

***Interactive comment on* “Secondary organic aerosol formation from the photooxidation of isoprene, 1,3-butadiene, and 2,3-dimethyl-1,3-butadiene under high NO_x conditions” by K. Sato et al.**

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Thank you very much for your valuable comments. We reply your comments as follows:
“Page 4321-line 24ff: SOA yield of isoprene without H₂O₂ is given as 0.006. As mentioned by the authors in the same chapter, SOA formation is dependent on the extent of reaction of methacrolein. Since measurements by PTRMS were performed the authors know how much methacrolein had reacted. Probably much less had reacted and a comparison between experiments with and without H₂O₂ is not fair.”

The PTR-MS signal of m/z 71 in the absence of H₂O₂ maintained 69% of its maximum level at the end of the experiment, whereas that in the presence of H₂O₂ (EPA1078W) decreased to 18% of its maximum level at the end of experiment (Fig. 2c); the extent of reaction in the absence of H₂O₂ is lower than in the presence of H₂O₂. The change in extent of reaction is a possible reason of the H₂O₂ addition effect on the SOA yield. These are explicitly described in section 3.2 of the new manuscript.

“Page 4324-line 5: It says that from butadiene chromatographic peaks of the series 1B and 5B oligomers were observed. A comparison of Figure 5c with Figures 5a and 5b puts some doubt on this statement. The two peaks m/z 193 and 281 show a retention time much higher than the corresponding peaks m/z 221 and 323 from isoprene. It is also improbable that the two peaks m/z 193 and 281 appear so much later than m/z 105 in the chromatogram. The shift in retention time for the series 5B seems also rather large compared to 5A.”

Thank you for the comments. We also wonder these results. However, further discussion on retention time results is difficult because a retention time cannot be predicted referring only a molecular size. Taking into account these comments, we tone down descriptions of 1B and 5B product identifications in section 4.3.

“Section 4.3: The authors say that the 5A oligomers were produced by the dehydration reaction between nitrooxypolyols and 2-methylglyceric acid. Thereafter it is stated that nitrooxypolyols and methylglyceric acid are formed by hydrolysis of 5A oligomers and then converted to tetrols. Thus, it does not need to form first the 5A oligomers to obtain tetrols from nitrooxypolyols as they are already needed to form the oligomers.”

We describe that nitrooxypolyols are directly produced by the gas phase isoprene oxidation and/or the particle phase hydrolysis of 5A oligomers in the new manuscript.

“Section 5.2, last paragraph: Oligomers of series 1A-4A were also detected from DMB oxidation. The authors speculate on the formation of methylglyceric acid from this compound. Could it be that DMB also contains isoprene as an impurity which would

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explain the oligomers.”

As you suggested, SOA formation from the oxidation of isoprene impurity cannot be ruled out. This is also a possible SOA formation process in experiments with DMB. This description is added in the same place of the new manuscript.

“Section 7: From the temperature dependence experiments the authors conclude that besides gas/particle partitioning also changes in chemical composition lead to higher SOA yield. Gas/particle partitioning is higher at lower temperatures leading itself to a change in chemical composition. If reaction R2 is favored at low temperature then one should see a lower production of methacrolein. Was this observed by PTR-MS?”

Unfortunately, we did not use the PTR-MS instrument in the low-temperature experiment. From GC-FID data, the methacrolein yields at 278 and 300 K were estimated, and the gaseous product yield was confirmed to be basically constant between 278 and 300 K. This indicates that the observed temperature dependence of particulate chemical composition is mainly determined by the changes in gas/particle partitioning of semi-volatile compounds. The lower temperature will result in higher condensation of 2-methylglyceric acid precursors and much higher condensation of nitrooxypolyols. We add a new paragraph in section 7 to describe these. Original discussion of temperature dependence of chemical composition described in section 5.1 was removed.

“The authors also argue that the VFR does not decrease as much as the SOA yield increases. This needs to be checked very cautiously. The VFR measurement is influenced by the residence time of the aerosol in the heater and the fraction which evaporate is kinetically limited. Can the authors show that their instrument would evaporate all the high volatile fraction which condensed at the lower temperature on the aerosol and additionally the lower volatile fraction of the 300 K aerosol?”

The residence time of the present instrument (17 s) is sufficiently long when the chamber temperature is 278 K and the thermodenuder temperature is 373 K (the temperature difference is 95 K) because An et al. (2007) reported α -pinene SOA was suffi-

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ciently evaporated in 15.8 s even when the chamber temperature was 298 K and thermodeuder was 473 K (the temperature difference is 175 K). This is briefly explained in section 2.3 of the new manuscript.

“Abstract and Page 4332-line 8: It is stated that oligoesters are the major fraction of particle-phase products. This is an important statement and needs to be supported by numbers.”

What we indicate in these places is that the signals of the oligoesters identified comprise a major fraction of the signals of the SOA products observed from all dienes investigated. From data of Fig. 4, the signal ratios of the oligomers identified to the total products observed were determined to be 0.33 (isoprene at 300 K), 0.28 (isoprene at 278 K), 0.20 (isoprene-13C), 0.10 (1,3-butadiene), and 0.14 (2,3-dimethyl-1,3-butadiene). These descriptions are added in section 4.1 of the new manuscript. The sentences in abstract and conclusions are also revised.

“Page 4328-line5-7 & Figure 10: It is a nice demonstration of the relative change of monomers and oligomers. Why should monomer and dimer formation become complete in Figure 10 (Page 4328-line5)? Had methacrolein already been consumed after 180-240 min? If no formation of monomers occurs anymore then its concentration should decrease due to the oligomerization reactions as proposed.”

Thank you for the comment. We think this comment is written for a sentence in Page 4330-line 4-6. Our original description that monomer and dimer formation become complete is incorrect. Methacrolein still remained after 180-240 min (e.g., see Fig. 2c); thus monomer and dimer formation occur in this period. The production of timer or higher oligomers is competitive with monomer and dimer formation after 180-240 min. We correct this sentence in the new manuscript.

“Page 4328-lines 24-28, & Figure 11: The authors state that there is a time lag between lights off and the suppression of oligomer formation. I can not see that since there is no measurement at the time of lights off.”

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“Page 4332-line22-27: The interpretation of the different time trends between Figures 10 and 11 is not clear to me. Regarding Figure 10 the authors conclude that oligomerization involves successive reactions as assumed in their mechanism. I understand that these are produced by dehydration reactions between for instance 2-methylglyceric acid molecules to form dimers and oligomers (Series 1A). This mechanism occurs even when the formation of the monomer ceases. However, in Figure 11 this effect is not observed after the formation of precursors of 2-MG stops due to lights off. The authors state that an unsaturated aldehyde intermediate reacts with OH radicals to form oligoesters in the particle phase. Does that mean there is a direct formation of oligoesters when lights are on? Are oligomers now formed by successive reactions from monomers, directly from OH radicals in the gas phase or both mechanisms?”

In the proposed mechanism, products of the gas-phase OH + methacrolein reaction are absorbed in the particle phase and undergo monomer formation. Then, the monomer undergoes successive oligomerizations in the particle phase.

If oligomer formation in the particle phase involves successive reactions, the concentration of the monomer might decrease more rapidly than that of a higher oligomer immediately after the lights were turned off. However, no such result was obtained. After the lights are turned off, the reactions of isoprene oxidation products with O₃ and NO₃ occur to form SOA. Particulate 2-methylglyceric acid is known to be produced by the O₃ + isoprene reaction (Kleindienst et al., 2007). Formation of the 2-methylglyceric acid monomer by the reaction with O₃ would affect the oligomer time profiles in the dark. These descriptions are added in section 6.3 of the new manuscript.

References

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