

The authors sincerely thank the Reviewer for the careful review and thoughtful comments, which are very helpful in improving our manuscript. Comments from the Reviewer are reproduced in black font. [Our point-by-point responses to the comments raised by the Reviewer are indicated in blue font below](#) and [the revised text in the manuscript is shown in red.](#)

Reviewer: 1

The manuscript by Yang et al. describes a set of laboratory measurements, in which they investigated SO₂ effects on the formation and chemical composition of particles from anthropogenic volatile organic compound ozonolysis. Various monomeric and dimeric products with C, H, and O atoms were observed under SO₂-free conditions. The authors found that SO₂ presence can induce the formation of sulfur-containing compounds. They suggested that the observed sulfur-containing compounds have stronger ability for particle formation than corresponding precursors, leading to an enhancement of particle formation. Structures and reasonable formation mechanisms of these sulfur-containing compounds were also proposed. Overall, the experimental design, results, and discussion of this manuscript are presented in a logical sequence that is easy to follow and understand. The paper provides new and valuable results for our understanding of the details of SO₂ roles in aerosol formation, and also guidance and inspiration for the community that reads ACP. Therefore, I would recommend the publication of this work if the author consider the minor comments below.

Specific comments:

The authors did a great job of explaining the reasons why their study would be of importance and interest. However, there is just brief text regarding the influences of SO₂ on aerosol chemistry. Some recent literatures should be considered.

Deng, P. S. J. Lakey, Y. Wang, P. Li, J. Xu, H. Pang, J. Liu, X. Xu, X. Li, X. Wang, Y. Zhang, M. Shiraiwa and S. Gligorovski, Daytime SO₂ chemistry on ubiquitous urban surfaces as a source of organic sulfur compounds in ambient air, *Sci. Adv.*, 2022, 8,

eabq6830.

Wang, T. Liu, J. Jang, J. P. D. Abbatt and A. W. H. Chan, Heterogeneous interactions between SO₂ and organic peroxides in submicron aerosol, *Atmos. Chem. Phys.*, 2021, 21, 6647-6661.

Response:

The literatures recommended by the Reviewer have been cited in the revised manuscript.

The following text was also added in the Introduction section to complement the influences of SO₂ on aerosol composition.

Page 2, Line 39:

Recently, the impacts of inorganic gases on aerosol chemistry have received significant attention (Deng et al., 2022).

Page 2, Line 51:

For instance, under humid condition, the reactive uptake of SO₂ onto organic aerosols was obvious and reactions of SO₂ with organic peroxides could contribute to organosulfate (OS) formation (Wang et al., 2021a; Ye et al., 2018). H₂SO₄ originated from sCI-induced oxidation of SO₂ is also linked to OS production (Stangl et al., 2019).

P4, L92. The authors mentioned that cyclohexane was injected into the chamber to scavenge OH radical. It is also worth mentioning how did the authors determine that OH had been successfully scavenged.

Response:

Aerosol yield from OH oxidation of cyclohexane is relatively low, and cyclohexane hardly reacts with O₃. Therefore, cyclohexane is commonly employed to isolate SOA formation from the additional impacts of OH formed in the gas-phase reaction of O₃ with alkenes (Bracco et al., 2019; Carlsson et al., 2012; Sato et al., 2013; Ng et al., 2006).

In this work, cyclohexane was introduced into the chamber at sufficient concentration (~130 ppm) so that more than 98% of OH generated during the ozonolysis of cyclooctene were scavenged. Control experiments were also carried out,

and the corresponding results showed that the presence of cyclohexane could lead to the significant decrease in particle volume concentration (Fig. R1).

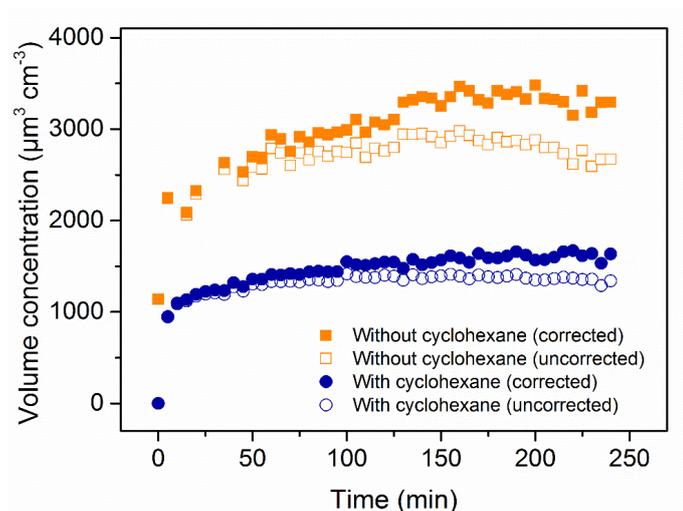


Figure R1. Particle volume concentration as a function of time during the ozonolysis of cyclooctene with and without cyclohexane addition.

For clarification, the following text was inserted in the experimental method section, and Fig. R1 was added in the revised supplement.

Page 4, Line 95:

Cyclohexane (99.5%, Aladdin) was injected in excess (~130 ppm) into the chamber so that more than 98% of OH generated during the ozonolysis of cyclooctene were scavenged. Control experiments showed that the presence of cyclohexane could lead to the significant decrease in particle volume concentration (Fig. S1).

P5, L118 and L128. Particle production experiments were carried out as batch mode experiments. Therefore, the chemical reaction systems were evolving during the ozonolysis of anthropogenic volatile compound. During which reaction period of the experiments did the authors collect aerosol particles? Please indicate this information.

Response:

Aerosol particles were collected 300 min after the reaction initiation. For clarification, the following sentence was added in the method section.

Page 5, Line 115:

The particle formation experiments proceeded for 300 min before the collection of aerosol particles.

P6, L130. It should be also stated clear how the extraction was done (i.e., whole filter or punches? device?)

Response:

The original sentence has been revised to show more details about the extraction method.

Page 6, Line 139:

The whole sample filters were extracted twice into 5 mL of methanol (Optima[®] LC-MS grade, Fisher Scientific) by ice sonication (KQ5200E, Kunshan Ultrasonic Instruments, China) for 20 min.

P7, L162–167. Perhaps it is better for the understanding of readers to include some relevant citations.

Response:

The KMD method has been widely applied for the analysis of mass spectra of organic aerosols. For clarification, the following sentence and references were added in the revised manuscript.

Page 7, Line 178:

The KMD value is same for homologous species that differ from each other only by their base units.

Kenseth, C. M., Hafeman, N. J., Huang, Y., Dalleska, N. F., Stoltz, B. M., and Seinfeld, J. H.: Synthesis of Carboxylic Acid and Dimer Ester Surrogates to Constrain the Abundance and Distribution of Molecular Products in alpha-Pinene and beta-Pinene Secondary Organic Aerosol, *Environ. Sci. Technol.*, 54, 12829-12839, 10.1021/acs.est.0c01566, 2020.

Kundu, S., Fisseha, R., Putman, A. L., Rahn, T. A., and Mazzoleni, L. R.: Molecular formula composition of β -caryophyllene ozonolysis SOA formed in humid and dry

conditions, *Atmos. Environ.*, 154, 70-81, 10.1016/j.atmosenv.2016.12.031, 2017.

P7, L168. Full equation from Li et al. (2016) should be given.

Response:

The following formulation has been updated in the revised manuscript.

$$\log_{10} C_i^o = (n_C^0 - n_C^i) b_C - n_O^i b_O - 2 \frac{n_C^i n_O^i}{n_C^i + n_O^i} b_{CO} - n_N^i b_N - n_S^i b_S$$

P9, L225. From Fig. S2, the volume concentration of aerosol particles reached its maximum within 240 min. So, what is the definition of the initial stage of particle production experiment?

Response:

Once O₃ was introduced into the reactor, cyclooctene began to be oxidized and aerosol particles were produced rapidly. Based on the initial concentrations of O₃ (~800 ppb) and cyclooctene (~200 ppb) as well as the reaction rate constant ($4.51 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), the reaction of cyclooctene with O₃ could be completed within several minutes. GC-FID measurements also indicated that cyclooctene was completely consumed within 10 minutes after the ozonolysis was initiated. When cyclooctene was depleted, aerosol particle mass increased slowly. Therefore, the initial stage of particle formation in this work was defined as the time (~10 min) from reaction initiation to the complete consumption of cyclooctene.

Now, the definition of the initial stage of particle production experiment is provided in the revised manuscript.

Page 10, line 242:

Once O₃ was introduced into the reactor, aerosol particles were produced rapidly. After cyclooctene was depleted, the aerosol particle mass increased slowly. The initial stage of particle formation was then defined as the time from reaction initiation to the complete consumption of cyclooctene (~10 min).

The authors mentioned that the enhancement of aerosol particles was mainly due to the formation of inorganic and organic sulfates. Although wall losses of organic vapors may be negligible as the author discussed, previous studies suggest that increased particle surface area by SO₂ may cause the increase in particle volume concentration. Would this be a possible clarification?

Response:

As suggested by the Reviewer, condensation of organic vapors onto aerosol particles can compete with wall losses of organic vapors. To better investigate the roles of SO₂ via increasing particle surface in promoting particle formation, we calculated the timescales associated with gas-particle partitioning equilibrium (τ_{g-p} , s) and gas-wall equilibrium (τ_{g-w} , s) based on the method of Zhang et al. (2014). More details about this method are shown below.

(a) Gas-wall equilibrium. The wall-loss process of gas-phase products is generally taken into account to be first-order and the first-order wall-loss coefficient of gas-phase products, k_w (s⁻¹), can be calculated as

$$k_w = \frac{A}{V} \times \frac{0.25\alpha_w\bar{c}}{1.0 + \frac{\pi}{2} \times \frac{\alpha_w\bar{c}}{4(k_e D_{gas})^{0.5}}} \quad (R1)$$

where A/V (5.55 m⁻¹) is the surface to volume ratio of Teflon reactor; α_w is the mass accommodation coefficient of gas-phase products onto the inner wall and an α_w value of 10⁻⁵ was employed (Matsunaga and Ziemann, 2010; Zhang et al., 2014); \bar{c} (m s⁻¹) is the molecules' mean thermal speed; k_e (s⁻¹) and D_{gas} (m² s⁻¹) are the eddy diffusion coefficient and the molecular diffusivity, respectively. A k_e value of 0.02 s⁻¹ was adopted (McMurry and Grosjean, 1985). D_{gas} was estimated to be 6 × 10⁻⁶ m² s⁻¹ (Krechmer et al., 2017; Tang et al., 2015). MW (g mol⁻¹) is molecular weight of the given gas-phase product. An average molecular weight of 200 g mol⁻¹ for gas-phase products was used to estimate the influence of vapor wall loss (Sarrafzadeh et al., 2016).

The mean thermal speed could be determined according to the following equation:

$$\bar{c} = \sqrt{\frac{8RT}{\pi MW}} \quad (R2)$$

where R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T (K) are the ideal gas constant and experimental temperature, respectively.

The time required to approach gas-wall equilibrium (τ_{g-w} , s) can be calculated as:

$$\tau_{g-w} = \frac{1}{k_w} \quad (\text{R3})$$

(b) Gas-particle equilibrium. The time associated with approaching gas-particle equilibrium (τ_{g-p} , s) can be determined using the following equation:

$$\tau_{g-p} = \frac{1}{2\pi N_p \overline{D_p} D_{gas} \overline{F_{FS}}} \quad (\text{R4})$$

where N_p ($\# \text{ m}^{-3}$) and $\overline{D_p}$ (m) are the number concentration and mean diameter of aerosol particles, respectively; D_{gas} ($\text{m}^2 \text{ s}^{-1}$) is the molecular diffusivity. $\overline{F_{FS}}$ is the Fuchs-Sutugin correction and it is equal to:

$$\overline{F_{FS}} = \frac{0.75\alpha_p(1+k_n)}{k_n^2 + k_n + 0.283k_n\alpha_p + 0.75\alpha_p} \quad (\text{R5})$$

where α_p is the mass accommodation coefficient of gas-phase products onto aerosol particles. An α_p value of 0.7 was adopted (Krechmer et al., 2017). K_n is the Knudsen number, which can be calculated as:

$$k_n = \frac{2\lambda}{D_p} \quad (\text{R6})$$

The gas mean free path (λ , nm) of gas-phase product is defined as:

$$\lambda = \frac{3D_{gas}}{\overline{c}} \quad (\text{R7})$$

The value of τ_{g-w} was determined to be around 20.4 ± 0.01 min. The estimated τ_{g-p} value decreased from 0.13 ± 0.01 to 0.07 ± 0.01 min when SO_2 concentrations increased from 0 to 129 ppb. Gas-particle partitioning could dominate the wall deposition of gas-phase products for particle number concentrations in our chamber experiments. Therefore, the roles of SO_2 via increasing particle surface in promoting particle formation may be negligible.

For clarification, the following details about the calculation of gas-particle

partitioning equilibrium and gas-wall equilibrium were inserted into the revised supplement.

S1. Estimation of wall losses of organic vapors

(a) Gas-wall equilibrium. The wall-loss process of gas-phase products is generally taken into account to be first-order and the first-order wall-loss coefficient of gas-phase products, k_w (s^{-1}), can be calculated as

$$k_w = \frac{A}{V} \times \frac{0.25\alpha_w\bar{c}}{1.0 + \frac{\pi}{2} \times \frac{\alpha_w\bar{c}}{4(k_e D_{gas})^{0.5}}} \quad (S1)$$

where A/V (5.55 m^{-1}) is the surface to volume ratio of Teflon reactor; α_w is the mass accommodation coefficient of gas-phase products onto the inner wall and an α_w value of 10^{-5} was employed (Matsunaga and Ziemann, 2010; Zhang et al., 2014); \bar{c} (m s^{-1}) is the molecules' mean thermal speed; k_e (s^{-1}) and D_{gas} ($\text{m}^2 \text{ s}^{-1}$) are the eddy diffusion coefficient and the molecular diffusivity, respectively. A k_e value of 0.02 s^{-1} was adopted (McMurry and Grosjean, 1985). D_{gas} was estimated to be $6 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ (Krechmer et al., 2017; Tang et al., 2015). MW (g mol^{-1}) is molecular weight of the given gas-phase product. An average molecular weight of 200 g mol^{-1} for gas-phase products was used to estimate the influence of vapor wall loss (Sarrafzadeh et al., 2016).

The mean thermal speed could be determined according to the following equation:

$$\bar{c} = \sqrt{\frac{8RT}{\pi MW}} \quad (S2)$$

where R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T (K) are the ideal gas constant and experimental temperature, respectively.

The time required to approach gas-wall equilibrium (τ_{g-w} , s) can be calculated as:

$$\tau_{g-w} = \frac{1}{k_w} \quad (S3)$$

(b) Gas-particle equilibrium. The time associated with approaching gas-particle equilibrium (τ_{g-p} , s) can be determined using the following equation:

$$\tau_{g-p} = \frac{1}{2\pi N_p \bar{D}_p D_{gas} F_{FS}} \quad (S4)$$

where N_p ($\# \text{ m}^{-3}$) and \overline{D}_p (m) are the number concentration and mean diameter of aerosol particles, respectively; D_{gas} ($\text{m}^2 \text{ s}^{-1}$) is the molecular diffusivity. \overline{F}_{FS} is the Fuchs-Sutugin correction and it is equal to:

$$\overline{F}_{FS} = \frac{0.75\alpha_p(1+k_n)}{k_n^2 + k_n + 0.283k_n\alpha_p + 0.75\alpha_p} \quad (\text{S5})$$

where α_p is the mass accommodation coefficient of gas-phase products onto aerosol particles. An α_p value of 0.7 was adopted (Krechmer et al., 2017). K_n is the Knudsen number, which can be calculated as:

$$k_n = \frac{2\lambda}{D_p} \quad (\text{S6})$$

The gas mean free path (λ , nm) of gas-phase product is defined as:

$$\lambda = \frac{3D_{gas}}{\overline{c}} \quad (\text{S7})$$

The value of τ_{g-w} was determined to be around 20.4 ± 0.01 min. The estimated τ_{g-p} value decreased from 0.13 ± 0.01 to 0.07 ± 0.01 min when SO_2 concentrations increased from 0 to 129 ppb. Gas-particle partitioning could dominate the wall deposition of gas-phase products for particle number concentrations in our chamber experiments.

P17, L378. Could you provide some more details about the IR absorption of different functional groups? Perhaps in the Supplement?

Response:

The IR absorption of assigned functional groups are summarized in the following Table, and they have been inserted in the revised supplement.

Table R1. IR absorption of functional groups.

Assignment	Wavenumber	References
	(cm ⁻¹)	
H-bonding of OH in alcohol	3600–3200	(Hung et al., 2013)
H-bonding of carboxylic acid	3200–2400	(Sax et al., 2005)
aliphatic CH	3000–2800	(Sax et al., 2005)
C=O in carboxylic acid/ketone/aldehyde/ester	1750–1685	(Hung et al., 2013)
OH of alcohol in-plane deformation vibration	1440–1260	
C-O stretching in primary alcohol	1090–1000	
C-O stretching in secondary alcohol	1150–1075	
C-O stretching in tertiary alcohol	1210–1100	
C-O stretching in carboxylic acid	1320–1210	
C-O stretching in peroxide	1150–1030	
asymmetric SO ₂ stretching	1415–1370	
C-O-C stretching	1050–1010	(Liu et al., 2015)
C-O-C stretching in acetal	1085	(Lal et al., 2012)
symmetric SO ₂ stretching	1064	(Lal et al., 2012)
C-O vibration of C-O-S	1050–1030	(Hung et al., 2013)
asymmetric SO stretching	1020–850	(Hung et al., 2013)
C-O-C stretching in ether	950	(Lin et al., 2014)
O-O stretching in peroxide	900–800	(Hung et al., 2013)
asymmetric C-O-S stretching	875	(Tammer, 2004)
symmetric C-O-S stretching	750	

P19, L 396. The Reviewer would recommend the author to present briefly the strengths of ESI-MS in characterizing organosulfate. This may be significant in supporting the production of organosulfate.

Response:

Traditional analytical methods, for example GC-MS techniques, failed to measure organosulfates (Surratt et al., 2007). In contrast, UHPLC-HRMS coupled with ESI has been recognized as a robust and effective method for the analysis of organosulfate in aerosol samples (Riva et al., 2016; Bruggemann et al., 2020; Wang et al., 2021b). Organosulfates could undergo highly efficient ionization to give deprotonated

molecular ions in negative ion mode without derivatization. Orbitrap MS with high sensitivity and molecular specificity allows us to accurately assign an amount of mass spectral signals to organosulfates (Eliuk and Makarov, 2015; Bruggemann et al., 2020). Furthermore, unambiguous identification of organosulfates can be achieved based on tandem mass spectrometry analysis because organosulfates could give characteristic fragment ions at m/z 80 (SO_3^-), 81 (HSO_3^-), and/or 97 (HSO_4^-).

The following text has been added to enrich the description about ESI-MS in the revised manuscript.

Page 20, Line 415:

OS could undergo highly efficient ionization to give deprotonated molecular ions in negative ion mode. Based on MS/MS analysis, unambiguous identification of OS can be achieved since OSs could give characteristic fragment ions at m/z 80 (SO_3^-), 81 (HSO_3^-), and/or 97 (HSO_4^-) in their MS/MS spectra.

P22, Figure 7. The legend “Precursor” is confusing since cyclooctene is also referred to as a precursor in this manuscript. Suggest different legend such as organosulfate precursor or something else.

Response:

Legend has been updated in the revised manuscript as follows:

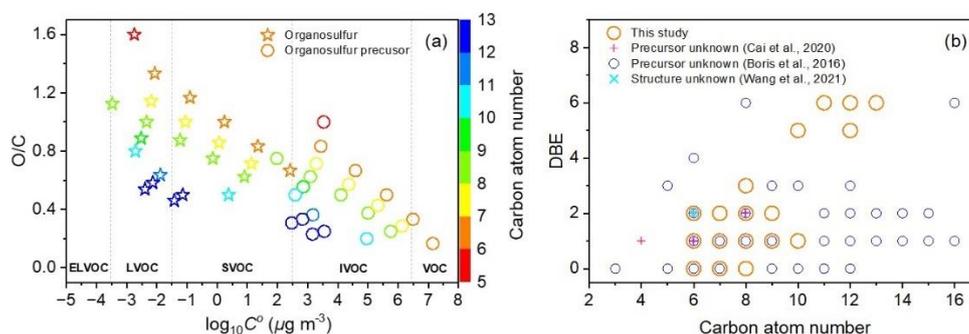


Figure 7. (a) Two dimensional volatility–oxidation space of the identified organosulfurs and their precursors. (b) Carbon atom number distribution of organosulfurs observed in the current work and in the studies of Cai et al. (2020), Boris et al. (2016), and Wang et al. (2021). Detailed formulae of these OSs can be found in Table S3. Organosulfurs from previous studies are of unknown origin or unknown structure.

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Wang, Y., Zhao, Y., Wang, Y., Yu, J.-Z., Shao, J., Liu, P., Zhu, W., Cheng, Z., Li, Z., Yan, N., and Xiao, H.: Organosulfates in atmospheric aerosols in Shanghai, China: seasonal and interannual variability, origin, and formation mechanisms, *Atmos. Chem. Phys.*, 21, 2959-2980, 10.5194/acp-21-2959-2021, 2021b.

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The authors sincerely thank the Reviewer for the careful review and thoughtful comments, which are very helpful in improving our manuscript. Comments from the Reviewer are reproduced in black font. Our point-by-point responses to the comments raised by the Reviewer are indicated in blue font below and the revised text in the manuscript is shown in red.

Reviewer: 2

General comments:

This paper describes the enhancement of aerosol formation in the presence of SO₂ during cyclooctene ozonolysis. The composition of the formed SOA was investigated by means of ATR-FTIR and LC-MS/MS and the authors found that the enhancement was largely attributed to the formation of H₂SO₄ and organosulfates (OSs). By using high-resolution MS/MS, the molecular structures of many OSs were proposed in this work. I think that this study was well-conducted and that the data presented here are valuable for the understanding of the SOA formation. In addition, the paper is generally well-written. I recommend this paper to be published in Atmospheric Chemistry and Physics after the authors' consideration of my minor comments detailed below.

Specific comments:

Page 4, Section 2.1: It is better to show the rate constant for the reaction of cyclooctene with O₃.

Response:

We provided the reaction rate constant (k) for the reaction of cyclooctene with O₃ ($k_{298\text{K}} = 4.51 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) in the Introduction section in the original text. For clarity, this rate constant was also showed in Section 2.1 in the revised manuscript.

Page 5, Table 1: There is no information about the reaction time. Is it 300 min?

Response:

Particle formation experiments were operated in a batch mode and aerosol particles were collected at 300 min after reaction initiation. For clarification, the following sentence was added in the method section.

Page 5, Line 115:

The particle formation experiments proceeded for 300 min before the collection of aerosol particles.

I guess that the reaction of cyclooctene with O₃ was completed within several minutes. Why did the authors measure for such the long reaction time?

Response:

The reaction of cyclooctene with O₃ is rapid. Once O₃ was introduced into the reactor, cyclooctene began to be oxidized and aerosol particles were produced accordingly.

Here, particle production experiments were performed in a batch mode. Therefore, the reaction systems were complicated over the course of particle formation. Cyclooctene could be completely consumed within 10 min based on GC-FID measurements but aerosol growth did not stop at the time when cyclooctene was depleted. As shown in Fig. R1, the uncorrected particle volume concentration can reach its maximum at 100 min after reaction initiation and remain constant at 100–200 min. If the apparent aerosol volume concentration measured by SMPS reaches its maximum and remains constant, it means aerosol production has not stopped yet. We would expect the aerosol volume concentration to go down once the wall loss processes take over. Thus, the aerosol volume concentration was measured continuously until we observed the decrease in aerosol volume concentration within 300 min. After wall loss correction was applied, the particle volume concentration reached its maximum at 240 min (Fig. R1).

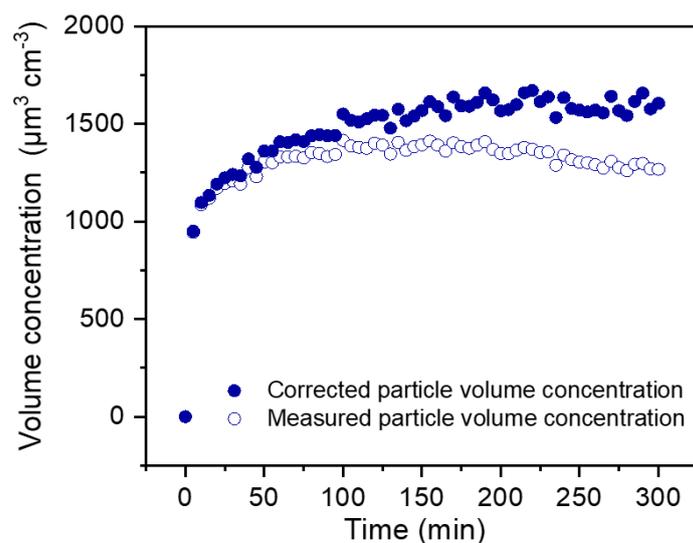


Figure R1. Time series of the volume concentration of aerosol particles during the ozonolysis of cyclooctene.

To further clarify the goal of our experiments, the following text has been inserted in the revised manuscript

Page 4, Line 92:

Particle formation experiments were operated in a batch mode.

Page 4, Line 114:

The particle volume concentration was measured continuously until we observed a decrease.

Page 17, Lines 383-387: In Hawkins et al (2010), an absorption band at 876 cm^{-1} was mentioned for organosulfates. There is no mention about an absorption band of organosulfates in Coury and Dillner (2008). How did the authors attribute absorption bands at 1413 and 1095 cm^{-1} to organosulfates? Is there any additional evidence?

Response:

We summarized IR absorption peak assignments in Table R1. The IR spectra of organosulfates may have different absorption bands. For example, asymmetric and symmetric stretching of $-\text{SO}_2-$ could result in strong absorbances at 1415–1370 cm^{-1} and $\sim 1064 \text{ cm}^{-1}$, respectively. The S=O vibration occurs at 1020–850 cm^{-1} . The asymmetric and symmetric stretching vibration of C-O-S could contribute to weak absorbances around at 875 cm^{-1} and 750 cm^{-1} , respectively. It should be noted that the

specific positions of these absorption bands could be affected by electronegative substituents and the nature of alkyl groups (Tammer, 2004).

Table R1. IR absorption of functional groups.

Assignment	Wavenumber	References	
	(cm^{-1})		
H-bonding of OH in alcohol	3600–3200	(Hung et al., 2013)	
H-bonding of carboxylic acid	3200–2400	(Sax et al., 2005)	
aliphatic CH	3000–2800	(Sax et al., 2005)	
C=O in carboxylic acid/ketone/aldehyde/ester	1750–1685	(Hung et al., 2013)	
OH of alcohol in-plane deformation vibration	1440–1260		
C-O stretching in primary alcohol	1090–1000		
C-O stretching in secondary alcohol	1150–1075		
C-O stretching in tertiary alcohol	1210–1100		
C-O stretching in carboxylic acid	1320–1210		
C-O stretching in peroxide	1150–1030		
asymmetric SO_2 stretching	1415–1370		(Tammer, 2004)
C-O-C stretching	1050–1010		(Liu et al., 2015)
C-O-C stretching in acetal	1085		(Lal et al., 2012)
symmetric SO_2 stretching	1064	(Lal et al., 2012)	
C-O vibration of C-O-S	1050–1030	(Hung et al., 2013)	
asymmetric SO stretching	1020–850	(Hung et al., 2013)	
C-O-C stretching in ether	950	(Lin et al., 2014)	
O-O stretching in peroxide	900–800	(Hung et al., 2013)	
asymmetric C-O-S stretching	875	(Tammer, 2004)	
symmetric C-O-S stretching	750		

Here, the IR absorptions by sulfur-containing functional groups were detected at 1413, 1095, and 617 cm^{-1} in the ATR-FTIR spectra of particles formed in the presence of SO_2 . Xu et al. (2021) measured the functional groups of β -pinene SOA in the absence and presence of SO_2 and also observed similar IR results. Absorption bands at 1413 and 1095 may be associated with the asymmetric and symmetric stretching of $-\text{SO}_2-$ while inorganic sulfates could give rise to strong absorption at 617 cm^{-1} . In the study of

Hawkins et al. (2010), the absorbance of C-O-S group at 876 cm^{-1} was measured and used to quantify the relative contribution of organosulfates to organic aerosols. However, detectable absorption bands of C-O-S did not appear in our spectra. Maria et al. (2003) showed that the IR absorptivity of C-O-S group at 876 cm^{-1} (0.031) is 10 times smaller than that of inorganic sulfate at 618 cm^{-1} (0.41). The weak absorption peak of C-O-S at $\sim 876\text{ cm}^{-1}$ may be overlapping by the absorption of other functional groups and is thus difficult to identify. Therefore, we further performed high-resolution MS measurements of aerosol particles to determine whether organosulfates were produced in the presence of SO_2 .

We have double checked our citation and the inappropriate reference that was cited accidentally has been deleted. Now, right references have been added in the revised manuscript.

Table R1 was added as Table S1 in the revised supplement, and the original text was revised as follows:

Page 18, Line 401:

Three additional absorption bands at 1413 , 1095 , and 617 cm^{-1} were observed in ATR-FTIR spectra of particles formed with the introduction of SO_2 (Tammer, 2004; Lal et al., 2012). Absorption bands at 1413 and 1095 cm^{-1} may be associated with the asymmetric and symmetric stretching of $-\text{SO}_2-$ while inorganic sulfates could give rise to strong absorption at 617 cm^{-1} . The presence of absorption band of sulfur-containing groups suggests that SO_2 addition can result in the production of sulfur-containing compounds.

Page 21, Figure 6: In this figure, the formation of many kinds of compounds having hydroxy groups is proposed. Actually, many of ion signals obtained by LC-MS/MS were assigned to compounds having hydroxy groups. But it seems that the peak of alcohol-COH in the ATR-FTIR ($3500\text{-}3200\text{ cm}^{-1}$) is quite smaller than that of carbonyl at 1702 cm^{-1} . Is it reasonable?

Response:

FTIR has been widely employed to investigate the chemical composition of SOA. Similar ATR-FTIR spectra of SOA were observed in previous laboratory studies (Fig. R2). For example, Zhao et al. (2016) identified multifunctional compounds containing hydroxy groups as important components of SOA formed from the ozonolysis of α -cedrene (Table R2). Carbonyl group ($\sim 1700\text{ cm}^{-1}$) also had strongest intensity among all characterized functional groups (Fig. R2b).

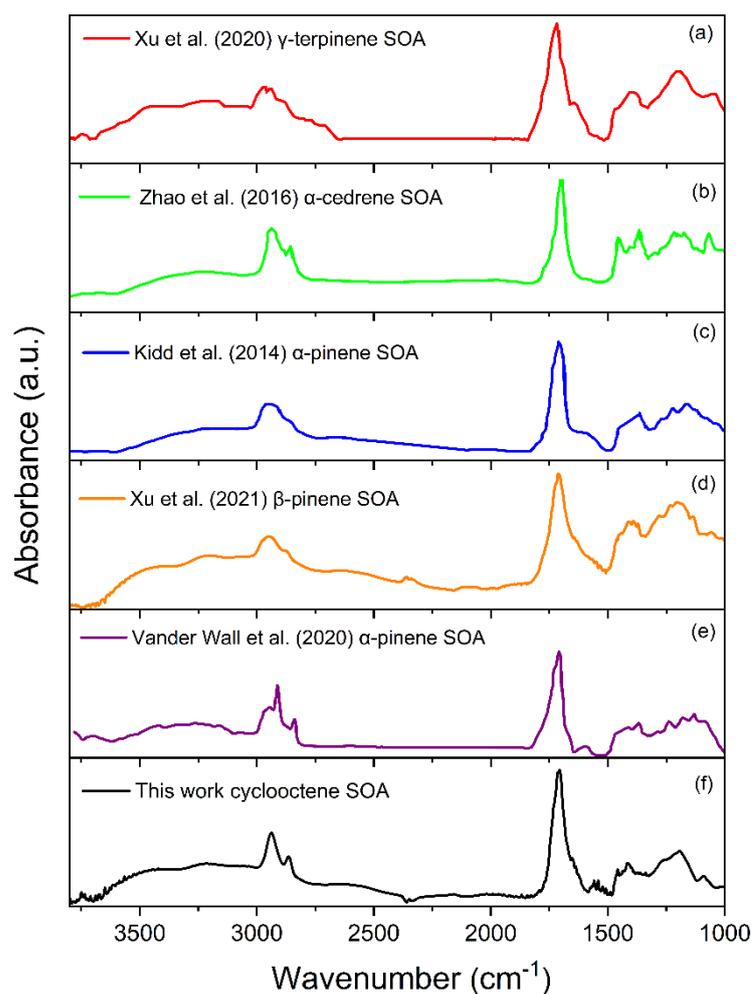


Figure R2. ATR-FTIR spectra for SOA generated from the ozonolysis of different alkenes. (a) γ -terpinene SOA (Xu et al., 2020); (b) α -cedrene SOA (Zhao et al., 2016); (c) α -pinene SOA (Kidd et al., 2014); (d) β -pinene SOA (Xu et al., 2021); (e) α -pinene SOA (Vander Wall et al., 2020); (f) cyclooctene SOA (this work). Initial experimental conditions are given in detail in Table R3.

Table R2. Potential structures of identified monomers and dimers in Zhao et al. (2016).

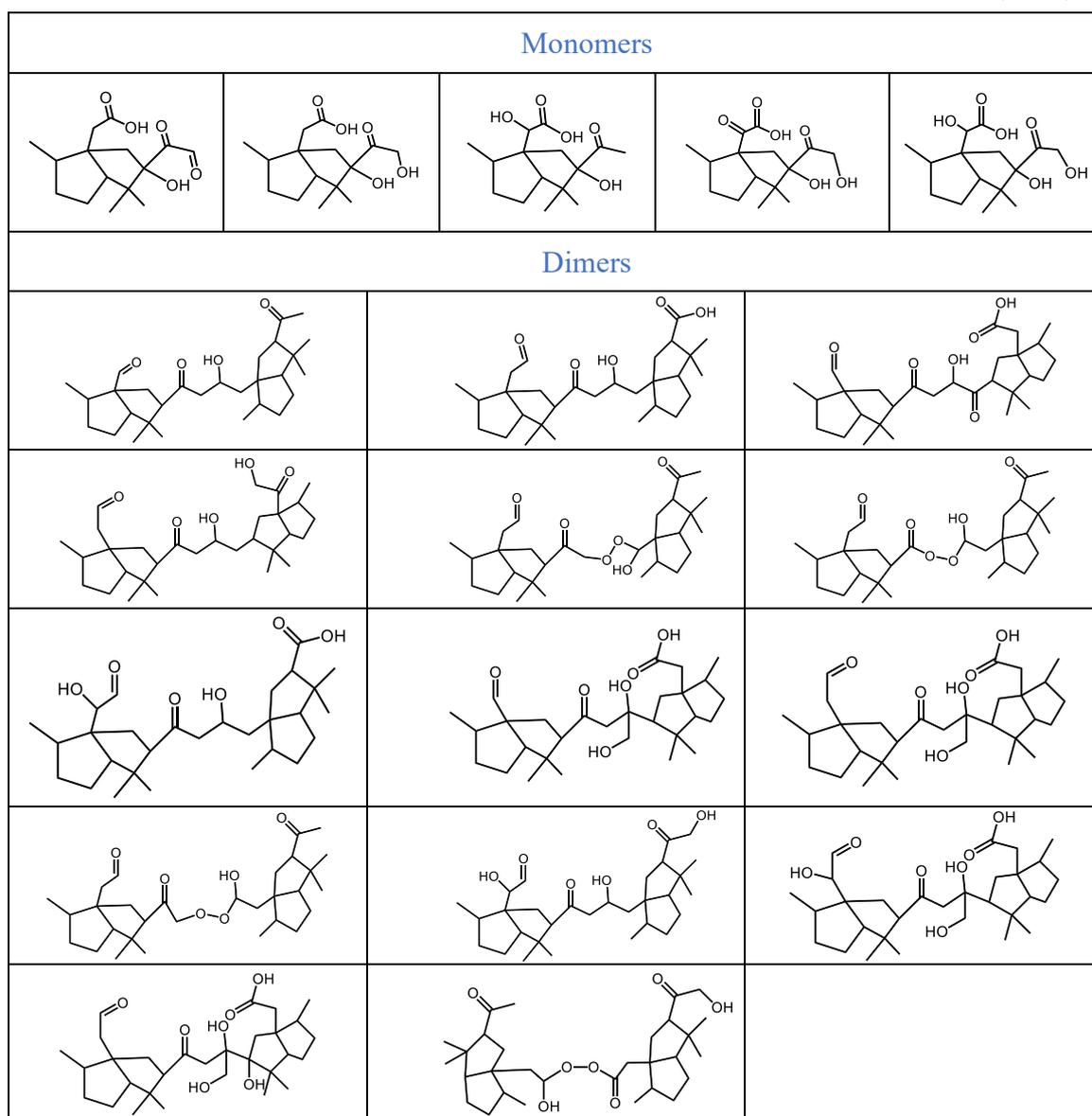


Table R3. Initial experimental conditions of SOA formation from the ozonolysis of alkenes.

VOC type	[VOC] ₀	[O ₃] ₀	T	RH	OH scavenger	Reference
	(ppb)	(ppb)	(K)	(%)		
γ-terpinene	302	1236	292	17	cyclohexane	(Xu et al., 2020)
α-cedrene	215	1500	295 ± 1	< 5	/	(Zhao et al., 2016)
α-pinene	1000	1000	297 ± 2	< 3	/	(Kidd et al., 2014)
β-pinene	154	624	300	22	cyclohexane	(Xu et al., 2021)
α-pinene	250	250–300	295–298	< 5	cyclohexane	(Vander Wall et al., 2020)
cyclooctene	195	839	296	25	cyclohexane	This work

In this work, we used FTIR to determine the overall functional groups of aerosol particles rather than individual oxidized products. At the molecular level, SOA is significantly complex as it may include hundreds to thousands of oxidized products. The results shown in Fig. 6 do not represent the entire aerosol components or compounds of high concentration but are some possible precursors with alcohol group for organosulfate formation. Carbonyl groups are also present in these alcohol skeletons. Furthermore, the ozonolysis of alkene could produce organic species containing one or more carbonyl groups (Mackenzie-Rae et al., 2018; Zhao et al., 2016). Therefore, it is reasonable that the peak intensity of alcohol group (3600-3200 cm^{-1}) is lower than that of carbonyl group ($\sim 1702 \text{ cm}^{-1}$).

Page 22, Figure 7: I think that the calculation of DBE (eqn. (1)) cannot be applied to organosulfates. I think that the DBE of precursors of OSs is meaningful.

Response:

The DBE value of a compound could reflect its unsaturation degree. For a given compound with elemental composition of $\text{C}_c\text{H}_h\text{O}_o\text{N}_n\text{S}_s$, the DBE value (number of rings and double bonds) could be calculated based on the following equation (Deng et al., 2022; Vandergrift et al., 2022; Wang et al., 2019).

$$\text{DBE} = 1 + c + \frac{n - h}{2} \quad (\text{R1})$$

We have double checked and read our references. Many studies on organosulfate formation used eq. R1 to calculate the DBE value of organosulfates and the two S=O bonds in each sulfate group of organosulfates were not taken into account (Wang et al., 2016; Riva et al., 2016; Kuang et al., 2016). Therefore, the DBE value of organosulfates reflects the degree of unsaturation for the side carbon chain. For example, in the study of Riva et al. (2016), the $\text{C}_{10}\text{H}_{18}\text{O}_6\text{S}$ organosulfate was characterized during the photooxidation of dodecane. Riva et al. (2016) reported that $\text{C}_{10}\text{H}_{18}\text{O}_6\text{S}$ corresponded to two DBEs, which arose from a six-membered ring and an internal carbonyl group (Fig. R3).

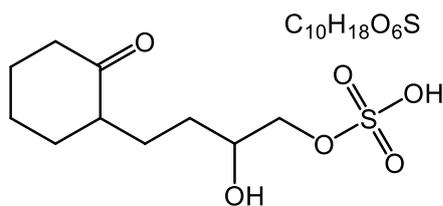


Figure R3. Structure of organosulfate ($C_{10}H_{18}O_6S$), which was extracted from Figure 2 in Riva et al. (2016).

We calculated the DBE value of organosulfates for the same consideration as in the previous studies (Wang et al., 2016; Riva et al., 2016; Kuang et al., 2016). The following notes have been added in the revised manuscript.

Page 7, Line 172:

For organosulfate, the two S=O bonds in the sulfate group were not considered based on calculations in previous studies (Wang et al., 2016; Riva et al., 2016; Kuang et al., 2016). The DBE value of organosulfate reflects the unsaturation degree of its side carbon chain.

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SO₂ enhances aerosol formation from anthropogenic volatile organic compound ozonolysis by producing sulfur-containing compounds

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Abstract. Sulfur dioxide (SO₂) can affect aerosol formation in the atmosphere, but the
10 underlying mechanisms remain unclear. Here, we investigate aerosol formation and
composition from the ozonolysis of cyclooctene with and without SO₂ addition in a
smog chamber. Liquid chromatography equipped with high-resolution tandem mass
spectrometry measurements indicate that monomer carboxylic acids and corresponding
dimers with acid anhydride and aldol structures are important components in particles
15 formed in the absence of SO₂. A 9.4–12.6 time increase in particle maximum number
concentration is observed in the presence of 14–192 ppb SO₂. This increase is largely
attributed to sulfuric acid (H₂SO₄) formation from the reactions of stabilized Criegee
intermediates with SO₂. In addition, a number of organosulfates (OSs) are detected in
the presence of SO₂, which are likely products formed from the heterogeneous reactions
20 of oxygenated species with H₂SO₄. The molecular structures of OSs are also identified
based on tandem mass spectrometry analysis. It should be noted that some of these OSs
have been found in previous field studies but were classified as compounds from
unknown sources or of unknown structures. The observed OSs are less volatile than
their precursors and therefore are more effective contributors to particle formation and
25 growth, partially leading to the increase in particle volume concentration under SO₂-
presence conditions. Our results provide an in-depth molecular-level insight into how
SO₂ alters particle formation and composition.

1 Introduction

Secondary organic aerosol (SOA) accounts for a large fraction of the organic aerosol mass. The atmospheric oxidation of anthropogenic volatile organic compounds (AVOCs) can produce low-volatility organic products that contribute to SOA formation and growth (Kelly et al., 2018; Fan et al., 2020). The oxidation of AVOCs can dominate SOA formation under severe haze episodes (Nie et al., 2022; He et al., 2020; Huang et al., 2019; Qiu et al., 2020). Thus, AVOCs have been commonly considered as significant SOA precursors. SOA can negatively impact air quality, global climate, and public health (Nault et al., 2021; Zhu et al., 2017). To better understand air pollution and develop effective particle control strategies, it is necessary to investigate the formation mechanism and molecular composition of anthropogenic SOA.

Recently, the impacts of inorganic gases on aerosol chemistry have received significant attention (Deng et al., 2022). In particular, there is increasingly much evidence that sulfur dioxide (SO_2) can modulate SOA formation and composition (Ye et al., 2018; Stangl et al., 2019; Liu et al., 2017). Liu et al. (2017) reported that SOA formation from cyclohexene photooxidation was inhibited by atmospherically relevant concentrations of SO_2 , as a result of the reaction of hydroxyl radical ($\cdot\text{OH}$) with SO_2 (to form sulfuric acid (H_2SO_4)) competing with the $\cdot\text{OH}$ reaction with cyclohexene. They demonstrated that H_2SO_4 -catalyzed SOA enhancement was not sufficient to compensate for the loss of $\cdot\text{OH}$ reactivity towards cyclohexene, leading to the suppression in cyclohexene SOA formation. On the other hand, SO_2 can enhance SOA formation and alter SOA composition by interacting with organic peroxides or stabilized Criegee intermediate (sCI) during the ozonolysis of alkenes (Stangl et al., 2019; Ye et al., 2018). For instance, under humid condition, the reactive uptake of SO_2 onto organic aerosols was obvious and reactions of SO_2 with organic peroxides could contribute to organosulfate (OS) formation (Wang et al., 2021a; Ye et al., 2018). H_2SO_4 originated from sCI-induced oxidation of SO_2 is also linked to OS production (Stangl

55 *et al.*, 2019). OSs have been detected in different SO₂-alkene interaction areas (Hettiyadura *et al.*, 2019; Wang *et al.*, 2018; Bruggemann *et al.*, 2020). Ubiquitous OSs may be used as tracers of SOA influenced by SO₂ emissions (Bruggemann *et al.*, 2020). To further gain mechanistic insights into the complex roles of SO₂ in SOA formation, it is important to explore the chemical nature and formation mechanism of OSs.

60 Cycloalkenes emitted from diesel vehicles and industrial processes are a crucial class of AVOCs in the atmosphere. They can be used to explore key chemical processes involved in atmospheric oxidation and SOA formation (Räty *et al.*, 2021). However, SOA formation chemistry from cycloalkenes has received less attention than that from linear or branched alkenes, leading to significant uncertainties in our understanding of
65 SOA. Recent studies have reported that ozonolysis of cycloalkenes could form highly oxidized products and have considerable SOA yield (Räty *et al.*, 2021; Rissanen, 2018). Among the most common cycloalkenes (with 5 to 8 carbon atoms), cyclooctene has the largest potential to SOA formation (Keywood *et al.*, 2004). Ozonolysis is the dominant oxidation pathway of cyclooctene with a reaction rate constant of $4.51 \times 10^{-16} \text{ cm}^3$
70 $\text{molecule}^{-1} \text{ s}^{-1}$ (298 K). Urban atmosphere is highly complex and may contain various concentrations of cycloalkenes and SO₂, which complicates SOA formation and composition. While most previous studies have identified compounds containing carbon, hydrogen, and oxygen atoms (CHO compounds) as important contributors to cycloalkene SOA (Hamilton *et al.*, 2006; Gao *et al.*, 2004; Räty *et al.*, 2021), the
75 potential of OS formation from the ozonolysis of cyclooctene in the presence of SO₂ and the chemical processes behind OS formation remain unclear.

Given the significance of cycloalkene and SO₂ emissions in aerosol formation, we investigated the SO₂ effects on the formation and chemical composition of cyclooctene SOA. Aerosol particles were formed from the ozonolysis of cyclooctene in the absence
80 and presence of SO₂ in a smog chamber. Structural identifications of the observed products were reported and corresponding formation mechanisms were proposed. We report the mechanism showing how SO₂ impacts particle formation and growth based

on the observation of sulfuring-containing compounds. Our results provide a more comprehensively mechanistic understanding of the roles of SO₂ in modulating SOA formation and composition.

2 Experimental methods

2.1 Particle production

Particle formation from the ozonolysis of cyclooctene ($k_{298\text{ K}} = 4.51 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) was carried out under dark conditions in a 1.2 m³ Teflon chamber housed in a temperature-controlled room. A summary of experimental conditions and results is listed in Table 1. Detailed experimental equipment and methods have been described in our previous studies (Yang et al., 2022; Yang et al., 2021). Particle formation experiments were operated in a batch mode. Briefly, cyclooctene was introduced into the chamber by passing zero air through a tube containing a known volume of cyclooctene (95%, Alfa). Then, cyclohexane (99.5%, Aladdin) was injected in excess (~130 ppm) into the chamber so that more than 98% of OH generated during the ozonolysis of cyclooctene were scavenged. Control experiments showed that the presence of cyclohexane could lead to the significant decrease in particle volume concentration (Fig. S1). When desired, SO₂ was added to the chamber from a SO₂ calibration cylinder. Initial concentration ratios of SO₂ to cyclooctene were in the range of ~0.07–1 ppb ppb⁻¹ to simulate different polluted atmospheric conditions. The reactor was stabilized for 20 min under dark conditions to allow for mixing of species. Finally, ozonolysis of cyclooctene was initiated by introducing O₃ produced via a commercial ozone generator (WH-H-Y5Y, Wohuan, China). All experiments were performed at room temperature (~295 K) and atmospheric pressure (~1 atm) without seed particles. Temperature and relative humidity (RH) inside the chamber were measured with a hygrometer (Model 645, Testo AG, Germany). O₃ and SO₂ concentrations over the course of ozonolysis were monitored by a Thermo Scientific model 49i O₃ analyzer and a Thermo Scientific model 43i-TLE SO₂ analyzer, respectively. The detection limits of

110 O₃ analyzer and SO₂ analyzer were 0.5 ppb and 0.05 ppb, respectively. Size
distributions and volume concentrations of particles were continuously recorded using
a scanning mobility particle sizer (SMPS), which consisted of differential mobility
analyzer (Model 3082, TSI, USA) and ultrafine condensation particle counter (Model
3776, TSI, USA). The particle volume concentration was measured continuously until
115 we observed a decrease. The particle formation experiments proceeded for 300 min
before the collection of aerosol particles.

Table 1. Experimental conditions and results for particle formation experiments.

[Cyclooctene] ₀ (ppb)	[O ₃] ₀ (ppb)	T (K)	RH (%)	SO ₂ (ppb)	ΔSO ₂ ^a (ppb)	V _{H₂SO₄} ^b (μm ³ cm ⁻³)	N _{max} ^c ×10 ⁶ (cm ⁻³)	V _{particle} ^d (μm ³ cm ⁻³)
195	839	296	25	-	-	-	0.14	151 ± 2.9
195	770	294	24	14	3.7	9.4	1.31	170 ± 5.7
195	800	294	22	28	8.9	22.6	1.05	191 ± 5.5
195	792	293	21	50	9.6	24.5	1.06	228 ± 4.2
195	730	292	20	100	9.5	24.3	1.54	264 ± 7.4
195	790	293	23	154	17.2	43.8	1.28	270 ± 5.0
191	743	295	24	192	14.2	35.9	1.77	280 ± 8.2

^a ΔSO₂ represents the consumed SO₂ concentration during the ozonolysis of cyclooctene.

120 ^b The volume concentration of particle-phase H₂SO₄ assuming a full conversion of SO₂ to
H₂SO₄ with a density of 1.58 g cm⁻³ under moderate humidity conditions (Wyche et al., 2009; Ye et
al., 2018).

^c N_{max} denotes the maximum number concentration of aerosol particles during the ozonolysis
of cyclooctene.

125 ^d V_{particle} is the volume concentration of aerosol particles, which has been corrected for wall
loss of particles. Errors represent standard deviation for particle formation experiments.

2.2 Particle collection and chemical characterization

Aerosol particles were collected on aluminum foils using a 14-stage low-pressure impactor (DLPI+, Dekati Ltd, Finland). All samples were stored in -20 °C freezer until
130 analysis. Offline functional group measurements of aerosol particles were performed using an attenuated total reflectance-Fourier transform infrared spectrometer (ATR-FTIR, Vertex 70, Bruker, Germany). Before each measurement, the diamond crystal was thoroughly cleaned with ethanol and ultrapure water to eliminate the interference of ambient contaminants on functional group measurements of aerosol particles. ATR-
135 FTIR spectra of blank aluminum foils and aerosol samples were recorded in the range of 4000–600 cm⁻¹ at a resolution of 4 cm⁻¹ with 64 scans. The data of ATR-FTIR spectra were recorded with the OPUS software.

Aerosol particles were also collected on polytetrafluoroethylene (PTFE) filters (0.22 µm pore size, 47 mm diameter, TJMF50, Jinteng, China). **The whole sample filters were extracted twice into 5 mL of methanol (Optima® LC-MS grade, Fisher Scientific) by ice sonication (KQ5200E, Kunshan Ultrasonic Instruments, China) for 20 min.** Extracts were then filtered, concentrated to near dryness and subsequently reconstituted in 200 µL of 50:50 (v/v) methanol and ultrapure water. Blank filters were also subjected to the same extraction and preparation procedure. Obtained extracts of blank and
145 sample filters were analyzed using a Thermo Scientific ultrahigh-performance liquid chromatograph, which was coupled with a high-resolution Q Exactive Focus Hybrid Quadrupole-Orbitrap mass spectrometer equipped with an electrospray ionization (ESI) source (UHPLC/ESI-HRMS). Samples were first separated on an Atlantis T3 C18 column (100 Å pores, 3 µm particle size, 2.1 mm × 150 mm, Waters, USA) at 35 °C.
150 The used binary mobile phase system consisted of ultrapure water with 0.1% (v/v) formic acid (A) and methanol with 0.1% (v/v) formic acid (B). The LC gradient employed was as follows: 0–3 min at 3% B, 3–25 min increased linearly to 50% B, 25–43 min ramped linearly to 90% B, 43–48 min returned to 3% B, and 48–60 min B held constant at 3% to re-equilibrate the column. The injected volume of samples and flow

155 rate were 2 μL and 200 $\mu\text{L min}^{-1}$, respectively. The ESI source was operated in both
positive (+) and negative (-) ion modes to ionize analyte components with a scan range
of mass-to-charge (m/z) 50 to 750. LC/ESI-MS parameter settings were as follows: 3.5
kV spray voltage (+), -3.0 kV spray voltage (-), 50 V S-lens radio frequency (RF) level
(+), 50 V S-lens RF level (-), 320 $^{\circ}\text{C}$ capillary temperature, 2.76×10^5 Pa sheath gas
160 (nitrogen) pressure, and 3.33 L min^{-1} auxiliary gas (nitrogen) flow. Data-dependent
tandem mass spectrometry (MS/MS) analysis were also carried out by high-energy
collision-induced dissociation (CID) with stepped collision energies of 20, 40, and 60
eV. For MS/MS experiments, an isolation width of 2 m/z units was applied. Other
parameters were also selected in MS/MS experiments as follows: 2×10^5 automatic
165 gain control (AGC) target, 50 ms maximum IT, 3 loop count, 1×10^5 minimum AGC
target, 2–6 s apex trigger, and 6 s dynamic exclusion. The mass resolution of MS and
MS/MS were 70000 (full width at half maximum, FWHM, at m/z 200) and 17500,
respectively. Detailed data processes are reported elsewhere (Yang et al., 2021; Yang et
al., 2022).

170 The double bond equivalent (DBE) value is the combined number of rings and
double bonds in the product $\text{C}_c\text{H}_h\text{O}_o\text{N}_n\text{S}_s$ and could be calculated according to eq. 1.
For organosulfate, the two S=O bonds in sulfate group were not considered based on
calculations in previous studies (Wang et al., 2016; Riva et al., 2016b; Kuang et al.,
2016). The DBE value of organosulfate reflects the unsaturation degree of its side
175 carbon chain.

$$\text{DBE} = 1 + c + \frac{n - h}{2} \quad (1)$$

Kendrick mass defect (KMD) analysis could provide chemical insights into
chemical compositions of complex organic mixtures (Kundu et al., 2017; Kenseth et al.,
2020). The KMD value is same for homologous species that differ from each other only
by their base units. CH_2 and the oxygen atom (O) are usually chosen as base units for
180 Kendrick analysis of complex organic mass spectra. Kendrick mass (KM) could be
converted into a new mass scale from the IUPAC mass (eq. 2 and 4). KMD is

determined as the difference between the nominal mass of a compound (the rounded integer mass) and KM (eq. 3 and 5).

$$\text{KM}_{\text{CH}_2} = m/z \times \frac{14.00000}{14.01565} \quad (2)$$

$$\text{KMD}_{\text{CH}_2} = \text{Nominal mass} - \text{KM}_{\text{CH}_2} \quad (3)$$

$$\text{KM}_{\text{O}} = m/z \times \frac{16.00000}{15.99492} \quad (4)$$

$$\text{KMD}_{\text{O}} = \text{Nominal mass} - \text{KM}_{\text{O}} \quad (5)$$

The saturation mass concentration (C° , $\mu\text{g m}^{-3}$) of product i was also calculated based on its elemental composition using the following expression (Li et al., 2016):

$$\log_{10} C_i^{\circ} = (n_{\text{C}}^0 - n_{\text{C}}^i) b_{\text{C}} - n_{\text{O}}^i b_{\text{O}} - 2 \frac{n_{\text{C}}^i n_{\text{O}}^i}{n_{\text{C}}^i + n_{\text{O}}^i} b_{\text{CO}} - n_{\text{N}}^i b_{\text{N}} - n_{\text{S}}^i b_{\text{S}} \quad (6)$$

where n_{C}^0 is the reference carbon number; n_{C}^i , n_{O}^i , n_{N}^i , and n_{S}^i represent the numbers of carbon, oxygen, nitrogen, and sulfur atoms, respectively; b_{C} , b_{O} , b_{N} , and b_{S} denote the contribution of each carbon, oxygen, nitrogen, and sulfur atom to $\log_{10} C_i^{\circ}$; and b_{CO} is the carbon–oxygen nonideality.

2.3 Wall loss corrections

The wall loss rates of O_3 and SO_2 inside the chamber were determined to be $2.05 \times 10^{-4} \text{ min}^{-1}$ and $2.02 \times 10^{-4} \text{ min}^{-1}$ (Fig. S2), respectively, indicating that the losses of these two gas-phase species to the chamber walls were negligible over the course of experiments. The wall loss of cyclooctene ($5.23 \times 10^{-6} \text{ min}^{-1}$) was also negligible while its oxidation products may deposit to the inner walls. However, wall losses of gas-phase products could be mitigated due to excess O_3 concentration (Sect. S1). The quick oxidation and nucleation could provide attractive condensation surfaces for oxidation products, thereby reducing the product wall losses to some extent (Stirnweis et al., 2017). Although wall losses of organic vapors may underestimate the particle mass, this work mainly focuses on the characterization of particle composition rather than the absolute SOA yield.

Independent wall-loss experiments of ammonium sulfate $((\text{NH}_4)_2\text{SO}_4)$ particles

were also performed to determine the size-dependent wall-loss rate constants of particles inside the chamber. An aqueous $(\text{NH}_4)_2\text{SO}_4$ solution was added to a TSI Model 205 3076 atomizer to produce droplets. The droplets were passed through a silica gel diffusion dryer to get dry $(\text{NH}_4)_2\text{SO}_4$ particles and then were injected into the chamber. The size distributions of $(\text{NH}_4)_2\text{SO}_4$ particles were characterized using the SMPS for 6 h. The relationship between the wall-loss rate (k , h^{-1}) of particles and their size (d_p , nm) can be expressed as $k(d_p) = 1.20 \times 10^{-7} \times d_p^{2.32} + 20.59 \times d_p^{-1.39}$ based on size-dependent 210 particle wall-loss correction method.

3 Results and discussion

3.1 SO_2 effects on aerosol formation

Insights into SO_2 effects on particle formation could be gained through investigating the number and volume concentration as well as size distribution of 215 particles under various SO_2 level conditions. In the absence of SO_2 , the particle number concentration increased burst within the first 20 min of cyclooctene ozonolysis and then decreased because of their coagulation and wall depositions, while the particle volume concentration increased gradually and reached its maximum within 240 min (Fig. S3). Elevating SO_2 level can result in significant increases in the number and volume 220 concentration of particles (Fig. 1a), which is consistent with observations from previous studies (Ye et al., 2018; Yang et al., 2021). We observed a 9.4–12.6 time increase in particle maximum number concentration in the presence of 14–192 ppb SO_2 (Table 1). The promoted effect of SO_2 is shown more clearly in Fig. 1b, where SO_2 was seen to be consumed on similar timescale as particle formation. Specifically, upon initiation of 225 cyclooctene ozonolysis, SO_2 concentration decreased and the particle volume concentration increased simultaneously. After cyclooctene was completely consumed, both SO_2 consumption and particle production slowed down. SO_2 consumption and particle formation resumed when more cyclooctene was introduced into the reactor. This result indicates that SO_2 may react with certain highly reactive species produced

230 from cyclooctene ozonolysis. For instance, reactions of SO_2 with sCI could form H_2SO_4 (Boy et al., 2013), which is a key specie for new particle formation (Lehtipalo et al., 2018; Yao et al., 2018). Inorganic sulfate absorption at 617 cm^{-1} was observed in the ATR-FTIR spectra of particles formed in cyclooctene/ O_3 / SO_2 systems (Fig. 2) (Hawkins et al., 2010; Coury and Dillner, 2008), indicating the formation of H_2SO_4 . We
235 assumed that all consumed SO_2 was converted to particle-phase H_2SO_4 , which represents an upper limit of the H_2SO_4 formation (Wyche et al., 2009; Ye et al., 2018). The amount of H_2SO_4 produced could not fully account for the enhancement of particle volume concentration (Table 1). H_2SO_4 has been considered as an important driver of particle acidity (Tilgner et al., 2021). Acid catalysis induced by H_2SO_4 may also
240 promote the formation of additional organic products, leading to the increase in particle volume concentration (Deng et al., 2021).

SO_2 can also affect the growth of new aerosol particles (Fig. 1c). **Once O_3 was introduced into the reactor, aerosol particles were produced rapidly. After cyclooctene was depleted, the aerosol particle mass increased slowly. The initial stage of particle**
245 **formation was then defined as the time from reaction initiation to the complete consumption of cyclooctene (~10 min).** From Fig. 1c, in the initial stage of ozonolysis (10 min), particles formed in cyclooctene/ O_3 / SO_2 systems had a smaller size mode than those formed in cyclooctene/ O_3 system, which may be attributed to the following two factors. First, oligomers formed from sCI reactions with organic species could partition
250 into the condensed phase to contribute to particle growth (Riva et al., 2017). SO_2 presence may lead to the decrease in these oligomers because SO_2 can compete with organic species to react with sCI. Second, counterbalancing the reduction of oligomers via sCI + SO_2 reactions is the production of H_2SO_4 . The production of more new particles in cyclooctene/ O_3 / SO_2 systems could provide more condensation sinks.
255 Organic vapors that can condense onto particles are dispersed via new particles, resulting in small particle size at the initial phase of cyclooctene/ O_3 / SO_2 systems (Stangl et al., 2019). Interestingly, particles could grow quickly in the presence of SO_2 .

At 300 min reaction time, particles formed in the presence of SO₂ even had slightly larger sizes than those formed in the absence of SO₂. H₂SO₄-catalyzed heterogeneous reactions could produce lower-volatile organic species from higher-volatile reactants in the aerosol phase (Yang et al., 2020; Han et al., 2016). Semi-volatile species could undergo evaporation after partitioning to the aerosol phase while low-volatile products generally have a negligible evaporation rate from the aerosol phase. Low-volatile products formed via H₂SO₄-catalyzed heterogeneous reactions could build particle mass at a rate almost equal to the condensation rate and thus effectively facilitate the particle growth in cyclooctene/O₃/SO₂ systems (Apsokardu and Johnston, 2018).

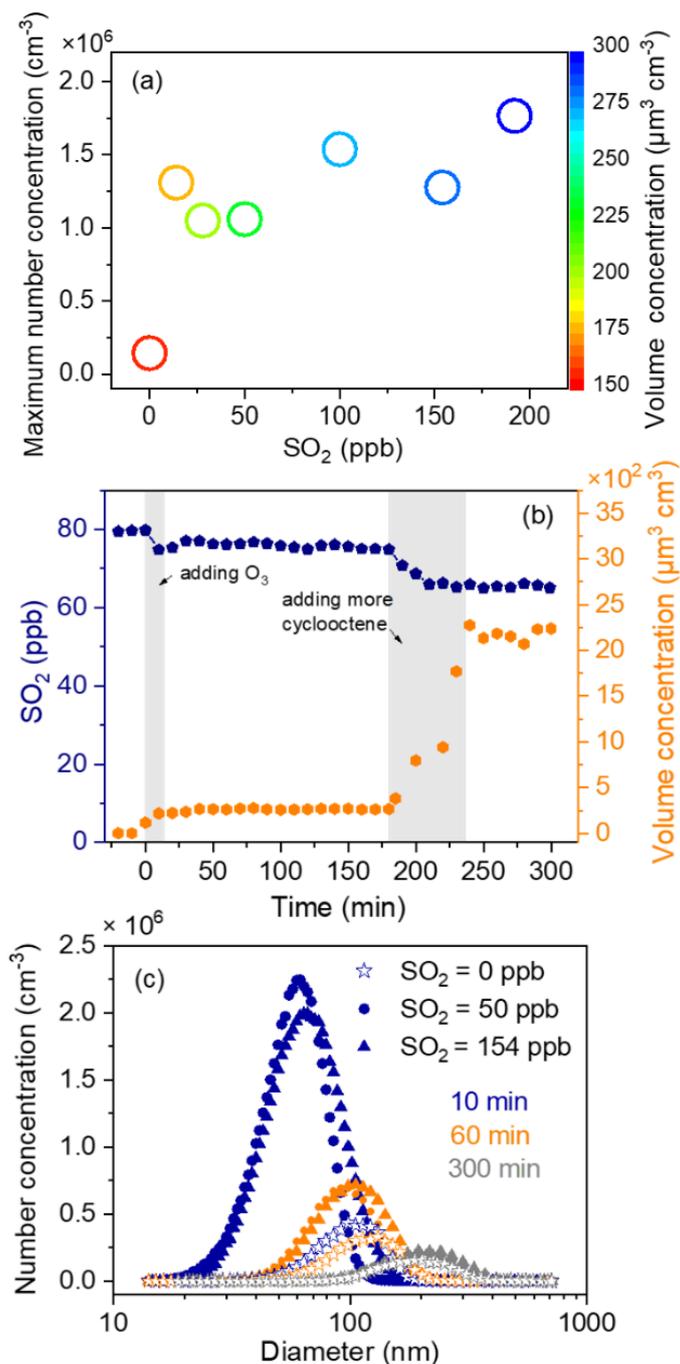
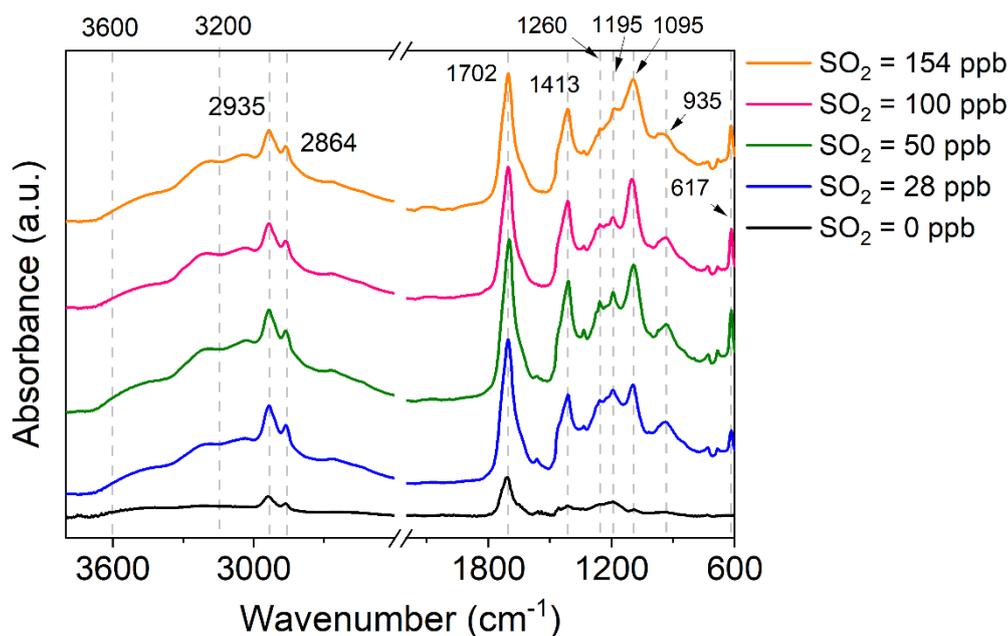


Figure 1. Particle formation from the ozonolysis of cyclooctene under various SO₂ conditions. (a) Maximum particle number concentration as a function of initial SO₂ level. Circle color represents particle volume concentration. (b) Temporal profiles of SO₂ concentration and particle volume concentration. (c) Size distributions of aerosol particles formed with various SO₂ concentrations at 10, 60, and 300 min after the after the initiation of cyclooctene ozonolysis.



275 **Figure 2.** ATR-FTIR spectra of aerosol particles generated from cyclooctene ozonolysis
in the presence of different SO₂ concentration.

3.2 Aerosol chemical composition under SO₂-free condition

Figure 3 shows the base peak chromatograms (BPCs) of cyclooctene-derived particles in the absence of SO₂. The chromatograms of blank filter showed clearly no peaks eluted at retention times (RTs) between 0 and 30 min while there were several significant peaks for cyclooctene SOA chromatograms in both positive and negative ion modes. Each chromatogram peak of cyclooctene SOA represents at least one ion, and major peaks are only labeled with the mass of the most abundant single ion. Compared to the negative chromatogram of cyclooctene SOA, the corresponding label ions in the positive chromatogram were 24 Da higher in mass. This is consistent with the fact that many ions produce adducts with sodium ion ($[M + Na]^+$) in positive ion mode, while negative ion mode leads to the production of deprotonated ions ($[M - H]^-$) (Mackenzie-Rae et al., 2018). From Fig. 3, products with molecular weight (MW) < 200 Da eluted from the column at shorter RT than those with MW > 200 Da. Low-molecular-weight products (MW < 200 Da) likely correspond to small monomer type compounds (hereafter termed as monomeric products), which are directly originated

from the ozonolysis of cyclooctene. Compounds with MW > 200 Da mainly dominate the later part of the chromatogram, and they may be homo or heterodimeric species (hereafter noted as dimeric products) formed using two monomeric products as building blocks.

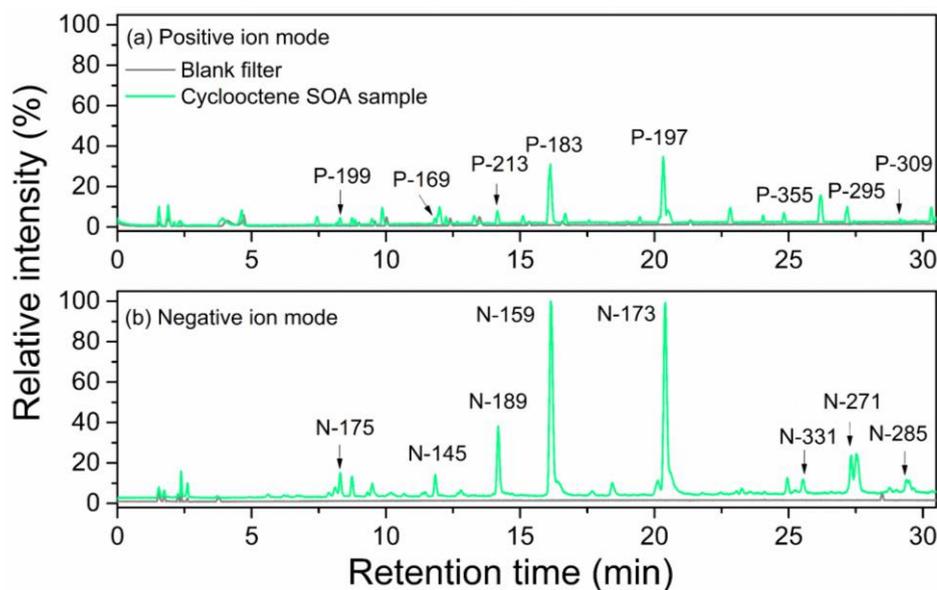
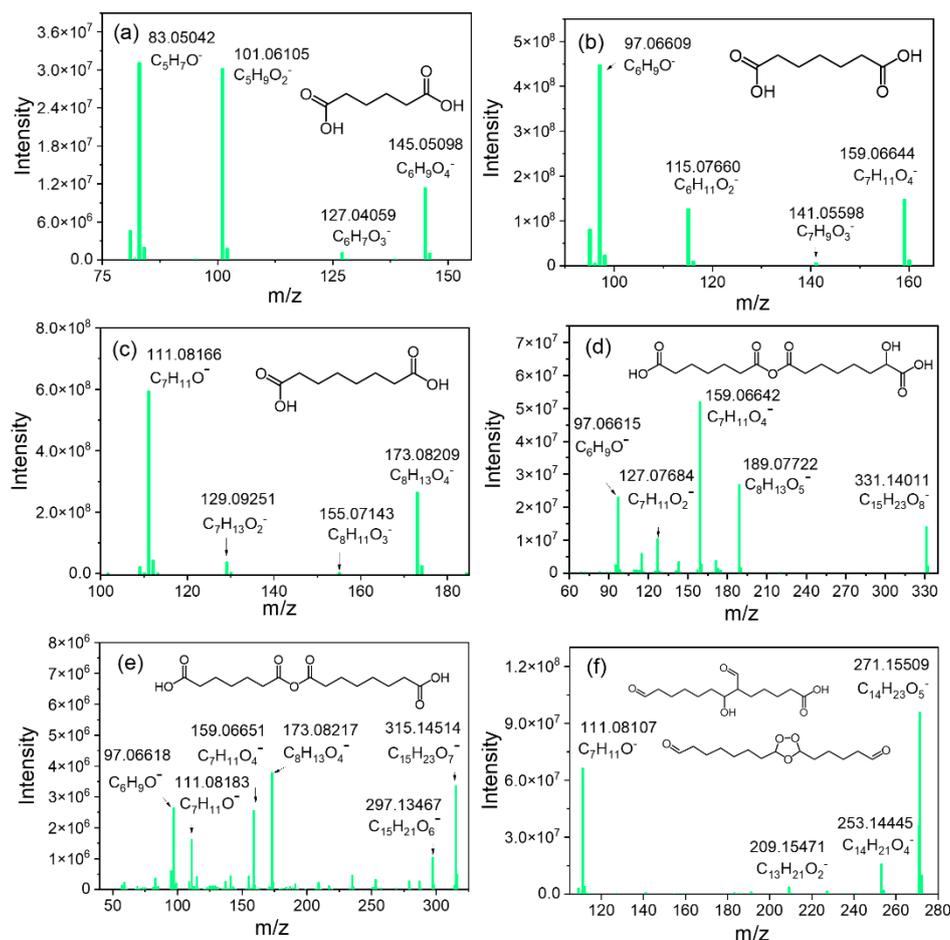


Figure 3. Base peak chromatograms of both blank filter and particles generated from the ozonolysis of cyclooctene in the absence of SO₂. Labels represent the most abundant single ion of each peak. (a) Positive ion mode. (b) Negative ion mode.

Possible structures of major monomeric products were proposed based on their accurate m/z , fragmentation mass spectra, and previous mechanistic insights. Note that the fragmentation of $[M + Na]^+$ is relatively difficult (Zhao et al., 2016) and, thus, the positive ion mode was not further analyzed in providing structural insights in the current study. The negative chromatogram peaks with RT at 11.85 min (N-145), 16.13 min (N-159), and 20.41 min (N-173) were significant peaks for cyclooctene SOA (Fig. 3b), and they were assigned neutral formulas of C₆H₁₀O₄, C₇H₁₂O₄, and C₈H₁₄O₄, respectively. As shown in Fig. 4, MS/MS spectra of monomer C₆H₁₀O₄, C₇H₁₂O₄, and C₈H₁₄O₄ were similar. Taking C₈H₁₄O₄ as example (Fig. 4c), its fragmentation mass spectrum was characterized by a loss of 44 Da (CO₂), suggesting the presence of carboxyl group. The neutral loss of 18 Da (H₂O) upon fragmentation of the parent ion (C₈H₁₃O₄⁻, m/z =

173.08209) led to the production of an ion with m/z 155.07143. The loss of H₂O is an unspecific fragmentation mechanism, which is likely originated from a carboxyl or hydroxyl group (Noziere et al., 2015). The fragment ion ($m/z = 111.08166$) representing the simultaneous neutral losses of CO₂ and H₂O was also formed. MS/MS spectra can be resulted from multiple isomeric structures in many cases (Wang et al., 2019). Yasmeeen et al. (2011) showed the detailed fragmentation spectrum for the dicarboxylic acid standard (azelaic acid) and indicated that deprotonated azelaic acid also showed losses of H₂O, CO₂, and CO₂ + H₂O. In addition, Noziere et al. (2015) showed that the neutral losses of CO₂ and H₂O indicates two carboxyl groups. Thus, monomer C₈H₁₄O₄ was tentatively assigned to suberic acid and the corresponding fragmentation pathways for C₈H₁₃O₄⁻ is proposed in Fig. S4. The fragment ions originated from losses of H₂O, CO₂, and CO₂ + H₂O were also observed in MS/MS spectra of C₆H₁₀O₄ and C₇H₁₂O₄, indicative of adipic acid and pimelic acid, respectively. Carboxylic acids have also been observed in SOA produced from previous alkene ozonolysis (Hamilton et al., 2006; Kenseth et al., 2020; Mackenzie-Rae et al., 2018; Zhang et al., 2015). Carboxylic acids represent a significant class of aerosol components, and they play a significant role in particle chemistry by their influences on particle acidity and through direct involvement in certain heterogeneous reactions to produce low volatile species (Millet et al., 2015). More experiments using available authentic standards are necessary to better understand their structures, sources, and formation mechanism. Other prominent monomer peaks at RTs 8.30 min (N-175) and 14.18 min (N-189) corresponded to compounds with neutral formula, namely C₇H₁₂O₅ and C₈H₁₄O₅. The losses of H₂O, CO, and CO₂ in MS/MS spectrum of C₇H₁₂O₅ indicated hydroxyl, terminal carbonyl, and carboxyl group, respectively (Mackenzie-Rae et al., 2018; Riva et al., 2016a), and C₇H₁₂O₅ was identified as hydroxy-containing oxoheptanoic acid (Fig. S5a and S5c). Monomer C₈H₁₄O₅ only showed losses of H₂O and CO (Fig. S5b), and it is difficult to determine the specific type and positioning of oxygen-containing functionalities within C₈H₁₄O₅ with 5 oxygen atoms based on its MS/MS spectrum.



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Figure 4. MS/MS spectra of major monomers and dimers. Monomers: (a) $C_6H_{10}O_4$, (b) $C_7H_{12}O_4$, and (c) $C_8H_{14}O_4$. Dimers: (d) $C_{15}H_{24}O_8$, (e) $C_{15}H_{24}O_7$, and (f) $C_{14}H_{24}O_5$.

The labeled dimer peaks in negative ion mode corresponded to $[M - H]^-$ ion masses of 271, 285, and 331 (Fig. 3b), which were assigned neutral formulas of $C_{14}H_{24}O_5$, $C_{15}H_{26}O_5$, and $C_{15}H_{24}O_8$, respectively. The number of fragment ions of dimers are generally limited, and determining the exact structure of dimers is less certain compared to monomers (Witkowski and Gierczak, 2017). Therefore, only a decrease in molecular structure possibilities is provided. For dimer $C_{15}H_{24}O_8$, fragment ions m/z 159.06642 ($C_7H_{11}O_4^-$) and m/z 189.07722 ($C_8H_{13}O_5^-$) were detected in its MS/MS spectrum (Fig. 4d). When dimers are subjected to CID, fragment ions corresponding to their building blocks are commonly observed (Witkowski and Gierczak, 2017; Hall and Johnston, 2012). Based on this rule, it could be concluded that dimer $C_{15}H_{24}O_8$ was an association product of $C_7H_{12}O_4$ and $C_8H_{14}O_5$. Similarly, for dimer $C_{15}H_{24}O_7$, there were two

350

significant product ions of $C_{15}H_{23}O_7^-$ with accurate masses of m/z 159.06651 ($C_7H_{11}O_4^-$)
355 and 173.08217 ($C_8H_{13}O_4^-$) (Fig. 4e). Furthermore, fragment ions corresponding to
secondary loss of $CO_2 + H_2O$ from product ions $C_7H_{11}O_4^-$ and $C_8H_{13}O_4^-$ were also
observed. The fragmentation spectrum of $C_{15}H_{24}O_7$ was similar to the MS/MS spectra
of $C_7H_{12}O_4$ and $C_8H_{14}O_4$ (Fig. 4b and 4c), suggesting again that $C_7H_{12}O_4$ and $C_8H_{14}O_4$
may be the building blocks of $C_{15}H_{24}O_7$. Acid-catalyzed heterogeneous processes can
360 result in the formation of high-molecular-weight dimers in both biogenic and
anthropogenic systems (Barsanti et al., 2017). Carboxylic acid monomers formed could
be important sources of particle acidity in the absence of SO_2 . Dimers $C_{15}H_{24}O_7$ and
 $C_{15}H_{24}O_8$ may be produced by heterogeneous reactions involving the loss of a water
molecule, and the linkage between building blocks is an acid anhydride (Fig. S6)
365 (Hamilton et al., 2006). Another abundant dimer peak (N-271) in negative
chromatogram was identified as $C_{14}H_{23}O_5^-$ with mass accuracy of -0.02492 ppm.
 $C_{14}H_{23}O_5^-$ could dissociate to the product ions of $C_{14}H_{21}O_4^-$, $C_{13}H_{21}O_2^-$, and $C_7H_{11}O^-$.
(Fig. 4f). Both secondary ozonide and aldol structures shown in Fig. 4f could match the
assigned elemental formula of $C_{14}H_{24}O_5$. However, the neutral losses of H_2O and CO_2
370 were not easily produced by secondary ozonide, but more likely for the aldol structure
(Hall and Johnston, 2012). Aldol condensation products were also one of the most
commonly observed species in previous ozonolysis of alkenes (Zhao et al., 2016;
Kenseth et al., 2018; Kristensen et al., 2016). Therefore, $C_{14}H_{24}O_5$ shown in Fig. 4f is
likely an aldol condensation product.

375 To examine the overall composition of particles, average mass spectra (Fig. S7)
corresponding to the chromatogram where particle components eluted were also
analyzed. Figure 5 summarizes the oxidation products observed in particles mapped in
O-KMD and van Krevelen plot. The molecular formulas of identified oxidation
products could be largely classified into homologous series of monomers and dimers
380 (Fig. 5a and 5b). The elemental composition distribution of products measured in
positive and negative ion modes was similar, with most monomers and dimers having

O/C ratios ranging from 0.2 to 0.8, and H/C ratios ranging from 1.2 to 1.8 (Fig. 5c). Lines with slopes of 0, -0.5, -1, and -2 in Fig. 5c can be used to illustrate the addition of hydroxyl/peroxide, carboxylic acid (with fragmentation), carboxylic acid (without
385 fragmentation), and carbonyl groups to a saturated carbon chain, respectively (Heald et al., 2010). As shown in Fig. 5c, cyclooctene SOA occupied a relatively wide range in the van Krevelen diagram, and the large number of points scattered in the space between lines with slopes of -0.5 and -2. This behavior is consistent with the importance of high abundance carboxylic acids in the above analysis.

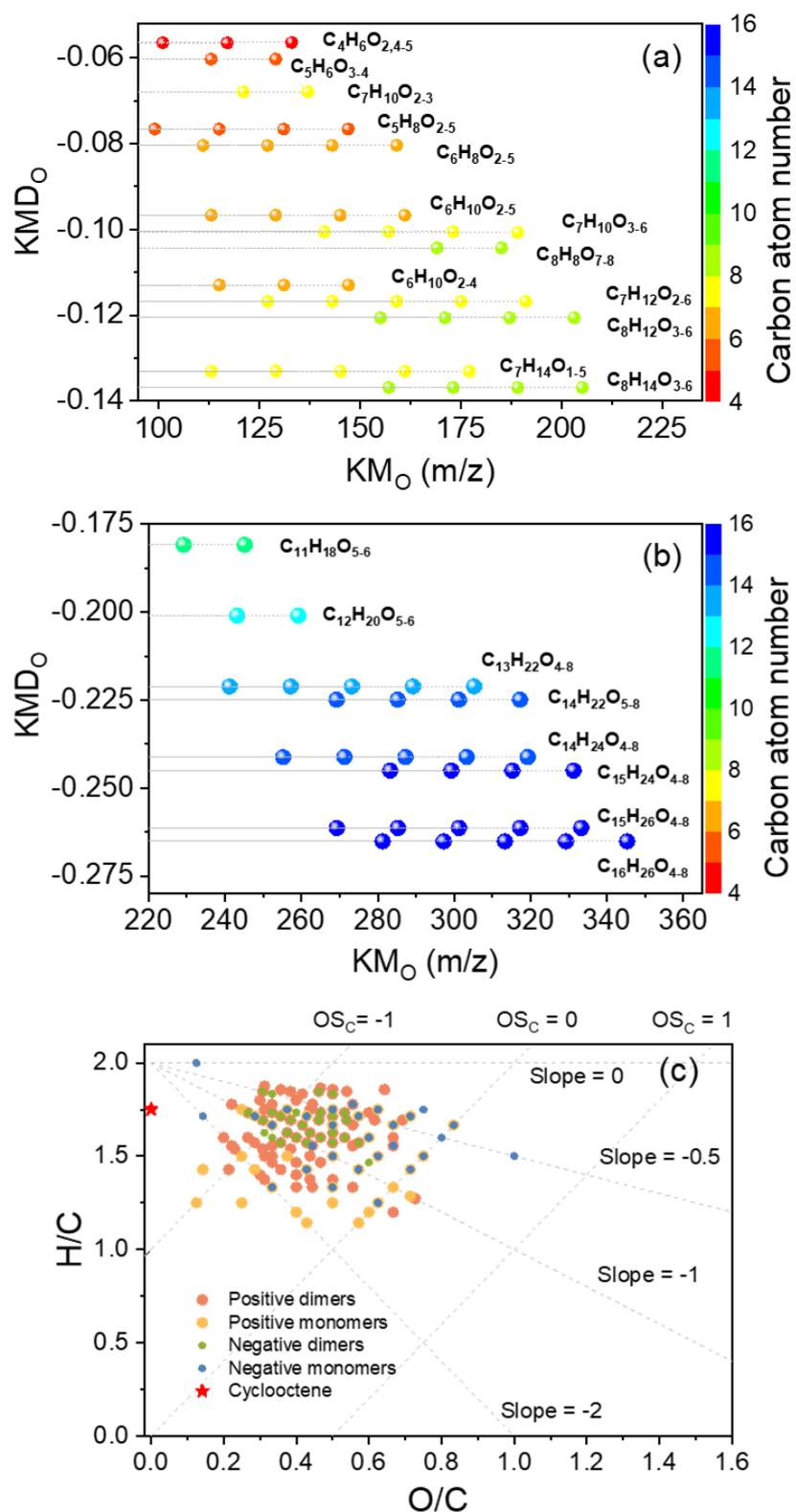
390 **3.3 SO₂ effects on aerosol chemical composition**

To further get detailed mechanisms about SO₂ effects and determine whether heterogeneous processes occurred, aerosol samples were analyzed using ATR-FTIR and LC/ESI-MS. Both IR and MS analysis of particles revealed changes in aerosol chemical composition induced by SO₂ addition.

395 **3.3.1 Characteristics of functional group in aerosol-phase products**

Figure 2 shows ATR-FTIR spectra of aerosol particles. Hydroxy (3600–3200 cm⁻¹), alkyl (2935 and 2864 cm⁻¹), and carbonyl (1702 cm⁻¹) were identified in particles collected from the cyclooctene/O₃ system (Table S1). These particles also had a broad absorption across the 1500–800 cm⁻¹ region, which may arise from C–H deformation in 1480–1350 cm⁻¹, C–C stretching in 1250–1120 cm⁻¹, and C–O stretching in different
400 regions for various oxygenated species (Hung et al., 2013). **Three additional absorption bands at 1413, 1095, and 617 cm⁻¹ were observed in ATR-FTIR spectra of particles formed with the introduction of SO₂ (Tammer, 2004; Lal et al., 2012). Absorption bands at 1413 and 1095 cm⁻¹ may be associated with the asymmetric and symmetric stretching of -SO₂- while inorganic sulfates could give rise to strong absorption at 617 cm⁻¹. The presence of absorption band of sulfur-containing groups suggests that SO₂ addition can result in the production of sulfur-containing compounds.**

405



410 **Figure 5.** Oxidation products observed in particles produced from the ozonolysis of cyclooctene in the absence of SO_2 . Oxygen (O)-Kendrick mass defect plots of (a) monomers and (b) dimers. (c) Van Krevelen diagram.

3.3.2 Organosulfate formation in the presence of SO₂

In addition to CHO compounds, products with C_cH_hO_oS_s elemental formulas were identified in the presence of SO₂ (Fig. S8). OS could undergo highly efficient ionization to give deprotonated molecular ions in negative ion mode. Based on MS/MS analysis, unambiguous identification of OS can be achieved since OSs could give characteristic fragment ions at *m/z* 80 (SO₃⁻), 81 (HSO₃⁻), and/or 97 (HSO₄⁻) in their MS/MS spectra (Figs. S9–S17). Accurate mass measurements of OSs as well as their retention times and DBE values are provided in Table S2. The proposed structure and fragmentation scheme of each OS and corresponding precursor are presented in Figs. S9–S17. For instance, OS-209 and OS-223 showed prominent product ions for losses of HSO₄⁻ and SO₃⁻ (Figs. S11–S12), confirming the organosulfate moiety. Neither a hydroxyl nor a carboxyl group fragment ion (i.e., -H₂O or -CO₂) was observed in their MS/MS spectra. C₆H₁₀O₃ and C₇H₁₂O₃ were proposed as the precursor of OS-209 and OS-223, respectively. MS/MS spectra of C₆H₁₀O₃ and C₇H₁₂O₃ were characterized by loss of CO, indicating terminal carbonyl group (Figs. S11–S12). Considering structural features of OS precursor measurements as well as OS-209 and OS-223 all corresponding to DBE = 2, two terminal carbonyl groups could explain well the observed MS/MS spectra of OS-209 and OS-223. The organosulfate substituent was expected to attach to internal carbon atom. Although the carbonyl group is more readily observed in positive ion mode, ESI-MS is also highly sensitive to carbonyl compounds containing sulfate substituents and thereby gives intense [M – H]⁻ ions in negative ion mode (Riva et al., 2016b).

Relatively high abundance of OS is helpful for the acquisition of MS/MS data, and therefore high abundance [M – H]⁻ ions were chosen as representative candidates to clarify the precursors and formation pathways of OSs. Simplified chemical mechanism describing OS production from the ozonolysis of cyclooctene (C₈H₁₄) is proposed in Fig. 6. The ozonolysis of cyclooctene (C₈H₁₄) can be initiated by O₃ addition to the endocyclic double bond, forming an energy-rich primary ozonide (POZ). POZ can

decompose rapidly to an excited CI containing both a terminal carbonyl and carbonyl oxide group. The excited CI could lead to the formation of sCI, vinylhydroperoxide, and dioxirane, illustrating the multiplicity and the complexity of cyclooctene ozonolysis. SCI is mainly capable of involving in bimolecular reactions to form carboxylic acids and acid esters. Vinylhydroperoxide rapidly decomposes into an alkyl radical ($C_8H_{13}O_2\cdot$) and an $\cdot OH$. Molecular oxygen could be subsequently added to $C_8H_{13}O_2\cdot$ to produce an alkyl peroxy radical (RO_2 , $C_8H_{13}O_4\cdot$). Dioxirane intermediate may also undergo decomposition and produce a $C_7H_{13}O_3\cdot$. $C_8H_{13}O_4\cdot$ and $C_7H_{13}O_3\cdot$ are considered as the starting point of the $RO_2\cdot$ and alkoxy radical ($RO\cdot$) chemistry, resulting in termination CHO compounds with hydroperoxy, carbonyl, or hydroxy groups (Fig. 6). Acid-catalyzed heterogeneous reactions of CHO products have been evidenced to play a major role in OS formation in the atmosphere (Riva et al., 2016c; Riva et al., 2016b). Although acidic seed particles were not directly injected into the reactor during cyclooctene ozonolysis, SO_2 -induced H_2SO_4 may create acidic conditions for the occurrence of heterogeneous reaction. In the case of CHO products with hydroxyl group, H_2SO_4 could protonate the hydroxyl group, leading to the formation of OS and water. The low RH ($\sim 20\%$) of ozonolysis was helpful for shifting the reaction equilibrium in favor of OS production.

Detailed information about the volatility of oxidation products is necessary to evaluate their potential to contribute to aerosol formation. As shown in Fig. 7a, the products could be categorized into intermediate volatility OCs (IVOCs), semi-volatile OCs (SVOCs), low-volatile OCs (LVOCs), and extremely low-volatile OCs (ELVOC) with C° in the range of $300-3 \times 10^6$, $0.3-300$, $3 \times 10^{-4}-0.3$, and $< 3 \times 10^{-4} \mu g m^{-3}$, respectively (Donahue et al., 2011). The saturation mass concentration of OSs spanned more than 6 orders of magnitude (Fig. 7a), suggesting their inherent chemical complexity of them. A large number of OSs are SVOCs and LVOCs while their precursors are classified as IVOCs and SVOCs, indicating that the SO_2 presence facilitates the reduction of product volatility (Yang et al., 2020; Han et al., 2016).

Lower-volatile OSs generated from acid-catalyzed heterogenous reactions may build
 470 particle mass at a faster rate compared to their higher-volatile precursors, and thereby
 benefit the formation and growth of particles in the presence of SO₂.

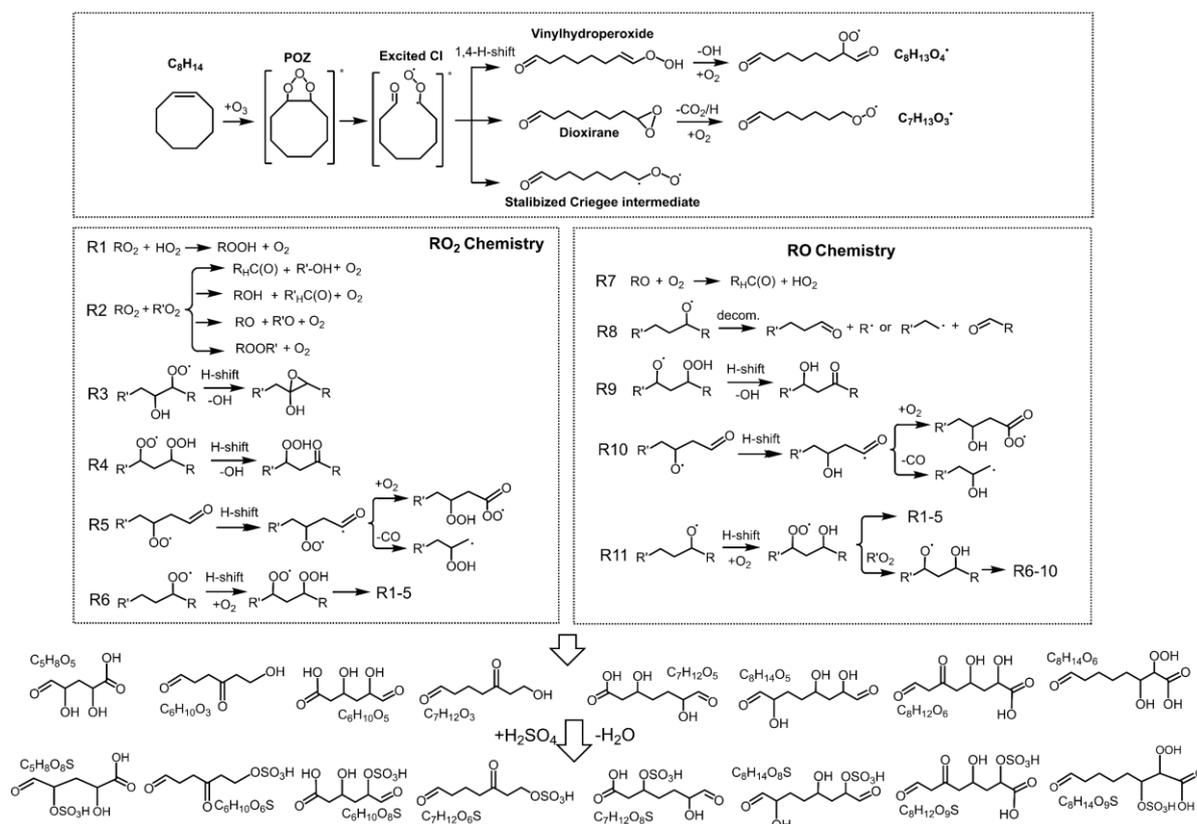


Figure 6. Simplified formation schemes for the selected organosulfates formed from
 475 the ozonolysis of cyclooctene.

Figure 7b displays the DBE–carbon atom number space for organosulfur
 compounds. There are some overlaps of organosulfur compounds detected in this work
 with previous data from field observations (Wang et al., 2021b; Boris et al., 2016; Cai
 480 et al., 2020). For example, Wang et al. (2021b) comprehensively analyzed OS in PM_{2.5}
 filter samples collected in an urban site in Shanghai, China and observed the presence
 of C₆H₁₀O₆S (Fig. 7b, cyan cross). In the absence of chromatographic data such as
 retention times, C₆H₁₀O₆S was tentatively assigned to diesel vapor-derived OS. Alkenes
 are important components of diesel and cyclooctene may be also responsible for

485 $C_6H_{10}O_6S$ formation in the atmosphere. The overlaps of organosulfur compounds indicate that the ozonolysis of cycloalkenes in the presence of SO_2 is likely an important source of organosulfur compounds in the ambient atmosphere. In addition, our work further suggests that the sources of OS cannot be determined only based on their elemental formula, and techniques that enable the identification of molecular structures
 490 (e.g., MS/MS) are greatly beneficial in field studies. The identified molecular structures of OSs in this study are also helpful in the source apportionment in field studies.

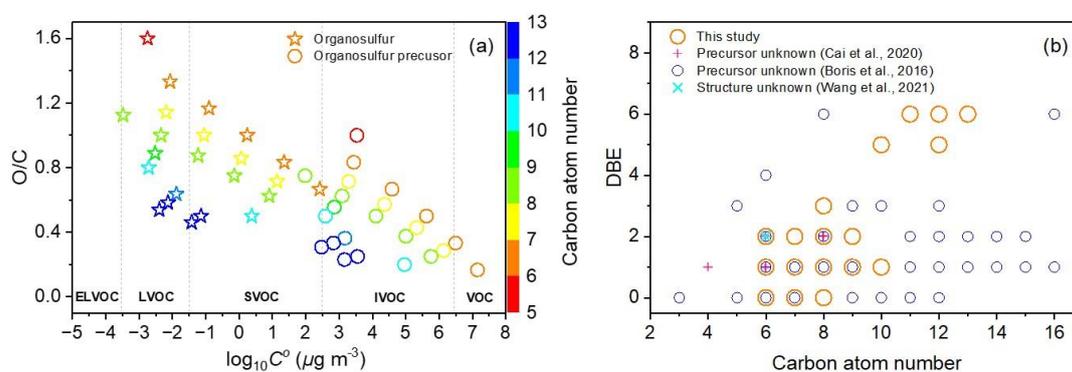


Figure 7. (a) Two dimensional volatility–oxidation space of the identified
 495 organosulfurs and their precursors. (b) Carbon atom number distribution of organosulfurs observed in the current work and in the studies of Cai et al. (2020), Boris et al. (2016), and Wang et al. (2021b). Detailed formulae of these OSs can be found in Table S3. Organosulfurs from previous studies are of unknown origin or unknown structure.

500 4 Conclusion

We have explored O_3 -initiated oxidation of cyclooctene in the absence and presence of SO_2 , with a focus on the mechanism by which SO_2 impacts particle formation and composition. Cyclooctene can produce a large number of particles upon reacting with O_3 . Higher SO_2 concentration led to higher particle number concentration
 505 as a result of H_2SO_4 formation from the reactions of sCI with SO_2 .

Cyclooctene SOA mainly consisted of carboxylic acids and corresponding dimers

with acid anhydride and aldol structures when SO₂ was not added. SO₂ addition can induce the changes in particle chemical composition through the formation of OSs. Some OSs, classified as compounds of unknown origin or unknown structure in previous field studies, were also observed in this work. The OSs found here are less volatile than their precursors, indicating the stronger ability of OS for particle formation. The formation of OSs can in part lead to the increase in particle volume concentrations in the presence of SO₂.

The results here suggest that SO₂ can influence aerosol particle formation and composition by producing sulfur-containing compounds (i.e., H₂SO₄ and OSs). Nevertheless, the observed number of OSs may be amplified by the high SO₂ concentration used in the present work. In order to determine the actual mass yields of OSs and better quantify SO₂ roles in particle formation, further experiments using ambient SO₂ levels and authentic standards are warranted.

520

Data availability.

Experimental data are available upon request to the corresponding author.

Supplement.

525 The supplement related to this article is available online at:

Author contribution.

ZY designed the experiments and carried them out. ZY performed data analysis with assistance from XL, NTT, KL, and LD. ZY prepared the paper with contributions from all co-authors. NTT, KL, and LD commented on the paper.

530 **Declaration.**

The authors declare that they have no conflict of interest.

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