

# ***Interactive comment on “CRI-HOM: A novel chemical mechanism for simulating Highly Oxygenated Organic Molecules (HOMs) in global chemistry-aerosol-climate models” by James Weber et al.***

## **Anonymous Referee #2**

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### General comments:

This manuscript describes the development of a new mechanism module for the simulation of highly oxygenated molecules (HOMs) from the oxidation of alpha-pinene by ozone and OH in the gas phase. Such HOMs have recently been demonstrated to contribute substantially to new particle formation in certain environments, and (highly uncertain) measurements are beginning to constraint the dependence of HOM formation on temperature, NO<sub>x</sub>, the presence of other peroxy radicals, and other parameters. By developing a mechanism that fits easily within a larger mechanism already in use

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in models (the Common Representative Intermediates or CRI mechanism), the study described herein will hopefully provide a precursor from which further research efforts can both fine-tune the mechanism and apply it to broader investigations of HOM impacts on atmospheric chemistry and climate. The mechanism adds 12 species and 66 reactions to CRI, which is both reduced from the full complexity of the HOM system and retains the most salient aspects of HOM formation and its chemical dependencies. The authors first describe the construction of the mechanism in detail, including the sources of and assumptions made about certain parameters (e.g. branching ratios and rate constants), after which they discuss the tuning of the various unknown mechanism parameters for optimization against laboratory experiments. Finally, they demonstrate the applicability of their mechanism by using it to model the role of HOMs in the ambient environment, simulating alpha-pinene chemistry in vertical profiles over the Finnish boreal forest and the Southeast United States

The manuscript represents a valuable addition to the recent surge in literature reports regarding HOM formation from monoterpenes, as it synthesizes inputs from various sources into a modular chemical mechanism that can be applied to further research into the role of HOMs in the atmosphere. However, with an eye toward those future projects to which this mechanism will surely make an important contribution, it is imperative that the authors make clear the remaining uncertainties, sensitivities, and assumptions inherent to the key parameters and output of this CRI-HOM mechanism. The mechanism is an important first step, but in order for future fine-tuning to be conducted, it will be necessary to not just acknowledge but to actively advertise the aspects of the mechanism that remain most uncertain. This will give the critical dialog between models, observations, and laboratory studies room to improve this mechanism as new constraints become available. To that end, I think a number of efforts could be made in this manuscript to clarify the sources and magnitudes of uncertainty, the origins of certain specific assumptions, the sensitivity of mechanism parameters (e.g. branching ratios, rate coefficients) to assumptions made, and the ranges of parameter values that would be consistent with the limited and/or highly uncertain HOM and RO<sub>2</sub> observa-

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tions.

As has already been alluded to, the mechanism relies on a number of assumptions and extrapolations between species for many branching ratios and reactions rates. That in itself isn't bad and doesn't invalidate any of this, but requires careful attention to the sensitivity to those assumptions and the resulting uncertainty in the mechanism's parameterizations and output. I would hate to suggest running more models; instead I think (a) some of this sensitivity analysis already exists in the SI (e.g. L 364-366) and should be given a more prominent billing; (b) some parameters and model output could benefit from bootstrap back-of-envelope calculations (or comparisons to previous literature, as I suspect exists for e.g. the first-generation pinene ozonolysis yields) as to their sensitivities to certain inputs or ranges that would be consistent with observations, and (c) descriptions of the mechanism would benefit from more careful attention to what can be stated with certainty and what results of the simulations are so sensitive to highly uncertain numbers that they can't be considered conclusive. Along these lines, see especially the comments to L222-224, 304-314, 341-347, 507-508 below.

The large uncertainty bounds on measurements to which the mechanism was compared (as noted in L 428-429) suggests a need for reporting a range of mechanistic parameterizations consistent with the measurements, rather than single values. The kind of analysis you do on L 364-366 of the SI is hugely useful for these purposes, and should be incorporated into the main text (and, as mentioned below, the ranges and sources reported in Table S6 would also be useful in the main text). However, these sensitivity studies could benefit from more detailed descriptions. It sounds as though the uncertainties were only estimated by changing one rate at a time and comparing the resulting changes in the concentration of the peroxy radical in question with the upper and lower bounds of the experimental uncertainty. This would neglect any compounding effects from simultaneous changes in multiple autoxidation coefficients, or in both autoxidation coefficients and alkoxy decomposition : isomerization branching ratios, correct? This should be acknowledged (or, if possible without too much additional

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work, the cumulative uncertainties could be estimated and reported). Also, if similar sensitivities exist to show the range of HOM yields from RO<sub>2</sub>-RO<sub>2</sub> chemistry that is consistent with the large uncertainty bounds shown in Figure 5, those would be useful to see as well.

Finally, it's somewhat unclear without reading the whole paper and SI very carefully what branching ratios / rates are fit, which are plugged in from measured values or extrapolated from similar species, and which are educated guesses. Someone wanting to use this mechanism or adapt it for their own uses might want to know which coefficients are flexible and which are most tightly constrained (or measured). Can a quick representation of that be provided? Either as an expanded Table 4 / Table S6 (with, say, a superscript character on each rate or branching ratio to denote which come from what sources) or additional annotations to figures 1 and 2 that make it clear (e.g. colour-coded arrows corresponding to which rates and branching ratios come from which sources).

Specific comments:

L 154-155: For mass conservation and to fit with the explanation in L 145-147, I assume reactions 3-4 are supposed to have C<sub>10</sub>RO<sub>2</sub> + C<sub>5</sub>RO<sub>2</sub> as the reactants?

L 194-195: Figure 1 implies that these TNCARB<sub>26</sub> and RCOOH<sub>25</sub> co-products, along with the major products of RN<sub>26</sub>BO<sub>2</sub> and RTN<sub>24</sub>O<sub>2</sub>, are formed in fixed yields from pinene ozonolysis. However, this sentence (and my understanding of Criegee intermediates) would imply that the branching ratios to these products depends on the relative abundance of the Criegee intermediates' reaction partners, such as water. Could you clarify here and/or in the caption to Figure 1 whether/how this Criegee chemistry is represented, and whether it matters?

L 199: This sentence refers to "RTN<sub>24</sub>BO<sub>2</sub>", but the co-product in Figure 1 is "RTN<sub>24</sub>O<sub>2</sub>".

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L 222-224: Are there any constraints or uncertainty bounds on this 50:50 ratio of decomposition and isomerization pathways used here? It seems that in environments where reaction with NO is competitive with the other reaction pathways (and even in very low-NO conditions, since the alkoxy radicals are formed in RO<sub>2</sub>-RO<sub>2</sub> reactions as well), the resulting HOM yield could be highly sensitive to this branching ratio. In the absence of concrete evidence for these specific alkoxy intermediates' branching ratios, can you provide some estimate of the sensitivity of your mechanism's output to the chosen ratio? This would be useful either here or later, when you describe the important of this NO-derived HOM in the context of the model output (~L 505-511)

L 244-246: Should equation 9 (and the line preceding it) read C10x or C10z? I realize the difference is described in Table 1, but it would be helpful to spell it out in the text as well so the reader doesn't get confused on this point.

L 283-294: Either this semicolon is meant to be a colon, or something's missing in the description of the UCARB10/UCARB12 products that would turn it into a standalone clause.

L 287: Does this "me" mean medium? If so, doesn't this contradict the statement (previous page, L272-3) that medium peroxy radicals react individually with each peroxy radical pool too?

L 304-314: The citation of MCM implies that k<sub>14</sub> and k<sub>15</sub> were derived from Jenkin et al. 2019a, but the citation two lines later implies they are from Molteni et al. 2018. Which were they? Also, this presents another fixed input in the mechanism to which the model output and parameter fitting might be highly sensitive. Are there uncertainty bounds on the rate coefficients from Molteni et al. or Roldin et al. 2019 that can be used to estimate this sensitivity? Are there constraints on the 50:50 branching between R14 and R15, or any particular reason to have chosen that branching? Can any estimates be made of the mechanism's sensitivity to this branching?

L 325 & L309: You report a range of chosen fitted values for k<sub>13</sub> and k<sub>16</sub>. Is this range

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of different values for the different peroxy radicals within each group, or does it represent some sort of uncertainty? Referring forward to section 3.1.3 as suggested here does not clarify the fitting procedure. The repeated use of "chosen" and "assigned" sounds more like the values were user-selected out of a pre-defined range rather than fit to data, and the model output then compared favourably to the highly uncertain aggregate HOM measurements (which, as far as I can tell, don't distinguish between the generation in which the HOM was formed). How was the initial range over which to "fit" chosen?

L 321: Why doesn't R16 conserve mass the same way R13 does?

L 341-347: What is the rate coefficient for the reaction of RTN28OOH + OH (and was it measured?), and why is this the one to stand in for the HOMs? Where did the MCM photolysis frequencies come from – were they measured or also extrapolated from other species? Again, are there any estimates of the uncertainty in these photolysis/reactions rate coefficients or the sensitivity of the mechanism to them? While your reasoning that their gas phases losses are unlikely to affect OH or O<sub>3</sub> seems reasonable, the loss rates should be very important to new particle formation in some circumstances.

L 392-397: As mentioned in the comment above to L 194-195, couldn't these yields be variable instead of static, and dependent on the environmental conditions that affect the branching pathways of the Criegee intermediates? Numerous past experimental efforts have quantified product yields from  $\alpha$ -pinene ozonolysis; are these branching ratios consistent with those past efforts? With what certainty is the 0.206 s<sup>-1</sup> autoxidation rate coefficient known, and how sensitive are all the subsequent steps in this mechanism to it?

L 404-406: This sentence seems grammatically incomplete. Perhaps the "and" isn't needed?

L 406-408: This is a crucial point for the present study, and one that I don't think should

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be so quickly discarded. How (i.e. to what extent) would this change the autoxidation coefficients?

L 416-418: This type of sensitivity study is very helpful for understanding the strength of the constraints on your mechanism parameters, but I am confused by the wording of "realistic deviations". Are these the maximum deviations consistent with the autoxidation coefficients, or the maximum deviations consistent with the experiments? If the former, do we have reason to believe that the experiments fell within this range? And if the latter, how were they deemed "realistic"?

L 426: Should this refer to Fig. 3b instead of a?

L 428-429: Why are these measurements believed to be so drastically underestimated? Whether or not they are, the results suggest that some element of the first-generation OH-derived peroxy radical chemistry is substantially biased in the mechanism; do you have any indication of what this might be?

L 490: This sentence mentions 4 mechanism versions, but the rest of the paragraph only seems to describe 3.

L 507-508: See comment above on lines 222-224: this NO<sub>x</sub>-dependent behaviour derives from a highly uncertain 50:50 alkoxy radical decomposition : isomerization branching ratio, but is described here as an important consequence of the mechanism. Would this behaviour hold true for a range of reasonable estimates of the branching ratio? How sensitive is it to the chosen branching?

L 516: Are the model uncertainty ranges reported here for the different temperature dependences? It's very important to distinguish this from some sort of total uncertainty estimate.

L 518: Missing a word in "comparing favourably to yield measured by" ?

L 527: What explains the drastic decrease in the simulated acetone production?

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L 571: "We also at the effect" ... something's wrong here.

L 588: What does it mean for a result to be semi-qualitative? That even some non-quantitative qualities of the simulated vertical profiles are expected to be erroneous? What ones?

Table 4: The uncertainties and sources of these rates are important enough that I think Table S6 should be combined into Table 4

Figure 3: Why are there no error bars on the 3rd and 4th generation O3RO2 observations? Where do the error bars come from (e.g. are they instrument uncertainty on the measurements or something else)?

L 979-980: While the note that first-generation OHRO2 are poorly reproduced is appreciated, it seems misleading not to put them on the graph, and deprives the reader of a visual representation of this important element of the mechanism. Are the concentrations too high to fit on this graph?

Figure 5: Can the y-axes be adjusted to show the reader the extent of the measurement uncertainty? The large uncertainties suggest that a wide range of HOM yields would be consistent with the observations, including some yield parameterizations that wouldn't display the much-heralded decrease in C20 (and total) accretion products and increase in C15 products. Were any sensitivity estimates made regarding HOM yields in the mechanism that could be shown here?

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