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Comment on acp-2021-890

Anonymous Referee #3

Referee comment on "OH-initiated atmospheric degradation of hydroxyalkyl hydroperoxides: mechanism, kinetics, and structure–activity relationship" by Long Chen et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-890-RC3, 2021

Review of *OH-Initiated Atmospheric Degradation of Hydroxyalkyl Hydroperoxides: Mechanism, Kinetics, and Structure-Activity Relationship* by Chen, L. et al.,

This work concerns the atmospheric degradation of the three smallest hydroxyalkyl hydroperoxides (HHPs) by OH radical. I think the work is interesting and timely, and is likely performed with adequate methodology, yet the documentation is lacking and it does not become fully clear from the presented why the initial mechanistic steps seem to change so much between analogous radical reactions. However, it is not clear from the text if this is a real result, or due to way of present representation, as it is not exactly clear if the authors have considered all the correct reaction steps. Most of the issues with the draft are likely solved by just adding more text to several places, assuming that what was originally left out did not contain errors and overlooks. Let me elaborate a bit further below.

Major comments:

I see two major issues with the work. First, it is generally known that the internal H-shift isomerizations become important only at larger carbon structures than studied here. The rather extensive previous literature amply points out that the H-shifts (discussed in older literature often as H transfer) are not competitive from the same, or adjacent, C-bearing functional groups. Thus it is rather surprising this was even considered here, and I think the whole discussion about RO2 autoxidation does not make any sense for these small systems. Additionally, the resulting accretion products ROOR are important for aerosol growth only at larger sizes. Thus, these small systems are not expected to play any practical role in atmospheric particulate matter formation (unless the second RO2 forming the ROOR is a very big and polar molecule). Moreover, one H-shift reaction does not really constitute autoxidation sequence, but is rather just a single isomerization / rearrangement reaction. Thus the whole word “autoxidation” should not be associated with the current work. All that said, for the sake of completeness, the current calculations could/should be left in, but it has to be made crystal clear that autoxidation is not expected here, and

these are only common isomerization (by H-shift) reactions.

Another major issue connects to Figure 2: Are you sure you get the RC's and PC's right in the mechanism shown? Seems strange that such analogous reactions with so similar reaction partners (i.e., substituting -H with -CH3 in adjacent sp3 C-atom is not expect have a profound influence) would have so different pre-reaction complexes. How was this specifically verified. I mean, is it possible you were doing a too constrained original conformer search / optimization and missed certain RC's? Did you try what the energetics would be if the RC spatial structure would be close to identical in every system? Especially RC3 really stands out, but others differ too. The whole issue might be better visualized, if you would show these with the actual reagent structures, and not just with grey symbols. After all there is only 3 systems, so this would not increase the space demands much.

Furthermore, it feels a bit strange that in the methylated radicals, the C-H abstraction does not play a bigger role, as seen in some older work on OH + alcohols and OH + amines. From the same previous work it seems somewhat strange that abstraction from -OH is the next likely pathway, and still no C-H abstraction. Moreover, the conclusion that one methyl group substitution does not really matter, but two groups do, seem evenly strange as the methyl groups seem to be rather in the by-stander position, and are likely to influence little on what is occurring at the C-O-OH functionality. What type of sensitivity tests were made to ensure you have found the correct pathways? The IRC computation only ensures you are connecting the right reactants with the correct products, but it does not tell if you have found the most likely pathway or not.

Figures: Symbol fonts should be increased in all figures showing potential energy surfaces. Currently they are in many places unreadable. Moreover, the molecular figures are too small to follow the mechanism from the figures with this symbolism. To make matters worse, it is difficult to see what peroxy radicals are reacting to make the tetroxides in the figures, and there is no help from the captions. There must be a better way to make these readable. The easiest way is to split the figures in parts (i.e., Figure 3 becomes, for example, Figures 3a to 3c) and at the same time considerably increase the amount of text in the captions.

Figure 2 caption: Far more details of this figure should be included. Currently I am having very hard time understanding it based on the manuscript text. Why, for example, the RC is uphill in energy although you go from separated reactants into a pre-reactive (=favorable binding) complex? Currently the caption does not help.

Although the message comes "mostly clear" throughout the text, the text should be language edited. Again, I do understand it quite well being a non-native speaker, but I assume native speakers will not agree with me.

Specific comments:

Hydroxyalkyl hydroperoxides (HHPs) are formed in several other reactions too, especially in OH addition initiation with subsequent HO2 termination. This could be mentioned in the intro too.

Line 69: What is the difference between vapor pressure and volatility?

In the Abstract, please reword the following sentence: "In urban environments, the rate-limiting step is the hydrogen abstraction by O2 in the processes of HOCH2OO radical reaction with NO, while it becomes the O-O bond scission when one or two methyl substitutions occur at the C1-position of HOCH2OO radical." I think I know what this means, but I can't be sure.

The sentence: " Previous literatures have been confirmed that the 141 energies obtained from unrestricted DFT are comparable to the multi-reference 142 CASSCF method (Lee et al., 2016; Bach et al., 2005)." seems to indicate that "unrestricted DFT" gives similar results to "CASSCF". Is this really the case, and why it is so? Does not the choice of active space factor in?

Please embed figures into text. It helps no one if they are positioned after the text.

Why is there four reactions in Figure 2, although there are 3 title reactions handled in the paper? In fact, the fourth option is hinted in the text "Considering the different chemical environments of hydrogen atoms, the atmospheric transformation of HHPs initiated by OH radical should have four types of H-abstraction pathways as presented in Figure 2." but I did not observe an explanation what is meant by it. In any case it would be good to break the Figure 2 into several separate figures - one for each reaction.

The following statement: " pseudo-first-order rate constant k'HO2 of ~ 10-2 s -1 in the forest environments" is completely condition dependent and cannot be represented by a single value. A range of values would be equally ambiguous, yet still better.

I am not sure if I can follow what is meant by this: " (e) The rate-limiting step is the hydrogen abstraction by O2 in the processes of HOCH2OO radical reaction with NO, while it becomes the O-O bond scission when one or two methyl substitutions occur at the C1-position of HOCH2OO radical." Please clarify and reword the statement.

It is unclear what is meant by the following statement "One reason for the barrier difference could lie in the fact that the bond dissociation energies (BDE) of different types of bonds are significantly different in the HOCH2OOH molecule."

I would like to see the rates obtained (k vs T) also in Figures in relation to each other, and not just as Tables. I think this could be very useful to the reader, as the tabular format is more difficult to compare.

I find it a bit odd to state that a single channel of hydroxymethylperoxy radical oxidation giving HO2 radical is "a new source of HO2 radical in the troposphere". I mean, can this specific radical have even a minute influence on the tropospheric HO2 burden?

In the beginning of chapter 3.2., you are missing the second RO produced in the reaction.

Chapter 3.2.1: Mark all radicals the same way (i.e., with similar dot).

It is rather disappointing to hear that "It is worth noting that the termination products are not found in the HO(CH3)2COO radical reaction system owing to the absence of alpha hydrogen atom." when it was just in previous sentence stated that: " is not discussed in detail to avoid redundancy." Please explain further these currently missing channels.

It is stated that "The main primary sources of HO2 radical in the atmosphere are from the photolysis of CH2O and OVOCs, and the ozonolysis reactions". I guess the authors meant "photo-oxidation" rather than "photolysis" here.

I wonder if you could find a better reference for [HO2] (and other atmospheric concentrations) than Bianchi et al. 2019. To me it seems that those numbers are somewhat questionable, or perhaps better to say that it feels odd that you can give such a "common value" for a whole type-of-an-environment. Is single value really realistic?

According to "HOM review" by Bianchi et al, almost none of the compounds in the work of Noziere and Vereecken would be labelled HOMs, and thus I would strongly advice to change the referencing of the following sentence: "…one after the other, and the resulting finally HOMs (Nozière and Vereecken, 2019; Vereecken and Nozière, 2020)."

What is meant by: "It deserves mentioning that the conformers HOCH2OO-c and HOCH2OO-d are not proceed H-shift reactions."

Where is the SAR mentioned in the title?