

This manuscript on different roles of water in toluene and isoprene SOA formation presents interesting results. Overall, the results are consistent with previous studies: toluene SOA formation is enhanced by higher RH due to aqueous-phase reactions and isoprene SOA formation is enhanced by lower RH due to oligomer formation. The main finding suggests that the isoprene SOA (ozonolysis and NO<sub>2</sub> irradiation) formation is largely controlled by the “SCI → oligomer” process that is influenced by water. The manuscript is well written and provides sufficient measurements supporting the main conclusion, but a few issues need to be addressed before considered publication in ACP.

#### Main Comments:

1. On page 2, line 14, the authors claimed that “the relationship between RH and SOA formation from isoprene is still not very clear”. However, from the previous studies listed in this paragraph, it appears that a pretty clear understanding has been established: (1) oligomers have always been found to enhance under low RH; and (2) SOA yield may not always enhance accordingly, because the competing pathways such as glyoxal SOA or organosulfate formation are increased under high RH and the overall SOA mass vary with the relative contributions from different pathways. Thus, it is problematic to say the RH effect on isoprene SOA is “not very clear”. Instead, what remains a question is, whether the known MAE-derived oligomers explain all oligomers. The authors’ findings fit right into this question and should thus set up this direction in the introduction. Also, in the introduction, the authors should provide more details of previous work that has found SCI as key oligomeric chain unit and give more credit to these studies (e.g., Sadezky et al., 2008 ACP and a few other studies). Right now, it was only briefly mentioned that SCI-derived products have been found in SOA, but considering the results of this work, the relationship between SCI and oligomers should be elaborated in more detail.

2. In section 3.1, the authors stated that the similar RH effect on isoprene SOA from ozonolysis and NO<sub>2</sub> irradiation experiments suggest that the ozonolysis of isoprene is a key pathway influencing the SOA formation in isoprene-NO<sub>2</sub> irradiations. This is not necessarily true. In the isoprene-NO<sub>x</sub> experimental conditions used in Zhang et al. (2011 ACP), most isoprene were reacted with OH before ozone was formed. In the Lewandowski et al. (2015 ACP) study, continuous mode was used and thus minimal ozone is expected to form. Nguyen et al. (2011 ACP) does not produce much O<sub>3</sub> and still observe enhanced oligomers under dry conditions (despite SOA yield was not affected). In these studies, ozonolysis play a small role in isoprene oxidation and observed similar results (or the authors may provide MCM simulations and prove otherwise). Even for the studied condition, as the authors stated, isoprene reacts with OH (59%) and O<sub>3</sub> (25%) and the SOA yield from the OH channel was over 2 (5) times greater than that from the O<sub>3</sub> channel under dry (humid) conditions. Thus, at most 10-15% of isoprene SOA are from the O<sub>3</sub> channel. This contradicts to the observed doubled SOA formation under dry conditions if all the RH effect is from the O<sub>3</sub> channel.

3. It appears that the authors used MCM simulation a few times in this study. I feel it might be worthwhile adding a section describing what they did. Particularly, SCI + RO<sub>2</sub> reactions and SCI-derived oligomer formation were added by the authors in the mechanism. Quantitatively, how much could the modeled total SCI-derived oligomers account for the measured total isoprene

SOA? Other references include, for example, the authors claiming MPAN+OH needs extra OH source. This is not the case in the Lin et al. (2013 PNAS). Without clearly show the MCM simulations, it is hard to draw the conclusion. These are very important aspects in the results and should be provided in more detail.

4. The mass spectral data suggest “the SCI based oligomers are almost 2 times larger than that from 2-MG”. However, the data are not quantitatively calibrated. It is unclear which is more important.

Overall, the authors reporting isoprene SCI-derived oligomers in SOA is well justified and important. These oligomers can be important fractions of oligomers under isoprene high-NO<sub>x</sub> conditions and might explain previously observed oligomers in isoprene SOA besides those derived from MAE. However, based on the results provided in this work, it is not convincing that the SCI-derived oligomers are the dominant part in isoprene SOA, especially under isoprene-NO<sub>2</sub> irradiation conditions.

Minor comment:

1. Page 2, line 16. The term “isoprene-NO<sub>x</sub> (x=1, 2)” is odd. Suggest using “isoprene-NO<sub>x</sub> (NO and NO<sub>2</sub>)”.

2. Page 2, line 19. Nguyen et al. (2011) did not find a RH influence on SOA yield, but did observe enhancement of oligomers under low RH, which is consistent with Zhang et al. This should be mentioned in this sentence.

3. Figures. The 4 plots in Figure 1 need to be numbered. The authors have consistently used red colors for low-RH results and black for high-RH results in many figures which is very helpful. I suggest use the same color scheme in Figures 6 (replace the blue line with a black dashed line), 10 (use colors for symbols and lines), 11, and 12.

4. Page 7, line 3. There are other possible reasons accounting for the lower SOA yield. For example, this study uses higher temperature than the two previous studies mentioned.

5. Page 8, line 5. Is this based on MCM simulation? Please add clarification in the text.

6. Page 13, line 17. “MPAN can be oxidized by OH to form 2-methyltetrols” is wrong. The products are 2-methylglyceric acid and related oligomers. This is repeated by later sentences in this paragraph. The authors should consider consolidate/rewrite this paragraph.

7. Page 14, line 6. “Thus, IEPOX is not the major contributor to SOA in isoprene-NO<sub>2</sub> system. This clearly demonstrates that MPAN and IEPOX related reactions were not dominant pathways for SOA formation in our isoprene-NO<sub>2</sub> irradiations”. The logic in this sentence is problematic. It cannot suggest MPAN reactions are not important in isoprene-NO<sub>2</sub> irradiations. Again, a figure showing simulated MPAN, SCI, and a few other important products is needed at least.

8. Page 18, line 9. C<sub>4</sub>H<sub>6</sub>O<sub>3</sub> is not formed from dehydration of 2-MG, but MAE (Lin et al., 2013 PNAS).