

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.

Anonymous Referee #4

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This manuscript presents chamber studies on the SOA formation of conjugated dienes. Different analytical techniques and experimental designs were used to elucidate mechanistic features and composition of SOA. The paper contains interesting observations and new results which contribute to our understanding of SOA formation. An interesting approach is the use of labeled compounds to investigate oligomer formation. The manuscript is well written and of interest to the community. There are a few issues related to interpretation of the data which need to be addressed prior to publication.

Page 4321-line 24ff: SOA yield of isoprene without H₂O₂ is given as 0.006. As men-

C855

tioned 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.

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.

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.

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 explain the oligomers.

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? 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 influ-

C856

enced by the residence time of the aerosol in the heater and the fraction which evaporates 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?

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.

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.

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.

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?

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C857