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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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Received and published: 29 June 2011

Thank you very much for your valuable comments. We reply your comments as follows:

“- 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

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useful to compare NO₂/NO ratio as suggested by Surratt et al. (2010) to see if that explains the variability in the yields.”

The SOA yields are compared to Kroll et al. 2006 in the new manuscript. The irradiation duration of Kroll et al. 2006 was about 7 hr and was close to the present study. Further, the NO₂ photolysis rate of Kroll et al. 2006 is higher than the present study (Cocker et al., 2001). Thus, we do not conclude that the extent of the reaction is a reason of present high SOA yields. We conclude that the difference in the aerosol loading is a possible reason of present high yields (please see reply to referee #3). This is discussed in section 3.2 of the new manuscript. Following the comment, the description of the wall loss of semi-volatile precursor is removed in the new manuscript. NO_x used in this study was pure NO. Unfortunately, we cannot discuss the dependence of SOA yield on the NO to NO₂ ratio from available data. We give information of the initial NO/NO₂ ratio in Table 1 of the new manuscript.

“- 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). “

We remove descriptions of the mechanism from MPAN to aerosol from the text. We also remove it from Fig. 7.

“- 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.”

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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.

“- Section 5.1: AMS measures total nitrate (HNO_3). Could the lower temperature result in higher condensation of HNO_3 ? Despite the low RH, organic acids can retain water and provide a medium for HNO_3 to condense. Given the high NO_x concentrations in these experiments, that is a concern. Injection of gas phase HNO_3 could be a worthwhile check.”

Thank you for the comment and the suggestion. We checked HNO_3 condensation by the ToF-AMS signal ratio of m/z 30 to m/z 46. This ratio is 3–5 for organic nitrates and <3 for inorganic nitrates (Rollins et al., 2009; Sato et al., 2010). The m/z 30 to m/z 46 ratio at 300 K (EPA1078W) was 4.7 ± 1.2 , whereas that at 278 K (EPA1148W) was 4.7 ± 0.6 , indicating HNO_3 is a minor particulate component both at 278 and 300 K. These descriptions are added in the new manuscript. Whole the paragraph is moved to section 7.

“- Section 6.3: The lights-off experiment is interesting. One cannot rule out NO_3 or O_3 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 NO_3 and O_3 ($\text{NO} + \text{NO}_3$ and $\text{NO} + \text{O}_3$ are very rapid) to rule out any dark reaction involving these species.”

Thank you for the comment and the suggestion. As you commented, the reactions

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of methacrolein with NO₃ or O₃ cannot be ruled out. We add descriptions of influence from reactions with NO₃ and O₃ in section 6.3 and will tone down the original conclusion in the conclusion section (please see also replies to referees 3 and 4).

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

No, it isn't. No seed aerosol was used in all experiments. This explanation is added in section 2.2 of the new manuscript.

“- 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?”

Yes, the TOF-AMS is a high resolution instrument. We basically operated this instrument in V mode. This mode was selected to detect oligomers with a high sensitivity. We used the HR analysis program for calculations of HR_NO₃ data described in section 5.1 of the original manuscript. The mass resolution in V mode was typically ~2700, and this enabled us to resolve the peaks of NO⁺ (m/z 29.997) and CH₂O⁺ (m/z 30.010). It is appropriate to analyze present data using the HR analysis program. These are briefly explained in section 2.3.

“- 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?)”

Carter et al. (2005) reported a typical concentration of background particle matter formation of the present chamber is 0–1 μg m⁻³. Detectable level SOA (4–7 μg m⁻³) was produced in the experiments with DMB in the range of 250–291 ppb of diene concentration, but the measured SOA yield (0.005–0.007) was significantly lower than that of isoprene and 1,3-butadiene. These are described in section 3.2 of the new manuscript. A yield value 0.003 was essentially zero; descriptions concerning this are removed.

“- Fig. 7: In the mechanism, there is a missing step from methacrolein to

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hydroxynitrooxy-PAN. There should be a step from methacrolein (+OH/O₂/NO₂) to MPAN first.”

We add a step from methacrolein to MPAN in Fig. 7 of the new manuscript.

References

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