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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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Thank you very much for your valuable comments. We reply your comments as follows:
“Role of H₂O₂ in the system as a radical source. What is the radiation spectrum of the bulbs and was any effort made to see over what time period H₂O₂ photolyzed?”

Black light spectrum is peaked at 350 nm with 40 nm FWHM. The H₂O₂ photolysis rate when 276 lights are used was evaluated to be $6.4 \times 10^{-4} \text{ min}^{-1}$ from the NO₂ photolysis rate, the black light spectrum, and the H₂O₂ and NO₂ absorption spectra (DeMore

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et al., 1997). The total amount of photolyzed H₂O₂ in 6 h at the initial concentration of 3 ppm is estimated to 0.62 ppm. These data are briefly described in the first paragraph of section 2.2 in the new manuscript.

“Was there any independent knowledge of the NO₂ concentrations during the experiments? Figure 2a shows essentially no loss of NO_x (i.e., NO₂) during the six hour irradiation following the removal of NO after about 90 min.”

Unfortunately, we do not have any independent knowledge of NO₂ concentrations during the experiments. Sato (2008) measured the time series of NO₂ in the isoprene/NO_x system by using FT-IR; Fig. 2 of this previous paper shows the NO₂ level decreases with time after the NO level decreases to zero. Similar NO_x curves would also be measured in this study if we use an instrument that can directly detect NO₂ (such as FT-IR, LIF, and so on). However, the NO_x analyzer we used was a chemiluminescence type; NO_x signals of this instrument include not only the signals of NO and NO₂ but also the signals of NO_y species (e.g., nitric acid). For readers' understanding, we explain this in the caption of Fig. 2a of the new manuscript.

“Carlton et al. (2009) has written a review and summarized the isoprene yield under different conditions particularly in the presence and absence of NO_x. How would this work fit into that comparison?”

The present results are compared with the previous results of isoprene/NO_x/H₂O₂ system by Kroll et al. (2006) in the new manuscript. Their experimental data are also referred in Carlton et al. (2009) and are used for discussion on aerosol yield. A part of our yield results are higher than Kroll et al. (2006); however, this is consistently explained by the difference in aerosol loadings (please see reply to referee #3). These are discussed in section 3.2 of the new manuscript.

The present yield results obtained at various NO_x levels suggest that the SOA yield depends strongly on the NO_x level. This is consistent with conclusions of Carlton et al. (2009). These are discussed in section 3.2 of the new manuscript.

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“With 36 experiments and four precursors, the data in Table 1 should be structured in a more logical fashion than simply by chronological order of experiments. I would suggest grouping by precursor in order of yield for the standard conditions ($\text{H}_2\text{O}_2 = 3$ ppm; $T = 300\text{K}$; $\text{NO}_2(\text{pr}) = 0.12 \text{ min}^{-1}$) followed by the experimental variants to these standard conditions.”

We fix Table 1.

“Some added discussion of the significance of the VFR result should be given. Right now, there is simply a one sentence observation of Figure 12c that provides no insight.”

A new paragraph is added in section 7. In this paragraph, not only the VFR results but also a purpose of VFR measurements and a conclusion from the VFR measurements are described as follows:

We measured the 373 K VFR in the experiments at 300 and 278 K, and confirmed the VFR was independent of the diameter. If the temperature dependence of SOA yield (Y) is purely determined by the gas/particle partitioning of semi-volatile compounds, the $\text{VFR}(300 \text{ K})/\text{VFR}(278 \text{ K})$ ratio would be the same as the $Y(278 \text{ K})/Y(300 \text{ K})$ ratio. Thus, a comparison of the temperature dependence of Y with that of VFR will provide us information on reactions of aerosol constituents in the particle phase. In the present study, the $\text{VFR}(300 \text{ K})$ was 0.45–0.56, whereas the $\text{VFR}(278 \text{ K})$ was 0.26–0.43 (Fig. 12c). The change in SOA yield cannot be solely explained by changes in the VFR (SOA yield increased 2–3 times while the VFR changes by less than a factor of 2). Although the temperature dependence of SOA yield is largely explained by gas/particle partitioning of semi-volatile compounds, the present VFR results suggest that reactions of aerosol constituents occur in the particle phase.

“Yields appear high when compared to Kroll et al. (2005). Could this be due to the addition of H_2O_2 to generate additional OH initially? Is it possible that H_2O_2 is not being photolyzed substantially but is playing a role to increase aerosol mass through heterogeneous reactions? Again note that an aerosol density of $1.0 \mu\text{g cm}^{-3}$ is used;

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if densities closer to Kroll of 1.3 were used, the yield would be higher by that factor.”

Kroll et al. (2005) examined isoprene/NO_x/HONO system, and our original description that they examined isoprene/NO_x system was incorrect. We cite only a paper of Dommen et al. (2006) and remove the citation of Kroll et al. (2005).

By the addition of an OH radical source, the OH concentration during the reaction increases and thus the rate of semi-volatile compound formation also increases. Increases in both the OH concentration and the rate of semi-volatile compound formation are possible reasons of the H₂O₂ addition effect on the SOA yield. Further, increase in extent of reaction is also a possible reason of the H₂O₂ addition effect (please see reply to referee #4). These are discussed in section 3.2 in the new manuscript.

The SOA might be formed from the heterogeneous reactions of isoprene oxidation products with H₂O₂ (e.g. Carlton et al., 2006) in the presence of H₂O₂; however, these processes are less significant under dry conditions. These descriptions are also added in the new manuscript.

The density value employed affects the evaluated SOA yields. This is mentioned in section 2.3 of the new manuscript.

“Some discussion of the uncertainty (particularly, the precision) of these measurements is needed. It would appear that Runs 1148W and 1148E are duplicate experiments and yet the precision of the yields are at best 50%. The authors might suggest some factors leading to these differences.”

Typically, SOA concentrations of duplicate experiments agreed within 8% precision at the same reaction time. The experimental duration of EPA1148E was shorter than EPA1148W due to the difference in chamber leakage. The SOA yield is underestimated by a low extent of reaction in EPA1148E. These are explained in section 3.2 of the new manuscript.

“A few sentences addressing the atmospheric implications of the present findings is

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warranted.”

We added descriptions addressing the atmospheric implications of the present findings in a newly added section (section 8 of the new manuscript).

“It is unclear of the value of Figure 1.”

Thank you for the comment. Readers of this journal will include scientists from a wide range of background. We believe that this figure (involving the structure of isotope-labeled isoprene) helps readers’ understanding.

References

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