**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.

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RC C441: 'Review on the manuscript Âń Radical mechanisms of methyl vinyl ketone oligomerisation. . . Âż by Renard et al.', Anonymous Referee #2, 08 Mar 2013

The authors appreciate many important comments raised by Reviewer 2 which have been considered in the new version of the manuscript. The authors' answers to the questions/comments of Reviewer 2 are presented below.

General comment Question: This manuscript reports a very thorough investigation of

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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. Answer: We fully agree on these general comments, and we have modified the introduction and conclusions accordingly (see answers to detailed comments).

1 – Implications of the results to atmospheric aerosols

Motivation for the study. Question: 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. Answer: As mentioned in the manuscript, in order to determine the reaction mechanism, we used a complete set of analytical strategies to identify the oligomers produced. The analytical methods used are complementary, and allowed us for a thorough identification of the reaction products, oligomers, and their kinetics. Although none of the analytical methods used is able to detect radicals, a precise determination of the time profiles of reactants and reaction products strengthened the proposed radical mechanism.

Question: 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

C2016

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.

Answer: We agree on this and we have modified the introduction accordingly, here is the new introduction: "Although Secondary Organic Aerosol (SOA) represents a substantial part of organic aerosol, which affects air quality, climate and human health, the understanding of its formation pathways and its properties is still limited due to the complexity of the physicochemical processes involved. It is now accepted that one of the important pathways of SOA formation occurs through aqueous phase chemistry (Hallquist et al., 2009; Carlton et al., 2009; Ervens et al., 2011). In particular, a number of studies have observed the formation of large molecular weight compounds in atmospheric aerosols (see for example Clayes et al., 2004, and 2010; Baduel et al., 2011) and in cloud/fog droplets (Herckes et al., 2002 and 2007), and the presence of HUmic-LIke Substances (HULIS) in atmospheric aerosol particles, fog and cloud water has been reviewed by Graber and Rudich (2006). Recent studies have shown that aqueous phase chemistry of glyoxal (Volkamer et al., 2007 and 2009; Ervens and Volkamer, 2010; Lim et al., 2010), methylglyoxal (Tan et al., 2012), pyruvic acid (Guzmàn et al., 2006; Tan et al., 2012) glycolaldehyde (Ortiz-Montalvo et al., 2012), methacrolein and methyl vinyl ketone (El Haddad et al., 2009; Liu et al., 2012) can produce significant amounts of SOA. In particular, Volkamer et al., (2007 and 2009) and Ervens and Volkamer, (2010) have shown that SOA production can occur via liquid phase processes of glyoxal in deliquesced particles named wet aerosol, where ambient relative humidity (RH) range from 50 to 80%. These findings give an extremely large set of conditions where organic liquid phase processes can occur, i.e. from rain drop, cloud and fog droplet to wet aerosol, for which atmospheric lifetimes (< 1 minute – days), liquid water content (LWC : 108 - 1 μg m-3), surface area (10-2 – 10-10 cm^2), particle number concentration (10-4 – 104 cm-3) and individual organic and inorganic chemical concentrations (10-2 – 106 μM) vary over orders of magnitude (Ervens and Volkamer, 2010). In their review, Lim et al. (2010) report that liquid phase reactions of glyoxal with OH radicals performed under high initial concentrations tend to be faster

C2017

and form more SOA than non-radical reactions. They conclude that in clouds/fog conditions (i.e. diluted concentrations of 10-2 – 1 mM), radical reactions yield organic acids, whereas in wet aerosols (i.e. concentrated conditions of 10 mM – 10 M) they yield large multifunctional humic-like substances, or oligomers, formed via radical-radical reactions. An oligomer is a molecule that consists of a few monomer units (from 2 to up to 30). Lim et al. (2010) and Tan et al. (2012) propose that radical-radical reactions to form oligomers are alkyl-alkyl radical additions, which always compete with O2 addition reactions. This explains why oligomer formation is observed only at high initial precursor concentrations, inducing high alkyl radical concentrations (after initial OH-oxidation of the precursor) which are required for radical-radical reactions to take place in competition with the reaction of O2. However, O2 concentrations were supposed to stay constant at saturation (i.e. Henry's law equilibrium) in these studies, as they were only measured and the beginning and at the end of the reaction. In the present study, in order to determine the atmospheric relevance of radical reactions, we explore in details the radical mechanisms and the influence of O2 concentrations on this chemistry using a slightly different precursor, i.e. methyl vinyl ketone. This compound is an α,β-unsaturated carbonyl that is water soluble, it bears a highly reactive function (i.e. carbon-carbon double bond) which is likely to play a major role on radical chemistry and oligomer formation, as it was preliminarily shown by Liu et al. (2012). The reactivity of olefin compounds has been scarcely studied in the liquid phase up to now, although a number of field measurements have observed them in atmospheric waters: unsaturated diacids were detected in rain and fog samples (7-14% of the total mass of diacids: Kawamura et al., 1993 and 1994 and Sempéré et al., 1996) and in marine aerosols (2-7% of the total mass of diacids; Fu and Kawamura, 2013). In clouds, it was observed that 1-18% of the total mass of carbonyls were unsaturated carbonyls (among which methyl vinyl ketone) (van Pinxteren et al., 2005), and in biogenic aerosols, unsaturated polyols (C5-alkene-triols) represented 2-5% of the total mass of identified polyols (Claeys et al., 2010). Finally, using NMR spectroscopy, Decesari et al. (2000) detected that 10-35% (respectively 7-37%) of the organic chemical functions were unsaturated

C2018

in fog samples (respectively aerosols) in the Po Valley. In view of these numbers, one can reasonably suppose that 2-20% of the organic matter concentration is unsaturated in atmospheric waters. Therefore, assuming total water soluble organic compounds (WSOC) concentrations of 0.01-1 μM in rain drops, 1-100 μM in cloud droplets, 1-100 mM in fog droplets and 1-10 M in wet aerosol, one obtains a range of unsaturated organic compounds of 0.002-0.2 μM in rain drops, 0.02-20 μM in cloud droplets, 0.02-20 mM in fog droplets and 0.02-2 M in wet aerosol. The aim of the present study was to determine the radical mechanism involved in the oligomerization of MVK, and to identify the oligomers formed via this chemistry. MVK was used as a model compound for unsaturated organic compounds present in atmospheric waters, its initial concentrations were varied from 0.2 to 20 mM, thus representing the total concentrations of unsaturated organic compounds in fog droplet and wet aerosol. In order to determine the atmospheric relevance of this radical chemistry, the influence of temperature and dissolved oxygen concentrations were studied."

Relevance and implications of the results

Question: 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. 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

C2019

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.

Answer: We agree on this and we have modified the conclusions accordingly. Here are the new conclusions, which have been renamed "atmospheric implications", and which contain a new figure (Fig. 12) and a new table (Table 3): "The proposed mechanism allowed for explaining the particular role of dissolved O2 under our experimental conditions. Each iRâĂć radical underwent competition kinetics between O2 addition (reaction R1) and oligomerization (reaction R2):

iRâĂć + O2 → LMWC kR1 (R1)

iRâĂć + n(MVK) → oligomers kR2 (R2)
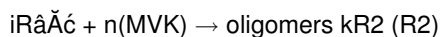
Supersaturated (by a factor of 155%) initial O2 concentrations inhibited radical oligomerization by fast addition on iRâĂć resulting in the formation of LMWC (such as acetic acid and methylglyoxal), which were further OH-oxidized and formed other iRâĂć radicals. The fast O2 addition reactions resulted in a fast decrease of O2 concentrations in the vessel, faster than O2 renewal from the gas phase and from the reactivity of H2O2, and even faster than MVK consumption. At initial MVK concentrations higher than 0.2 mM, the decrease of O2 concentrations resulted in the dominance of reaction (2) after several minutes, and oligomerization started, even when O2 concentrations were still higher than Henry's law equilibrium with atmospheric O2. The paradoxical role of O2 resides in the fact that while it intensely inhibits oligomerization, it produces more iRâĂć radicals, which contribute to O2 consumption, and thus lead to oligomerization. These processes, together with the large ranges of initial concentrations investigated ($60 - 656$ μM of dissolved O2 and $0.2 - 20$ mM of MVK concentrations) show the fundamental role that O2 likely plays in atmospheric waters. In order to scale the relative importance of reactions R1 and R2 from the laboratory to

C2020

the atmospheric conditions, one has to compare the rates of R1 and R2: vR1 = kR1 × [iR\•Ăć] × [O2] vR2 = kR2 × [iR\•Ăć] × [MVK] The dominance of oligomerization over O2 addition is determined by "v" _"R2" /"v" _"R1" "=" "k" _"R2 " /"k" _"R1" "×" ["MVK"]/["O" _"2"] . Assuming that the ratio "k" _"R2 " /"k" _"R1" does not vary from the laboratory conditions to the atmospheric ones, one can simply predict the oligomerization to occur from the [MVK] / [O2] ratio. In our experiments, the detailed study of the time profiles of O2 and MVK together with the kinetics of oligomer formation allowed us to determine that radical oligomerization dominates over O2 addition for [MVK] / [O2] ratios (in M/M) equal or higher than 32 (at 5°C) and 54 (at 25°C). In atmospheric waters, assuming that dissolved O2 concentrations are saturated (i.e. at Henry's Law equilibrium) everywhere from 0 to 5 km in altitude, and from -20 to +25°C, gives a range of 190-391 μM for [O2]. Furthermore, taking the concentrations of unsaturated organic compounds ([UNS]) in atmospheric waters as stated in the introduction, one obtains [UNS] / [O2] ratios as indicated in Fig. 12 (Ervens et al., 2012). In this figure, radical oligomerization occurs when [UNS] / [O2] ratios are equal or higher than 32 or 54. It is thus concluded that radical oligomerization will always occur in wet aerosols, and in sometimes in fogs: in most polluted fogs, where [UNS] > 6 mM. This result, added to the fact that the lifetime of wet aerosols in the atmosphere are several days, shows the extreme relevance of radical oligomerization of unsaturated organic compounds in the atmosphere. Another point of view for atmospheric implications is the fate of MVK. In general, aqueous phase OH-oxidation is known to drastically reduce WSOCs atmospheric lifetimes, compared to their gas phase reactivity (Monod et al., 2005). As it was shown in the present study, once in the liquid phase, MVK can undergo OH-oxidation. In fogs and wet aerosols, it can additionally undergo oligomerization with a first order kinetic rate constant of koligo = 7.6 ($\pm$ 0.3) x 10-4 s-1, (which is not temperature dependent between 5 and 25°C) as derived in the present work from the MVK decay during oligomerization, under all conditions (figures 5 and 9). Although MVK is weakly water soluble, its aqueous phase reactivity may impact its overall atmospheric lifetime. In Table 3, we compare MVK atmospheric lifetimes between its gas phase reactivity

only (taking into account both OH-oxidation and ozonolysis) and its multiphase reactivity. The latter takes into account MVK air/water partitioning at Henry's Law equilibrium, and its liquid phase reactivity: oligomerization is considered only in fogs and aerosol media. Table 3 shows that liquid phase reactivity impacts the overall atmospheric lifetime of MVK by 2 to 13%. Compared to these numbers, the rate of heterogeneous ozonolysis of MVK on SiO2 or ïĄą-Al2O3 particles under various relative humidity (ïĄğ = 10-10 to 10-9, Shen et al., 2013) calculated for a number of 100 nm particles of 5000 particles cm-3, would deplete its atmospheric lifetime by less than 0.00006%. Thus, liquid phase photooxidation seems more efficient, but this needs to be confirmed by more studies of both bulk and heterogeneous reactivity of olefin compounds. The results obtained in Figure 12 and Table 3 show the atmospheric relevance of liquid phase reactivity of unsaturated water soluble organic compounds (even for low soluble ones like MVK), and their ability to activate radical oligomerization chemistry, which is extremely fast and is able to form macromolecules as high as 1800 Da in polluted fogs and wet aerosols. For an unsaturated compound 10 times more soluble than MVK, we anticipate that its overall atmospheric lifetime would be depleted by 13 to 79%, thus showing the need for further studies of oligomer formation from other relevant unsaturated compounds, and their mixtures under various conditions (especially inorganic content and ionic strength). Further studies are also needed to investigate the oligomer yields, their oxidizing states, and their aging (Siekmann et al., in preparation).

Fig. 12: Estimated ranges of the ratios of unsaturated dissolved organic carbon concentration to oxygen concentration (in M M-1) in atmospheric waters. The straight lines delimit the values for which radical oligomerization dominates over O2 addition, as determined by the present work (see text).

Table 3: Comparison of MVK atmospheric lifetimes between its gas phase reactivity only and its multiphase reactivity, taking into account its air/water partitioning at Henry's Law equilibrium, its gas and liquid phase reactivity: oligomerization is considered only in fogs and aerosol media, with koligo values derived from our experimental results.

2 – Terminology

Question: 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.

Answer: We replaced the term "aqueous phase" by "liquid phase" for wet aerosol chemistry.

Question: - 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.

Answer: In the new introduction, the term is not used anymore, but we would replace

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the term "accretion reactions" by "condensation reactions". We prefer this term than "bond-forming" reactions because the radical mechanisms we are describing are also bond forming.

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. Answer: The word "supremacy" was replaced by the word "dominance"

- 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"? Answer: Yes, the modification was done in the revised version of the manuscript

- title of section 2.3: this should be "mass spectrometric" (adjective) not "mass spectrometry" (substantive) Answer: The modification was done in the revised version of the manuscript

- 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. Answer: The modification was done in the revised version of the manuscript

- li 27/28 section 3.3: the last sentence seems to repeat point 2). Answer: The modification was done in the revised version of the manuscript

- li 29/30 section 3.3: I do not understand this sentence. Is something missing there? Answer: In section 3.3, there are no li 29/30! âĂČ References

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Fig. 12: Estimated ranges of the ratios of unsaturated dissolved organic carbon concentration to oxygen concentration (in M M^{-1}) in atmospheric waters. The straight lines delimit the values for which radical oligomerization dominates over O$_2$ addition, as determined by the present work (see text).
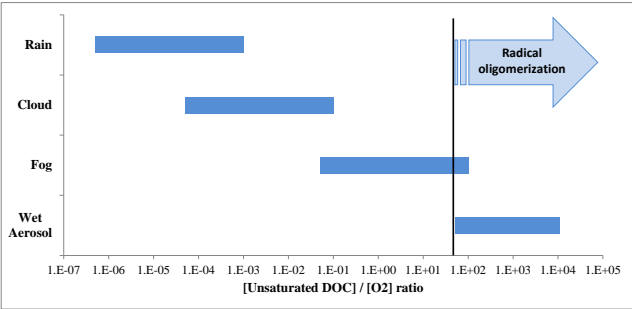

Fig. 1. Figure 12

Table 3: Comparison of MVK atmospheric lifetimes between its gas phase reactivity only and its multiphase reactivity, taking into account its air/water partitioning at Henry's Law equilibrium, its gas and liquid phase reactivity: oligomerization is considered only in fogs and aerosol media, with k$_{oligo}$ values derived from our experimental results.

	gas	cloud	fog		aerosol	
OH concentration	10^6 molec cm^{-3}	10^{-13} M	10^{-12} M		10^{-11} M	
O$_3$ concentration	1,23.10^{12} molec cm^{-3} (50 ppbV)	-	-		-	
Radical oligomerization reactions	No	No	Yes [a]		Yes [a]	
Henry's Law constant (M atm^{-1})	-	41 [b]	41 [b]		7100 [c]	
LWC (g m^{-3})	-	5	1	0.4	0.1	2.5 x 10^{-5}
Atmospheric lifetimes (h) at 298 K	12	10.4	11.6	10.4	11.5	11.8
% impact of liquid phase reactivity	-	-13%	-3%	-13%	-4%	-2%

[a] k$_{oligo}$ = 8 x 10^{-4} s^{-1}; [b] Iraci et al., 1999; [c] Nozière et al., 2006.

Fig. 2. Table 3