Photooxidation of cyclohexene in the presence of SO$_2$: SOA yield and chemical composition

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Received: 12 January 2017 – Discussion started: 15 February 2017
Revised: 28 September 2017 – Accepted: 8 October 2017 – Published: 9 November 2017

Abstract. Secondary organic aerosol (SOA) formation from a cyclohexene/NO$_x$ system with various SO$_2$ concentrations under UV light was investigated to study the effects of cyclic alkenes on the atmospheric environment in polluted urban areas. A clear decrease at first and then an increase in the SOA yield was found with increasing SO$_2$ concentrations. The lowest SOA yield was obtained when the initial SO$_2$ concentration was in the range of 30–40 ppb, while higher SOA yield compared to that without SO$_2$ could not be obtained until the initial SO$_2$ concentration was higher than 85 ppb. The decreasing SOA yield might be due to the fact that the promoting effect of acid-catalysed reactions on SOA formation was less important than the inhibiting effect of decreasing OH concentration at low initial SO$_2$ concentrations, caused by the competition reactions of OH with SO$_2$ and cyclohexene. The competitive reaction was an important factor for SOA yield and it should not be neglected in photooxidation reactions. The composition of organic compounds in SOA was measured using several complementary techniques including Fourier transform infrared (FTIR) spectroscopy, ion chromatography (IC), and Exactive Plus Orbitrap mass spectrometer equipped with electrospray interface (ESI). We present new evidence that organosulfates were produced from the photooxidation of cyclohexene in the presence of SO$_2$.

1 Introduction

Alkenes are widely emitted from biogenic and anthropogenic sources (Kesselmeier et al., 2002; Chin and Batterman, 2012), and their gas-phase oxidation reactions with OH, NO$_3$, or O$_3$ are among the most important processes in the atmosphere (Atkinson, 1997; Stewart et al., 2013; Paulson et al., 1999). Reactions of ozone with alkenes are an important source of free radicals in the lower atmosphere and thus highly influence the oxidative capacity of the atmosphere (Paulson and Orlando, 1996). Some products of these reactions have sufficiently low vapour pressure, allowing them to condense with other gaseous species, and contribute to the secondary organic aerosol (SOA) mass (Sarwar and Corsi, 2007; Sakamoto et al., 2013; Nah et al., 2016; Kroll and Seinfeld, 2008; Hallquist et al., 2009). SOA formation from the oxidation of VOCs has been receiving significant attention in recent years due to its large implication in the formation of atmospheric fine particulate matter (Jimenez et al., 2009). SOA has significant impacts on human health (Pope III and Dockery, 2006), air quality (Kanakidou et al., 2005; Jaoui et al., 2012; McFiggans et al., 2006), and global climate change (Hansen and Sato, 2001; Adams et al., 2001; Pokhrel et al., 2016).

Although cyclic alkenes widely exist in the atmosphere, their gas-phase oxidation has received less attention than that of linear or branched alkenes (Sipilä et al., 2014). Cyclohexene is an important industrial chemical (Sun et al., 2013) and is also widespread in urban areas (Grosjean et al., 1978). Cyclohexene has been extensively studied as a monoterpene surrogate for inferring oxidation mecha-
nisms and aerosol formation characteristics, because it has the basic structural unit in abundant biogenic monoterpenes and sesquiterpenes (Carlsson et al., 2012; Keywood et al., 2004b). The rate constants for gas-phase reactions of cyclohexene with OH, O₃, and NO₃ were measured at room temperature to be \((6.4 \pm 0.1) \times 10^{-11}, \ (8.1 \pm 1.8) \times 10^{-17}, \) and \((5.4 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\), respectively (Stewart et al., 2013; Aschmann et al., 2012), and a correlation between the logarithm of the rate constants and the molecular orbital energies for simple cyclic alkenes was observed. The effect of pressure and that of the presence of SO₂ on the formation of stable gas-phase products and SOA from the ozonolysis of cyclohexene were investigated (Carlsson et al., 2012). It was found that the collisional stabilization of initial clusters was an important aspect for SOA formation processes involving sulfuric acid (H₂SO₄) and organic compounds. The effect of the structure of the hydrocarbon parent molecule on SOA formation was investigated for a series of cyclic alkenes and related compounds (Keywood et al., 2004b), and the SOA yield was found to be a function of the number of carbons present in the cyclic alkenes ring. The relative SOA yields from ozonolysis of cyclic alkenes can be quantitatively predicted from properties of the parent hydrocarbons, like the presence of a methyl group and an exocyclic double bond.

SO₂, one of the most important inorganic pollutants in urban areas, plays an important role in SOA formation (Wang et al., 2005; Lonsdale et al., 2012; Liu et al., 2016). Seasonal variations of SO₂ concentrations were found to be consistent with seasonal variations of PM₂.₅ concentration (Cheng et al., 2015). Smog chamber simulations have indicated that SO₂ could enhance the formation of SOA from the oxidation of VOCs under acidic conditions by increasing aerosol acidity and ammonium sulfate aerosol formation (Edney et al., 2005; Liu et al., 2016; Attwood et al., 2014). Anthropogenic SO₂ emissions can impact new particle formation, and SOA composition (Lonsdale et al., 2012).

Although the existence of organosulfates in ambient aerosols was first observed in 2005 (Romero and Oehme, 2005), proper identification of these aerosols was done 2 years later. In a series of laboratory chamber studies, it was shown that organosulfates present in ambient aerosols collected from various locations mostly originate from acid-catalysed reactions of SOA formed from photooxidation of α-pinenene and isoprene (Surratt et al., 2007). Recently, different kinds of organosulfates have been observed in SOA around the world, and organosulfates have been identified as a group of compounds that have an important contribution to the total amount of SOA in the atmosphere (Surratt et al., 2008; Froyd et al., 2010; Kristensen and Glasius, 2011; Tololka and Turpin, 2012; Wang et al., 2016). Laboratory chamber studies showed that OH / NO₃ / O₃-initiated reactions of BVOCs, such as isoprene, α-pinenene, β-pinenene, and limonene with sulfates or sulfuric acid are the main processes for organosulfate formation (Surratt et al., 2007, 2008; Hatch et al., 2011). Despite the well-recognized presence of organosulfates in SOA, their formation and transformation processes can be complex and varied, depending on the nature of the original organic compound involved. Extensive studies on their formation have been performed and several mechanisms based on a variety of reactions have been proposed. Using nuclear resonance techniques, isoprene-derived epoxides formed during isoprene photooxidation reactions were found to be important intermediates for organonitrates and organosulfate formation via potential SOA reactions (Darer et al., 2011; Hu et al., 2011). The authors further found that organonitrates could easily be transformed to organosulfates during hydrolysis in the presence of sulfate. Some studies also showed that 2-methyl-3-buten-2-ol (MBO), due to its emissions that are larger than isoprene in some regions (Baker et al., 1999), is an important precursor for organosulfates and SOA in the atmosphere through its reactions with OH under NO and aerosol acidity conditions and from acid-catalysed reactive uptake of MBO-based epoxides formed during MBO photooxidation (Mael et al., 2015; Zhang et al., 2012, 2014). Organosulfate formation was also found from oxidation of hydroxycycroperoxides (Riva et al., 2016) and from heterogeneous reactions of SO₂ with selected long-chain alkenes and unsaturated fatty acids (Passananti et al., 2016).

Reactions with sulfates or H₂SO₄ were the main formation processes of organosulfates. Qualitative analyses of organosulfates in SOA have been gaining more attention and development in recent years (Lin et al., 2012; Shalamzari et al., 2013; Staudt et al., 2014). Riva et al. (2015) investigated the formation of organosulfates from photooxidation of polycyclic aromatic hydrocarbons and found that, in the presence of sulfate aerosol, this photooxidation was a hitherto unrecognized source of anthropogenic secondary organosulfur compounds (Riva et al., 2015). A more complete structural characterization of polar organosulfates that originate from isoprene SOA was performed (Shalamzari et al., 2013), and an organosulfate related to methyl vinyl ketone and minor polar organosulfates related to croton aldehyde were identified. However, there have been no reports on the yield and chemical composition of SOA obtained from photooxidation of cyclohexene in the presence of SO₂.

In the present work, we investigated the yields and chemical composition of SOA during cyclohexene photooxidation under different SO₂ concentrations conditions. A better understanding of the magnitude and chemical composition of SOA from different SO₂ concentrations will contribute to a more accurate SOA prediction from anthropogenic sources and provide valuable information related to air pollution in urban environments.
2 Methods

2.1 Chamber description

The experiments were performed in a 400 L Teflon FEP film chamber (wall thickness 125 µm) at the Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing. The details of the chamber, including the experimental set-up and analysis techniques, have been described elsewhere (Du et al., 2007; Jia and Xu, 2014), and only a brief description is presented here. The reactor was surrounded by 12 black light lamps (GE F40BLB) with emission bands centred at 365 nm, which were used to simulate the spectrum of the UV band in solar irradiation. Stainless steel covered the chamber interior walls to maximize and homogenize the interior light intensity. The effective light intensity near the ultraviolet region plays a decisive role in the formation of photochemical smog (Presto et al., 2005b). The effective light intensity of the chamber was represented by the photolysis rate constant of NO2. In our study, the average effective light intensity was determined to be 0.177 min−1. Both the inlet and outlet of the chamber were made of Teflon material. Atmospheric pressure was maintained in the chamber at all times. All experiments were performed at room temperature (307 ± 2 K) under dry conditions (RH < 10 %). The wall loss is the decrease of the concentration of reactive gas-phase species caused by adsorption on the inner wall of the reactor. Possible reaction of residual reactants and products on the inner wall with gas-phase species is another major reason for wall loss. The wall loss can directly affect the quantitative evaluation of the photooxidation rate and SOA yield. A correct estimation of the wall loss is therefore necessary for a reliable analysis of the experimental results of the SOA yield. In the present study, the wall loss of cyclohexene in the chamber could be neglected, since no decrease in its concentration was observed. The wall losses of O3, NOx, and SO2 were of the first order, because ln([X]0/[X]t) had a good correlation with time (R² = 0.994, 0.944, 0.999 for O3, NOx, and SO2, respectively). The measured wall loss rate constants for O3, NOx, and SO2 were 5.05 × 10−6, 7.04 × 10−6, and 6.39 × 10−6 s−1, respectively. The average value of the wall loss rate constant of particles was 4.7 × 10−5 s−1, and the measured particle concentrations in this study were corrected using the same method as in Pathak et al. (2007). Typical profiles of the gas and particle phases are given in Fig. S1.

Prior to each experiment, the chamber was cleaned by being purged with purified dry air for at least 8 h until residual hydrocarbons, O3, NOx or particles could not be detected in the reactor. Known amounts of cyclohexene were injected into a 0.635 cm diameter Teflon FEP tube and dispensed into the chamber by purified dry air. Typical initial cyclohexene concentrations were 500 ppb. NOx was injected with a gastight syringe, so that the mixing ratio of NOx in the reactor would be around 95 ppb in all experiments. The mixed concentration ratios of cyclohexene / NOx were in the range 4.4–6.9. SOA formation experiments were carried out under UV irradiation in the presence of NOx to produce O3 and OH radicals for cyclohexene oxidation. Although initial VOCs, NOx, and average OH concentrations were different from typical urban conditions, efforts were made to maintain initial concentrations of the reactants that were as similar as possible to make sure the effect of SO2 was the main reason for changes in the SOA yield. More details on the experimental conditions are shown in Table 1.

2.2 Gas and particle measurements

Ozone concentration in the reactor was measured using an ozone analyser (model 49C, Thermo Electron Corporation, USA). A NO-NO2-NOx analyser (model 42C, Thermo Electron Corporation, USA) was used to monitor the NOx concentration. The measurement of SO2 concentration was taken using a SO2 analyser (model 43i-TLE, Thermo Electron Corporation, USA). The uncertainty of the O3, NOx, and SO2 measurements was less than ±1 %. The detection limits of the different monitors were 0.40, 0.50, and 0.05 ppb for NOx, O3, and SO2, respectively.

Two Tenax absorption tubes (150 mm length × 6 mm O.D., 0.2 g sorbent) were used to collect the sample before the UV lights were turned on and at the end of each experiment. The volume of the sample was 60 mL and the sampling time was 3 min. The concentrations of cyclohexene were analysed by thermal desorption – gas chromatography – mass spectrometry (TD–GC–MS). A thermal desorption unit (Master TD. Dani, Italy) was combined with a 6890A gas chromatograph (6890A, Agilent Tech., USA) interfaced to a 5975C mass selective detector (5975C, Agilent Tech., USA). The GC was equipped with a HP-5MS capillary column (30 m × 0.25 mm. 0.25 µm film thickness). The TD temperature was 280°C, and the sampling time was 3 min. The GC–MS temperature programme was as follows: the initial temperature of 40°C was held for 4 min, and then raised to 300°C at a rate of 20°C min−1. The inlet temperature was set at 250°C and the transfer line at 200°C. The ionization method in MS was electron impact ionization, and helium was used as the carrier gas at a constant flow (1.2 mL min−1). Because a very diverse range of compounds might be present in the samples, the SCAN mode (36–500 amu) was used in the MS detector. This mode is known to be a classical and typical detection method for GC–MS analysis. The results were analysed with MSD Productivity ChemStation.

Particle number concentrations and size distributions were measured with a scanning mobility particle sizer (SMPS), which consists of a differential mobility analyser (DMA model 3081, TSI Inc., USA) and a condensation particle counter (CPC model 3776, TSI Inc., USA). A sheath flow – aerosol flow relationship of 3.0/0.3 L min−1 was used for the measurements. The particle size was measured in the range of 14 to 710 nm, and each scan was 180 s. An aerosol density of 1.2 g cm−3 was assumed to convert the particle vol-
Table 1. Experimental conditions for the photooxidation of a cyclohexene / NOx / SO2 system. All experiments were performed under dry conditions (relative humidity < 10 %).

<table>
<thead>
<tr>
<th>Exp.</th>
<th>T (K)</th>
<th>SO2 (ppb)</th>
<th>cyclohexene (ppb)</th>
<th>NOx (ppb)</th>
<th>cyclohexene/NOx</th>
<th>ΔM0 (µg m⁻³)</th>
<th>Y (%)</th>
</tr>
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<tr>
<td>1b</td>
<td>308</td>
<td>0.0</td>
<td>596</td>
<td>122.0</td>
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<tr>
<td>2b</td>
<td>305</td>
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<td>651</td>
<td>93.7</td>
<td>6.9</td>
<td>79.7</td>
<td>3.40</td>
</tr>
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<td>3b</td>
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<td>2.4</td>
<td>553</td>
<td>95.7</td>
<td>5.8</td>
<td>62.6</td>
<td>3.15</td>
</tr>
<tr>
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<td>307</td>
<td>5.8</td>
<td>612</td>
<td>92.7</td>
<td>6.6</td>
<td>41.0</td>
<td>1.87</td>
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<td>5a</td>
<td>309</td>
<td>9.3</td>
<td>599</td>
<td>93.5</td>
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<td>48.1</td>
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<td>96.3</td>
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<td>472</td>
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<td>5.2</td>
<td>22.6</td>
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<td>10a</td>
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<td>44.3</td>
<td>592</td>
<td>98.6</td>
<td>6.0</td>
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<tr>
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<td>497</td>
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<td>4.4</td>
<td>77.3</td>
<td>2.16</td>
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<td>577</td>
<td>96.7</td>
<td>6.0</td>
<td>44.3</td>
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<td>49.2</td>
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<td>1048</td>
<td>198.0</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>18b,c</td>
<td>306</td>
<td>93.7</td>
<td>1235</td>
<td>215</td>
<td>5.7</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

a The experiment was initiated by NO.
 b The experiment was initiated by NO2.
 c The formed particles were detected by Exactive Plus Orbitrap MS.

volume concentration into the mass concentration (Zhang et al., 2015). Size distribution data were recorded and analysed using the TSI AIM software v9.0.

2.3 SOA composition analysis

The chemical composition of SOA was important for analysing the degree of cyclohexene oxidation, and it was used to evaluate the transformation from gas phase to particle phase. Particle-phase chemical composition was studied by means of Fourier transform infrared (FTIR) spectroscopy (Nicolet iS10, Thermos Fisher, USA). Aerosols were sampled through a Dekati low-pressure impactor (DLPI, DeKati Ltd, Finland). The impactor was connected to a pump working at a flow rate of 10 L min⁻¹ while sampling a total volume of 300 L of gas for each experimental run. Aerosols, from 108 to 650 nm in diameter, were collected on an ungreased zinc selenide (ZnSe) disk (25 mm in diameter) for FTIR measurements.

The characteristic bands of inorganic and organic sulfates overlapped in the IR spectrum. In order to distinguish between these inorganic and organic sulfates, an ion chromatograph (IC, Dionex ICS-900, Thermo Fisher, USA) was used to analyse the inorganic sulfate anion (SO₄²⁻) in SOA. The limit of detection for the IC analysis was 0.005 µg mL⁻¹. SOA collected on ZnSe disks was firstly dissolved in high purity water (7 mL) and then measured by IC for SO₄²⁻ concentrations. Anions were analysed with a Dionex IonPac AS14A analytical column and a Dionex anion self-regenerating suppressor (ASRS) was used as eluent. The flow rate was 1.0 mL min⁻¹ with a mixture of 8.0 mmol L⁻¹ Na₂CO₃ and 1.0 mmol L⁻¹ NaHCO₃ for anions analyses. The suppressing current was 50 mA.

Chemical characterization of aerosols from photooxidation of cyclohexene was performed using an Exactive Plus Orbitrap mass spectrometer equipped with electrospray interface (ESI) (Thermo Fisher Scientific, USA) operated in negative (⁻) ion mode, which was calibrated using the manufacturer’s calibration standards mixture, allowing for mass accuracies < 5 ppm in external calibration mode. The capillary voltage was set to 3 kV. The desolvation gas flow was 200 µL min⁻¹, and the desolvation gas temperature was 320 °C. SOA was collected on the aluminium foil using the same method as FTIR analysis and then extracted with 1 mL of acetonitrile. The aluminium foil was used due to its ease of use and its non-reactivity with the sample. A total volume of 300 L was sampled at a flow rate of 10 L min⁻¹. A volume of 5 µL of the extraction and a direct injection were used for the measurement. Xcalibur 2.2 software (Thermo Fisher, USA) was used for the calculation of chemical formulae from accurate measurement of m/z values.

2.4 Chemicals

The chemicals used and their stated purities were as follows: cyclohexene (99 %) was obtained from Aldrich and used...
3 Results and discussion

3.1 Effect of SO\textsubscript{2} on SOA number concentrations

The particle number concentrations at the maximum SOA yield for the cyclohexene / NO\textsubscript{x} / SO\textsubscript{2} system with different initial SO\textsubscript{2} concentrations are shown in Fig. 1, while the cooperation of the maximum number concentration and the particle number concentrations at the maximum SOA yield are shown in Fig. S2. After the black light lamps were turned on, the SO\textsubscript{2} number concentrations increased rapidly to reach the maximum within 0.5 h in each experiment. Subsequently, the particle number concentrations gradually decreased, accompanied by the growth in particle size by coagulation. The SOA mass concentration kept increasing until its maximum was reached (after ~ 2h). Both types of particle number concentration had similar trends against initial SO\textsubscript{2} concentrations. In general, maximum particle number concentrations were three times higher than the particle number concentrations at the maximum SOA yield. In the remainder of this paper, in order to better elaborate the effect of SO\textsubscript{2} on the formation of particles, the particle number concentration refers to the particle number concentrations at the maximum SOA yield.

The particle number concentration increased with initial SO\textsubscript{2} concentration, and this increase could be divided into two stages: increasing stage and stable stage. In the increasing stage, with the initial SO\textsubscript{2} concentration increasing from 0 to 30 ppb, the particle number concentration grew significantly under low initial SO\textsubscript{2} concentration (< 5 ppb), then the growth rate reduced gradually. In the stable stage, when the SO\textsubscript{2} concentrations were varied systematically between 30 and 105 ppb, particle number concentrations were practically maintained at a steady level, and there was no further obvious growth as shown in Fig. 1. For experiments with high initial SO\textsubscript{2} concentrations, the particle number concentrations were 10 times higher than those without SO\textsubscript{2}, indicating enhanced new particle formation (NPF) when adding SO\textsubscript{2}. It is evident from Fig. 1 that even small amounts of SO\textsubscript{2} affect the new particle formation substantially, as observed in previous studies (Chu et al., 2016; Liu et al., 2016).

Figure 1. Particle number concentrations of SOA in the photooxidation of the cyclohexene / NO\textsubscript{x} / SO\textsubscript{2} system with different initial SO\textsubscript{2} concentrations.
condensation onto existing aerosol particles was favoured compared to the formation of new particles, and this condensation would be the main contribution to the increase in SOA mass.

3.2 Effect of SO$_2$ on SOA yields

SOA yield ($Y$) is defined as $Y = \Delta M_0 / \DeltaHC$, where $\Delta M_0$ is the produced organic aerosol mass concentration (µg m$^{-3}$), and $\DeltaHC$ is the mass concentration of reacted cyclohexene (µg m$^{-3}$). The SOA yields of cyclohexene at different SO$_2$ concentration as determined by SMPS are shown in Fig. 2. The numerical values of the aerosol mass concentration and SOA yields at different conditions are shown in Table 1.

The SOA yields in the absence of SO$_2$ were in the range of 2.7–3.4 %, which were an order of magnitude lower than those reported in previous studies (Warren et al., 2009; Keywood et al., 2004b; Kalberer et al., 2000). There are three possible explanations for this phenomenon. (1) SOA formation is closely related to the oxidation capacity in the photooxidation experiments and, therefore, is affected by the ratio of $[\text{VOC}]_0 / [\text{NO}_x]_0$ (Pandis et al., 1991). Experiments performed with different SO$_2$ concentrations indicate that the SOA formation is partly controlled by the ability of the system to oxidize cyclohexene and contribute to the particle mass. As indicated in Fig. S3, even at 0 ppb of SO$_2$, the mass concentration of SOA quickly reaches its maximum. Experiments with higher NO$_x$ levels have been proved to obtain considerably lower SOA yields than those with lower NO$_x$ levels at the same VOC concentration (Song et al., 2005). Reactions of organoperoxy radicals (RO$_2$) with NO and NO$_2$ instead of peroxy radicals (RO$_2$ or HO$_2$) under high NO$_x$ conditions resulted in the formation of volatile organic products and a decreased SOA yield (Lane et al., 2008). It was reported that SOA yield was constant for $[\text{VOC}]_0 / [\text{NO}_x]_0 > 15$ but decreased considerably (by a factor of more than 4) as $[\text{VOC}]_0 / [\text{NO}_x]_0$ decreased (Presto et al., 2005a). In this study, the $[\text{VOC}]_0 / [\text{NO}_x]_0$ ratio was maintained at about 4.4 to 6.9. Recently, the NO$_x$ dependence of SOA formation from photooxidation of β-pinene was comprehensively investigated (Sarrafzadeh et al., 2016), and it was shown that the NO$_x$-induced OH concentration was the greatest factor influencing the SOA yield. The impacts of NO$_x$ on SOA formation were only moderate if the impact of NO$_x$ on OH concentration was eliminated. The OH concentration in our study was relatively insufficient, which was the main limiting factor for SOA formation. (2) UV light is another factor influencing the SOA yield. SOA yields between dark and UV-illuminated conditions were reported to be different (Presto et al., 2005b). Exposure to UV light could reduce SOA yield by 20–40 %, while more volatile products were formed (Griffin et al., 1999). (3) The temperature may have a pronounced influence on SOA yield (Qi et al., 2010; Emanuelsson et al., 2013). At low temperatures, semi-volatile organic compounds would favour the condensation of gas-phase species and a higher SOA yield could be expected. Raising the chamber temperature by 10 K should cause a decrease of 10 % in aerosol yield (Pathak et al., 2007). SOA yields reported in the present study were obtained at a higher temperature (307 ± 2 K) than 298 K used in most previous studies. On the basis of the discussion above, the SOA yield from cyclohexene in this study was lower than observed in the previous studies.

SOA yields for the cyclohexene / NO$_x$ / SO$_2$ system were measured for initial SO$_2$ mixing ratios of 0–105 ppb. Due to the error associated with the SO$_2$ concentrations measurement, with stronger impact on low values than on higher values, several experiments were performed at SO$_2$ concentrations below 40 ppb. The experimental results showed a clear decrease at first and then an increase in the SOA yield with increasing SO$_2$ concentrations (Fig. 2). When SO$_2$ concentrations increased from 0 to 40.8 ppb, there was a remarkable decrease in SOA yield, dropping by about half with the increase in SO$_2$ concentration. For SO$_2$ concentrations higher than 40.8 ppb, the SOA yield increased with increasing SO$_2$ concentration. The highest SOA yield was found to be 3.5 %, and was at 104.7 ppb SO$_2$ concentration. The lowest SOA yield of cyclohexene photooxidation was obtained at an initial SO$_2$ concentration of 40 ppb. Although the SOA yield increased gradually with the initial SO$_2$ concentration at concentrations higher than 40 ppb, a higher SOA yield than that in the absence of SO$_2$ could not be obtained when the initial SO$_2$ concentration was lower than 85 ppb.

Both NO and NO$_2$ were used as NO$_x$ for repeated experiments in the current study. Although the photooxidation reaction could not happen in the case of NO until it was oxidized to NO$_2$, which means that both NO- and NO$_2$-initiated
photooxidation reactions were actually triggered by NO₂, the chemistry of SOA formation from both processes is similar. Despite the time of occurrence of the maximum SOA concentration for the experiment with NO₂ being half an hour earlier than that for the experiment with NO, the results of the SOA yield were similar.

In the presence of SO₃, enhanced SOA formation could be attributed to acid-catalysed heterogeneous reactions (Jang et al., 2002; Xu et al., 2014). When studying the effect on acidic seed of the growth of isoprene- and α-pinene-based SOA, it was shown that FTIR peaks at 1180 cm⁻¹ (C-O-C stretch of hemiacetals and acetalts) and 1050 cm⁻¹ (C-O asymmetric stretch of alcohols) are indicators of acid-catalysed heterogeneous reactions, since these peaks could not otherwise be observed in non-acidic conditions (Jang et al., 2002; Czoschke et al., 2003). These peaks are prominent in IR spectra from SOA formation in an acidic particle environment. In the current study, similar peaks were observed at 1195 and 1040 cm⁻¹ (see Fig. S4). Their intensities were very weak when initial SO₂ concentrations were lower than 44 ppb, indicating that acid-catalysed reactions were not facilitated at these conditions.

However, there were some undiscovered processes that could inhibit the formation of SOA in the cyclohexene/NOₓ/SO₂ system. The competitive reaction between SO₂ and cyclohexene might be among the reasons for the decrease in the SOA yield. For example, SO₂ could be oxidized by OH to form H₂SO₄ (Somnitz, 2004). Due to the presence of O₃ in our system, the formation of Criegee intermediates (CIs) and their reactions with SO₂ could equally be expected (Criegee, 1975). The rate constants of O₃ + cyclohexene and OH + cyclohexene reactions were determined to be 7.44 × 10⁻¹⁷ and 6.09 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹, corresponding to 5.5 and 2.5 h lifetimes for cyclohexene (Treacy et al., 1997; Rogers, 1989). Hence, it is likely that the cyclohexene reaction with O₃ would be less important than the reaction with OH in this study. However, the importance of SO₂ reactions with stabilized CIs could be limited due to the kinetics and low yield of the latter (Stewart et al., 2013; Keywood et al., 2004a; Hatakeyama et al., 1984). As mentioned above, the photooxidation in this study was at high-NOₓ conditions and the OH was the main limiting factor for SOA formation because of its relatively low concentration. The change of cyclohexene concentration with time at different initial SO₂ concentrations is shown in Fig. S5. It is seen that in the first half hour, the amount of cyclohexene consumed is almost similar for different SO₂ concentrations. Regarding the difference between initial cyclohexene concentrations, the similar amount of reacted cyclohexene in the first half hour indicates that low and high OH concentrations were used at high and low SO₂ conditions, respectively. The consuming rate of cyclohexene was slightly higher without SO₂ in the chamber, which means that if there was a competition reaction, its effect was very limited. Under a lower OH concentration condition, caused by the reaction between SO₂ and OH, the formation of SOA was inhibited.

The rate constant for the OH + SO₂ reaction was estimated to be 2.01 × 10⁻¹² cm³ molecule⁻¹ s⁻¹, corresponding to a SO₂ lifetime of 69 h (Atkinson et al., 1997). This reaction is much slower than the cyclohexene + OH reaction, suggesting that OH + SO₂ reaction has very little impact on the OH concentration in the system. In our experiment, the decrease in the SOA yield with SO₂ addition might then not be attributed to its reaction with OH. It is also possible that the SO₂ addition could change the chemistry of the photooxidation process and suppress the oxygenation of products (Friedman et al., 2016; Liu et al., 2015). Comparing the MS results at different initial SO₂ concentrations, the proportion of low molecular weight components increases with increasing SO₂ concentration. Molecular weights have negative correlation with volatility, which could also make the SOA yield to decrease. Moreover, in real atmospheric situations where O₃ is found in much higher proportions than OH, cyclohexene would mainly react with O₃ to produce Criegee intermediates, which are good SO₂ oxidizers, and significantly less SOA than in the chamber would be formed. Accordingly, SOA yield showed a descending trend with an increase in SO₂ concentrations when they are below 40 ppb.

When the initial SO₂ concentration was greater than 40 ppb, the acid-catalysed heterogeneous formation of SOA became more significant (Fig. 2). The same SOA yield was obtained in the absence of SO₂ and at 85 ppb initial SO₂ concentration. The competitive reaction plays an important role in SOA formation, and it should be taken into account in SOA simulation models or air quality models for more accurate predictions. Acid-catalysed reactions gradually became important as the initial SO₂ concentration for SOA yield increased. The formation of low-volatile organics (e.g. organosulfates) by photooxidation in the presence of SO₂ might be another reason for the increase in the SOA yield.
Figure 4. IR spectra of aerosols from the cyclohexene / NOx / SO2 system under different SO2 concentrations.

3.3 Organosulfate formation

When SO2 was added to the chamber, acidic aerosol particles were formed by photooxidation of SO2 in a reaction initiated by OH. The amount of SO42− in particle phase and the consumption of SO2 (ΔSO2) with varying initial SO2 concentrations are shown in Fig. 3. The changes with initial SO2 concentrations were not uniform between the SO42− concentration and ΔSO2, which indicates that besides SO42−, other products were formed from the reaction of SO2. Typical IR spectra of aerosols from the cyclohexene / NOx / SO2 system under different SO2 concentrations are presented in Fig. 4. Based on the peak positions in the IR spectra, different functional groups were assigned. The broadband at 3100 to 3300 cm\(^{-1}\) is assigned to the O–H stretching of hydroxyl and carboxyl groups (Coury and Dillner, 2008), while the peak at 1717 cm\(^{-1}\) represents the C=O stretching of aldehydes, ketones, and carboxylic acids. The peaks at 1622 and 1278 cm\(^{-1}\) show good correlation and both are assigned to the -ONO2 stretching (Liu et al., 2012; Jia and Xu, 2014). The characteristic absorption band at 1500–1350 cm\(^{-1}\) is the C–O stretching and O–H bending of the COOH group (Ofner et al., 2011), and the absorption peak of sulfate exists in the range of 1200–1000 cm\(^{-1}\) (Wu et al., 2013). The band at 1100 cm\(^{-1}\) in the IR spectra can be attributed to the sulfate group in organic compounds and sulfate. It has been confirmed that the S=O absorption band in organic sulfate monoesters appears around 1040–1070 cm\(^{-1}\) (Chihara, 1958). Although, more studies on band assignments in organosulfates are not currently available from the literature for further comparison, the 1100 cm\(^{-1}\) band from the current FTIR study can reasonably be assigned to S=O in the sulfate group.

The intensities of most absorption bands, such as O–H at 3100–3300 cm\(^{-1}\), C=O at 1717 cm\(^{-1}\), -ONO2 at 1622 and 1278 cm\(^{-1}\), and C-H at 2930 cm\(^{-1}\), have similar trends with the change of SOA yield for initial SO2 concentrations between 11 and 105 ppb. However, the band of sulfate at 1100 cm\(^{-1}\) in IR spectra increases with the rise of initial SO2 concentration rather than the SOA yield, which suggests the formation of a sulfate group in organic compounds and a sulfate product from SO2 photooxidation, since only the relative difference in the intensities of FTIR peaks were studied here. The relative intensity of the band at 1100 cm\(^{-1}\) increased 1.8 times when the initial SO2 concentration rose from 0 to 44 ppb, and increased 7.2 times when the initial SO2 concentration was 105 ppb. This intensity band grew slowly at low SO2 concentrations due to the decrease in the formation of aerosols. To clearly show the number of sulfate groups and amount of sulfate in aerosols, the intensity of the band at 1100 cm\(^{-1}\) and the amount of SO42− were compared in the same aerosol mass, as shown in Fig. 5. The relative intensity was set to 1 when the initial SO2 concentration was 44.3 ppb.

The relative intensities of the band at 1100 cm\(^{-1}\), which represented the intensity of both SO42− and the sulfate group in organic compounds, increased approximately in a linear form with the increase in initial SO2 concentration \((R^2 = 0.91)\). If the 1100 cm\(^{-1}\) band originated solely from SO42−, the change of the band intensity would be consistent with SO42− concentration in unit mass of aerosols. Figure 5 shows the inconsistency between the trends of FTIR band at 1100 cm\(^{-1}\) and the amount SO42− as the initial SO2 concentration increases, which implies that the 1100 cm\(^{-1}\) band originated not only from SO42− but also from other organosulfur compounds. These include organosulfates, which also have the S=O bond, and might therefore contribute to the 1100 cm\(^{-1}\) band in the FTIR spectrum. The difference between the trends of FTIR band at 1100 cm\(^{-1}\) and the amount of SO42− with increasing initial SO2 concentration can be attributed to the formation of organosulfates.
The composition of cyclohexene SOA was examined with Exactive Plus Orbitrap MS using negative ion mode ESI and the mass spectrum was recorded at a resolution of $10^5$ (Fig. 6). The OH addition to the $\text{C}=$C bond produces an alkyl peroxy ($\text{RO}_2^-$) radical that can react with NO to yield organonitrates (Perring et al., 2013). Although the formation of organonitrates was highly expected, there was no evidence of the presence of N-containing compounds from the main peaks of Fig. 6, indicating that organonitrates would be formed at very low concentrations, if at all. A similar conclusion could be observed from Fig. 4, in which the -ONO$_2^-$ stretching peaks at 1622 and 1230 cm$^{-1}$ have very low intensities. The presumed low concentrations of organonitrates might be due to the low concentration of NO when SOA was formed. RO$_2$ radicals also react with NO$_2$ to form peroxy nitrates (RO$_2$NO$_2$) on timescales comparable to RONO$_2$ formation. However, RO$_2$NO$_2$ are thermally labile and rapidly dissociate at ambient temperatures (Perring et al., 2013). Organosulfates were identified in the particle phase from the chamber experiments. Accurate mass fittings for measured ions of organosulfates in ESI negative ion mode are given in Table 2. As shown in Fig. 6 and Table 2, 10 different organosulfates were successfully detected and identified from cyclohexene SOA. These results not only first prove the formation of organosulfates from cyclohexene photooxidation at high-NO$_2$ condition in the presence of SO$_2$ but also provide evidence and reference for organosulfates identification by FTIR-IC joint technique. A deprotonated molecular ion at $m/z = 195.03322$ ($C_6H_{11}O_5S^-$) had the highest content (more than 60%) of all the organosulfates detected in this study. Its intensity was 6.5 times higher than that of the second-highest abundant organosulfate. The intermediate product of cyclohexene + OH reaction, i.e. CH(O)CH$_2$CH$_2$CH$_2$CH$_2$CHOH, has a hydroxyl group, and the organosulfate product ($m/z = 195.03322$) would likely form from the intermediate product, not from the end product. This organosulfate, together with organosulfates with $m/z = 179.00181$ and 209.01257 measured in this study were also measured in the Arctic sites but with unknown sources (Hansen et al., 2014). This study further supports the formation of organosulfates from cyclohexene in the atmosphere.

Table 2. Accurate mass fittings for main products and measured organosulfates ions in ESI negative ion mode from cyclohexene photooxidation in the presence of SO$_2$ under high-NO$_2$ conditions.

<table>
<thead>
<tr>
<th>Measured$^a$</th>
<th>Ion</th>
<th>Proposed ion formula</th>
<th>Delta$^b$ (ppm)</th>
<th>RDB$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$115.03942$</td>
<td>(M$^-$H)$^-$</td>
<td>C$<em>8$H$</em>{13}O_3^-$</td>
<td>$-5.628$</td>
<td>$2$</td>
</tr>
<tr>
<td>$145.05019$</td>
<td>C$_6$H$_7$O$_4^-$</td>
<td>$-3.048$</td>
<td>$2$</td>
<td></td>
</tr>
<tr>
<td>$131.03444$</td>
<td>C$_6$H$_7$O$_4^-$</td>
<td>$-4.136$</td>
<td>$2$</td>
<td></td>
</tr>
<tr>
<td>$101.06006$</td>
<td>C$_6$H$_7$O$_4^-$</td>
<td>$-7.351$</td>
<td>$1$</td>
<td></td>
</tr>
<tr>
<td>$87.04433$</td>
<td>C$_4$H$_4$O$_2^-$</td>
<td>$-9.453$</td>
<td>$1$</td>
<td></td>
</tr>
<tr>
<td>$129.05515$</td>
<td>C$_6$H$_7$O$_4^-$</td>
<td>$-4.397$</td>
<td>$2$</td>
<td></td>
</tr>
<tr>
<td>$99.04439$</td>
<td>C$_5$H$_5$O$_2^-$</td>
<td>$-7.702$</td>
<td>$2$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Sort by abundance intensity. $^b$Delta: label the peak with the difference between the theoretical and measured $m/z$. $^c$RDB: ring and double-bond equivalent.
The mass spectra show a great abundance of peaks, detected as deprotonated molecular ions (M−H)^− and formed via proton abstraction. Most cyclohexene SOA contained carboxylic acid and/or aldehyde moieties. The products of the reaction of OH radicals with cyclohexene in the presence of NO were investigated and were identified as cyclic 1,2-hydroxynitrates and 1,6-hexanediol (Aschmann et al., 2012). These products could not be detected by Exactive Plus Orbitrap MS in our study. Aldehydes could be oxidized by OH radicals to form carboxylics, which have been intensively identified in previous studies (Cameron et al., 2002; Goldsmith et al., 2012). 1,6-hexanediol might be further oxidized in the atmospheric photooxidation reactions to form 1,6-adipic acid (C_6H_{10}O_4) and 6-oxohexanoic acid (C_6H_{10}O_3), which were both observed in this study. In addition to the C_6 compounds observed in this study, a C_5H_7O_3 ion was detected with higher abundance than the C_6 compounds. Although the formation of C_5H_7O_3 might be due to a carbonyl cleavage from a six-carbon atoms chain, a proper mechanism for its formation could not be determined. A C_4 compound was also detected likely as a result of a carbonyl cleavage from a C_5 compound. However, there was no evidence of the formation of compounds with less than four carbon atoms.

The Exactive Plus Orbitrap MS spectra of species formed from different initial SO_2 concentrations are shown in Fig. S6. We found no obvious difference in the composition and response of organosulfates with different initial SO_2 concentrations. The relative intensity of the peak at m/z = 97, which corresponds to sulfate, was set to 100% in both Exactive Plus Orbitrap MS spectra. The relative intensities of organosulfate peaks in both spectra were almost unchanged regardless of the initial SO_2 concentration. However, Minerath and Elrod (2009) and Hatch et al. (2011) observed an increase in organosulfate yields with increasing sulfate concentration, and sulfate can be regarded as a key parameter, which influences the formation of organosulfates (Minerath and Elrod, 2009; Hatch et al., 2011). Since sulfate is formed as a result of SO_2 oxidation in the current study, quantification of organosulfates formed from cyclohexene photooxidation will be investigated in further studies in order to examine the effect of increasing SO_2 concentration on organosulfate formation. Comparing Exactive Plus Orbitrap MS data when SO_2 initial concentrations were 0 ppb and 236 ppb reveals that the bands representing organosulfates do not appear at 0 ppb of SO_2. Peaks at m/z larger than 150 were undetectable at initial SO_2 concentration of 0 ppb, while products without sulfur peaked at both concentrations, with the only difference being their relative intensities. This implies that the process of SOA formation strongly depends on initial SO_2 concentrations.

4 Conclusion

We report a series of laboratory chamber studies on the formation of SOA from the mixture of cyclohexene and SO_2. The experiments were based on Fourier transform infrared spectroscopy, ion chromatography, and electrospray ionization high-resolution quadrupole mass spectrometry, and were performed under NO_x conditions. Although new particle formation was found to be enhanced with increasing SO_2 concentration, the yield of SOA was not enhanced for all SO_2 concentrations between 0 and 105 ppb. SOA formation decreased at first and then was enhanced for all SO_2 concentrations above 40 ppb. Both acid-catalysis and competitive OH reactions with cyclohexene and SO_2 were found to have important effects on the SOA formation and hence should be taken into account in SOA simulation models or air quality models for a better understanding of haze pollution. The formation of organosulfates, an important part of atmospheric organic aerosol components, was first observed from cyclohexene SOA. However, quantification of these organosulfates and precursors to their formation should be determined in further studies. The formation of organosulfates has a great significance for the particulate matter formation under high SO_2 concentrations in the atmosphere.

Data availability. Data are available by contacting the corresponding author.

The Supplement related to this article is available online at https://doi.org/10.5194/acp-17-13329-2017-supplement.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgements. This work was supported by the National Natural Science Foundation of China (91644214, 21577080, 41375129), Shenzhen Science and Technology Research and Development Funds, China (JCYJ20150402105524052), and the Strategic Priority Research Programme (B) of the Chinese Academy of Sciences (XDB05010104).

Edited by: Jason Surratt
Reviewed by: four anonymous referees
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