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Comment on acp-2021-901

Anonymous Referee #1

Referee comment on "Global simulations of monoterpene-derived peroxy radical fates and the distributions of highly oxygenated organic molecules (HOMs) and accretion products" by Ruochong Xu et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-901-RC1, 2021

Review of the manuscript "Global simulations of monoterpene-derived peroxy radical fates and the distributions of highly oxygenated organic molecules (HOM) and accretion products" by Xu et al.

This is overall a very interesting and well written global model study about peroxy radical autoxitation and the formation of Highly Oxygenated organic Molecules (HOM) from monoterpenes. The authors should be honored for that this is one of the first attempts to provide a global model assessment of the contribution of HOM from monoterpenes to the atmospheric SOA levels. The model sensitivity runs clearly demonstrate the large uncertainties that still exists about the HOM SOA production from monoterpenes. I think the manuscript is well worth to be published in atmospheric chemistry and physics after some relatively minor but essential revision.

General comment:

You perform a comprehensive set of global model sensitivity runs with different RO2 autoxidation rates, RO2+RO2 termination rate coefficients and initial RO2 branching ratios as listed in Table 1. But why do you not compare and try to constrain the mechanism uncertainties using existing observations from laboratory experiments? E.g. in the global chemistry transport model study by Weber et al. (2020) the mechanism was tested and compared against existing laboratory experiments and then after this used for global model simulations. Also it would be suitable to discuss your results a bit more in the context of existing atmospheric modelling studies about HOM formation such as Zhu et al. (2019), Roldin et al., (2019) and Weber et al. (2020). What are the major differences and similarities of the present mechanism and these other existing peroxy radical autoxidation and HOM formation mechanisms?

When I started to read the manuscript I thought that the modelled HOM concentrations you mention were gas-phase concentrations but on L238-239 it is indicated that it is the total gas+particle phase HOM concentrations you model. I think this should be clearly stated earlier in the manuscript. This assumption will of course also influence the dry and wet deposition losses of HOM and their chemical degradation. As I am sure that you are aware of, not all HOMs are ELVOCs and they will not partition irreversible to the particle phase.

Specific comments

Abstract L31-34: "Within the bounds of formation kinetics and HOM photochemical lifetime constraints from laboratory studies, predicted HOM concentrations in MT-rich regions and seasons reach 10% or even exceed total organic aerosol as predicted by the standard GEOS-Chem model."

I had some problem to understand the meaning of this sentence. Can it be reformulated? I guess that the meaning is that, according to the model simulations, HOM from monoterpenes contribute to a SOA increase of between 10 % and up to more than 100% depending on the model assumptions.

L166-168: "The fraction of first-generation MT-RO2 able to undergo unimolecular H-shifts, and thus autoxidation (MT-bRO2), is 20% from MT + OH and 3% from MT + O3, in the base simulation (Table S3)."

Too me this sounds like a very low fraction of MT-bRO2 formation from MT+O3. The experimental results from Ehn et al., (2014) and Jokinen et al. (2015) for different monoterpenes and the detailed modelling of α-pinene + O3 experiments at variable NO levels by Roldin et al. (2019) indicate that the HOM yields and HOM SOA formation from MT + O3 are substantially higher. I think this motivates a model sensitivity run with higher HOM production from MT+O3 "HighProd" while keeping the default "LowProd" MT+OH fraction in the model. It would be interesting to compare the modelled diurnal trends from such a run with the existing HOM observations.

L180. “These MT-HOM-RO2 undergo only bimolecular reactions with HO2, RO2, and NO2, NO3.”

I guess you mean NO and not NO2 or?

Figure 1. “I do not see any specific HOM closed shell products formed from RO2+ RO2 reactions in the schematic figure. Did you not consider C10 HOM formation from RO2+RO2 reactions? Why do not HOM-RO2 react with other RO2 according to this scheme?

L287-289: “For HOM measurements, molecular formulas of compounds contain 10 carbon atoms and greater than or equal to 7 oxygen atoms were selected as HOM for comparisons.”

Are the closed shell HOM products with 7 or more O atoms not primarely expected to be products from MT+O3? I thought that the MT+OH oxidation primarely are expected to results in closed shell HOM products with 6 or possibly 7 O atoms. In the manuscript you do not call the ROOR dimers HOM but accretion products. Did you not compare modelled and observed HOM (accretion products) with >10 C atoms? This would maybe provide some constraints on the importance of ROOR for the atmospheric SOA production.

Table 4 and L427-429: “Interestingly, even for a small branching to accretion products, MT-RO2 derived accretion products are a substantially larger fate than HOM, suggesting either that the rates and branching are too high or that the chemical loss pathways of associated products are not well represented.” This, seems a bit strange. I think this should motivates some sort of box-model tests and evaluation of the present mechanism against existing HOM dimer (C18-C20) gas-phase observations from laboratory smog chamber experiments. Does this imply that most RO2s that undergo autoxidation are lost by RO2+RO2 reactions leading to ROOR before they become HOM-RO2 in the present mechanism? The model do seem to overestimate the Isoprene concentrations in Centreville and Amazon quite a bit according to Figure S8. Can this result in overestimated RO2 +RO2 cross reactions and ROOR formation?

L533-539 “We scale the predicted HOM concentrations in the lowest model level by the ratio of observed to predicted monoterpene concentrations in order to account for potential biases in the monoterpene emissions (Figure S8). For SOAS and GoAmazon, we use the hourly average measured monoterpene data to compare with the hourly GEOS-Chem predictions, while for the BAECC campaign at SMEAR II station, we use the campaign average of measured monoterpene concentrations.”

First, I do not understand this approach completely. You also state that the particulate HOM potentially represent the integral of multiple days of formation. Thus, most HOM PM will not be formed at the station but upwind the station where the monoterpene concentrations will be different.

Second, does not the absolute BVOCs concentrations and RO2 pool also influence the fate of the MT-bRO2, MT-cRO2 and HOM-RO2 concentrations and the relative fraction of C10 HOM and HOM accretion products (ROOR)? I think that the relatively large differences/uncertainties in the observed and modelled BVOC concentrations could be mentioned as an additional source of error in the absolute HOM SOA formation. Maybe the uncertainties in the absolute BVOC emissions are even greater than the HOM SOA yields? I suggest that you extend the discussion about these uncertainties in the paper.

Figure 9. I did not find a definition of the Rmt scaling factor used do generate the results in Fig. 9 in the manuscript. I think it would be good to also provide the reader with some information about the modelled and observed absolute HOM-ON and HOM-non-ON C10 concentrations at each station e.g. in the form of a table. This would then provide some information about the total uncertainties in the surface layer HOM SOA concentrations. It is not clear to me which altitude above the ground that the observed and modelled HOM concentrations and MT, NO and O3 concentrations in Fig. S8 are taken from. The observed NO concentrations seem to be close to the detection limit of conventional NO monitors and I also wonder why the observed and modelled NO concentrations do not go down to 0 in the nighttime at some of the stations. Can you please add a short discussion about this in the SI?

SI, “MT-RO2 reactions with NO/NO3”

"Yet for MT-aRO2, a 5% branching of MT-bRO2 formation was added. This is because in polluted regions, the formation of HOM may well be facilitated by certain NO reactions through the alkoxy channel"

I agree that such pathways probably are important to consider but what do you base this assumption on? Did you consider some experimental observations or other existing mechanism that have been evaluated and constrained this pathway to HOM production in the presence of NO? The near explicit Peroxy Radical Autoxidation Mechanism (PRAM, Roldin et al., 2019), which was constrained using a-pinene ozonolysis experiments at variable NO concentrations, also take into account such RO2+ NO -> RO and RO + O2 – bRO2 formation pathways.

List of a few additional HOM formation atmospheric modelling studies that are appropriate to consider and refer to when discussing the presented mechanism and modelled HOM SOA concentrations:

Öström et al. Atmos. Chem. Phys., 17, 8887–8901, 2017

Zhu, Nat. Commun., 10, 423, https://doi.org/10.1038/s41467-019-08407-7, 2019.

McFiggans et al, Nature, 565, 587–593, https://doi.org/10.1038/s41586- 018-0871-y, 2019

Roldin, et al. Nat. Commun., 10, 1–15, https://doi.org/10.1038/s41467-019-12338-8, 2019

Weber et al. Atmos. Chem. Phys., 20, 10889–10910, 2020