

## Response to Reviewer 1

We greatly appreciate the time and effort that reviewer 1 spent in reviewing our manuscript. The comments are really thoughtful and helpful to improve the quality of our paper. Reviewer 1 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.

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.

We agree with the reviewer that the relationship between RH and SOA from isoprene is clear. However, the mechanism for the influence of RH on SOA derived from radicals is not very clear. Following the reviewer's comments, we have deleted the original sentence of line 14 on page 2: "the relationship between RH and SOA formation from isoprene is still not very clear".

We have added some sentences to introduce the important SOA precursor of MAE in the Introduction section on page 2.

MPAN is one of key precursors of SOA from isoprene under high NO<sub>x</sub> conditions (Surratt et al., 2010), which can react with OH to produce epoxides (methacrylic acid epoxide (MAE), hydroxymethyl-methyl- $\alpha$ -lactone (HMML)). Lin et al. (2013) reported that MAE was an important precursor to 2-MG, a tracer of isoprene-derived SOA. Nguyen et al. (2015) showed that HMML could form SOA. Since SCIs, IEPOX, MPAN, HMML and MAE co-exist in isoprene-NO<sub>2</sub> irradiations, there are cross reactions in the system. Thus, the study is still needed to demonstrate the role of these precursors in oligomer formation from isoprene-NO<sub>2</sub> irradiations.

In addition, we have added a new paragraph to review the progress on the SCI-derived oligomer in SOA.

Sadezky et al (2006, 2008) reported that SCIs (CH<sub>2</sub>OO, C<sub>2</sub>H<sub>4</sub>OO, C<sub>3</sub>H<sub>6</sub>OO and C<sub>4</sub>H<sub>8</sub>OO) play a central role in SOA formation from the ozonolysis of ethyl butenyl ether, trans-3-hexene, 2, 3-dimethyl-2-butene, and trans-4-octene. They further suggested that SCI-derived oligomers are formed by the reactions of RO<sub>2</sub> with SCI. Sakamoto et al. (2013) showed that the reactions of SCI (CH<sub>2</sub>OO) with hydroperoxides (ROOH) from ethylene can form SOA. Inomata et al (2014) showed that the reaction

of an SCI with carboxylic acids or hydroperoxides can contribute to SOA formation from the ozonolysis of isoprene. Zhao et al. (2015, 2016) also showed that the SOA generated from the ozonolysis of trans-3-hexene and  $\alpha$ -cedrene is primarily composed of oligomers formed from the addition of SCI to RO<sub>2</sub> radicals. Although these studies have demonstrated the importance of SCI-derived oligomers in SOA formation from the ozonolysis of alkenes, the role of SCI in SOA formation from isoprene-NO<sub>2</sub> irradiations has not been reported.

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.

We agree with the reviewer that ozonolysis is not necessarily to be the key channel influencing SOA in isoprene-NO<sub>2</sub> systems, which obviously depends on specific experimental conditions, including extra OH sources. Indeed, our statement is based on our experimental conditions, where the yield of SCI was much higher than those of IEPOX, MPAN, HMML and MAE. Taking the reviewer's advice, the original statement that "This shows that the ozonolysis of isoprene is a key pathway influencing the SOA formation in isoprene-NO<sub>2</sub> irradiations." has been changed to

Thus, it shows that the ozonolysis of isoprene may be a key pathway influencing SOA formation in isoprene-NO<sub>2</sub> irradiations in our experimental conditions, which will be further discussed in latter section.”

In these studies mentioned by the reviewer, their experimental conditions are different from our ones. For example, in the study by Zhang et al. (2011), artificial seed particles were used. In Nguyen et al. (2011 ACP) H<sub>2</sub>O<sub>2</sub> was added. Thus, the role of ozonolysis in these studies is different from that in our study. Since there are synergistic or competing mechanisms for SOA formation when NO<sub>2</sub> and O<sub>3</sub> are both present, we cannot deduce SOA contribution simply by initial ratios of isoprene oxidized by OH and O<sub>3</sub>. However, since SOA was mainly formed by the secondary or later generation products, we can evaluate SOA contributions by precursors of SOA from different channels.

As discussed in the section of Introduction in our manuscript, SCI can be taken as SOA precursor from the O<sub>3</sub> channel, while IEPOX, MPAN, HMML and MAE as SOA precursors from the OH channel. Following the reviewer’s suggestion, we simulated the concentrations of IEPOX, MPAN, HMML, MAE and total yield of SCI using MCM (based on Exp. 25). Results 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-NO<sub>2</sub>. Therefore, in the system of isoprene-NO<sub>2</sub>, even though 59% of isoprene was consumed by OH and only 25% by O<sub>3</sub>, the formation of SOA was still mainly from the O<sub>3</sub> channel.

To make it more clearly, we have following sentences on page 7:

There are cross reactions when NO<sub>2</sub> and O<sub>3</sub> are both present. Thus, we cannot deduce SOA contribution simply by initial ratios of isoprene oxidized by OH and O<sub>3</sub>. 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 O<sub>3</sub> 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-NO<sub>2</sub>. Therefore, even though 59% of isoprene were consumed by OH and only 25% by O<sub>3</sub>, the formation of SOA in isoprene-NO<sub>2</sub> was mainly 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.

We cannot quantify the contribution from SCI-derived oligomers to isoprene SOA because many species can react with SCI, but details are not known so far. We can only simulate the reactions of SCI with glyoxylic acid and ACETOL that have been identified by our MS. The purpose of our simulation was to evaluate the role of RH in the formation of SOA. The original sentences at lines 9~ 12 on page 14 have been deleted, and a figure and some sentences have been added on page 20:

Following the reviewer's suggestion, we have added a paragraph in Experimental section to describe the model simulation on page 5:

To evaluate the potential contribution of SOA precursors (e.g. glyoxal, IEPOX, MPAN, HMML, MAE and SCI) from toluene and isoprene reaction systems, a model of the Master Chemical Mechanism (MCM v3.3.1, website: <http://mcm.leeds.ac.uk/MCM>, Jenkin et al., 2015) was used, which includes the chamber dependent reactions. To examine the influence of RH on oligomer formation from SCI, the reactions of SCI

with carbonyls were added to MCM, which were expressed with  $X+SCI=X(SCI)_1$ ,  $X(SCI)_1+SCI=X(SCI)_2\dots X(SCI)_{n-1}+SCI=X(SCI)_n$ , where  $n=1-10$  and  $X$  represents carbonyls. The rate constant for these reactions was set to be  $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Vereecken et al., 2012). Since most of  $RO_2$  was consumed by  $NO_x$ ,  $SCI+RO_2$  reactions were not included in our model. The carbonyls were chosen based on the results of mass spectra data from isoprene- $NO_2$  irradiations shown in section 3.4.1. A set of ordinary differential equations was built and solved using Matlab.”

To quantify the contribution from SCI-derived oligomers to SOA, we have made MCM simulations. The original sentences on page 14 line 9~ 12 have been deleted, and a figure and some sentences have been added on page 18:

To quantify the RH effect of SOA and relatively possible contribution of SCI-derived oligomers from 2 species in isoprene- $NO_2$  irradiations, the reactions of SCI with formic acid, glyoxylic acid and ACETOL were added into MCM. Simulations show that the total mass concentration of oligomers from these reactions was 558.4 (271.2)  $\mu\text{g}/\text{m}^3$  at 7% (80%) RH. The mass concentrations of SCI -derived oligomers reduced by 51% as RH increased from 7% to 80%, while the concentrations of other precursors had little change under different RH conditions. In addition, simulation also shows that the mass concentrations form other SOA precursors IEPOX, MPAN, HMML and MAE were 182.8(167.0), 27.4(28.9), 28.1(27.4), and 11.2(10.9)  $\mu\text{g}/\text{m}^3$  at 7% (80%) RH (Figure 13). It is obvious that SCI-derived oligomers from glyoxylic acid and ACETOL should have a great potential for formation of SOA, compared to other precursors.

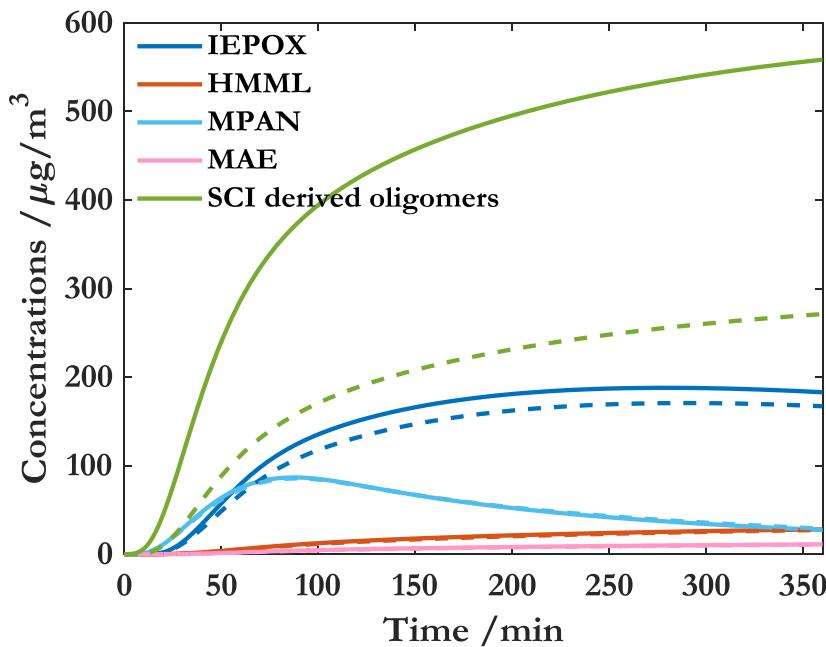


Figure 13 the MCM simulated the time profiles of SOA precursors in isoprene- $\text{NO}_2$  irradiation.

Indeed, Lin et al. (2013, PNAS) did not use an extra OH source in their study. We made the mistake. This has been corrected: “(Surratt et al., 2010; Lin et al., 2013; Nguyen et al., 2015) at lines 17-18, page 13” has been changed to

(Surratt et al., 2010; Nguyen et al., 2015)

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.

It is true that the MS data were not quantitatively calibrated in our study. The HR-MS data show that the SOA from isoprene- $\text{NO}_2$  irradiations is mainly composed of hundreds of oligomers. It is very difficult to prepare the standard substances for so many compounds. Since the oligomers from SCI and 2-MG (or MAE) have similar structures, we considered that their peak heights in MS reflect equivalent mass. Thus, the total peak heights from SCI-based oligomers were used to compare with those from 2-MG in our work.

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.

We have pointed out in our revised manuscript that our conclusion about important ozonolysis influencing SOA formation in isoprene-NO<sub>2</sub> systems was made under our experimental conditions, which is not only based on the yields between isoprene-NO<sub>2</sub> with isoprene-O<sub>3</sub> under dry and humid conditions, but also on the following facts: (1) The FTIR spectra of SOA from isoprene-NO<sub>2</sub> irradiations show that the absorbance ratios of O-H/C=O are 0.35 (0.36) under dry (humid) conditions, which are almost the same as the corresponding values in isoprene-O<sub>3</sub> but totally different from the values in isoprene-H<sub>2</sub>O<sub>2</sub> (the ratio are 1.63 (dry) and 1.45 (humid)). In addition, the similar features of IR spectra between isoprene-NO<sub>2</sub> and isoprene-O<sub>3</sub> reaction systems also demonstrate that the O<sub>3</sub> channel plays an import role in isoprene-NO<sub>2</sub> irradiations. (2) The mass spectrum of SOA from the isoprene-NO<sub>2</sub> system is similar to the one from the ozonolysis of isoprene, which all shows obviously regular structures of the peaks for oligomers with SCI as a base unit; while the spectrum of SOA from isoprene-H<sub>2</sub>O<sub>2</sub> does not such regular structures, which shows a feature different from that of the SOA from isoprene-NO<sub>2</sub>. (3) The MCM simulation further demonstrates the importance of the SCI-derived oligomers in the formation of isoprene SOA under our experimental 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>)”.

We have corrected it.

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.

We have added following words “but they observed enhancement of 2-MG -derived oligomers under low RH, which was consistent with Zhang et al. (2011a)”

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.

It is very good suggestions! We have numbered plots in Figure 1, and changed the color in Figure 6, 10, 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.

We have added following words: “In addition, the temperature in this study is higher than the previous studies, which may be another reason accounting for the lower SOA yields in this work”

5. Page 8, line 5. Is this based on MCM simulation? Please add clarification in the text. Yes, it is based on MCM simulation, to clarify it, we have added the following words to the original sentence: “based on MCM simulation”

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.

We have rewritten the paragraph:

The yield of MACR is generally greater in isoprene-NO<sub>2</sub> irradiations and isoprene-O<sub>3</sub> systems than that in isoprene-H<sub>2</sub>O<sub>2</sub> irradiations. MACR can react to form MPAN in the presence of NO<sub>2</sub>, which can be oxidized by OH to form SOA precursors of epoxides (e.g., HMML, MAE), such as in the Nguyen et al. (2011) work with H<sub>2</sub>O<sub>2</sub> as an extra OH source. Epoxides can further be oxidized to produce 2-MG and related oligomers (Surratt et al., 2010; Lin et al., 2013; Nguyen et al., 2015). 2-MG-derived oligomers can be enhanced under lower RH (Zhang et al., 2011). Both the results from Nguyen et al. (2014) and MCM simulations further show that if there are enough OH radicals, most of MPAN can be further oxidized by OH to produce epoxides. However, since there were no extra OH sources in our systems, MCM simulations show that only 12% (24%) of MPAN under dry (humid) conditions was oxidized by OH to produce HMML and MAE. The maximum concentrations of HMML and MAE were only 6.8 and 2.7 ppb under dry conditions (Figure 4), which is too small to explain the yields of SOA in isoprene-NO<sub>2</sub> systems.”

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.

The logic of the original sentence is indeed problematic. Following the reviewer’s comments, the original sentence “This clearly demonstrates that MPAN and IEPOX related reactions were not dominant pathways for SOA formation in our isoprene-NO<sub>2</sub> irradiations.” has been deleted. As our response to main comment 2, we believe that MPAN has a small contribution to SOA in our reaction system because the reacted MPAN is low in our experimental conditions. In addition, based on data from FTIR and MS spectra we suggest that SCI-based oligomer are major components of SOA in isoprene-NO<sub>2</sub> irradiations. We have added a figure (Figure 4) to show the concentrations of the products in our system.

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).

Taking the reviewer's comment, we have added the following sentences on page 18:

Lin et al. (2013) has reported that C<sub>4</sub>H<sub>6</sub>O<sub>3</sub> was from MAE in MACR-NO<sub>x</sub> irradiations. Thus, C<sub>4</sub>H<sub>6</sub>O<sub>3</sub> is probably formed from dehydration of 2-MG and MAE in oligomers. Considering the low yield of MAE in our system, we considered that most of C<sub>4</sub>H<sub>6</sub>O<sub>3</sub>-based oligomers is probably contributed by 2-MG in our work.