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Atmospheric Chemistry and Physics Discussions

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 #2

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In this manuscript, the authors study photooxidation of conjugated dienes, in order to elucidate the SOA formation mechanism of isoprene, one of the most important hydrocarbon emitted in the atmosphere. They conducted smog chamber experiments in the presence of NOx and found a few different series of oligomers involving methyl-glyceric acid monomers, similar to those characterized in previous studies. The chemistry of oligomer formation is probed by varying temperature and lights. The experiments carried out are well designed and show very interesting results. The manuscript is clearly written, and is within the scope of this journal. The analysis of the results can be

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more complete, but I recommend publication at ACP after considering the following comments.

Specific comments:

- Section 3.2, last paragraph: The SOA yields should be compared to Kroll et al. 2006, since the experimental conditions are most similar. The yields presented here are twice those of Kroll et al. 2006. I believe the true reason behind that is the reaction extent, as in these experiments methacrolein is almost fully reacted. The wall loss of semivolatile precursor is less significant under dry conditions (see Loza et al., 2010). Also, it is useful to compare NO2/NO ratio as suggested by Surratt et al. (2010) to see if that explains the variability in the yields.

- Section 5.1: Chan et al. (2010) showed that aerosol formation is NOT from hydroxynitrooxy-MPAN, as the SOA yields did not correlate with its abundance. They propose a cyclic intermediate from oxidation of MPAN based on indirect evidence. The mechanism from MPAN to aerosol is still unclear, and the mechanism described here should be removed (and from Fig. 7 too).

- Section 5.1: The temperature dependence of chemical composition is intriguing. If this is true, then the bottom route in the proposed mechanism (Fig. 7) should be favored over the top route under lower temperatures. Did the yield of methacrolein (m/z 71) decrease under lower temperatures? How much does the branching ratio depend on temperature? Series 5A still involves oligomerization with 2-MG. If 2-MG yield is decreased at lower temperatures, why would series 5A still increase? In general, I think addressing these issues would make the argument much stronger.

- Section 5.1: AMS measures total nitrate (HRNO3). Could the lower temperature result in higher condensation of HNO3? Despite the low RH, organic acids can retain water and provide a medium for HNO3 to condense. Given the high NOx concentrations in these experiments, that is a concern. Injection of gas phase HNO3 could be a worthwhile check.

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11, C717–C719, 2011

- Section 6.3: The lights-off experiment is interesting. One cannot rule out NO3 or O3 playing a role, given the decay of methacrolein (which can still produce MPAN via abstraction of aldehydic hydrogen). I suggest adding a large amount of NO to suppress both NO3 and O3 (NO+NO3 and NO+O3 are very rapid) to rule out any dark reaction involving these species.

Minor comments:

- Section 2.2: Is seed aerosol used in these experiments?

- Section 2.3: Is the TOF-AMS a high resolution instrument? None of the AMS data presented here are high-resolution. Is it appropriate to analyze them using the HR Analysis program?

- Section 3.2: It is claimed here that the yield from DMB is 0.003–0.007. How is that compared to experimental uncertainty? (Is it essentially zero?)

- Fig. 7: In the mechanism, there is a missing step from methacrolein to hydroxynitrooxy-PAN. There should be a step from methacrolein (+OH/O2/NO2) to MPAN first.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 4313, 2011.