

Interactive comment on “Peroxy Radical Chemistry and the Volatility Basis Set” by Meredith Schervish and Neil M. Donahue

Anonymous Referee #1

Received and published: 11 September 2019

This is a very timely paper given the widespread use of the VBS combined with the lack of auto-oxidation chemistry in most chemical transport models and box models. Guidance for how to treat auto-oxidation in the VBS is needed. The temperature dependent aspects (for RO₂ dimerization and auto-oxidation rate constants) are particularly novel and interesting. Overall, the work is useful, but could be better tied to other studies to determine more concrete parameters and steps forward for the community.

Major comments:

1. Where does the gas-phase chemistry leave and the VBS take over? Page 2 highlights how auto-oxidation is similar to other RO₂ fates (+NO or +HO₂) whose products can be treated by a VBS. The RO₂+HO₂, etc is not predicted by the VBS, but a gas-phase mechanism. Would it be more accurate (e.g. to state in the abstract) that “a new

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implementation of the VBS that explicitly resolves peroxy radical (RO₂) PRODUCTS formed via auto-oxidation”? When do the kernels take over? At a specific volatility? Would a chemical transport model use the VBS (or kernels) to predict auto-oxidation?

2. The work is highly idealized and hypothetical and could be informed by recent mechanistic work on the α -pinene system. Future work (aimed at, for example, estimating auto-oxidation rate constants and RO₂+RO₂ dimer rates) could also be better informed if some of the already published parameters were considered in this work.

a. The authors assert OH radical-derived RO₂ do not auto-oxidize as readily as ozone-initiated ones with a reference to Ehn et al. 2014 (page 4). Berndt et al. 2016 found that quantification of the OH-initiated HOMs from α -pinene are highly sensitive to the detection technique and that previous work likely underestimated them. Revise in consideration of this more recent work.

b. Rather than specifying one value per oxidant for the fraction of RO₂ able to undergo auto-oxidation (α , page 6), can the authors provide insight into a plausible range? For example, the α for OH is set at 0.1 while Vereecken et al. 2007, Berndt et al. 2016, and Pye et al. 2019 all suggest values on the order of 0.2. Can one of those values (0.1 or 0.2) be ruled out or are they both plausible?

c. You may want to consider examining faster auto-oxidation rate constants (3-10 1/s) and add α -pinene RO₂+RO₂ specific values (Section 3.1.3-3.1.5) based on literature (Zhao et al. 2019).

d. How does the value of γ (page 8) predicted in this work match up with γ from mechanistic work (e.g. Zhao et al. 2019)?

e. Why wasn't an actual α -pinene experiment simulated? How well would the parameterization perform?

f. Page 12, line 33: “NO_x suppresses dimer yields more aggressively than it does HOM monomer yields.” How likely is this to be generally applicable to the atmosphere? Can

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you modify rate constants and branching to state with more/less confidence what the NO_x modulation of HOM is?

g. Page 13, line 23: what bounds do you propose for the auto-oxidation rate coefficient? The bounds on the carbon yield in Fig 9 can be quite large (the min/max bound is also hard to see and link with monomer vs dimer).

3. How generalizable are the parameters within the α -pinene system and to other systems? Previous work (e.g., Kurten et al., 2017) has highlighted how structure-specific product distributions can be. Can the α -pinene system be treated with a series of general kernels or will we eventually need an explicit mechanism that replaces the specified values of α , the dimer kernel, etc. with individual species and unique yields? How important is it to capture the diversity of barriers and rate constants (page 6)? Can you provide some bounds for what might be good enough?

Minor comments:

1. Page 2, line 9-add units after 300
2. Page 2, clarify C_0 is volatility at temperature, T?
3. Page 6, section 3.1.2: what are the parameters (A) based on?
4. Section 3.1.3 and 3.1.5 both cover RO₂ cross reactions. How are they connected?
5. Page 9, line 9-add units after 300. Note additional appearances of 300 should be 300 K throughout the manuscript.
6. Page 11, near line 20, Does the LVOC characterization apply based on the C^* at Tref or C^* at T? Is the definition of LVOC, ELVOC, etc environment dependent or unique to the species? Also page 11, line 32 "...the volatility classes shift toward higher C_0 (300) at lower temperature..." is a bit confusing.

References:

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Berndt et al. 2016: Hydroxyl radical-induced formation of highly oxidized organic compounds, <https://doi.org/10.1038/ncomms13677>

Kurten et al. 2017: Alkoxy Radical Bond Scissions Explain the Anomalously Low Secondary Organic Aerosol and Organonitrate Yields From α -Pinene + NO₃, <https://doi.org/10.1021/acs.jpcllett.7b01038>

Pye et al. 2019: Anthropogenic enhancements to production of highly oxygenated molecules from autoxidation, <https://doi.org/10.1073/pnas.1810774116>

Vereecken et al. 2007: Low-volatility poly-oxygenates in the OH-initiated atmospheric oxidation of α -pinene: impact of non-traditional peroxy radical chemistry, <https://doi.org/10.1039/B708023A>

Zhao et al. 2019: Quantitative constraints on autoxidation and dimer formation from direct probing of monoterpene-derived peroxy radical chemistry, <https://doi.org/10.1073/pnas.1812147115>

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