Formation of secondary aerosols from gasoline vehicle exhaust when mixing with SO\textsubscript{2}

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Abstract. Sulfur dioxide (SO\textsubscript{2}) can enhance the formation of secondary aerosols from biogenic volatile organic compounds (VOCs), but its influence on secondary aerosol formation from anthropogenic VOCs, particularly complex mixtures like vehicle exhaust, remains uncertain. Gasoline vehicle exhaust (GVE) and SO\textsubscript{2}, a typical pollutant from coal burning, are directly co-introduced into a smog chamber, in this study, to investigate the formation of secondary organic aerosols (SOA) and sulfate aerosols through photooxidation. New particle formation was enhanced, while substantial sulfate was formed through the oxidation of SO\textsubscript{2} in the presence of high concentration of SO\textsubscript{2}. Homogenous oxidation by OH radicals contributed a negligible fraction to the conversion of SO\textsubscript{2} to sulfate, and instead the oxidation by stabilized Criegee intermediates (sCIs), formed from alkenes in the exhaust reacting with ozone, dominated the conversion of SO\textsubscript{2}. After 5 h of photochemical aging, GVE's SOA production factor revealed an increase by 60–200\% in the presence of high concentration of SO\textsubscript{2}. The increase could principally be attributed to acid-catalyzed SOA formation as evidenced by the strong positive linear correlation ($R^2 = 0.97$) between the SOA production factor and in situ particle acidity calculated by the AIM-II model. A high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS) resolved OA's relatively lower oxygen-to-carbon (O:C) (0.44 ± 0.02) and higher hydrogen-to-carbon (H:C) (1.40 ± 0.03) molar ratios for the GVE/SO\textsubscript{2} mixture, with a significantly lower estimated average carbon oxidation state (OS\textsubscript{c}) of $-0.51 ± 0.06$ than $-0.19 ± 0.08$ for GVE alone. The relative higher mass loading of OA in the experiments with SO\textsubscript{2} might be a significant explanation for the lower SOA oxidation degree.

1 Introduction

Sulfate and organic aerosols (OA) can lead to serious and complex air pollution (Parrish and Zhu, 2009) as the main components of fine particles or PM\textsubscript{2.5}, conveying negative effects on human health (Nel, 2005). Sulfate and OA additionally affect radiative forcing on a global scale (Andreae et al., 2005; Shindell et al., 2009). Thus, a detailed understanding of the magnitude and formation pathways of sulfate and OA is critical to formulate control strategies and to accurately estimate their impact on air quality and climate. Complications often arise due to missing or underestimated oxidation pathways of sulfur dioxide (SO\textsubscript{2}) (Berglen et al., 2004), the precursor of sulfate, and the unclear formation mechanisms of secondary organic aerosols (SOA) (de Gouw et al., 2005; Heald et al., 2005; Johnson et al., 2006; Volkamer et
Recent smog chamber studies have demonstrated that the amount of SOA formed from dilute gasoline vehicle exhaust often exceeds primary OA (POA) (Nordin et al., 2013; Platt et al., 2013; Gordon et al., 2014; Liu et al., 2015). Aromatic hydrocarbons were found to be vital SOA precursors in gasoline vehicle exhaust. Up to 90 % of SOA from idling Euro 1–4 vehicle exhaust could be attributed to aromatics (Nordin et al., 2013; Liu et al., 2015). Gordon et al. (2014) concluded that traditional precursors could fully explain the SOA production from old vehicles with model years prior to 1995. Multiple studies have shown that modeled SOA can only explain a fraction of the measured SOA from gasoline vehicle exhaust (Platt et al., 2013; Tkacik et al., 2014). Platt et al. (2013) found that predicted SOA accounted for approximately 20 % of the SOA formed from Euro 5 gasoline vehicle exhaust. Hence, more studies are needed to bridge the gap between modeled and measured SOA from gasoline vehicle exhaust. Emitted primarily from coal-fired power plants and coal-burning boilers, SO2, when mixed with gasoline vehicle exhaust containing the precursors for secondary nitrates and organic aerosols, NOx and aromatics, may react, complicating the formation of sulfate and SOA. Alkenes present in gasoline vehicle exhaust can react with ozone to form stabilized Criegee intermediates (SCIs), recently considered to significantly oxidize SO2 and influence sulfate formation (Mauldin et al., 2012; Welz et al., 2012). On the other hand, recent smog chamber simulations indicated that SO2 could enhance SOA formation from typical biogenic precursors, such as monoterpenes and isoprene through acid-catalyzed reactions (Edney et al., 2005; Kleindienst et al., 2006; Jaoui et al., 2008), but the influence of acid-catalyzed reactions on SOA formation from aromatics still remains debatable (Cao and Jang, 2007; Ng et al., 2007). Combinations of several pure chemicals, additionally, are not fully representative of SO2 mixing, with vehicle exhaust containing thousands of gaseous and particle-phase components (Gordon et al., 2014) in the formation of secondary aerosols under real atmospheric conditions. Until now, there have been no reports about the influence of SO2 on secondary aerosol formation from complex vehicle exhaust.

Here we directly introduced pipe exhaust from light-duty gasoline vehicles (LDGVs) and SO2 into a smog chamber with a 30 m3 Teflon reactor (Wang et al., 2014) to study the production of secondary aerosols: the influence of LDGV exhaust on SO2 oxidation to form sulfate aerosols and reciprocally that of SO2 on SOA formation from primary organics in LDGV exhaust.

2 Materials and methods

2.1 Vehicles and fuel

In Europe, vehicle emissions are classified by “Euro standards”, currently ranging from Euro 1 to Euro 6. China implemented the Euro 1, Euro 2, Euro 3, and Euro 4 emission standards in 2000, 2004, 2007, and 2012 for LDGVs, and the Euro 5 standard will be implemented in 2018. Three LDGVs were utilized in this study: one Euro 1 and two Euro 4 vehicles. They are all port-fuel-injected vehicles with model years ranging from 2002 to 2011. Further vehicle details are listed in Table 1. All vehicles were fueled with grade 93# gasoline, which complies with the Euro 3 gasoline fuel standard. Details of the gasoline composition can be found elsewhere (Zhang et al., 2013).

2.2 Smog chamber experiments

Six photochemical experiments with LDGV exhaust were conducted in a 30 m3 indoor smog chamber at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIG-CAS). Details of the smog chamber are described in Wang et al. (2014). Briefly, black lamps (1.2 m long, 60 W Philips/10R BL, Royal Dutch Philips Electronics Ltd., the Netherlands) are used as a light source, providing a NO2 photolysis rate of 0.49 min−1. Two Teflon-coated fans are installed inside the reactor to guarantee thorough mixing of the introduced gas species and particles within 120 s. Temperature and relative humidity in the reactor were controlled at approximately 25 °C and 50 %, respectively. A schematic of the experiment setup is presented in Fig. 1. Eight thermocouples are placed between the enclosure and the reactor walls to control the temperature. The temperature inside the reactor (T9) was measured by a Siemens QFM2160 (Siemens AG, Germany). Vehicles were first operated on-road to warm up the three-way catalysts for a minimum of half an hour prior to introducing the vehicle exhaust. Idling vehicle exhaust was then introduced directly by two oil-free pumps (Gast Manufacturing Inc., USA) into the reactor at a flow rate of 40 L min−1. Losses of volatile organic compounds (VOCs) and particles in the transfer lines were estimated to be less than 5 % (Liu et al., 2015). Prior to each experiment, the chamber was evacuated and filled with purified dry air at least 5 times, and then the reactor was flushed with purified dry air for a minimum of 48 h until no residual hydrocarbons, O3, NOx, or particles were detected in the reactor. The exhaust in the reactor was diluted by a factor of 13–94 compared to the tailpipe.

SO2 was injected by a gas-tight syringe following introduction of exhaust to create a mixing ratio of SO2 in the reactor of approximately 150 ppb during three experiments with the three vehicles. Experiments without additional SO2 were also conducted for each vehicle for comparison, and additional NO was added to adjust the VOC/NOx ratios.
Table 1. Detailed information of the three LDGVs.

<table>
<thead>
<tr>
<th>ID</th>
<th>Emission standard class</th>
<th>Vehicle</th>
<th>Model year</th>
<th>Mileage (km)</th>
<th>Displacement (cm³)</th>
<th>Power (kW)</th>
<th>Weight (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Euro 4</td>
<td>Golf</td>
<td>2011</td>
<td>25 000</td>
<td>1598</td>
<td>77</td>
<td>1295</td>
</tr>
<tr>
<td>II</td>
<td>Euro 4</td>
<td>Sunny</td>
<td>2011</td>
<td>9448</td>
<td>1498</td>
<td>82</td>
<td>1069</td>
</tr>
<tr>
<td>III</td>
<td>Euro 1</td>
<td>Accord</td>
<td>2002</td>
<td>237 984</td>
<td>2298</td>
<td>110</td>
<td>1423</td>
</tr>
</tbody>
</table>

Figure 1. Schematic of the GIG-CAS smog chamber facility and vehicle exhaust injection system.

(ppb / ppb) to between 4.9 and 10.8 (Table 2). VOC / NOₓ ratios in experiments with the same vehicle were similar with initial concentrations of NOₓ ranging from 300.8 to 458.5 ppb. After more than half an hour of primary characterization, the exhaust was exposed to black light continuously for 5 h. The formed SOA was characterized for another 2 to 3 h after the black lamps were switched off to correct the particles’ wall loss. OH precursor and seed particles were not introduced in this study.

An array of instruments was used to characterize gas and particle-phase compounds in the reactor. Gas-phase NOₓ, O₃, and SO₂ were measured with dedicated monitors (EC9810, 9841T, Ecotech, Australia, and Thermo Scientific model 43iTLE, USA). The detection limit and accuracy of the SO₂ instrument are 0.2 ppb and ±1 %, respectively. Methane and CO concentrations were determined using a gas chromatograph (Agilent 6890GC, USA) with a flame ionization detector and a packed column (5A molecular sieve 60/80 mesh, 3 m × 1/8 in.) (Zhang et al., 2012). CO₂ was analyzed with a HP 4890D gas chromatograph (Yi et al., 2007). Gas-phase organic species were measured with a model 7100 pre-concentrator (Entech Instruments Inc., USA) coupled with an Agilent 5973N gas chromatograph–mass selective detector/flame ionization detector/electron capture detector (GC-MSD/FID, Agilent Technologies, USA) (Wang and Wu, 2008; Zhang et al., 2010, 2012, 2013) and a commercial proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS, model 2000, Ionicon Analytik GmbH, Austria) (Lindinger et al., 1998; Jordan et al., 2009). C₂–C₃ and C₄–C₁₂ hydrocarbons were measured by GC-FID and GC-MSD, respectively. PTR-TOF-MS was used to determine the time-resolved concentrations of VOCs such as aromatics. The decay curve of toluene was used to derive the average hydroxyl radical (OH) concentration during each experiment.

Particle number concentrations and size distributions were measured with a scanning mobility particle sizer (SMPS, TSI Incorporated, USA, classifier model 3080, CPC model 3775). An aerosol density of 1.4 g cm⁻³ was assumed to convert the particle volume concentration into the mass concentration (Zhang et al., 2005). A high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-MS, Aerodyne Research Incorporated, USA) was used to measure the particle chemical compositions and nonrefractory PM mass (Jayne et al., 2000; DeCarlo et al., 2006). The instrument was operated in the high-sensitivity V mode and high-resolution W mode alternatively every 2 min. The toolkit Squirrel 1.51H was used to obtain time series of various mass components (sulfate, nitrate, ammonium, and organics). We used the toolkit Pik a 1.1H to determine the average element ratios of organics, including H : C, O : C, and N : C (Aiken et al., 2007, 2008). The contribution of gas-phase CO₂ to the m/z 44 signal was corrected with measured CO₂ concentrations. The HR-TOF-MS was calibrated using 300 nm monodisperse ammonium nitrate particles.

A summary of initial experimental conditions and final results is presented in Tables 2 and 3, respectively. Total wall-loss-corrected OA varied from 17.8 to 91.4 µg m⁻³, which spans the typical urban PM concentrations in heavy polluted megacities with poor air quality. POA concentrations of the experiments ranged from 0.13 to 0.31 µg m⁻³ and are negligible compared with the formed SOA. Initial mixing ratios of non-methane hydrocarbons (NMHCs) in the reactor were between 2.2 and 4.3 ppm, much higher than typical urban conditions. The average OH concentrations during photooxidation ranged from 0.73 to 1.29 × 10⁶ molecules cm⁻³, approximately 5 times lower than that during summer daytime (Seinfeld and Pandis, 1998). Initial concentrations of the reactants were maintained as similar as possible for the same vehicle, though initial NMHCs, NOₓ, and average OH concentrations are different from typical urban conditions, so all
2.3 SOA production factors

The SOA production factor (PF) (mg kg\(^{-1}\)) is calculated on a fuel basis:

\[
PF = 10^6 \cdot [\text{SOA}] \cdot \frac{[\Delta \text{CO}_2] \cdot [\Delta \text{CO}] \cdot [\Delta \text{HC}]}{\text{MW}_{\text{CO}_2} \cdot \text{MW}_{\text{CO}} \cdot \text{MW}_{\text{HC}}} \cdot \frac{\omega_C}{\text{MW}_C},
\]

where \([\Delta \text{CO}_2]\), \([\Delta \text{CO}]\), and \([\Delta \text{HC}]\) are the background-corrected concentrations of \(\text{CO}_2\), \(\text{CO}\), and the total hydrocarbons in the reactor in \(\mu g m^{-3}\); \([\text{SOA}]\) is the concentration of wall-loss-corrected SOA in \(\mu g m^{-3}\); and \(\text{MW}_{\text{CO}_2}\), \(\text{MW}_{\text{CO}}\), \(\text{MW}_{\text{HC}}\), and \(\text{C. } \omega_C\) are the molecular weights of \(\text{CO}_2\), \(\text{CO}\), \(\text{HC}\), and \(C\). \(\omega_C\) (0.85) is the carbon intensity of the gasoline (Kirchstetter et al., 1999). Total hydrocarbons measured in this study include methane and \(C_2-C_{12}\) hydrocarbons. The carbon content of each hydrocarbon was calculated and then summed in Eq. (1).

2.4 Determination of OH concentration

Decay of toluene measured by PTR-TOF-MS is used to determine the average OH concentration during each experiment. Changes in the toluene concentration over time can be expressed as

\[
\frac{d[\text{toluene}]}{dt} = -k \cdot [\text{OH}] \cdot [\text{toluene}],
\]

where \(k\) is the rate constant for the reaction between toluene and OH radical. The value of \(k\) is obtained from the Master Chemical Mechanism version 3.3 (MCM v3.3, http://www.chem.leeds.ac.uk/MCM) (Jenkin et al., 2003). Assuming a constant OH concentration during an experiment, we can integrate Eq. (2) to get Eq. (3):

\[
\ln \left( \frac{[\text{toluene}]_0}{[\text{toluene}]_t} \right) = k \cdot [\text{OH}] \cdot t.
\]

Thus, by plotting \(\ln([\text{toluene}]_0)/[\text{toluene}]_t\) vs. time \(t\), we can obtain a slope that equals \(k \cdot [\text{OH}]\). The average OH concentration is then calculated as

\[
[\text{OH}] = \frac{\text{slope}}{k}.
\]

Average OH concentrations were determined when the black lamps were on. Segmented OH concentrations were also estimated (Fig. S1 in the Supplement) and listed in Table S1 for experiments with the addition of \(\text{SO}_2\). Similar concentrations of \(\text{SCIs}\) were determined subsequently (Sect. 2.5) when average and segmented OH concentrations were individually used for the same experiment.
2.5 Determination of the steady-state concentration of sCIs

Ozonolysis of alkenes will form a primary ozonide through a 1,3-cycloaddition of ozone across the olefinic bond. The primary ozonide then rapidly decomposes to two carbonyl compounds, called excited CIs, which can be stabilized by collision to form sCIs (Heard et al., 2004; Johnson and Marston, 2008):

\[ \text{alkene} + \text{O}_3 \rightarrow \phi \text{sCIs} + \text{products}, \]  

where \( \phi \) represents the yield of sCIs from ozonolysis of alkenes. The four main losses of sCIs are reactions with H\(_2\)O, SO\(_2\), and NO\(_2\) and unimolecular decomposition.

\[ \text{sCIs} + \text{H}_2\text{O} \rightarrow \text{products}, \]  
\[ \text{sCIs} + \text{SO}_2 \rightarrow \text{SO}_3 + \text{products}, \]  
\[ \text{sCIs} + \text{NO}_2 \rightarrow \text{products}, \]  
\[ \text{sCIs} \rightarrow \text{products}. \]

The steady-state concentration of sCIs will be

\[ \text{sCIs}_{\text{steady-state}} = \frac{\phi K_{R1} \text{[alkene]}}{K_{R2} \text{[H}_2\text{O]} + K_{R3} \text{[SO}_2] + K_{R4} \text{[NO}_2] + K_{R5}}, \]  

where \( K_{R1} \) is the rate coefficient for the ozonolysis of alkene; \( K_{R2}, K_{R3}, K_{R4}, \) and \( K_{R5} \) represent the rate constant for reactions of sCIs with H\(_2\)O, SO\(_2\), NO\(_2\), and decomposition, respectively. This equation has been widely used to predict the steady-state concentration of sCIs in the atmosphere (Welz et al., 2012; Newland et al., 2015).

The steady-state concentration of sCIs throughout the entire experiment was estimated in this study. The production rate of sCIs was dependent on both the concentrations and composition of alkenes in the exhaust. Detailed gas-phase mechanisms of alkenes from the MCM v3.3 were run to determine the time-resolved concentrations of sCIs in the experiments. The concentrations of alkenes included in the model and the category of sCIs are presented in Table 4. No alkenes and branched alkenes respectively contributed 89.9-93.0 % and 7.0-10.1 % of the alkenes, with ethene and propene as two main components accounting for 66.8-81.3 %.

The emission of black carbon (BC) from LDGVs was negligible according to a previous study (Liu et al., 2015). The loss of particles onto the walls was treated as a first-order process (McMurry and Grosjean, 1985). The wall loss rate constant was determined separately for each experiment by fitting the SMPS and AMS data with first-order kinetics when UV lamps were switched off. By applying this rate to the entire experiment, we use the same method as Pathak et al. (2007) to correct the wall loss of the particles. The wall loss of particles is a size-dependent process; therefore, the presence of nucleation would influence wall loss correction of the particles due to the rapid loss of nucleation-mode particles. As shown in a previous study, particle wall loss rates could not be accurately quantified for the particles generated in the nucleation event (Keywood et al., 2004). The impact of the nucleation event on wall loss estimate is considered to be negligible as less than 5 % of the particle mass is in the nucleation-mode 20 min after nucleation for all experiments in this study.

Wall deposition of organic vapors can lead to the underestimation of SOA production (Matsunaga and Ziemann, 2010; X. Zhang et al., 2014, 2015). Wall deposition of a compound has recently been established as related to its volatility (X. Zhang et al., 2015). The extent that wall deposition of organic vapors impacts on SOA production depends on the competition of organic vapors depositing onto walls and suspended particles. Here, we assumed that gas–particle partitioning of organic vapors dominated their wall depositions and thus organic vapors were considered to only partition onto suspended particles.

As the collection efficiency of sulfate in the HR-TOF-AMS can vary due to the coating of OA onto sulfate, we used AMS data combined with SMPS data to derive the time-resolved concentrations of OA, sulfate, ammonium, and nitrate. The emission of black carbon (BC) from LDGVs was negligible according to a previous study (Liu et al., 2015); thus the ratio of OA to inorganic aerosols from the AMS was used to split the total particle mass measured by SMPS into the mass of OA, sulfate, ammonium, and nitrate (Gordon et al., 2014; Liu et al., 2015).
3 Results and discussion

3.1 Formation of sulfate

Figure 2 shows the temporal evolution of gas- and particle-phase species during the photochemical aging of emissions from vehicle III with and without adding SO$_2$. NO was injected to adjust the VOC / NO$_x$ ratio at approximately time = −0.25 h for both experiments. After the black lamps were switched on, NO was rapidly consumed in less than 1 h. Mass concentrations of secondary aerosols rapidly increased following photooxidation with or without SO$_2$ for approximately 1 h, stabilizing after approximately 4 h of photooxidation (Figs. 2, 3, and 4). Substantial sulfate was formed synchronously with OA for experiments with SO$_2$ with the maximum particle number concentrations at 5.4−48 times of those without SO$_2$ (Table 1, Fig. 5), indicating enhanced new particle formation (NPF) when adding SO$_2$. As the precursor of sulfuric acid (H$_2$SO$_4$), SO$_2$ at higher concentrations would lead to additional formation of H$_2$SO$_4$, thereby increasing the nucleation rates and total particle number concentrations (Sipila et al., 2010). The S-bearing organic fragments C$_n$H$_m$O$_s$S determined by HR-TOF-AMS can be used as marker ions to quantify organosulfates (Huang et al., 2015). In this study the fragments C$_n$H$_m$O$_s$S were almost not appreciable. Using the methods of Huang et al. (2015), we estimated that the mass ratio of organosulfates to sulfate was less than 0.5 %. Thus the formation of organosulfates could be negligible in this study.

Substantial nitrates were formed for vehicles I and II (Figs. 3a and 4a) and could be attributed to ammonium or organic nitrates. The identification of ammonium and organic nitrates may be obtained from the NO$^+/NO_2^+$ ratio, which is typically substantially higher for organic nitrates compared with ammonium nitrate (Farmer et al., 2010; Sato et al., 2010). The NO$^+/NO_2^+$ ratios for experiments I-2 and II-2 were 1.99−2.60, within the range of 1.08−2.81 for ammonium nitrate (Farmer et al., 2010; Sato et al., 2010), suggesting that nitrates detected in the two experiments could be attributed to ammonium nitrate. Ammonium nitrate was likely formed by reactions of nitric acid formed from NO$_x$ oxidation and ammonia, which is substantially higher in China’s LDGV exhaust (Liu et al., 2014). The NO$^+/NO_2^+$ ratios for experiments with SO$_2$ were 3.9−5.0, significantly higher than ratios measured for ammonium nitrate and also similar to ratios for organic nitrates (3.82−5.84) from the photooxidation of aromatic hydrocarbons (Sato et al., 2010), indicating organic nitrates dominated nitrate formation in these experiments. High concentration of SO$_2$ suppressed the formation of ammonium nitrate in experiments with SO$_2$ as NH$_3$ was liable to react with sulfuric acid rather than nitric acid (Pathak et al., 2009).

### Table 4. Concentrations of alkenes included in the model and the category of sCIs.

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (ppb)</th>
<th>sCIs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I-2</td>
<td>II-2</td>
</tr>
<tr>
<td>Ethene</td>
<td>333.1</td>
<td>113.8</td>
</tr>
<tr>
<td>Propene</td>
<td>95.8</td>
<td>50.3</td>
</tr>
<tr>
<td>1-Butene</td>
<td>30.9</td>
<td>49.1</td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>7.6</td>
<td>4.8</td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>9.9</td>
<td>6.4</td>
</tr>
<tr>
<td>1-Pentene</td>
<td>3.8</td>
<td>0.3</td>
</tr>
<tr>
<td>cis-2-Pentene</td>
<td>5.2</td>
<td>1.2</td>
</tr>
<tr>
<td>trans-2-Pentene</td>
<td>8.5</td>
<td>2.6</td>
</tr>
<tr>
<td>2-Methyl-1-butene</td>
<td>11.9</td>
<td>5.4</td>
</tr>
<tr>
<td>3-Methyl-1-butene</td>
<td>2.4</td>
<td>0.8</td>
</tr>
<tr>
<td>2-Methyl-2-butene</td>
<td>17.8</td>
<td>10.9</td>
</tr>
<tr>
<td>cis-2-Hexene</td>
<td>0.8</td>
<td>0</td>
</tr>
</tbody>
</table>

### Table 5. Rate constants of sCIs used in the model.

<table>
<thead>
<tr>
<th>Stabilized CIs</th>
<th>$K_{R2}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>$K_{R3}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>$K_{R4}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>$K_{R5}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$OO</td>
<td>0.025a</td>
<td>3.9b</td>
<td>7.0b</td>
<td>0c</td>
</tr>
<tr>
<td>CH$_3$CHOO</td>
<td>7.0d</td>
<td>4.55d</td>
<td>2.0d</td>
<td>67.5e</td>
</tr>
<tr>
<td>(CH$_3$)$_2$COO</td>
<td>2.1c</td>
<td>2.4c</td>
<td>2.0c</td>
<td>151c</td>
</tr>
</tbody>
</table>

* Ouyang et al. (2013); Welz et al. (2012); Newland et al. (2015); Taatjes et al. (2013); average of $K_{R5}$ from Fenske et al. (2009) and Newland et al. (2015).
Formation rates of sulfate, derived from the differential of concentration–time plots of sulfate, exhibited burst increases at the initial stage of sulfate formation and then decreased to nearly zero 5 h after sulfate formation initiated (Fig. 6a). The maximum formation rate of sulfate in experiments I-2, II-2, and III-2 was 61.5, 21.6, and 113 µg m$^{-3}$ h$^{-1}$, respectively, considerably higher than the rate of 0.17–0.37 ppbv h$^{-1}$ (0.73–1.59 µg m$^{-3}$ h$^{-1}$ under normal temperature and pressure (NTP) conditions) through gas-phase oxidation of SO$_2$ during the daytime in the Pearl River Delta (PRD) region of China in the summer of 2006 (Xiao et al., 2009), and also more than 10 times higher than the maximum sulfate formation rate of 4.79 µg m$^{-3}$ h$^{-1}$ observed at an urban site in Beijing during the Beijing Olympic Games in 2008 (Zhang et al., 2011). The formation rate of sulfate was related to the concentrations of SO$_2$ and OH, which were respectively approximately 7 times higher and 2–16 times lower than those in the study of Xiao et al. (2009). Significant differences of sulfate formation rates between chamber and ambient observations could, however, indicate that there might be other processes dominating the oxidation of SO$_2$ rather than gas-phase oxidation by OH in this study.

SO$_2$ was typically deemed to be oxidized by OH radicals through homogeneous reactions in the gas phase (Calvert et al., 1978), or by H$_2$O$_2$ and O$_3$ through in-cloud processes in the aqueous phase (Lelieveld and Heinzenberg, 1992), which, however, could be negligible in this study due to RH of approximate 50%. As shown in Fig. 7, the loss rate of SO$_2$...
Figure 5. Evolution of particle number concentrations during the aging experiments of LDGV exhaust for vehicle I (a), II (b) and III (c). At time = 0 h, the black lamps were turned on. “W/o SO₂” and “with SO₂” in the figures represent experiments without and with addition of SO₂, respectively.

through homogeneous reactions with OH radicals in the three experiments ranged from 0.0023 to 0.0034 h⁻¹, accounting for only 2.4–4.6% of the total loss rate of SO₂. The initial concentrations of alkenes in the experiments with SO₂ varied from 248 to 547 ppb, contributing 7.7–23.5% of the total NMHCs. The high content of alkenes in the exhaust might form a mass of sCIs through the reaction with ozone. Recent studies have indicated the rate coefficient of CH₂OO with SO₂ to be 50 to 10 000 times larger than that used in tropospheric models (Welz et al., 2012). The oxidation of SO₂ by sCIs may be as significant as that by OH radicals in the atmosphere. The oxidation rate of SO₂ for experiments I-2 and III-2, through the reactions with sCIs, was calculated to be 0.065 ± 0.029 and 0.042 ± 0.020 h⁻¹ (Fig. 7), respectively, accounting for 66.9 and 61.4% of the total loss rate of SO₂. Considering the variability of sCIs throughout the entire experiment, we concluded that sCIs were virtually responsible for the formation of secondary aerosols from gasoline vehicle exhaust.
for the oxidation of SO$_2$ in experiments I-2 and III-2. The oxidation rate of SO$_2$ through the reactions with sCIs for the experiment II-2 was estimated to be 0.028 ± 0.015 h$^{-1}$, contributing 31.5% of the total loss rate of SO$_2$. The unexplained loss of SO$_2$ might be a result of heterogeneous oxidation in the presence of LDGV exhaust containing thousands of aerosols and gaseous species. He et al. (2014) found that SO$_2$ could react with NO$_2$ on the surface of mineral dust to promote the conversion of SO$_2$ to sulfate. As shown in Fig. 5, the initial particle number for vehicle II was approximately 5000 cm$^{-3}$, nearly 40–50 times higher than for vehicle I and III, providing larger aerosol surface areas for the oxidation of SO$_2$ by NO$_2$. However, quantification of SO$_2$ oxidation by NO$_2$ on the surface of existing aerosols is difficult due to the lack of reaction rate constant (He et al., 2014). We speculate that the reaction between SO$_2$ and NO$_2$ on the surface of existing aerosols might explain the difference between the total loss rate of SO$_2$ and the sum of sCIs and OH oxidation for vehicle II.

3.2 SOA production

Fuel-based SOA production factors (PFs), expressed as SOA production in milligrams (mg) after 5 h photooxidation of LDGV exhaust emitted per kilogram (kg) of gasoline burned, all increased substantially when adding SO$_2$, 60–200% above that without SO$_2$ (Fig. 8a), although the selected cars’ emission standards varied from Euro 1 to Euro 4. The in situ particle acidities at the time when SOA formation rate peaks were calculated as H$^+$ concentrations based on AIM-II model H$^+$–NH$_4^+$–SO$_4^{2−}$–NO$_3^{−}$–H$_2$O with gas–aerosol partitioning disabled (http://www.aim.env.uea.ac.uk/aim/model2/model2a.php) (Clegg et al., 1998; Wexler and Clegg, 2002). Inputs to the model include temperature, RH, [SO$_2^+$], [NO$_2^+$], [NH$_4^+$], and [H$^+$]$_{total}$, calculated based on ion balance. SO$_4^{2−}$, NH$_4^+$ and NO$_3^−$ contributed virtually all of the aerosol-phase ions mass in this study, thus determining the aerosol acidity. Though other ions (i.e., Ca$^{2+}$, Mg$^{2+}$, K$^+$ and Na$^+$) had a negligible influence on the aerosol acidity, it is worth noting that the reported values of H$^+$ may be the upper bound.

The in situ particle acidities with the addition of SO$_2$ were 1.6–3.7 times as high as those without the addition of SO$_2$ (Table 3). This elevated particle acidity could largely explain the higher PFs of SOA from LDGV exhaust with SO$_2$, supported by the strong positive linear correlations ($R^2 = 0.965$, $P < 0.01$) between SOA PFs and the in situ particle acidities (Fig. 8b). Aromatic hydrocarbons are vital SOA precursors in gasoline vehicle exhaust (Nordin et al., 2013; Gordon et al., 2014; Liu et al., 2015). The influence of particle acidity on SOA formation from aromatics is still debatable. Cao and Jang (2007) found that the presence of acid seeds with [H$^+$] concentrations of 240–860 nmol m$^{-3}$ significantly increased the SOA yields from oxidation of toluene and 1,3,5-trimethylbenzene compared with yields using neutral seed aerosols. However, Ng et al. (2007) observed no influence of particle acidity on SOA yields from the aromatics, possibly due to the low content of aerosol water. SOA production from gasoline vehicle exhaust was enhanced in this study, even at a low level of [H$^+$] concentrations ranging from 7.4 to 27.1 nmol m$^{-3}$. Gas-phase oxidation products of aromatic hydrocarbons in the exhaust, like multifunctional carboxyl glyoxal, would be transformed more rapidly into low-volatility products through acid-catalyzed heterogeneous reactions (Jang et al., 2002; Cao and Jang, 2007) and thus caused increasing SOA production. Aerosol water is needed for the hydration of carbonyls and therefore influences the acid-catalyzed reactions. Liquid water content (LWC) in this study was not measured but instead predicted by the AIM-II model, with an average value of 5.5 ± 4.5 µg m$^{-3}$ when SOA formation rate peaks, ensuring the occurrence of acid-catalyzed reactions. Figure 9 shows the ion intensity of fragment m/z 88 that can arise only from a glyoxal oligomer formed through acid-catalyzed heterogeneous reactions (Liggio et al., 2005). The scatter of the data might be due to the low intensity of m/z 88. It may not be possible to take the low intensities of m/z 88 as an indication that oligomers formed from glyoxal are not important. It is more likely that these fragments are thermally unstable at the vaporization temperature of HR-TOF-AMS (600°C) and readily decompose to monomer or gem-diol forms before passing into the ionization region. The experiment with the addition of SO$_2$, with higher particle acidity, exhibited relatively higher m/z 88 intensities. This indicated the important role of acid-catalyzed heterogeneous reactions in SOA formation from gasoline vehicle exhaust. A photooxidation experiment of exhaust from vehicle I in the presence of ammonium sulfate seeds (53.3 µg m$^{-3}$) with RH of 59% (Table 2) was conducted to explore the effect of sulfate on SOA formation as particle acidity is typically driven by sulfate. The SOA production factor was 22.2 mg kg$^{-1}$ fuel, comparable with...
Figure 9. Time evolution of m/z 88 during the aging of LDGV exhaust from vehicle III. Solid lines are derived from the average values of every five data points.

26.2 mg kg$^{-1}$ fuel for experiment I-1, indicating that sulfate may not directly influence SOA production. Thus, the SOA production was indeed dependent on the particle acidity.

Recent studies have indicated that the presence of high concentrations of seed aerosols might decrease the loss of organic vapors to the walls and thus increase the SOA formation (Kroll et al., 2007; X. Zhang et al., 2014, 2015). However, Cocker et al. (2001) observed that the presence of ammonium sulfate seed aerosols had no impact on SOA formation from the photooxidation of m-xylene and 1,3,5-trimethylbenzene. Li et al. (2015) also suggested that no measurable differences were observed in SOA formation from m-xylene between non-seeded and seeded experiments. In this study, comparable SOA PFs for experiments with and without seed aerosols indicated that wall loss of organic vapors did not significantly impact SOA production from gasoline vehicle exhaust.

SOA formation rates, derived from the differential of concentration-time plots of SOA, exhibited similar trends to sulfate with a burst increase at the initial stage of SOA formation (Fig. 6b). The average SOA formation rates for vehicles I, II, and III with SO$_2$ were 1.1, 1.2, and 4.4 times as high as those without SO$_2$, respectively, although the maximum rate for vehicle II with SO$_2$ was lower. Here we particularly focused on the burst increase stage of SOA and sulfate, which may be related to fast increase in PM$_{2.5}$ and occurrence of haze (He et al., 2014). Figure 10 shows the correlation between SOA formation rate and particle acidity. Plotted data corresponded to data selected from Fig. 6 when SOA formation rate was higher than zero to when the rate reached the maximum value. Significant linear correlations ($P < 0.05$, $R^2 > 0.88$) between SOA formation rate and particle acidity during this stage for experiments with SO$_2$ suggest that acid-catalyzed heterogeneous reactions might play an important role in the rapid formation of SOA (Jang et al., 2002). The fitted slopes for vehicle I, II, and III were 3.96, 0.82, and 3.14, respectively, suggesting other factors, including alkene abundance, may influence the SOA formation rate. The initial concentration of alkenes for experiments I-2, II-2, and III-2 was 547, 248, and 353 ppb, respectively, consistent with the variation of the slopes. Higher alkene content would increase the formation rate of sCIs, which could rapidly oxidize SO$_2$ to sulfuric acid, thus influencing the aerosol acidity.

3.3 Oxidation state

After 5 h of photooxidation, SOA’s molar ratios of oxygen to carbon (O:C) and hydrogen to carbon (H:C) resolved by HR-TOF-AMS were plotted on a Van Krevelen diagram.
Thus decrease the oxidation degree of OA. The O : C ratios in the experiments with SO\(_2\) vehicle (Table 2), the relative higher mass loading of OA in that the average OH concentrations were similar for the same generation. Kang et al. (2011) also observed that the oxidation degree of OA decreased rapidly as the OA mass concentration increased for the same amount of OH exposure. Given the average OH concentrations were similar for the same vehicle (Table 2), the relative higher mass loading of OA in the experiments with SO\(_2\) may lead to the lower O : C and thus decrease the oxidation degree of OA. The O : C ratios were observed to decrease 0.1 with an increase of approximately 50 µg m\(^{-3}\) of OA concentrations for m-xylene and p-xylene (Kang et al., 2011). However, in this study the slope was 0.1 ΔO : C for approximately 26 µg m\(^{-3}\) ΔOA. The differences may be due to some other precursors than aromatics contributing to SOA formation from gasoline vehicle exhaust (Liu et al., 2015).

The slope of −0.87 (Fig. 11) for the mixture of SO\(_2\) and exhaust, slightly higher than for exhaust alone (Liu et al., 2015), indicates that SOA formation in these experiments is a combination of carboxylic acid and alcohol/peroxide formation (Heald et al., 2010; Ng et al., 2011). The slope of −0.87 and intercept of approximately 1.8 are similar to the observation for ambient data with a slope of approximately −1 and intercept of approximately 1.8 (Heald et al., 2010), suggesting that SOA chemistry for the mixture of SO\(_2\) and gasoline vehicle exhaust is atmospherically relevant.

4 Conclusions

A series of chamber experiments investigating the formation of secondary aerosols from the mixture of SO\(_2\) and gasoline vehicle exhaust were conducted. The high content of alkenes in gasoline vehicle exhaust formed numerous sCIs, dominating the formation of sulfate, while elevated particle acidity, resulting from the formation of sulfuric acid, enhanced SOA production from the gasoline vehicle exhaust. We conclude that SO\(_2\) and gasoline vehicle exhaust can enhance each other in forming secondary aerosols. High concentration of SO\(_2\) and high levels of aerosol acidity combined with rapid increase in LDGVs in heavily polluted cities such as Beijing (Pathak et al., 2009; He et al., 2014) might consequently worsen the air quality in the absence of stricter control strategies on emissions of SO\(_2\) and vehicle exhaust. Previous studies have indicated that a high content of alkenes in China’s gasoline oil is detrimental for the control of ozone in ambient air (Y. Zhang et al., 2013, 2015). Our results suggested that the incomplete combustion of gasoline with a high content of alkenes might also induce the formation of sCIs, facilitating the production of secondary aerosols. The limit of alkenes content in China was lowered to 24 % by volume in the newly established Level V gasoline fuel standard from 28 % by volume in the Level IV gasoline fuel standard. This limit remains substantially higher when compared to those limits in the USA or in Europe and, in particular, 6 times higher than that in California, USA. Thus, limiting the content of alkenes in China’s gasoline might benefit the control of both ozone and secondary aerosols.

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