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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.

Anonymous Referee #1

Received and published: 5 March 2019

This manuscript discusses structure-activity relationships for peroxy radicals with its most common co-reactants in atmospheric conditions. The SARs are developed based on a selection of the available literature (mostly experimental data), and aim to provide site-specific rate coefficients and product distributions as appropriate for the reactions studied. The derivation of the SARs is well developed and explained, and the SARs strike a good balance between covering the mechanistic aspects of the target reactions on the one hand, and a pragmatic approach fitting data to a suitable function on the other hand, with good recovery of the training set. The data used as the training set

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is not an exhaustive literature tabulation. Some experimental data is missing (see also the comment by B. Nozière), and while some theoretical data is used, the potential of combing theoretical and experimental data has not been fully exploited. Overall, however, I feel that reasonable choices were made, giving a good summary of the reactivity trends discernible from the literature data, even if one could have a different view on what data to include in the training set, what weight to assign to each datum (which is not all that obvious especially for theoretical data at lower levels of methodology), or how to parameterize the SAR. What was missing a bit in places is reference to existing SARs and their approaches, but I recognize this paper is focused on presenting a new SAR, and need not be made longer by rigorous review or historic overview.

To put the usability of the SARs to the test, I have applied them in the development of a small mechanism ($\sim$100 reactions). The SARs prove to be quite usable even with a simple calculator, though during these efforts I found that adding a few additional subheadings would have made it easier to locate the desired information in the text: e.g. rate coefficients vrs. product distribution; self-reactions versus cross-reactions versus product distributions, etc.

Overall, this paper presents a good overview of the status quaestionis, and presents a set of very valuable SARs. Publication of the paper after minor revisions is recommended.

Specific comments:

p. 3, line 22: The generic rate coefficient for RO2 + NO is appropriate for many peroxy radicals, but RO2 derived from aromatics have been reported to have slightly higher rate coefficients. The difference may not warrant a different class, but a short mention might be useful.

p. 4, line 17: State explicitly (again) that nCON does not include the peroxy radical oxygen atoms, as an equally logical choice could have been a nCON based on the full molecular stoichiometry, i.e. including all functionalities. It might be useful to have a

short reminder in other places as well.

p. 4: The parameterization of the nitrate yield may need to be updated soon following recent work of John Orlando et al (NCAR). No publication is available to my knowledge, but interesting results were presented at conferences; I suggest contacting these authors to see if there is a need for alternative SAR parameters.

p. 7, line 13: formation of CI from CH3O2 + OH: Also state that the small to negligible yield of CI is consistent with theoretical data.

p. 8, R6c and R6e: R-HO is perhaps better written as R-H=O, unless the authors mean to imply that the H-atom transferred is not necessarily adjacent to the peroxy radical group.

p. 10: readability might be improved if using a notation for kRO2RO2 that indicates whether an expression pertains to self-reactions vrs. cross-reactions. Additional subheadings might be useful to make finding specific topics easier when applying the SAR (reference self reactions, self reactions, cross reactions, branching ratios,...).

p. 11: line 29: "... if the peroxy radical contains more than one benzyl group". A benzyl group is C6H5-C.H2, and there can be only one. The authors probably mean multiple beta-phenyl groups?

p. 11, line 29: the formula for calculating alpha and beta needs an equation number to allow unambiguous references in implementations.

p. 12: line 7: "This is regarded as a logical choice, because CH3O2 is the most abundant organic peroxy radical in the atmosphere". An explicit or semi-explicit mechanism as seems to be the target here is not used all that often for global modeling or even regional modeling as they tend to be too large. Without having access to any reliable statistical data, I would guess that e.g. the MCM is more often used to model specific experiments such as environmental chambers or lab studies, where CH3O2 is not necessarily the dominant proxy radical, if it is present at all in non-negligible concentration.

In many studies, only one or a few primary VOCs are present, and the RO2 population pool is heavily biased towards one or a few of the reactivity classes presented in the SI, especially in the early stages of the oxidation. Such consideration might be mentioned in the main paper. For me personally, given what I perceive as the main use of mechanisms of the envisioned detail, the most logical choice would be to separate the RO2 pool into reactivity classes.

Figures: While I recognize that adding uncertainty intervals on all the underlying data would make the figures visually cluttered, it could be useful to indicate somewhere in the caption what the typical uncertainty or scatter is on the data points underlying the fitting parameters.

SI, page 7, "The reaction of OH with ROOOH is expected to occur significantly by initial addition to the OOOH group". There are no free orbitals to accommodate an addition of OH, only abstraction, complexation, and substitution. I propose "... by initial attack on the OOOH group".

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