REVIEWER #2

`Remarks by the authors: We thank the reviewer for the detailed comments and thoughts on our paper. We have carefully revised the manuscript and added sensitivity studies and further discussion on the most sensitive parameters in the mechanism. In addition, we fully revised and shortened the section of multiphase simulations. In order to better constrain the mechanism by more accurate laboratory results, as asked by Reviewer #1, additional experiments were performed. Because of this, a coauthor was added and several figures were replotted.`

`In the following response, our comments are marked with 'Response' (Courier New font); all reviewer comments are in` 'Times New Roman' `font. Line and figure numbers refer to the revised manuscript.`

This paper is a follow-up to a recent paper describing laboratory studies of aqueous SOA from the OH oxidation of methyl vinyl ketone (MVK) in bulk solutions. In the current paper, the authors develop a box model to describe the laboratory results and apply it to atmospheric aqueous aerosol conditions. The model does a good job of replicating the laboratory results. Applying the model to atmospheric conditions suggests that the OH oxidation of MVK in aqueous particles could be a significant source of SOA in regions with isoprene emissions.

However, the key to MVK having any significance as an aqueous source of SOA is the Henry’s law constant, K(H). The authors have assumed that K(H) for MVK is approximately 50,000 times higher in aerosol water than the measured value in pure water (41 M/atm). They cite this factor of 50,000 as mimicking "...the enhanced partition- ing of carbonyl compounds into aerosol water as compared to pure water...", but they are vague on the details. The authors need to give more justification for their factor of 50,000. What is the range of K(H) enhancements seen for carbonyls? Is there a difference between aldehydes and ketones? Since the latter have much smaller hydration equilibrium constants generally, I would think that they would have much smaller K(H) enhancements in aerosols. Thus the enhancement factor for the poster child of enhanced Henry’s law constants - glyoxal (a di-aldehyde) - might be much larger than the enhancement seen for MVK (a ketone). The K(H) value of 3000 M/atm for MVK in 80% H2SO4, an enhancement of 80 over the water value, suggests that the assumed enhancement of 50,000 for MVK in aerosol water is too high.

Since the Henry’s law constant is the key factor, it needs more discussion and justification. A table of K(H) values for carbonyls in water, and the enhancements in aerosol particles, would help give a clearer picture of a reasonable value for MVK. The authors indicate that if K(H) is 100 times lower than assumed that no significant aqueous SOA is formed.

This idea should be expanded to show a sensitivity study of the MVK-derived SOA mass across the likely values of K(H) in aerosol water. It is suggested in the text (e.g., p. 21580) that the assumed very high enhancement in K(H) relative to pure water might be due to accumulation of MVK at the air-water interface of particles. However, based on the structure of MVK and its high volatility, it seems unlikely that this compound partitions significantly to the air-water interface.

Response: We agree with the reviewer that the choice of the effective Henry's law constants for the oligomer precursor likely represents the largest uncertainty in the multiphase model simulations and therefore in our previous conclusions on the atmospheric implications. We have revised Section 3 (and combined it with the previous Section 4) and discuss the efficiency of salting-in and salting-out effects. Using the new Figure 2-1 (Figure 6 in the manuscript), we estimate now that in saturated ammonium sulfate solutions (~ 2.7 mol kg^{-1}) the enhancement of solubility (K_H*/K_H) is at most a factor ~100 for ketones. Using this factor, we have performed new model simulations and show that oligomerization from MVK and MACR alone might not be a significant SOA source. However, we have extended the discussion and take into account the possibility of additional oligomer precursors that might undergo similar reactions. We give an estimate of the concentration that might be required to initiate efficient oligomer formation in aerosol water and add a considerable amount to total SOA loading (Section 3).

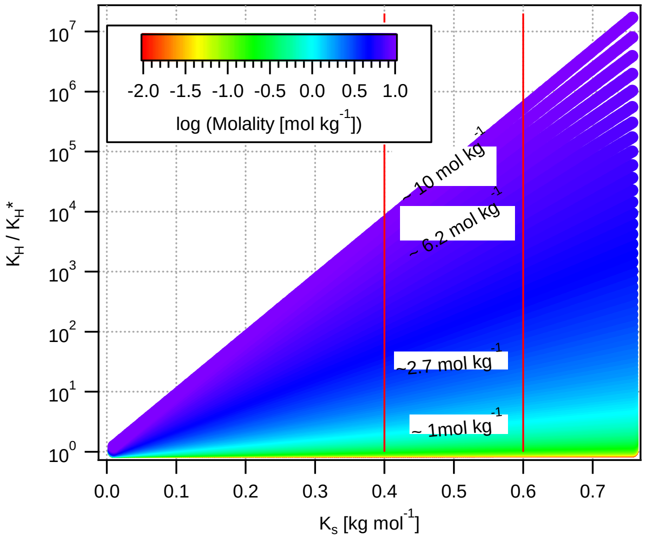

Figure R2-1 (= Figure 6 in the revised manuscript): Reduction of solubility due to ionic strength effects as a function of Setchenov coefficient K_s according to Equation 4. The vertical lines show the range of K_s values for ketones (Wang et al., 2014). The intermediate molalities (2.7 mol kg^{-1}, 6.2 mol kg^{-1}) refer to saturated ammonium sulfate and sodium chloride solutions, respectively.

>Other comments<

1. Line 11 of the abstract states “If oxygen is consumed too quickly or its solubility is kinetically or thermodynamically limited, oligomerization is accelerated, in agreement with the laboratory studies.” If the Henry’s law constant for O2 is decreased in high ionic strength solutions then the aqueous O2 concentration will be lower. But it’s difficult to believe that there is any kinetic limitation to establishing Henry’s law equilibrium for O2, i.e., that any chemical reaction in the aqueous phase can be faster than mass transport of O2 to the particles. This is especially true if the aqueous oxidation process is initiated by OH from the gas phase: since the O2 concentration in the gas phase is approximately a trillion times higher than OH(g), transport of O2 will be enormously faster than OH transport to the particles.

Response: The reviewer is right. O_2 limitation is rather unlikely in atmospheric aerosol particles – unlike in laboratory bulk experiments in which the surface-to-volume ratio is very small. We have changed the abstract as follows (p. 1, l. 26):

"While in laboratory experiments oxygen limitation accelerated oligomer formation, such conditions are likely not met in the atmosphere. ~~*If oxygen is consumed too quickly or its solubility is kinetically or thermodynamically*~~

~~*limited, oligomerization is accelerated, in agreement with the laboratory studies."*~~

On a related note, in Figure 6b it's surprising that O2 is not always in equilibrium with gaseous O2. Is mass transport of O2 limited by interfacial transport or aqueous diffusion? What is the time scale for these steps and for chemical reaction of O2 in the particles?

Response: During revision, we noticed that the former Figure 6b included wrong data (it was not oxygen that was displayed). This error led us to false conclusions. Now, we state that the atmospheric aqueous phase is always saturated with oxygen. However, uncertainties exist about its equilibrium concentration. Potential oxygen limitation is now discussed in Section 3.3.3.

2. Are products from the MVK + OH reaction allowed to evaporate in the model? If so, what are the assumed values for K(H)? In the atmosphere the large oligomers will remain in the aqueous phase, but smaller, intermediate products are likely to volatilize, which might significantly decrease the production of aqueous SOA in particles.

Response: We assume that all oligomers, independently of their chain length, remain in the aqueous phase. The reviewer is right that potentially, smaller, more volatile products might evaporate to the gas phase. However, our simple box model does not include the gas phase chemistry of such compounds (e.g. pyruvic acid, acetic acid). Since they are not initialized in the gas phase, their evaporation flux to the gas phase would be unlimited due to the artificially strong gradient.
The omission of potential evaporation might indeed lead to an overestimate of oligomerization in the condensed phase. However, on the other hand, formation processes of these compounds in the gas phase might also lead to additional uptake and therefore sources of oligomer precursors in addition to MVK.

Since our study can be considered an exploratory feasibility study, we assume that these effects in the real atmosphere might approximately cancel. We added some text explaining this omission (p. 18, l. 26ff).

3. The H2O2 concentrations that were used in the laboratory experiments are extraordinarily high: from 4 mM (in the 0.2 mM MVK solution) to 400 mM (in the 20 mM MVK). In contrast, a typical aqueous HOOH concentration in the atmosphere is 100 uM or less. At the very high experimental concentrations are there thermal reactions between H2O2 and either MVK or some of the intermediate products? I wonder if such reactions are making a significant contribution to the formation of SOA. A comment in the manuscript about this possibility would be helpful.

Response: We are not aware of any measurements of H_2O_2 in ambient aerosol water. The hydrogen peroxide concentrations were chosen such that the MVK/H_2O_2 ratio is constant for all experiments and favors the MVK + OH reaction rather than H_2O_2+OH reaction. The resulting OH concentrations are in the range of atmospherically reasonable concentrations.
We added the following text in order to give an estimate of possible contributions of the H2O2 reactions (p. 13, l. 1-20):

"Control experiments were conducted to check for any reactivity of H_2O_2 towards MVK: MVK (20 mM) and H_2O_2 (400 mM) were mixed together for 300 min in the dark. MVK was not significantly consumed, and no oligomers were formed.
Among the intermediate reaction products formed, the only reactive species towards H_2O_2 are pyruvic acid, glycolaldehyde and glyoxal (2-4%, 11% and 4%

molar yield, respectively Zhang et al. 2010 and Schöne et al 2014). Under our experimental conditions, the second-order-rate constants of reaction of these species towards H_2O_2 (taken from Schöne and Herrmann, 2014) induce life times of 22 seconds for pyruvic acid, 62 sec for glycolaldehyde and more than 4h for glyoxal. While the latter is greater than our experimental time scales, the two former ones are certainly occurring in the vessel during our experiments. The reaction of pyruvic acid towards H_2O_2 leads to the production of acetic acid with a ~molar yield (Schöne and Herrmann, 2014; Stefan and Bolton, 1999). Because acetic acid is one of the identified oligomer contributor, the reaction of pyruvic acid with H_2O_2 might, thus, artificially increase the amount of oligomers formed. Taking into account the molar yields of acetic acid (57%) and pyruvic acid (2-4%) (Zhang et al. 2010; Schöne et al 2014), one can conclude that this increase in the amount of oligomers formed should be of negligible importance. The reaction of glycolaldehyde with H_2O_2 leads to the production of formic acid with a ~molar yield (Schöne and Herrmann, 2014; Stefan and Bolton, 1999). However, formic acid was not identified as a precursor of oligomers in our experiments; therefore, the reaction of glycolaldehyde with H_2O_2 is not assumed to influence the amount of SOA detected."

4. In Figure 8 there is very little SOA made after 2 hours (in either the gas phase or aqueous phase), but approximately 10 times more after 6 hours, even in the gas phase. Why is the formation of SOA increasing so quickly between 2 and 6 hours? This effect is not apparent in the laboratory results.

Response: The concentration of MVK in the multiphase simulations (Section 4) were much lower than in the lab experiments. Therefore, the increase in oligomers is delayed. In addition, it should be noted that in the multiphase simulations, an 'infinite' supply of MVK is assumed (constant isoprene concentration) whereas in the lab experiments MVK is continuously consumed until it is completely reacted.
These differences and the resulting differences in MVK/OH ratios lead to the differences in the temporal behavior of oligomer increase.
We added text accordingly on p. 20, l. 18.

>Minor issues<

1. p. 21569, line 6: O2 should be H2O2. Also, the portion “, for MVK and ::: ” at the end of the sentence is repetitive and can be deleted.

Response: We clarified that indeed MVK, H2O2 and O2 concentrations were recorded. We added 'H2O2' (p. 4, l. 10). Only for MVK and H2O2, UPLC-UV was used; therefore, we did not change the end of the sentence.

2. A major channel from the reaction of RO2 with HO2 is formation of an akyl hydroperoxide, ROOH. Does this imply that Oligomer II is a hydroperoxide? If not, what is it likely to be?

Response: Yes, we assume that Oligomer II is a hydroperoxide. It was the only oligomer with hydroperoxide group that was identified. The fact that the corresponding compounds for the other oligomer series were not found, suggests that they were not formed (or only to negligible amounts). We added this information to the text (p. 8, l. 15).

3. Is the reaction of HOOH with OH the only source of HO2? In the mechanism is HO2 formed from OH + organic?

Response: HO2 is produced in all reactions of OH with organics, i.e. speciated individual compounds and WSOC. Reviewer #1 pointed out the possibility that the stoichiometry of the conversion of OH to HO2 in the reaction of WSOC + OH might not be 1:1.
However, since the revised version of the manuscript does not include the discussion of sensitivity to OH(aq) concentrations anymore, this reaction is not included in the manuscript.

4. Section 2.2.1. Related to the depletion of dissolved oxygen in the laboratory solutions, are solutions in air-tight containers or are they open to air? Why are the initial O2 concentrations different in the different MVK solutions?

Response: Our stirred reactor was tightly closed between samplings (where the reactor was opened for several tens of seconds) that were performed every ~1 to ~10 minutes.
Each experiment started with H_2O_2 photolysis alone for ~ 10 min, and then, MVK was injected in the irradiated solution. Due to the reaction mechanism of H_2O_2 photolysis (HO_x reactions in Table R2-1 = Table 1 in the manuscript), dissolved O_2 concentrations increased during the first 10 minutes, and this increase was faster with higher initial H_2O_2 concentrations. As a consequence, supersaturation of dissolved O_2 was systematically observed prior MVK introduction (Figure R2-2). This also explains why the amount of O_2 produced increased with increasing initial H_2O_2 concentration (Figure S2), as the experiments were performed with different MVK and H_2O_2 concentrations, using a constant initial [MVK]/[H_2O_2] ratio. When MVK was introduced and during the rest of the experiment, the reactor was opened periodically for sampling, thus inducing aqueous/air exchanges of O_2, but these were less efficient than the reaction of O_2 consumption by the reaction as shown by the O_2 depletion observed.

We added this information to the supplemental information, Section S2.

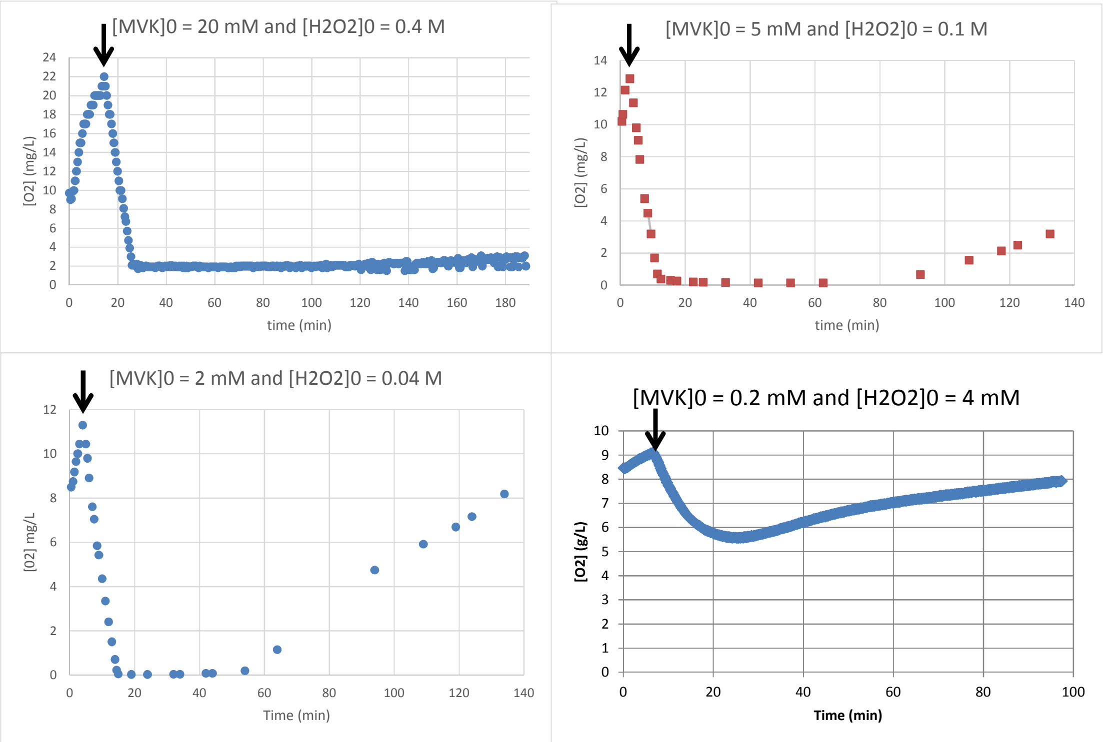

Figure R2-2: Time profiles of dissolved O_2 concentrations during H_2O_2 + MVK photooxidation, for 4 different initial conditions. Time 0 is H_2O_2 injection. The black arrow shows the time when MVK was introduced in the vessel

HO_x reactions		
$H_2O_2 + h\nu \rightarrow 2\ OH$	$j_{H2O2} = f([MVK]_0)$	Estimated based on experiments, cf. Figure 3
$H_2O_2 + OH \rightarrow HO_2 + H_2O$	$3\cdot10^{7}\ M^{-1}\ s^{-1}$	(Christensen et al., 1982)
$HO_2 + HO_2/O_2^- \rightarrow O_2 + H_2O_2$	$8\cdot10^{5}\ M^{-1}\ s^{-1}\ (HO_2)$ $9.7\cdot10^{7}\ M^{-1}\ s^{-1}\ (O_2^-)$	(Bielski et al., 1985)
$OH + HO_2/O_2^- \rightarrow H_2O + O_2$	$10^{10}\ M^{-1}\ s^{-1}$	(Elliot and Buxton, 1992)

Table R2-1: Reaction scheme for the photolysis of H_2O_2 and formation of O_2. (= HO_x reactions in Table 1 of the manuscript)

5. p. 21575, line 10. I don’t see blue arrows in Figs. 2a and b, as is stated in the text.

Response: We apologize for this omission. The revised figure 2b includes arrows; we did not add any to Figure 2a as the revised figure might look too busy with the additional symbols.

6. p. 21575, line 25. The wording should be modified to clarify that the authors measured the transmitted intensity through the MVK solution, rather than the intensity of the lamp (which is independent of what is occurring downstream).

Response: We thank the reviewer for pointing this out. Of course, it is the intensity as measured through the solution and not of the lamp itself. However, we revised the figure and now compare experimental data and actinometry calculations in absence and in presence of MVK (Section 2.2.2, and Figure 3).

7. The rate constants for oligomer + OH and WSOC + OH are based on results from Arakaki et al. (2013). However in the Arakaki work the rate constant is based on per mole of carbon, while in the current work it appears that the authors are using this rate constant as if it were on a basis of per mole of compound. Given the large number of carbons in each oligomer, this is a significant difference.

Response: We changed the reference for k_{loss} (reaction of oligomers with OH) and refer now to Doussin and Monod (2013) where the reactivity of carbonyl compounds towards the OH radical is discussed. In that paper, it is shown that many organic compounds have rate constants on the order of magnitude of ~10^8 M^{-1} s^{-1}, independent of their carbon chain length. To our knowledge, no data are available for oligomers; however, since there is no clear trend with chain length, we think that our estimate for k_{loss} is justified.
The reviewer is right that the rate constant by Arakaki et al. was given in $M(carbon)^{-1}$ s^{-1}. However, given the high variability of WSOC concentration in atmospheric particles and the fact that a large fraction is composed of relatively small compounds (e.g.(Herckes et al., 2013)), we think that our treatment of k_{WSOC} was reasonable. Note that in the revised manuscript, the sensitivity to OH concentrations is not further explored and the reaction was omitted.

8. I cannot understand the value of the mass accommodation coefficient in Table 2.

Response: This mistake occurred during typesetting. We thank the reviewer for pointing it out. We'll make sure that in the revised copyedited version, all symbols will be printed correctly.

9. The first line of the caption in Figure 3 indicates “3” wavelengths, but the correct number appears to be 8.

Response: We have changed Figure 3 including its caption and do not show any wavelength-dependent data anymore (cf. also response to comment #6).

10. In Figure 6, it would be helpful to add a few-word description to each case (A – E) in an expanded legend. It's difficult to have to keep flipping between the text, figure, and Table while reading this section.

`Response: Since we now explore fewer cases with the multiphase model, we omitted Table 3 and added the description of the cases to the new Figure 8.`

References

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