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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Estimation of rate coefficients and branching ratios for reactions of organic peroxy radicals for use in automated mechanism construction" *by* Michael E. Jenkin et al.

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In this study, Jenkin and colleagues describe the formulation of 'rules' for the rate coefficients and product yields for reactions of organic peroxy radicals for use in mechanism construction. This manuscript documents how these rules are created and is not intended as a full review of the state-of-knowledge of such reactions. As a result of this scope (which is understandable and indeed necessary), at times this reviewer wishes for more detailed discussion of the choices made and critical review of the background literature. Clearly, however, this is not necessary within the context of the goals of this

paper. That said, below I highlight a few areas where I believe the authors might go further in justifying and improving their description of the RO2 chemistry. It would also be helpful if the authors address at the onset what is meant that these 'rules' are meant to "guide" the mechanism development. Please explain, for example, how, within the new MCM / GECKO framework, the authors intend to reconcile differences between specific reactions where experimental data exist and the rules/SAR based estimates (e.g. will the latter take precedent or the former in setting the rates / products?).

Specific comments (Page#.Line#):

2.22 In general where the competition is with NO, I'd suggest using 'NO' rather than 'NOx'.

2.29 HOMs: Include reference to Bianchi, 2019 - https://pubs.acs.org/doi/10.1021/acs.chemrev.8b00395

4.13 I believe that Teng was the first to point out that for multifunctional compounds, the nitrate branching ratios should (and do) scale more closely with heavy atoms than just carbon. Perhaps "updated by Arey et al. (2001) and Teng et al. (2015)"? In your definition of n(NCO), does the peroxy radical moiety count towards the 'O'? I'd suggest being explicit.

7.16 Should note that Caravan (2018) found a somewhat larger R5b/R5 (to methanol) at higher pressure.

7.17&7.22 Worth noting that Muller (2016) calculate that R5c/R5 is ∼.1 for CH3OO and Caravan (2018) suggest that they do see some CH3OOOH from this reaction.

8.8 Given that your fit to kHO2RO2 vs nCON is identical to that shown in Wennberg et al., 2018, figure 2, I guess that nCON does not include the peroxy moiety? We didn't weight our fit by the stated uncertainty - perhaps that should be done? Also, although we didn't consider this in our isoprene review, I expect that the T-dependence will depend on nCON at some level (presumably less strong for large nCON). For large n and low T, for example, the current parameterized rate will exceed that for kAPHO2 – this seems unreasonable.

8.24 “is taken to be the default where no information is available”. This is the type of comment that I do not know how to interpret. In this context, does that mean for any RO2 + HO2 not described in Table 8?

9.17 (section 2.6). Thank you for engaging with Barbara Noziere’s comment on this manuscript. I concur with her that the reported uncertainties in many RO2 + RO2 studies are underestimated given the (often) under-constrained observations of only bulk RO2 abundances. Thus, using reported uncertainty as a screen for which studies to include in formulating the SAR needs to be done critically. While the data shown in Figs. 4 and 5 gives some confidence in the resulting parameterizations, the log-log presentation hides the disagreement somewhat. Perhaps worth including a residual (fit-measure/measure) as a second panel.

13.20 Add Ng et al. to list of ‘ROOR’ studies - https://www.atmos-chem-phys.net/8/4117/2008/

13.16 Given all the recent results (e.g. those listed in 13.20), I don’t see a reason not to recommend (generically) a few percent branching yield for R’OOR formation. I suspect that this is more correct than assuming 0% as is currently done.

14.1 Recognizing that this is a fast-moving area of research, Section 3 still seems a bit cursory and could be advanced using some recent literature as guidance. I believe that this is worth the time as there is now wide recognition that H-shift and endocylization reactions are important in many systems.

To more accurately capture this chemistry, the parameterization used could be improved using new observations and theoretical calculations (the section is currently based largely on older literature). Here are some of the recent literature I am aware of that could be used to broaden and deepen the recommendations:

Mohamed, 2018: https://pubs.acs.org/doi/pdfplus/10.1021/acs.jpca.7b11955 Otkjaer, 2018: https://pubs.acs.org/doi/abs/10.1021/acs.jpca.8b06223 Praske, 2017: https://www.pnas.org/content/115/1/64 Praske, 2018: https://pubs.acs.org/doi/10.1021/acs.jpca.8b09745 Bianchi, 2019: https://pubs.acs.org/doi/10.1021/acs.chemrev.8b00395 Xu, 2019: https://pubs.acs.org/doi/10.1021/acs.jpca.8b11726 Moller, 2019: https://pubs.acs.org/doi/10.1021/acs.jpca.8b10432

14.22 Xu, 2019 offers new experimental and theoretical calculations for peroxy radical unimolecular chemistry following addition of OH and O2 to alpha and beta pinene that could be added to Table 14.

14.28 Otkjaer, 2018 offers high-level calculations of ring-size and constituent dependence of the H-shift chemistry for a number of organic substrates that should provide guidance for a first estimate for the rates of these reactions for consideration in the auto-generated mechanism.

14.28 Table 15. Should make clear what are calculated and experimental determinations. Also, k298K of alpha-formyl peroxy radicals the rate should be 0.57 s-1 (typo).

15.22 (and in SI) Assuming that the new mechanism will retain at least to the two radical pools produced following OH addition to isoprene, I do not understand why the 1,6 H-shift rates are not treated separately given there is significant evidence (Crounse, Teng) that a much larger fraction of the chemistry following addition at C4 will undergo this H-shift. Because the H-shift rates (not rate coefficients) for the C1 and C4 addition differ by an order of magnitude, use of the geometric mean will yield significant errors. Thus, I suggest it would be prudent to follow the recipe (if not the rates) described in Wennberg et al., 2018; Teng et al., 2018.

16.1-9 The literature cited above goes some way towards meeting the recommendations presented in this paragraph. I’d recommend considering them in the ‘rules’ developed in this work.

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