

General comments

Overall, this is a very well written and clearly structured manuscript about a novel semi-automated method used to constrain autoxidation reaction schemes, including both unimolecular peroxy/alkoxy radical reactions and all related biomolecular reactions that influence the autoxidation reaction mechanisms. The presented novel autoCONSTRAINT tool seem to be a potentially very useful software for the construction of realistic, theoretically consistent and clearly documented and reproduceable peroxy/alkoxy radical autoxidation mechanisms for a large number of VOC + oxidation systems. Currently such a tool is not existing and hence this manuscript provide a substantial contribution to scientific progress within the scope of atmospheric chemistry and secondary organic aerosol formation.

Specific comments

Comment #1:

“L105 “Reactions R2a to R2c do only change the reacting peroxy radical and have no effect on the $\Sigma\text{RO}_2\bullet$.” Consider to reformulate this sentence. Reactions R2a to R2c only influence the concentration of the reacting peroxy radical and has only minor effect on the $\Sigma\text{RO}_2\bullet$ ”

I think that reacting peroxy radical is also part of ΣRO_2 , so some minor impact R2a to R2c should also have on the $\Sigma\text{RO}_2\bullet$ or am I wrong?”

Answer:

We fully agree. Reactions R2a – R2c do effect the ΣRO_2 by reducing the reacting peroxy radical's concentration. We will reformulate the respective sentence as suggested.

Changes in the manuscript:

The respective sentence is reformulated: “Reactions R2a to R2c do change the reacting peroxy radical's concentration and have only minor effect on the $\Sigma\text{RO}_2\bullet$.”

Comment #2:

“Page 4: Why do you consider that fragmentation products can form from $\text{RO}_2\bullet + \text{HO}_2\bullet$ and $\text{RO}_2\bullet + \text{NO}\bullet$ reactions but not $\text{RO}_2\bullet + \Sigma\text{RO}_2\bullet$?”

Answer:

Thanks for pointing out this inconsistency. The reaction pathway $\text{RO}_2\bullet + \Sigma\text{RO}_2\bullet$ leading to fragmentation of the product was omitted unintentionally in the text and, actually, is part of the reaction pathways covered by the current version of the autoAPRAM-fw. We will add the missing reaction as reaction R2d to the manuscript.

Changes in the manuscript:

The following additions/changes are made, starting from reaction equation (R2c):

“ \rightarrow fragmentation products (+ $\Sigma\text{RO}_2\bullet$) (R2d)

Reactions R2a to R2d do change ...”

Comment #3:

“L260: “In the current work we assumed $k_{\text{autox,high}} = 2 \text{ s}^{-1}$. We chose this conservative upper limit as most H-shifts are significantly slower”. What would the consequences be if you would allow considerably higher autoxidation reaction rates? “

Answer:

The consequence would be a reduction in the expected initiation flux (i.e., production of the species $\text{RO}_{2,k}$ from MCM species). As outlined in the last paragraph of section 2.2, the “...H-shift of $\text{RO}\bullet$ and $\text{RO}_2\bullet$, together with the initiation-flux form an equation with three unknowns.” Accordingly, a single experimental data-set will only allow for determining the range of production of $\text{RO}_{2,k}$ but not for determining specific magnitudes of the fluxes. The higher the considered $k_{\text{autox,high}}$, the larger will be the 2D surface of potential solutions. However, equ. (4) & (5) do not aim to quantify the influx required but aim to highlight situations where influx very likely is needed.

Comment #4:

“Page 9: The description and use of the potential initiation flux (P), equ. 4-5 need to be described more clearly. It is not easy to understand how equ. 4-5 was derived and what these equations represents. I guess that they are derived from equ. 3 or? These equations do not seem to represent the potential initiation flux (units of molecules $\text{cm}^{-3} \text{ s}^{-1}$) but ratios (potentials) of how much RO autoxidation and RO_2 autoxidation may contribute to the production of a specific RO_2 peak.”

Answer:

We agree. First of all we will change the name from “potential initiation flux”, which indicates a mass flux to “initiation flux probability”. Further we will add a description of how this probability relates to equ. (3) to relate the potential to prior considerations.

Changes in the manuscript:

In the sentence above equ. (4): “The initiation flux **probability** (P) ...”

In equ. (4), there was a mistake (missing “1 - ...”), thus, we added “1 - ...” : “ $P(\text{RO}\bullet) = \frac{1 - (L_{\text{chem}} + L_{\text{phys}} - S_{\text{in}})}{(L_{\text{chem}} + L_{\text{phys}} + S_{\text{in}})}$ ”

From line 259 we add: “ S_{in} is a source term of the $\text{RO}_{2,k}\bullet$ **via the alkoxy pathway.**”

From line 262 we add: “The initiation flux probabilities of $\text{RO}\bullet$ and $\text{RO}_2\bullet$ relate to equ. (3) as all are based on considerations of mass conservation. While equ. (3) is explicitly balancing mass fluxes, P is meant to highlight the imbalances in fluxes by considering a) mass fluxes via the RO pathway for $P(\text{RO}\bullet)$, and b) expected limitations of the fluxes from $\text{RO}_2\bullet$ within the autoAPRAM scheme for $P(\text{RO}_2\bullet)$.”

Comment #5:

“Should not equ. 3 also have a separate term for the RO autoxidation source of $\text{RO}_{2,k}$ or is the RO autoxidation source included in S_k ?”

Answer:

Yes, the equ. (3) has to consider the source of $\text{RO}_{2,k}$ via the alkoxy pathway and, yes, this pathway is part of the term S_k . We will add a statement specifying explicitly that RO autoxidation is part of S_k to increase clarity.

Changes in the manuscript:

Sentence starting from line 213 is reformulated: “Where $C(\text{RO}_{2,k}\bullet)$ is the concentration of the peroxy radical k . S_k is a source term considering all potential contributions including wall sources as well as autoAPRAM- $\text{RO}\bullet$ autoxidation, MCM- $\text{RO}\bullet$ and MCM- $\text{RO}_2\bullet$ pathways. L_k is a loss term (physical as well as chemical but not including $\text{RO}_2\bullet$ autoxidation).”

Comment #6:

“I guess you don’t need to constrain the RO autoxidation rate since this is assumed to be very fast. Is this why it is omitted in equ. 3-5?”

Answer:

Yes, we assume that the alkoxy reactions are very fast ($\sim 10^6 \text{ s}^{-1}$). As a result, the limiting rate is the formation of alkoxy radicals. This seems to be true at least for the model data, where reactions of the alkoxy radicals are considered explicitly (i.e., they have a specific rate) while in the analysis, using autoCONSTRAINT, we consider instantaneous formation of the products via the alkoxy pathway. The results (Fig. 3 and Figs. S3 to S6) show that this assumption does not introduce a notable error (the maximum error found among all rate coefficients determined is roughly 0.5% which will not matter in any experimentally derived results where much larger errors are expected to result from the measurement).

Technical corrections**Comment #7:**

L34: “a drop of the saturation vapor pressure”. Consider if it maybe better to write a decrease in the saturation vapor pressure.

Answer:

We changed from “drop” to “decrease”

Comment #8:

L106-107: ... those equations difficult to constrain. Change to: those equations difficult to constrain that are difficult to constrain.

Answer:

We changed from “... those reaction equations difficult to constrain.” to “... those reaction equations that are difficult to constrain.”

Comment #9:

L203: “Although direct inclusion of the fragmentation products is beyond the scope of this work, the effect of this reaction can be investigated.” Change to:

“Although direct inclusion of reactions leading to fragmentation products is beyond the scope of this work, the effect of such reactions can be investigated.”

Answer:

We partly agree. The reactions leading to the formation of fragmentation products are included. However, predicting the reactant-specific atomic composition of fragmentation products is beyond the scope of this work.

Changes in the manuscript:

We reformulate the respective sentence: “... inclusion of **reactant-specific** fragmentation products is beyond the scope of this work ...”

Comment #10:

L272: “see Fig. Worklfow_1.pdf”. Change to see Fig. 2

Answer:

we changed to “Fig. 2”

Comment #11:

L272-273: “The autoCONSTRAINT tool reads in a chemical scheme with no rate coefficients, together with a NO_3^- obtained mass spectrum” I am not exactly sure what you want to state with this sentence, but would it not be better to write:

The autoCONSTRAINT tool reads in a chemical scheme with no rate coefficients, together with a mass spectrum obtained e.g. with a NO_3^- CIMS.

Answer:

we agree and changed accordingly

Changes in the manuscript:

Line 275: “The autoCONSTRAINT tool reads in a chemical scheme with no rate coefficients, together with a mass spectrum obtained e.g. with a NO_3^- CIMS.”

Comment #12:

L299: “datat” should be data

Changes in the manuscript:

“datat” was changed to “data”