

Response to Reviewer 2

We greatly appreciate the time and effort that reviewer 2 spent in reviewing our manuscript. The comments are really thoughtful and helpful to improve the quality of our paper. Reviewer 2 has provided both major comments and other specific comments. Below we make a point-by-point response to these comments. According to editor's requirement, the response to the referee is structured in the following sequence: (1) comments from the referee in black color, (2) our response in blue color, and (3) our changes in the revised manuscript in red color.

The manuscript is comprehensive and provides useful information about the chemical composition of SOA formed from various pathways. However, there are a few points that the author should consider when making these arguments, and these issues should be addressed before the article is published in ACP.

Major Comments

First, the author draws the conclusion that RH does not have an effect on isoprene SOA yield under the OH oxidation pathway. However, Gaston et al. (2014) clearly show that RH has an effect on isoprene epoxydiols (IEPOX) reactive uptake into the acidic sulfate particles due to the dilution effect at higher RH. Because IEPOX is one of the main oxidation products of isoprene under OH pathway, the yield should show a negative correlation with RH. But the author's experimental results seem to not agree with those of past studies. I believe the main reason for non-RH dependence observed in this study is that the acidity of the H₂SO₄ particles generated by this study is too low, resulting in RH not having an additional acidity dilution effect. The author should at least mention the discrepancy between this work and other studies, and point out limitations of this study. For instance, page 7, line 19-20: the author made a conclusion that RH had little effect on the yield of isoprene with OH reactions. Please note that this is probably true for generating self-nucleated isoprene SOA, but may not be true for isoprene SOA that are formed on acidic sulfate seed particles, as shown by a few other studies (Gaston,

Riedel et al. 2014, Riedel, Lin et al. 2015, Zhang, Chen et al. 2018). These studies suggest that RH has an important effect on the formation of isoprene OH-heterogeneous generated SOA, due to the change of RH affecting the acidity of the seed particles. The author should include the literature and clarify the difference of RH effects on experiments because the seed particles in this study probably do not have enough concentration to undergo full heterogeneous reactions.

We agree with the reviewer that there is discrepancy between our work and other studies. The initial burst of new particles happened at 10 min after the start of irradiation in isoprene-H₂O₂ system in our work and maximum number concentration was over 10⁴. These new particles were considered to be H₂SO₄ particles. Both theoretical simulation and experiments have confirmed the formation of these new particles. We ever did the experiment. If the SO₂ concentration in background air was removed to be below 50 ppt, the number concentration of H₂SO₄ would be below 1000 /cm³. In addition, using the extra-purified background air, the mass concentration of SOA would be greatly reduced by one order of magnitude in isoprene-OH system. We have added the curve in the revised Figure 2 to show the variation of number concentrations of particle with time from the experiment of ISO-H₂O₂, indicating the formation of H₂SO₄ and heterogeneous generated SOA. As the reviewer pointed out, the mass concentration of H₂SO₄ was much smaller as compared to previous studies. Although the heterogeneous formation of SOA occurred in our system, compared with other studies the acid dilution effect was not obvious under higher RH condition. To make it clear, we have added the following sentences on page 7 and references to clarify the differences between our work and previous studies.

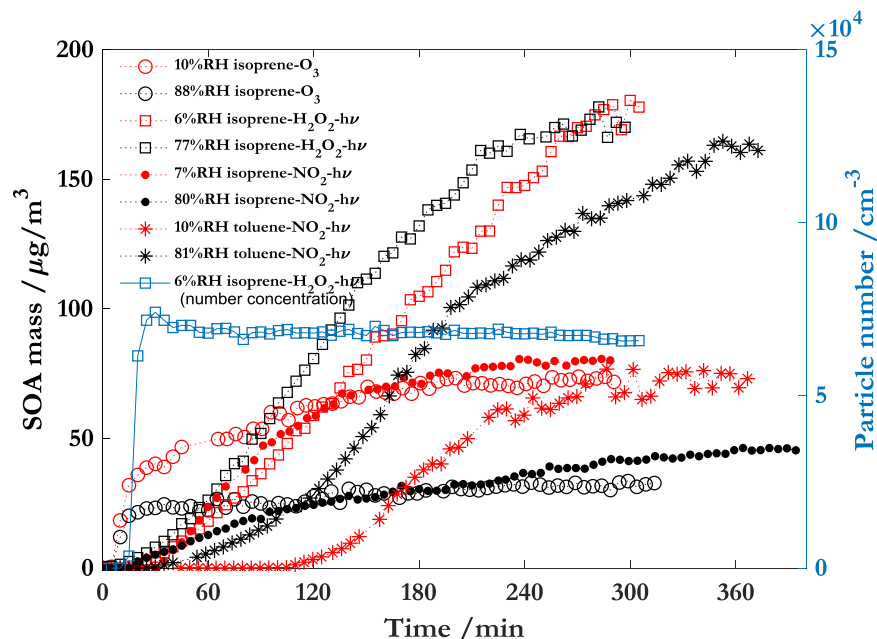


Figure 1 Figure 2 in our manuscript

In addition, some other previous studies (Gaston et al., 2014; Riedel et al. 2015; Zhang et al. 2018) showed that RH has a negative effect on the formation of SOA from isoprene-OH systems due to acid dilution effect. In these studies, acidic sulfate seed particles were used and the acid-catalyzed effect was very obvious. Thus, higher RH can reduce the acidity of the seed particles by particle water. In our study acidic seed particles were from a little amount of H_2SO_4 formed from the gas-phase reaction of SO_2 and OH. It was estimated that the mass concentration of H_2SO_4 particles was less than $1 \mu\text{g}/\text{m}^3$. When liquid water content increased from $1 \mu\text{g}/\text{m}^3$ to the maximum $54 \mu\text{g}/\text{m}^3$ under humid conditions, the pH value was estimated to be in the range of 2 to 3.7, indicating that the pH variation was small in our experimental conditions. Therefore, compared with previous studies, the acid dilution effect was not remarkable in our work.

Riedel, T. P., Lin, Y. H., Budisulistiorini, S. H., Gaston, C. J., Thornton, J. A., Zhang, Z., Vizuete, W., Gold, A. and Surratt, J. D.: Heterogeneous reactions of isoprene-derived epoxides: Reaction probabilities and molar secondary organic aerosol yield estimates, *Environ. Sci. Technol. Lett.*, 2(2), 38–42, doi:10.1021/ez500406f, 2015.

Zhang, Y., Chen, Y., Lambe, A. T., Olson, N. E., Lei, Z., Craig, R. L., Zhang, Z.,

Gold, A., Onasch, T. B., Jayne, J. T., Worsnop, D. R., Gaston, C. J., Thornton, J. A., Vizuete, W., Ault, A. P. and Surratt, J. D.: Effect of the Aerosol-Phase State on Secondary Organic Aerosol Formation from the Reactive Uptake of Isoprene-Derived Epoxydiols (IEPOX), *Environ. Sci. Technol. Lett.*, 5(3), [acs.estlett.8b00044](https://doi.org/10.1021/acs.estlett.8b00044), doi:10.1021/acs.estlett.8b00044, 2018.

Page 7, lines 10-11: the author concludes that ozonolysis is the key pathway influencing SOA formation in isoprene-NO₂ systems. How does the author draw such conclusion? It seems that the author just compares the yields of isoprene-NO₂ with isoprene-O₃ under dry and humid conditions, and finds out the yields were similar. But similar yields do not mean that the reaction mechanisms are similar. The ozone concentrations in the two conditions could be different. There might also be synergistic or competing mechanisms for SOA formation when NO₂ and O₃ are both present. Besides, the author also shows on page 7, lines 21-22 that NO₂ and O₃ pathway each contributes to isoprene oxidation for certain extent. Therefore, the author cannot rule out the possibility that NO₂ and O₃ pathways having similar yields, rather than O₃ pathway dominates the NO₂ pathway. I think the author should either provide more evidence in this part to show isoprene-O₃ really dominates, or make a more conservative the conclusion and state the limitations.

The reviewer is absolutely right. We can't draw this conclusion only based on the comparison of SOA yields between isoprene-NO₂ and isoprene-O₃ systems. Actually, our conclusion was based on mass yields, chemical information provided by FTIR and HR-MS data, and MCM simulations.

Just as reviewer pointed out, there are synergistic or competing mechanisms for SOA formation when NO₂ and O₃ are both present. Since SOA was mainly formed by the secondary or later generation products, we could evaluate the contributions of SOA precursors from different channel. As discussed in the section of Introduction in our manuscript, SCI can be taken as SOA precursor from the O₃ channel, while IEPOX,

MPAN, HMML and MAE as SOA precursors from the OH channel. The MCM model simulation (based on Exp. 25) showed that the total yield of SCI is dominant as compared to OH channel precursors such as IEPOX, MPAN, HMML and MAE. The former (SCI) accounts for 70% and the remaining precursors (IEPOX+MPAN+HMML+MAE) 30% at the end of reaction in isoprene-NO₂. Therefore, in the system of isoprene-NO₂, even though 59% of isoprene was consumed by OH and only 25% by O₃, the formation of SOA was still mainly from the O₃ channel.

Following the reviewer's suggestion, the original sentence of Page 7, lines 10-11 has been changed as:

Thus, these results show that high RH can reduce the maximum yields of SOA from the reaction channel of isoprene with O₃ (O₃ channel) and that RH has little effect on the maximum yields from the reaction channel of isoprene with OH (OH channel) without sufficiently high mass concentrations of acid particles. This shows that the ozonolysis of isoprene is probably a key pathway influencing the SOA formation in isoprene-NO₂ irradiations.

To make it clear, we have added the following sentences on page 7:

There are cross reactions when NO₂ and O₃ are both present. Thus, we cannot deduce SOA contribution simply by initial ratios of isoprene oxidized by OH and O₃. Since SOA was mainly formed by the secondary or later generation products, we could evaluate the contribution of reaction pathways to formation of SOA in terms of SOA precursors from different channels. As described previously, SCI can be taken as the SOA precursor from the O₃ channel, while IEPOX, MPAN, HMML and MAE can be used as SOA precursors from the OH channel. The MCM simulations show that the total yield of SCI was dominant as compared to OH channel precursor such as IEPOX, MPAN, HMML and MAE. The former accounts for 70% of SOA precursors while the latter (IEPOX+MPAN+HMML+MAE) 30% at the end of reaction in isoprene-NO₂. Therefore, even though 59% of isoprene were consumed by OH and only 25% by O₃, the formation of SOA in isoprene-NO₂ was mainly from the O₃ channel.

Page 7, line 23: the author points out that RH has little effects on NO₃ pathway. Please

list any evidence (such as references) to support this point.

We have added 3 references and the following sentence to support our statement on page 7. Previous studies have shown that humid has little effect on SOA formation from NO₃ oxidation of alkenes (Bonn and Moorgat 2002; Fly et al., 2009; Boyd et al., 2015).

Boyd, C. M., Sanchez, J., Xu, L., Eugene, A. J., Nah, T., Tuet, W. Y., Guzman, M. I. and Ng, N. L.: Secondary organic aerosol formation from the β -pinene+NO₃ system: Effect of humidity and peroxy radical fate, *Atmos. Chem. Phys.*, 15(13), 7497–7522, doi:10.5194/acp-15-7497-2015, 2015.

Bonn, B. and Moorgat, G. K.: New particle formation during α - and β -pinene oxidation by O₃, OH and NO₃, and the influence of water vapour: particle size distribution studies, *Atmos. Chem. Phys.*, 2(3), 183–196, doi:10.5194/acp-2-183-2002, 2002.

Fry, J. L., Rollins, a W., Wooldridge, P. J., Brown, S. S., Fuchs, H. and Dub, W.: Organic nitrate and secondary organic aerosol yield from NO₃ oxidation of β -pinene evaluated using a gas-phase kinetics/aerosol partitioning model, *Atmos. Chem. Phys.*, 9(3), 1431–1449, doi:10.5194/acp-9-1431-2009, 2009.

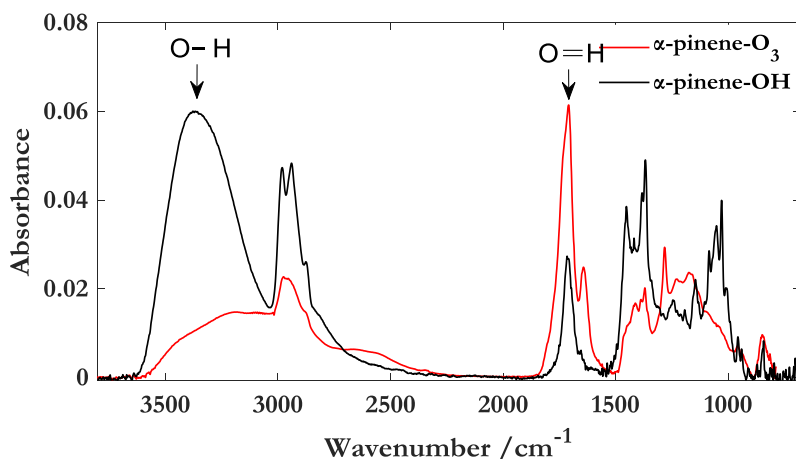
Page 12, line 9: this paragraph the author compares the RH effects of this experiments with Gaston et al. Please note that due to the difference in experimental conditions, such comparison may not be meaningful. For previous studies about heterogeneous uptake of IEPOX onto acidic particles (Gaston, Riedel et al. 2014, Riedel, Lin et al. 2015, Zhang, Chen et al. 2018), the acidic particles are in excess. But for this study, based on the mass concentration of the H₂SO₄ particles that the author provides, the concentration of H₂SO₄ particles might be limited, leading the majority of the isoprene SOA particles coming from self-nucleation. Therefore, the isoprene-OH SOA formation mechanisms between this study and past studies are quite different. The author should either provide SMPS data to show that there is no significant number concentration increase (i.e., isoprene SOA formed from heterogeneous reaction rather

than self-nucleation), or revise the statement in this paragraph and point out the difference between this study and Gaston et al. Moreover, according to Gaston et al., when $\text{pH} > 2$, the uptake coefficient is already very small. The pH of the particles in this study is estimated to be “2-3.7”, which makes a comparison with Gaston et al. not meaningful.

We totally agree with the reviewer that our experimental conditions are different from those by previous studies. As discussed in the response to the first comment by the reviewer, though the mass concentration of acid particles was not high in our system, it is considered that SOA was still mainly formed by heterogeneous reaction in our isoprene-OH systems. To avoid needless repetitions, the original paragraph of page 12, lines 9-18 has been deleted.

Page 11, line 10: the author states “Since O-H-containing products from terpene are 10 more enriched from the OH channel oxidation than from the O_3 one (Calogirou et al., 1999), here the absorption ratio of O-H to C=O was used to examine the difference between the O_3 and OH oxidation channels.” Could the author provide any rationale that why the IR results of terpene SOA could be used to infer the IR results of isoprene SOA?

Considering isoprene is the basic chain unit of terpenes, similar abundance of functional groups in oxidation products from isoprene and terpenes can be expected. In fact, we also measured the IR spectra of SOA from α -pinene oxidized by O_3 and OH (see below Figure). The similar characteristics of IR spectra of SOA from both isoprene and α -pinene was observed. The peak height ratio of O-H/C=O is 0.24 in SOA from α -pinene- O_3 system, while it is as high as 2.19 in α -pinene- OH system. This demonstrates that the absorption ratios of O-H to C=O from α -pinene are similar to SOA from isoprene. To make it clear, we have modified original sentences of page 11, lines 10-13.



The IR spectra of SOA from α -pinene- O_3 and α -pinene-OH systems under dry conditions.

Since isoprene is the chain unit of terpenes, the abundance of functional groups in oxidation products from isoprene and terpenes is expected to be close. O-H-containing products from terpene are 10 more enriched from the OH channel oxidation than from the O_3 one (Calogirou et al., 1999). Our extra experiments show the similar characteristics of IR spectra of SOA from both isoprene and α -pinene (figure not shown). Here the absorption ratio of O-H to C=O was used to examine the difference between the O_3 and OH oxidation channels. Higher values of O-H/C=O ratio should be expected to be more from the OH channel than from the O_3 channel. Our experiment shows that the peak height ratio of O-H/C=O is 0.24 in SOA from α -pinene- O_3 system, while it is as high as 2.19 in α -pinene-OH system.

Minor Comments

Page 6, lines 18-20: this part of the manuscript is a bit confusing. The author talked about the maximum mass concentrations ratios when comparing humid v.s. dry conditions for toluene- NO_2 and isoprene- NO_2 reactions. However, the author did not report such maximum mass concentration ratios of humid v.s. dry conditions for isoprene- O_3 and isoprene- H_2O_2 conditions. The author should list all the ratios together for readers to understand and compare.

We have added the maximum mass ratios for isoprene-O₃ and isoprene-H₂O₂ on page 6.

The ratio is 0.45 for isoprene-O₃ and 1.01 for isoprene-H₂O₂.

Page 8, line 15: please define E2/E3

We have added following words to define E2/E3 on page 8:

(absorbance at 250 nm divided by absorbance at 365 nm)

Page 8, lines 20-24: This part is a bit confusing to read. First, the author uses “why is the maximum yield from isoprene-H₂O₂ irradiations unchanged under humid conditions.” Shouldn’t there be a question mark instead of a period at the end of the sentence? Then the author should provide some explanation to this question rather than just leaving the statement unattended. Next, the author talks about RH influence on aromatic SOA. At the end of this paragraph (page 9, line 1), the author changes back to isoprene SOA again. It can be difficult for readers to follow the thought process of this paragraph. I suggest the author revise this part to make it flow better.

We thanks the reviewer for the careful reading and good suggestions. According to the reviewer’s suggestions, we have added the question mark at the end of the sentence, and also briefly explained it. Further discussion is given in later sections. This part has been revised on page 9.

Nevertheless, if the suppression of the oligomerization reactions under humid conditions is the main reason for the decrease in SOA yield from isoprene, why is the maximum yield from isoprene-H₂O₂ irradiations unchanged under humid conditions? Besides the weak acid dilution effect in our experimental conditions, there must be an intrinsic mechanism regarding the influences of RH on the SOA yield from isoprene. In addition, oligomers have been also identified as important products of SOA from aromatics, and water is a byproduct during oligomerization process (Lim et al., 2010; Gaston et al., 2014; Kalberer et al., 2004). However, a negative effect of RH on SOA yield from aromatics has never been observed. This is because there are likely competing processes that are responsible for SOA formation from aromatics under

humid conditions. Oligomers are generally inhibited by higher RH, while the organics formed by aqueous reactions are enhanced.

Page 9, line 22: the author states that SOA mass concentration increased by 16%. Was this increase due to LWC, or was it actually organic mass? The author should explain it more clearly.

It was organic mass. To make it clear, the original sentence has been modified on page 9.

The particles were mainly consistent of NaNO_3 , LWC and SOA at the end of reaction. the major changes for SOA were all the bands assigned to O–H, C=O and C–OH (错误!未找到引用源。 e), which were enhanced by 50%, 29% and 35% respectively. After considering the mass contributions from NaNO_3 and LWC, the organic mass concentrations of SOA were increased by 16%, compared to those in humid conditions without extra LWC.

‘Page 14, line 19: I believe the author had the statement inversed. It should be: “the range of 300 to 800 m/z under humid conditions is reduced by 75% as compared to that under dry conditions.”

The reviewer is right. We had the statement inversed. It has been corrected in our revised manuscript.

Page 19, line 11: there should be a space between 5% and RH.

It has been corrected.

Page 19, line 11: there is an extra parenthesis.

The extra parenthesis has been deleted.