Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-1064-RC2, 2018

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Different roles of water in secondary organic aerosol formation from toluene and isoprene" *by* Long Jia and Yongfu Xu

Anonymous Referee #2

Received and published: 9 February 2018

This article examines the influence of relative humidity (RH) on selected toluene and isoprene SOA formation pathways. Through yield calculations, the author discovers toluene-NO2 system has a higher SOA yield at high humidity environment while isoprene has a lower yield at higher RH for NO2 and O3 pathways. This study involves various techniques and methods such as Master Chemical Mechanism (MCM) modeling, Fourier Transform Infrared Spectroscopy (FTIR), ultraviolet-visible spectroscopy, and EST-HRMS. The author concludes that the higher yield of toluene SOA at high RH is due to aqueous reactions of water-soluble components, while the decreasing yield of isoprene SOA under NO2 and O3 pathways is due to reduced oligomer formation from Criegee intermediate (SCI) reacting with water.

This study combines both experimental techniques and modeling to support the above

Printer-friendly version

Discussion paper

arguments that the authors are trying to make. The modeling results add more credibility to the arguments. 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.

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.

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.

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 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.

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 O3 one (Calogirou et al., 1999), here the absorption ratio of O−H to CïijİO was used to examine the difference between the O3 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?

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-NO2 and isoprene-NO2 reactions. However, the author did not report such maximum mass concentration ratios of humid v.s. dry conditions for isoprene-O3 and isoprene-H2O2 conditions. The author should list all the ratios together for readers to understand and compare.

Page 8, line 15: please define E2/E3

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.

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.

‘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."

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

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

References

Gaston, C. J., et al. (2014). "Reactive Uptake of an Isoprene-Derived Epoxydiol to Submicron Aerosol Particles." Environ. Sci. Technol. 48(19): 11178-11186.

Riedel, T. P., et al. (2015). "Heterogeneous Reactions of Isoprene-Derived Epoxides: Reaction Probabilities and Molar Secondary Organic Aerosol Yield Estimates." Environ. Sci. Technol. Lett. 2(2): 38-42.

Zhang, Y., et al. (2018). "Effect of Aerosol-Phase State on Secondary Organic Aerosol Formation from the Reactive Uptake of Isoprene-Derived Epoxydiols (Iepox)." Environ. Sci. Technol. Lett.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-1064, 2017.

Printer-friendly version

Discussion paper