

## ***Interactive comment on* “Low-volatility compounds contribute significantly to isoprene SOA under high-NO conditions” by Rebecca H. Schwantes et al.**

### **Anonymous Referee #2**

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Comments: This manuscript aimed to address contributions of isoprene SOA under high-NO conditions through forming the “low-volatility” organic nitrate compounds. The authors found that the isoprene SOA yields under tailored NO<sub>x</sub> conditions and substantial seed aerosol surface areas indeed are higher than previously estimated. The results are important and the paper is overall well written. But there are a few important issues that need to be addressed before published.

Major: 1. The authors concluded in the abstract that the LV pathway which produces organic nitrates and dinitrates likely contribute to isoprene SOA under high-NO conditions more substantially than previously thought under typical atmospheric conditions.

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But some components of the typical atmospheric conditions were not thoroughly discussed. For example, how does hydrolysis of the organic nitrates affect this contribution? How would aerosol acidity affect the contribution from the 2MGA pathway? Would low particle surface areas in real atmosphere impede partitioning of the products that the authors discussed? In addition, as the authors have claimed themselves that the yields of these LV organic nitrates are highly uncertain, the MCM model assumes a yield of 10.4%. Estimation of LV pathway yield using this model is thus also highly uncertain. The results from this model that LV pathway yield of  $\sim 0.15$  is rather hypothetical and I suggest leave it out of the abstract. Moreover, the partitioning behavior can be very different in the atmosphere compared to the chamber studies.

2. Validation is needed to explain why the authors only studied the 2MGA pathway using methacrolein as the initial VOC. I understand that the authors tried to tailor the conditions to separate the two pathways and measure SOA yield from each pathway. This is a really good idea. But then, a direct comparison between the two pathways is also needed, which is more straightforward and reasonable to start with isoprene and vary NO/NO<sub>2</sub> between different experiments. For example, using the many analytical tools in the authors' lab, they can show that as NO/NO<sub>2</sub> decreases, the gas-phase (CIMS) and particle-phase (AMS) organic nitrates and dinitrates decrease, while the HMML and 2MGA increase. Comparing with the isolated experiments, quantification of the two pathways is probably possible too. In this way, the same OH oxidation extent and seed particle surface area will be used and variations can be better controlled. Although the 2MGA pathway from isoprene and methacrolein oxidation is the same mechanistically, in direction isoprene photooxidation experiment, the 2MGA pathway products are formed in later generation and that may change the dynamics (e.g., OH availability at different times) in the SOA formation. Also, how signature SOA product ions (both CIMS and AMS) from the LV pathway and the 2MGA pathway in the same isoprene photooxidation experiments as NO/NO<sub>2</sub> ratio varies is a more desired and direct way to present the results.

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3. Page 12, line 22. It is very interesting that SOA yield does not vary too much as temperature changes between 13 and 32 C. The authors mention two reconciling effects: enhanced vapor wall loss and enhanced organic nitrate yields from RO<sub>2</sub> + NO reaction under lower temperatures. Can the authors provide some quantitative constraints on these two effects? How different are the organic nitrate yields and wall loss rates under this range of temperatures? Another point to add, is that at lower temperature, more semi-volatile species may partition into the particle phase. I think this is a major effect. Previous studies using very similar temperature range and found a difference of 2-10 times in SOA yields (Clark et al., 2016 ES&T; Takekawa et al., 2003 Atmos. Environ.; Sheehan and Bowman, 2001 ES&T.). Some of these studies use isoprene, some use hydrocarbons that likely produce less volatile SOA than isoprene. The authors should think about addressing this question. Is it because the LV SOA have surprisingly low volatility that they are already mostly in the particle-phase at 30C? Can the authors estimate the vapor pressure of the nitrate and dinitrate compounds and see if this hypothesis make sense? Note that there are only two experiments at different temperatures and the lower temperature experiment started forming SOA much earlier than the higher temperature experiment. But they ended up forming similar SOA mass. From that perspective, there is a clear temperature influence. I hope the authors can address this question with more detailed discussion. The same case for the 2MGA pathway. The authors found little temperature influence on SOA mass yield. But again, that was based on only one high temperature and one low temperature experiment. The two experiments have very different seed particle surface areas too. The data provided are not sufficient to draw conclusions on temperature effects.

4. The authors use “low-volatility” to describe the organic nitrates. But they should also justify this by providing some estimates of the vapor pressures or C\* of the molecules in Figure 1.

Minor: 1. Title and abstract: HMML is formed not only under high-NO, but also high-NO<sub>2</sub> (MPAN is their precursor). It is thus inaccurate to term “high-NO” as the condition.

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As the authors also point out in the text, NO<sub>2</sub>/NO ratio is an important indicator of the two pathways. From the experimental list, NO and NO<sub>2</sub> are indeed adjusted to optimize different conditions. Thus, it seems more appropriate to use “high-NO<sub>x</sub>” rather than “high-NO” in this manuscript.

2. Page 3, line 2. The 2MGA pathway should refer to particle-phase products (2-MGA, its oligomers, and its organosulfates) from further oxidation of MPAN or uptake of HMML.

3. Page 5, line 27. Whether the NO<sub>2</sub> signal can be interferences from nitrous acid or CH<sub>3</sub>ONO can be easily tested using the standards.

4. Page 12, line 14. It is unclear what is referred to as “the 2-MGA precursor” here. Is it MACR? MPAN? HMML? This information was obtained from the kinetic mechanism. I think the author should at least provide the simulations in the supporting information and mention it in the main text.

5. Page 12, line 26-27. Exceptions are when temperature was low and initial seed particle surface area was high.

6. Page 12, line 31. Based on the earlier description, the kinetic model combines MCM and some other gas-phase reactions that are listed in Table 2. So the kinetic model seems to be a pure gas-phase model. It is thus unclear when the authors mentioned that the kinetic model can predict the SOA mass yield. This sentence needs to be re-phrased to something like: “The kinetic model predicts that the formation of gas-phase dinitrates from experiment D7 is similar to the other experiments”. Then the followed issue is whether this single species can represent the overall SOA in the studied condition. The authors may want to also compare other proposed LV-pathway products from the model.

7. Page 15, line 9. The authors may also want to consider that organosulfate formation in the presence of ammonium sulfate seed particles.

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8. Page 15, line 15. HMML/reacted MACR = 0.25 does not mean the SOA yield from HMML uptake is 0.25. HMML is a C<sub>4</sub>H<sub>6</sub>O<sub>3</sub> lactone. If you think about its vapor pressure, it is probably on the more volatile side of the SVOC range. It will have a large fraction in the gas phase.

9. Page 17, line 30 to Page 18, line 2. The description is unclear. A brief but better explanation (better than just saying “highly uncertain”) is needed here to explain why the Lee et al. used upper limit yields 10 times higher than their measurements? Are there other studies supporting the yields?

10. Page 18, line 17. The Lee et al., 2016 PNAS study provide some constraints on isoprene nitrate yields and should be cited here.

11. Figures 9 and 10. What do the rest unlabeled ions represent?

12. Page 25, line 23. The authors provided evidence that MAE is not a product from MPAN oxidation, but then use MCM which assumes MAE has a 21% yield from MPAN oxidation, to estimate contribution to the 2MGA pathway. Why not modify the MCM model and provide an estimate that the authors are more confident about?

13. The CIMS data are shown for the LV pathway. CIMS can also measure HMML in the 2MGA pathway and I'm curious why the data were not shown.

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