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.

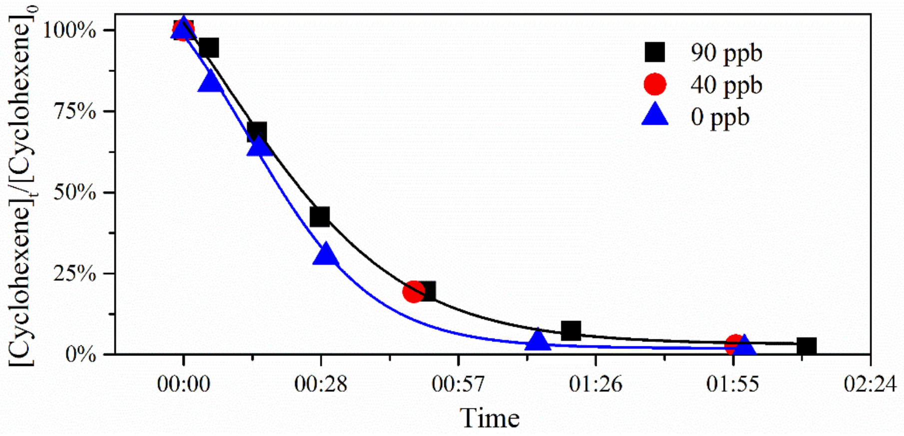

Figure S4: Change of cyclohexene concentration with time at different initial SO_2 concentrations.

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.

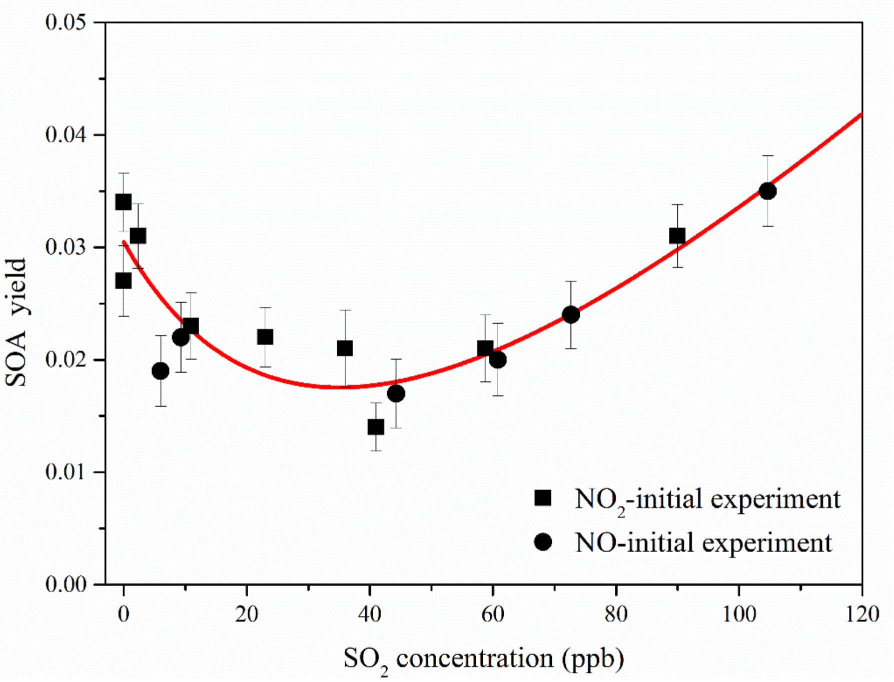

Figure 2: SOA yields of cyclohexene photooxidation in the presence of NOx at different initial SO_2 concentrations. The solid line is the least-square fitting to the data. The error bars were determined on the basis of propagation of uncertainties arising in the ΔHC measurements, including GC calibration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

References

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