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 #1

This manuscript described photooxidation of cyclohexene with changing SO_2 concentration and concluded that both SO_2 competing OH and acid-catalyzed heterogeneous reactions are important to result in the observed SOA yield trend. Organosulfates are also observed in SOA composition. The main results are clearly stated, but the discussion could have been more comprehensive and in depth, regarding the complementary measurements. I think there are a few major issues that the authors need to address before the manuscript can be published.

Major comments:

1. As initial SO_2 concentration increases, it becomes more competitive of OH radicals against cyclohexene, whose initial concentration remain stable. Note cyclohexene could also react with O_3. From the Figure S1 in supplemental, it seems O_3 concentration was already high at 20 min. If OH is mostly reacted with SO_2, when cyclohexene remains, cyclohexene + O_3 could become the dominant pathway for cyclohexene loss. At page 9, line 8-9, the authors argued that the ozonolysis rate is 6 orders of magnitude lower than OH oxidation. But the much higher O_3 concentration than OH could offset this difference, especially in the case of the current study where OH was insufficient. Therefore, varying only initial SO_2 could cause very different cyclohexene chemistry (OH oxidation vs. ozonolysis). I think this is important to discuss. The authors at least need to provide convincing data to show ozonolysis is not important in this study. A statement like "In addition to the kinetic limitation of the cyclohexene reaction with O_3, the typical concentration of O_3 in our chamber was 200 ppb and hence the importance of cyclohexene reaction with O_3 was expected to be less significant than that of its reaction with OH under any relevant SO_2 conditions" is too vague.

We agree with the Referee that cyclohexene can be oxidized by both ozone and OH. Although SOA can be formed from ozonization, but O_3 cannot react with SO_2. Moreover, the ozone concentrations in every experiment with different initial SO_2 concentrations were almost unchanged. So, the effect of SO_2 on O_3 concentration was not obvious. In a similar study involving β-pinene, Sarrafzadeh et al. proved that the increasing SOA yield was likely due to the increase in OH concentration though the concentration of O_3 was not mentioned in their experiment (Sarrafzadeh et al., 2016). However, it is worth noting that O_3 was added in their experiment. It has also been proved that the OH yield from β-pinene reacting with O_3 was about 30% (Nguyen et al., 2009; Ma and Marston, 2008), and the OH yield from the reaction of O_3 with cyclohexene was 60% (Presto and Donahue, 2004). In the study of Sarrafzadeh, when [VOCs]/[NOx] was about 5, the OH concentration in the chamber was about 3.7×10^{7} cm^{-3}. This concentration was higher in our experiment. Furthermore, the ratio of [OH]/[O_3] was higher in our experiments than in Sarrafzadeh's experiments. All in all, these are in favor to our argument that the SOA formed from cyclohexene was likely due to the OH reaction, and the SOA yield was likely due to the changing of OH concentration in our study.

The authors did not include cyclohexene concentration in the supplementary figure, which is an important indicator of the VOC chemistry. Also, it will be evident if the authors could show cyclohexene decay curves at different initial SO_2 concentrations. It might be best if the authors could provide a figure (could include that in Figure 2) estimating how much cyclohexene reacts with OH vs. O_3 under the studied SO_2 concentrations.

We have patched new experiments. Figure S4 below shows the change of cyclohexene concentration with time, at different initial SO_2 concentrations.

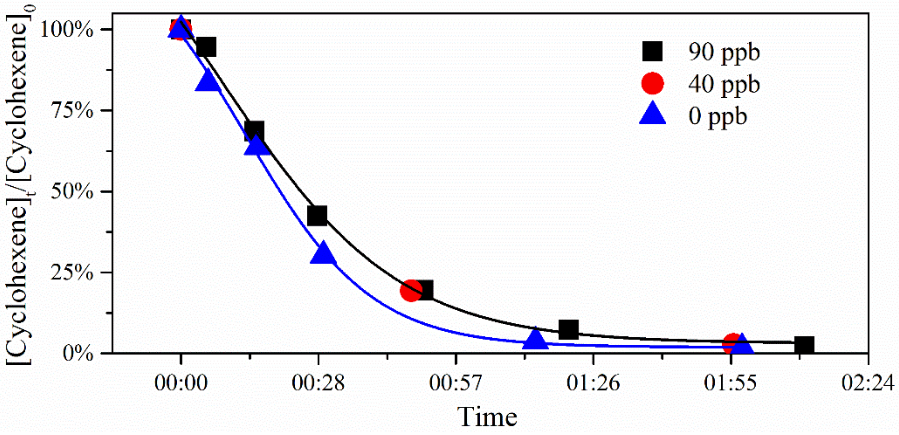

Figure S4: Change of cyclohexene concentration with time at different initial SO_2 concentrations.

As shown in Figure S4, the reacted cyclohexene concentration at 0 ppb initial SO_2 concentration was slightly higher than that at 90 ppb. The consuming rate of cyclohexene was higher without SO_2 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 SO_2, they could not be fitted. However, they fell between the fitted data at 0 and 90 ppb initial SO_2 concentration, being closer to the fit at 90 ppb. This further indicates that the presumed competition reaction was more obvious at low SO_2 concentrations than that at high SO_2 concentrations. The particle number concentration, which is related to the sulfate formed from SO_2 reaction with OH was also increased quickly at low SO_2 concentrations. This result explains why the SOA yield was decreased at low initial

SO_2 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 SO_2 concentrations is shown in Figure S4, wherefrom it can be seen that the reacted cyclohexene concentration at 0 ppb initial SO_2 concentration was slightly higher than that at 90 ppb. The consuming rate of cyclohexene was higher without SO_2 in the chamber, which means that if there was a competition reaction, its effect was very limited."

2. Comparing Figure 3 and Figure 5, it is unclear to me what the amount of sulfate indicates in either case and they obviously represent different measurements. Is the amount of sulfate in Figure 3 only from IC measurement (inorganic SO_4^{2-})? And the amount of sulfate in Figure 5 from IC measurement normalized to SOA mass? I think it is the main results of this manuscript and need to be clearly stated in the figure caption. Also I wonder how does the ratio of the FTIR band 1100 cm^{-1} to IC SO_4^{2-} as a function of initial SO_2 look like? This ratio might tell how efficiently organosulfates are formed under changing SO_2 concentrations.

The amount of sulfate in Figure 3 is only from IC measurement (inorganic SO_4^{2-}), while the amount of sulfate from IC measurement in Figure 5 is normalized to the SOA mass, as stated at page 10, lines 18-21. For further clarifications, the caption of Figure 5 was modified to be:
"Figure 5: The relative intensity of the FTIR band at 1100 cm^{-1} (square) and the amount of SO_4^{2-} (triangle) normalized to SOA mass. The 1100 cm^{-1} band intensity and the amount of SO_4^{2-} were divided by the formed SOA mass. Subsequently, the results of both FTIR band at 1100 cm^{-1} and the amount of SO_4^{2-} divided by SOA mass were set to 1 when the initial SO_2 concentration was 44.3 ppb."

The intensity of FTIR band at 1100 cm^{-1} can be used for quantitative analysis of the S=O bond in the particulate phase. The components having the S=O bond can be inorganic (sulfate) and organic (sulfate group in organosulfates). Although sulfate was quantified by IC, the relationship between SO_4^{2-} concentration and FTIR band could not be determined. This means that the ratio function of the FTIR band at 1100 cm^{-1} to IC SO_4^{2-} here can only represent the relative variation of these two results, with no actual dimension.

As shown in Figure 5 in the main manuscript, when initial SO_2 concentrations are higher than 50 ppb, the opposite relationship between the 1100 cm^{-1} band and the sulfate concentration normalized to SOA mass indicates that the band at 1100cm^{-1} does not fully contribute to sulfate, but also to the sulfate group in organosulfates. The following sentence was inserted at page 10 line 27.
"Figures 5 shows the inconsistency between the FTIR band at 1100 cm^{-1} and the amount of SO_4^{2-} as the initial SO_2 concentration changes, which implies that the 1100 cm^{-1} band originated not only from SO_4^{2-}, but also from other organosulfur

compounds. These include organosulfates, which also have the S=O bond, and might contribute to the 1100 cm^{-1} band in the FTIR spectrum. The gap between the FTIR band at 1100 cm^{-1} and SO_4^{2-} can be attributed to the formation of organosulfates."

3. As indicated by the title, I think more discussion regarding chemical composition is needed. From the results, only organosulfates are focused. From Figure S1, it looks NOx gets lost to organic nitrates. From Figure 4, the IR data suggest –ONO2 presents in SOA. I suggest the authors discuss more on organic nitrate in SOA. Only a paragraph at the very end seems insufficient. For example, does –ONO2 IR data correlate better with SOA yield? What N-containing chemical formulae present in the ESI-HR-MS data? Any suggested mechanisms?

SOA formed by cyclohexene photooxidation was a mixture of different kinds of compounds, whose functional groups were assigned using FTIR as can be seen in page 10, lines 2-6. As shown in Figure 4, the bands at 1622 and 1230 cm^{-1}, assigned to $–ONO_2$, were the evidence for the existence of organonitrates. But, the intensity of $–ONO_2$ bands were very low, and this result was consisted with the ESI-HR-MS data that there was no evidence of the presence of N-containing compounds from the main peaks. The following was inserted at page 10 line 31 for clarification.
"The OH addition to the C=C bond produces an alkyl peroxyl (RO_2) radical that can react with NO to yield organonitrates (Perring et al., 2013). Although the formation of organonitrates was highly expected, there was no evidence of the presence of N-containing compounds from the main peaks of Figure 6, indicating that organonitrates would be formed at very low concentrations, if at all. A similar conclusion could be observed from Figure 4, when noticing that the $-ONO_2$ stretching peaks at 1622 and 1230 cm^{-1} have very low intensities. The presumed low concentrations of organonitrates might be due to the low concentration of NO when SOA was formed. RO_2 radicals also react with NO_2 to form peroxy nitrates (RO_2NO_2) on time scales comparable to $RONO_2$ formation. However, RO_2NO_2 are thermally labile and rapidly dissociate at ambient temperatures (Perring et al., 2013)."

4. Based on Page 8, Line 35, it seems both NO- and NO2-initiated experiments were conducted. But it is unclear according to Table S1. The authors used NOx in most experiment description. I think it is better to state clearly whether they used NO or NO2. The SOA yields might be similar, but chemistry and timescales of SOA formation might be different, as the authors already indicated.

NO and NO_2 both initiated the experiments but, the photooxidation reaction could not happen in the case of NO until it was oxidized to NO_2, which means that both NO- and NO_2-initiated photooxidation reactions were actually triggered by NO_2. Hence, the chemistry of SOA formation from both processes is similar. It takes about 0.5 hour for NO to be fully converted to NO_2. Both O_3 and SOA formation occurred 0.5 later in the NO-initiated photooxidation than in the NO_2-initiated photooxidation.

We have distinguished the NO- and NO_2-initiated experiments in Figure 2 and Table 1 and added related comments.

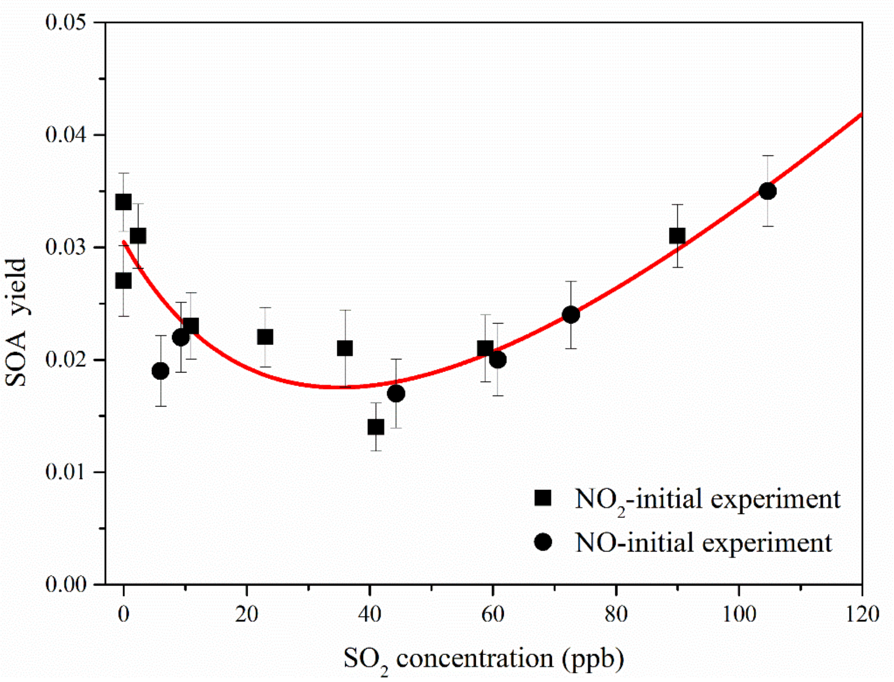

Figure 2: SOA yields of cyclohexene photooxidation in the presence of NOx at different initial SO_2 concentrations. The solid line is the least-square fitting to the data. The error bars were determined on the basis of propagation of uncertainties arising in the ΔHC measurements, including GC calibration uncertainties propagation and the variance in the initial cyclohexene measurements.

Table 1 Experimental conditions for the photooxidation of cyclohexene/NOx/SO_2 system. All experiments were performed under dry conditions (relative humidity < 10 %). ΔM_0 is the produced organic aerosol mass concentration and Y is the SOA yield.

Exp.	T (K)	SO_2 (ppb)	cyclohexene (ppb)	NOx (ppb)	cyclohexene/NOx	ΔM_0 ($\mu g\ m^{-3}$)	Y (%)
1 [b]	308	0.0	596	122.0	4.9	57.0	2.66
2 [b]	305	0.0	651	93.7	6.9	79.7	3.40
3 [b]	309	2.4	553	95.7	5.8	62.6	3.15
4 [a]	307	5.8	612	92.7	6.6	41.0	1.87
5 [a]	309	9.3	599	93.5	6.4	48.1	2.23
6 [b]	309	11.0	574	94.7	6.1	47.1	2.28
7 [b]	309	23.0	514	90.5	5.7	42.6	2.30
8 [b]	305	36.6	665	99.7	6.7	96.3	2.01
9 [b]	308	40.8	472	91.4	5.2	22.6	1.33
10 [a]	308	44.3	592	98.6	6.0	35.3	1.66
11 [b]	305	55.0	497	113.0	4.4	77.3	2.16
12 [b]	308	58.8	577	96.7	6.0	44.3	2.13
13 [a]	309	60.8	626	102.0	6.1	43.9	1.95
14 [a]	308	72.7	581	98.4	5.9	49.2	2.35
15 [b]	306	90.0	543	99.6	5.4	102.0	2.62
16 [a]	309	104.7	608	93.7	6.5	77.1	3.52
17 [bc]	305	236.0	1048	198.0	5.3	-	-
18 [bc]	306	93.7	1235	215	5.7	-	-

a: the experiment was initiated by NO.

b: the experiment was initiated by NO_2.

c: the formed particles were detected by ESI-HR-MS.

Moreover, Table S1 was moved to the main manuscript as Table 1. Further, the following was inserted at page 9, line 1:

"Although the photooxidation reaction could not happen in the case of NO until it was oxidized to NO_2, which means that both NO- and NO_2-initiated photooxidation reactions were actually triggered by NO_2, the chemistry of SOA formation from both processes is similar."

Minor comments:

I have a big issue with the literature citing quality of this manuscript (and I do not know how to make suggestions because there are too many of those). Some examples: Page 1, Line 27. A few important review papers need to be cited in the first paragraph of introduction, such as the Halliquist et al. 2009 ACP, Kroll et al., 2008 AE. Page 8, Line 33. Many papers were published demonstrating acid-catalyzed heterogeneous reactions and enhanced SOA formation before and around 2010. The authors did not cite the most important studies.

This was fixed.

Page 2, Line 1. Jaoui et al., 2012 citation was not in the reference list.

Jaoui et al., 2012 citation was in the reference list at page 13, line 32.

Page 4, Line 6. It should be specified, whether NO or NO2 was injected.

We have distinguished the NO- and NO_2-initiated experiments in Figure 2 and Table 1. This is further detailed in our response to comment number 4.

Page 4, Line 23. What were the TD temperature and time?

The TD temperature was 280 °C, and the sampling time was 3 min. The following sentence was inserted at page 4 line 25 to clarify.
"The TD temperature was 280 °C, and the sampling time was 3 min."

Page 5, Line 9. FTIR analysis uses 300L of air sample, >75% of total chamber volume. Discuss potential artifact.

When the air sample was collected for FTIR analysis, and the volume of chamber was reduced, specific surface area of chamber decreased, and consequently, the wall loss of particles increased. However, SOA sampling was started after the maximum mass concentration was observed, and the change of chamber volume had no effect on the result of SOA yield. Although wall loss was increased, the collected SOA was still consistent with SOA yield between different experiments because of the same volume of sampling air.

Page 8. Line 8. It is problematic to say "NO_3-initiated reaction was a poor source of SOA". Presto et al., 2005a and some later studies did find out that NO3 oxidation of alpha-pinene does not make a lot of SOA, but not necessarily for cyclohexene.

The sentence "NO_3-initialed reaction was not a poor source of SOA for all kinds of VOCs" was deleted in order to cancel the contradiction.

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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 SO_2 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 SO_2 and cyclohexene.

Specifically, heterogeneous uptake is responsible for aerosol mass increase in the presence of acid seed aerosol. Sulfate oxidant from SO_2 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 SO_2 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 SO_2 concentrations, caused by the competition reactions of OH with SO_2 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 SO_2 concentrations.

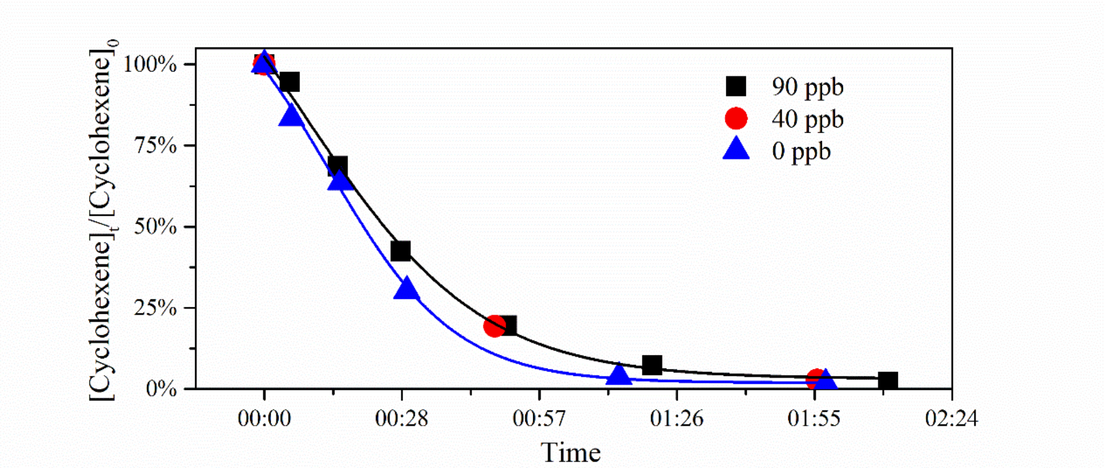

Figure S4: Change of cyclohexene concentration with time at different initial SO_2 concentrations.

As shown in Figure S4, the reacted cyclohexene concentration at 0 ppb initial SO_2 concentration was slightly higher than that at 90 ppb. The consuming rate of cyclohexene was higher without SO_2 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 SO_2, they could not be fitted. However, they fell between the fitted data at 0 and 90 ppb initial SO_2 concentration, being closer to the fit at 90 ppb. This further indicates that the presumed competition reaction was more obvious at low SO_2 concentrations than that at high SO_2 concentrations. The particle number concentration, which is related to the sulfate formed from SO_2 reaction with OH was also increased quickly at low SO_2 concentrations. This result explains why the SOA yield was decreased at low initial SO_2 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 SO_2 concentrations is shown in Figure S4, wherefrom it can be seen that the reacted cyclohexene concentration at 0 ppb initial SO_2 concentration was slightly higher than that at 90 ppb. The consuming rate of cyclohexene was higher without SO_2 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 SO_2 and cyclohexene can be important in environment enriched with O_3. For example, when OH reacts with SO_2 while cyclohexene and O_3 are present, cyclohexene + O_3 reaction will become the dominant pathway for cyclohexene loss. Since SOA was mainly formed from the reaction of cyclohexene with OH and SO_2, the OH competition reaction would then lead to less SOA forming. In real atmospheric situations where O_3 is found in much higher proportion than OH, more cyclohexene will react with O_3 to form Criegee intermediates, which are good SO_2 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 O_3 is found in much higher proportion than OH, cyclohexene would mainly react with O_3 to produce Criegee intermediates, which are good SO_2 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 SO_2? Without the initial input of SO_2, the SOA yield was already substantial. It appears that with and without SO_2 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 SO_2 concentrations. This means that in addition to organic sulfate formation, the remainder of the chemical composition is almost the same regardless of the initial SO_2 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 SO_2 concentration rather than the SOA yield, which suggests the formation of sulfonic acid group and sulfate product from SO_2 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 SO_2 to study the composition of organosulfates under different SO_2 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 SO_2 concentrations.

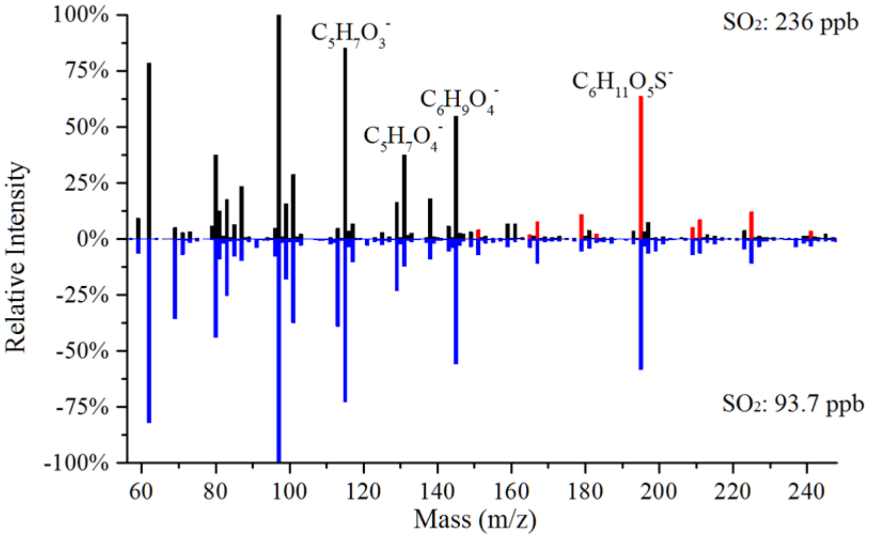

Figure S5: Comparison of SOA ESI-HR-MS spectra with different initial SO_2 concentrations.

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 SO_2 concentrations: "The ESI-HR-MS spectra of particles formed from two different initial SO_2 concentrations are shown in Figure S5. We found no obvious difference in the composition and response of organosulfates with different initial SO_2 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 SO_2 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 μg 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 μg m^{-3}) (Czoschke et al., 2003). In our chamber, the concentration of sulfuric acid was greater than 5 μg m^{-3} when the initial SO_2 concentration was greater than 40 ppb. This indicates that acid-catalyzed reactions were evident in our experiment."

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We have revised our manuscript according to the suggestions of the Referee's comments. For clarity, the Referee' 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 #4

This manuscript presents interesting new results on atmospheric reactions of photooxidation of cyclohexene in the presence of SO2. Unfortunately the quality of the presentation is not suitable for publication in ACP regarding scientific discussion and interpretation of results. The manuscript must be rewritten to discuss the results from a more objective, scientific point, which to a higher degree takes data uncertainty into account before reaching conclusions. Furthermore, there are many grammatical errors. In the following I have explained some of the major points.

In addition to the many comments responded below, the whole manuscript has been checked, several errors have been fixed, to improve the quality of the manuscript.

Introduction the introduction should include more references to relevant previous work. One example is in line 23 page 1, where only one study (on measurement methods for VOC from vehicles) is used as reference for the general statement about emission of alkenes from biogenic and anthropogenic sources.

We carefully reviewed the citations and several relevant previous works were added, some of which are given below:

Chin, J. Y., and Batterman, S. A.: VOC composition of current motor vehicle fuels and vapors, and collinearity analyses for receptor modeling, Chemosphere, 86, 951-958, doi: 10.1016/j.chemosphere.2011.11.017, 2012.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155-5236, doi: 10.5194/acpd-9-3555-2009 2009.

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

Kesselmeier, J., Kuhn, U., Rottenberger, S., Biesenthal, T., Wolf, A., Schebeske, G.,

Andreae, M. O., Ciccioli, P., Brancaleoni, E., Frattoni, M., Oliva, S. T., Botelho, M. L., Silva, C. M. A., and Tavares, T. M.: Concentrations and species composition of atmospheric volatile organic compounds (VOCs) as observed during the wet and dry season in Rondonia (Amazonia), J. Geophys. Res., 107, LBA 20-21–LBA 20-13, doi: 10.1029/2000jd000267, 2002.

Kroll, J. H., and Seinfeld, J. H.: Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, Atmos. Environ., 42, 3593-3624, doi: 10.1016/j.atmosenv.2008.01.003, 2008.

Paulson, S. E., Chung, M. Y., and Hasson, A. S.: OH radical formation from the gas-phase reaction of ozone with terminal alkenes and the relationship between structure and mechanism, J. Phys. Chem. A, 103, 8125-8138, doi: 10.1021/Jp991995e, 1999.

The reference Jimenez et al. (page 1 line 28) on reactions of polyfluorinated compounds is not relevant for a general statement on SOA formation in the atmosphere, and it should thus be removed.

This reference was deleted.

On page 2 (lines 27-30) it is stated that a substantial amount of organosulfates have been observed. Most measurements estimate up to 10% of aerosol mass, and typically much lower in most places, which in my opinion is not a "substantial amount".

The original meaning of “substantial amount” was wrong. Our aim was to point out that different organosulfates were observed. Hence, "substantial amount" has been changed to “different kinds”.

Why so much focus on organosulfate formation from MBO, which is typically not found in high concentrations? Page 2 lines 11-21: This section has a good number of relevant references.

We agree that MBO is not among the major molecules responsible for organosulfates formation. From the literature, laboratory chamber studies showed that OH/NOx/O_3-initiated reactions of BVOCs, such as isoprene, α-pinene, β-pinene, and limonene with sulfates or sulfuric acid are the main formation processes for organosulfates formation. Although organosulfates formation from MBO photooxidation is not as important as from isoprene and pinene reactions, MBO emissions were found to be larger than isoprene emissions in some regions (Baker et al., 1999). Hence, organosulfates formation from MBO reactions would not be negligible in those conditions. To take this into account in the manuscript, the text at page 2 lines 24 to page 3 line 10 was modified as:

“Despite the existence of organosulfates in ambient aerosols was first observed in

2005 (Romero and Oehme, 2005), proper identification of these aerosols was made two years later. In a series of chamber experiments studies, it was shown that organosulfates present in ambient aerosols collected from various locations mostly originate from acid-catalyzed reactions of SOA formed from photooxidation of α-pinene and isoprene (Surratt et al., 2007). Recently, different kinds of organosulfates have been observed in SOA around the world, and organosulfates have been identified as a group of compounds that have an important contribution to the total amount of SOA in the atmosphere (Surratt et al., 2008; Froyd et al., 2010; Kristensen and Glasius, 2011; Tolocka and Turpin, 2012; Wang et al., 2015). Laboratory chamber studies showed that OH/NOx/O_3-initiated reactions of BVOCs, such as isoprene, α-pinene, β-pinene, and limonene with sulfates or sulfuric acid are the main processes for organosulfates formation (Surratt et al., 2007; Surratt et al., 2008; Hatch et al., 2011). Despite the well-recognized presence of organosulfates in SOA, their formation and transformation processes can be complex and varied, depending on the nature of the original organic compound involved. Extensive studies on their formation have been performed and several mechanisms based on a variety of reactions have been proposed. Using nuclear resonance techniques, isoprene-derived epoxides formed during isoprene photooxidation reactions were found to be important intermediates for organonitrates and organosulfates formation via potential SOA reactions (Darer et al., 2011; Hu et al., 2011). The authors further found that organonitrates could easily be transformed to organosulfates during hydrolysis in the presence of sulfate. Some studies also showed that 2-Methyl-3-buten-2-ol (MBO), due its larger emissions than isoprene in some regions (Baker et al., 1999), is an important precursor for organosulfates and SOA in the atmosphere, through its reactions with OH under NO and aerosol acidity conditions, and from acid-catalyzed reactive uptake of MBO-based epoxides formed during MBO photooxidation (Mael et al., 2015; Zhang et al., 2012; Zhang et al., 2014). Organosulfates formation was also found from oxidation of hydroxyhydroperoxides (Riva et al., 2016) and from heterogeneous reactions of SO_2 with selected long-chain alkenes and unsaturated fatty acids (Passananti et al., 2016)."

Experimental Page 4 line 8: The VOC/NOx ratio was not about 5, but varied from 4.4 to 7.

The ratio of VOCs/NOx has been fixed.
The sentence at page 4, line 8 "The mixed concentration ratios of VOCs/NOx were adjusted to be about 5" was changed to "The mixed concentration ratios of VOCs/NOx were in the range 4.4-6.9."

Section 2.3: Why were only aerosols in the range 108-650 nm collected? What was the limit of detection of the IC analysis?

The particles were collected by a Dekati low pressure impactor (DLPI, DeKati Ltd, Finland). The size range of particles collected by this device was 0.03-10μm, which was divided into thirteen segments. According to the results of particle size range measured by SMPS as shown in Figure R1 below, the mass of particles formed were in the range of 75-300 nm. These were in the 108-650 nm range, which corresponds to the third segment, within which most of the particles from our measurements could be collected. The particles in this range constitutes about 97% of the total mass, both measured (black bars) and simulated (red line).

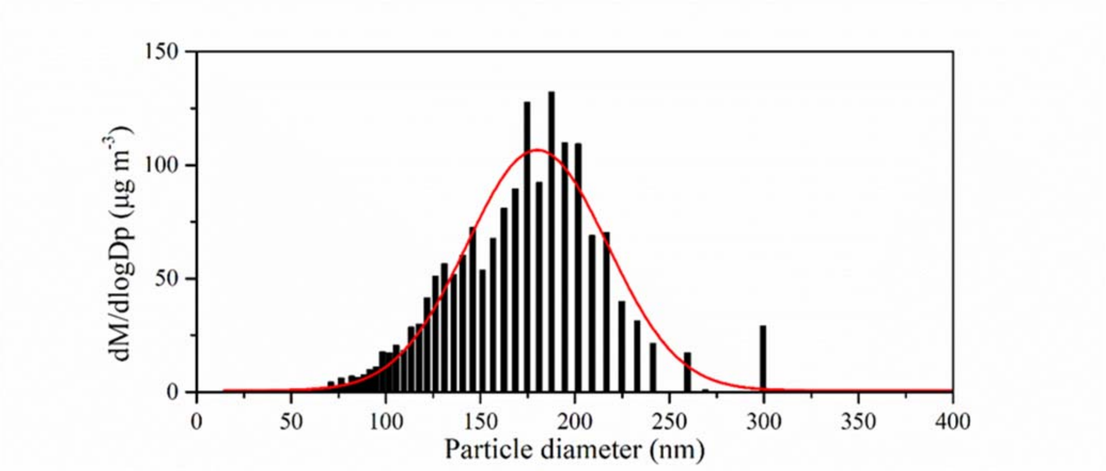

Figure R1. Particle size distribution

For the IC analysis, the limit of detection was 0.2 mg mL^{-1}.
The following is added in the manuscript at page 5 line 13 to clarify:
"For the IC analysis, the limit of detection was 0.2 mg mL^{-1}."

Were samples for FTIR and SOA analysis collected right after each other?

No. While FTIR is very sensitive and does not require high concentrations of the samples, the SOA analysis needs higher concentrations. For SOA analysis, the concentrations were increased in order to have more SOA formation. Hence, the samples for SOA analysis were collected after the samples for FTIR analysis. However, both samples types were collected using the same method, and all experiments were conducted using the same procedure.

Results and discussion Section 3.1 should be moved to the experimental section.

We have moved the content of Section 3.1 to the experimental section.

Section 3.2 Page 6 line 22. The trend is not clear, especially regarding maximum particle number, which shows quite some scatter.

Page 6 line 26-32: The conclusions in this section are beyond what I see in the data, given the scatter.
Why are some of the experiments not shown in Figure 1? Only 11 out of 17 experiments can be seen.

Based on the available data and despite the scattered behavior of the maximum particle number concentration relative to the particle number concentration at maximum yield with increasing SO_2 concentration, we can find an acceptable correlation between the two types of number concentrations, as we mentioned at page 6 lines 21-22. The change in the trend of SOA number concentrations is quite evident from the particle number concentrations at the maximum SOA yield as can be observed in Figure R2 below.

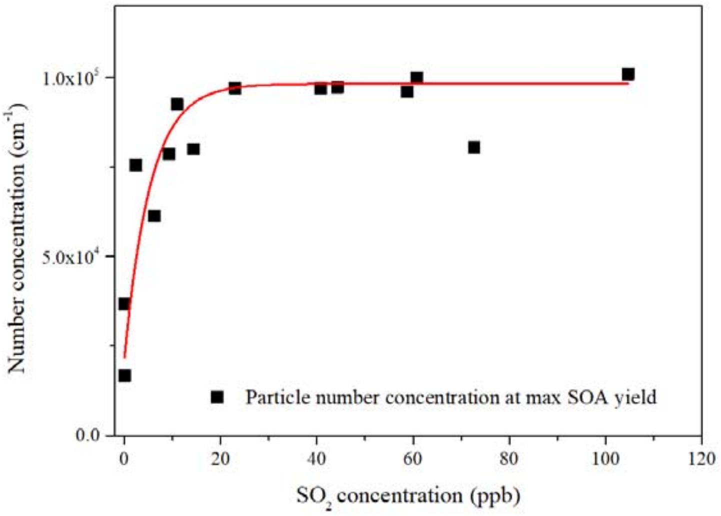

Figure R2: Particle number concentrations of SOA in the photooxidation of the cyclohexene/NOx/SO_2 system with different initial SO_2 concentrations.

The scattered behavior of the maximum particle number concentrations was likely caused by measurement errors. These concentrations were obtained upon particles formation after the black light lamps were switched on. SOA number concentrations increased rapidly to reach the maximum, and subsequently, the particle number concentrations decreased, as shown in Figure S1. The particles were collected by SMPS at a sampling interval of 5 min. The decrease rate of the particle number concentration was very fast, about 25% after 5 min, which also corresponds to the time at which the maximum number concentration was obtained.
To avoid any misinterpretation of our data and our conclusions due to the data being scattered, Figure 1 of the main manuscript was replaced by Figure R2 in this response.

There are two main reasons why there are some maximum particle number concentrations were missing. Firstly, as shown in Figure S1, the maximum number concentration was obtained in the beginning of SOA formation, but the maximum mass concentration was obtained one hour later. For our experiments, we focus on the

ultimate yield of SOA and hence, the SMPS analysis was not performed immediately after the UV light was turned on.
Secondly, the collection volume by the impactor was slightly smaller than the volume of the chamber. In order to reduce gas consumption in the smog chamber, the particles were not sampled continuously by SMPS from the beginning of the experiment. Despite the missing data on the maximum particle number concentration the trend of SOA number concentration with initial SO_2 is obvious.

Page 7 lines 1-4: This discussion is very unclear.

We re-wrote this as:
"It is evident from Figure 1 that even small amounts of SO_2 affect the new particle formation substantially. This is in agreement with the finding that wood soot, a minor source of SO_2 (Reddy and Venkataraman, 2002), resulted in a measurable positive deviation to the VOCs/NOx photooxidation reaction system without background aerosol (Jang et al., 2002)."

Page 7 line11: It is of course difficult to reproduce concentrations of VOC and NOx in an experiment, which is also clear from the present work. Therefore the statement of "similar" conditions is too strong. VOC concentration varies from 472 to 665 ppb, which also affects SOA formation to some degree (seen by plotting the data presented here).

We agree that the statement with "similar" can be misleading. Because this statement does not actually give extra information on the stated finding, it was deleted, however, without changing the meaning of the main result.

Page 7 line 18-19: This seems speculative.

This sentence was deleted.

Page 7 line 22-23: This meaning is unclear.
This was re-written as:
"New particles were formed by vapor condensation onto existing aerosol particles."

Section 3.3. Page 7 line 30: According to your data in Table S1 the SOA yield without SO2 present was 2.7-3.4%, not 2.5-2.7% as stated here.

This was fixed.

Page 8 line 10: The ratio was 4.4-7 according to Table S1, not 5 as stated here.

This was fixed.

Figure 2. The SOA yield shows a trend, but only to some degree, since the values for low SO2 concentrations are somewhat scattered, while experiments at high concentrations have not been repeated. This means that conclusion about a trend in the data is based on very few data points at high SO2 concentrations. The discussion e.g. on page 8 lines 23-31 should be revised considerably with this in mind.

Due to the error associated with measuring SO_2 concentrations, many experiments were needed at low concentrations (below 40 ppb) for a better reproducibility of the experimental data since even 1 ppb error in SO_2 concentration can have significant effects. However, this error is less important at higher SO_2 concentrations and hence, few data points were used. The scattered behavior of the SOA yield at low SO_2 concentrations is primarily a consequence of the errors due to measuring the concentrations, and the trend of Figure 2 is not expected to change. Based on this, the discussion on page 8 lines 23-31 is modified as:

"SOA yields for the cyclohexene/NOx/SO_2 system were measured for initial SO_2 mixing ratios of 0-105 ppb. Due to the error associated with the SO_2 concentrations measurement, with stronger impact on low values than on higher values, several experiments were performed at SO_2 concentrations below 40 ppb. The experimental results showed a clear decrease at first and then an increase in the SOA yield with increasing SO_2 concentrations (Figure 2). When SO_2 concentrations increased from 0 to 40.8 ppb, there was a remarkable decrease in SOA yield, dropping by about half with the increase of SO_2 concentration. For SO_2 concentrations higher than 40.8 ppb, SOA yield increased with increasing SO_2 concentration. The highest SOA yield was obtained to be 3.5%, at 104.7 ppb SO_2 concentration. The lowest SOA yield of cyclohexene photooxidation was obtained at the initial SO_2 concentration of 40 ppb. Although the SOA yield increased gradually with the initial SO_2 concentration at concentrations higher than 40 ppb, a higher SOA yield than that in the absence of SO_2 could not be obtained when the initial SO_2 concentration was lower than 85 ppb."

Page 9 line 1-3: Which experiments were with NO and which with NO2?

A new plot for Figure 2 was made, in which experiments initiated with NO and NO_2 are clearly distinguished. Also, different NO- and NO_2-initiated experiments are marked in Table 1.

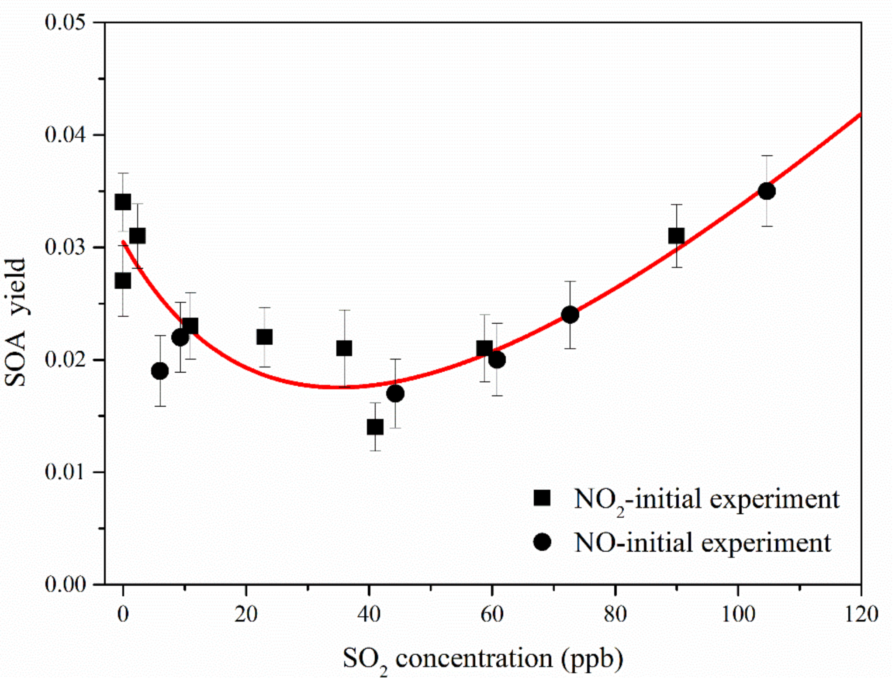

Figure 2: SOA yields of cyclohexene photooxidation in the presence of NOx at different initial SO_2 concentrations. Solid line is least-square fitting to the data. The error bars were determined on the basis of propagation of uncertainties arising in the ΔHC measurements, including GC calibration uncertainties propagation and the variance in the initial cyclohexene measurements.

Table 1 Experimental conditions for the photooxidation of cyclohexene/NOx/SO_2 system. All experiments were performed under dry conditions (relative humidity < 10%). ΔM_0 is the produced organic aerosol mass concentration and Y is the SOA yield.

Exp.	T (K)	SO_2 (ppb)	cyclohexene (ppb)	NOx (ppb)	cyclohexene/NOx	ΔM_0 ($\mu g\ m^{-3}$)	Y (%)
1 [b]	308	0.0	596	122.0	4.9	57.0	2.66
2 [b]	305	0.0	651	93.7	6.9	79.7	3.40
3 [b]	309	2.4	553	95.7	5.8	62.6	3.15
4[a]	307	5.8	612	92.7	6.6	41.0	1.87
5[a]	309	9.3	599	93.5	6.4	48.1	2.23
6 [b]	309	11.0	574	94.7	6.1	47.1	2.28
7 [b]	309	23.0	514	90.5	5.7	42.6	2.30
8 [b]	305	36.6	665	99.7	6.7	96.3	2.01
9 [b]	308	40.8	472	91.4	5.2	22.6	1.33
10[a]	308	44.3	592	98.6	6.0	35.3	1.66
11 [b]	305	55.0	497	113.0	4.4	77.3	2.16
12 [b]	308	58.8	577	96.7	6.0	44.3	2.13
13[a]	309	60.8	626	102.0	6.1	43.9	1.95
14[a]	308	72.7	581	98.4	5.9	49.2	2.35
15 [b]	306	90.0	543	99.6	5.4	102.0	2.62
16[a]	309	104.7	608	93.7	6.5	77.1	3.52
17[bc]	305	236.0	1048	198.0	5.3	-	-
18[bc]	306	93.7	1235	215	5.7	-	-

a: the experiment was initiated by NO.

b: the experiment was initiated by NO_2.

c: the formed particles were detected by ESI-HR-MS.

Section 3.4 Please distinguish between sulfonate and organosulfate and make this more clear in the text.

Sulfonate and organosulfates are all members of organosulfur compounds, with respective formulae $R\text{-}SO_3^-$ and $R\text{-}O\text{-}SO_3^-$, where R is an organic alkyl or aryl group. The two terms are distinguished in the text.

Figure 3: The line for ratio should be removed as it is based on very few data points. Figure 5: This figure is very confusing. Some data points are placed on top of each other. Information on the secondary axis (scale + label) is missing. Furthermore the uncertainty on the measurements should be presented. I suggest to make two figures instead of one.

The ratio line from Figure 3 was removed. The discussion at page 9 lines 30-32 was modified as:

"Figure 3 shows that the changes with initial SO_2 concentrations were not uniform between the SO_4^{2-} concentration and ΔSO_2, which indicates that besides SO_4^{2-}, other products were formed from SO_2."

In Figure 5, all the results were normalized to SOA mass. In order to compare the changes of the results with different initial SO_2 concentrations and the relationship between the different results at the same SO_2 concentration, all the results were set as 1 at the initial SO_2 concentration of 44 ppb. This led to some points being overlapped in Figure 5. For clarification, we used different colors, Figure 5 was remade as follows. We do not need the secondary axis here since the magnitudes of the band at 1100 cm^{-1} and SO_4^{2-} are similar. The results of ΔSO_2 were measured before DPLI sampling, both the volume of the chamber and the sampling time being inconsistent with those of the measurement of the band at 1100 cm^{-1} and SO_4^{2-}. Hence, in order to be more rigorous, we deleted the results on ΔSO_2 in Figure 5.

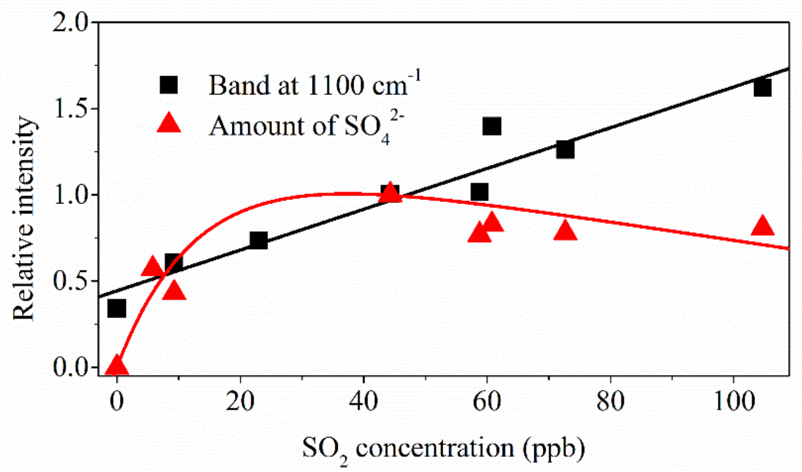

Figure 5: The relative intensity of the FTIR band at 1100 cm^{-1} (square) and the amount of SO_4^{2-} (triangle) normalized to SOA mass. The 1100 cm^{-1} band intensity and the amount of SO_4^{2-} were divided by the formed SOA mass. Subsequently, the results of both FTIR band at 1100 cm^{-1} and the amount of SO_4^{2-} divided by SOA mass were set to 1 when the initial SO_2 concentration was 44.3 ppb.

To clarify these changes, the statement at page 10 lines 23-24 was deleted. The statement at page 10 lines 27-28 was changed to "Figure 5 show the inconsistency between the FTIR band at 1100 cm^{-1} and the amount SO_4^{2-} as the initial SO_2 concentration, which implies that the 1100 cm^{-1} band originated not only from SO_4^{2-}, but also from other organosulfur compounds. These include organosulfates, which also have the S=O bond, and might contribute to the 1100 cm^{-1} band in the FTIR spectrum. The gap between the FTIR band at 1100 cm^{-1} and SO_4^{2-} can be attributed to the formation of organosulfates."

Page 10 line 30- and Figure 6: Did the composition and response of organosulfates vary between samples?

We investigated the composition and response of organosulfates between samples by performing another experiment with different initial SO_2 concentrations. We found that these did not vary much with the change in initial SO_2 concentrations, as can be seen in Figure S5 below.

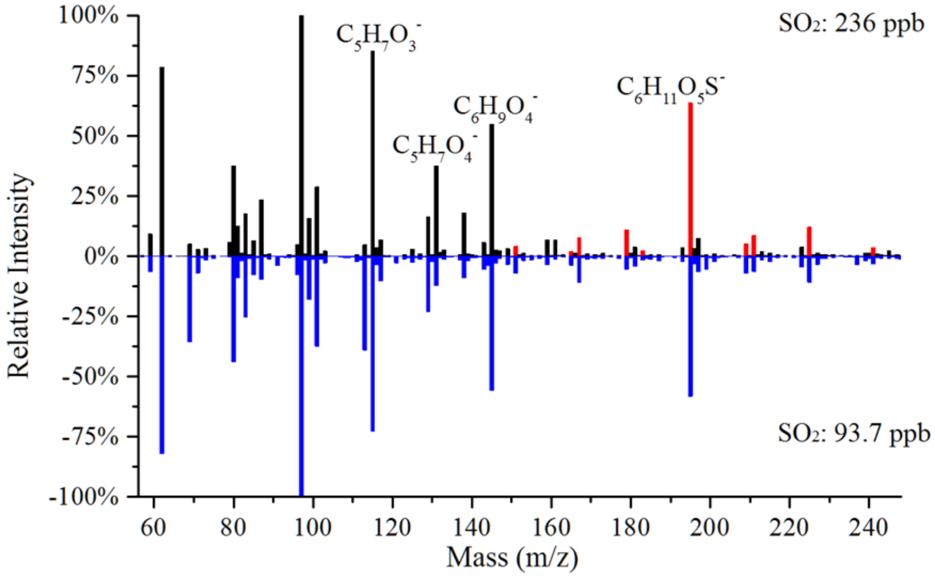

Figure S5: Comparison of SOA ESI-HR-MS spectra with different initial SO_2 concentrations.

The following was added at page 11 line 18 for clarification.

"The ESI-HR-MS spectra of particles formed from two different initial SO_2 concentrations are shown in Figure S3. We found no obvious difference in the composition and response of organosulfates with different initial SO_2 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 SO_2 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."

In conclusion, some of the results are interesting, but the quality of the presentation and discussion is not adequate for publication of this work in ACP.

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

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Abstract. Secondary organic aerosol (SOA) formation from cyclohexene/NOx system with various SO_2 concentrations under UV light was investigated to study the effects of cyclic alkenes on the atmospheric environment in polluted urban areas. A clear decrease at first and then increase of the SOA yield was found with increasing SO_2 concentrations. The lowest SOA yield was obtained when initial SO_2 concentration was in the range of 30-40 ppb, while higher SOA yield compared to that without SO_2 could not be obtained until the initial SO_2 concentration was higher than 85 ppb. 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 SO_2 concentrations, caused by the competition reactions of OH with SO_2 and cyclohexene. The competitive reaction was an important factor for SOA yield and it should not be neglected in photooxidation reactions. The composition of organic compounds in SOA was measured using several complementary techniques including Fourier transform infrared (FTIR) spectrometer, ion chromatograph (IC) and electrospray ionization high-resolution quadrupole mass spectrometer (ESI-HR-MS). We present the first evidence that organosulfates were produced from the photooxidation of cyclohexene in the presence of SO_2.

1 Introduction

Alkenes are widely emitted from biogenic and anthropogenic sources (Kesselmeier et al., 2002; Chin and Batterman, 2012), and their gas-phase oxidation reactions with OH, NO_3, or O_3 are among the most important processes in the atmosphere (Atkinson, 1997; Stewart et al., 2013; Paulson et al., 1999). The reactions of ozone with alkenes are an important source of free radicals in the lower atmosphere, which influence the oxidative capacity of the atmosphere (Paulson and Orlando, 1996). Some of the products have sufficiently low vapor pressures to condense with other gaseous species, and contribute to the secondary organic aerosol (SOA) mass (Sarwar and Corsi, 2007; Sakamoto et al., 2013; Nah et al., 2016; Kroll and Seinfeld, 2008; Hallquist et al., 2009). SOA formation from VOCs oxidation has been receiving significant attention since recent years due to its large implication in the formation of atmospheric fine particulate matter (Jimenez et al., 2009). SOA has significant impacts on human health (Pope III and Dockery, 2006), air quality (Kanakidou et al., 2005; Jaoui et al., 2012; McFiggans et al., 2006), and global climate change (Hansen and Sato, 2001; Adams et al., 2001; Pokhrel et al., 2016).

Although cyclic alkenes widely exist in the atmosphere, their gas-phase oxidation has received less attention than that of linear or branched alkenes (Sipilä et al., 2013). Cyclohexene is an important industrial chemical (Sun et al., 2013), and is also widespread in urban areas (Grosjean et al., 1978). Cyclohexene has been extensively studied as a monoterpene surrogate for inferring oxidation mechanisms and aerosol formation characteristics, because it has the basic structural unit in abundant biogenic monoterpenes and sesquiterpenes (Carlsson et al., 2012; Keywood et al., 2004). The rate constants for gas-phase reactions of cyclohexene with OH, O_3 and NO_3 were measured at room temperature to be $(6.4\pm0.1)\times10^{-11}$, $(8.1\pm1.8)\times10^{-17}$ and $(5.4\pm0.2)\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, respectively (Stewart et al., 2013; Aschmann et al., 2012), and a correlation between the logarithm of the rate constants and the molecular orbital energies for simple cyclic alkenes was observed. The effect of pressure and that of the presence of SO_2 on the formation of stable gas-phase products and SOA from ozonolysis of cyclohexene were investigated (Carlsson et al., 2012). It was found that the collisional stabilization of initial clusters was an important aspect for SOA formation processes involving sulfuric acid (H_2SO_4) and organic compounds. The effect of the structure of the hydrocarbon parent molecule on SOA formation was investigated for a series of cyclic alkenes and related compounds (Keywood et al., 2004), and the SOA yield was found to be a function of the number of carbons present in the cyclic alkenes ring. The relative SOA yields from ozonolysis of cyclic alkenes can be quantitatively predicted from properties of the parent hydrocarbons, like the presence of a methyl group and an exocyclic double bond.

SO_2, one of the most important inorganic pollutants in urban area, plays an important role on SOA formation (Wang et al., 2005; Lonsdale et al., 2012; Liu et al., 2016). Seasonal variations of SO_2 concentrations were found to be consistent with seasonal variations of $PM_{2.5}$ concentration (Cheng et al., 2015). Smog chamber simulations have indicated that SO_2 could enhance the formation of SOA from VOCs oxidation under acidic conditions by increasing aerosol acidity and ammonium sulfate aerosol formation (Edney et al., 2005; Liu et al., 2016; Attwood et al., 2014). Anthropogenic SO_2 emissions can impact new particle formation, and SOA composition (Lonsdale et al., 2012).

Despite the existence of organosulfates in ambient aerosols was first observed in 2005 (Romero and Oehme, 2005), proper identification of these aerosols was made two years later. In a series of chamber experiments studies, it was shown that organosulfates present in ambient aerosols collected from various locations mostly originate from acid-catalyzed reactions of SOA formed from photooxidation of α-pinene and isoprene (Surratt et al., 2007). Recently, different kinds of organosulfates have been observed in SOA around the world, and organosulfates have been identified as a group of compounds that have an important contribution to the total amount of SOA in the atmosphere (Surratt et al., 2008; Froyd et al., 2010; Kristensen and Glasius, 2011; Tolocka and Turpin, 2012; Wang et al., 2015). Laboratory chamber studies showed that OH/NOx/O_3-initiated reactions of BVOCs, such as isoprene, α-pinene, β-pinene, and limonene with sulfates or sulfuric acid are the main processes for organosulfates formation (Surratt et al., 2007; Surratt et al., 2008; Hatch et al., 2011). Despite the well-recognized presence of organosulfates in SOA, their formation and transformation processes can be complex and varied, depending on the nature of the original organic compound involved. Extensive studies on their formation have been performed and several mechanisms based on a variety of reactions have been proposed. Using nuclear resonance techniques, isoprene-derived epoxides formed during isoprene photooxidation reactions were found to be important intermediates for organonitrates and organosulfates formation via potential SOA reactions (Darer et al., 2011; Hu et al., 2011). The authors further found that organonitrates could easily be transformed to organosulfates during hydrolysis in the presence of sulfate. Some studies also showed that 2-methyl-3-buten-2-ol (MBO), due to its larger emissions than isoprene in some regions (Baker et al., 1999), is an important precursor for organosulfates and SOA in the atmosphere, through its reactions with OH under NO and aerosol acidity conditions, and from acid-catalyzed reactive uptake of MBO-based epoxides formed during MBO photooxidation (Mael et al., 2015; Zhang et al., 2012; Zhang et al., 2014). Organosulfates formation was also found from oxidation of hydroxyhydroperoxides (Riva et al., 2016) and from heterogeneous reactions of SO_2 with selected long-chain alkenes and unsaturated fatty acids (Passananti et al., 2016).

Reactions with sulfates or H_2SO_4 were the main formation processes of organosulfates. Qualitative analyses of the organosulfates in SOA have been gaining more attention and development since recent years (Lin et al., 2012; Shalamzari et al., 2013; Staudt et al., 2014). Riva et al. investigated the formation of organosulfates from photooxidation of polycyclic aromatic hydrocarbons and found that, in the presence of sulfate aerosol, this photooxidation was a hitherto unrecognized source of anthropogenic secondary organosulfur compounds (Riva et al., 2015). A more complete structural characterization of polar organosulfates that originate from isoprene SOA was performed (Shalamzari et al., 2013), and an organosulfate related to methyl vinyl ketone and minor polar organosulfates related to croton aldehyde were identified. However, there was no report about the yield and chemical composition of SOA obtained from photooxidation of cyclohexene in the presence of SO_2.

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

2 Methods

2.1 Chamber description

The experiments were performed in a 400 L Teflon FEP film chamber (wall thickness 125 μm) at the Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing. The details of the chamber, including the experimental setup and analysis techniques have been described elsewhere (Du et al., 2007; Jia and Xu, 2014), and only a brief description is presented here. The reactor was surrounded by 12 black light lamps (GE F40BLB) with emission band centered at 365 nm, which were used to simulate the spectrum of the UV band in solar irradiation. Stainless steel was covered on the chamber interior walls to maximize and homogenize the interior light intensity. The effective light intensity near the ultraviolet region plays a decisive role in the formation of photochemical smog (Presto et al., 2005a). The effective light intensity of the chamber was represented by the photolysis rate constant of NO_2. In our study, the average effective light intensity was determined to be 0.177 min^{-1}. Both inlet and outlet of the chamber were made of Teflon material. Atmospheric pressure was maintained in the chamber at all times. All the experiments were performed at room temperature (307±2 K) under dry conditions (RH < 10%). The wall loss is the decrease of the concentration of reactive gas phase species caused by adsorption on the inner wall of the reactor. Residual reactant and product on the inner wall can also react with the gas phase species, which is another important reason for wall loss. The wall loss can directly affect the quantitative evaluation of the photooxidation rate and SOA yield. A correct estimation of the wall loss is therefore necessary in a reliable analysis of the experimental results of SOA yield. In the present study, the wall loss of cyclohexene in the chamber could be neglected since no decrease in its concentration was observed. The wall loss of O_3, NOx, and SO_2 were first order because $\ln([X]_0/[X]_t)$ had a good correlation with time (R^2=0.994, 0.944, 0.999 for O_3, NOx, and SO_2, respectively). The measured wall loss rate constants for O_3, NOx and SO_2 were 5.05×10^{-6}, 7.04×10^{-6} and 6.39×10^{-6} s^{-1}, respectively. The average value of the wall loss rate constant of particles was 4.7×10^{-5} s^{-1}, and the measured particle concentrations in this study were corrected using the same method as Pathak et al. (Pathak et al., 2007). Typical profiles of the gas and particle phases are given in Figure S1 of the Supplementary material.

Prior to each experiment, the chamber was cleaned by purging with purified dry air for at least 8 h until residual hydrocarbons, O_3, NOx or particles could not be detected in the reactor. Known amounts of cyclohexene was injected into a 0.635 cm diameter Teflon FEP tube and dispensed into the chamber by purified dry air. Typical initial cyclohexene concentrations were 500 ppb. NOx was injected by a gas-tight syringe to make the mixing ratio of NOx in the reactor around 95 ppb during all the experiments. The mixed concentration ratios of cyclohexene/NOx were in the range 4.4-6.9. SOA formation experiments were carried out under UV irradiation in the presence of NOx to produce O_3 and OH radicals for cyclohexene oxidation. Although initial VOCs, NOx and average OH concentrations were different from typical urban conditions, efforts were made to maintain the initial concentrations of the reactants as similar as possible to make sure the effect of SO_2 was the main reason for the changes in the SOA yield. More details on the experimental conditions are shown in Table 1.

2.2 Gas and particle measurements

Ozone concentration in the reactor was measured using ozone analyzer (Model 49C, Thermo Electron Corporation, USA). A NO-NO_2-NOx analyzer (Model 42C, Thermo Electron Corporation, USA) was used to monitor the NOx concentration. Measurement of SO_2 concentration was made using a SO_2 analyzer (Model 43i-TLE, Thermo Electron Corporation, USA). The uncertainty of the O_3, NOx and SO_2 measurement was less than ±1%. The detection limits of the different monitors were 0.40 ppb, 0.50 ppb, and 0.05 ppb for NOx, O_3, and SO_2, respectively.

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

Particle number concentrations and size distributions were measured with a scanning mobility particle sizer (SMPS), which consists of a differential mobility analyzer (DMA model 3081, TSI Inc., USA) and a condensation particle counter (CPC model 3776, TSI Inc., USA). A sheath flow/aerosol flow relationship of 3.0/0.3 L min^{-1} was used for the measurements. The particle size was measured in the range of 14 to 710 nm, and each scan was 180 s. An aerosol density of 1.2 g cm^{-3} was assumed to convert the particle volume concentration into the mass concentration (Zhang et al., 2015). Size distribution data were recorded and analyzed using the TSI AIM software v9.0.

2.3 Products composition analysis

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

The characteristic bands of inorganic and organic sulfates overlap in the IR spectrum. In order to distinguish between the inorganic and organic sulfates, ion chromatograph (IC, Dionex ICS-900, Thermo Fisher, USA) was used to analyze the inorganic sulfate anion (SO_4^{2-}) in SOA. For the IC analysis, the limit of detection was 0.2 mg mL^{-1}. SOA collected on ZnSe disks was firstly dissolved in high purity water (7 mL) and then measured by IC for SO_4^{2-} concentrations. The anions were analyzed with a Dionex IonPac AS14A analytical column and an anion self-regenerating suppressor Dionex ASRS was used as eluent. The flow rate was 1.0 mL min^{-1} with a mixture of 8.0 mmol L^{-1} Na_2CO_3 and 1.0 mmol L^{-1} $NaHCO_3$ for anions analyses. The suppressing current was 50 mA.

Chemical characterization of aerosols from photooxidation of cyclohexene was performed using an electrospray ionization high-resolution quadrupole mass spectrometer (ESI-HR-MS, Thermo Fisher, USA) operated in negative (-) ion mode, which was calibrated using the manufacturer's calibration standards mixture allowing for mass accuracies <5 ppm in external calibration mode. The ionization voltage was 4.2 kV and the capillary temperature was set at 300 °C. N_2 was used as both the sheath gas (70 U) and auxiliary gas (30 U). SOA was collected on the aluminium foil using the same method as FTIR analysis and then extracted with 1 mL of acetonitrile. The aluminium foil was used due to its ease to handle and its non-reactivity with the sample. A total volume of 300 L was sampled at a flow rate of 10 L min^{-1}. A volume of 5 μL of the extraction and a direct injection were used for the measurement. Xcalibur 2.2 software (Thermo Fisher, USA) was used for the calculation of chemical formula from the accurate measurement of m/z values.

2.4 Chemicals

The chemicals used and their stated purities were as follows: cyclohexene (99%) was obtained from Aldrich and used without further purification. A zero air generator (Model 111, Thermo Scientific, USA) was used to generate clean air. The zero air has no detectable non-methane hydrocarbons (NMHC < 1 ppb), NOx (< 1 ppb), low O_3 concentration (< 3 ppb), and low particle numbers (< 5 cm^{-3}), and relative humidity (RH) below 10%. Ozone was produced from O_2 via electrical discharge using a dynamic gas calibrator (Model 146i, Thermo Scientific, USA). NO_2 (510 ppm), NO (50 ppm) and SO_2 (25 ppm) with ultra-pure N_2 (99.999%) as background gas was purchased from Beijing Huangyuan Gas Co., Ltd., China.

3 Results and discussion

3.1 Effect of SO_2 on SOA number concentrations

The particle number concentrations at the maximum SOA yield for the cyclohexene/NOx/SO_2 system with different initial SO_2 concentrations are shown in Figure 1. The cooperation of the maximum number concentration and the particle number concentrations at the maximum SOA yield is shown in Figure S2. After the black light lamps were turned on, the SOA number concentrations increased rapidly to reach the maximum within 0.5 h in each experiment. Subsequently, the particle number concentrations gradually decreased accompanied by the growth of particle size by coagulation. The SOA mass concentration kept increasing until its maximum was reached (after ~2 h). Both types of particle number concentrations had similar trends against initial SO_2 concentrations. In general, maximum particle number concentrations were three times higher than the particle number concentrations at the maximum SOA yield. In the remainder of this paper, in order to better elaborate the effect of SO_2 on the formation of particles, the particle number concentration refers to the particle number concentrations at the maximum SOA yield.

The particle number concentration increased with initial SO_2 concentration, and this increase could be divided into two stages: increasing stage and stable stage. In the increasing stage, with the initial SO_2 concentration increasing from 0 ppb to 30 ppb, the particle number concentration grew significantly under low initial SO_2 concentration (<5 ppb), then the growth rate reduced gradually. In the stable stage, when the SO_2 concentrations were varied systematically between 30 and 105 ppb, particle number concentrations were practically maintained steady, and there was no further obvious growth as shown in Figure 1. For experiments with high initial SO_2 concentrations, the particle number concentrations were 10 times higher than those without SO_2, indicating enhanced new particle formation (NPF) when adding SO_2. It is evident from Figure 1 that even small amounts of SO_2 affect the new particle formation substantially. This is in agreement with the finding that wood soot, a minor source of SO_2 (Reddy and Venkataraman, 2002), resulted in a measurable positive deviation to the VOCs/NOx photooxidation reaction system without background aerosol (Jang et al., 2002).

Nucleation is a fundamental step in the atmospheric new particle formation. Nucleation of particles in the atmosphere has been observed to be strongly dependent on the abundance of H_2SO_4 (Sihto et al., 2006; Xiao et al., 2015). Normally, SO_2 was deemed to be oxidized by OH radicals to form H_2SO_4 through homogeneous reactions in gas phase (Calvert et al., 1978), or by H_2O_2 and O_3 through in-cloud processes in aqueous phase (Lelieveld and Heintzenberg, 1992). The aqueous phase formation of H_2SO_4 is negligible in this study (RH<10%). As the precursor of H_2SO_4, SO_2 at high concentrations would lead to more H_2SO_4 formation, and thereby increase the nucleation rates and total particle number concentrations (Sipilä et al., 2010). Because of the similar initial conditions for each experiment except SO_2, the amount of OH radicals produced was assumed to be almost equal. In the presence of high concentrations of SO_2, new particle formation was not enhanced. This feature may indicate that no more sulfates were formed when SO_2 was in large excess (>30 ppb) and the OH radicals were insufficient. The quantity of OH radicals is the main restraint on H_2SO_4 formation at high initial SO_2 concentrations, which could not lead to more H_2SO_4 formation in the present study. Therefore, the particle number concentration was maintained steady, and it was independent of the SO_2 concentrations in the second stage.

Besides, the mean diameter of particles increased with photooxidation reaction time, which suggests that not many new particles were generated after a burst increase at the initial stage of SOA formation. Once new particles are formed, there is a competition between growth of existing particles by uptake of the precursors and formation of new particles. Our result agrees with previous studies that there was no obvious increase in aerosol number concentration when additional VOCs were injected, but a significant increase in SOA mass concentration (Presto et al., 2005a). New particles were formed by vapor condensation onto existing aerosol particles. If there was enough seed particle surface area, observation of new particles formation would not be expected.

3.2 Effect of SO_2 on SOA yields

SOA yield (Y) is defined as $Y=\Delta M_0/\Delta HC$, where ΔM_0 is the produced organic aerosol mass concentration (μg m^{-3}), and ΔHC is the mass concentration of reacted cyclohexene (μg m^{-3}). The SOA yields of cyclohexene at different SO_2 concentration as determined by SMPS are shown in Figure 2. The numerical values of the aerosol mass concentration and SOA yields at different conditions are shown in Table 1.

The SOA yields in the absence of SO_2 were in the range of 2.7-3.4%, which were an order of magnitude lower than those reported in previous studies (Warren et al., 2009; Keywood et al., 2004; Kalberer et al., 2000). There are three possible explanations to this phenomenon. (1) SOA formation is closely related to the oxidation capacity in the photooxidation experiments and, therefore, is affected by the ratio of $[VOC]_0/[NOx]_0$ (Pandis et al., 1991). Experiments performed with different SO_2 concentrations indicate that the SOA formation is partly controlled by the ability of the system to oxidize cyclohexene and contribute to the particle mass. As indicated in Figure S3 of the Supplementary material, even at 0 ppb of

SO_2, the mass concentration of SOA quickly reaches its maximum. Experiments with higher NOx levels have been proved to get considerably lower SOA yield than those with lower NOx levels at the same VOCs concentration (Song et al., 2005). The reactions of organo-peroxy radicals (RO_2) with NO and NO_2 instead of peroxy radicals (RO_2 or HO_2) under high NOx conditions resulted in the formation of volatile organic products and a decreased SOA yield (Lane et al., 2008). It was reported that SOA yield was constant for $[VOC]_0/[NOx]_0>15$, but decreased considerably (by a factor of more than 4) as $[VOC]_0/[NOx]_0$ decreased (Presto et al., 2005b). In our study, the $[VOC]_0/[NOx]_0$ ratio was maintained at about 4.4 to 6.9. Recently, the NOx dependence of SOA formation from photooxidation of β-pinene was comprehensively investigated (Sarrafzadeh et al., 2016), and it was shown that the NOx-induced OH concentration was the major factor influencing the SOA yield. The impacts of NOx on SOA formation were only moderate if the impact of NOx on OH concentration was eliminated. OH concentration in our study was relatively insufficient, which was the main limiting factor for SOA formation. (2) UV light is another factor influencing the SOA yield. SOA yields between dark and UV-illuminated conditions were reported to be different (Presto et al., 2005a). Exposure to UV light could reduce SOA yield by 20-40%, while more volatile products were formed (Griffin et al., 1999). (3) The temperature may have a pronounced influence on SOA yield (Qi et al., 2010; Emanuelsson et al., 2013). At low temperatures, semi-volatile organic compounds would favor the condensation of gas phase species and a higher SOA yield could be expected. Raising the chamber temperature by 10 K should cause a decrease of 10% in aerosol yield (Pathak et al., 2007). SOA yields reported in the present study were obtained at a higher temperature, (307±2 K) than 298 K used in most previous studies. On the basis of the discussion above, the SOA yield from cyclohexene in our study was lower than observed in the previous studies.

SOA yields for the cyclohexene/NOx/SO_2 system were measured for initial SO_2 mixing ratios of 0-105 ppb. Due to the error associated with the SO_2 concentrations measurement, with stronger impact on low values than on higher values, several experiments were performed at SO_2 concentrations below 40 ppb. The experimental results showed a clear decrease at first and then an increase in the SOA yield with increasing SO_2 concentrations (Figure 2). When SO_2 concentrations increased from 0 to 40.8 ppb, there was a remarkable decrease in SOA yield, dropping by about half with the increase of SO_2 concentration. For SO_2 concentrations higher than 40.8 ppb, SOA yield increased with increasing SO_2 concentration. The highest SOA yield was found to be 3.5%, and was at 104.7 ppb SO_2 concentration. The lowest SOA yield of cyclohexene photooxidation was obtained at an initial SO_2 concentration of 40 ppb. Although the SOA yield increased gradually with the initial SO_2 concentration at concentrations higher than 40 ppb, a higher SOA yield than that in the absence of SO_2 could not be obtained when the initial SO_2 concentration was lower than 85 ppb.

SOA formation was enhanced by the presence of SO_2 (Jang et al., 2002), which has been previously attributed to acid-catalyzed heterogeneous reactions and produced an increase of the total organic aerosol mass (Xu et al., 2014). Even small amounts of acid are capable of catalyzing heterogeneous reactions. Both NO and NO_2 were used as NOx for the repeated experiments in our study. Although the photooxidation reaction could not happen in the case of NO until it was oxidized to NO_2, which means that both NO- and NO_2-initiated photooxidation reactions were actually triggered by NO_2, the chemistry of SOA formation from both processes is similar. Despite the time of occurrence of the maximum SOA concentration for the experiment with NO_2 was half an hour earlier than that for the experiment with NO, the results of SOA yield were similar. However, there were some undiscovered processes in the cyclohexene/NOx/SO_2 system that offset potential multifold increases in the SOA yield by acid-catalyzed heterogeneous reactions. The competitive reaction between SO_2 and VOCs might be the reason for the decrease of the SOA yield. SO_2 could be oxidized by OH radicals to form H_2SO_4 (Somnitz, 2004). Due to the presence of O_3 in our system, the formation of intermediates and their reactions with SO_2 could be expected (Criegee, 1975). However, the importance of these reactions can be kinetically limited. The reaction of cyclohexene with ozone has a rate constant of 8.1×10^{-17} cm^3 $molecule^{-1}$ s^{-1} (Stewart et al., 2013), considerably slower than e.g., its reaction with OH, which has a rate constant of 6.4×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Aschmann et al., 2012). In addition to the kinetic limitation of the cyclohexene reaction with O_3, the typical concentration of O_3 in our chamber was 200 ppb and hence the importance of cyclohexene reaction with O_3 was expected to be less significant than that of its reaction with OH under any relevant SO_2 conditions. The competitive reaction resulted in a decrease of the concentration of OH radicals, which was one of the main oxidizers for the photooxidation in the chamber. As mentioned above, the photooxidation in this study was at high-NOx conditions and the OH was the main limiting factor for SOA formation because of its relatively low concentration. The change of cyclohexene concentration with time at different initial SO_2 concentrations is shown in Figure S4, wherefrom it can be seen that the reacted cyclohexene concentration at 0 ppb initial SO_2 concentration was slightly higher than that at 90 ppb. The consuming rate of cyclohexene was higher without SO_2 in the chamber, which means that if there was a competition reaction, its effect was very limited. Moreover, in real atmospheric situations where O_3 is found in much higher proportion than OH, cyclohexene would mainly react with O_3 to produce Criegee intermediates, which are good SO_2 oxidizers, and significantly less SOA than in the chamber will be formed. At lower OH radical concentration condition caused by the reaction between SO_2 and OH radical, the formation of SOA was inhibited. It was also found that during the Investigation of Sulfur Chemistry in the Antarctic Troposphere, the OH tends to increase when the influx of SO_2 from above decreases (Mauldin et al., 2004), which means that there is a negative correlation between OH and SO_2 in real atmosphere. Accordingly, SOA yield showed descending trend with the increase of SO_2 concentration when the initial SO_2 concentration was lower than 40 ppb.

When the initial SO_2 concentration was greater than 40 ppb, the acid-catalyzed heterogeneous formation of SOA became more significant (Figure 2). The lowest SOA yield was obtained at 40 ppb initial SO_2 concentration. At this concentration, there was a balance between the inhibition of SOA formation by competitive reactions and the promotion by acid-catalyzed reactions. The same SOA yield was obtained in the absence of SO_2 and at 85 ppb initial SO_2 concentration. The competitive reaction plays an important role on SOA formation, and it should be taken into account in SOA simulation models or air quality models for more accurate prediction. The formation of low volatile organics (e.g. organosulfates) by photooxidation in the presence of SO_2 might be another reason for the increase of the SOA yield.

3.3 Organosulfates formation

When SO_2 was added into the chamber, the acidic aerosol particles were formed by photooxidation of SO_2 in a reaction initiated by OH. The changes in the amounts of SO_4^{2-} in particle phase and the consumption of SO_2 (ΔSO_2) with different initial SO_2 concentrations are shown in Figure 3. The amounts of SO_4^{2-} grew rapidly at low concentration of SO_2, but the relative growth rate became steady in the range of 20-60 ppb initial SO_2 concentrations. It was demonstrated that acid-catalyzed processes could take place when there is a small amount of acid catalyst (5 μg m^{-3}) (Czoschke et al., 2003). In our chamber, the concentration of sulfuric acid was greater than 5 μg m^{-3} when the initial SO_2 concentration was greater than 40 ppb. This indicates that acid-catalyzed reactions were evident in our experiment. However, both the amount and the growth rate of ΔSO_2 increased with initial SO_2 concentrations. Figure 3 shows that the changes with initial SO_2 concentrations were not uniform between the SO_4^{2-} concentration and ΔSO_2, which indicates that besides SO_4^{2-}, other products were formed from the reaction of SO_2.

Typical IR spectra of aerosols from the cyclohexene/NOx/SO_2 system under different SO_2 concentrations are presented in Figure 4. Based on the peak positions in the IR spectra, the functional groups represented by each peak are summarized as follows: the broadband at 3100 to 3300 cm^{-1} is assigned to the O–H stretching of hydroxyl and carboxyl groups (Coury and Dillner, 2008). The peak at 1717 cm^{-1} represents the C=O stretching of aldehydes, ketones, and carboxylic acids. The peaks at 1622 and 1278 cm^{-1} show good correlation and both are assigned to the $-ONO_2$ stretching (Liu et al., 2012; Jia and Xu, 2014). The characteristic absorption band at 1500-1350 cm^{-1} is the C–O stretching and O–H bending of COOH group (Ofner et al., 2011). The absorption peak of sulfate exists in the range of 1200-1000 cm^{-1} (Wu et al., 2013). The band at 1100 cm^{-1} in the IR spectra can be attributed to the sulfate group in organic compounds and sulfate. It has been confirmed that the S=O absorption band in organic sulfate monoesters appears around 1040-1070 cm^{-1} (Chihara, 1958). Although, more studies on bands assignments in organosulfates are not currently available from the literature for further comparison, the 1100 cm^{-1} band from the current FTIR study can reasonably be assigned to S=O in the sulfate group.

The intensities of most absorption bands, such as O-H at 3100-3300 cm^{-1}, C=O at 1717 cm^{-1}, $-ONO_2$ at 1622 and 1278 cm^{-1}, and C-H at 2930 cm^{-1}, have similar trends with the change of SOA yield for initial SO_2 concentrations between 11 and 105 ppb. However, the band of sulfate at 1100 cm^{-1} in IR spectra increases with the rise of initial SO_2 concentration rather than the SOA yield, which suggests the formation of sulfate group in organic compounds and sulfate product from SO_2 photooxidation since, only the relative difference in the intensities of FTIR peaks were studied here. The relative intensity of the band at 1100 cm^{-1} increased by 1.8 times when the initial SO_2 concentration rose from 0 to 44 ppb, while the band increased by 7.2 times when the initial SO_2 concentration was 105 ppb. The intensity of 1100 cm^{-1} band grew slowly at low SO_2 concentrations due to the decrease in the formation of aerosols. To clearly show the amount of sulfate group and sulfate in aerosols, the intensity of the band at 1100 cm^{-1} and the amount of SO_4^{2-} were compared in the same aerosol mass, as shown in Figure 5. The relative intensity was set to 1 when the initial SO_2 concentration was 44.3 ppb.

With the increase of SO_2 concentration, the amount of SO_4^{2-} in unit mass of aerosols increased first and then decreased, which was in negative correlation with SOA yield. The relative band intensities at 1100 cm^{-1}, which represented the intensity of both SO_4^{2-} and the sulfate group in organic compounds, also increased approximately in a linear form with the increase of initial SO_2 concentration (R^2=0.91). If the 1100 cm^{-1} band originated from SO_4^{2-} only, the change of the band intensity would be consistent with SO_4^{2-} concentration in unit mass of aerosols. Figure 5 shows the inconsistency between the FTIR band at 1100 cm^{-1} and the amount SO_4^{2-} as the initial SO_2 concentration, which implies that the 1100 cm^{-1} band originated not only from SO_4^{2-}, but also from other organosulfur compounds. These include organosulfates, which also have the S=O bond, and might contribute to the 1100 cm^{-1} band in the FTIR spectrum. The gap between the FTIR band at 1100 cm^{-1} and SO_4^{2-} can be attributed to the formation of organosulfates.

The composition of the cyclohexene SOA was examined with HR-MS using negative ion mode ESI and the mass spectrum was recorded at a resolution of 10^5 (Figure 6). The OH addition to the C=C bond produces an alkyl peroxyl (RO_2) radical that can react with NO to yield organonitrates (Perring et al., 2013). Although the formation of organonitrates was highly expected, there was no evidence of the presence of N-containing compounds from the main peaks of Figure 6, indicating that organonitrates would be formed at very low concentrations, if at all. A similar conclusion could be observed from Figure 4, when noticing that the -ONO_2 stretching peaks at 1622 and 1230 cm^{-1} have very low intensities. The presumed low concentrations of organonitrates might be due to the low concentration of NO when SOA was formed. RO_2 radicals also react with NO_2 to form peroxy nitrates (RO_2NO_2) on time scales comparable to $RONO_2$ formation. However, RO_2NO_2 are thermally labile and rapidly dissociate at ambient temperatures (Perring et al., 2013). Organosulfates were identified in the particle phase from the chamber experiments. Accurate mass fittings for measured ions of organosulfates in ESI negative ion mode are given in Table 2. As shown in Figure 6 and Table 2, 10 different organosulfates were successfully detected and identified from cyclohexene SOA. These results not only first prove the formation of organosulfates from cyclohexene photooxidation at high-NOx condition in the presence of SO_2, but also provide evidence and reference for organosulfates identification by FTIR-IC joint technique. A deprotonated molecular ion at m/z=195.03322 ($C_6H_{11}O_5S^-$) had the maximum content (more than 60%) of all the organosulfates detected in our study. Its intensity was 6.5 times higher than that of the second highest abundant organosulfate. The intermediate product of cyclohexene reaction with OH, i.e., $CH(O)CH_2CH_2CH_2CH_2\dot{C}HOH$, has a hydroxyl group, and the organosulfate product (m/z=195.03322) would likely form from the intermediate product, not from end product.

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

The ESI-HR-MS spectra of particles formed from two different initial SO_2 concentrations are shown in Figure S5. We found no obvious difference in the composition and response of organosulfates with different initial SO_2 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 SO_2 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.

4 Conclusion

We report a series of chamber experiments studies on the formation of secondary aerosols from the mixture of cyclohexene and SO_2. The experiments were based on Fourier transform infrared spectrometer, ion chromatography and electrospray ionization high-resolution quadrupole mass spectrometer, and were performed under NOx conditions. Although new particle formation was found to be enhanced with increasing SO_2 concentration, the yield of SOA was not enhanced for all SO_2 concentrations between 0 and 105 ppb. The SOA formation decreased at first and then was enhanced for all SO_2 concentration above 40 ppb.

Both acid-catalysis and competitive OH reactions with cyclohexene and SO_2 were found to have important effects on the SOA formation and hence, should be taken into account in SOA simulation models or air quality models for a better understanding of haze pollution. The formation of organosulfates, an important part of atmospheric organic aerosol components, was first observed from cyclohexene SOA. The formation of organosulfates has a great significance for the particulate matter formation under high SO_2 concentrations in the atmosphere.

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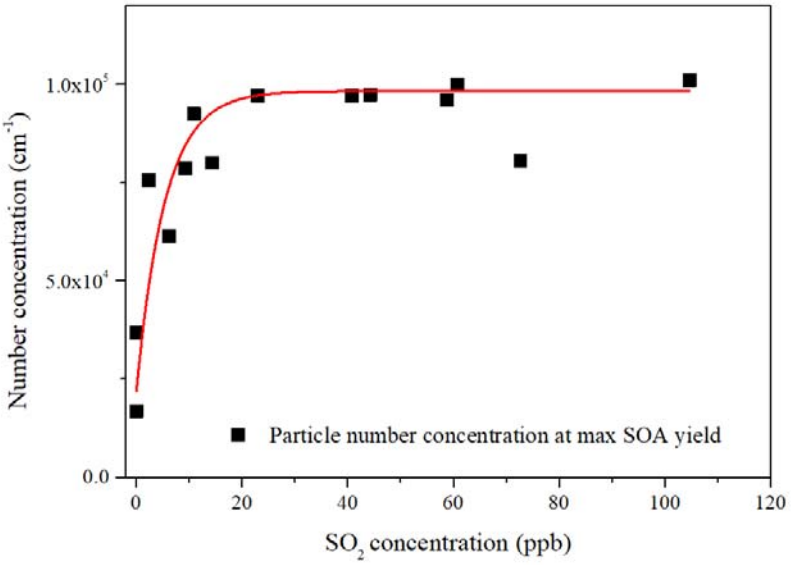

Figure 1: Particle number concentrations of SOA in the photooxidation of the cyclohexene/NOx/SO_2 system with different initial SO_2 concentrations.

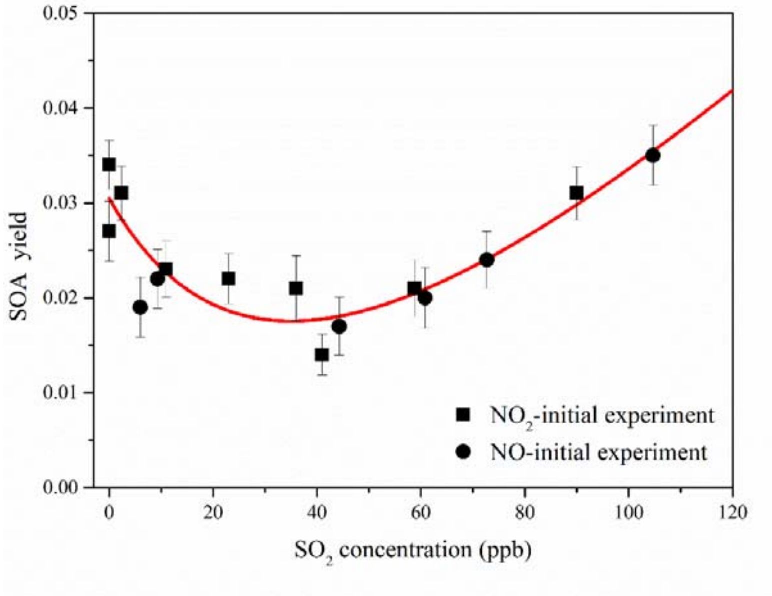

Figure 2: SOA yields of cyclohexene photooxidation in the presence of NOx at different initial SO_2 concentrations. Solid line is the least-square fitting to the data. The error bars were determined on the basis of propagation of uncertainties arising in the ΔHC measurements, including GC calibration uncertainties propagation and the variance in the initial cyclohexene measurements.

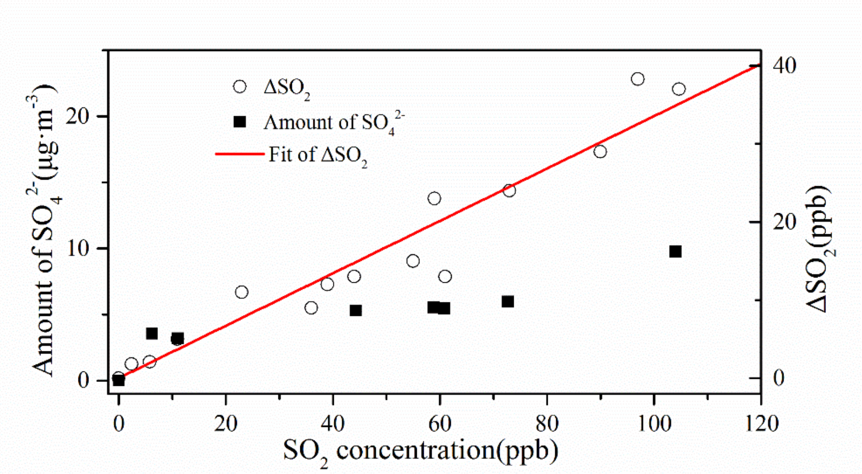

Figure 3: The amount of SO_4^{2-} in aerosols in the chamber, consumption of SO_2 (ΔSO_2) and the ratio of the amount of SO_2 for SO_4^{2-} formation to ΔSO_2 with different initial SO_2 concentrations.

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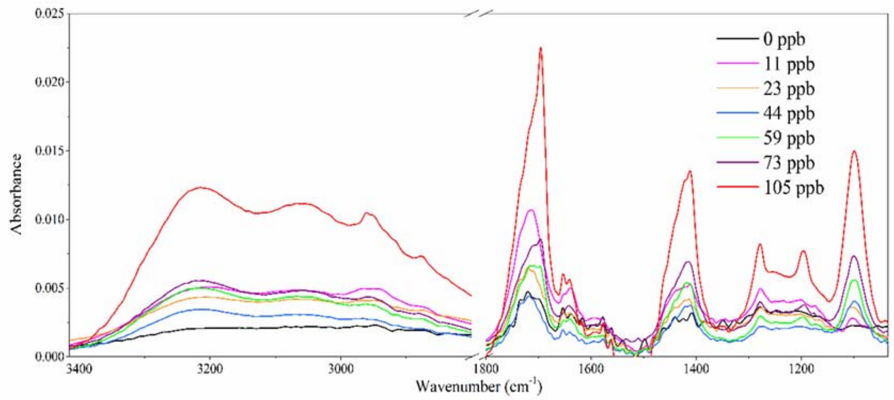

Figure 4: IR spectra of aerosols from the cyclohexene/NOx/SO_2 system under different SO_2 concentrations.

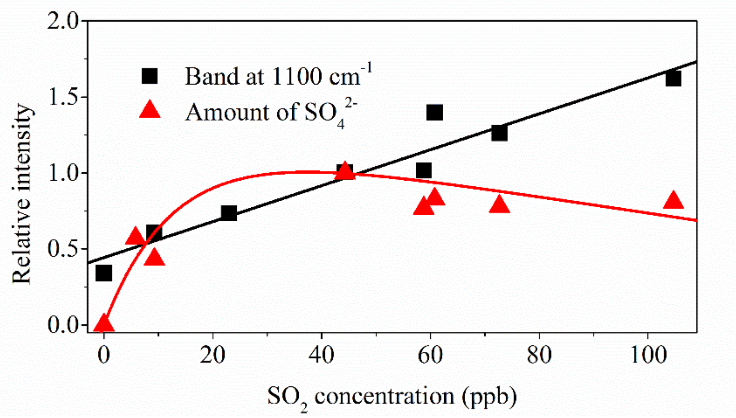

Figure 5: The relative intensity of the FTIR band at 1100 cm^{-1} (square) and the amount of SO$_4^{2-}$ (triangle) normalized to SOA mass. The 1100 cm^{-1} band intensity and the amount of SO$_4^{2-}$ were divided by the formed SOA mass. Subsequently, the results of both FTIR band at 1100 cm^{-1} and the amount of SO$_4^{2-}$ divided by SOA mass were set to 1 when the initial SO$_2$ concentration was 44.3 ppb.

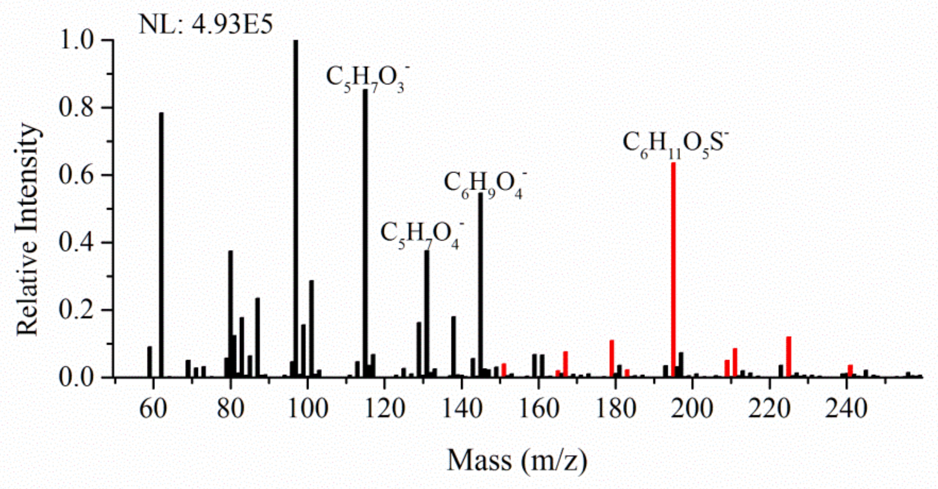

Figure 6: Negative ion mode ESI mass spectrum of SOA generated from the photooxidation of cyclohexene in the presence of SO$_2$. Red peaks correspond to organic compounds containing the sulfate group. The mass resolution is 10^5.

Table 1 Experimental conditions for the photooxidation of cyclohexene/NOx/SO_2 system. All experiments were performed under dry conditions (relative humidity < 10 %). ΔM_0 is the produced organic aerosol mass concentration and Y is the SOA yield.

Exp.	T (K)	SO_2 (ppb)	cyclohexene (ppb)	NOx (ppb)	cyclohexene/NOx	ΔM_0 (μg m^{-3})	Y (%)
1[b]	308	0.0	596	122.0	4.9	57.0	2.66
2[b]	305	0.0	651	93.7	6.9	79.7	3.40
3[b]	309	2.4	553	95.7	5.8	62.6	3.15
4[a]	307	5.8	612	92.7	6.6	41.0	1.87
5[a]	309	9.3	599	93.5	6.4	48.1	2.23
6[b]	309	11.0	574	94.7	6.1	47.1	2.28
7[b]	309	23.0	514	90.5	5.7	42.6	2.30
8[b]	305	36.6	665	99.7	6.7	96.3	2.01
9[b]	308	40.8	472	91.4	5.2	22.6	1.33
10[a]	308	44.3	592	98.6	6.0	35.3	1.66
11[b]	305	55.0	497	113.0	4.4	77.3	2.16
12[b]	308	58.8	577	96.7	6.0	44.3	2.13
13[a]	309	60.8	626	102.0	6.1	43.9	1.95
14[a]	308	72.7	581	98.4	5.9	49.2	2.35
15[b]	306	90.0	543	99.6	5.4	102.0	2.62
16[a]	309	104.7	608	93.7	6.5	77.1	3.52
17[bc]	305	236.0	1048	198.0	5.3	-	-
18[bc]	306	93.7	1235	215	5.7	-	-

[a]: the experiment was initiated by NO.

[b]: the experiment was initiated by NO_2.

[c]: the formed particles were detected by ESI-HR-MS.

Table 2. Accurate mass fittings for main products and measured organosulfates ions in ESI negative ion mode from cyclohexene photooxidation in the presence of SO_2 under high-NOx conditions

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

[a] Sort by abundance intensity.

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

[c] RDB: ring and double bond equivalent.