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Atmospheric Chemistry and Physics Discussions

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

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Reviewer responses are repeated below, followed by authors' responses.

Referee #1: 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 ug m-3 of seed organic aerosol in the second part. After each of the limonene/oxidant injections (i.e., at âĹij3 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 hetero-

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geneous 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 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 ïňĄrst- 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?

– AUTHORS' RESPONSE: The reviewer's point is well-taken: analysis of the kinetics

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in this experiment would have been made significantly simpler if there were not a high concentration of O3 completing with NO3 reactions. Nevertheless we would like to point out, that unlike the Ng et al study we performed direct measurements of NO3 concentrations throughout the experiment. Therefore in this experiment NO3 concentrations are known with a high accuracy rather than estimated. Furthermore Ng et al had to deal with ∼10% HNO3 and ∼4% NO2 impurities from the synthesized N2O5 in their approach. Since NO3 is formed from O3 + NO2 reactions in the atmosphere via the process used in our experiment, the relative importance of NO3 and O3 in SOA formation should be realistic for ambient night time situations. In future work, we would certainly like to address the questions the reviewer poses about dominant RO2 chemistry in the real atmosphere. –

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. 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 where

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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?

– AUTHORS' RESPONSE: During this experiment, the PTR-MS measurement was optimized for high time resolution for precursor decay rather than scanning for products; hence we do not have additional information on the products of limonene oxidation in the gas phase. Please see response to reviewer #2's second point below (similar to this suggestion) for some additional composition information gleaned from AMS O/C ratio. –

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.

– AUTHORS' RESPONSE: We respectfully disagree with the reviewer on this point. The SAPHIR simulation chamber was extensively characterized with respect to wall losses, wall effects and impurities in previous and the present campaign. A broad range of experiments was conducted to characterize the NO3 and N2O5 chemistry in the otherwise empty chamber (Dorn et al, in preparation) and revealed no artifacts from the chamber. Also the SOA formation experiments for other BVOCs (b-pinene (Fry et al) and isoprene (Rollins et al)) show that the chemistry in SAPHIR is well understood and reproducible. While experiments covering a range of initial conditions are certainly useful in many respects, SAPHIR with its long experiment times and high purity environment is more applicable to observations on time scales and concentrations not accessible with other simulation chambers. Certainly other experiments such as flow tube studies or smog chamber studies of the NO3 + limonene system would be desirable to further investigate aspects of the work presented here. –

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4.) Heterogenous 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 dom- inated 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 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.

– AUTHORS' RESPONSE: The experiments performed focused on the gas phase oxidant and RONO2 analysis. No detailed chemical analysis on individual molecules in the particle phase is available. Nevertheless the correlation of PMF factor 3 with [NO3]x[O3LIMaero] and with [NO3]xSA together with the mass spectral signatures of factor three strongly supports the interpretation of this fraction of SOA being formed via heterogeneous NO3 uptake. –

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.: Secondar y organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO3), Atmos. Chem. Phys., 8, 4117-4140, 2008.

– AUTHORS' RESPONSE: Added to discussion, with speculation about unsaturated RO2/RO2 products. –

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 ïňĄgure what the dashed vertical lines mean in each subfigure either by labeling the ïňĄgure or saying

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what these dashed lines mean in the figure caption.

– AUTHORS' RESPONSE: Done. This was a consequence primarily of the constraints of the ACPD landscape format and will be larger in the ACP version. Added text to 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.

– AUTHORS' RESPONSE: Will do, in revised ACP-format manuscript. Thank you! –

Referee #2: This is an excellent paper that should be published after some minor revisions. Specifically, the authors should take note of a relevant study by Zhang et al., JPCA, 2006 and they miss the opportunity to calculate the atomic composition of the SOA using the HR-AMS at their disposal.

The Zhang paper addresses limonene ozonolysis and includes a discussion of heterogeneous uptake by ozone to unsaturated limonene-derived SOA as well as interpretation of (unit mass resolution) AMS spectra under low and high NOx conditions. Those topics seem germane here. Zhang et al. concluded that ozone uptake to limonene SOA is very rapid under low-NOx conditions (this was confirmed in the Maksymiuk paper cited by Fry et al.) but that it is quite slow under high-NOx conditions. Without slow ozone uptake to the SOA in this experiment, it is likely that ozone would rapidly scavenge any double bonds available for NO3 uptake. Thus, on the face of it, these studies appear to be consistent with each other ; however, this should be discussed.

– AUTHORS' RESPONSE: Added text to discussion of uptake, citing Zhang: "The availability of these aerosol-phase double bonds for heterogeneous reaction with NO3 relies on their not being rapidly consumed by O3 . This was found to be the case by Zhang et al. (2006), who found rapid ozone uptake by limonene SOA under low-NOx conditions, but not under high-NOx conditions. Hence, in the present experiments, without ozone scavenging, the unsaturated aerosol-phase organics remain available

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for NO3 uptake." –

In addition, Zhang et al. make use of PTRMS data to assess the loss of limonene at m/z = 137 as well as the loss of a first-generation product (evidently unsaturated) at m/z = 81 with an apparent ozone rate constant about a factor of 30 lower than limonene. Given the uncertainties in gas-phase chemistry discussed here, it would be nice to see more use of the PTRMS data than simple observation of the limonene loss.

– AUTHORS' RESPONSE: Please see response to reviewer #1: our PTR-MS measurements were optimized for high time resolution and therefore only measuring m/z 137 and 81. m/z 81 showed a small interference and was therefore unable to be evaluated as in Zhang et al. –

Also, given that the authors invoke additional oxidation as a potential explanation for the discrepancy between predicted and observed SOA levels, it would be very interesting to see a comparison between the bulk atomic composition of the SOA, as observed by the AMS using the relationships discussed by Aiken et al., EST 2008, and the atomic compassion inferred from the surrogates used to represent the SOA. Is the AMS-derived O:C higher than that of the surrogates? Would adding two carbonyl groups fix this? What about the mean oxidation state of carbon, as proposed by Kroll et al. in Nature Chemistry this year? Are the surrogate products sufficiently oxidized?

– AUTHORS' RESPONSE: We thank the reviewer for this suggestion. We have calculated the O/C ratio in the AMS-observed total aerosol for the length of the experiment, and calculated the same ratio from the modeled surrogate compounds. Interestingly, with the proposed model chemistry, the O/C ratio largely matches observations. The AMS measures on average 0.4 for the whole experiment with a slight increasing trend over time, while modeled O/C ranges from 0.33 to about 0.5 at 25 hours, slightly underpredicting the oxidation of initial aerosol formed and slightly overpredicting later aerosol oxidation level (see figure attached), as product species are re-equilibrating in a diluting chamber.

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The broad agreement between measured and modeled O/C validates our assumption of the average structure and molecular weight of condensing species (p. 12 in ACPD manuscript, assumed MW = 250 g/mol), and suggests that the surrogate species are, in fact, sufficiently oxidized.

We have modified discussion in section 5.3 “Aerosol chemical composition” to include a paragraph discussing this (new paragaph #2 in that section):

“Comparison of bulk atomic composition of the SOA observed by the AMS (Aiken et al., EST 2008) to calculated composition based on the surrogate model compounds reveals broad agreement on the level of oxidation of the aerosol components. Both measurement and model have an average O/C ratio of about 0.4, increasing gradually over the course of the experiment (observed O/C rises from about 0.3 to 0.45). This suggests that the model chemistry at least accurately captures the bulk oxidation level of the condensing species.”

In addition, a sentence has been added to section 5.1.2. where modeled vapor pressures are discussed:

“Because bulk oxidation state of the modeled species agrees with AMS observations (see Section 5.3), it seems unlikely that additional oxidation is the explanation for these underestimates.”

and I have removed from Table 3 the “equivalent functional group change”, since this newest analysis suggests that the explanation lies elsewhere than oxidation chemistry.
–

Finally, the dramatic behavior of N2O5 really does require a little more discussion. Assuming that the ozone and NO2 did not do anything strange during this period, it would seem that some relatively labile reservoir of nitrate may have appeared as an intermediate species (between hours 11 and 16, as discussed by the authors). This is exactly when the total AN peaks, and it is even roughly consistent with the

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period and magnitude of the discrepancy between the total AN model and the total AN measurements shown in Fig. 6. If one simply takes measurement - model for total AN from Fig. 6 and plots that on Fig. 7, how much of the mysterious divot is filled in?

– AUTHORS' RESPONSE: This is an excellent point – the area between measured/modeled curves matches quite tantalizingly. We have iterated so many times with the model that we can be confident it is not simply a small variation of some chemical process we already have in the model, but this does seem to suggest that there is some additional, temporary alkyl-nitrate-type gas-phase species formed from NO3 during the "divot". We have added text pointing this out and describing this speculation: "It is notable that the remaining discrepancy between measured and modeled alkyl nitrate (Fig. 6, green data and solid line) is essentially identical in magnitude, opposite in sign, and synchronous in time with the discrepancy between measured and modeled N2 O5 (Fig. 7, blue traces). What remains mysterious is what process could induce this temporary source of volatile alkyl nitrate intermediate. " Thank you! –

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

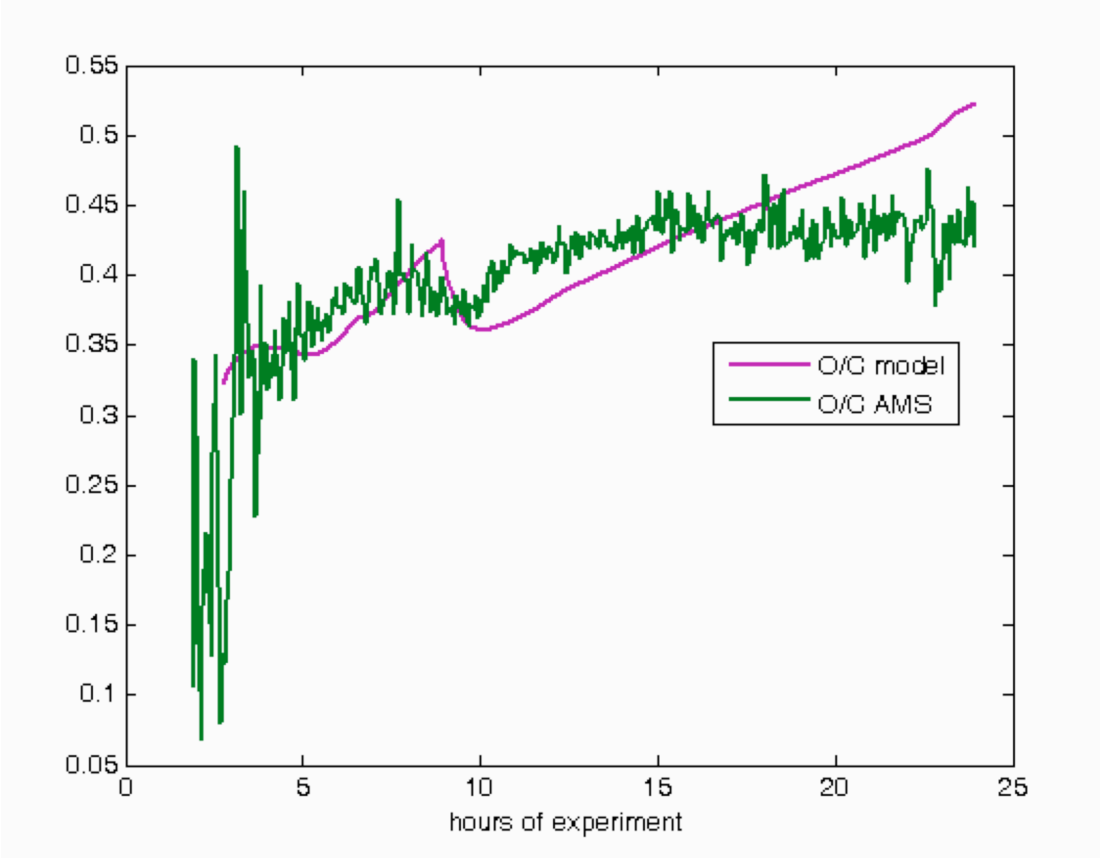

Fig. 1. OC/EC measured by AMS vs. in modeled aerosol.

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