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Interactive comment on "Influence of NO$_2$ on secondary organic aerosol formation from ozonolysis of limonene" *by* Changjin Hu et al.

Anonymous Referee #2

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In this work, the authors studied the effect of NO2 on secondary organic formation from limonene. Specifically they conducted chamber experiments with limonene and ozone, and investigated the effect of added NO2. They followed up with a gas-phase explicit oxidation model (Master Chemical Mechanism) and gas-particle partitioning calculations to corroborate the experimental findings. While the topic explored in this work is relevant to the scope of Atmospheric Chemistry and Physics, the new scientific understanding gained by this work is limited, and there are some major issues with the relevance of the modeling work. I therefore do not recommend publication of this manuscript in ACP.

Major comments:

My biggest issue with this paper is whether or not this work advances scientific under-

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Discussion paper

standing of SOA mechanisms. Here the authors use explicit mechanisms outlined in MCM to model SOA formation. The most important lesson from this exercise is that as NO2 and O3 concentrations increase, the contribution of NO3 oxidation increases, leading to higher SOA from limonene + NO3. It has been shown in many studies (since Griffin et al., 1999) that terpenes + NO3 have substantially higher SOA yields than OH oxidation. Also work by Fry et al., has shown large contributions of organic nitrate to SOA. It is therefore not surprising that as NO3 increases, the amount of SOA from limonene + NO3 increases. Using a model to verify these experimental observations is hardly insightful, as the model is merely a synthesis and a reflection of what the user already understands. I am therefore highly critical about any broader impacts that this work may carry. I do not find this modeling exercise to add any value to the field.

The authors would need to dig deeper and ask more impact research questions. For example, what would be the NO2 concentration or relative ratios of NO2/limonene/O3 that would divide the different regimes (limonene + NO3 dominated vs limonene + O3 dominated) and what would be the implications? Would different regions in the world fall under these different regimes?

I also have issues with the use of MCM coupled to gas-partitioning calculations based on vapor pressures, which are in turn calculated by estimation methods that have 1-2 orders of magnitude in error. More important, many processes, such as oligomerization and heterogeneous phase reactions, vapor losses to the walls, are not represented in the model. I understand that there is somewhat of an agreement in SOA yields between the MCM model and experiments, but constraining with yields is hardly the only goal. One suggestion I have for the authors would be to quantify the functional group abundances shown by the FTIR data. It would be very useful to demonstrate the MCM can also successfully predict the abundances of different functional groups, which would make the model much more powerful.

I should also stress that a lot of work has been done since Chan et al. (2010) to demonstrate the formation of epoxide intermediates from MPAN that are important

for SOA formation. Lin et al. (2013) suggested the role of methacrylic acid epoxide, and Nguyen et al. (2015) and Kjaergaard et al (2012) suggested the role of HMML. These pathways are quite specific to isoprene, and may not apply to limonene. The authors need to justify how one can extrapolate results from isoprene to limonene. One notable difference between the two systems are the positions of the double bonds. Isoprene has conjugated double bonds, leading to intermolecular reaction mechanisms to ultimately to lead to low-volatility products. It is not clear if limonene would do the same.

I would imagine with the large excess of butanol, butanol would dominate the NO_3 reactivity. Therefore, the reaction of NO_3 with limonene would be minimized. Is the reaction of butanol with NO_3 included in the model? Also, if the main argument is that as NO_2 increases, the role of NO_3 oxidation increases, the authors should demonstrate evidence either experimentally (very difficult) or in the MCM model (easy to show).

I am not sure if there are any specific recommendations or outcomes from this work for experimentalists or modelers. It seems that message is "the mechanism is complex", but do not offer any suggestions as to how to reduce that complexity, or how to design specific experiments to probe important branches of the mechanisms. These suggestions are absolutely needed to make the modeling exercise worthwhile.

Other comments:

I was wondering about particle wall loss correction, but did not see it until Supporting Information. It would be useful to mention that wall loss has been corrected in the methods and refer to the supporting information.

I assume there are no seed particles (e.g. ammonium sulfate) added. In that case, vapor wall loss will be an even bigger issue since there is an induction period associated with nucleation. Have the authors tried using ammonium sulfate seed to investigate whether or not SOA yields would be higher?

What is the interference of NOy species in the NOx analyzer? They may affect the NO2 measurements and skew the model-experiment comparison

Line 327: why is there an increase in particle number concentration? How reproducible are these increases in mode diameter and number concentration?

In general, the FTIR data show what one would expect. Carbonyl groups (and hydroxyl groups) are what one would expect in SOA, and it has been shown in numerous studies that low-volatility organic nitrates can form in the presence of NOx. Is there any indication from the FTIR data about specific reaction pathways? For example, PANs and organic hydroperoxides would produce peroxy (O-O) groups may give a unique peak in the data.

Section 3.3.2: I would take one step back and explore some more basic questions. First, what is the concentration of NO3 or total NO3 produced as a function of NO2 added? Second, what is the fraction of limonene that reacted with O3 and what is the fraction that reacted with NO3? These would help support the explanation presented in the conclusions.

Section 3.3.3: The modeled results about 20 species dominating the particle mass (93-96%) is intriguing. This result may merely be a reflection of what we understand about particle composition, rather than a true representation of the particle composition. The citation stating that a majority of organic nitrates are unidentified (Lines 543-544) seems to support the notion that we simply don't have sufficient chemical understanding to model this system explicitly.

Technical comments:

Line 78: "low volatile" should be "low volatility"

Line 78: stylistic suggestion "when react with" should be "upon reaction with"

Line 87: "molecular bone" should be "molecular backbone"

Line 89: awkward language "a major part from vegetation"

Line 99: double bond is unsaturated, saying "unsaturated double bonds" is redundant

Line 170 – 173: is it necessary to cite these papers? It seems like these self citations are here to inflate citation numbers. These papers should only be cited if they help describe the experiment methods. Even so, one citation should be sufficient.

Line 175 and 179: what is the difference between dry zero air and purified air?

Line 181: excessive should be excess. How much butanol is in excess?

Line 187: what is TEI? I assume it is the ThermoFisher NOx analyzer (42i).

Line 229-230: I am not sure what this statement means. Oligomerization reactions do happen for larger molecules too. Why are they not considered? The SOA yields here are on average around 40%, meaning that there is still a lot of mass that are in the gas phase and can potentially condense upon further oxidation, or oligomerization.

Line 286: what does typical mean? Is it typical of polluted regions? If so, how much limonene is typically present in high NO2 areas? Limonene has very short lifetimes and therefore may not be present in high concentrations outside of forested areas. One exception could be indoor environments where limonene is used in air fresheners.

Line 330: form should be from

Line 347: passways should be pathways

Line 368-369: slope does not makes sense. Just because the slope is 1.4 it does not mean yields are overestimated across the board. There is an intercept for the best fit line.

Lines 415-416: why can NO be ruled out? Is it because of high O3 and NO3 levels? What are the measured levels of NO?

Line 419: Ng et al. (2007) does not show PAN formation.

Line 423: awkward language "learn" should be "study"

Line 448 typo: oxidation

Line 484: what does "semi-qualitative" mean?

Line 583: typo in the second set of parentheses

Line 597: stylistic suggestion: do not start a sentence with actually.

Line 599: what is whenas? Maybe "whereas"?

Figure 2: what are the error bars?

Figure 4: the red line is not the 1:1 line. For these model-experiment comparison, it would be useful to show a 1:1 line. The best fit line is not useful.

References:

Lin, Y.-H., et al. Epoxide as a Precursor to Secondary Organic Aerosol Formation from the Photooxidation of Isoprene in the Presence of Nitrogen Oxides.ÂăPNAS, 2013, 110 (17), 6718–6723.

H. G. Kjaergaard, H. C. Knap, K. B. Ørnsø, S. Jørgensen, J. D. Crounse, F. Paulot and P. O. Wennberg, J. Phys. Chem. A, 2012, 116, 5763–5768.

T. B. Nguyen, K. H. Bates, J. D. Crounse, R. H. Schwantes, X. Zhang, H. G. Kjaergaard, J. D. Surratt, P. Lin, A. Laskin, and J. H. Seinfeld, Phys. Chem. Chem. Phys., 2015, 17, 17914–17926