Review of Luo et al. ACP submission: Formation of highly oxygenated organic molecules from the oxidation of limonene by OH radical: significant contribution of H- abstraction pathway

Significance:

This is a well-motivated study about an important general process that is currently neglected in atmospheric chemistry models. The common chemistry models assume that an OH radical will always find its way to a double bond although several well-known facile H-abstractions would be available in the same molecule; the same double bond catalyzes the H-abstraction adjacent to it forming an allylic alkyl radical. This is quite well understood effect, but practically completely neglected in the current models describing atmospheric processes. This lack is likely most severe for secondary aerosol modelling, in which the condensing vapors are generated in-situ by rapid chain like oxidation chemistry, which likelihood is controlled by the oxidizing hydrocarbon structure. Only a fraction of the overall pathways leads to low volatile, condensable products, and thus describing the correct paths becomes critically important. Thus the study and analysis are timely and well-motivated.

While I find the topic worthwhile and certainly interesting for the readers of ACP, I am poorly convinced that such a parameter could be derived in a setup like SAPHIR. By reading the work through, I am sadly not much more convinced. Several crucial approximations have to be made to get started with the analysis, and with such a long processing times it becomes a tedious task to fill in the gap between the first reaction step (i.e., the reaction that is studied), and the chain like chemistry progressing to observed products through a complex and convoluted mechanism. I want to emphasize that the whole mechanism is littered with uncertainty, and with longer time scale this uncertainty only grows. Additionally, there seems to be some confusion with the presentation and some worrying observations about NOx have been made that put the final result in doubt. I'll detail my concerns below.

Major comments:

So first of all: Can you estimate such a quantity with this platform and experimental setup? Ideally this sort of work should be performed with techniques capable of seeing the primary radical products at short reaction times (e.g., resonance fluorescence, photoionization mass spectrometry, IR-spectrometry, etc.,), and not deduce the value from a very complex mechanism at very long reaction times (note that it seems the reaction time is not given in the manuscript text), with several assumptions about the mechanism and the detection. Such long residence times are arguably poorly suited to study details of chemical mechanisms, and are far more better equipped to study, for example, SOA forming potential. A large volume implies long time-scales, which leaves open the possibility for even slow processes to make a dent. The bare minimum is that the caveats of this approach should be discussed.

Several details seem to be missing which prevent understanding how the work was performed and analyzed. First of all, what was the OH source? You are reporting OH oxidation experiments but it appears you do not even mention the OH source in the main text. The method of OH production should be discussed extensively especially if you claim the current work was done better than the previous. Also, what was the source of HO_2? How was it controlled? Was it? What were the used limonene concentrations? What was the time-scale of the experiment? Where is the HONO originating from? Does it prevent making such a study as apparently the chamber has always appreciable NOx present. To clarify, it is really difficult to put the results into any context when the most important parameters are left out. I hope you remember that the study should reproducible with the given information, and that the ACP format does not require for a shorter length. Also, please remember that the supplemental material is for adding information that is not pertinent for understanding the work, but is a place to add additional information supporting the claims.

How well does the "HOM measured under 17 ppb of NOx in a one chamber setup" represent the general "high NOx" yield of limonene HOM? Is this realistic to use for atmospheric modelling? Would some sort of fit between the conditions be better, or is it sufficient to use a one value for all the environments?

On the same lines: What does "a HOM yield of a single molecule" actually signify? Can you apply it for an air quality study, or how is it a useful quantity? How much does it depend on the individual configuration of the experiment and the instruments? When you consider that individual HOM measurement is affected by the transmission and fragmentation of the instrument, the detection sensitivity due to changes in diffusion of bulky HOM, detection (=charging) probability that depends on the exact molecular structure, and so on… So to sum it up: how realistic is any given HOM yield, and how useful it is for others to utilize? This should be discussed.

The given range for "low NO" spans over 3 orders of magnitude(!), whereas the "high NO" is only about 80 times higher than highest low. This seems a bit strange. Even more strange is that you obtain 33% yield for the nitrates even with the low NO conditions – to me it would imply that your low and high conditions were far closer that what you assume here. Also it raises the question that is it possible to deduce the OH reaction influence with such a high persistent background levels of NOx? A sensitivity analysis based on the model chemistry would improve the credibility.

I generally find the discussion around this NO influence confusing. For example you state that "to estimate the impact of ozone oxidation during photoxidation, we calculated the reaction rates of VOC+ OH and VOC+O3 in low and high NO conditions of this study.." without explaining where this difference comes from. Obviously the NO has nothing to do with the VOC + OH and VOC + O3 rates unless you consider the secondary chemistry. This can be very misleading to a reader without a prior good grasp on the ongoing processes. Please connect these statements to the chemical phenomenon you're describing.

To consider:

*Do you consider the $RO_2 + HO_2 \rightarrow RO + O_2 + OH$ pathway for any of the RO_2 in the mechanism? This should be possible as you follow the structures explicitly.

*Why can't the $C_{10}H_{17}O_x$ produce an $C_{10}H_{16}O_y$ alcohol by $RO_2 + RO_2$?

*Is it really the case you saw no trimer species? By looking at the Figure 1, it appears that dimers are high, and four a two double bond systems trimers have been reported (e.g., Molteni et al. https://acp.copernicus.org/articles/18/1909/2018/)). So if you would provide me a Zoom of the 700-900 Th – are there no apparent bands of peaks present?

*The method (Fuchs et al. 2012) used to determine [RO2] and [HO2] has been debated to be prone to artefacts from different RO2 propagation reactions. For example, a tertiary RO2 will not lead into HO2 and is thus miscounted, especially here when your most facile reaction advances through a tertiary RO2. Was any correction applied to the values of [RO2] and [HO2]? If not, the caveat of not doing so should be the very least discussed.

*Line 348: Yes, the alkoxy-peroxy step removes the geometrical constraint, but it also imposes a limitation on the efficiency of this path, as the bimolecular step is needed to allow for autoxidation, whereas losses by wet and dry scavenging, photolysis and reactions with other trace gases might as well happen. Postulating several alkoxy-peroxy sequences will impose even greater limitations, as the radicals may be lost in each step and the OH is mainly lost with the high [VOC]. This caveat on the way to HOM should be clearly stated.

*How good is the assumption to use “the same kuni, kRO2+RO2, kRO2+HO2, and α for a given C10H15Ox• and C10H17Ox• family.”? Easy examples where this does not hold are: H-shift across the ring vs H-shift in a linear chain after ring breaking. RO2 + RO2 for a primary RO2 vs oxygenated RO2. How big of an uncertainties these assumption generate?

*How does the shifting detection sensitivity of CIMS affect your conclusions (e.g. Hyttinen et al. https://pubs.acs.org/doi/10.1021/acs.jpca.7b10015), as the C10H17Ox is likely detected better than the C10H15Ox products, especially at the lower end of the oxygen content?

*It seems unlikely that the SAR will reproduce the rates of the highly oxygenated molecule H-shift rates. This is due to intramolecular interactions (mainly H-bonding) that influences the thermochemistry; a favorable interaction on the reactant side will increase the barrier to reaction, and can significantly decrease the H-shift rate. Looking at the schemes of the paper with the given SAR rates can leave a very wrong picture for the reader. This influence is hinted in the manuscript but, still the uncertain numbers are presented in the schemes. Is this reasonable?

*The secondary OH reaction is generally inherently less likely in lab systems, as I would expect to be here as well (i.e., how much would you need to accumulate the product before it’ll find the second OH at a rate sufficient for measurable product formation?). Yet, with the missing documentation about the used concentration ranges it is not possible to even roughly estimate this fraction.

*Line 323: “However, this extra bimolecular OH reaction takes time, and can delay formation of HOM. An analysis of the secondary chemistry is outside the scope of this work, …” As mentioned above, not all pathways lead to HOM, and the whole paper is an analysis of secondary chemistry if you are studying OH abstraction vs OH addition through a complex mechanism. Please sharpen your words and thinking.

*Line 328: Here you imply that the low NO is actually the highest of your reported range (0.2 ppb) and quote a value of 29% for RONO2 which is not in line with the previously given 33%.

At these conditions this seems like a very high value. Have you considered, for example, that your CIMS could be more sensitive to nitrates than to HOM devoid of -ONO2? There are some hints in the recent literature about this.

*Finally, it is very difficult for me to see why higher NO can lead to higher abstraction vs addition rates. These issues seem uncoupled (i.e., no amount NO can increase an OH abstraction rate) and rather point into being misunderstood RO2 + NO (or indeed RO + NO) chemistry connected to the long processing time-scales.

Minor comments:

*Consider changing the “dimer” into “accretion product”.
*Line 66: “Biomolecular” is an error. (Other places as well).
*Line 150: What “organic” are you referring to? The identity matters a lot, as has been shown in this chamber setup previously.
*Line 158: delta symbol is usually reserved for a changing quantity.
*Line 210: How should one understand the statement: “Briefly, we only consider a limited oxidation network by considering all possible reaction channels, …”
*Don’t mix -y and -yl endings, i.e., if you choose to use “peroxyl” then use “alkoxyl” as well.
*Line 394: Didn’t catch why you presume the disproportionation of RO2 + RO2 would favor carbonyls over alcohols.
*Plural of formula is formulae.