Effects of seed aerosols on the growth of secondary organic aerosols from the photooxidation of toluene

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Abstract

Hydroxyl radical (·OH)-initiated photooxidation reaction of toluene was carried out in a self-made smog chamber. Four individual seed aerosols such as ammonium sulfate, ammonium nitrate, sodium silicate and calcium chloride, were introduced into the chamber to assess their influence on the growth of secondary organic aerosols (SOA). It was found that the low concentration of seed aerosols might lead to high concentration of SOA particles. Seed aerosols would promote rates of SOA formation at the start of the reaction and inhibit its formation rate with prolonging the reaction time. In the case of ca. 9000 pt/cm^3 seed aerosol load, the addition of sodium silicate induced a same effect on the SOA formation as ammonium nitrate. The influence of the four individual seed aerosols on the generation of SOA decreased in the order of calcium chloride>sodium silicate and ammonium nitrate>ammonium sulfate.

Key words: toluene; photooxidation; secondary organic aerosol; seed aerosol

Introduction

Ambient aerosol can adversely affect atmospheric visibility, the climate and human health. Its source includes the primary aerosol from direct emissions and secondary aerosols through secondary processes. The secondary organic aerosol (SOA) is a key component in secondary aerosols and accounts for as much as 50% of the total aerosol mass. It is produced mainly through the ·OH initiated photooxidation reaction, acid catalyzed reaction on the surface of particle, and gas/particle partitioning or self-nucleating of semi-volatile reaction products (Kleindienst et al., 1999; Edney et al., 2005; Wang et al., 2005).

The SOA formation is related to the primary aerosol, which is one of seed aerosols and can act as the absorption or adsorption centers of SOA formation. The number size distribution of these seed aerosols is the dominant factor for condensation and coagulation process of the reaction products, and the surface area of the particle can also play an important role in the adsorption and catalytic reactions (Oh and Andino, 2000). Over the last decade, laboratory studies have been conducted to assess whether the presence of pre-existing submicron seed aerosols can affect the SOA formation. Cocker's studies indicated the presence of ammonium sulfate seed aerosol with little relative humility (RH) variation has a negative impact on the SOA yield

(Cocker et al., 2001). His conclusion disagreed with the results by Oh and Andino (2000) and by Koehler et al. (2004). Under the condition of the high RH, Edney et al. (2000) suggested that the presence of water on the seed aerosol did not significantly affect the SOA yield, which was also discrepant with the results of Cocker et al. (2001). Besides, in the atmosphere, there are some seed aerosols with different concentration and constituents. However, studies as regards how these seed aerosols affect SOA formation are less reported at present.

In this article, the effects of concentration and composition of four seed aerosols such as $(NH_4)_2SO_4$, NH_4NO_3, Na_2SiO_3 and $CaCl_2$ on the SOA formation were studied respectively during the UV-irradiation of toluene/CH_3ONO/NO/air mixtures in a self-made smog chamber. The experiments were conducted using pre-existed seed aerosols inside the smog chamber to simulate the SOA formation. The aim of this study was to determine the extent to which the SOA yields were affected by compositions and concentrations of seed aerosols as previously mentioned.
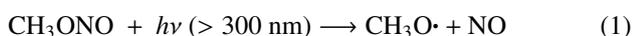
1 Experimental

1.1 Materials

Toluene (>99%) was obtained from the Sigma-Aldrich Chemistry Corporation, Germany; nitrogen oxide (99.9%) was purchased from the Nanjing Special Gas Factory, China. Purity of agents of $(NH_4)_2SO_4$, NH_4NO_3, Na_2SiO_3

and CaCl$_2$ (Shanghai Chemical and Medical Corporation, China) was >99.7%. Methyl nitrite (CH$_3$ONO) was synthesized by dropping sulfuric acid into a methanol solution of sodium nitrate (Hao *et al*., 2005; Wang *et al*., 2006) and collected by a condenser of liquid nitrogen at 77 K.

1.2 Experimental methods

Experiments were performed in an 850-L sealed collapsible polyethylene smog chamber. Its ratio of surface to volume was 5.8 m^{-1}. Around the chamber, there was equipped with 12 sets of 40-W fluorescent black lamps symmetrically that provide radiation in the 300–400 nm region. The bag and lamps were housed inside a highly reflective enclosure to enhance light distribution.

Prior to the start of experiment, the chamber was continuously flushed with purified laboratory compressed air for 40 min. The compressed air was processed through three consecutive packed-bed scrubbers, which contain activated charcoal, silica gel and a Balston DFU® filter (Grade BX) respectively, to remove trace hydrocarbon compounds, moisture and particles. The four individual seed aerosols were generated by aspirating 0.0067 mol/L aqueous solution through a stainless steel, constant rate atomizer (TSI 3076, USA), respectively. The mean diameter of each kind of seed aerosols was approximately 80 nm. In all cases, the seed aerosols were passed through a diffusion dryer (TSI 3062) with exiting RH lower than 20%, followed by an ^{85}Kr neutralizer (TSI 3012) before entering the chamber. After obtaining the desired initial seed particles concentration, 1.35 μl/L toluene, 24.0 μl/L CH$_3$ONO, 2.0 μl/L NO were injected into the chamber, mixed with the pre-existing seed aerosol. And again the chamber was filled with the purified air to 850 L full volume. Turn on four black lamps and initiate the photooxidation reaction. Hydroxyl radicals will be generated by the photolysis of methyl nitrate in air at wavelengths longer than 300 nm (Hao *et al*., 2005; Wang *et al*., 2006). The chemical reactions leading to the formation of the ·OH radical are as follows:

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

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

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

·OH-initiated toluene photooxidation reaction will lead to the formation of the SOA particles. During the course of reaction, the number concentration of SOA particles was detected by an aerodynamic particle size spectrometer (TSI APS 3321) quickly.

1.3 Datum processing methods

Similar experimental procedures for the four individual seed aerosols were designed to assess their influence on the formation of SOA and the concentration of SOA particles were measured by APS 3321directly. Figs.2a, 3a and 4a show the growth of SOA particles as the functions of reaction time. The model lines through the data were chosen to fit the data points of measurement using Sigmoidal-Fit method. The curves in Figs.2b, 3b and 4b represent the incremental rate of SOA particles concentration as functions of reaction time, and they were obtained by making the first derivative of the corresponding curves in Figs.2a, 3a and 4a, respectively.

2 Results

2.1 Size distribution of secondary organic aerosols

Fig.1 shows the size distributions of SOA in the presence/absence of the four individual seed aerosols. These aerosol particles are distributed in the range of 0.5–1.4 μm and belong to ultra fine particles, which can affect health problems due to humans' inhalation of high particle matter.
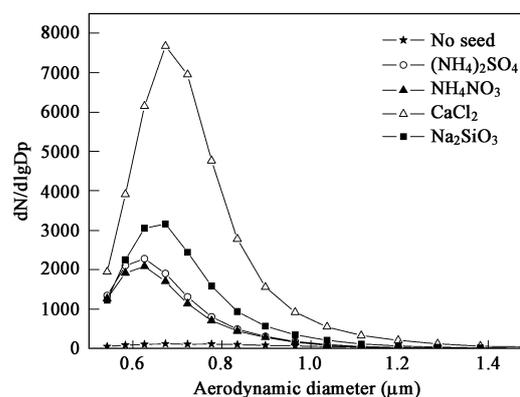

Fig. 1 Size distribution of SOA particles from toluene photooxidation reaction. Reaction time: 60 min; seed concentration: cv. 9000 pt/cm^3; dN/dlgDp displays differential or normalized particle size distribution, normalized to one decade of particle size.

2.2 Effect of (NH$_4$)$_2$SO$_4$ seed aerosol on the SOA formation

Fig.2 shows the influence of (NH$_4$)$_2$SO$_4$ seed aerosol on the formation of SOA particles at the level of three concentrations of particles. By comparison, the SOA formation can be affected by (NH$_4$)$_2$SO$_4$ seed aerosol in three different ways:

Firstly, the presence of seed aerosol shortens the time to reach the gas-particle partitioning equilibrium. In the absence of (NH$_4$)$_2$SO$_4$ seed aerosol, it takes 197 min to reach the gas-particle partitioning equilibrium between gas/particle phases with the ultimate aerosol concentration maintaining 2128 pt/cm^3. In the presence of ca. 27000 pt/cm^3 seed aerosol, the period to reach such equilibrium status is 135 min, and the lower the number concentration of seed aerosol is, the longer the time to reach an equilibrium state is. Secondly, the presence of (NH$_4$)$_2$SO$_4$ seed aerosol can accelerate the growth rate of SOA at the initial stage of the photochemical reaction, followed by decreasing the growth rate of SOA with prolonging reaction time. In Fig.2b, the growth rate of SOA is faster in the initial 45 min than that one in the absence of seed aerosols, which indicates that there is a stimulating effect of seed aerosol on the SOA formation. After 45 min, SOA particle concentration grows at a lower rate in the presence than in the absence of seed aerosol, which shows that there is an inhibition effect of the seed aerosol on the
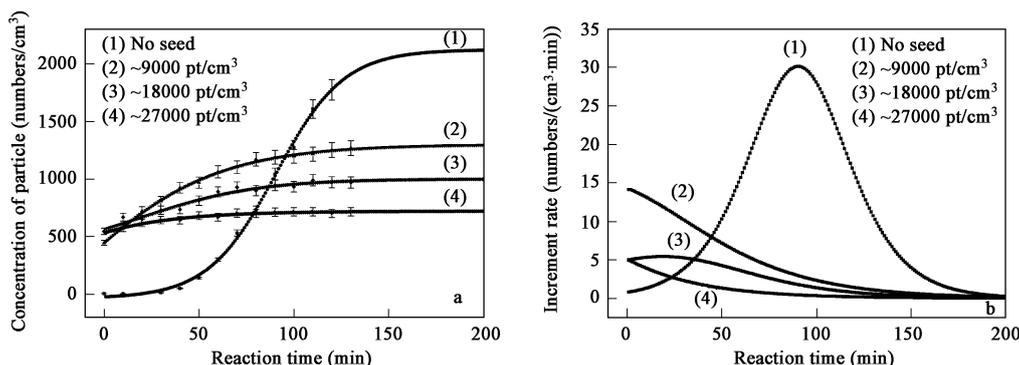
Fig. 2 Impact of ammonium sulfate seed aerosol on the formation of secondary organic aerosol. (a) growth curve; (b) increment curve.

SOA formation. Similar results for the ca. 18000 pt/cm³ seed aerosol experiments are shown in curve (3) of Fig.2b. The SOA particles grow faster initially, then undergo a 35 min period of growth and ultimately decrease. For the case of ca. 27000 pt/cm³ seed aerosol, the stimulating time is only 25 min as shown in curve (4). Lastly, the finial equilibrium number concentration of SOA particle in the presence of seed aerosol is lower than that in the absence of seed aerosol. The finial SOA particle concentrations will become lower as the number concentrations of seed aerosols are higher, which indicates that the presence of $(NH_4)_2SO_4$ seed aerosol will reduce the amount of SOA and the degree of reduction is dependent on the concentrations of seed aerosols.

2.3 Effect of $CaCl_2$ seed aerosol on the SOA formation

Fig.3 shows the influence of $CaCl_2$ seed aerosols on the SOA formation. It can be seen that in the present experiments, the presence of $CaCl_2$ seed shorten the time to reach the gas/particle equilibrium state, and the $CaCl_2$ seed aerosol also acts as an accelerator in the process of SOA formation at the initial stage of the reaction and inhibits the formation of SOA particles while the reaction keeps on. When the number concentration of $CaCl_2$ seed aerosol is low, its stimulating effect on the SOA formation will be much larger. These results are in good agreement with those of $(NH_4)_2SO_4$ seed.

2.4 Potentials of four individual seed aerosols in the SOA formation

The effects of four individual seed aerosols on the SOA formation are shown in Fig.4. In each curve, the

particle number concentration is increased as a function of reaction time in the presence and absence of seed aerosol, respectively. The primary number concentration of each kind of the seed aerosol was ca. 9000 pt/cm³. It can be seen that $CaCl_2$ seed has the most prominent stimulating effect on the SOA formation. The effect of sodium silicate on the SOA formation was the same as the ammonium nitrate seed aerosol. The stimulatory effect of seed aerosol on the SOA formation increased in the order of $CaCl_2 > NH_4NO_3/Na_2SiO_3 > (NH_4)_2SO_4$.

3 Discussion

3.1 Dependence of the formation of SOA on seed aerosols

The experimental results show that all the four seed aerosols have effects on the formation of SOA from the oxidation products of toluene. These can be interpreted using the expression for the overall SOA yields from the ·OH initiated photooxidation reaction of toluene and some subsequent reactions are as follows (Odum *et al.*, 1997):

$$Y_{SOA} = \sum_i Y_i = M_o \sum_i \left(\frac{\alpha_i K_{i,om}}{1 + K_{i,om} M_o} \right) \qquad (4)$$

Where, Y_i and Y_{SOA} are the yield of an individual product and the total SOA yield respectively; α_i is the proportionality constant relating the concentration of ROG that reacts to the concentration of product i (C_i) that is formed; $K_{i,om}$ is the gas-particle partitioning coefficient, which is inversely proportional to the compounds vapor
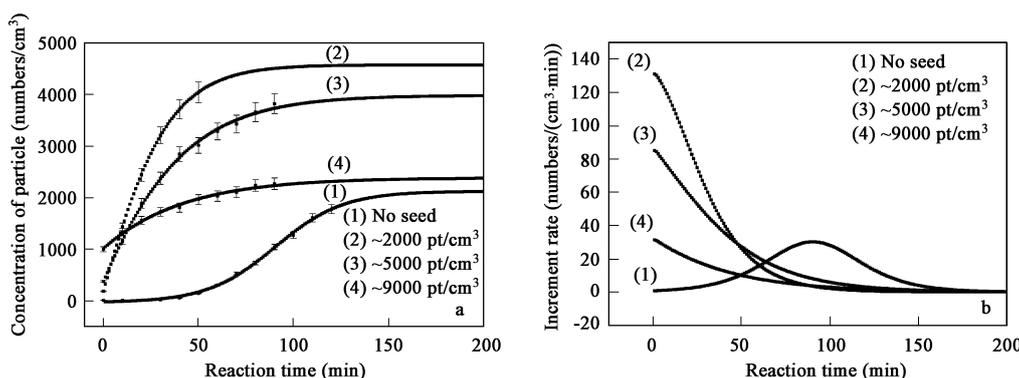

Fig. 3 Impact of calcium chloride seed aerosol on the formation of secondary organic aerosol. (a) growth curve; (b) increment curve.
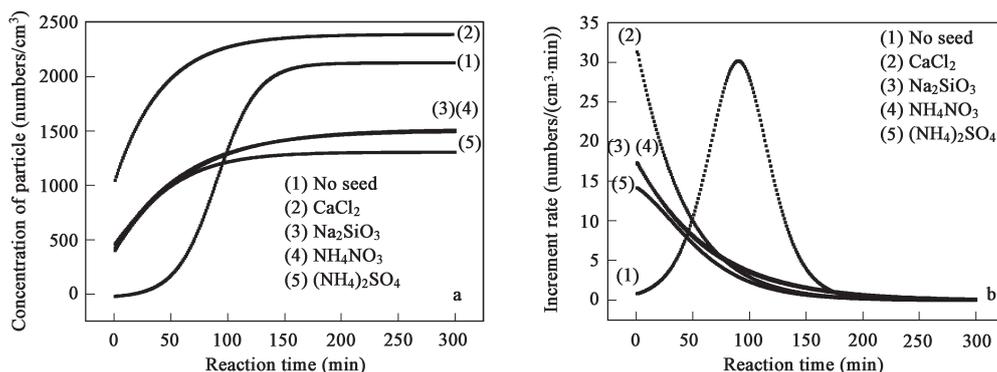
Fig. 4   Impact of four individual seed aerosols on the formation of secondary organic aerosols. (a) growth curve; (b) increment curve.

and pressure, and M_o is the absorbing organic aerosol mass concentration, including the organic/inorganic material and associated water present in the aerosol phase.

For model Equation (1), it has two limiting conditions based on the value for $K_{i,om}M_o$. Firstly, it is suggested that for low organic mass concentration and for products that have relatively small partitioning coefficients, that is $K_{i,om}M_o \ll 1$, then the SOA yield will be directly proportional to the total aerosol organic mass concentration M_o:

$$Y_{SOA} = M_o \sum_i (\alpha_i K_{i,om}) \qquad (5)$$

secondly, for very non-volatile products and/or for large organic mass concentration , that is $K_{i,om}M_o \gg 1$, the individual product yields will be independent of the organic mass concentration and will be equal to α_i, then,

$$Y_{SOA} = \sum_i \alpha_i \qquad (6)$$

In the absence of seed, M_o is very small at the initial stage of the photooxidation reaction of toluene, that is, $K_{i,om}M_o \ll 1$, the low-yield of SOA will lead to the low number concentration of SOA particle which can be predicted from the Equation (2). As the reaction keeps on, the formed SOA particles can also act as the absorbing material M_o. The SOA yield will increase with M_o and the number concentration will become much high. When it comes to the case of $K_{i,om}M_o \gg 1$, the SOA yield is only related to α_i as described by Equation (3), so the SOA yield did not change and the finial number concentration of SOA particle will keep constant.

In the presence of seed aerosols, the value of M_o is larger than that in the absence of seed aerosols at the initial stage of the oxidation reaction. According to the Equation (2), Y_{SOA} is higher than that in the absence of seed aerosols, which shows that the SOA number concentration is larger. As a result of the higher concentration SOA particles, the situation of $K_{i,om}M_o \gg 1$ will appear soon during a shorter period due to the rapid increase of M_o. Thus, the reaction system will account for a shorter time to maintain a gas/particle partitioning equilibrium state and the SOA number concentration will remain constant.

3.2 Stimulating effect of CaCl₂ seed aerosol on the SOA formation

Among the four individual seed aerosols, the $CaCl_2$ aerosol shows the strongest hygroscopic behavior, and the most significant promotion effect on the formation of SOA. For example, at 50% RH, the liquid water amount of the existing seed aerosol $CaCl_2$ mol^{-1} is about three times greater than that within $(NH_4)_2SO_4$ (Cocker et al., 2001). At 75%–80% RH, the level of the relative humidity is above the deliquescence point of calcium chloride. The retention of water on the $CaCl_2$ aerosol surface increased dramatically which results in a highly hydrated aerosol. For the hydrophilic oxidant compounds, more gas-phase products will dissolve in the aerosol water according to the Henry's Law, therefore, the SOA yield is increased.

4 Conclusions

Secondary organic aerosol is one of the important members in the atmospheric particle matters. Its formation will make a main contribution to the ambient aerosol concentration. Based on our experimental results, it can be inferred that SOA might be a minor source of the atmospheric aerosol in the regions with high concentrations of background aerosols. These results might have potential applications to the air pollution control strategies.

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