Ozone and Secondary Organic Aerosol Formation of Toluene/NO\textsubscript{x} Irradiations under Complex Pollution Scenarios

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ABSTRACT

Toluene is one of the most important precursor contributors to ozone and secondary organic aerosol (SOA), both of which greatly affect the air quality and human health. In this study, the effects of toluene on ozone and SOA formation were investigated in the presence of NO\textsubscript{x} in the CAPS-ZJU (Complex Air Pollution Study-Zhejiang University) smog chamber. Three comparison groups of experiments were conducted under the gas-phase environments of toluene/NO\textsubscript{x}, toluene/isoprene/NO\textsubscript{x}, and toluene/ethylene/NO\textsubscript{x}. The ozone concentration and physical properties of SOA such as mass concentration, aerosol yield, effective density, extinction and scattering were measured simultaneously. A toluene-dependent mechanism of ozone formation was found at ratios of toluene and NO\textsubscript{x} between 3.1 and 11.3 with the initial NO\textsubscript{x} concentration about 30 ppb. With further increase of the toluene concentration, the maximum value of ozone concentration remained almost stabilized. The maximum SOA yields decreased with increase of toluene, while the SOA effective density was concentrated at 1.3–1.4 g cm\textsuperscript{-3}. The presence of isoprene or ethylene can promote the formation of ozone and SOA. The SOA nucleation was delayed under different initial toluene concentrations and the yield was reduced at the same mass concentration. A linear increase of extinction and scattering was observed with the increase of SOA mass concentration in both the toluene/isoprene/NO\textsubscript{x} and toluene/ethylene/NO\textsubscript{x} systems. A rapid increase of single scattering albedo reflects the process of SOA nucleation and growth. In addition, organic aerosol oxidation products tend to carboxylic acids in toluene/isoprene/NO\textsubscript{x} system according to Van Krevelen.

Key words: Smog chamber; Toluene; Ozone; Secondary organic aerosol; NO\textsubscript{x}.

INTRODUCTION

Ozone and secondary organic aerosol (SOA) are of great importance in the atmosphere due to their strong impacts on air quality (Tong et al., 2016a, b), climate change and public health (Srebot et al., 2009; Lv et al., 2015; Yin et al., 2015; Briggs et al., 2016; Kanaya et al., 2016; Tong et al., 2017). Toluene, as one of the dominant aromatic hydrocarbons, is a potential source of photo-oxidation of ozone and SOA formation in urban air (Cheng, 2016; Sahu et al., 2016; Yang et al., 2016; Deng et al., 2017). Ozone formation potential (OFP) and aerosol formation potential (AFP) are used to assess the ability of VOCs to generate ozone and SOA, reflecting the relative contribution of ozone and SOA precursors. According to analysis of the AFP and OFP during August and September of 2016 in Hangzhou, toluene is the most contributor not only for ozone formation, but also for SOA as well (the average of OFP and AFP of toluene is 12.4 µg m\textsuperscript{-3} and 0.9 µg m\textsuperscript{-3}, respectively).

Many studies have shown that the VOCs or NO\textsubscript{x} concentrations have a great influence on the formation of ozone and SOA. Johnson et al. (2004) observed a decreasing trend of toluene SOA yield with decreasing toluene to NO\textsubscript{x} ratio, with the NO\textsubscript{x} concentration ranging from 45 ppb to 1300 ppb and toluene concentration ranging from 500 ppb to 6600 ppb. Meanwhile, the decreasing trend of toluene SOA yield with increasing NO\textsubscript{x} concentration ranging from 45 ppb to 1300 ppb and toluene concentration ranging from 500 ppb to 6600 ppb. Meanwhile, the decreasing trend of toluene SOA yield with increasing NO\textsubscript{x} concentration is less obvious in Xu et al. (2015), which might be due to the different initial reactant concentrations. A similar phenomenon was also found in other VOCs, such as m-xylene, isoprene and propylene (Song et al., 2005; Hu et al., 2011; Beardsley and Jang, 2016; Ge et al., 2017). The previous studies mainly focus on the impact of the toluene/NO\textsubscript{x} ratio on SOA formation under different initial NO\textsubscript{x} concentrations in the photo-oxidation reaction (Ng et al., 2007; Sato et al., 2007), and chamber experiments were conducted under non-atmospherically relevant conditions (see Table 1). The influence of the toluene/NO\textsubscript{x} ratio with different initial toluene concentrations at atmospheric conditions on ozone and SOA formation has been little studied.
The ozone and SOA produced from individual VOCs precursor irradiations can be significantly affected by the presence of other VOCs (Jaoui et al., 2008). The presence of toluene and other atmospheric VOCs can affect the gas phase chemistry of toluene and influence the oxidation products (Chen and Jang, 2012). Jaoui et al. (2008) found that adding isoprene to α-pinene/toluene/NOx system significantly lowered the reacted amount of toluene, and increased the ozone concentration. Zhou et al. (2011) found that the HC mix system (o-, p-xylene and toluene with NOx) under natural sunlight showed the highest SOA yield in the α-xylene system compared to toluene and p-xylene. These studies show that the effects of various VOCs precursors on ozone and SOA generation are not simply linearly superimposed. Thus, it is expected that the mixed VOCs will affect the formation of ozone and SOA in toluene photo-oxidation reactions.

In this study, the progress of the photo-oxidation of toluene was investigated in a smog chamber. The influence of the toluene/NOx ratio with different initial toluene concentrations and mixed VOCs on the ozone and SOA formation was studied.

### EXPERIMENT SECTION

The photo-oxidation of toluene was performed in the absence of seed aerosol in the Complex Air Pollution Study-Zhejiang University (CAPS-ZJU) smog chamber, which has been previously described (Li et al., 2017a). The volume of the Teflon bag reactor of the experiments was 3 m³, which had a surface/volume of 4.32 m⁻¹. The experiments were performed for around 8 h at a light intensity equivalent to Jsol of 0.17 min⁻¹ with 20 black lamps (GE F40BLB, peak intensity at 365 nm) opened. Prior to each experiment, the chamber was flushed continuously by zero-air, which was provided through an Aadco 737 series air purification system. The background particles number concentration of the reactor was below 10 # cm⁻³ and the concentration of NOx was below 2 ppb. The temperature was relatively constant at 25°C before the experiments began and increased to a stable value (approximately 30–32°C) after the lamps were turned on. The relative humidity (RH) inside the chamber stabilized at approximately 15–20%. A fan inside the chamber was used to help the components in the reactor to mix well after injection.

Standard gases such as toluene, isoprene, ethylene, NO and NO2 were injected into the chamber precisely by mass flow meters. The standard concentration of each standard gases is 100 ppm, and nitrogen was used as the background gas. The concentrations of gas-phase NOx and ozone were measured with an interval of 1 min by gas analyzers (Thermo 42i, 49i). The rate constants for the wall loss of NOx and ozone were (1.642 ± 0.004) × 10⁻⁴ min⁻¹ and (8.987 ± 0.067) × 10⁻⁴ min⁻¹, respectively. Toluene, isoprene and ethylene were measured by an automated Preconcentrator (Entech 7100A), coupled with a gas chromatography-mass spectrometry instrument (GC-MS, Agilent 7890B-5977A).

The aerosol particle size distributions and number concentration were monitored by using a Scanning Mobility Particle Sizer (SMPS, TSI 3936), with a long Differential Mobility Analyzer (DMA, TSI 3081) in combination with a butanol Condensation Particle Counter (CPC, TSI 3776). Effective density was determined by the SMPS coupled with an Aerosol Particle Mass Analyzer (APM, Kanomax 3601). The wall loss constant of particles was obtained to be (3.52 ± 0.031) × 10⁻³ min⁻¹. Meanwhile, the chemical composition of SOA and the non-refractory submicron aerosol mass was measured using a high resolution time-of-flight aerosol mass spectrometer (Aerodyne, HR-TOF-AMS). The optical properties of SOA were measured with a Cavity Attenuated Phase Shift equipment (Aerodyne, CAPS PMssa).

### RESULTS AND DISCUSSION

According to analysis of AFP and OFP during August and September of 2016 in Hangzhou, toluene, isoprene and ethylene are the important contributors for ozone and SOA formation. The average concentration of NOx in August to September from 2013 to 2015 at 11 sites in Hangzhou was about 25–30 ppb. Based on the atmospheric environments of Hangzhou, a series of toluene photo-oxidation reactions was conducted with different initial toluene concentrations and mixed VOCs to evaluate the ozone and SOA formation from the toluene/NOx system. The temperature in the progress of the reaction was controlled at 303–305 K and relative humidity was maintained at 15–20%. The initial experimental conditions are listed in Table 2.

### The Effect of Initial Toluene Concentration on Ozone Formation

In order to investigate the influence of the initial concentration ratios of toluene/NOx (ppbC/ppb) on the peak ozone concentration, a series of experiments were conducted (Exps. 1–8). The results in Fig. 1 show that the maximum ozone concentration has two different trends with the increasing toluene/NOx ratio (increasing the toluene concentration at relatively constant NOx concentrations).
Table 2. Initial conditions for each experiment.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>VOCs species</th>
<th>NO&lt;sub&gt;2&lt;/sub&gt; (ppb)</th>
<th>NO (ppb)</th>
<th>VOCs/NO&lt;sub&gt;x&lt;/sub&gt; (ppbC:ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Toluene</td>
<td>14.2</td>
<td>27.5</td>
<td>4.8</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>24.5</td>
<td>26</td>
<td>4.9</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>37.2</td>
<td>24.5</td>
<td>4.5</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>49.7</td>
<td>25.7</td>
<td>4.9</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>58.6</td>
<td>24.7</td>
<td>5.3</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>66</td>
<td>25.3</td>
<td>4.6</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>84</td>
<td>24.4</td>
<td>5.3</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>107</td>
<td>24.5</td>
<td>5.7</td>
</tr>
<tr>
<td>9</td>
<td>Toluene/isoprene</td>
<td>17.6/14.4</td>
<td>24.6</td>
<td>6.4</td>
</tr>
<tr>
<td>10</td>
<td>Toluene/ethylene</td>
<td>17.5/14.4</td>
<td>26.1</td>
<td>5.4</td>
</tr>
</tbody>
</table>

* Each experiment used preconcentrator, GC-MS and gas analyzers. Expt. 3, 5, 8 did not use SMPS and APM, CAPS is used in Expt. 9, 10, and AMS is used in Expt. 9.

At toluene/NO<sub>x</sub> ratio values from 3.1 to 11.3, the maximum ozone concentration increases linearly from 35.1 ppb to 136.2 ppb (the maximum ozone concentration = 5.3 + 11.6 × toluene/NO<sub>x</sub> ratio, R<sup>2</sup> = 0.97), which is controlled by the initial toluene concentration. Meanwhile, the maximum ozone concentration remained unchanged when the toluene/NO<sub>x</sub> ratio was from 15.5 to 24.8, this regime being controlled by the initial NO<sub>x</sub> concentration. However, the maximum ozone concentration is different from these two ranges when the ratio is 13.6. Jiménez (2004) and Mazzuca et al. (2016) observed that there is a transition regime, in which the ozone concentration is controlled by VOCs and NO<sub>x</sub> at the same time. This inspires us, and a plausible explanation may be like this: when toluene/NO<sub>x</sub> ratio is between 11.3 and 15.5 (the concentration of toluene was from 49.7 ppb to 66 ppb, and NO<sub>x</sub> was constant), the ozone concentration is influenced by toluene and NO<sub>x</sub>, which leads to the different trend of maximum ozone concentration.

Meanwhile, the appearance of the maximum ozone concentration was advanced to 225 min with the increase of the toluene/NO<sub>x</sub> ratio. 5.6%–58.3% of the initial toluene is consumed, and the attenuation rate of the toluene increases from 1.1 × 10<sup>−4</sup> to 1.6 × 10<sup>−3</sup> min<sup>−1</sup>. When the ratio is greater than 13.6, the decay rate of toluene tends to stabilize (see Table 3). Such phenomena might mean that more toluene is oxidized by OH radicals at the high toluene/NO<sub>x</sub> ratio. At the same time, the organo-peroxide radicals (RO<sub>2</sub>) concentration increased due to the restriction of conversion of NO to NO<sub>2</sub> (Jia et al., 2010), leading to the accumulation of ozone concentration. In addition, the initial toluene concentration is excessive with the increase of the toluene/NO<sub>x</sub> ratio, which causes the attenuation rate of toluene to become gradually gentler.

**The Effect of Initial Toluene Concentration on SOA Formation**

Fig. 2 shows the typical photo-oxidation of toluene and NO<sub>x</sub>. In this experiment, with the initial toluene/NO<sub>x</sub> ratio ~3:1 (ppbC:ppb), 0.8 ppb of toluene is reacted, and the initial NO<sub>2</sub> and NO concentrations are 27.5 ppb and 4.8 ppb, respectively. In the absence of initial HONO, OH radicals are likely to drive the photolysis of HONO, which is formed from the heterogeneous reaction of NO<sub>2</sub> on the chamber wall, or generated through recycling via NO<sub>x</sub>/HO<sub>x</sub> chemistry (Ng et al., 2007). Aerosol growth did not occur immediately, but was observed after the semi-volatile or nonvolatile organic matter formed and accumulated to a certain concentration by photo-oxidation.

The particle size distributions from five toluene/NO<sub>x</sub> photo-oxidation experiments are shown in Fig. 3 (initial toluene concentrations in Figs. 3(a)–3(e) are 14.2 ppb, 24.5 ppb, 49.7 ppb, 66.0 ppb, and 84.0 ppb, respectively.). It was observed that the aerosol formation increases with increasing of the initial toluene concentration, the particles size grows further, and the total number concentration of our chamber experiments reached the level of 10<sup>3</sup>–10<sup>4</sup> # cm<sup>−3</sup>. The toluene/NO<sub>x</sub> system shows a 50–100 min induction period (no significant SOA growth), the time to reach the saturation of the gas-phase toluene oxidation products, this suggesting that SOA is further oxidized from toluene photo-oxidation products (Song et al., 2005; Chen and Jang, 2012).

Li et al. (2017b) used two methods of Log Normal and Max Concentration to derive the particle size evolution. The asymptotic fit with merging data was used to decrease
Table 3. Summary of the chamber experiment results.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>$\Delta$Tol$^a$</th>
<th>$O_{\text{max}}$</th>
<th>Time of $O_{\text{max}}$</th>
<th>$N_{\text{total, max}}$</th>
<th>$M_{\text{O, max}}$</th>
<th>$k_{\text{toluene}}$</th>
<th>Yield$^b_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>3.1</td>
<td>480</td>
<td>$1.9 \times 10^3$</td>
<td>1.6</td>
<td>$1.1 \times 10^{-4}$</td>
<td>0.38</td>
</tr>
<tr>
<td>2</td>
<td>11.3</td>
<td>75.9</td>
<td>480</td>
<td>$2.3 \times 10^3$</td>
<td>7.8</td>
<td>$2.5 \times 10^{-4}$</td>
<td>0.37</td>
</tr>
<tr>
<td>3</td>
<td>3.1</td>
<td>104.5</td>
<td>480</td>
<td>--</td>
<td>--</td>
<td>$1.1 \times 10^{-3}$</td>
<td>--</td>
</tr>
<tr>
<td>4</td>
<td>73.4</td>
<td>136.2</td>
<td>480</td>
<td>$1.3 \times 10^4$</td>
<td>14.3</td>
<td>$1.0 \times 10^{-3}$</td>
<td>0.22</td>
</tr>
<tr>
<td>5</td>
<td>126.8</td>
<td>128.9</td>
<td>450</td>
<td>--</td>
<td>--</td>
<td>$1.5 \times 10^{-3}$</td>
<td>--</td>
</tr>
<tr>
<td>6</td>
<td>137.2</td>
<td>120.3</td>
<td>324</td>
<td>$2.1 \times 10^4$</td>
<td>17.5</td>
<td>$1.5 \times 10^{-3}$</td>
<td>0.21</td>
</tr>
<tr>
<td>7</td>
<td>190.6</td>
<td>117.7</td>
<td>306</td>
<td>$2.7 \times 10^4$</td>
<td>20.6</td>
<td>$1.6 \times 10^{-3}$</td>
<td>0.19</td>
</tr>
<tr>
<td>8</td>
<td>234.9</td>
<td>120.5</td>
<td>225</td>
<td>--</td>
<td>--</td>
<td>$1.6 \times 10^{-3}$</td>
<td>--</td>
</tr>
</tbody>
</table>

$a$: $\Delta$Tol is calculated at the end of each experiment, and each experiment is irradiated for 6–8 h;
$b$: In the experiment, if the ozone concentration does not reach the maximum, we take 480 min as the appearance time of maximum ozone concentration.

The SOA yield was estimated using the total organic aerosol mass concentration and consumption of toluene. Fig. 5 shows the curves of SOA yield ($Y$) versus organic aerosol mass concentration ($M_0$) under different initial toluene concentrations. It is noticeable that the high initial toluene concentration tends to have lower yields at the same mass concentration (see Table 3, where the maximum yield of SOA decreased from 0.38 to 0.19). The SOA yield shown in Exps. 6–7, which increased first and then decreased, might be because the deposition of particles in the reactor wall is greater than the generation of SOA, so SOA would decline after reaching the maximum in the experiment, yet toluene was still oxidized, which contributed to the different yields.

The yields measured in our experiments are higher than previous measurements (Takekawa et al., 2003; Song et al., 2005; Song et al., 2007). According to the SOA growth curve under different initial toluene concentrations, when
the SOA yields are consistent, the experiment with a high initial toluene concentration produces more aerosol mass concentration and consumes a greater amount of toluene. If $M_0$ is the same, the lower the initial toluene concentration (lower toluene/NOx ratio), the higher the SOA yields, which was also observed by Chen et al. (2016), who found that the SOA yields were 0.49 and 0.28 when 2-methylnaphthalene was 20.0 ppb and 29.1 ppb, respectively. This is different from the phenomenon that the yield increased with the increase of the VOCs/NOx ratio. Possible reasons maybe as follows. (1) The SOA yields measured under low-NOx (< 100 ppb) conditions are higher than high-NOx conditions in toluene/NOx system or m-xylene/NOx system (Ng et al., 2007; Chen et al., 2016). In our experiments, the initial NOx,
Fig. 4. Diameter variations of SOA effective densities under different initial toluene concentrations (a) and frequency distributions of particle counts in different effective density ranges (b).

Fig. 5. SOA yields from toluene photo-oxidation as a function of $M_0$ in different toluene regimes. Black line represents allometric fit (initial toluene concentration is 14.2 ppb, 24.5 ppb, 49.7 ppb, 66.0 ppb, 84.0 ppb, respectively.).

concentration is about 30 ppb, which is low-NO$_x$ condition; (2) The initial toluene concentrations change the oxidation pathways, which leads to different yields. In high initial toluene concentration conditions, the reaction rate is higher, which means more oxidation products are generated and may stay more in gas-phase, while the photo-oxidation products may be more in the particle-phase in low toluene/NO$_x$ ratio conditions; (3) Ng et al. (2007) suggest that the VOCs/NO$_x$ ratio may be a useful metric of photochemistry for experiments with similar oxidation conditions, while it is less useful when comparing systems in different oxidative conditions. The relationship between the VOCs/NO$_x$ ratio and SOA yields, on which most previous studies report, were based on the NO$_x$ level or changing VOCs and NO$_x$ at the same time. In our study, the initial NO$_x$ concentration of each experiment is the same, and the initial toluene concentration level has a significant effect on the SOA yields.

The Effect of Multiple VOCs Components on Ozone Formation

In the toluene/NO$_x$, toluene/isoprene/NO$_x$ and toluene/ethylene/NO$_x$ systems, the maximum ozone concentration significantly increases due to the photo-oxidation of isoprene and ethylene. Detailed results of ozone and SOA formation under mixed precursor are listed in Table 4.

In these three comparison experiments, 5.6%, 32% and 25% of the initial toluene were consumed, respectively. NO was completely oxidized in the toluene/isoprene/NO$_x$ system at the end of the experiment. As shown in Fig. 6, isoprene and ethylene could promote the formation of ozone, and it is clear that isoprene has a greater effect on ozone formation than that of ethylene in the toluene/NO$_x$ system.

Farmer et al. (2011) and Valin et al. (2014) reported that when the photochemical reaction system is converted from a high NO$_x$ condition ($[NO_x]_0/[VOCs]_0 > 1$) to a low NO$_x$ condition ($[NO_x]_0/[VOCs]_0 < 1$), it can promote the photo-oxidation reaction and increase the concentration of organo-peroxide radicals (RO$_2$). So adding isoprene or ethylene in the toluene/NO$_x$ system significantly increases the initial ratio of VOCs/NO$_x$, enhancing the formation of ozone. Carter (1994) detected that the dynamic reaction of isoprene (reaction rates of VOCs and OH radicals) is higher than ethylene in 12 cities of the United States, while the ozone concentration in the photochemical reaction system would not rise very high with the presence of NO (Kiros et al., 2016). Therefore, adding isoprene or ethylene has a positive effect on ozone, and isoprene is more favorable than ethylene for the formation of ozone under the same conditions.

The Effect of Multiple VOCs Components on SOA Formation

The SOA formation from the three comparison experiments is compared in Fig. 7. The peak particle size and peak number concentration is still growing in these three systems. This might be due to the low initial reactants concentration in the three systems, which caused the slow
Table 4. Summary of the chamber experiment results.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>(\Delta Tolu)</th>
<th>(\Delta Iso)</th>
<th>(\Delta Ethy)</th>
<th>(O_3_{\text{max}})</th>
<th>(N_{\text{total max}})</th>
<th>(M_0_{\text{max}})</th>
<th>Yield(_{\text{max}})</th>
<th>NO(_2)</th>
<th>NO(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>3.1</td>
<td>--</td>
<td>--</td>
<td>35.1</td>
<td>1.9 \times 10^4</td>
<td>1.6</td>
<td>0.38</td>
<td>19.4</td>
<td>4.6</td>
</tr>
<tr>
<td>Toluene/Isoprene</td>
<td>22.2</td>
<td>51.1</td>
<td>--</td>
<td>106.5</td>
<td>6.9 \times 10^4</td>
<td>15.7</td>
<td>0.17</td>
<td>17.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Toluene/Ethylene</td>
<td>14.8</td>
<td>--</td>
<td>6.6</td>
<td>72.2</td>
<td>5.0 \times 10^3</td>
<td>7.1</td>
<td>0.27</td>
<td>19.7</td>
<td>1.4</td>
</tr>
</tbody>
</table>

a: Reactants consumption is calculated at the end of each experiment.
b: The concentration of NO\(_2\) and NO at the end of experiments.

The growth curve of SOA yields from these three systems is focused on in Fig. 9(b). When the SOA yields are consistent, the aerosol mass concentration and organic products consumed are the highest in the toluene/isoprene/NO\(_x\) system. If \(M_0\) is the same, the SOA yields in the toluene/isoprene/NO\(_x\) and toluene/ethylene/NO\(_x\) system are lower than that in the toluene/NO\(_x\) system. The reasons for this phenomenon may be as follows: (1) Isoprene and ethylene possess few carbon atoms and produce highly volatile oxides, so organic products produced by photooxidation reactions are more likely to stay in gas-phase. (2) The oxidation pathways are changed when various VOCs coexist. For example, isoprene, ethylene and their gas-phase products compete for the oxidants (e.g., OH, O\(_3\), NO\(_3\)) with toluene and toluene gas-phase products, which could produce different amounts of oxidants and radicals (Chen and Jang, 2012).

Furthermore, we find extinction and scattering of SOA using CAPS in the toluene/isoprene/NO\(_x\) and toluene/ethylene/NO\(_x\) systems. Fig. 10(a) shows that the aerosol mass concentration has a high correlation with extinction and scattering, suggesting that the chemical and physical properties of the particles are stable. The slope of linear regression between the mass concentration and extinction (scattering) is defined as the mass extinction (scattering) coefficient, and the larger the slope, the stronger the mass extinction (scattering) coefficient (Moise et al., 2015; Wang et al., 2015). The mass extinction coefficient and mass scattering coefficient in toluene/isoprene/NO\(_x\) are 5.4 and 4.4, respectively, and in toluene/ethylene/NO\(_x\) systems are 6.2 and 5.1, respectively. This means that the SOA generated in the toluene/ethylene/NO\(_x\) system has a stronger mass extinction coefficient and mass scattering coefficient.

The single scattering albedo (SSA) reflects the proportion of the scattering and absorption of aerosol (Paredes-Miranda et al., 2009; Han et al., 2016). It is observed that the SSA value was lower at the beginning of the experiment, and the main component of SOA was aerosol with absorbability. With the progress of the reaction, the SSA value rises rapidly, reaching 0.8 and 0.73 at the end of the experiments, respectively. This may be caused by the growth of the particle size and the change of particle composition, and further studies are needed to clarify the possible causes.

The temporal profiles of the mass concentration results of the toluene/isoprene/NO\(_x\) system from SMPS and AMS are compared in Fig. 9(a), and both have a high consistency. Moreover, we collected the data of H:C, O:C, f\(_{43}\) and f\(_{44}\) to explore the degree of oxidation of SOA. According to the element ratio, the slope of H: C vs. O: C of organic reaction rate. The fact that the mass concentration and peak size growth curve shown in Fig. 8 still maintain a growth trend in the experiment period also proved this point. Besides, the maximum mass concentrations at the end of the experiments on toluene/NO\(_x\), toluene/isoprene/NO\(_x\) and toluene/ethylene/NO\(_x\) are 1.6 \(\mu\)g m\(^{-3}\), 15.7 \(\mu\)g m\(^{-3}\) and 7.1 \(\mu\)g m\(^{-3}\), respectively. The presence of isoprene or ethylene delays the nucleation time of SOA, which indicates that isoprene or ethylene inhibits the SOA nucleation of the toluene/NO\(_x\) system.

The addition of isoprene or ethylene in the toluene/NO\(_x\) system increases the initial VOCs concentration, promotes the photochemical reaction, and produces a large number of organic products. The reason that isoprene is more favorable than ethylene for the formation of SOA might be that two of the isomers produced by the reaction of isoprene with OH radicals are polyhydroxy compounds, which are highly hygroscopic and can improve the nucleation ability of aerosols (Claeys et al., 2004). For hydrocarbon that has a lower carbon number, Eq. (1) > Eq. (2), while if C \(\geq\) 4, the reaction Eq. (2) > Eq. (1) (Johnson et al., 2004). Therefore, in the case of more isoprene being reacted (97% of the isoprene is consumed and 46% of ethylene is reacted), the toluene/isoprene/NO\(_x\) system is more capable of generating more SOA than the toluene/ethylene/NO\(_x\) system.

\[
\begin{align*}
RO_2 + NO & \rightarrow RO + NO_2 \\
RO_2 + NO & \rightarrow RONO_2
\end{align*}
\]
aerosol in Van Krevelen in Fig. 11(a) is about −1.3, which is steeper, and close to (~−2). The possible reason may be that organic aerosol oxidation products tend to be carboxylic acids and with less cracking reactions in a low oxidation condition (Lambe et al., 2012). The research shows that the generation of organic aerosol changes in the order:

**Fig. 7.** Temporal profiles of particle size distribution in toluene/NOx, toluene/isoprene/NOx and toluene/ethylene/NOx systems.

**Fig. 8.** Total number concentration and diameter evolution for toluene/NOx, toluene/isoprene/NOx and toluene/ethylene/NOx systems. The time-dependent diameter uses the fitting curve from merging data of Log. Nor. and Max. Conc.
Fig. 9. Mass concentration and SOA yields for toluene/NOx, toluene/isoprene/NOx and toluene/ethylene/NOx systems.

Fig. 10. Extinction, scattering (a) and single scattering albedo (b) for toluene/isoprene/NOx and toluene/ethylene/NOx systems.

HOA → SV-OOA → LV-OOA, from the bottom to the top of the triangle in the diagram of f44 vs. f43 (Jimenez et al., 2009). As shown in Fig. 11(b), the data points were mainly concentrated in the middle of the triangle, which is lower than aging SOA in the actual environment, which may be caused by a lower concentration of precursor or a shorter reaction time (Hu et al., 2012), further studies of the detailed reasons for the oxidation of organic aerosols are needed. Besides, it is necessary to further study the aerosol composition measurements with AMS and the comparison between AMS and SMPS under complex pollution condition in detail, and providing effective data for the complex atmospheric pollution.

CONCLUSIONS

Three comparison groups of experiments were conducted under the gas-phase environments of toluene/NOx, toluene/isoprene/NOx, and toluene/ethylene/NOx in a smog chamber. Experimental results show that under toluene limited conditions, the effect of the toluene/NOx ratio on the maximum ozone concentration shows two different trends. When the ratio is within 3.1–11.3, the maximum ozone greatly increases with the increasing ratio, whereas for the ratio of 15.5–24.8, it remains unchanged as the ratio increases. The same phenomenon was observed in the propene photochemical reaction (Hu et al., 2011). The appearance of the maximum ozone concentration was advanced to 225 min, and the decay rate of toluene increased from 1.1 × 10–4 to 1.6 × 10–3 min–1 with increase of the toluene concentration. The toluene SOA was greatly influenced by the initial toluene concentrations. The particle size and total number concentrations increased with increase of the initial toluene concentration. The SOA effective density was concentrated around 1.3–1.4 g cm–3, which has the highest frequency of 50.8%. Possibly due to the difference of oxidative conditions and oxidation pathways, the yield is higher at the same mass concentration under lower initial toluene concentrations, and a similar case was observed in Chen et al. (2016).
In the mixed VOCs system, the presence of isoprene or ethylene in the low initial concentration toluene/NOx system will promote ozone formation and SOA. Isoprene has a greater effect on ozone formation than that of ethylene, while the nucleation time of SOA is delayed, and the maximum SOA yield was reduced at the same mass concentration. In the toluene/isoprene/NOx and toluene/ethylene/NOx systems, the SSA rapidly increases with the progress of the reaction and reaches 0.8 and 0.73 at the end of the experiments, respectively. The mass extinction coefficient and mass scattering coefficient are weaker in the toluene/isoprene/NOx system. The slope of H/C and O/C of organic aerosol in Van Krevelen (V-K) is about −1.3, which suggests that organic aerosol oxidation products tend to carboxylic acids in the toluene/isoprene/NOx system. Therefore, it is concluded from our study that the different initial toluene concentrations and coexisting VOCs are most important for ozone and SOA formation from toluene.

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