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## ***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 C740: 'Review of the manuscript', Anonymous Referee #3, 23 Mar 2013

The authors appreciate many important comments raised by Reviewer 3 which have been considered in the new version of the manuscript. The authors' answers to the questions/comments of Reviewer 3 are presented below.

General comment

Question: Overall, this work is very well done and can be publishable. However, the  
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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.

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: 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 radicalradical oligomerization to produce high molecular weight products with aqueous-phase OH oxidation as an initiation step. This is particularly important for readers to build 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.

Answer: We agree on this and we have modified the introduction accordingly, here is

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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 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 :  $108 - 1 \mu\text{g m}^{-3}$ ), 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 and form more SOA than non-radical reactions. They conclude that in clouds/fog conditions (i.e. diluted concentrations of  $10^{-2} - 1 \text{ mM}$ ), radical reactions yield organic acids, whereas in wet aerosols (i.e. concentrated conditions of  $10 \text{ mM} - 10 \text{ M}$ ) they yield

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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 O<sub>2</sub> 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 O<sub>2</sub>. However, O<sub>2</sub> 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 O<sub>2</sub> concentrations on this chemistry using a slightly different precursor, i.e. methyl vinyl ketone. This compound is an  $\alpha,\beta$ -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 (C<sub>5</sub>-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 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

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(WSOC) concentrations of 0.01-1  $\mu\text{M}$  in rain drops, 1-100  $\mu\text{M}$  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  $\mu\text{M}$  in rain drops, 0.02-20  $\mu\text{M}$  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.”

Question: 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.

Answer: Alarifi, A. and Aouak, T.: Homopolymerization of benzylmethacrylate and methylvinylketone using Ni(acac)<sub>2</sub>–methylaluminumoxane catalyst system, Arabian Journal of Chemistry 2, 87– 93, 2009.

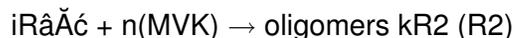
Ziaee, F., Bouhendi, H. and Ziaie, F.: NMR Study of Polyacrylamide Tacticity Synthesized by Precipitated Polymerization Method, I. Poly. J., 18 (12), 947-956, 2009.

Question: 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

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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?

Answer: We agree on these comments 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 O<sub>2</sub> under our experimental conditions. Each iR• radical underwent competition kinetics between O<sub>2</sub> addition (reaction R1) and oligomerization (reaction R2):



Supersaturated (by a factor of 155%) initial O<sub>2</sub> concentrations inhibited radical oligomerization by fast addition on iR• resulting in the formation of LMWC (such as acetic acid and methylglyoxal), which were further OH-oxidized and formed other iR• radicals. The fast O<sub>2</sub> addition reactions resulted in a fast decrease of O<sub>2</sub> concentrations in the vessel, faster than O<sub>2</sub> renewal from the gas phase and from the reactivity of H<sub>2</sub>O<sub>2</sub>, and even faster than MVK consumption. At initial MVK concentrations higher than 0.2 mM, the decrease of O<sub>2</sub> concentrations resulted in the dominance of reaction (2) after several minutes, and oligomerization started, even when O<sub>2</sub> concentrations were still higher than Henry’s law equilibrium with atmospheric O<sub>2</sub>. The paradoxical role of O<sub>2</sub> resides in the fact that while it intensely inhibits oligomerization, it produces more iR• radicals, which contribute to O<sub>2</sub> consumption, and thus lead to oligomerization. These processes, together with the large ranges of initial concentra-

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tions investigated (60 – 656  $\mu\text{M}$  of dissolved  $\text{O}_2$  and 0.2 – 20 mM of MVK concentrations) show the fundamental role that  $\text{O}_2$  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:  $v_{\text{R1}} = k_{\text{R1}} \times [\text{O}_2]$   $v_{\text{R2}} = k_{\text{R2}} \times [\text{MVK}]$ . The dominance of oligomerization over  $\text{O}_2$  addition is determined by  $v_{\text{R2}}/v_{\text{R1}} = k_{\text{R2}}/k_{\text{R1}} \times [\text{MVK}]/[\text{O}_2]$ . Assuming that the ratio  $k_{\text{R2}}/k_{\text{R1}}$  does not vary from the laboratory conditions to the atmospheric ones, one can simply predict the oligomerization to occur from the  $[\text{MVK}]/[\text{O}_2]$  ratio. In our experiments, the detailed study of the time profiles of  $\text{O}_2$  and MVK together with the kinetics of oligomer formation allowed us to determine that radical oligomerization dominates over  $\text{O}_2$  addition for  $[\text{MVK}]/[\text{O}_2]$  ratios (in M/M) equal or higher than 32 (at  $5^\circ\text{C}$ ) and 54 (at  $25^\circ\text{C}$ ). In atmospheric waters, assuming that dissolved  $\text{O}_2$  concentrations are saturated (i.e. at Henry's Law equilibrium) everywhere from 0 to 5 km in altitude, and from  $-20$  to  $+25^\circ\text{C}$ , gives a range of 190–391  $\mu\text{M}$  for  $[\text{O}_2]$ . Furthermore, taking the concentrations of unsaturated organic compounds ( $[\text{UNS}]$ ) in atmospheric waters as stated in the introduction, one obtains  $[\text{UNS}]/[\text{O}_2]$  ratios as indicated in Fig. 12 (Ervens et al., 2012). In this figure, radical oligomerization occurs when  $[\text{UNS}]/[\text{O}_2]$  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  $[\text{UNS}] > 6$  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  $k_{\text{oligo}} = 7.6 (\pm 0.3) \times 10^{-4} \text{ s}^{-1}$ , (which is not temperature dependent between 5 and  $25^\circ\text{C}$ ) as derived in the present work from the MVK decay during oligomerization, under all conditions (figures

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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<sub>2</sub> or γ-Al<sub>2</sub>O<sub>3</sub> particles under various relative humidity ( $\bar{RH} = 10^{-10}$  to  $10^{-9}$ , Shen et al., 2013) calculated for a number of 100 nm particles of 5000 particles cm<sup>-3</sup>, 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<sup>-1</sup>) in atmospheric waters. The straight lines delimit the values for which radical oligomerization dominates over O<sub>2</sub> addition, as determined by the present work (see text).

Table 3: Comparison of MVK atmospheric lifetimes between its gas phase reactivity

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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.

Minor comments:

Page 2918, line 19-20: Please briefly describe the method used for H<sub>2</sub>O<sub>2</sub> detection.

Answer: We used UPLC-UV at 265nm for H<sub>2</sub>O<sub>2</sub> detection.

Table 1: I am wondering if the dissolved oxygen concentration without H<sub>2</sub>O<sub>2</sub> was measured. This can confirm the supersaturation of dissolved oxygen.

Answer: Dissolved oxygen concentrations were continuously monitored in the solution before, during and after H<sub>2</sub>O<sub>2</sub> introduction. This is visible on Figure 9, where one can see that O<sub>2</sub> was saturated prior to H<sub>2</sub>O<sub>2</sub> introduction. Just after H<sub>2</sub>O<sub>2</sub> introduction, dissolved O<sub>2</sub> concentrations increased and reached a supersaturation concentration, certainly due to the following reactions:  $\text{H}_2\text{O}_2 + \text{HO} \cdot \rightarrow \text{HO}_2 \cdot + \text{H}_2\text{O}$   $\text{HO}_2 \cdot + \text{HO}_2 \cdot \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$   $\text{HO}_2 \cdot + \cdot \text{O}_2 \text{ (} +\text{H} \cdot \text{)} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$  Then, when MVK was introduced, dissolved O<sub>2</sub> concentrations decreased due to addition on alkyl radicals. All this is explained in the manuscript (sections 2.2.3 and 3.3.2).

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

Answer: This paragraph was rewritten to avoid duplicate information.

Figure 9: In order to visualize the delay of oligomer formation in the case of high dissolved O<sub>2</sub> concentration, it is recommended to add the time series profile of total signal from oligomers in Figure 9a-c.

Answer: These changes have been done in the new version of Fig. 9

Page 2933, line 11: Perhaps typos. “: : :Supplement 2: : :”

Answer: The typo concerned the reaction number (R7 instead of R2). The sentence

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has been replaced the following one: this method of identification, applied to the synthetic oligomers of MVK formed from the V-50 initiator, allowed us to identify the most intense series of oligomers as the one shown in reaction 2 R7 (in Supplementary Information 2), thus showing the robustness of the method.

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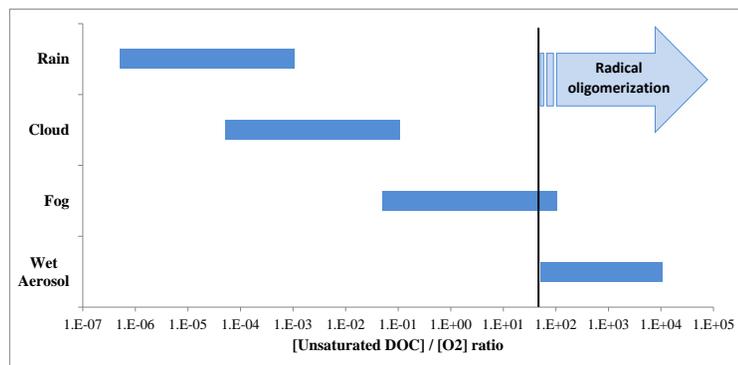
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**Fig. 12:** Estimated ranges of the ratios of unsaturated dissolved organic carbon concentration to oxygen concentration (in  $M M^{-1}$ ) in atmospheric waters. The straight lines delimit the values for which radical oligomerization dominates over  $O_2$  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  $k_{\text{oligo}}$  values derived from our experimental results.

	gas	cloud	fog		aerosol	
OH concentration	$10^7$ molec $\text{cm}^{-3}$	$10^{13}$ M	$10^{12}$ M		$10^{11}$ M	
$\text{O}_3$ concentration	$1.23 \cdot 10^{17}$ molec $\text{cm}^{-3}$ (50 ppbV)	-	-		-	
Radical oligomerization reactions	No	No	Yes <sup>a</sup>		Yes <sup>a</sup>	
Henry's Law constant ( $\text{M atm}^{-1}$ )	-	$41^b$	$41^b$		$7100^c$	
LWC ( $\text{g m}^{-3}$ )	-	5	1	0.4	0.1	$2.5 \times 10^{-3}$
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%

<sup>a</sup>  $k_{\text{oligo}} = 8 \times 10^{-4} \text{ s}^{-1}$ ; <sup>b</sup> Iraci et al., 1999; <sup>c</sup> Nozière et al., 2006.

Fig. 2. Table 3

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