

## ***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<sub>x</sub> conditions” by K. Sato et al.***

**Anonymous Referee #6**

Received and published: 4 April 2011

Review of Sato et al. 2011 APCD, “Secondary organic aerosol formation from the photooxidation of isoprene, 1,3-butadiene, and 2,3-dimethyl-1,3-butadiene under high NO<sub>x</sub> conditions.”

Synopsis: The paper describes laboratory experiment to examine the laboratory yields for the three title compounds. Experiments are conducted in the presence of high concentrations of NO<sub>x</sub>. In an effort to increase the availability of OH radicals in the system, the investigators add ppm levels of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) to the system which are expected to photolyze to give OH directly. Based on the distribution of exper-

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iments, the paper is clearly focused on products and yields from isoprene (23 expts); a much lower focus is on the other diene precursors: 1,3-butadiene (8 expts), 2,3-dimethyl-1,3-butadiene (3 expts), and (13C1)-isoprene (2 expts). Of the 23 isoprene experiments, 15 were conducted under their “typical” conditions where differences in yields with respect to initial NO<sub>x</sub> conditions can be examined. LC-TOFMS analysis was conducted to study the formation of oligoesters during the photooxidation. Notable parameter changes included changes in system temperature, radiation intensity, and the presence or absence of H<sub>2</sub>O<sub>2</sub>.

General Comments: By and large, the experiments appear to have been carefully performed and important aerosol parameters and products were measured. The interpretation of the data is rather restrained and is largely consistent with prior work. However, the reported yields tend to be higher than that prior work (e.g., as reviewed by Carlton et al., 2009), particularly when realizing an aerosol density of 1.0 g cm<sup>-3</sup> is used in the present work. Thus, the discussion should be expanded to more completely compare the yield data of this work with prior studies, notwithstanding the comment of incomparability between studies made on p. 4321, line 26. With the presence of four other reviews, the addition of a fifth review may look like “piling on” so I will limit the detail in this review. The work warrants publication and subsequent comments are mostly minor criticisms.

Specific Comments: Role of H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> photolyzed?

Was there any independent knowledge of the NO<sub>2</sub> concentrations during the experiments? Figure 2a shows essentially no loss of NO<sub>x</sub> (i.e., NO<sub>2</sub>) during the six hour irradiation following the removal of NO after about 90 min.

Carlton et al. (2009) has written a review and summarized the isoprene yield under different conditions particularly in the presence and absence of NO<sub>x</sub>. How would this

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work fit into that comparison?

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.

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.

Yields appear high when compared to Kroll et al. (2005). Could this be due to the addition of  $\text{H}_2\text{O}_2$  to generate additional OH initially? Is it possible that  $\text{H}_2\text{O}_2$  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; if densities closer to Kroll of 1.3 were used, the yield would be higher by that factor.

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.

A few sentences addressing the atmospheric implications of the present findings is warranted.

It is unclear of the value of Figure 1.

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

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