacklamps for 10 min, the effect of concentration of CH$_3$ONO on the formation of SOA can be studied through the concentration change of CH$_3$ONO within the range of 30.1—375.2 ppm. Their results are shown in Fig. 12—14. At 30.1 ppm for [CH$_3$ONO]$_0$, a
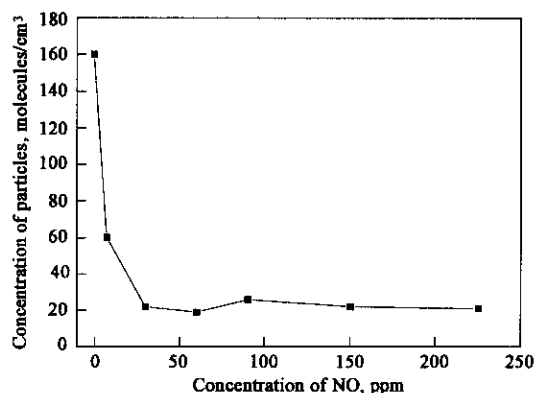
minor concentration of particles was formed due to the low concentration of OH radical generated. The sum of particles was increased with increasing [CH$_3$ONO]$_0$. A maximum concentration of particles, 235 molecule/cm^3, was obtained when [CH$_3$ONO]$_0$ was 225.4 ppm, followed by a prominent decrease of particle concentration with increasing [CH$_3$ONO]$_0$ continuously. A higher concentration of CH$_3$ONO might resulte in substantially higher concentration of OH·, and as a result, it is not suitable for the formation of SOA particle due to more volatile compounds of small molecules from the OH-initiated photooxidation of toluene.
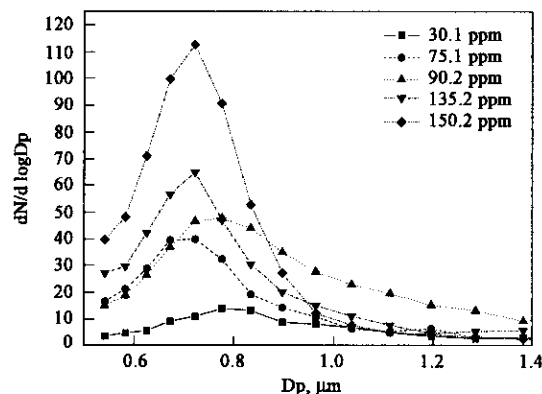

Fig.12   Size distribution of SOA particles with φ > 0.523 μm by increasing the concentration of CH$_3$ONO(30.1—150.2 ppm)

3   Conclusions
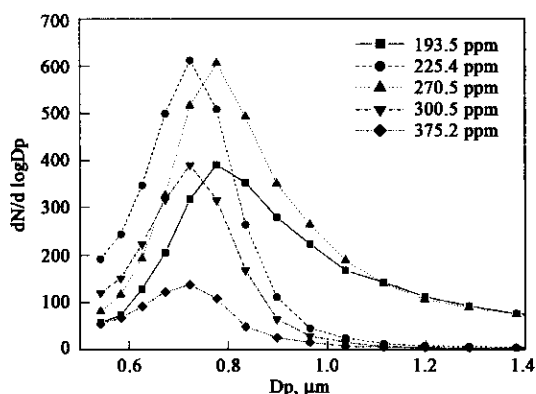
The formation of SOA is one of the most important

Fig.13   Size distribution of SOA particles with φ > 0.523 μm by increasing the concentration of CH_3ONO(193.5—375.2 ppm)
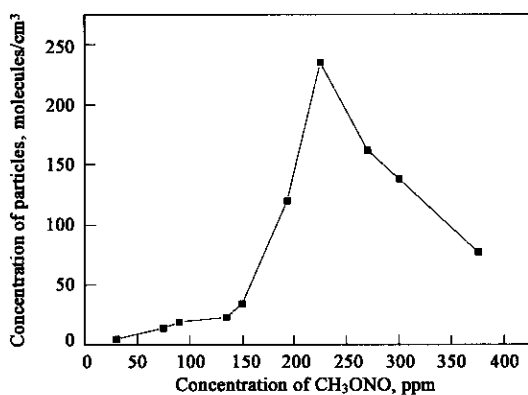

Fig.14   Number density of SOA particles vs concentration of CH_3ONO

features of photochemical smog in urban atmosphere and there is a growing concern over the role of SOA in the atmospheric chemistry. In this paper, the effect of five factors on the

formation of SOA from the photooxidation of toluene has been investigated by the direct detection of products with aerodynamic particle sizer spectrometer, and some useful information were obtained also. Improvements of the detection and analysis technologies of SOA will be performed and the formation mechanism of SOA from the photooxidation of aromatic hydrocarbons will be investigated further in our laboratory.

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