

Review: Aqueous phase oligomerization of methyl vinyl ketone through photooxidation, by B. Ervens, P. Renard, S. Ravier, J.-L. Clément, and A. Monod, submitted to ACPD, Ms # acp-2014-607

General

This is a study on the oligomer formation originating from MVK. It is undertaken at an early point in time as only limited process information on all the steps involved is available. Clearly stated, it might be too early to try to model this system. Some process information which is now available from the literature is not used and there is a wrong treatment of the branching ratio of the OH initiation reaction. I would advise the authors to clearly mark the very explorative nature of this contribution from its beginning and throughout. Clearly, all results will be strongly dependent on the chosen input and one possible variant to be added to the manuscript would be a sensitivity study which variation of input parameter would lead to which change in the results. To some extent this has been done for oxygen concentration but there are many more variables which are critical to the results of the model.

The possible depletion of oxygen in tropospheric particles seems to be a non-proven hypothesis, the fulfillment of which, however, is required, as otherwise the calculated oligomer formation will be much below its possible maximum. In my view the results obtained with a non-depleted oxygen concentration are most realistic and this should be clearly stressed within the manuscript.

The paper contains plain errors.

Overall, the manuscript needs revision at many points and should generally be seen as an explorative study.

Details

Introduction: 'gasSOA' is a strange acronym

Pages 21567, 21568 The selection of references in this part seems somewhat arbitrary. I feel the author should give a better coverage of work related to the presented study. Recent studies are missing.

Page 21568, line 15 Great care has to be taken following this approach: By just fitting observables to a mechanism without detailed knowledge of the chemical steps involved, a detailed process model cannot be deduced. The fitted mechanistic scheme is a parameterization. Whether the parameterization is valid for environmental conditions has to be proven independently. It cannot be only postulated that such parameterization can be applied direct to environmental systems. This, even though this approach has been followed recently quite often, might potentially represent a strong systematic error in the work described here.

Page 21569, section2: As for the processes listed in Table 1:

$J_{\text{H}_2\text{O}_2}$: A value derived from actinometry should be given and compared to this maximum value. Why is just a maximum value given ?

$k_{\text{MVKOH(a)}}$ and $k_{\text{MVKOH(b)}}$ 'abstraction from allyl group' is wrong and must be replaced by "addition reaction ..." or something similar. As the abstraction from the allyl group is wrongly mentioned here: What will be the branching ratio considering addition and H-abstraction via both pathways, i.e. at the methyl group and at the allylic H abstraction at the allylic H is not considered, but only the first pathway being treated in analogy to acetone. Splitting the measured rate constant just between addition and methyl group H-abstraction does not make sense.

In the OH addition pathway (MVKOH(a)), all formed organic radical products react with O_2 to form a peroxy radical. In the other pathway (MVKOH(b)), the $\text{RO}_2\cdot$ formation is not included for all formed organic radical products (see e.g., Mgly(MVK)_i , MVK(MVK)_i , HAc(MVK)_i). This inconsistency has to be revised.

As for the kinetics: The overall rate constant measured by Schöne et al. (2014) covers all occurring pathways but they are not all discussed in the present manuscript. Any branching ratio must cover all of the three occurring pathways. Schöne et al. (2014) are discussing mechanisms for the reaction of OH with MVK which are not reflected at all in this contribution. This needs to be fully revised. The revision of this includes the possibility that any model calculation must be repeated with corrected values.

J_{ROOH} : How valid is the applied approximation? Please please put „estimated“ into the comment column

$k_{1\text{st}}$ for the conversion of oligomer products to stable products. Is this just an estimate? Give a sound reason for the order of magnitude of this conversion rate constant.

k_{recomb} : This value appears way too low. Give a justification.

k_{HAcOH} : Is this the best available value? compare with others and justify choice.

Could you please explain the basis of the estimation of the rate constants of the recombination of RO_2 with HO_2/O_2^- radicals.

In the WSOC reactions: $\text{WSOC} + \text{OH} \rightarrow \text{R}\cdot + \text{HO}_2$. Please discuss the approximated HO_2 formation. How realistic is a 1:1 stoichiometry?

k_{MVK} is not listed in Table1.

Overall, the applied mechanism appears very uncertain and includes a huge number of tuning parameters. What would the meaning of the result be if, in the end, the mechanism reproduces measurements? It would only show that this is one possible solution. The authors should scan the parameter space and search for other solutions (see the above general comment) – include a sensitivity study. Is the one given by the listed set of parameters an absolutely best solution? Rank

different solution sets. Discuss all the uncertainties of the parameters in detail. Give ranges of possible values.

p.21570, l 28: Please rephrase the sentence. Replace “There is a lack of exact reaction rate constants for the different branching reactions” by “There is a lack of branching ratios for the...”.

Section 2.2. How is the concentration of oxygen in aqueous solution treated in the model ?

P 21579, 21580 The estimates about the phase partitioning are chosen in such a way to lead to maximum uptake. How are they justified ? This is adding additional uncertainty to the results of the study.

The authors assume an effective Henry’s law constant of $2.1 \cdot 10^6$ for the uptake of MVK. Please, specify how this value has been derived! Is there any evidence from laboratory or field measurements for such high Henry’s law constants of MVK or represents the chosen value just a tool to tune the results?

Moreover, an effective Henry’s law constant means that certain processes shift the phase partitioning towards the aqueous phase. But in this case, MVK might not necessarily be present in its monomer form. It might be hydrated or in its dimer form or in other forms. However, this might have effects on the reaction mechanism. In the present work, the authors consider an effective Henry’s law constant, but consider all of the dissolved MVK in its monomer form. This might be incorrect and questionable with regards to the proposed chemical mechanism. Can you, e.g., exclude to have dimers to be present in you system? Please provide proper answers to the questions and discuss them in the paper.

p.21580, line 13: What do the authors want to say with the sentence “... an aqueous phase concentration of 2 mM, that can be considered as being typical for organics in aerosol water (Lim et al., 2010)”? The work of Lim et al. (2010) is mostly related to glyoxal and does not present data related to MVK. Why do the authors use the data given in Lim et al. (2010) for MVK? Do the authors think that MVK and glyoxal behave similar? The authors should keep in mind that the physico-chemical properties of MVK and glyoxal are not identical such as the different effective Henry’s law constants which have been measured for both compounds.

p.21581/9: Please add “+ H₂O” to the right hand side of (R1).

p.21581/11-13: The authors consider (R 1-2) to account for additional OH and O₂ sinks. However, the authors should keep in mind that O₂ is at least partly recycled during peroxy-peroxy radical recombination’s (see, e.g. Alfassi, 1997). In case of a chemical system, where the amount of dissolved O₂ might be important, this recycling should be considered in a proper mechanism.

p. 21585, line 27:

Table 4:

- a) There is no uptake data given for H_2O_2 and O_2 in the manuscript. However, in the manuscript it is mentioned: "However, instead of initializing MVK, H_2O_2 and O_2 in the aqueous phase, gas phase species are initialized, and their uptake into the aqueous phase of aerosol particles is described by the 10 resistance model (Schwartz, 1986)".
- b) Please, put the used K_H values in the Table and not the measured data of Iraci et al. (1999) since they were not really applied in the mechanism. This is misleading and the small comment below is not sufficient enough.

Figure 1:

- a) From the reviewer's point of view, it might be better, for the sake of clarity, to provide both Figure 1 and a detailed revised Table 1 with all single reactions considered in the mechanism.
- b) For the compound $(\text{CH}=\text{CH}_2)\text{C}(\text{O})\text{C}\cdot\text{H}(\text{OH})$ the $\text{RO}_2\cdot$ formation and subsequent HO_2 elimination reaction is missing.
- c) Moreover, the mechanism in its current version does include $\text{RO}_2\cdot$ recombinations for all formed $\text{RO}_2\cdot$ radicals. For some single species only the reaction with HO_2 is considered. However, also the $\text{RO}_2\cdot$ recombination should be considered as potential sink as well as source of O_2 . Without this recycling process of O_2 , the presented result in Figure 6b is inadequate. Moreover, it is mentioned that the formation of some end-products given in Figure 1 (for example: Products, small molecular weight compounds, ..) represents an artificial loss of O_2 . This issue needs at least to be mentioned.
- d) The oxygen addition reactions for the alkyl radicals formed after the MVK addition (Pathway leading to oligomer III, IV, V, VI, VII) are missing. Could you please explain why the RO_2 reaction with HO_2 radicals in one pathway forms the oligomer II and in a second pathway a thermodynamic unfavorable hydroperoxid, which undergoes a subsequent photolysis reaction. It is more likely that this reaction produce an alkoxy radical, a hydroxyl radical and molecular oxygen. Can you please elaborate the possibility of the addition reaction of peroxy radical with double bond of MVK.

Figure 4:

The right part of the Figure (4b) needs a legend.

Supplement

The page numbers of the supplement are not in the correct order.

On page S1, Line 11 there is a typo. The space between (Figure S1.2) obtained is missing. Also in line 13: mL.min⁻¹ instead of mL·min⁻¹ and on page S2, Line 4: mL.min⁻¹ instead of mL·min⁻¹

The layout of equation e) on page S5 is different in comparison with equation d).