Atmospheric
Chemistry
and Physics
Discussions

Photooxidation of cyclohexene in the presence of SO_2: SOA yield and chemical composition

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Abstract. Secondary organic aerosol (SOA) formation from cyclohexene/NOx system with various SO_2 concentrations under UV light was studied to understand the effects of cyclic alkenes on the atmospheric environment in polluted urban areas. A clear decrease at first and then increase of the SOA yield was found with increasing SO_2 concentrations. The lowest SOA yield was obtained when 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. SOA formation was enhanced by the acid-catalyzed heterogeneous reactions, which lead to an increase in the total organic aerosol mass. The competitive reaction of OH radicals with SO_2 and VOCs was the reason for the SOA yield decrease even under acidic conditions. The competitive reaction was an important factor for SOA yield and it should not be neglected in photooxidation, especially when acid-catalyzed mechanism could not significantly improve SOA yield. The composition of organic compounds in SOA was measured using several complementary techniques including Fourier transform infrared (FTIR) spectrometer, ion chromatograph (IC) and electrospray ionization high-resolution quadrupole mass spectrometer (ESI-HR-MS). We present the first 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 (Zielinska et al., 1996), and their gas-phase oxidation reactions with OH, NO_3, or O_3 are among the most important processes in the atmosphere (Atkinson, 1997). The reactions of ozone with alkenes are an important source of free radicals in the lower atmosphere, which influences the oxidative capacity of the atmosphere (Paulson and Orlando, 1996). Some of the products have sufficiently low vapor pressures 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; Jimenez et al., 2016). SOA formation from VOCs oxidation has been receiving significant attention due to its large implication in the formation of atmospheric fine particulate matter. SOA has significant impacts on

Atmospheric
Chemistry
and Physics
Discussions
Open Access

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 received less attention than those of linear or branched alkenes (Sipilä et al., 2013). Cyclohexene is an important industrial chemical (Sun et al., 2013), and is also

5 widespread in urban areas (Grosjean et al., 1978). Cyclohexene has been extensively studied as a monoterpene surrogate for inferring oxidation mechanisms and aerosol formation characteristics, because it shows the basic structural unit in abundant biogenic monoterpenes and sesquiterpenes (Carlsson et al., 2012; Keywood et al., 2004). The rate constants for gas-phase reactions of cyclohexene with OH, O_3 and NO_3 were measured at room temperature to be $(6.4\pm0.1)\times10^{-11}$, $(8.1\pm1.8)\times10^{-17}$ and $(5.4\pm0.2)\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, respectively (Stewart et al., 2013; Aschmann et al., 2012). A correlation between the

10 logarithm of the rate constants and the molecular orbital energies for simple cyclic alkenes was observed. The effect of the pressure and that of the presence of SO_2 on the formation of stable gas-phase products and SOA from 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 (H_2SO_4) 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

15 compounds (Keywood et al., 2004). 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.

SO_2, one of the most important inorganic pollutants in urban area, plays an important role on SOA formation (Wang et al., 2005; Lonsdale et al., 2012; Liu et al., 2016). Seasonal variations of SO_2 concentrations were found to be consistent with

20 seasonal variations of $PM_{2.5}$ concentration (Cheng et al., 2015). Smog chamber simulations have indicated that SO_2 could enhance the formation of SOA from VOCs oxidation 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 SO_2 emissions can impact new particle formation, and SOA composition (Lonsdale et al., 2012).

Despite the existence of organosulfates in ambient aerosols was first observed in 2005 (Romero and Oehme, 2005), proper

25 identification of these aerosols was made two years later. In a series of chamber experiments studies, it was shown that organosulfates present in ambient aerosols collected from various locations mostly originate from acid-catalyzed reactions of SOA formed from photooxidation of α-pinene and isoprene (Surratt et al., 2007). Recently, substantial amount of organosulfates have been observed in SOA around the world, and organosulfates have been identified as a group of compounds which have an important contribution to the total amount of SOA in the atmosphere (Surratt et al., 2008; Froyd

30 et al., 2010; Kristensen and Glasius, 2011; Tolocka and Turpin, 2012; Wang et al., 2015). However, the formation and transformation process of organosulfates 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. 2-Methyl-3-buten-2-ol (MBO) has been found to be an important precursor for organosulfates in the atmosphere. Smog chamber studies of OH-initiated oxidation of MBO under nitric oxide and aerosol

acidity conditions revealed the formation of organosulfates and SOA (Mael et al., 2015; Zhang et al., 2012). Chemical characterization of laboratory-generated MBO SOA revealed that an organosulfate species ($C_5H_{12}O_6S$) was formed and its formation was significantly enhanced with elevated aerosol acidity (Zhang et al., 2012). It has also been demonstrated that substantial formation of organosulfates could derive from acid-catalyzed reactive uptake of MBO-based epoxides formed

5   during MBO photooxidation (Zhang et al., 2014). Using nuclear resonance techniques, isoprene-derived epoxides formed during isoprene photooxidation reactions were found to be important intermediates for organonitrates and organosulfates 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. Organosulfates formation was also found from oxidation of hydroxyhydroperoxides (Riva et al., 2016) and from heterogeneous reactions of SO_2 with selected

10   long-chain alkenes and unsaturated fatty acids (Passananti et al., 2016).

Laboratory chamber studies showed that organosulfates were formed in the products of OH/NOx/O_3-initiated reactions with biogenic VOCs (BVOCs), such as isoprene (Surratt et al., 2007; Surratt et al., 2008; Hatch et al., 2011), monoterpenes (Surratt et al., 2007; Gomez-Gonzalez et al., 2008; Iinuma et al., 2007) and sesquiterpenes (Chan et al., 2011). Reactions with sulfates or H_2SO_4 were the main formation processes of organosulfates. Qualitative analyses of the organosulfates in

15   SOA have been gained more attention and development (Lin et al., 2012; Shalamzari et al., 2013; Staudt et al., 2014). Riva et al. 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 (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

20   organosulfates related to croton aldehyde were identified. However, there was no report about the yield and chemical composition of SOA obtained from photooxidation of cyclohexene with the presence of SO_2.

In the present work, we investigated the SOA yields and chemical composition during cyclohexene photooxidation under different SO_2 concentrations. A better understanding of the magnitude and chemical composition of SOA from different SO_2 concentrations will contribute to more accurate SOA prediction from anthropogenic sources and give valuable information

25   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 setup

30   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 band centered at 365 nm, which were used to simulate the spectrum of the UV band in solar irradiation. Stainless steel was covered on the chamber

interior walls to maximize and homogenize the interior light intensity. Both inlet and outlet of the chamber were made of Teflon material. Atmospheric pressure was maintained in the chamber at all times. All the experiments were performed at room temperature (307±2 K) under dry conditions (RH < 10%). Prior to each experiment, the chamber was cleaned by purging with purified dry air for at least 8 h until residual hydrocarbons, O_3, NOx or particles could not be detected in the

5   reactor. Known amounts of cyclohexene was 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 by a gas-tight syringe to make the mixing ratio of NOx in the reactor around 95 ppb during all the experiments. The mixed concentration ratios of VOCs/NOx were adjusted to be about 5. SOA formation experiments were carried out under UV irradiation in the presence of NOx to produce O_3 and OH radicals for cyclohexene oxidation. Although initial VOCs, NOx and average OH

10   concentrations were different from typical urban conditions, efforts were made to maintain the initial concentrations of the reactants as similar as possible to make sure the effect of SO_2 was the main reason for the changes in the SOA yield. More details on the experimental conditions are shown in Table S1 of the Supplementary material.

2.2 Gas and particle measurements

Ozone concentration in the reactor was measured using ozone analyzer (Model 49C, Thermo Electron Corporation, USA). A

15   NO-NO_2-NOx analyzer (Model 42C, Thermo Electron Corporation, USA) was used to monitor the NOx concentration. Measurement of SO_2 concentration was made using a SO_2 analyzer (Model 43i-TLE, Thermo Electron Corporation, USA). The uncertainty of the O_3, NOx and SO_2 measurement was less than ±1%. The detection limits of the different monitors were 0.40 ppb, 0.50 ppb, and 0.05 ppb for NOx, O_3, and SO_2, 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

20   lights were turned on and at the end of each experiment, respectively. The volume of the sample was 60 mL and the sampling time was 3 min. Concentrations of cyclohexene and the main gas phase products were analyzed 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

25   thickness). The temperature program 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, 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 analyzed

30   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 analyzer (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

Atmospheric
Chemistry
and Physics
Discussions

particle size was measured in the range of 14 to 710 nm. Each scan was 180 s. An aerosol density of 1.2 g cm^{-3} was assumed to convert the particle volume concentration into the mass concentration (Zhang et al., 2015). Size distribution data were recorded and analyzed using the TSI AIM software v9.0.

2.3 Products composition analysis

5   The chemical composition of SOA was important for analyzing the degree of VOCs 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) spectrometer (Nicolet iS10, Thermos Fisher, USA). The 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 diameter, were

10 collected on an ungreased zinc selenide (ZnSe) disk (25 mm in diameter) for FTIR measurements.
The characteristic bands of inorganic and organic sulfates overlap in IR spectrum. In order to distinguish between the inorganic and organic sulfates, ion chromatograph (IC, Dionex ICS-900, Thermo Fisher, USA) was used to analyze the inorganic sulfate anion (SO_4^{2-}) in SOA. SOA collected on ZnSe disks was firstly dissolved in high purity water (7 mL) and then measured by IC for SO_4^{2-} concentrations. The anions were analyzed with a Dionex IonPac AS14A analytical column

15 and an anion self-regenerating suppressor Dionex ASRS was used as eluent. The flow rate was 1.0 mL min^{-1} with a mixture of 8.0 mmol L^{-1} Na$_2$CO$_3$ and 1.0 mmol L^{-1} NaHCO$_3$ for anions analyses. The suppressing current was 50 mA.
Chemical characterization of aerosols from photooxidation of cyclohexene was performed using an electrospray ionization high-resolution quadrupole mass spectrometer (ESI-HR-MS, Thermo Fisher, USA) operated in negative (-) ion mode, which was calibrated using the manufacturer's calibration standards mixture allowing for mass accuracies <5 ppm in external

20 calibration mode. The ionization voltage was 4.2 kV and the capillary temperature was set at 300 °C. N$_2$ was used as both the sheath gas (70 U) and auxiliary gas (30 U). SOA was collected on the aluminum foil using the same method as FTIR analysis and then extracted with 1 mL of acetonitrile. The aluminum foil was used due to its ease to 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

25 the calculation of chemical formula from the 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 without further purification. A zero air generator (Model 111, Thermo Scientific, USA) was used to generate clean air. The zero air has no detectable non-methane hydrocarbons (NMHC < 1 ppb), NOx (< 1 ppb), low O$_3$ concentration (< 3 ppb), and

30 low particle numbers (< 5 cm^{-3}), and relative humidity (RH) below 10%. Ozone was produced from O$_2$ via electrical discharge using a dynamic gas calibrator (Model 146i, Thermo Scientific, USA). NO$_2$ (510 ppm), NO (50 ppm) and SO$_2$ (25 ppm) with ultra-pure N$_2$ (99.999%) as background gas was purchased from Beijing Huangyuan Gas Co., Ltd., China.

Atmospheric
Chemistry
and Physics
Discussions

3 Results and discussion

3.1 Characterization of the chamber

The effective light intensity in the near ultraviolet region plays a decisive role in the formation of photochemical smog (Presto et al., 2005a). The effective light intensity of the chamber was represented by the photolysis rate constant of NO_2. In
5   our study, the average effective light intensity was determined to be 0.177 min^{-1}.

Wall loss is the decrease of the concentration of reactive gas phase species caused by adsorption on the inner wall of the reactor. Residual reactant and product on the inner wall can also react with the gas phase species, which is another important reason for wall loss. Wall loss can directly affect the quantitative calculation of photooxidation rate and SOA yield. Correct evaluation of wall loss is therefore necessary to explain the experimental results of SOA yield. In the present study, the wall

10   loss of cyclohexene in the chamber could be neglected. The wall loss of O_3, NOx, and SO_2 were first order because $\ln([X]_0/[X]_t)$ had a good correlation with time (R^2=0.994, 0.944, 0.999 for O_3, NOx, and SO_2, respectively). The measured wall loss rate constants for O_3, NOx and SO_2 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 Pathak et al (Pathak et al., 2007). Typical profiles of the gas and particle phases are given in

15   Figure S1 of the Supplementary material.

3.2 Effect of SO_2 on SOA number concentrations

The maximum particle number concentrations for cyclohexene/NOx/SO_2 system with different initial SO_2 concentrations and the particle number concentrations at the maximum SOA yield are shown in Figure 1. After the black light lamps were turned on, SOA number concentrations increased rapidly to reach the maximum within 0.5 h in each experiment.

20   Subsequently, the particle number concentrations gradually decreased accompanied by the growth of particle size by coagulation. The SOA mass concentration kept increasing until its maximum was reached (after ~2 h). Both types of particle number concentrations had similar trends against initial SO_2 concentrations. In general, maximum particle number concentrations were three times higher than the particle number concentrations at the maximum SOA yield. In the rest part of this paper, in order to better elaborate the effect of SO_2 on the formation of particles, the particle number concentration

25   refers to the maximum particle number concentration.

The particle number concentration increased with initial SO_2 concentration, and this increase could be divided into two stages: increasing stage and stable stage. In the increasing stage, with the initial SO_2 concentration increasing from 0 ppb to 30 ppb, the particle number concentration grew significantly under low initial SO_2 concentration (<5 ppb), then the growth rate reduced gradually. In the stable stage, when the SO_2 concentrations were varied systematically between 30 and 105 ppb,

30   particle number concentrations practically maintained steady (2.5×10^5-3.8×10^5 cm^{-3}), and there was no obvious growth as shown in Figure 1. For experiments with high initial SO_2 concentration, the maximum particle number concentrations were 10 times of those without SO_2, indicating enhanced new particle formation (NPF) when adding SO_2. It was found that wood

soot, a minor source of SO_2 (Reddy and Venkataraman, 2002), resulted in a measurable positive deviation to the VOCs/NOx photooxidation reaction system without background aerosol (Jang et al., 2002). Our result was consistent with a range of previous studies (Jang et al., 2002; Liu et al., 2016), in which even small amount of SO_2 could affect the new particle formation.

5   Nucleation is a fundamental step in the atmospheric new particle formation. Nucleation of particles in the atmosphere has been observed to be strongly dependent on the abundance of H_2SO_4 (Sihto et al., 2006; Xiao et al., 2015). Normally, SO_2 was deemed to be oxidized by OH radicals to form H_2SO_4 through homogeneous reactions in gas phase (Calvert et al., 1978), or by H_2O_2 and O_3 through in-cloud processes in aqueous phase (Lelieveld and Heintzenberg, 1992). The aqueous phase formation of H_2SO_4 is negligible in this study (RH<10%). As the precursor of H_2SO_4, SO_2 at higher concentrations would

10   lead to more H_2SO_4 formation, and thereby increase the nucleation rates and total particle number concentrations (Sipilä et al., 2010). Because of the similar initial conditions for each experiment except SO_2, the amount of OH radicals produced was assumed to be almost equal. In the presence of high concentration of SO_2, new particle formation was not enhanced. This feature may indicate that no more sulfates formed when SO_2 was in large excess (>30 ppb) and the OH radicals were insufficient. The quantity of OH radicals is the main restraint on H_2SO_4 formation at high initial SO_2 concentrations, which

15   could not lead to more H_2SO_4 formation in the present study. Therefore, the particle number concentration maintained steady, and it was independent of the SO_2 concentrations in the second stage.

Besides, the mean diameter of particles increased with photooxidation reaction time, which suggests that not many new particles were generated after a burst increase at the initial stage of SOA formation. The burst increase stage of SOA may be related to fast increase of $PM_{2.5}$ and occurrence of haze (He et al., 2014). Once new particles are formed, there is a

20   competition between growth of existing particles by uptake of the precursors and formation of new particles. Our result agrees with previous studies that there was no obvious increase in aerosol number concentration when additional VOCs were injected, but a significant increase in SOA mass concentration (Presto et al., 2005a). Condensation onto existing aerosol particles was prior to the occurrence of new particle formation. If there was enough seed particle surface area, no new particles formation was expected to be observed.

25   **3.3 Effect of SO_2 on SOA yields**

SOA yield (Y) is defined as $Y=\Delta M_0/\Delta HC$, where ΔM_0 is the produced organic aerosol mass concentration (μg m^{-3}), and ΔHC 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 Figure 2. The numerical values of the aerosol mass concentration and SOA yields at different conditions are shown in Table S1 of the Supplementary material.

30   The SOA yields in the absence of SO_2 were in the range of 2.5% to 2.7%, which were an order of magnitude lower than those reported in previous studies (Warren et al., 2009; Keywood et al., 2004; 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 $[VOC]_0/[NOx]_0$ (Pandis et al., 1991). Experiments performed with

Atmospheric
Chemistry
and Physics
Discussions

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 Figure S2 of the Supplementary material, even at 0 ppb of SO_2, the mass concentration of SOA quickly reaches its maximum. Experiments with higher NOx levels have been proved to get considerably lower SOA yield than those with lower NOx levels at the same VOCs concentration (Song et al., 2005).

5   The reactions of organo-peroxy radicals (RO_2) with NO and NO_2 instead of peroxy radicals (RO_2 or HO_2) under high NOx conditions resulted in the formation of volatile organic products and a decreased SOA yield (Lane et al., 2008). For $[VOC]_0/[NOx]_0$ ratios between 3 and 10, a greater amount of nitrate radical (NO_3) was available to react with VOCs, and the NO_3-initiated reaction was a poor source of SOA, which may also contribute to the reduction of SOA yield (Presto et al., 2005b). It was reported that SOA yield was constant for $[VOC]_0/[NOx]_0 > 15$, but decreased dramatically (by a factor of more than 4) as $[VOC]_0/[NOx]_0$ decreased (Presto et al., 2005b). In our study, the $[VOC]_0/[NOx]_0$ ratio was maintained at about 5.

10   Recently, the NOx dependence of SOA formation from photooxidation of β-pinene was comprehensively investigated (Sarrafzadeh et al., 2016), and it was shown that the NOx-induced OH concentration was the major factor influencing the SOA yield. The impacts of NOx on SOA formation were only moderate if the impact of NOx on OH concentration was eliminated. OH concentration in our study was relatively insufficient, which was the main limiting factor for SOA formation.

15   (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., 2005a). Exposure to UV light could reduce SOA yield by 20%-40%, while more volatile products were formed (Griffin et al., 1999). (3) Temperature may have a pronounced influence on SOA yield (Qi et al., 2010; Emanuelsson et al., 2013). At lower temperature, semi-volatile organic compounds would favor the condensation of gas phase species and a higher SOA yield could be expected. Raising the chamber temperature by 10 K should cause a

20   decrease of 10% in aerosol yield (Pathak et al., 2007). SOA yields reported in the present study were obtained at higher temperature, 307±2 K, instead of 298 K in most previous studies. On the basis of the discussion above, SOA yield from cyclohexene in our study was lower than observed in the previous studies.

SOA yields for the cyclohexene/NOx/SO_2 system were measured for initial SO_2 mixing ratios of 0-105 ppb. The experimental results showed a clear decrease at first and then an increase in the SOA yield with increasing SO_2

25   concentrations (Figure 2). When SO_2 concentrations increased from 0 to 40.8 ppb, there was a remarkable decrease in SOA yield with the increase of SO_2 concentration. The SOA yield dropped from 2.7% to 1.2%, reduced by 56%. For SO_2 concentrations higher than 40.8 ppb, SOA yield increased with increasing SO_2 concentration. The highest SOA yield was obtained to be 3.5%, at 104.7 ppb SO_2 concentration. The lowest SOA yield of cyclohexene photooxidation was obtained at the initial SO_2 concentration of 40 ppb. Although the SOA yield increased gradually with the initial SO_2 concentration at

30   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.

SOA formation was enhanced by the presence of SO_2 (Jang et al., 2002), which has been previously attributed to acid-catalyzed heterogeneous reactions and produced an increase of the total organic aerosol mass (Xu et al., 2014). Even small amounts of acid are capable of catalyzing heterogeneous reactions. Both NO and NO_2 was used as NOx for the repeated

Atmospheric
Chemistry
and Physics
Discussions

experiments in our study. Despite the time of occurrence of the maximum SOA concentration for the experiment with NO_2 was half an hour earlier than that for the experiment with NO, the results of SOA yield were similar. However, there were some undiscovered processes in the cyclohexene/NOx/SO_2 system that offset potential multifold increases in the SOA yield by acid-catalyzed heterogeneous reactions. The competitive reaction between SO_2 and VOCs might be the reason for the

5 decrease of the SOA yield. SO_2 could be oxidized by OH radicals to form H_2SO_4 (Somnitz, 2004). Due to the presence of O_3 in our system, the formation of Criegee intermediates and their reactions with SO_2 could be expected (Criegee, 1975). However, the importance of these reactions can be kinetically limited. The reaction of cyclohexene with ozone has a rate constant of 8.1×10^{-17} cm^3 $molecule^{-1}$ s^{-1} (Stewart et al., 2013), considerably slower than e.g., its reaction with OH, which has a rate constant of 6.4×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Aschmann et al., 2012). In addition to the kinetic limitation of the

10 cyclohexene reaction with O_3, the typical concentration of O_3 in our chamber was 200 ppb and hence the importance of cyclohexene reaction with O_3 was expected to be less significant than that of its reaction with OH under any relevant SO_2 conditions. The competitive reaction resulted in a decrease of the concentration of OH radicals, which was one of the main oxidizers for the photooxidation in the chamber. 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. At lower

15 OH radical concentration condition caused by the reaction between SO_2 and OH radical, the formation of SOA was inhibited. Accordingly, SOA yield showed descending trend with the increase of SO_2 concentration when the initial SO_2 concentration was lower than 40 ppb.

When the initial SO_2 concentration was greater than 40 ppb, the acid-catalyzed heterogeneous formation of SOA became more significant (Figure 2). The lowest SOA yield was obtained at 40 ppb initial SO_2 concentration. At this concentration,

20 there was a balance between the inhibition of SOA formation by competitive reactions and the promotion by acid-catalyzed reactions. The same SOA yield was obtained in the absence of SO_2 and at 85 ppb initial SO_2 concentration. The competitive reaction plays an important role for SOA formation, and it should be taken into account in SOA simulation models or air quality models for more accurate prediction. The formation of low volatile organics (e.g. organosulfates) by photooxidation in the presence of SO_2 might be another reason for the increase of the SOA yield.

25 **3.4 Organosulfates formation**

When SO_2 was added into the chamber, the acidic aerosol particles were formed by photooxidation of SO_2 initiated by the reaction with OH. The amounts of SO_4^{2-} in particle phase and the consumption of SO_2 (ΔSO_2) with different initial SO_2 concentrations are shown in Figure 3. The amounts of SO_4^{2-} grew rapidly at low concentration of SO_2, but the relative growth rate dramatically decreased in the range of 20-60 ppb initial SO_2 concentrations. However, both the amount and the

30 growth rate of ΔSO_2 increased with initial SO_2 concentrations. The ratio of the amount of SO_2 for SO_4^{2-} formation to ΔSO_2 reduced gradually with the increase of initial SO_2 concentrations (Figure 3), which indicated that other products formed from SO_2 besides SO_4^{2-} in the aerosols.

Atmospheric
Chemistry
and Physics
Discussions

Typical IR spectra of aerosols from cyclohexene/NOx/SO$_2$ system under different SO$_2$ concentrations are presented in Figure 4. Based on the peak positions in the IR spectra, the functional groups represented by each peak are summarized as following. The broadband at 3100 to 3300 cm^{-1} is assigned as the O–H stretching of hydroxyl and carboxyl groups (Coury and Dillner, 2008). The peak at 1717 cm^{-1} represents the C=O stretching of aldehydes, ketones, and carboxylic acids. The peaks at 1622

5   and 1278 cm^{-1} show good correlation and both are assigned to the ONO$_2$ 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 COOH group (Ofner et al., 2011). 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 sulfonic acid group 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 bands assignments in

10   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 sulfonic acid group.

The intensities of most absorption bands, such as O-H at 3100-3300 cm^{-1}, C=O at 1717 cm^{-1}, ONO$_2$ at 1622 and 1278 cm^{-1}, and C-H at 2930 cm^{-1}, have similar trends with the change of SOA yield for initial SO$_2$ concentrations between 11 and 105 ppb. However, the band of sulfate at 1100 cm^{-1} in IR spectra increases with the rise of initial SO$_2$ concentration rather than

15   the SOA yield, which suggests the formation of sulfonic acid group and sulfate product from SO$_2$ photooxidation. The relative intensity of the band at 1100 cm^{-1} increased by 1.8 times when the initial SO$_2$ concentration rose from 0 to 44 ppb, whereas the band increased by 7.2 times when the initial SO$_2$ concentration was 105 ppb. The intensity of 1100 cm^{-1} band grew slowly at low SO$_2$ concentrations due to the decrease of the formation of aerosols. To clearly show the amount of sulfonic acid group and sulfate in aerosols, the intensity of the band at 1100 cm^{-1} and the amount of SO$_4^{2-}$ were compared in

20   the same aerosol mass, and are shown in Figure 5, where the amount of ΔSO$_2$ in the aerosols are also included. The relative intensity was set to 1 when the initial SO$_2$ concentration was 44.3 ppb.

With the increase of SO$_2$ concentration, the amount of SO$_4^{2-}$ in unit mass of aerosols increased first and then decreased, which was negative correlation with SOA yield. However, ΔSO$_2$ was in a linear relationship with the initial SO$_2$ concentration (R^2=0.94). The relative band intensities at 1100 cm^{-1}, which represented the intensity of both SO$_4^{2-}$ and

25   sulfonic acid group, also increased approximately in a linear form with the increase of initial SO$_2$ concentration (R^2=0.91). If the 1100 cm^{-1} band originated from SO$_4^{2-}$ only, the change of the band intensity was consistent with SO$_4^{2-}$ concentration in unit mass of aerosols. Combined with the ratio of the amount of SO$_2$ for SO$_4^{2-}$ formation to ΔSO$_2$, it was reasonable to believe that the 1100 cm^{-1} band originated not only from SO$_4^{2-}$, but also from the sulfonic acid group. Organosulfates might be the products from the photooxidation of cyclohexene in the presence of SO$_2$ under high-NOx conditions.

30   The composition of the cyclohexene SOA was examined with HR-MS using negative ion mode ESI and the mass spectrum was recorded at a resolution of 10^5 (Figure 6). Organosulfates were identified in the particle phase from chamber experiments. Accurate mass fittings for measured ions of organosulfates in ESI negative ion mode are given in Table 1. As shown in Figure 6 and Table 1, 10 kinds of organosulfates were successfully detected and identified from cyclohexene SOA. The result not only first proved the formation of organosulfates from cyclohexene photooxidation at high-NOx condition

Atmospheric
Chemistry
and Physics
Discussions

with SO_2, but also provided 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 maximum content (more than 60%) of all the organosulfates detected in our study. Its intensity was 6.5 times higher than that of the second highest abundant organosulfate. The intermediate product of cyclohexene with OH, i.e., $CH(O)CH_2CH_2CH_2CH_2\dot{C}HOH$, has a hydroxyl group,

5 and the organosulfate product (m/z=195.03322) might form from the intermediate product, not from end product.

The mass spectra showed a great abundance of peaks, detected as deprotonated molecular ions $(M-H)^-$ 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 the products were identified as cyclic 1,2-hydroxynitrates and 1,6-hexanedial (Aschmann et al., 2012). These products couldn't be detected by ESI-HR-MS in our

10 study. Aldehydes could be oxidized by OH radicals to form carboxyls, which have been intensively identified in previous studies (Cameron et al., 2002; Goldsmith et al., 2012). The 1,6-hexanedial might be further oxidized in the atmospheric photooxidation reactions to form the 1,6-adipic acid ($C_6H_{10}O_4$) and 6-oxohexanoicacid ($C_6H_{10}O_3$), which were both observed in our MS results. 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 this C_5 compound might be due to a carbonyl cleavage from a six-carbon

15 atoms chain, a proper mechanism for its formation could not be determined. A C_4 compound was also detected in this study, 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.

4 Conclusion

We report a series of chamber experiments studies on the formation of secondary aerosols from the mixture of cyclohexene

20 and SO_2. The experiments were based on Fourier transform infrared spectrometer, ion chromatography and electrospray ionization high-resolution quadrupole mass spectrometer, and were performed under NOx 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. The SOA formation decreased at first and then was enhanced for all SO_2 concentration above 40 ppb.

25 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. The formation of organosulfates has a great significance for the particulate matter formation under high SO_2 concentrations in the atmosphere.

Atmospheric
Chemistry
and Physics
Discussions

5 **References**

Adams, J. M., Constable, J. V., Guenther, A. B., and Zimmerman, P.: An estimate of natural volatile organic compound emissions from vegetation since the last glacial maximum, Chemosphere, 3, 73-91, doi: 10.1016/S1465-9972(00)00023-4, 2001.

Aschmann, S. M., Arey, J., and Atkinson, R.: Kinetics and products of the reactions of OH radicals with cyclohexene, 1-
10 methyl-1-cyclohexene, cis-cyclooctene, and cis-cyclodecene, J. Phys. Chem. A, 116, 9507-9515, doi: 10.1021/jp307217m, 2012.

Atkinson, R.: Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and alkenes, J. Phys. Chem. Ref. Data., 26, 215-290, doi: 10.1063/1.556012, 1997.

Attwood, A., Washenfelder, R., Brock, C., Hu, W., Baumann, K., Campuzano-Jost, P., Day, D., Edgerton, E., Murphy, D.,
15 and Palm, B.: Trends in sulfate and organic aerosol mass in the southeast US: Impact on aerosol optical depth and radiative forcing, Geophys. Res. Lett., 41, 7701-7709, doi: 10.1002/2014GL061669, 2014.

Calvert, J. G., Su, F., Bottenheim, J. W., and Strausz, O. P.: Mechanism of the homogeneous oxidation of sulfur dioxide in the troposphere, Atmos. Environ., 12, 197-226, doi: 10.1016/0004-6981(78)90201-9, 1978.

Cameron, M., Sivakumaran, V., Dillon, T. J., and Crowley, J. N.: Reaction between OH and CH_3CHO. Part 1. Primary
20 product yields of CH_3 (296 K), CH_3CO (296 K), and H (237-296 K), Phys. Chem. Chem. Phys., 4, 3628-3638, doi: 10.1039/b202586h, 2002.

Carlsson, P. T., Dege, J. E., Keunecke, C., Kruger, B. C., Wolf, J. L., and Zeuch, T.: Pressure dependent aerosol formation from the cyclohexene gas-phase ozonolysis in the presence and absence of sulfur dioxide: a new perspective on the stabilisation of the initial clusters, Phys. Chem. Chem. Phys., 14, 11695-11705, doi: 10.1039/c2cp40714k, 2012.

25 Chan, M. N., Surratt, J. D., Chan, A. W. H., Schilling, K., Offenberg, J. H., Lewandowski, M., Edney, E. O., Kleindienst, T. E., Jaoui, M., Edgerton, E. S., Tanner, R. L., Shaw, S. L., Zheng, M., Knipping, E. M., and Seinfeld, J. H.: Influence of aerosol acidity on the chemical composition of secondary organic aerosol from β-caryophyllene, Atmos. Chem. Phys., 11, 1735-1751, doi: 10.5194/acp-11-1735-2011, 2011.

Cheng, N., Zhang, D., Li, Y., Chen, T., Li, J., Dong, X., Sun, R., and Meng, F.: Analysis about spatial and temporal
30 distribution of SO_2 and an ambient SO_2 pollution process in Beijing during 2000-2014, Environ. Sci., 36, 3961-3971, doi: 10.13227/j.hjkx.2015.11.004, 2015.

Chihara, G.: Characteristic infrared absorption band of organic sulfate esters, Chem. Pharm. Bull., 6, 114, doi: 10.1248/cpb.6.114, 1958.

Coury, C., and Dillner, A. M.: A method to quantify organic functional groups and inorganic compounds in ambient aerosols
35 using attenuated total reflectance FTIR spectroscopy and multivariate chemometric techniques, Atmos. Environ., 42, 5923-5932, doi: 10.1016/j.atmosenv.2008.03.026, 2008.

Criegee, R.: Mechanism of ozonolysis, Angew. Chem. Int. Edit., 14, 745-752, doi: 10.1002/anie.197507451, 1975.

Darer, A. I., Cole-Filipiak, N. C., O'Connor, A. E., and Elrod, M. J.: Formation and stability of atmospherically relevant isoprene-derived organosulfates and organonitrates, Environ. Sci. Technol., 45, 1895-1902, doi: 10.1021/es103797z, 2011.

40 Du, L., Xu, Y. F., Ge, M. F., and Jia, L.: Rate constant for the reaction of ozone with diethyl sulfide, Atmos. Environ., 41, 7434-7439, doi: 10.1016/j.atmosenv.2007.05.041, 2007.

Edney, E., Kleindienst, T., Jaoui, M., Lewandowski, M., Offenberg, J., Wang, W., and Claeys, M.: Formation of 2-methyl tetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NOx/SO_2/air mixtures and their detection in ambient $PM_{2.5}$ samples collected in the eastern United States, Atmos. Environ., 39, 5281-5289, doi:
45 10.1016/j.atmosenv.2005.05.031, 2005.

Emanuelsson, E. U., Watne, A. K., Lutz, A., Ljungstrom, E., and Hallquist, M.: Influence of humidity, temperature, and radicals on the formation and thermal properties of secondary organic aerosol (SOA) from ozonolysis of β-pinene, J. Phys. Chem. A, 117, 10346-10358, doi: 10.1021/jp4010218, 2013.

Froyd, K. D., Murphy, S. M., Murphy, D. M., de Gouw, J. A., Eddingsaas, N. C., and Wennberg, P. O.: Contribution of isoprene-derived organosulfates to free tropospheric aerosol mass, Proc. Natl. Acad. Sci. U. S. A., 107, 21360-21365, doi: 10.1073/pnas.1012561107, 2010.

Goldsmith, C. F., Green, W. H., and Klippenstein, S. J.: Role of O_2 + QOOH in low-temperature ignition of propane. 1. Temperature and pressure dependent rate coefficients, J. Phys. Chem. A, 116, 3325-3346, doi: 10.1021/jp210722w, 2012.

Gomez-Gonzalez, Y., Surratt, J. D., Cuyckens, F., Szmigielski, R., Vermeylen, R., Jaoui, M., Lewandowski, M., Offenberg, J. H., Kleindienst, T. E., Edney, E. O., Blockhuys, F., Van Alsenoy, C., Maenhaut, W., and Claeys, M.: Characterization of organosulfates from the photooxidation of isoprene and unsaturated fatty acids in ambient aerosol using liquid chromatography/(-) electrospray ionization mass spectrometry, J. Mass Spectrom., 43, 371-382, doi: 10.1002/jms.1329, 2008.

Griffin, R. J., Cocker, D. R., Flagan, R. C., and Seinfeld, J. H.: Organic aerosol formation from the oxidation of biogenic hydrocarbons, J. Geophys. Res., 104, 3555-3567, doi: Doi 10.1029/1998jd100049, 1999.

Grosjean, D., Cauwenberghe, K. V., Schmid, J. P., Kelley, P. E., and Pitts, J. N.: Identification of C3-C10 aliphatic dicarboxylic acids in airborne particulate matter, Environ. Sci. Technol., 12, 313-317, doi: 10.1021/es60139a005, 1978.

Hansen, J. E., and Sato, M.: Trends of measured climate forcing agents, Proc. Natl. Acad. Sci. U. S. A., 98, 14778-14783, doi: 10.1073/pnas.261553698, 2001.

Hatch, L. E., Creamean, J. M., Ault, A. P., Surratt, J. D., Chan, M. N., Seinfeld, J. H., Edgerton, E. S., Su, Y. X., and Prather, K. A.: Measurements of isoprene-derived organosulfates in ambient aerosols by aerosol time-of-flight mass spectrometry-part 1: Single particle atmospheric observations in atlanta, Environ. Sci. Technol., 45, 5105-5111, doi: 10.1021/es103944a, 2011.

He, H., Wang, Y., Ma, Q., Ma, J., Chu, B., Ji, D., Tang, G., Liu, C., Zhang, H., and Hao, J.: Mineral dust and NOx promote the conversion of SO_2 to sulfate in heavy pollution days, Sci. Rep., 4, 4172, doi: 10.1038/srep04172, 2014.

Hu, K. S., Darer, A. I., and Elrod, M. J.: Thermodynamics and kinetics of the hydrolysis of atmospherically relevant organonitrates and organosulfates, Atmos. Chem. Phys., 11, 8307-8320, doi: 10.5194/acp-11-8307-2011, 2011.

Iinuma, Y., Muller, C., Berndt, T., Boge, O., Claeys, M., and Herrmann, H.: Evidence for the existence of organosulfates from beta-pinene ozonolysis in ambient secondary organic aerosol, Environ. Sci. Technol., 41, 6678-6683, doi: 10.1021/es070938t, 2007.

Jang, M., Czoschke, N. M., Lee, S., and Kamens, R. M.: Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions, Science, 298, 814-817, doi: 10.1126/science.1075798, 2002.

Jaoui, M., Kleindienst, T. E., Offenberg, J. H., Lewandowski, M., and Lonneman, W. A.: SOA formation from the atmospheric oxidation of 2-methyl-3-buten-2-ol and its implications for $PM_{2.5}$, Atmos. Chem. Phys., 12, 2173-2188, doi: 10.5194/acp-12-2173-2012, 2012.

Jia, L., and Xu, Y. F.: Effects of relative humidity on ozone and secondary organic aerosol formation from the photooxidation of benzene and ethylbenzene, Aerosol. Sci. Tech., 48, 1-12, doi: 10.1080/02786826.2013.847269, 2014.

Jimenez, E., Gonzalez, S., Cazaunau, M., Chen, H., Ballesteros, B., Daele, V., Albaladejo, J., and Mellouki, A.: Atmospheric degradation initiated by OH radicals of the potential foam expansion agent, $CF_3(CF_2)_2CH$ horizontal line CH_2 (HFC-1447fz): kinetics and formation of gaseous products and secondary organic aerosols, Environ. Sci. Technol., 50, 1234-1242, doi: 10.1021/acs.est.5b04379, 2016.

Kalberer, M., Yu, J., Cocker, D. R., Flagan, R. C., and Seinfeld, J. H.: Aerosol formation in the cyclohexene-ozone system, Environ. Sci. Technol., 34, 4894-4901, doi: 10.1021/es001180f, 2000.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5, 1053-1123, doi: 10.5194/acp-5-1053-2005, 2005.

Keywood, M. D., Varutbangkul, V., Bahreini, R., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from the ozonolysis of cycloalkenes and related compounds, Environ. Sci. Technol., 38, 4157-4164, doi: 10.1021/es035363o, 2004.

Atmospheric
Chemistry
and Physics
Discussions

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Kristensen, K., and Glasius, M.: Organosulfates and oxidation products from biogenic hydrocarbons in fine aerosols from a forest in North West Europe during spring, Atmos. Environ., 45, 4546-4556, doi: 10.1016/j.atmosenv.2011.05.063, 2011.

Lane, T. E., Donahue, N. M., and Pandis, S. N.: Effect of NOx on secondary organic aerosol concentrations, Environ. Sci. Technol., 42, 6022-6037, doi: 10.1021/es703225a, 2008.

5 Lelieveld, J., and Heintzenberg, J.: Sulfate cooling effect on climate through in-cloud oxidation of anthropogenic SO_2, Science, 258, 117-120, doi: 10.1126/science.258.5079.117, 1992.

Lin, Y. H., Zhang, Z. F., Docherty, K. S., Zhang, H. F., Budisulistiorini, S. H., Rubitschun, C. L., Shaw, S. L., Knipping, E. M., Edgerton, E. S., Kleindienst, T. E., Gold, A., and Surratt, J. D.: Isoprene epoxydiols as precursors to secondary organic aerosol formation: acid-catalyzed reactive uptake studies with authentic compounds, Environ. Sci. Technol., 46, 250-258, 10 doi: 10.1021/es202554c, 2012.

Liu, S., Shilling, J. E., Song, C., Hiranuma, N., Zaveri, R. A., and Russell, L. M.: Hydrolysis of organonitrate functional groups in aerosol particles, Aerosol. Sci. Tech., 46, 1359-1369, doi: 10.1080/02786826.2012.716175, 2012.

Liu, T., Wang, X., Hu, Q., Deng, W., Zhang, Y., Ding, X., Fu, X., Bernard, F., Zhang, Z., and Lü, S.: Formation of secondary aerosols from gasoline vehicle exhausts when mixing with SO_2, Atmos. Chem. Phys., 16, 675-689, doi: 15 10.5194/acp-16-675-2016, 2016.

Lonsdale, C. R., Stevens, R. G., Brock, C. A., Makar, P. A., Knipping, E. M., and Pierce, J. R.: The effect of coal-fired power-plant SO_2 and NOx control technologies on aerosol nucleation in the source plumes, Atmos. Chem. Phys., 12, 11519-11531, doi: 10.5194/acp-12-11519-2012, 2012.

Mael, L. E., Jacobs, M. I., and Elrod, M. J.: Organosulfate and nitrate formation and reactivity from epoxides derived from 20 2-methyl-3-buten-2-ol, J. Phys. Chem. A, 119, 4464-4472, doi: 10.1021/jp510033s, 2015.

McFiggans, G., Artaxo, P., Baltensperger, U., Coe, H., Facchini, M. C., Feingold, G., Fuzzi, S., Gysel, M., Laaksonen, A., Lohmann, U., Mentel, T. F., Murphy, D. M., O'Dowd, C. D., Snider, J. R., and Weingartner, E.: The effect of physical and chemical aerosol properties on warm cloud droplet activation, Atmos. Chem. Phys., 6, 2593-2649, doi: 10.5194/acp-6-2593-2006, 2006.

25 Nah, T., Sanchez, J., Boyd, C. M., and Ng, N. L.: Photochemical aging of alpha-pinene and beta-pinene secondary organic aerosol formed from nitrate radical oxidation, Environ. Sci. Technol., 50, 222-231, doi: 10.1021/acs.est.5b04594, 2016.

Ofner, J., Kruger, H. U., Grothe, H., Schmitt-Kopplin, P., Whitmore, K., and Zetzsch, C.: Physico-chemical characterization of SOA derived from catechol and guaiacol-a model substance for the aromatic fraction of atmospheric HULIS, Atmos. Chem. Phys., 11, 1-15, doi: 10.5194/acp-11-1-2011, 2011.

30 Pandis, S. N., Paulson, S. E., Seinfeld, J. H., and Flagan, R. C.: Aerosol formation in the photooxidation of isoprene and β-pinene, Atmos. Environ., 25, 997-1008, doi: 10.1016/0960-1686(91)90141-S, 1991.

Passananti, M., Kong, L. D., Shang, J., Dupart, Y., Perrier, S., Chen, J. M., Donaldson, D. J., and George, C.: Organosulfate formation through the heterogeneous reaction of sulfur dioxide with unsaturated fatty acids and long-chain alkenes, Angew. Chem. Int. Edit., 55, 10336-10339, doi: 10.1002/anie.201605266, 2016.

35 Pathak, R. K., Stanier, C. O., Donahue, N. M., and Pandis, S. N.: Ozonolysis of alpha-pinene at atmospherically relevant concentrations: Temperature dependence of aerosol mass fractions (yields), J. Geophys. Res., 112, doi: 10.1029/2006jd007436, 2007.

Paulson, S. E., and Orlando, J. J.: The reactions of ozone with alkenes: An important source of HOx in the boundary layer, Geophys. Res. Lett., 23, 3727-3730, doi: 10.1029/96GL03477, 1996.

40 Pokhrel, A., Kawamura, K., Ono, K., Seki, O., Fu, P. Q., Matoba, S., and Shiraiwa, T.: Ice core records of monoterpene- and isoprene-SOA tracers from Aurora Peak in Alaska since 1660s: Implication for climate change variability in the North Pacific Rim, Atmos. Environ., 130, 105-112, doi: 10.1016/j.atmosenv.2015.09.063, 2016.

Pope III, C. A., and Dockery, D. W.: Health effects of fine particulate air pollution: lines that connect, J. Air Waste Manage. Assoc., 56, 709-742, doi: 10.1080/10473289.2006.10464485, 2006.

45 Presto, A. A., Hartz, K. E., and Donahue, N. M.: Secondary organic aerosol production from terpene ozonolysis. 1. Effect of UV radiation, Environ. Sci. Technol., 39, 7036-7045, doi: 10.1021/es050174m, 2005a.

Presto, A. A., Hartz, K. E., and Donahue, N. M.: Secondary organic aerosol production from terpene ozonolysis. 2. Effect of NOx concentration, Environ. Sci. Technol., 39, 7046-7054, doi: 10.1021/es050400s, 2005b.

Qi, L., Nakao, S., Tang, P., and Cocker, D. R.: Temperature effect on physical and chemical properties of secondary organic 50 aerosol from m-xylene photooxidation, Atmos. Chem. Phys., 10, 3847-3854, doi: 10.5194/acp-10-3847-2010, 2010.

Atmospheric
Chemistry
and Physics
Discussions

Reddy, M. S., and Venkataraman, C.: Inventory of aerosol and sulphur dioxide emissions from India. Part II-biomass combustion, Atmos. Environ., 36, 699-712, doi: Doi 10.1016/S1352-2310(01)00464-2, 2002.

Riva, M., Tomaz, S., Cui, T., Lin, Y. H., Perraudin, E., Gold, A., Stone, E. A., Villenave, E., and Surratt, J. D.: Evidence for an unrecognized secondary anthropogenic source of organosulfates and sulfonates: gas-phase oxidation of polycyclic aromatic hydrocarbons in the presence of sulfate aerosol, Environ. Sci. Technol., 49, 6654-6664, doi: 10.1021/acs.est.5b00836, 2015.

Riva, M., Budisulistiorini, S. H., Chen, Y., Zhang, Z., D'Ambro, E. L., Zhang, X., Gold, A., Turpin, B. J., Thornton, J. A., Canagaratna, M. R., and Surratt, J. D.: Chemical characterization of secondary organic aerosol from oxidation of isoprene hydroxyhydroperoxides, Environ. Sci. Technol., 50, 9889-9899, doi: 10.1021/acs.est.6b02511, 2016.

Romero, F., and Oehme, M.: Organosulfates – A new component of humic-like substances in atmospheric aerosols?, J. Atmos. Chem., 52, 283-294, doi: 10.1007/s10874-005-0594-y, 2005.

Sakamoto, Y., Inomata, S., and Hirokawa, J.: Oligomerization reaction of the Criegee intermediate leads to secondary organic aerosol formation in ethylene ozonolysis, J. Phys. Chem. A, 117, 12912-12921, doi: 10.1021/jp408672m, 2013.

Sarrafzadeh, M., Wildt, J., Pullinen, I., Springer, M., Kleist, E., Tillmann, R., Schmitt, S. H., Wu, C., Mentel, T. F., and Zhao, D.: Impact of NOx and OH on secondary organic aerosol formation from β-pinene photooxidation, Atmos. Chem. Phys., 16, 11237-11248, doi: 10.5194/acp-16-11237-2016, 2016.

Sarwar, G., and Corsi, R.: The effects of ozone/limonene reactions on indoor secondary organic aerosols, Atmos. Environ., 41, 959-973, doi: 10.1016/j.atmosenv.2006.09.032, 2007.

Shalamzari, M. S., Ryabtsova, O., Kahnt, A., Vermeylen, R., Herent, M. F., Quetin-Leclercq, J., Van der Veken, P., Maenhaut, W., and Claeys, M.: Mass spectrometric characterization of organosulfates related to secondary organic aerosol from isoprene, Rapid Commun. Mass Spectrom., 27, 784-794, doi: 10.1002/rcm.6511, 2013.

Sihto, S. L., Kulmala, M., Kerminen, V. M., Dal Maso, M., Petaja, T., Riipinen, I., Korhonen, H., Arnold, F., Janson, R., Boy, M., Laaksonen, A., and Lehtinen, K. E. J.: Atmospheric sulphuric acid and aerosol formation: implications from atmospheric measurements for nucleation and early growth mechanisms, Atmos. Chem. Phys., 6, 4079-4091, doi: 10.5194/acp-6-4079-2006, 2006.

Sipilä, M., Berndt, T., Petaja, T., Brus, D., Vanhanen, J., Stratmann, F., Patokoski, J., Mauldin, R. L., 3rd, Hyvarinen, A. P., Lihavainen, H., and Kulmala, M.: The role of sulfuric acid in atmospheric nucleation, Science, 327, 1243-1246, doi: 10.1126/science.1180315, 2010.

Sipilä, M., Jokinen, T., Berndt, T., Richters, S., Makkonen, R., Donahue, N. M., Mauldin, R. L., III, Kurten, T., Paasonen, P., and Sarnela, N.: Reactivity of stabilized Criegee intermediates (sCI) from isoprene and monoterpene ozonolysis toward SO_2 and organic acids, Atmos. Chem. Phys., 14, 3071-3098, doi: 10.5194/acpd-14-3071-2014, 2013.

Somnitz, H.: Quantum chemical and dynamical characterisation of the reaction $OH+SO_2 \rightleftharpoons HOSO_2$ over an extended range of temperature and pressure, Phys. Chem. Chem. Phys., 6, 3844-3851, doi: 10.1039/b317055a, 2004.

Song, C., Na, K., and Cocker, D. R., 3rd: Impact of the hydrocarbon to NOx ratio on secondary organic aerosol formation, Environ. Sci. Technol., 39, 3143-3149, doi: 10.1021/es0493244, 2005.

Staudt, S., Kundu, S., Lehmler, H. J., He, X., Cui, T., Lin, Y. H., Kristensen, K., Glasius, M., Zhang, X., Weber, R. J., Surratt, J. D., and Stone, E. A.: Aromatic organosulfates in atmospheric aerosols: synthesis, characterization, and abundance, Atmos. Environ., 94, 366-373, doi: 10.1016/j.atmosenv.2014.05.049, 2014.

Stewart, D. J., Almabrok, S. H., Lockhart, J. P., Mohamed, O. M., Nutt, D. R., Pfrang, C., and Marston, G.: The kinetics of the gas-phase reactions of selected monoterpenes and cyclo-alkenes with ozone and the NO_3 radical, Atmos. Environ., 70, 227-235, doi: 10.1016/j.atmosenv.2013.01.036, 2013.

Sun, H., Li, S., Zhang, Y., Jiang, H., Qu, L., Liu, Z., and Liu, S.: Selective hydrogenation of benzene to cydohexene in continuous reaction device with two reaction reactors in serie over Ru-Co-B/ZrO_2 catalysts, Chin. J. Catal., 34, 1482-1488, doi: 10.1016/S1872-2067(12)60637-8, 2013.

Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Edney, E. O., Claeys, M., Sorooshian, A., Ng, N. L., Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., and Seinfeld, J. H.: Evidence for organosulfates in secondary organic aerosol, Environ. Sci. Technol., 41, 517-527, doi: 10.1021/es062081q, 2007.

Surratt, J. D., Gomez-Gonzalez, Y., Chan, A. W., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Organosulfate formation in biogenic secondary organic aerosol, J. Phys. Chem. A, 112, 8345-8378, doi: 10.1021/jp802310p, 2008.

Atmospheric
Chemistry
and Physics
Discussions

Tolocka, M. P., and Turpin, B.: Contribution of organosulfur compounds to organic aerosol mass, Environ. Sci. Technol., 46, 7978-7983, doi: 10.1021/es300651v, 2012.

Wang, X. K., Rossignol, S., Ma, Y., Yao, L., Wang, M. Y., Chen, J. M., George, C., and Wang, L.: Identification of particulate organosulfates in three megacities at the middle and lower reaches of the Yangtze River, Atmos. Chem. Phys., 15,
5   21415-21448, doi: 10.5194/acpd-15-21415-2015, 2015.

Wang, X. M., Carmichael, G., Chen, D. L., Tang, Y. H., and Wang, T. J.: Impacts of different emission sources on air quality during March 2001 in the Pearl River Delta (PRD) region, Atmos. Environ., 39, 5227-5241, doi: 10.1016/j.atmosenv.2005.04.035, 2005.

Warren, B., Malloy, Q. G. J., Yee, L. D., and Cocker, D. R.: Secondary organic aerosol formation from cyclohexene
10   ozonolysis in the presence of water vapor and dissolved salts, Atmos. Environ., 43, 1789-1795, doi: 10.1016/j.atmosenv.2008.12.026, 2009.

Wu, L. Y., Tong, S. R., Zhou, L., Wang, W. G., and Ge, M. F.: Synergistic Effects between SO_2 and HCOOH on α-Fe_2O_3, J. Phys. Chem. A, 117, 3972-3979, doi: 10.1021/jp400195f, 2013.

Xiao, S., Wang, M. Y., Yao, L., Kulmala, M., Zhou, B., Yang, X., Chen, J. M., Wang, D. F., Fu, Q. Y., Worsnop, D. R., and
15   Wang, L.: Strong atmospheric new particle formation in winter in urban Shanghai, China, Atmos. Chem. Phys., 15, 1769-1781, doi: 10.5194/acp-15-1769-2015, 2015.

Xu, W., Gomez-Hernandez, M., Guo, S., Secrest, J., Marrero-Ortiz, W., Zhang, A. L., and Zhang, R.: Acid-catalyzed reactions of epoxides for atmospheric nanoparticle growth, J. Am. Chem. Soc., 136, 15477-15480, doi: 10.1021/ja508989a, 2014.

20   Zhang, H., Worton, D. R., Lewandowski, M., Ortega, J., Rubitschun, C. L., Park, J. H., Kristensen, K., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Jaoui, M., Offenberg, J. H., Kleindienst, T. E., Gilman, J., Kuster, W. C., de Gouw, J., Park, C., Schade, G. W., Frossard, A. A., Russell, L., Kaser, L., Jud, W., Hansel, A., Cappellin, L., Karl, T., Glasius, M., Guenther, A., Goldstein, A. H., Seinfeld, J. H., Gold, A., Kamens, R. M., and Surratt, J. D.: Organosulfates as tracers for secondary organic aerosol (SOA) formation from 2-methyl-3-buten-2-ol (MBO) in the atmosphere, Environ. Sci. Technol., 46, 9437-9446, doi:
25   10.1021/es301648z, 2012.

Zhang, H., Zhang, Z., Cui, T., Lin, Y. H., Bhathela, N. A., Ortega, J., Worton, D. R., Goldstein, A. H., Guenther, A., Jimenez, J. L., Gold, A., and Surratt, J. D.: Secondary organic aerosol formation via 2-Methyl-3-buten-2-ol photooxidation: evidence of acid-catalyzed reactive uptake of epoxides, Environ. Sci. Technol. Lett., 1, 242-247, doi: 10.1021/ez500055f, 2014.

30   Zhang, X., Schwantes, R. H., McVay, R. C., Lignell, H., Coggon, M. M., Flagan, R. C., and Seinfeld, J. H.: Vapor wall deposition in Teflon chambers, Atmos. Chem. Phys., 15, 4197-4214, doi: 10.5194/acp-15-4197-2015, 2015.

Zielinska, B., Sagebiel, J. C., Harshfield, G., Gertler, A. W., and Pierson, W. R.: Volatile organic compounds up to C20 emitted from motor vehicles; measurement methods, Atmos. Environ., 30, 2269-2286, doi: 10.1016/1352-2310(95)00116-6, 1996.
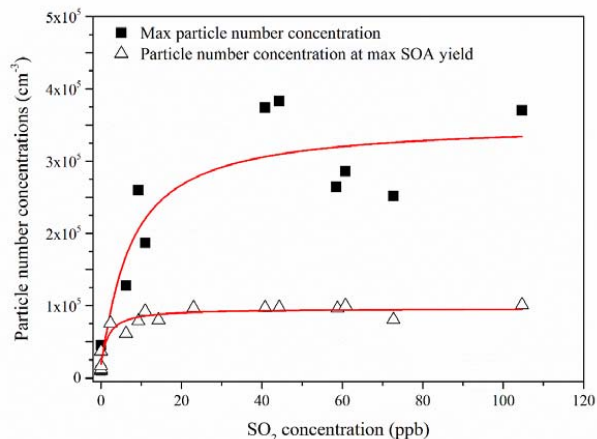
35

Figure 1: Particle number concentrations for cyclohexene/NOx/SO₂ system with different initial SO₂ concentrations.
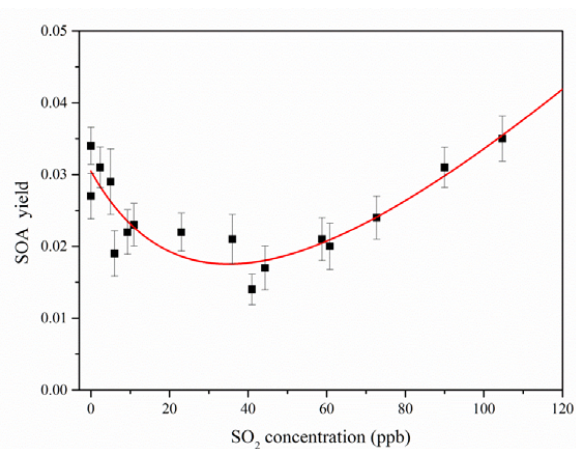
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Figure 2: SOA yields of cyclohexene photooxidation in the presence of NOx at different initial SO₂ concentrations. Solid line is least-square fitting to the data. The error bars were determined on the basis of propagation of uncertainties arising in the ΔHC measurements, including GC calibration uncertainties propagation and the variance

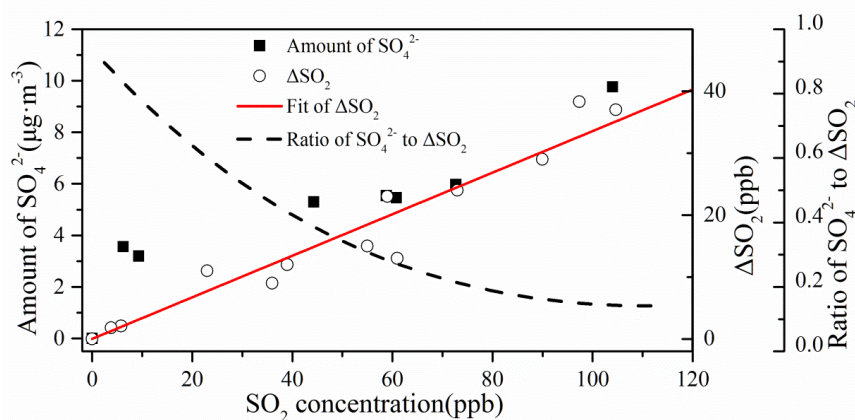10   **in the initial cyclohexene measurements.**

17

Atmospheric
Chemistry
and Physics
Discussions

Figure 3: The amount of SO_4^{2-} in aerosols, consumption of SO_2 (ΔSO_2) and the ratio of the amount of SO_2 for SO_4^{2-} formation to ΔSO_2 with different initial SO_2 concentrations.
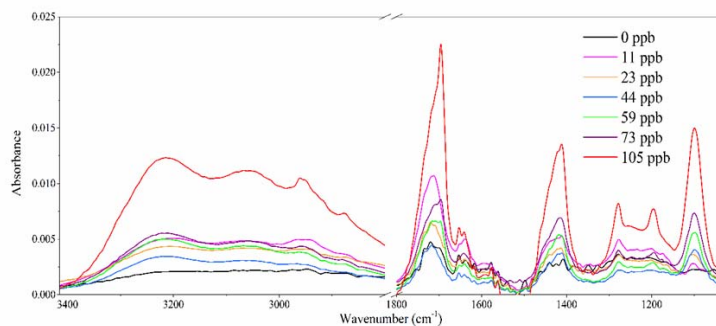
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Figure 4: IR spectra of aerosols from cyclohexene/NOx/SO₂ system under different SO₂ concentrations.
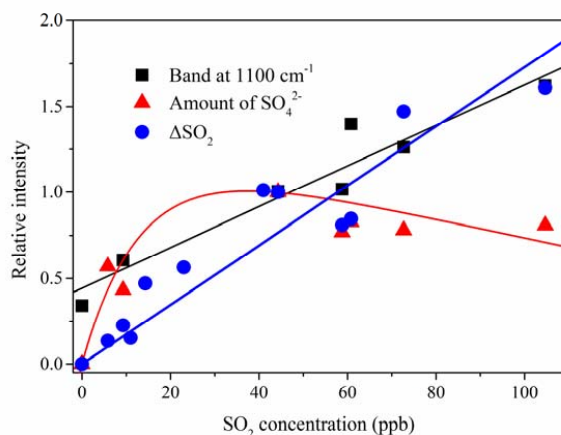
Figure 5: The relative intensity of the band at 1100 cm^{-1} (square), the amount of SO$_4^{2-}$ (triangle) and ΔSO$_2$ (circle) of unit mass of aerosols. The relative intensity was set to 1 when the initial SO$_2$ concentration was 44.3 ppb.
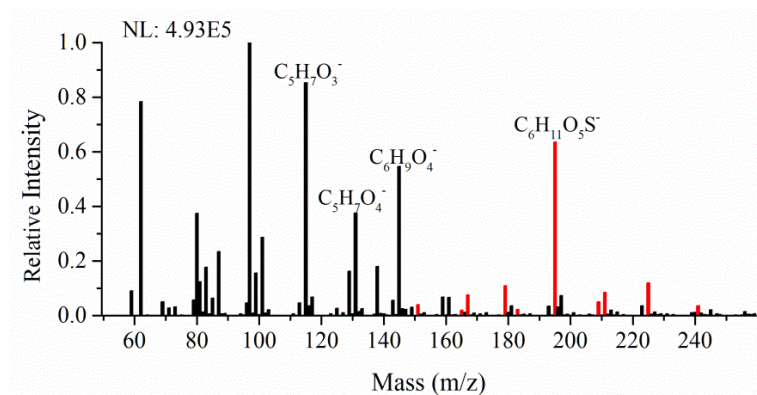
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Figure 6: Negative ion mode ESI mass spectrum of SOA generated from the photooxidation of cyclohexene in the presence of SO$_2$. Red peaks correspond to formulae containing sulfonic acid group. The mass resolution is 10^5.

10

19

Atmospheric
Chemistry
and Physics
Discussions

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Table 1. 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-NOx conditions

Measured [a] m/z	Ion	Proposed Ion Formula	Delta [b] (ppm)	RDB [c]
115.03942		$C_5H_7O_3^-$	-5.628	2
145.05019		$C_6H_9O_4^-$	-3.048	2
131.03444		$C_5H_7O_4^-$	-4.136	2
101.06006	(M−H)⁻	$C_5H_9O_2^-$	-7.351	1
87.04433		$C_4H_7O_2^-$	-9.453	1
129.05515		$C_6H_9O_3^-$	-4.397	2
99.04439		$C_5H_7O_2^-$	-7.702	2
Organosulfates				
195.03322		$C_6H_{11}O_5S^-$	-0.243	1
225.00771		$C_6H_9O_7S^-$	1.171	2
179.00181		$C_5H_7O_5S^-$	-0.0879	2
211.02828		$C_6H_{11}O_6S^-$	0.464	1
167.00167	(M−H)⁻	$C_4H_7O_5S^-$	-1.780	1
209.01257		$C_6H_9O_6S^-$	0.182	2
151.00658		$C_4H_7O_4S^-$	-3.130	1
241.00278		$C_6H_9O_8S^-$	1.738	2
182.99667		$C_4H_7O_6S^-$	-1.158	1
164.98594		$C_4H_5O_5S^-$	-2.287	2

[a] Sort by abundance intensity.

[b] Delta: label the peak with the difference between the theoretical and measured m/z.

5   [c] RDB: ring and double bond equivalent.