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Interactive comment on “Aqueous phase oligomerization of methyl vinyl ketone through photooxidation – Part 2: Development of the chemical mechanism and atmospheric implications” by B. Ervens et al.

Anonymous Referee #2

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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.

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[Interactive Discussion](#)

[Discussion Paper](#)

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 partitioning 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.

>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

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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.

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?

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.

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 μM 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.

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.

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>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.
2. A major channel from the reaction of RO₂ with HO₂ is formation of an alkyl hydroperoxide, ROOH. Does this imply that Oligomer II is a hydroperoxide? If not, what is it likely to be?
3. Is the reaction of HOOH with OH the only source of HO₂? In the mechanism is HO₂ formed from OH + organic?
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?
5. p. 21575, line 10. I don't see blue arrows in Figs. 2a and b, as is stated in the text.
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).
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.
8. I cannot understand the value of the mass accommodation coefficient in Table 2.
9. The first line of the caption in Figure 3 indicates “3” wavelengths, but the correct number appears to be 8.
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,

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and Table while reading this section.

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Discussion Paper

C8386

