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 O_3 ($k_{298\ K} = 4.51 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}) in the Introduction section. 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 O_3 is rapid. Once O_3 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).

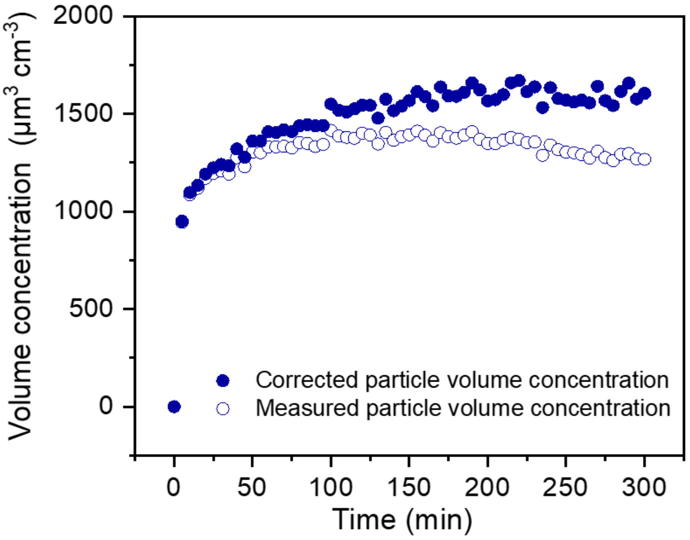

Figure R1. Time series of the volume concentration of aerosol particles during the ozonolysis of cyclooctene.

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

Page 4, Line 91:

Particle formation experiments were operated in 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 -SO_2- could result in strong absorbances at 1415–1370 cm^{-1} and ~1064 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 (cm^{-1})	References
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 $-SO_2-$ 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 ~876 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 -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 (3500-3200 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 also had strongest intensity among all characterized functional groups (Fig. R2b).

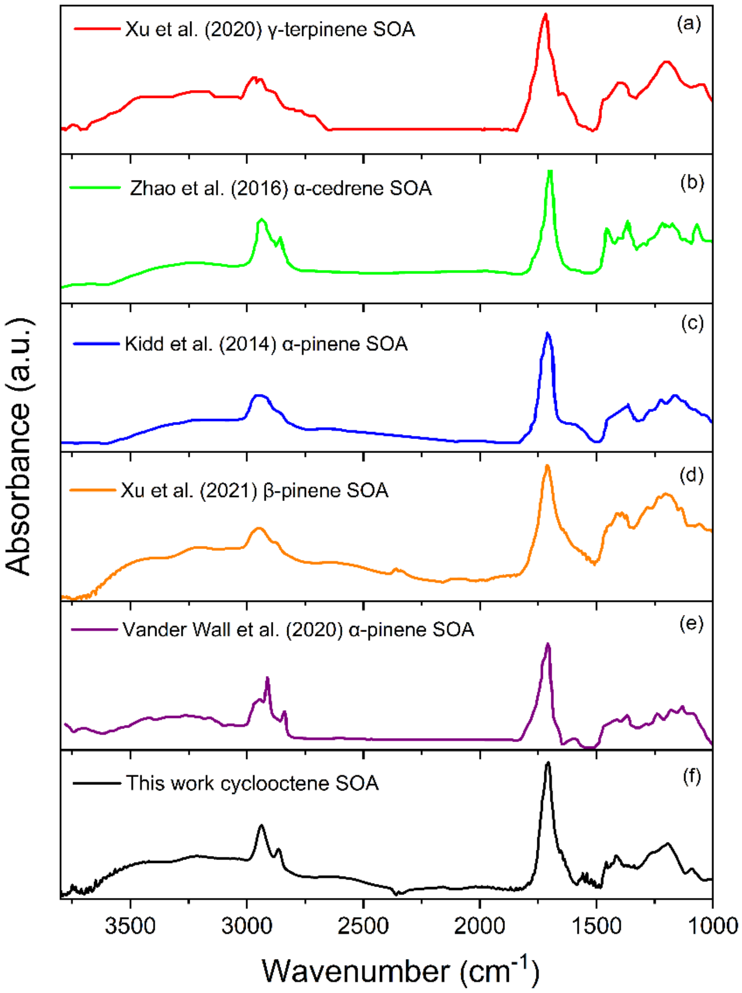

Figure R2. ATR-FTIR spectra for SOA generated from ozonolysis of different alkenes. (a) γ-terpinene SOA (Xu et al., 2020); (b) α-cedrene SOA (Zhao et al., 2016); (c) α-pinene SOA (Kidd et al., 2014); (d) β-pinene SOA (Xu et al., 2021); (e) α-pinene SOA (Vander Wall et al., 2020); (f) cyclooctene SOA (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).

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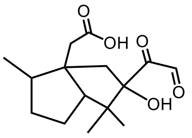
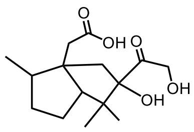
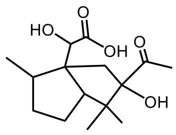
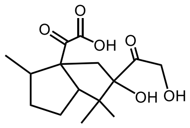
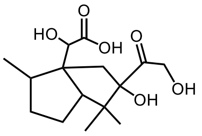
<td colspan="3"></td>
<td colspan="3"></td>
<td colspan="3"></td>
<td colspan="3"></td>
<td colspan="3"></td>
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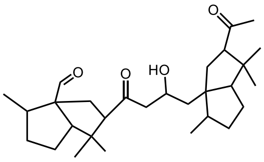
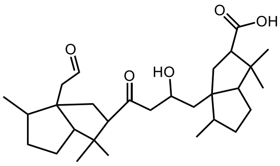
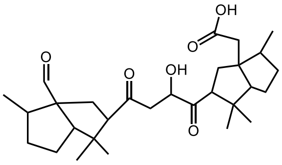
<td colspan="5"></td>
<td colspan="5"></td>
<td colspan="5"></td>
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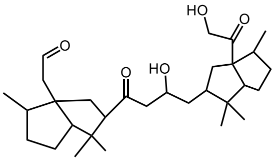
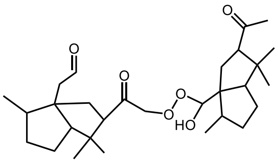
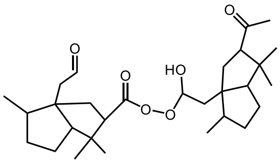
<td colspan="5"></td>
<td colspan="5"></td>
<td colspan="5"></td>
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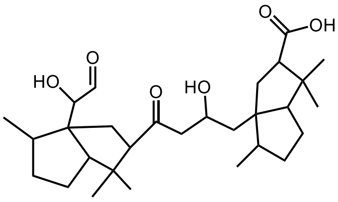
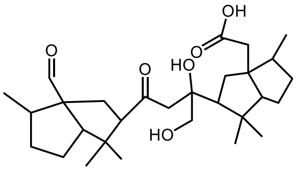
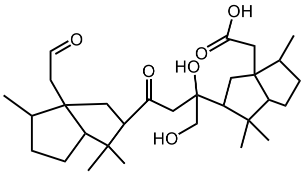
<td colspan="5"></td>
<td colspan="5"></td>
<td colspan="5"></td>
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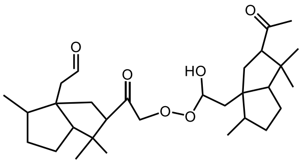
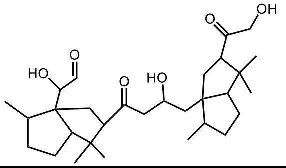
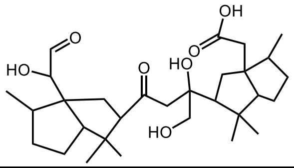
<td colspan="5"></td>
<td colspan="5"></td>
<td colspan="5"></td>
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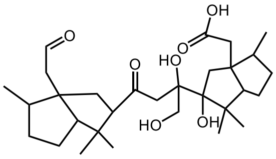
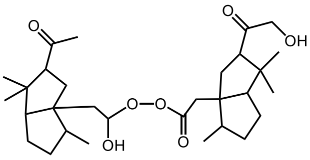
<td colspan="5"></td>
<td colspan="5"></td>
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Table R3. Initial experimental conditions of SOA formation from the ozonolysis of alkenes.

VOC type	$[VOC]_0$ (ppb)	$[O_3]_0$ (ppb)	T (K)	RH (%)	OH scavenger	Reference
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 FITR 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 is lower than that of carbonyl group.

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 $C_cH_hO_oN_nS_s$, 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).

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

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 $C_{10}H_{18}O_6S$ organosulfate was characterized during the photooxidation of dodecane. Riva et al. (2016) reported that $C_{10}H_{18}O_6S$ corresponded to two DBEs, which arose from a six-membered ring and an internal carbonyl group (Fig. R3).

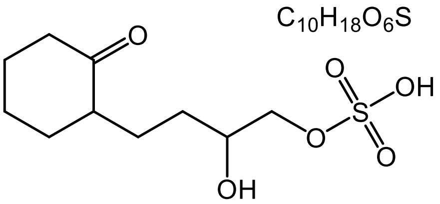

Figure R3. Structure of organosulfate ($C_{10}H_{18}O_6S$), which was extracted from Figure 2 in Riva et al. (2016).

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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