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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 #2

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General comment

This manuscript reports a very thorough investigation of the oligomerization of Methyl Vinyl Ketone initiated by OH radicals in aqueous media, involving systematic series of experiments and state-of-the-art analytical techniques. The work is very well performed, technically and methodologically. Impressive efforts have been invested in the identification of oligomer series and in studying the role of experimental conditions on the results, in particular the concentrations of oxygen and MVK. The conclusions are interesting. However the implications of the results for atmospheric aerosols need to

be further discussed. And a few points need to be improved in the introduction, mostly terminology. Provided that these changes are made, the manuscript is publishable.

Detailed comments

1 – Implications of the results to atmospheric aerosols

As emphasized above, the work presented is of good quality, both technically and methodologically. I will thus only address the few points that need improvement.

Motivation for the study.

The efforts invested in this study are impressive. Few studies of this type have involved two different Mass Spectrometric techniques, including high resolution, correlated NMR, and UV kinetics. This is positive, of course, but at the same time requires a better justification in the introduction and conclusion. For instance, the authors refer to one single paper (Mazzoleni et al. 2012) reporting non-oxidative high-molecular weight products in atmospheric aerosols as the motivation for this study. It is a very good strategy to refer to atmospheric observations, as this justifies the atmospheric relevance of the work. But one paper alone seems too little (their results could be biased, for instance). Isn't there more literature on large molecular weight compounds in atmospheric aerosols ? This problem shows in the last paragraph of the conclusion, which is not very convincing: the authors seems to run out of arguments to justify the atmospheric implication of the work.

Relevance and implications of the results.

Similarly, the importance of the results for atmospheric particles needs to be better discussed. There is nothing wrong with performing experiments under unrealistic conditions if necessary (which is not entirely the case here), but the extrapolation of the results to the atmosphere needs to be explained. Clearly here, varying the concentrations of MVK and oxygen was a way to obtain some information on the mechanism, and not meant to be atmospherically-relevant. But once we have this information, what

does it mean for atmospheric particles ? Obviously the later will always be saturated in oxygen, which suggests that the oxidative pathways producing small-chain products will always be favored ? This requires a discussion. That's where literature on compounds found in authentic atmospheric aerosols becomes important. The concentrations of MVK used do not need to be relevant for the atmosphere either, as they only affect the kinetics and the competition between the different reaction pathways. But what about the fact that MVK will always be mixed with many other compounds in atmospheric particles, none the least being MACR, but perhaps other unsaturated compounds with larger concentrations, thus more likely to react with MVK than with MVK itself. In that case, we should expect cross-polymerization, making many different series of oligomers and those found in this work might not be the most probable in atmospheric particles. All these points need to be discussed at the end of the discussion or in the conclusion.

2 – Terminology

This paper shows some real efforts in using the correct chemical terminology (for instance, first paragraph in 3.1), which is very commendable. However there are two terms in the introduction that are not used in the right way, or should not be used at all.

- The first one is "aqueous" and addresses the distinction between "aqueous" conditions and SOA (or aerosols in general). These are two VERY different conditions and, while the reactions investigated here might be relevant to both, it is important to understand these differences. Aqueous media are where the concentrations of solute do not exceed 0.1 M. This corresponds to a ratio of water molecules/solute molecules of at least 550. By contrast, in aerosols, especially those containing ammonium sulphate (SOA seeds for instance), the ratio water molecules/salt molecules is only 2 – 10. Thus any organic solute in these aerosol media would be subject to strong electrostatic interactions (going way beyond the ionic strength) that are not present in "aqueous" media. The chemistry is thus very different in these two media.

- the second term is "accretion" reactions, which does do correspond to any reality. This term was introduced a few years ago by atmospheric scientists who obviously had no chemical education. But it is NOT recognized by the IUPAC and has NEVER been used by any serious chemist. Just look in any chemistry textbook and you will find condensation reaction, addition reactions, substitution reactions, corresponding to actual mechanisms, but no "accretion" reactions. Simply because they do not correspond to anything. Worse, this term means something completely different in physics and astronomy, which is very misleading, as illustrated in the reference "Orthous-Daunay, (2011)" of this manuscript. Instead, one could use "bond-forming" reactions, for instance, which is perfectly correct.

Small comments:

A few sentences seem repetitive, awkward, or just unclear. Please, check and improve:

- li. 21 in the abstract: the word "supremacy" is very unusual in scientific papers – and rather unclear in this context.

- li 26 in section 2.2.3: not well written and unclear. Do you mean "to complete the investigation of the role of oxygen we also performed experiments with low initial O2 concentrations" ?

- title of section 2.3: this should be "mass spectrometric" (adjective) not "mass spectrometry" (substantive)

- li 4, section 2.3: in the experimental section one should avoid using personal pronouns such as "we". Try the passive form "An UHPLC column. . . was used". This is generally the rule for the entire text in all scientific papers.

- li 27/28 section 3.3: the last sentence seems to repeat point 2).

- li 29/30 section 3.3: I do not understand this sentence. Is something missing there ?

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 2913, 2013.