

Interactive comment on “Effects of NO_x and SO₂ on the Secondary Organic Aerosol Formation from Photooxidation of α -pinene and Limonene” by Defeng Zhao et al.

Anonymous Referee #2

Received and published: 18 June 2017

This chamber study investigated the effects of SO₂ and NO_x (NO) on SOA formation from photooxidation of α -pinene and limonene. It was found that SO₂ enhanced SOA yield while NO_x suppressed SOA yield. The suppression effect of NO_x was attributed to the suppressed new particle formation and thus a lack of particle surface area for organics to condense on. The authors concluded that SO₂ oxidation produced high number of particles and compensated for the suppression of SOA yield by NO_x. SOA composition measured by AMS was also presented and discussed.

This is an interesting study. The gas- and particle-phase measurements are comprehensive and include several important species that have not been typically character-

C1

ized in previous studies (e.g., OH, HO₂ and RO₂). The experiments appeared to be carefully conducted. However, I have major concerns regarding data interpretation and some conclusions in the manuscript.

One of the central themes of the manuscript is that the suppression effect of NO_x on SOA formation can be compensated by the presence of SO₂. This conclusion is not accurate based on all the data presented in this manuscript. For α -pinene, it appears that under high SO₂ conditions, the SOA yields under low vs. high NO_x conditions are comparable. However, this is not the case for limonene, where there is still a large difference in SOA yields between low vs. high NO_x conditions in the presence of high SO₂. The manuscript needs to be thoroughly revised to accurately reflect what the data are showing. If one set of data is showing one thing and another set of data is showing the opposite, the authors need to discuss both datasets equally and cannot conclude that SO₂ effect can compensate NO_x effect.

The authors concluded that the suppression effect of NO_x on SOA yields is mainly due to suppression of nucleation (absence of particle surface area as condensation sink) rather than decrease of condensable materials. If particle surface area plays a role, this will point to the importance of loss process of oxidation products via chemical reactions and/or chamber wall loss. However, the effect of loss of organic vapors on chamber walls is not considered in this study. Nevertheless, previous studies on α -pinene oxidation suggested that SOA yield is independent of particle surface area. In this regard, the interpretation that the suppression effect of NO_x arises from a lack of particle surface area appears to be at odds with previous studies. All in all, it is not clear how the absence of particle surface area can explain the suppressed SOA yields under high NO_x condition in this study.

The authors explained the effect of SO₂ as 1) inducing new particle formation and providing surface area for vapor condensation, 2) acid-catalyzed particle-phase reactions. I have the same question regarding the first explanation, i.e., what is the role of vapor wall loss (if any), and how does one reconcile this explanation with findings from previ-

C2

ous studies? Also, what is the effect of SO₂ on gas-phase chemistry and SOA yield? This is not considered.

It appears that the SOA yields in high SO₂ experiments might be overestimated by double counting the density of ammonium sulfate/ammonium bisulfate in the SOA mass calculation. This is not entirely clear.

Finally, the authors need to conduct a more careful and accurate comparison with previous studies. It was noted that in high SO₂ conditions, their findings that SOA yields are comparable under high NO_x and low NO_x conditions are in line with Sarrafzadeh et al. and Eddingsaas et al. I do not think that the data in Eddingsaas et al. showed this. SOA yields are also a function of ΔMo (as well as various experimental conditions and parameters) and this could play a role, see detailed comment below. Also, the α -pinene yields in this study under comparable NO_x/SO₂/OH exposure are much lower than Eddingsaas et al.. This is not mentioned and discussed in the manuscript.

Major revisions are needed before the manuscript can be published. Specific comments are listed below.

Detailed comments

1. Line 18-20. This statement is not true for limonene data presented in this study.
2. Line 79 -81. This sentence seems to imply that previous studies that used higher NO_x and SO₂ concentrations are not atmospherically relevant. I think these sentences should be revised and clarified to more accurately reflect the experimental design and results from previous studies. For instance, the use of high levels of NO_x (e.g., from HONO or CH₃ONO) in some studies is to push the RO₂ radical fate to the extreme (i.e., RO₂+NO or RO₂+NO₂) to investigate SOA yields and composition under such conditions. Thus, the use of high levels of NO_x do not necessarily mean that the results are not applicable to ambient conditions.
3. Line 132. Is the organic aerosol density 1.32 g/cm³ from Eddingsaas et al. (2012a)?

C3

If this is the case, note that this density used in Eddingsaas et al. is directly taken from the results in Ng et al. (2007), and that this density was obtained in the presence of seeds already. Therefore, it appears that there might be a double counting of the density of ammonium sulfate/ammonium bisulfate in the data presented here?

4. Line 162. How were OH and O₃ formed in the experiments (under each combination of NO_x/SO₂ condition). Please provide more info. Also, please provide typical time profiles of VOC (either α -pinene or limonene), O₃, OH, NO, NO₂, SO₂ for each combination of NO_x/SO₂ condition. These are important to help the readers obtain a better idea of the reaction pathways/regimes under each condition.
5. Line 163. Was all the VOC reacted in each experiment?
6. Lin 163. There is no "typical" experiment in this study, as each experiment was conducted under a different NO_x/SO₂ condition. Please clearly state that this is only for low NO_x condition. Also, what about high NO_x condition? Was it exclusively OH reaction? Please also specify clearly.
7. Line 173 – 177. Here, under low NO_x condition, RO₂+NO dominates throughout the entire experiment (RO₂+HO₂ only contributes to ~40% at most).
 - a. These sentences clearly demonstrate the shortcomings of classifying the experiments as low NO_x vs. high NO_x as discussed in Wennberg et al. (IGAC news, 2103). I suggest the authors to characterize reactions conditions by explicitly stating the RO₂ fates, rather than as low vs. high NO_x.
 - b. It is stated that under low NO_x conditions, in the beginning of the experiment, a trace amount of NO is formed from photolysis of HONO from the chamber wall. Is this just in the beginning of the experiment, or there is a continuous NO source from HONO photolysis throughout the entire experiment? Please specify.
8. Line 189. The authors attributed the lower particle number concentration and nucleation rate at high NO_x to the decreasing RO₂+RO₂ reaction in the presence of NO_x.

C4

However, in line 182, the authors noted that RO₂+RO₂ reaction is negligible in this study to start with. Please reconcile these seemingly contradictory statements. Also, can be suppressed nucleation under high NO_x due to the higher volatility of organic nitrates as compared to peroxides (from RO₂+HO₂)?

9. Line 205-206. There is nucleation (from organics) in the presence of NO_x as shown in Fig. 4. In this sense, “absence of nucleation” here is a bit confusing. Perhaps would be clearer to say “absence of seed particles”.

10. Line 211 and Figure 3. The author concluded that the suppression effect of NO_x on SOA yields was mainly due to suppression of nucleation, i.e., to the absence of particle surface as condensation sink. Many critical aspects are not discussed, making this conclusion not well-justified and well-supported.

a. If the absence of seed particle surface area is the reason for the low yield under high NO_x condition (at low SO₂), this will point to the importance of loss of semivolatile species via chemical reactions or chamber wall loss (Kroll et al., ES&T, 2007). However, the effect of vapor wall loss is not considered in this study. Zhang et al. (PNAS, 2014) first systematically investigated the effects of particle surface area and vapor wall loss on SOA yields. For α -pinene photooxidation and ozonolysis specifically, it was found that SOA yields are largely independent of seed surface area (McVay et al., 2016, Nah et al., ACP, 2016; Nah et al., ACP, 2017). Therefore, taken all these together, it is not clear how the absence of particle surface area can explain the suppressed SOA yields under high NO_x condition in this study.

b. The authors dismissed the “decrease of condensable organic materials” in high NO_x conditions as an explanation for the observed decrease in yield. Why? If more volatile organic nitrates are formed in high NO_x conditions, why can't this be an explanation for the suppressed SOA yield? For limonene data (Line 213-218), the authors appeared to embrace the role of volatility of oxidation products.

c. Line 217. How does the different range in VOC/NO_x for α -pinene and limonene

C5

experiments explain the differences in yields in high SO₂ conditions? Please elaborate and explain clearly.

11. Line 225-237. Comparisons with previous studies. Many critical details are not considered and discussed. I think the authors jumped to the conclusion on whether their study agree/disagree with previous studies too quickly.

a. Line 225. This sentence is only true for α -pinene data in this study, but not for limonene. Please state clearly.

b. Seed particles were generated via SO₂ oxidation in this study (for high SO₂ experiments). Previous studies directly injected seeds into the chamber. In comparing SOA yields, the author should also consider the role of gas-phase chemistry and particle-phase chemistry. For instance, what about the reaction of SO₂ and cregee intermediates? What about the effect of particle acidity on particle-phase reactions (in this study vs. previous studies)? Please discuss.

c. The experiments in this study were conducted in the presence of humidity but previous studies were mostly conducted under dry conditions. RH can affect gas-phase and particle-phase chemistry, and subsequently SOA yields.

d. The authors noted that the finding that SOA yields at high NO_x is comparable to that at low NO_x in high SO₂ conditions is in line with findings in Sarrafzadeh et al. (2016) and Eddingsaas et al. (2012a). I do not think that the data in Eddingsaas et al. showed that “in presence of seed aerosol, the difference in the SOA yield between low and high NO_x is much reduced”. SOA yield is also a function of Δ Mo. Considering the data in Table 1 of Eddingsaas et al., the difference in yields between low and high NO experiments for nucleation is 19%, and for seeded experiments are 15% and 10%. However, the difference in Δ Mo for the nucleation experiments is also the largest and this will play a role in the yield difference.

e. The SOA yields in this study are much lower than previous studies, why? Consid-

C6

ering the low NO_x low SO₂ experiment, with OH dose of 1e11 molecules cm⁻³ s, the yield in this study is 7%. However, the corresponding yield in Eddingsaas et al. is > 30% (Figure 3 of Eddingsaas et al.).

12. Line 238 onwards, effect of SO₂.

a. One of the proposed reasons to explain the effect of SO₂ is that it induces nucleation and provides more particle surface area for condensation. Again, if this is the case, it will point to the importance of loss of organic vapors to chamber walls, though previous studies suggested that this process does not effect SOA yields from a-pinene oxidations to a large extent. With this, it is not clear if this is indeed a reason for the observed SO₂ effect. Please explain.

b. Line 258. Is “counterbalance” the appropriate word? If the suppression effect of NO_x is counterbalanced by the enhancement effect SO₂, in going from “low NO_x low SO₂” to “high NO_x high SO₂” one shall not observe change in SOA yields? Also, note that the limonene data showed very different trends comparing to the a-pinene data. This needs to be accurately and clearly stated.

13. Line 315-318. This explanation is a stretch and not well-justified. There is extensive fragmentation in the AMS and so the H/C ratios of oxidation product molecules do not necessarily translate to the H/C ratios measured. As shown in Chhabra et al., not all experiments conducted under low NO_x condition have higher H/C ratios.

14. Line 262 onwards. Did the ratio of nitrate mass concentration to organics mass change over time?

Minor comments

1. Line 72. Why “in contrast”? 2. Line 84 citation. There are more studies on OH oxidations of a-pinene and they should also be cited here (for example, some of the studies cited in page 2). 3. Line 125. “mass” should be “volume”? SMPS measures volume concentration. 4. Line 126. Delete “with”. 5. Line 256. Sentence not clear. 6.

C7

Figure 1 caption should specify the SO₂ condition.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-294>, 2017.

C8