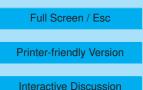**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Radical mechanisms of methyl vinyl ketone oligomerization through aqueous phase OH-oxidation: on the paradoxical role of dissolved molecular oxygen" *by* P. Renard et al.

Anonymous Referee #3

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This paper reported the radical oligomerization mechanisms of methyl vinyl ketone (MVK) that can be initiated by aqueous-phase OH oxidation. The experimental observations demonstrate that the initial concentrations of MVK and dissolved oxygen can play a significant role in affecting the production of oligomers in aqueous solution. In particular, the dissolved oxygen can quickly react with radical initiators, thus inhibiting the proposed oligomerization mechanisms (or in other words, leading to the formation of low molecular weight organics). On the basis of the ESI-MS measurements, many oligomeric series are identified with convincing explanations on the proposed

mechanisms. Overall, this work is very well done and can be publishable. However, the introduction should be improved to meet the publication standard. The authors should clearly state the motivation of this work with more comprehensive literature review. Furthermore, the atmospheric implications of their observations should be better discussed in the revised version. Some specific comments are shown below.

Specific comments:

1. Introduction: First of all, the introduction gives an overall impression that oligomerization process is highly relevant to all aqueous medium, including aerosol, fog and cloud water, in the atmosphere but this is actually inappropriate. Previous studies (e.g. Tan et al., 2009, Lim et al., 2010) have shown that high precursors concentration is a critical factor to facilitate radical mechanism for the formation of oligomeric products, which may only relevant to the aerosol scenario. The authors should provide more accurate interpretation on the literature findings.

Secondly, the authors attempt to use a single term "non-oxidative reaction pathways" (page 2916, line 24) to generalize the potential mechanisms of oligomerization without further interpretations. What types of "non-oxidative reaction pathways" has been suggested by Mazzoleni et al (2012) and other studies? Giving a few examples of potential mechanisms and other field/lab observations in the introduction is highly recommended. For example, Turpin and co-workers have illustrated the possibility of radical-radical oligomerization to produce high molecular weight products with aqueous-phase OH oxidation as an initiation step. This is particularly important for readers to built up their understanding on this specific research topic and the motivation of this study. Lastly, it is recommended to add the motivation of modifying the selected experimental conditions here instead of simply stating what have been done. This would definitely help to visualize the potential atmospheric implications of this work in the later part of manuscript.

2. Section 3.1.1, Page 2925, line 24-25: Formation of oligomers were clearly observed

based on the mass-spectrometric analysis. However, this statement implies that NMR can be used as a stand alone technique to at least qualitatively indicate the presence of oligomers in the reacting solution. It is worth to provide appropriate references to support the way to interpret the NMR spectra in this section.

3. Conclusions and atmospheric implications: The conclusion can be shorten because there are too many details of repeated information from the previous section. Instead, the authors should better discuss the atmospheric importance of their current observations. In particular, due to the fact that atmospheric droplets has much larger surface-to-volume ratio than that of the bulk solution, oxygen molecule in the droplets likely equilibrate with the surrounding air quickly, resulting in saturation of dissolved oxygen. This suggests that the proposed oligomerization mechanism may be significantly inhibited. The atmospheric relevance of the initial MVK concentrations (0.2, 2, and 20 mM) used in this study should be also addressed. In addition, ozone may react with the C=C bond of MVK quickly through heterogeneous processing, especially under high ozone concentration. Can the authors roughly estimated the relative importance between ozonolysis and the proposed oligomerization mechanisms on the consumption of C=C bond of MVK in the atmospherically relevant condition?

Minor comments:

1. Page 2918, line 19-20: Please briefly describe the method used for H2O2 detection.

2. Table 1: I am wondering if the dissolved oxygen concentration without H2O2 was measured. This can confirm the supersaturation of dissolved oxygen.

3. Page 2929, line 23-28: Duplicate information in this paragraph.

4. Figure 9: In order to visualize the delay of oligomer formation in the case of high dissolved O2 concentration, it is recommended to add the time series profile of total signal from oligomers in Figure 9a-c.

5. Page 2933, line 11: Perhaps typos. ". . .Supplement 2. . ."

References:

Lim, Y. B., Tan, Y., Perri, M. J., Seitzinger, S. P. and Turpin, B. J.: Aqueous chemistry and its role in secondary organic aerosol (SOA) formation, Atmos. Chem. Phys., 10, 10521-10539, 2010.

Tan Y., Perri, M. J., Seitzinger, S. P. and Turpin, B. J.: Effects of Precursor concentration and acidic sulfate in aqueous glyoxal OH radical oxidation and implications for secondary organic aerosol, Environ. Sci. Technol., 43,8105-8112, 2009.

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