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Atmospheric Chemistry and Physics Discussions

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 #1

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The article demonstrates the implementation of a reduced HOM mechanism into a reduced mechanism, CRI, which was derived from MCM3.3.1. HOM were discovered a few years ago. They are supposedly formed by a fast process called autoxidation. Since from their structure HOM and accretion products have low to extreme low vapor pressure, they are important candidates for SOA formation and persistence. This links HOM to relevant issues related to aerosol effects, e.g. for climate warming. The purpose of the presented work was to provide a simple enough version of HOM formation mechanism within a CRI for implementation in larger models.

The authors describe quite clearly the steps of the implementation with respect to the changes in the CRI. Their attention turned to the implementation of autoxidation in competition to bimolecular termination reactions. In addition they put efforts also in the implementation of HOM accretion products, as those may play a role in atmospheric nucleation. HOM accretion products are supposedly formed by recombination reactions of (HOM) peroxy radicals. By splitting the sum of peroxy radicals in three classes and considering class interactions they enabled a treatment of the recently described interaction of HOM peroxy radicals with low molecular weight peroxy radicals, specifically the interaction of a-pinene and isoprene. They further implemented the temperature dependence of HOM formation as recently observed. Aspects of their improvement of the CRI – HOM mechanism were tested against flow tube experiments by Berndt et al., with satisfying results. These parts of the work are very interesting and important.

The new CRI-HOM was then used to calculate vertical profiles over two stations in Hyytiälä and Manaus. Here the descriptions of the results are not fully congruent with the graphical representations. Overall, the vertical profiles of HOM and HOM accretion products are however in a reasonable range. That means within general experience it could be possible. Any verification of the height profiles by observation is missing. Things become even more speculative when the authors try to predict PI and PD nucleation and the role of biogenics and HOM. I am not sure if that part is really helpful. They authors admit that any validation is currently impossible (in the first sentence of the according paragraph). Depite of the latter, overall the article is timely, well written and can be published in ACP after addressing the comments below.

Comments:

line 53: Bianchi et al., is a review; here you reference to the original papers in order to give the authors the credits

line 199f: I think it must be RTN24O2, instead of RTN24BO2. Or it must be "RTN26BO2 - RTN23BO2". Or something else in the nomenclature is not consistent in this para-

graph.

line 204 and line 236: If you want to make the mechanism efficient, why do you start lumping O3-HOM from the 5th generation, while you starting for OH HOM with the 4th generation?

line 219f: “Alkoxy radicals are not represented explicitly due to their rapid reactions which, typically for larger peroxy radicals, are decomposition or isomerisation. “ The statement doesn’t make sense to me; alkoxy instead of peroxy?

line 339: How much effort would it be to implement and to test a range lifetimes typical for sticky molecules applied to your HOM species. Isn’t deposition always a week point in atmospheric models? If deposition is faster than upward transport, your vertical profiles would be obsolete.

line 403-409 and Table 4: If I understand the autoxidation process correctly, the autoxidation rate must slow down at the end as suited H atoms are already consumed in previous autoxidation steps. This is the case for OH, but not for ozone? The overprediction of the highest generations compared to Berndt et al. is not necessarily only due to missing loss processes, it can be also due to overestimated source strength, by your last step autoxidation rate coefficients.

line 426-429: Overpredicting the first generation of OHRO2 has nothing to do with the HOM-mechanism, correct? From this point of view it may be a severe principal failure of your CRI scheme. What could be reasons for that? This should be discussed a little more extensively.

line 467: In section 4, I do not understand the selections of sites for comparison. Why compare Alabama with Southern Finland at the ground, but calculating vertical profiles over Southern Finland and Amazonia. You should compare with the Manus ground data, too. Moreover, there were big campaigns over Amazonia and Finland, also with airplanes. Can’t you use data to validate at least parts of your vertical profiles, e.g. OH,

O3, NOX, a-pinene, isoprene, selected OVOC?

line 589: Do really mean “semi-qualitative”. That would implicate not even qualitatitve. . .? The profiles look quite reasonable, overall. And you highlight features of the profiles. . .

line 592-594: What is the sense of the comparison then (see comment above)? Can’t you split off from the observations the compounds which are in your model?

line 596-602 and Figure 7: In contrast to your statement, the OH data decrease with height and O3-HOM and OH-HOM do not have the same share there anymore. Why do the OH-HOM decrease in upper troposphere? It would be helpful to show vertical profiles for OH, O3 and possibly NO, too. Moreover, in legend of Figure 7 you describe features (arrows) which I cannot see. And the color code for O3-HOM is brown, while the line is orange.

line 672: There were no vertical profiles over Alabama, right?

Captions, Figure 1 and 2: I suggest to introduce the meaning of RO2s, m, b also in the captions.

Typos, errors:

line 70: reference Sindelarova et al., 2014, is missing in the reference list

line 141: reference Kiendler-Scharr, instead of Kiendler-Scherr

line 150-160: in the reaction equation 3 and 4: it should be C5RO2 instead of C10RO2

line 245: in equ. (9) 10x instead of 10z

line 274: Jenkin et al. 2019, a or b missing

line 287: m instead of me

line 306: than instead of that

line 625: you call the underestimation of H2SO4 slightly, I see 1-2 orders of magnitude

There are frequently passages in the text using a different font size. e.g. lines 57/58, line 378/379, line 421, line 422, line 458/459, line 464/465, line 561

Table 1: “gen.”

Table 3: needs reformatting of the text fields. . .

In general, some page formatting issues with Figures and Tables.

Figures S17, S18: The subscripts are too small.

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