

Interactive comment on “SOA from limonene: role of NO₃ in its generation and degradation” by J. L. Fry et al.

Anonymous Referee #1

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This manuscript by Fry et al. describes the formation of organic nitrates and SOA from a single two-part NO₃ + limonene experiment conducted in the SAPHIR smog chamber facility in Julich, Germany. This experiment was a 24-hr study that involved two injections of limonene and oxidants. As a result of the latter, the authors were able to measure the SOA yield in the absence of seed aerosol during the first part of the experiment and then measure the SOA yield in the presence of 10 µg m⁻³ of seed organic aerosol in the second part. After each of the limonene/oxidant injections (i.e., at ~3 and 9 hrs based on Figure 1), two separate increases in SOA mass were observed. Importantly, the authors find some chemical evidence to support the heterogeneous uptake of NO₃ onto unreacted alkene SOA constituents. This manuscript is well written, concise, and certainly suitable for publication in Atmospheric Chemistry and Physics, especially due to our lack of detailed knowledge on SOA formation from

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NO₃ reactions with various BVOCs. However, I kindly request that the authors respond to some major questions I have about the current manuscript:

1.) Why did the authors design the experiment to contain both NO₃ and O₃? I realize that the authors did this in order to generate N₂O₅, which serves as a source of NO₃. However, the problem I have with the current experimental design is that the oxidation of limonene is done by both NO₃ and O₃ (as clearly stated by the authors in the text), and as a result, this can really complicate things inside the chamber. Since the goal of the manuscript is to understand SOA formation only from NO₃-initiated oxidation of limonene, I was surprised to find that the authors did not consider a cleaner approach. Specifically, did the authors consider synthesizing N₂O₅ offline and then injecting N₂O₅ only into the chamber? Recently, Ng et al. (2008, ACP) did this for the study of SOA formation from isoprene + NO₃. This allowed Ng et al. (2008, ACP) to study only the reaction of isoprene only with NO₃ as well as conduct multiple injections of N₂O₅ in order to understand the behaviors of first- and second-generation gas-phase oxidation products in forming SOA. In addition, Ng et al. (2008, ACP) was able to design two different types of injections: (1) slow injection of N₂O₅ into a chamber already containing isoprene, which results in RO₂ + RO₂ chemistry dominating; and (2) slow injection of isoprene into a chamber already containing N₂O₅, which results in RO₂ + NO₃ chemistry dominating. From these two comparisons, these authors were able to show that the RO₂ + RO₂ reactions leads to more SOA formation from isoprene than the RO₂ + NO₃ reactions. The question that remains from this previous study is what gas-phase reaction(s) (i.e., RO₂ + RO₂ vs. RO₂ + NO₃ vs. RO₂ + HO₂ vs. RO₂ + NO) are important in the "real" atmosphere at night in forming SOA from BVOCs oxidized by NO₃?

2.) The authors use the proposed mechanism shown in Figure 3 to model their chamber results. One problem I have with this approach is the fact that the mechanism in Figure 3 appears to be based on the previous literature and not on detailed chemical characterization of both gas- and aerosol-phase constituents found in their chamber.

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Are the gas-phase products shown in Figure 3 detected by the PTR-MS measurements? Additionally, the authors state the following on page 31097: "As has been noted in previous studies, the predicted vapor pressures underestimates the aerosol produced. This suggests that the actual structures of limonene oxidation products are either more oxidized or oligomerized formed of the proposed structures, or that the group contribution method overestimates vapor pressure." Detailed chemical characterization of both the gas- and aerosol-phase constituents could have provided insights into this issue. The lack of detailed chemical characterization (at the molecular level) of both phases is probably the main weakness of this paper. By chemically characterizing both phases at the molecular level, Ng et al. (2008) were able to show how certain gas-phase products produced from isoprene + NO₃ lead to specific aerosol constituents. Interestingly, Ng et al. (2008, ACP) showed that when RO₂ + RO₂ reactions dominate in the gas-phase more aerosol forms over that when RO₂ + NO₃ dominates. Many of the aerosol constituents from the RO₂ + RO₂ reactions were high-MW organic nitrates. Many of these previously characterized products from isoprene likely had low vapor pressures. It would be interesting to know if this process also occurs when limonene is oxidized by NO₃; specifically, do we get more aerosol from limonene + NO₃ when RO₂ + RO₂ reactions dominate in the gas phase?

3.) Only one experiment is conducted and/or presented for this paper. For quality control purposes, it would be better if more experiments were conducted to make sure this chemistry is consistent from day to day. If the authors aren't willing to conduct (or present) more experiments, I think they should at least provide some word of caution for readers of this manuscript.

4.) Heterogeneous NO₃ uptake.

This is an important finding and it could be further validated if detailed chemical data was collected/presented from both phases. For example, if RO₂ + RO₂ reactions dominated in the gas-phase, it is possible that certain unsaturated ROOR products (similar to Ng et al. (2008, ACP) for the isoprene system) are of low enough volatility that they

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partition to the aerosol phase. Is there any detailed chemical data available for the authors to further explore this? Although AMS data is certainly useful (i.e., PMF analyses of AMS data), I'm not convinced these data are helpful in further understanding (or validating) the heterogeneous uptake of NO₃ radicals.

Minor Comments:

1.) Please cite and include the study by Ng et al. (2008, ACP) in your discussion.

Reference details:

Ng, N. L., Kwan, A. J., Surratt, J. D., Chan, A. W. H., Chhabra, P. S., Sorooshian, A., Pye, H. O. T., Crounse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO₃), *Atmos. Chem. Phys.*, 8, 4117-4140, 2008.

2.) Figure 1:

Very hard to read even when printed out. I would increase the size of the figures as well as the font so it is easier to read, especially since this is the main result of the study.

I would also consider indicating more clearly on this figure what the dashed vertical lines mean in each subfigure either by labeling the figure or saying what these dashed lines mean in the figure caption.

3.) Figures 3 and 4:

Again, very hard to read the text and figures. I would make these larger so they are easier to read.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 10, 31083, 2010.

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