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Comment on acp-2021-118

Anonymous Referee #1

Referee comment on "Evolution of OH reactivity in NO-free volatile organic compound photooxidation investigated by the fully explicit GECKO-A model" by Zhe Peng et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-118-RC1>, 2021

Review of "Evolution of OH reactivity in low-NO volatile organic compounds photooxidation investigated by the fully explicit GECKO-A model"

This study focuses on the investigation of the OH reactivity for several alkanes, m-xylene and isoprene by using fully explicit mechanisms generated with GECKO-A.

I find it rather difficult to appreciate the main goal and purpose of this study. The title is misleading and does not cover what is actually done within the study. The study is performed at zero NO, which is rather different than the mentioned "low-NO", where I think the majority of readers would assume this to mean below 100 pptv but not truly 0. The complete removal of NO from the model does not allow for nitrates, NO₂ and ozone to be formed through the normal channels accessible at any atmospheric NO level. While there is nothing wrong in studying this type of environment, it should be clearly stated in the title/abstract/introduction/conclusion that this does not represent any real ambient condition. In a similar way, although not clearly stated, the impression I formed when reading the title was that the OH reactivity for different species would be investigated at ambient like conditions. This was again not found in the text, not only because of the lack of NO but also as most of the organic compounds chosen are very unlikely to be found in low-NO environment as they are mainly anthropogenic emissions. A first question raised is then why the focus is on zero NO instead of investigating more realistic ambient conditions?

After reading the paper it became clear that the chosen reaction conditions are, in my opinion, more representative of what one can expect in oxidation flow reactors and certain simulation chambers, and the idea is to compare what happens in these laboratory devices against what would happen for similar conditions in ambient air. I think this a useful comparison, but I would recommend making that clearer in the title and introduction. I am stressing this point as in both the abstract and in the conclusion there is a strong remark about how OH reactivity is poorly constrained in the atmosphere, which is true, and how this study address, to some extent, all three issues raised by Williams and Brune (2015). I would recommend to state which these three issues are as I feel two main issues raised in the roadmap by Williams and Brune (2015) were the broader availability of instrumentation to measure OH reactivity, as well as improving and comparing the techniques measuring OH reactivity, neither of which was addressed in the current study. I assume this study refers mostly to the issue of the so-called "missing" OH reactivity

often observed in field studies when comparing the measured OH reactivity with what can be calculated from the measured trace gases. If this is the case, I would recommend being more clear in stating it was this that is being addressed. This study does not include measured OH reactivity but only simulated OH reactivity and it investigates the OH oxidation of single compounds at atmospherically not relevant conditions. I feel the statement "largely speciated the likely source of the missing reactivity" seems a bit of an overstatement. Despite the use of a full explicit mechanisms, in the plots provided there are often lumped multifunctional species which do not clarify about which species contribute to what amount to the OH reactivity. Wouldn't it be possible to actually list the individual species and how much they contributes, or a list of the most prominent ones making up the largest fraction of the total? After all, many studies in the field showed that when a modelling of the OH reactivity is performed, the presence of large quantities of unmeasured oxygenated VOC (precursors to or actual multifunctional species) help in strongly reducing if not closing the gap between measured and calculated OH reactivity (Yang et al., 2016).

Finally, I think there should be a better description of which simulation chambers (type, size, ...) this study refers to. The same holds for the oxidation flow reactors (OFR) discussed. Specifically: atmospheric simulation chambers can be as small as few m³ up to hundreds of m³ and their size and residence time of gases in the chamber and initial concentrations of reagent will strongly influence how lower-volatility compounds are lost on walls. Within this study only a value without wall effect, and one with a certain loss on walls of certain compounds is given but no explanation as to which chambers this could apply to. The largest atmospheric simulation chambers such as SAPHIR (Rohrer et al., 2005), Jülich, Germany, or EUPHORE (Siese et al., 2001), Valencia, Spain are much less affected by wall losses as compared to smaller chambers. In addition, this study seems to focus on simulation chambers where high concentrations of reagents and intermediates are used. This is again not what is investigated in chambers such as SAPHIR and EUPHORE where experiments are conducted with atmospheric like concentration of reagents and intermediates, and where indeed no large discrepancies have been observed between measured and calculated/modelled OH reactivity; see e.g. (Fuchs et al., 2013; Nölscher et al., 2014; Fuchs et al., 2017; Novelli et al., 2018). One of the reasons for the good agreement between measured and calculated/modelled OH reactivity found for these studies is clearly the lack of large amounts of oxygenated products, so these studies might not be representative examples for the topic of this study where the oxidation in the chamber is simulated up to 10 days. A more clear specification up front as to what type of experiments, which type of chambers, which reaction times, and which bracket of reaction conditions is examined would avoid the incorrect interpretation that this study applies to all chambers and most chamber studies.

The paper is well written but rather than recommending publication I suggest the authors consider the points mentioned above and attempt to better focus the study in such a way that makes it more clear how ambient OH reactivity values and the issue of "missing" OH reactivity is addressed by their modeling. In its current form, this link is not clear and while the data is interesting there seems to be little direct applicability for it.

Specific comments:

Abstract. The first sentence needs a bit of explanation of where it is poorly constrained. In every environment? In chamber experiments? For specific chemical regimes? What is the reason behind the chosen VOCs?

Page 2, Line 57. I do not understand the use of the Nehr et al. (2014) study here. It is true that the OH reactivity was measured but it is not compared with a calculated or

measured OH reactivity. The studies highlighted above (Fuchs et al., 2013; Fuchs et al., 2017; Novelli et al., 2018) would be in my opinion a better choice.

Page 6 Lines 223-230. It is not specified what the basis is for the implementation of the mechanisms. There is no reference to any previous study or to SAR. How is the rate coefficient between OH and MXYLOOH estimated to be $\sim 3e^{-11} \text{ cm}^3 \text{ s}^{-1}$? I would also refrain from using the notation of k_{OH} for the rate coefficient as many groups use that same notation for the OH reactivity. The same question applies for the estimated reaction rate of $\text{RO}_2 + \text{HO}_2$. Can a reaction with O_3 compete with the reaction paths normally available for alkoxy radicals? What is the rate of the reaction with O_3 and the alkoxy and could also reaction with OH compete? Are there appropriate references for adding this type of chemistry? In the schemes I would recommend keeping the orientation of the molecules always the same to enhance readability. E.g. MXCATEC10 has the methyl group pointing up, yet after reacting with O_3 the methyl group points down. As I understood there is zero NO in the model, but then how is the O_3 formed, as it is not stated explicitly that it is added as a reactant for all simulations? The OH in the OFR is produced from photolysis of O_3 (which is a hint O_3 is added as a reactant), which raises the question on how is OH produced in the ambient and the chamber cases? It would be good to describe these critical inorganic reactions, as well as how much O_3 is present in the different simulations.

Section 2.3. Such a tool would be extremely useful for the atmospheric community. Do the authors plan to share it?

Page 7, Line 270. For which temperature and pressure is the rate coefficient between OH and CO valid? Also, at which temperature were the simulations performed?

Page 8, line 310. I do not understand what the notation " $\times 3$ more rapidly" stands for.

Page 8, line 312. I think it should be "can be abstracted"?

Page 9 Lines 323 and 324. I do not feel this sentence is necessary; I would go ahead and explain what the reasons are without saying it is different reasons...

Page 10, Lines 379 and 380. I think realistic and unrealistic are not very good in constraining how different simulations chambers are affected by partitioning of volatile compounds on the walls. As mentioned above explanations about which chambers/type of chambers this study is referring to and how these are positioned within the variety of chambers used is needed to avoid giving the wrong impressions that all simulation chambers have (huge?) wall losses.

Summary and conclusions. I feel that bullet point 3 and 4 on page 16 don't belong to the conclusion. Aside from the impression they are saying the same, they are also merely the result of the modelled used. GECKO-A uses SAR and therefore explicitly incorporated that C atoms in $>\text{C}=\text{C}<$, $-\text{CH}_2-$, and $-\text{CH}_3$ have OHR per C atom on the order of 10^{-11} , 10^{-12} , and $10^{-13} \text{ cm}^3 \text{ s}^{-1}$; this "conclusion" is thus a given and does not seem to add much to the discussion, nor it is a new finding as it is well established in the SARs. As there is a long discussion about how wall losses can impact the findings of chamber experiments and need to be carefully accounted, I recommended once more to be clear about which chambers/type of chambers the study applies to, to avoid misinterpretation. As already mentioned above, I disagree that this study addresses the issues raised by the roadmap on OH reactivity by Williams and Brune (2015). As the paper in its current form has little applicability to real atmospheric conditions it is difficult to claim it helps understanding the source of the "missing" OH reactivity observed in various field studies.

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