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Differences of the oxidation process and secondary organic aerosol formation at low and high precursor concentrations

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ABSTRACT

Current atmospheric quality models usually underestimate the level of ambient secondary organic aerosol (SOA), one of the possible reasons is that the precursors at different concentrations may undergo different oxidation processes and further affect SOA formation. Therefore, there is a need to perform more chamber studies to disclose the influence. In this work, SOA formation over a wide range of initial precursor concentrations (tens of ppb to hundreds of ppb levels) was investigated in a 30 m³ indoor smog chamber, and mainly through the analysis of multiple generations of VOCs detected from HR-TOF-PTRMS to expound the difference in the oxidation process between low and high precursor concentrations. Compared to high initial concentrations, gas-phase intermediates formed at low concentrations had a higher formation potential due to the competition between semi-volatile intermediates and precursors with oxidants. In addition, the formed SOA was more oxidized with higher f_{44} value (0.14 ± 0.02) and more relevant to real atmosphere than that formed at high concentrations. This work should help to deeply understand SOA formation and improve the performance of air quality models for SOA simulation.

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Introduction

Secondary organic aerosol (SOA) is a dominant constituent of sub-micrometer atmospheric particulate matter (Jimenez et

al., 2009), and could contribute 44%–71% of organic aerosol (OA) (Huang et al., 2014) in the severe haze pollution in Beijing. In the past decades, great efforts have been made to investigate the composition and formation mechanism of

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SOA, because it has adverse effects on human health (Davidson et al., 2005), climate change (Thalman et al., 2017) and air quality (Huang et al., 2014).

However, the predicted SOA concentrations are always underestimated significantly by air quality models according to the parameters derived from experimental results, even 10fold lower than the atmospheric level (Jiang et al., 2012; Johnson et al., 2006). The significant uncertainty is mainly caused by insufficient consideration of different factors in the models, which could have direct or indirect effect on the oxidation processes of the precursors and SOA formation (Heald et al., 2005; Volkamer et al., 2006). Firstly, the OH exposure in a smog chamber is usually lower than that in real atmospheres (Chu et al., 2016), which is not favorable to SOA formation. Meanwhile, some unknown precursors (e.g., intermediate volatility organic compounds (IVOCs), semi-volatile organic compounds (SVOCs)) (Robinson et al., 2007; Zhao et al., 2014) and multiple-phase chemical processes (e.g., aqueous chemistry (Xu et al., 2017)) might contribute to the SOA formation. In addition, the differences between experimental conditions (e.g., the concentration of precursors (Alfarra et al., 2012)) and real atmospheric conditions (Deng et al., 2017) might greatly affect the oxidation processes and SOA formation in smog chamber. In view of the low concentration of precursors in the atmosphere, it is necessary to use the laboratory results cautiously to model predication applied for the real atmospheric ambient (Shilling et al., 2009). Therefore, to minimize the discrepancy between observations and model predictions, more chamber studies on SOA formation need to be conducted under lower precursor concentrations.

Anthropogenic aromatic hydrocarbons are ubiquitous in the atmosphere, mainly from fuel evaporation, vehicle exhaust and solvent using (Corrêa and Arbilla, 2006; Dumanoglu et al., 2014; Miracolo et al., 2012). The levels of toluene, xylene and trimethylbenzenes in urban environments could reach approximately 10 ppb (parts per billion) (Calvert et al., 2008), considered as the major anthropogenic SOA precursors (Henze et al., 2008; Wang et al., 2013). Many smog chamber studies have extensively investigated the SOA formation from the photo-oxidation of toluene, xylene and trimethylbenzenes under different experimental conditions. These studies have shown that the formation mechanisms of SOA not only depend on various physical parameters such as solar irradiance, temperature (T), and relative humidity (RH) (Cao and Jang, 2007; Cocker et al., 2001; Takekawa et al., 2003), but also depend on the type of oxidant (e.g., OH radicals, NO₃ radicals, Cl atoms, and O_3), NO_x levels, and the concentration of VOC precursors (Alfarra et al., 2012; Atkinson and Arey, 2003; Song et al., 2005; Xu et al., 2015). According to the reaction mechanisms of VOCs with OH radicals, the concentration of VOC precursors will affect the concentration of alkyl peroxy radicals (RO_2), which will determine the subsequent further reactions associated with the formation of low volatility species. However, there have been few reports on the effect of initial precursor concentration on the oxidation process and SOA formation, especially for the anthropogenic precursors. In addition, high concentrations of NO_x have been observed in China haze episodes (He et al., 2014; Zou et al., 2015). Therefore, in this work, under conditions of a wide range of precursor concentrations (30-690 ppb), SOA

formation from the photo-oxidation of toluene, m-xylene, and 1,3,5-trimethylbenzene in the presence of NO_x was carried out in an indoor smog chamber, with the aim of investigating the influence of initial precursor concentration on the photo-oxidation processes and SOA formation.

1. Experimental

Experiments were carried out in a 30 m³ indoor smog chamber located at the Research Center for Eco-Environment Sciences, Chinese Academy of Sciences (RCEES-CAS). Fig. S1 shows the schematic structure of the smog chamber, described in the Supplementary material. The reactor chamber is a cubic Teflon reactor (4.0 m (height) \times 2.5 m (width) \times 3.0 m (length)), placed in a temperature-controlled room. 120 UV lamps (365 nm, Philips TL 60/10R) were installed on the north and south inner walls of the thermostatic house. The maximum photolysis rate of NO₂ (J_{NO2}) was 0.55 min⁻¹ when all the UV lamps were turned on. This value was comparable to the irradiation intensity at noon in Beijing (Chou et al., 2011). The wall loss rates of NO₂, NO, O₃ and VOCs species $(1.67 \pm 0.25) \times 10^{-4}$, $(1.32 \pm 0.32) \times 10^{-4}$, were (3.32 ± 0.21) \times 10 $^{-4},$ and (2.20 \pm 0.39) \times 10 $^{-4}$ min $^{-1},$ respectively. The wall loss rate of particles (ammonium sulfate, AS) was in accordance with $k_{dep} = 4.15 \times 10^{-7} \times D_p^{1.89} + 1.39 \times D_p^{-0.88}$ (D_p is the particle diameter (nm)), which was measured according to the method in the literature (Takekawa et al., 2003) and used to correct the wall loss of SOA. In our study, wall loss experiments were conducted regularly, and these wall loss rates only have a slight change. SOA yield was calculated as the mass concentration ratio of corrected SOA to reacted hydrocarbon.

The initial concentrations of toluene, m-xylene, 1,3,5trimethylbenzene, and NO_x with a wide range in the chamber were 37-690, 34-656, 30-570, and 4-100 ppb, respectively. All the experiments were performed at a temperature (T) of 30 \pm 2°C and dry conditions (RH < 10.0%) with the absence of seeds. The equivalent OH concentration, which was generated from the photo-oxidation reaction of NO_x with VOCs precursor, was $1.92-4.38 \times 10^{6}$ molecule/cm³, estimated according to the decay curves of aromatic hydrocarbons. The detailed descriptions of experimental conditions are listed in the Table S1. The particle size distribution and number concentration were measured using a Scanning Mobility Particle Sizer (SMPS), consisting of a Differential Mobility Analyzer (DMA) (Model 3080, TSI, USA) and a Condensation Particle Counter (CPC) (Model 3776, TSI, USA). Assuming that particles are spherical and non-porous, the average effective particle density could be calculated to be 1.4 g/cm³ using the equation $\rho = d_{va}/d_{m}$ (Decarlo et al., 2004), where d_{va} is the mean vacuum aerodynamic diameter measured by Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and d_m is the mean volume-weighted mobility diameter measured by SMPS. And then the SOA mass concentration was calculated. At the same time, the mass concentration and chemical composition of SOA were measured by HR-ToF-AMS (Ng et al., 2010). Gas-phase hydrocarbons and their intermediate products were measured with a High-Resolution Time-of-Flight Proton Transfer Reaction Mass Spectrometry



Fig. 1 – Comparison of the gas phase mass spectra obtained from two toluene photo-oxidation experiments. (a) one higher initial concentration (690 ppb), (b) one lower initial concentration experiment (37 ppb), (c) difference of the intensity normalized mass spectra under these two limiting initial precursor concentration conditions (37 – 690 ppb, i.e., (b)–(a)) after 480 min of the photo-oxidation reaction. Each bar represented as an intensity normalized to m/z 93 (i.e., protonated toluene, $C_7H_9^+$).

(HR-ToF-PTRMS) (Ionicon Analytik GmbH). NO_x and O_3 were measured online with a NO_x analyzer (Model 42i-TL, Thermo Fisher Scientific, USA) and an O_3 analyzer (Model 49i, Thermo Fisher Scientific, USA), respectively. More detailed descriptions of instruments are summarized in Table S2. In addition, more details about the smog chamber experiments, and the instrument operation and data analysis protocols are also described in Supplementary material.

2. Results and discussion

2.1. Influence of initial precursor concentration on gas phase products

The evolution of gas-phase intermediates was monitored with HR-ToF-PTRMS, with the aim to understand the potential influence of initial precursor concentration on VOCs oxidation under the same experimental conditions (i.e., RH, T, UV light intensity, and $HC_0/NO_{x,0}$). Fig. 1 shows a comparison of the gas phase mass spectra derived from two experiments at low (37 ppb, Fig. 1a) and high (690 ppb, Fig. 1b) concentrations. The spectra were acquired at the end of the photo-oxidation reaction (i.e., 480 min after the UV lights on), and the intensities of all mass peaks were normalized to that at m/z93 (i.e., protonated toluene). As illustrated in Fig. 1, the intensities of mass peaks for low concentration were much higher than those for high concentration, especially for the high *m*/*z* range (>110 Da). Although the mass spectra obtained by HR-ToF-PTRMS could not distinguish the different structural isomers (Wyche et al., 2005), the significant difference in

the signal intensities of mass peaks suggests that precursors at different initial concentrations would be aged in different pathways.

Fig. 1c shows the difference of the normalized mass spectra in the m/z range of 50–150 Da at low and high concentrations (37-690 ppb) at 480 min after the UV light was switched on. The mass peaks at *m*/z 59, 73, 85, 99, 101, 115 and 129 were tentatively assigned to the protonated ions of C₂H₂O₂ (glyoxal), C₃H₄O₂ (methylglyoxal), C₄H₄O₂ (butenedial), $C_5H_6O_2$ (4-oxo-2-pentenal), $C_4H_4O_3$ (2,3-epoxybutandial), (2-methyl-2,3-epoxybutandial) and $C_5H_6O_3$ $C_6H_8O_3$ (2,3-epoxy-1,4-dicarbonyl), respectively. Their corresponding yields for the atmospheric oxidation of toluene were reported to be 13.0%, 40.9%, 33.3%, 8.8%, 7.4%, and 4.0%, respectively, estimated according to the quantum chemistry calculations by Wu et al. (2014). These products were also identified in the recent studies on the photo-oxidation of toluene (Ji et al., 2017; Pan and Wang, 2014; Wu et al., 2014).

Fig. 1c indicates that with similar ratios of hydrocarbon to NO_x, the oxygenated products could be more easily generated at low precursor concentration due to the relative abundance of OH radicals (~2-fold, Fig. S2), in which OH concentration could be estimated using the method described by Liu et al. (2016). As compared to the short reaction time (30 min) (Fig. S3), the signal intensities of C₂H₂O₂, C₃H₄O₂, C₄H₄O₂, $C_5H_6O_2$, $C_4H_4O_3$, $C_5H_6O_3$ and $C_6H_8O_3$ were about one order of magnitude lower than those obtained at long reaction time (480 min), indicating that the formation of oxygenated products is directly affected by OH exposure. The effect of OH exposure on the oxidation state of the products has also reported by Lambe et al. (2012), who found that under the higher OH exposure, more oxidized SOA with high O/C ratios would be generated. In this work, the concentration of OH radicals formed by the photochemical processes of NO_x and hydrocarbons was $1.92-4.38 \times 10^6$ molecule/cm³. Most recently, higher daytime average concentration of OH radicals in ambient atmosphere ((5.2–7.5) \times $10^6\,molecule/cm^3)$ have been revealed in Beijing and Heshan, China (Yang et al., 2017). In addition, even the lower initial precursor concentrations in our experiments were higher than those in the atmosphere. Therefore, it is reasonable to assume that toluene in the atmosphere could be oxidized more easily into oxygenated intermediates or products, subsequently tending to condense and contributing to the formation of SOA (Liu et al., 2013).

Fig. 2 shows the time-resolved concentrations of cresol $(m/z = 108, C_7H_8O)$ during photo-oxidation of toluene at different initial concentrations. Through the combined experimental and theoretical studies, Ji et al. (2017) have identified that the formation of cresol is dominant, with the molar yield 39.0% \pm 5.0%, during the OH-initiated oxidation of toluene in the presence of O₂ and NO. Similarly, the higher yield of cresol (32.0%) were also reported by Wu et al. (2014), who investigated the atmospheric oxidation mechanism of toluene initiated by OH radical addition via quantum chemistry calculations. As shown in Fig. 2, the concentrations of C₇H₈O increased as a function of the initial toluene concentration. For all experiments, the concentration of C₇H₈O increased firstly to a peak point (i.e., inflection point) and then decreased as a function of reaction time. In addition, a positive correlation $(R^2 = 0.97)$ between the maximum



Fig. 2 – Time-resolved concentrations of gas-phase intermediates (C₇H₈O)H⁺ derived from HR-ToF-PTRMS under different initial toluene concentrations (37–690 ppb).

concentration of C7H8O and the initial toluene concentration was observed (Fig. S4). The results also showed that the time to reach the inflection point was affected significantly by the initial toluene concentration, which decreased from 225 to 165 min for C₇H₈O when the initial concentration of toluene decreased from 690 to 37 ppb. The shorter time to reach the inflection point at lower initial precursor concentration suggested that the IVOCs could be earlier transformed into the next generation products with low volatility (e.g., SVOCs and LVOCs), consequently leading to SOA formation. Recently, Schwantes et al. (2017) has reported that the pathway of cresol oxidation by OH radicals could contribute a substantial fraction of highly oxygenated low-volatility products, which were estimated to contribute 20%-40% to toluene SOA. Ji et al. (2017) also identified that the prompt formation of cresol and its subsequent oxidation would have a significant effect on the atmospheric impacts of toluene oxidation. Additionally, the concentration of OH radicals was also affected by the initial concentration of toluene. The segmented OH concentrations were also estimated using the method expounded above (Liu et al., 2016), and the OH concentration showed a trend of first increasing and then decreasing for all different initial precursor concentrations (Fig. S2). Meanwhile, the higher OH concentration (2-fold, Fig. S2) was found at low initial precursor concentration, additionally the reaction rate constants between the precursors and OH radicals are one order of magnitude higher than that of the first generation products (e.g., cresol) (Atkinson and Arey, 2003). Therefore, it is a reasonable speculation that the extent of reactions between precursor and first generation products with OH radicals would be sufficiently altered, which will be beneficial to the formation of IVOCs, and then promote the SOA formation.

For the photo-oxidation of m-xylene and 1,3,5trimethylbenzene, similar influence of initial precursor concentration on gas phase products were observed (Figs. S5 and S6). In addition, we found that the time to reach the inflection point for $C_6H_8O_2$ (2-methyl-4-oxo-2-pentenal, m/z = 113), which was a typical intermediate (IVOCs), was also affected by the initial precursor concentration (Fig. S7). Recently, it has been indicated that organics with extremely low volatilities (ELVOCs) (saturation concentration, $C^* < 10^-$ ^{4.5} µg/m³) can drive the initial nucleation of particles (Kirkby et al., 2016), and organics with slightly higher volatility (10⁻ $^{4.5} < C^* < 10^{-0.5} \,\mu g/m^3$), i.e., highly oxygenated molecules (HOMs), contribute to their subsequent growth (Tröstl et al., 2016). Although it is impossible to directly measure the ELVOCs and HOMs with the HR-ToF-PTRMS in this study, it is reasonable to deduce that the high formation potential of IVOCs observed under low initial precursor concentrations should be in favor of the formation of these ELVOCs and LVOCs. Nevertheless, under high initial precursor concentrations, the competitive reactions between these IVOCs products and the precursor with OH might be significant, which would result in lower formation potential of these ELVOCs and LVOCs, subsequently reducing the SOA formation.

2.2. Influence of initial precursor concentration on SOA formation

Fig. 3 shows the growth curves of particle mass concentration (M_o) as a function of reacted toluene (Δ HC). In present work, the percentage of reacted toluene was about 75% at low initial concentration (37 ppb), which was clearly higher than that (about 48%) at high initial concentrations (425–690 ppb). As shown in Fig. 3, the slopes (~0.13) obtained at low concentration (37 ppb) are slightly larger than those (~0.07) obtained at high concentration (690 ppb), indicating that a smaller amount of reacted precursor at low concentration could form SOA compared with that at high concentration of precursor. Meanwhile, the higher slope indicates higher SOA yield to some extent. Similar results were reported by Ng et al. (2007), who found that the slopes of the SOA growth curves for photo-oxidation of m-xylene, toluene and benzene were



Fig. 3 – Growth curves for toluene photo-oxidation under different initial precursor concentration conditions. The values of ~40 and ~260 μ g/m³ were the Δ HC threshold obtained at the initial toluene concentrations of 37 and 425 ppb, respectively.

higher under high SOA yield conditions compared to those obtained under low SOA yield conditions.

During the initial stage of photo-oxidation reaction, the reacted toluene (i.e., ΔHC) were insufficient and could not generate particle matter via gas-particle partitioning. With the increasing of AHC, SOA forms gradually. And when the particle was just formed, the corresponding values of ΔHC was called the threshold. It is clearly shown in Fig. 3 that the threshold values of AHC at low initial precursor concentration (37-59 ppb) are much lower than those obtained at high initial precursor concentrations (425-690 ppb). For example, they were ~40 and ~260 μ g/m³, respectively, for the initial toluene concentrations of 37 and 425 ppb. For all experiments, SOA formation was not observed when the AHC was lower than the corresponding threshold. The possible explanation for this phenomenon is that OH radicals mainly react with the precursor at the initial stage, leading to the formation of SVOCs/IVOCs rather than ELVOC/LVOC. While the small threshold value of ΔHC indicated a high formation potential of ELVOCs/LVOCs from the oxidation of SVOCs/IVOCs. The results are well supported by the evolution of the inflection point of the gas phase intermediates observed by HR-ToF-PTRMS (Fig. 2 and Fig. S7). Similarly, an obvious gap in the threshold value of Δ HC was observed for the photo-oxidation of m-xylene (~60 vs. ~400 µg/m³) and 1,3,5-trimethylbenzene (~115 vs. ~570 μ g/m³), as shown in Fig. S8. Additionally, it is worth noting that with the increase of the methyl group number (i.e., from one to three), the threshold value of ΔHC showed an increase trend (from 40 to 115 µg/m³ and 260 to 570 μg/m³, respectively, under low and high initial concentrations). This phenomenon was in line with the previous experimental results, which observed a decreasing SOA yield with increasing number of methyl groups (Li et al., 2016).

In order to explore the oxidation degree of SOA, the organic mass fractions of m/z 44 (CO⁺₂) and m/z 43 (mostly C₂H₃O⁺) (Ng et al., 2010, 2011), named f_{44} and f_{43} , respectively, are used as the indicators of the oxidation state of SOA (Aiken et al., 2008; Loza et al., 2012; Ng et al., 2010) in this work. Fig. 4a shows the f_{44} vs. f_{43} of the SOA formed at different initial toluene concentrations. It is clearly shown that the f_{44} values (0.14 \pm 0.02) at low concentration (37 ppb) are larger than those at higher concentration, while the contrary trend is observed for the f_{43} values. In these experiments with higher concentrations (425–690 ppb), the values of f_{43} and f_{44} were comparable to the results reported by Li et al. (2016), who revealed that the f_{43} and f_{44} of toluene SOA derived from smog chamber study ranged from 0.08 to 0.11 and 0.13 to 0.17, respectively.

The triangular region drawn by the dashed line in Fig. 4 was obtained according to the results on the components of ambient oxygenated organic aerosol (OOA) reported by Ng et al. (2010). The f_{44} values for low-volatility OOA (LV-OOA) were 0.13–0.21, and its values for semi-volatile OOA (SV-OOA) were 0.03–0.11. As shown in Fig. 4a, high f_{44} values (0.14 ± 0.02) and low f_{43} values (0.05 ± 0.01) were observed at low concentration (37 ppb). This suggested that the SOA formed belonged to LV-OOA, which was mainly composed of more oxidized products (Ng et al., 2010, 2011). Alfarra et al. (2012) have also reported that the initial precursor of β -caryophyllene (from biogenic emissions) could directly affect the product composition of SOA, and the products formed at low concentration mainly



Fig. 4 – (a) f_{44} vs. f_{43} of under different initial toluene concentration conditions (37–690 ppb); (b) f_{44} vs. f_{43} of different monocyclic aromatic hydrocarbons under low initial precursor concentration conditions (i.e., 37 ppb Toluene, 34 ppb m-xylene and 28 ppb 1,3,5-trimethylbenzene). Colored solid circle markers represent the location of average f_{44} vs. f_{43} value.

consist of compounds with more oxidized, smaller carbon structures and higher average O/C, compared to those obtained at high concentration. Meanwhile, it could be clearly seen from Fig. 4a, with the initial toluene concentrations decreased, the f_{44} - f_{43} data points gradually approaching the results of field observation, which was located at an urban site in Beijing, China (Liu et al., 2018) with a much higher f_{44} values (0.17 ± 0.04) during a clean day (i.e., extremely low precursor concentrations condition). The similarly experimental results were obtained under the different initial concentrations of mxylene and 1,3,5-trimethylbenzene conditions (Fig. S9). For mxylene and 1,3,5-trimethylbenzene under low initial precursor concentration conditions, generally decreasing $f_{\rm 44}$ and increasing f_{43} were also observed with the increasing of the methyl group number in our present study (Fig. 4b), which was consist with the previous studies (Chhabra et al., 2011; Li et al., 2016; Ng et al., 2010). Furthermore, the f_{44} - f_{43} data points of toluene were much closer to the points of field observation, which was related to the relative abundant of toluene in the



Fig. 5 – Simplified oxidation process for SOA formation. Red arrows denote the major reaction pathway for the formation of SOA under low initial precursor concentrations. The black dotted arrow represents the pathway of SOA increase through the partition of IVOCs to the initial nuclei formed by the homogeneous nucleation of LVOCs under high initial precursor concentrations.

ambient air (Sun et al., 2016; Zou et al., 2015). In addition, the AMS spectrum profile of the SOA formed at low concentration of toluene was comparable to the ambient SOA observed in Beijing ($R^2 = 0.97$, Fig. S10), which was also derived from the same field observation. These phenomena further indicated that the SOA generated at low initial precursor concentration might be more atmospherically relevant. Under high initial toluene concentration conditions (425–690 ppb), low f_{44} values (~0.12) and high f_{43} values (0.11–0.13) were observed, and the f_{44} – f_{43} data points were at the right side of the triangular region. The possible explanation for this phenomenon is that the major components of SOA are less-oxidized products (i.e., SVOCS), formed due to the higher initial precursor concentration and lower OH exposure in the smog chamber compared to the typical atmospheric conditions.

2.3. Oxidation process of SOA formation at different initial precursor conditions

Based on the above analysis, a simplified oxidation process of SOA formation depending on the initial precursor concentration was proposed (As shown in Fig. 5). Intermediate products (IVOCs) with relatively high volatility were firstly formed through an oxidation reaction (Step 1), followed by further oxidization into low-volatility products (LVOCs) (Step 2). The formed LVOCs would generate the initial nucleation of particles through gas-particle partitioning, resulting in the formation of SOA (Step 3). The HR-ToF-PTRMS results shown in Figs. 1-2 and Figs. S3-S7 suggested that the contribution of IVOCs and LVOCs to the SOA was significantly different, depending on initial precursor concentration. At low initial concentration (37 ppb), the photo-oxidation products of toluene were mainly LVOCs, which could be easier to nucleate and subsequently contribute significantly to the SOA formation. For high initial concentrations (425-690 ppb), its major products were IVOCs, which could result in SOA increase through their gas-particle partitioning to the initial nuclei formed by the homogeneous nucleation of LVOCs. Previous

studies have revealed that the oxidation of low-volatility organic vapors (LVOCs) could greatly enhance the SOA mass (Liggio et al., 2016) and contribute to the initial growth of particles in the atmosphere (Tröstl et al., 2016). Meanwhile, Kirkby et al. (2016) have recently indicated that highly oxygenated molecules (HOMs, i.e., LVOCs) play a vital role in new particle formation and atmospheric particle nucleation. Thus, the major products (LVOCs) at low initial concentration would favor increasing SOA formation, while the limited gasto-particle partitioning of IVOCs to SOA might play a negative role in SOA formation at high initial concentration.

3. Conclusions and implications

As the dominant constituent of atmospheric particle matter, SOA has been recently demonstrated to play an important role in haze pollution in North China, especially in the Beijing-Tianjin-Hebei region (Han et al., 2015; He et al., 2014). Based on the present knowledge on SOA formation, the observed SOA levels in the atmosphere cannot be well explained, which reflects that many influencing factors are not taken into account in the atmospheric models (Baek et al., 2011; Kanakidou et al., 2005).

Our experimental results indicated that the oxidation process of precursors and SOA formation depended on the initial precursor concentration. Under low concentration conditions, the relative intensity of gas-phase intermediates was about one order of magnitude higher than that obtained under high concentration conditions. Meanwhile, the lowvolatility compounds and SOA both had a higher formation potential, which should was reasonably contributed from the competition between gas-phase intermediates and precursor with oxidants. Additionally, SOA formed at low concentration had a higher oxidation state with higher f_{44} value (0.14 ± 0.02), which would enhance SOA hygroscopicity (Chu et al., 2014), subsequently affecting the climate and air quality (Denjean et al., 2015). The findings on the preferred oxidation process of precursors and SOA formation in this work could provide a new perspective to better understand the SOA underestimation in atmospheric models.

According to our present findings, it is reasonable to deduce that when the yield parameters obtained at low initial precursor concentration are included in the air quality models, the predicted SOA results by the available atmospheric models would be more accurate; more importantly, the results would be more environmentally significant. Certainly, when the yield parameters obtained at high initial precursor concentration were incorporated into the atmospheric models, the predicted SOA formation would be inaccurate and even underestimated under typical atmospheric conditions. In fact, the atmospheric levels of these precursors are lower than those used in the present experiments. Meanwhile, compared to the atmospheric environment, the experimental conditions are greatly simplified. It has been reported that the SOA yields from toluene photooxidation are increased by 5.6-12.9 times with urban ambient air as matrix compared to those obtained with purified zero air as matrix (Deng et al., 2017). Therefore, more work on SOA formation should be carried out under simulated atmospheric conditions, the corresponding results would shed light on the mechanism of SOA formation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2018.11.011.

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