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Atmospheric
Chemistry
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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 #1

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General Comments

This paper closely examines methylvinylketone (MVK) oxidation by OH radicals in an aqueous phase reactor, and the subsequent oligomerization reactions that occur between organic radicals formed and excess MVK. Conclusions are supported by data from several different organic techniques, with the greatest reliance on ESI mass spectra. Many oligomer series are identified. The work is very well-done and thoroughly argued, and this reviewer is convinced that the explanations of the processes responsible for their observations are reasonable.

The main issues with the paper have to do with its applications to the atmosphere. There are major differences between experiment and atmospheric conditions for the availability of both MVK and dissolved oxygen that the authors tend to minimize or ignore. While field measurement of these species (and similarly reactive olefinic carbonyl species) in clouds and particles are relatively rare, and the authors wisely call for more measurements, more is known than it would appear from reading the manuscript. I think that this paper is publishable and will have high impact, once realistic distinctions are made between experimental and atmospheric conditions, and these distinctions are used to inform and qualify the conclusions.

Specific Comments

First, the experimental MVK concentrations used are 3 to 5 orders of magnitude higher than the highest cloudwater measurements of this compound (van Pinxteren, et al. 2005). In section 2.2.2 the authors attempt to justify experimental MVK concentrations by comparing them to total WSOC concentrations in atmospheric precipitation, cloudwater, and aqueous aerosol particles. However, the authors later argue in the discussion that radical chain reactions observed in this study could take place among olefins in atmospheric aqueous phase particles, which likely make up only a small fraction of the WSOC, at least in clouds (van Pinxteren, et al. 2005). Thus, the comparison of experimental MVK concentrations to atmospheric concentrations of WSOC is not relevant, and claims that the experiments represent atmospheric conditions (e.g. abstract line 10) are questionable, at best. This is a crucial issue since the amount of oligomerization observed in this and other studies depends strongly on MVK concentrations. If MVK (and olefin) concentrations in the atmosphere are indeed much lower than those used in this study, then one could use the same data to argue that these oligomerization processes are not atmospherically important. The manuscript should better estimate or summarize what is known about atmospheric aqueous-phase concentrations of MVK (and olefins), and use this information to describe the potential atmospheric importance of these oligomerization processes in a more nuanced, convincing fashion.

Second, the paper notes that O2 has the “paradoxical role” of initially depressing, and later accelerating (by its absence) oligomer formation. This is certainly true in these bulk-phase experiments: O2 is rapidly used up as it reacts with MVK, at which point oligomerization accelerates because the radicals initially formed no longer can react with O2. However, in aqueous atmospheric particles and/or droplets (with high surface-to-volume ratios), it would be surprising if dissolved O2 could ever fall much below equilibrium, except perhaps in solid-phase particles. Thus, oxygen depletion and its large effects in these bulk-phase experiments are probably not atmospherically relevant. This again means that radical-radical oligomerization would not be expected to proceed nearly as fast nor as far in the atmosphere. The “paradoxical role of O2” observed in these experiments would not likely be a paradox in the atmosphere. This needs to be made clear in the manuscript.

Abstract line 6 and p. 2916 lines 18-21: Tan et al. (2012) and Lim et al. (2010) found that radical-radical reactions were largely responsible for oligomer formation in the glyoxal + OH and methylglyoxal + OH systems at high concentrations. They carefully interpreted this observation to state that radical-radical reactions were likely dominant sources of glyoxal- and methylglyoxal-derived oligomers formed during daytime in atmospheric aqueous aerosol particles (not clouds). These important qualifiers seemed to have been lost in this manuscript when describing these studies, and should be restored.

Technical corrections:

p. 2921 line 10: What substance was used for the optimization of ESI conditions? MVK? Leucine enkephalin?

p. 2921 line 14: What was the source of sodium?

Figure 9: This figure could be clarified by inserting a vertical line at t = 0 to mark the

time at which oxygen concentrations are high or low. As it is, it misleadingly appears that all experiments start with the same oxygen concentrations (on the left side of the graph).

References

Lim, Y. B., Y. Tan, et al. (2010). "Aqueous chemistry and its role in secondary organic aerosol (SOA) formation." Atmospheric Chemistry and Physics 10: 10521-10539.

Tan, Y., Y. B. Lim, et al. (2012). "Mechanisms leading to oligomers and SOA through aqueous photooxidation: insights from OH radical oxication of acetic acid and methylglyoxal." Atmospheric Chemistry and Physics 12: 801-813.

van Pinxteren, D., A. Plewka, et al. (2005). "Schmucke hill cap cloud and valley stations aerosol characterisation during FEBUKO (II): organic compounds." Atmospheric Environment 39: 4305-4320.

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