

We have revised our manuscript according to the suggestions of the Referee's comments. For clarity, the Referee's comments are reproduced in blue, authors' responses are in black and changes in the manuscript are in red color text. Pages and lines of modified/inserted/deleted texts are relative to the previous version of the manuscript.

Anonymous Referee #2

This manuscript presents laboratory measurements on the photooxidation of cyclohexene, with a focus on the change of SOA yield and chemical composition as a function of SO₂ concentrations. The authors concluded that competitive reaction of OH radicals with SO₂ and VOCs was the main reason that dictates the cyclohexene SOA yields, and presented FTIR, IC, and ESI-HR-MS data to support the formation of organosulfates in this specific system. Overall, this study provides useful information relevant to a better understanding of cyclic alkene SOA formation. However, there are a few major concerns regarding the connections between the reported data and the speculated mechanisms that need to be addressed before publication can be considered. Also, more in depth discussions are needed to improve the current manuscript. Below I listed a few specific questions for the authors' clarification.

1) In the abstract line 14-17, these two sentences are very confusing and somewhat contradictory with other statements in the manuscript. What is the real impact of acid catalyzed-mechanisms on cyclohexene SOA formation?

Acid catalyzed reactions have been extensively proved to promote SOA formation (Jang et al., 2002; Jang and Kamens, 2002). At low SO₂ concentrations, the decreasing SOA yield might be due to the promoting effect of acid-catalyzed reactions on SOA formation. This effect was less important than the inhibiting effect of decreasing OH concentration, which was caused by the competition reaction of OH reactions with SO₂ and cyclohexene.

Specifically, heterogeneous uptake is responsible for aerosol mass increase in the presence of acid seed aerosol. Sulfate oxidant from SO₂ was the source of seed aerosol in our experiments. The oxygenated products of cyclohexene photooxidation including carbonyl and aldehyde group, which are able to react heterogeneously (Aschmann et al., 2012), are rapidly converted to low volatility products assigned to the particulate phase and increase the production of SOA (Cao and Jang, 2007). This additional accommodation of gas phase aldehydes to the particle phase progresses until no further heterogeneous reactions take place. Figure 5 shows that the sulfate amounts in unit mass of aerosols gradually decrease at high SO₂ initial concentration, which means that SOA formation can be promoted in acidic conditions.

To clarify the real effect of acid-catalyzed mechanisms in cyclohexene SOA formation, we modified the text in the Abstract lines 13-16 as:

“The decreasing SOA yield might be due to the fact that the promoting effect of acid-catalyzed reactions on SOA formation was less important than the inhibiting

effect of decreasing OH concentration at low initial SO₂ concentrations, caused by the competition reactions of OH with SO₂ and cyclohexene.”

2) Did cyclohexene react completely in each experiment? The experimental profile presented in Figure S1 didn't include the traces of VOC precursor and main gas phase products. Since in section 2.2 the authors mentioned that these compounds were measured by TD-GC-MS measurements, these data should be included in discussion.

Cyclohexene reacted completely in each of our experiments. Its concentration was measured at the beginning and at the end of each experiment. We have patched experiments for the changing trend of cyclohexene during reaction. Figure S4 below shows the change of cyclohexene concentration with time, at different initial SO₂ concentrations.

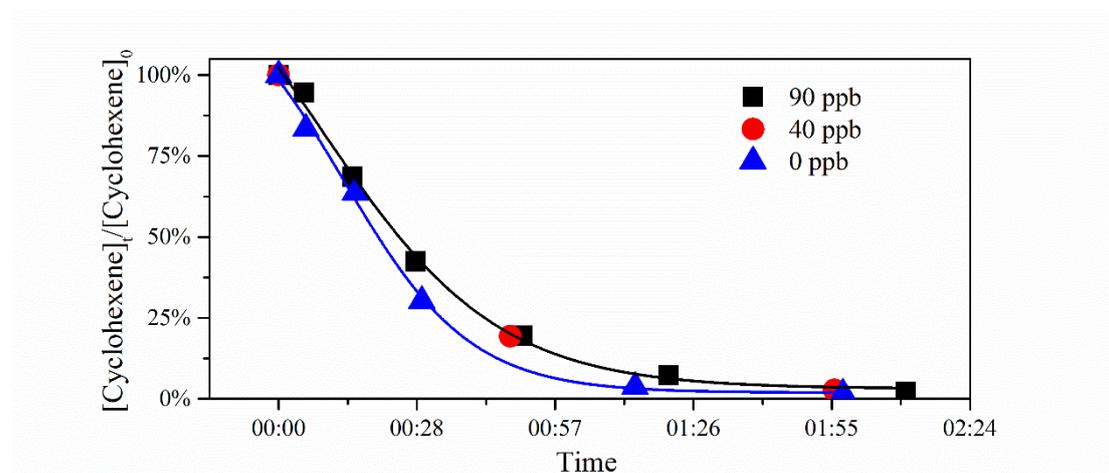


Figure S4: Change of cyclohexene concentration with time at different initial SO₂ concentrations.

As shown in Figure S4, the reacted cyclohexene concentration at 0 ppb initial SO₂ concentration was slightly higher than that at 90 ppb. The consuming rate of cyclohexene was higher without SO₂ in the chamber, which means that if there was a competition reaction, its effect was not significant. Due to the sparse data of cyclohexene concentration in the experiment with 40 ppb initial SO₂, they could not be fitted. However, they fell between the fitted data at 0 and 90 ppb initial SO₂ concentration, being closer to the fit at 90 ppb. This further indicates that the presumed competition reaction was more obvious at low SO₂ concentrations than that at high SO₂ concentrations. The particle number concentration, which is related to the sulfate formed from SO₂ reaction with OH was also increased quickly at low SO₂ concentrations. This result explains why the SOA yield was decreased at low initial SO₂ concentration as shown in Figure 3.

The following sentence was inserted at page 9 line 14.

“The change of cyclohexene concentration with time at different initial SO₂ concentrations is shown in Figure S4, wherefrom it can be seen that the reacted

cyclohexene concentration at 0 ppb initial SO₂ concentration was slightly higher than that at 90 ppb. The consuming rate of cyclohexene was higher without SO₂ in the chamber, which means that if there was a competition reaction, its effect was very limited.”

Only the cyclohexene concentration could be monitored with the GC-MS while other gaseous products could not, probably due to their low concentration not allowing their detection by the experimental device, and the selective adsorption of the Tenax tube.

For more clarifications on this, the sentence at page4, line 21 was modified as:

“The concentrations of cyclohexene were analyzed by thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS).”

We also did not find the organosulfates from the GC-MS spectra. Traditional analytical methods, such as GC-MS with prior derivatization, may not be well suited to identify organosulfates. It is likely that single derivatization protocols, such as trimethylsilylation, GC injection and column temperature could cause the degradation or misinterpretation of such species (Murray and Baillie, 1979). On the other hand, ESI-MS has been shown as an effective method for the detection of organosulfates species (Boss et al., 1999; Metzger et al., 1995). In this regard, only ESI-HR-MS data, as presented in Figure 6, were used for particle chemical composition discussion in this manuscript.

3) What is the connection between OH-limited scenario presented here (that leads to competitive reactions) and the real atmospheric environment? This is not clearly stated in the manuscript.

The competitive reaction of OH with SO₂ and cyclohexene can be important in environment enriched with O₃. For example, when OH reacts with SO₂ while cyclohexene and O₃ are present, cyclohexene + O₃ reaction will become the dominant pathway for cyclohexene loss. Since SOA was mainly formed from the reaction of cyclohexene with OH and SO₂, the OH competition reaction would then lead to less SOA forming. In real atmospheric situations where O₃ is found in much higher proportion than OH, more cyclohexene will react with O₃ to form Criegee intermediates, which are good SO₂ oxidizers. Hence, even less SOA would form. However, this was not the case in our chamber. To clarify the atmospheric implications of competitive reactions, we inserted the following at page 9 line 14:

“Moreover, in real atmospheric situations where O₃ is found in much higher proportion than OH, cyclohexene would mainly react with O₃ to produce Criegee intermediates, which are good SO₂ oxidizers, and significantly less SOA than in the chamber will be formed.”

4) How does the chemical composition of SOA change in the absence versus in the

presence of SO₂? Without the initial input of SO₂, the SOA yield was already substantial. It appears that with and without SO₂ addition, SOA was formed through different pathways (homogeneous nucleation versus heterogeneous uptake/partitioning). This needs to be discussed in more detail. Also, the authors provided a full set of FT-IR spectra and sulfate concentrations. Are the corresponding ESI-MS data available? These will be useful to strengthen the discussion on organosulfates formation.

Different particles were formed from cyclohexene photooxidation, and the particle chemical composition was very complex. Because of this complexity, the chemical composition could not be completely determined, making the understanding of the photooxidation mechanism incomplete. The overall chemical composition of particles was analyzed by FTIR, and it was found that the relative intensity of each characteristic peak did not show obvious change under different initial SO₂ concentrations. This means that in addition to organic sulfate formation, the remainder of the chemical composition is almost the same regardless of the initial SO₂ concentration.

For clarification, the sentence at page 10, lines 14-15 was modified as:

“However, the band of sulfate at 1100 cm⁻¹ in IR spectra increases with the rise of initial SO₂ concentration rather than the SOA yield, which suggests the formation of sulfonic acid group and sulfate product from SO₂ photooxidation since, only the relative difference in the intensities of FTIR peaks were studied here.”

Generated particles were collected on ZnSe, and then detected by FTIR. During ESI-HR-MS detection, particles were collected on the aluminum foil using the same method as FTIR analysis and then extracted with 1 mL of acetonitrile. Considering the volume of the chamber and the volume of particles collected, corresponding ESI-MS data and FT-IR spectra for each experiment were not available. In order to afford more information about organosulfates composition, we performed one more experiment with different initial SO₂ to study the composition of organosulfates under different SO₂ concentrations, and the HR-MS result is shown in Figure S3 to appear in the Supplementary material. It is seen from this figure that the composition and response of organosulfates vary weakly with change in initial SO₂ concentrations.

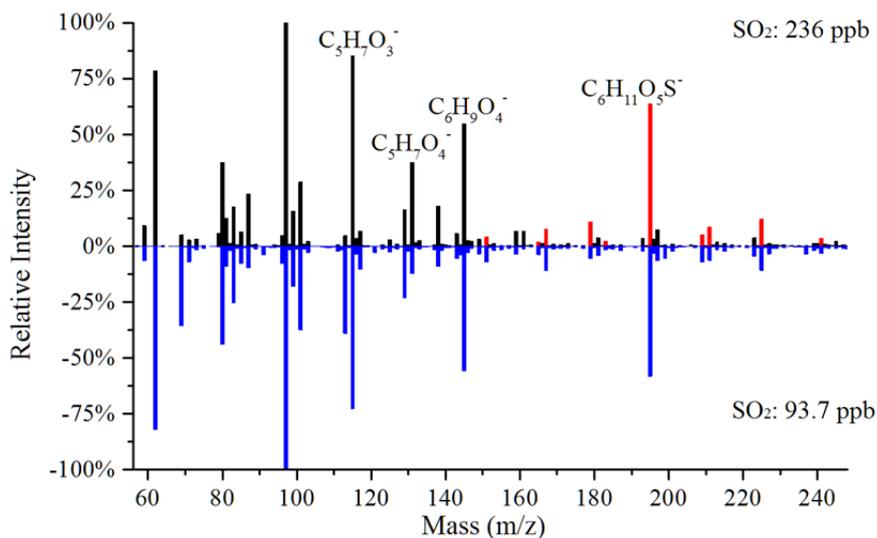


Figure S5: Comparison of SOA ESI-HR-MS spectra with different initial SO₂ concentrations.

The following text was added at page 11 line 18 to strengthen the discussion on the composition and response of organosulfates with change in initial SO₂ concentrations: “The ESI-HR-MS spectra of particles formed from two different initial SO₂ concentrations are shown in Figure S5. We found no obvious difference in the composition and response of organosulfates with different initial SO₂ concentrations. The relative intensity of m/z = 97, which corresponds to sulfate was set to 100% in both ESI-HR-MS spectra. The relative intensities of the organosulfates peaks in both spectra were almost unchanged regardless of the initial SO₂ concentration, indicating that the organosulfates yield was associated with sulfate content. Our result is consistent with the results of Minerath et al. and Hatch et al. who observed an increase in organosulfates yield with increasing sulfate concentration (Minerath and Elrod, 2009; Hatch et al., 2011). These observations demonstrate that particle sulfate content is likely a key parameter influencing organosulfates formation.”

5) In the last paragraph of section 3.2, the authors stated that SOA yield was enhanced by acid-catalyzed heterogeneous reactions when SO₂ concentrations are high. Is there direct evidence to support the proposed acid-catalyzed reactions? Was aerosol acidity measured or estimated? What is the potential role of particle sulfate contents for surface or bulk accommodation?

We did not measure the aerosol acidity due to the limitations of our experimental equipment. Although, aerosol acidity correlated well with sulfate and could be estimated using the same way as Zhou et al. (Zhou et al., 2012), Zhou et al. pointed that when ambient RH is lower than the deliquescence point (DRH), the particle is considered to exist as a pure solid phase. Czoschke et al. pointed that a catalytic process takes place by a small amount of acid catalyst (5 μg m⁻³) in dry conditions

(RH<10%) (Czoschke et al., 2003). As Figure 3 shows, the concentration of sulfuric acid in the chamber was greater than $5 \mu\text{g m}^{-3}$ when the initial SO_2 concentration was greater than 40 ppb. This indicates that acid-catalyzed reactions took place in our experiment.

Sulfate oxidant from SO_2 as the source of aerosol seed in our experiments, contributes to the increase of the aerosol mass through heterogeneous uptake. The following was inserted at page 9 line 29 for clarifications:

“It was demonstrated that acid-catalyzed processes could take place when there is a small amount of acid catalyst ($5 \mu\text{g m}^{-3}$) (Czoschke et al., 2003). In our chamber, the concentration of sulfuric acid was greater than $5 \mu\text{g m}^{-3}$ when the initial SO_2 concentration was greater than 40 ppb. This indicates that acid-catalyzed reactions were evident in our experiment.”

References

- Boss, B., Richling, E., Herderich, R., and Schreier, P.: HPLC-ESI-MS/MS analysis of sulfated flavor compounds in plants, *Phytochemistry*, 50, 219-225, doi: Doi 10.1016/S0031-9422(98)00526-3, 1999.
- Czoschke, N. M., Jang, M., and Kamens, R. M.: Effect of acidic seed on biogenic secondary organic aerosol growth, *Atmos. Environ.*, 37, 4287-4299, doi: 10.1016/S1352-2310(03)00511-9, 2003.
- Hatch, L. E., Creamean, J. M., Ault, A. P., Surratt, J. D., Chan, M. N., Seinfeld, J. H., Edgerton, E. S., Su, Y., and Prather, K. A.: Measurements of isoprene-derived organosulfates in ambient aerosols by aerosol time-of-flight mass spectrometry - part 1: single particle atmospheric observations in Atlanta, *Environ. Sci. Technol.*, 45, 5105-5111, doi: 10.1021/es103944a, 2011.
- Jang, M., Czoschke, N. M., Lee, S., and Kamens, R. M.: Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions, *Science*, 298, 814-817, doi: 10.1126/science.1075798, 2002.
- Jang, M., and Kamens, R. M.: Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst, 35, 4758-4766, 2002.
- Metzger, K., Rehberger, P. A., Erben, G., and Lehmann, W. D.: Identification And Quantification Of Lipid Sulfate Esters by Electrospray-Ionization Ms/Ms Techniques - Cholesterol Sulfate, *Analytical Chemistry*, 67, 4178-4183, doi: Doi 10.1021/Ac00118a022, 1995.
- Minerath, E. C., and Elrod, M. J.: Assessing the potential for diol and hydroxy sulfate ester formation from the reaction of epoxides in tropospheric aerosols, *Environ. Sci. Technol.*, 43, 1386-1392, 2009.
- Murray, S., and Baillie, T. A.: Direct Derivatization Of Sulfate Esters for Analysis by Gas-Chromatography Mass-Spectrometry, *Biomed Mass Spectrom*, 6, 82-89, doi: DOI 10.1002/bms.1200060209, 1979.
- Zhou, Y., Xue, L. K., Wang, T., Gao, X. M., Wang, Z., Wang, X. F., Zhang, J. M., Zhang, Q. Z., and Wang, W. X.: Characterization of aerosol acidity at a high mountain site in central eastern China, *Atmos. Environ.*, 51, 11-20, doi: 10.1016/j.atmosenv.2012.01.061, 2012.