

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 C97: 'Referee comment', Anonymous Referee #1, 07 Feb 2013

The authors appreciate many important comments raised by Reviewer 1 which have been considered in the new version of the manuscript. The authors' answers to the questions/comments of Reviewer 1 are presented below.

General comments

Question: The main issues with the paper have to do with its applications to the atmo-
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sphere. 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.

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

Specific comments

Question: 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 depend 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 poten-

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tial atmospheric importance of these oligomerization processes in a more nuanced, convincing fashion.

Answer: We agree on this. We have modified the introduction and the conclusions 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 (Guzmán et al., 2006; Tan et al., 2012) glycolaldehyde (Ortiz-Montalvo et al., 2012), methacrolein and methylvinyl 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 : $10^8 - 1 \mu\text{g m}^{-3}$), surface area ($10^{-2} - 10^{-10} \text{ cm}^2$), particle number concentration ($10^{-4} - 10^4 \text{ cm}^{-3}$) and individual organic and inorganic chemical concentrations ($10^{-2} - 10^6 \mu\text{M}$) 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

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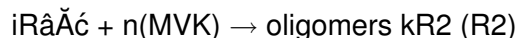
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and form more SOA than non-radical reactions. They conclude that in clouds/fog conditions (i.e. diluted concentrations of 10⁻² – 1 mM), radical reactions yield organic acids, whereas in wet aerosols (i.e. concentrated conditions of 10 mM – 10 M) they 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 at 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 methylvinylketone) (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

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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." 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 $\dot{\text{R}}$ radical underwent competition kinetics between O₂ addition (reaction R1) and oligomerization (reaction R2):



Supersaturated (by a factor of 155%) initial O₂ concentrations inhibited radical oligomerization by fast addition on $\dot{\text{R}}$ resulting in the formation of LMWC (such as acetic acid and methylglyoxal), which were further OH-oxidized and formed other $\dot{\text{R}}$ 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

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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 iR[•] 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 the atmospheric conditions, one has to compare the rates of R1 and R2: $v_{R1} = k_{R1} \times [iR^{\bullet}] \times [O_2]$ $v_{R2} = k_{R2} \times [iR^{\bullet}] \times [MVK]$ The dominance of oligomerization over O₂ addition is determined by $v_{R2}/v_{R1} = k_{R2}/k_{R1} \times [MVK]/[O_2]$. 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 $[MVK] / [O_2]$ 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 $[MVK] / [O_2]$ 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 $[UNS] / [O_2]$ ratios as indicated in Fig. 12 (Ervens et al., 2012). In this figure, radical oligomerization occurs when $[UNS] / [O_2]$ 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 reac-

tivity (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 $k_{\text{oligo}} = 7.6 (\pm 0.3) \times 10^{-4} \text{ s}^{-1}$, (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 SiO_2 or $\gamma\text{-Al}_2\text{O}_3$ particles under various relative humidity ($\bar{A}_{\text{g}} = 10^{-10}$ 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 con-
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centration 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).

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.

Question: Second, the paper notes that O_2 has the "paradoxical role" of initially depressing, and later accelerating (by its absence) oligomer formation. This is certainly true in these bulk-phase experiments: O_2 is rapidly used up as it reacts with MVK, at which point oligomerization accelerates because the radicals initially formed no longer can react with O_2 . However, in aqueous atmospheric particles and/or droplets (with high surface-to-volume ratios), it would be surprising if dissolved O_2 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 O_2 " observed in these experiments would not likely be a paradox in the atmosphere. This needs to be made clear in the manuscript.

Answer: We agree on the fact that O_2 depletion is not likely in the atmosphere, but the study of its influence was necessary in our experiments, as it is (hopefully) clearly written now. We want to insist here that our experiments evidenced that oligomerization processes start under super-saturated O_2 concentrations (see Fig. 9b and c). We have done some new calculations to scale these results to the atmospheric conditions. In the atmosphere (from -20 to $+25^\circ C$, and from 0 to 5 km altitude), at Henry's Law equilibrium, dissolved O_2 concentrations can vary over a narrow range from 190 to $391 \mu M$ whereas dissolved unsaturated organic compounds can vary over orders of magnitude (as shown in the new introduction), resulting in the ratios indicated in Fig. 12. No mea-

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surements of dissolved oxygen have been done up to now in atmospheric waters (to our knowledge), but one can think that respiration of microorganisms (Vařtilingoma et al., 2013) could deplete them in rain drops, cloud or fog droplets, while organic films at the air/water interface of deliquesced particles could slow down the air-to-water transfer of O₂ as it was shown to occur for acetic acid by Gilman and Vaida (2006).

Question: 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.

Answer: These changes have been done in the revised version of the manuscript (see above the new introduction). Here is also the new version of the abstract: "It is now accepted that one of the important pathways of Secondary Organic Aerosol (SOA) formation occurs through aqueous phase chemistry in the atmosphere. However, the liquid phase chemical mechanisms leading to macromolecules are still not well understood. For α -dicarbonyl precursors, such as methylglyoxal and glyoxal, radical reactions through OH-oxidation produce oligomers, irreversibly and faster than condensation reactions in wet aerosol. Methyl vinyl ketone (MVK) was chosen in the present study as it is an α,β -unsaturated carbonyl that can undergo radical oligomerization in the liquid phase. We present here experiments on the aqueous phase OH-oxidation of MVK, performed under various conditions. Using NMR and UV absorption spectroscopy, high and ultra-high resolution mass spectrometry, we show that the fast formation of oligomers up to 1800 Da is due to radical oligomerization of MVK, and 13 series of oligomers (out of a total of 26 series) are identified. The influence of atmospherically relevant parameters such as temperature, initial concentrations of MVK

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and dissolved oxygen are presented and discussed. In agreement with the experimental observations, we propose a chemical mechanism of OH-oxidation of MVK in the aqueous phase that proceeds via radical oligomerization of MVK on the olefin part of the molecule. This mechanism highlights the paradoxical role of dissolved O₂: while it inhibits oligomerization reactions, it contributes to produce oligomerization initiator radicals, which rapidly consume O₂, thus leading to the dominance of oligomerization reactions after several minutes of reaction. These processes, together with the large ranges of initial concentrations investigated show the fundamental role that radical oligomerization processes likely play in atmospheric aqueous and liquid phase media.”.

Technical corrections:

p. 2921 line 10: What substance was used for the optimization of ESI conditions? MVK? Leucine enkephalin? Answer: The ESI source has been optimized directly with the sample. These parameters allow increasing the signal to noise ratio, keeping soft ionization technique.

p. 2921 line 14: What was the source of sodium? Answer: Sodium comes from labware (glassware). Sodium adduct formation commonly occurs in electrospray. The H⁺ concentration is much higher than Na⁺ concentration, but some molecules have a strong affinity for Na⁺. It depends in particular on the molecules' steric hindrance.

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). Answer: These changes have been done in the new version of the manuscript.

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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).

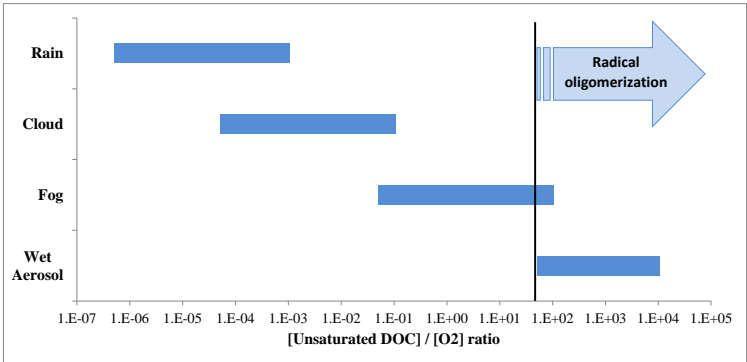


Fig. 1. Figure 12

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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	$10^6 \text{ molec cm}^{-3}$	10^{-13} M	10^{-12} M		10^{-11} M	
O_3 concentration	$1.23 \cdot 10^{-3} \text{ molec cm}^{-3}$ (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	2.5×10^{-3}
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 $k_{\text{oligo}} = 8 \times 10^{-4} \text{ s}^{-1}$; ^b Iraci et al., 1999; ^c Nozière et al., 2006.

Fig. 2. Table 3

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