

Interactive comment on “H-migration in peroxy radicals under atmospheric conditions” by Luc Vereecken and Barbara Nozière

The authors present an extensive structure activity relationship for the prediction of temperature-dependent rate coefficients for H-shift isomerisation reactions in substituted alkyl peroxy radicals under atmospheric conditions. Training data for the construction of the SAR is mainly based on (high level) theoretical calculations, supplemented with some experimental data. Both literature theoretical and experimental datasets are used to evaluate the SAR, including some product studies reported in this work.

This is an excellent, well written and thorough piece of work, providing much needed chemical insight into unimolecular RO₂ H-migration reactions. Such theoretical SARs, anchored to experimental studies, are crucial in developing our chemical understanding of atmospheric chemistry, providing focus for targeting research in areas of particular uncertainty and in deriving chemical mechanism for scientific and policy modelling. The development of the SAR is described well, including limitations, simplifications and thorough descriptions of the theoretical techniques applied. The SAR is presented in a form that is easy to read and implement into automatic mechanism development methodologies. There is a very useful and comprehensive supplementary folder supplied.

I recommend publication into ACP after the following suggestions and clarifications are considered and addressed:

- (1) In terms of chemical notation, I would recommend that IUPAC notation is followed through out. All rate expression terms given in italics e.g. $k_{298\text{ K}}$ or $k(298\text{ K})$, $k(T)$, A , etc...

It would also be useful to clarify and define the way you are using the modified form of the Arrhenius expression (Kooij formula) in the main text and the SAR tables. Why is $(T/K)^n$ used and not $(T)^n$?

- (2) This work seems to nicely follow on from discussions in Jenkin et al., (2019) [<https://doi.org/10.5194/acp-19-7691-2019>] on their SAR for “Estimation of rate coefficients and branching ratios for reactions of organic peroxy radicals” where they introduce discussions on the need for systematic structure–activity methods for a wide range of RO₂ radicals and their potential isomerization reactions. They also discuss that the rates of the reverse isomerization reactions are sometimes sufficiently rapid that the product radical may not be fully trapped by onward reaction (e.g. addition of O₂) under atmospheric conditions” The way the SAR in this work is set up is that the reverse reactions are not explicitly taken into account (for good reasons, given the theoretical complexities involved). More discussion on this is needed but I see that one of the Referees has brought this up and the authors have already responded.
- (3) It would be useful to the reader if more schematic figures and worked examples were shown in order to show exactly how the SARs work/ can be implemented and to illustrate how some of the more interesting reactions work

e.g. the effects of allyl resonance stability in unsaturated RO₂ species. It is also unclear to me how the product studies work really links into the evaluation of the SAR. Here, showing how the reaction mechanism for *n*-pentyl RO₂ is predicted by the SAR in Figure 10 would be useful. It would also be useful to add the structures associated with the masses show in Figure 9.

- (4) Test vs. Training dataset. It would be useful to highlight your strategy of picking what (Scarce) experimental data was used in the training vs. test datasets early on in the manuscript when talking about the development of the SARs. Some of this is brought out more in the evaluation section. It would also be useful to distill out the experimental dataset used into a fully referenced Table in the supplementary.