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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.

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RC C798: 'Interactive comment', Sarah Green, 26 Mar 2013

The authors appreciate important comments raised by Sarah Green, they have been considered in the new version of the manuscript. The authors' answers to the questions/comments of Sarah Green are presented below. General comments

Question: Oxygen concentrations were manipulated by changes in temperature to change the saturation concentration or by purging with argon. O2 was assumed (or

measured?) to become supersaturated with the decomposition of H2O2.

Answer: Dissolved oxygen concentrations were continuously monitored in the solution; before, during and after H2O2 introduction. This is visible on Figure 9, where one can see that O2 was saturated prior to H2O2 introduction. Just after H2O2 introduction, dissolved O2 concentrations increased and reached a supersaturation concentration, certainly due to the following reactions:

H2O2 + HO = HO2 + H2O

HO2 + HO2 = H2O2 + O2

HO2 + O2- (+H+) = H2O2 + O2

Then, when MVK was introduced, dissolved O2 concentrations decreased due to addition on alkyl radicals. All this is explained in the manuscript (sections 2.2.3 and 3.3.2)

Question: The relevance to atmospheric processes should be clarified. The concentrations of MVK used (0.2-20 mM) are extraordinarily high (which explains how NMR analysis was possible!). As has been pointed out in other comments, oxygen is likely to be near equilibrium in atmospheric aqueous phases. However, I presume that at higher altitudes O2 partial pressures are lower, and so aqueous levels would be proportionally lower as well. I am not expert enough in this area to assess the effects of altitude or the balance between decreasing pressure and the competing fact that lower T increases O2 solubility.

Answer: The variability of dissolved O2 concentrations is an excellent idea, which was used in our new conclusions where we investigated the range of possible O2 concentrations over -20 to +25° and 0 to 5 km altitude (see below). We have modified the introduction and the conclusions according to these comments, those from Yi Tan, and those from the reviewers.

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 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 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 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 or-

ganic 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 iR radical underwent competition kinetics between O2 addition (reaction R1) and oligomerization (reaction R2):

iR + O2 $\rightarrow$ LMWC kR1 (R1)

iR + n(MVK) $\rightarrow$ oligomers kR2 (R2)

Supersaturated (by a factor of 155%) initial O2 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 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 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: vR1 = kR1 $\times$ [iR] $\times$ [O2] vR2 = kR2 $\times$ [iR] $\times$ [MVK] The dominance of oligomerization over O2 addition is determined by vR2/vR1 =kR2/kR1$\times$[MVK]/[O2] . Assuming that the ratio kR2/kR1 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.

Question: While the experimental MVK concentrations are very high relative to atmospheric conditions, the time scales are very short. To what degree would very long reaction times at lower MVK levels give similar outcomes? Can some of the intermediates (e.g. alkyl peroxides) in Fig. 10 act as reservoirs for continuing radical chain reactions even at much lower initial reactant concentrations?

Answer: Aerosol lifetime is several days, but oligomers lifetimes are probably shorter (it is currently being investigated). As shown in the paper, high initial concentrations of unsaturated compounds are necessary for radical addition to the C=C bond, to compete with O2 addition. Nevertheless, we agree with the fact that some species (such as the long lived RO2 radicals, or hydroperoxides which are well known atmospheric radical reservoirs) act probably as reservoirs for continuing radical chain reactions when they encounter high concentrations of unsaturated compounds.

Question: Fig 8b is interesting, showing that in at least one aspect the effect of initial low O2 concentrations does not affect the products obtained after 50 minutes. Answer: Yes, this observation can be explained by the fact that O2 has depleted at the same level at the end of both experiments, and the reaction advancement (i.e. amount of consumed MVK) is also similar in both experiments.

Specific comments

p. 2918, line 16: I'm surprised to see a Pyrex flask used. Pyrex light transmission drops off below about 330 nm where the H2O2 absorbance band starts. Obviously this worked, since the H2O2 was effectively photolyzed.

Answer: Pyrex light transmission is sufficient to photolyse H2O2. Indeed, we determined photolysis rate constant J ($8.5\times10-6$ s-1). Under these conditions, we esti-

mated HOâĂć concentrations to approximately 4.3×10−14 M, which fall in the range of the estimated values for cloud droplets to deliquesced aerosol particles conditions by models (Herrmann et al., 2010; Ervens and Volkamer, 2010).

p. 2929, line 8 (and elsewhere). I assume "external" refers to the beta-carbon and "internal" means the alfa-C. I would assume that beta-addition would be greatly favored because resonance with the carbonyl gives it a stronger positive character.

Answer: The terms "external" and "internal" additions have been replaced by ïĄć- and ïĄą-additions respectively, and the argument for showing only ïĄć-additions have also been added in the new version of the manuscript.

p. 2918, lines 8-9. I assume "photostationary conditions" refers to HO2âĂć and HOâĂć concentrations. Correct? The HO2âĂć loss rate should be quite sensitive to pH (rxn R4, S1), so its concentration is expected to decrease rapidly as the pH drops from 6 to 3 (Fig 5).

Answer: Yes, "photostationary conditions" refers to HO2âĂć and HOâĂć concentrations. However, pH does not vary during the 10 min awaited prior to MVK introduction. After MVK introduction, pH decreases from 6 to 3, so this should decrease the reactivity of hydroperoxyl radicals as HO2âĂć are less reactive than âĂćO2- radicals, and their pKa is 4.8. As a consequence, their concentrations should increase; but on the same time, their source (H2O2 + OH) is dominated by the reaction MVK + OH. It is thus difficult to predict accurately the variations of these radical concentrations without a model.

p. 2919, line 13: Was O2 also measured with the Consort analyzer that was used for pH? Not clear.

Answer: Absolutely. Temperature, pH, and dissolved O2 were continuously monitored using a Consort C3020 multi-parameter analyzer. This was modified in the new version of the manuscript.

p. 2928, line 21: The formation of an oligomer containing a terminal vinyl group means there is an opportunity for additional radical reactions. Is that important for atmospheric timescales?

Answer: Yes, this means some of the oligomers themselves are still highly reactive. The study of their aging under atmospheric conditions is thus of high interest. This work is currently being done as mentioned in the new conclusions (Siekmann et al., in preparation).

Technical corrections

p. 2915, line 10: under atmospheric relevant conditions. –> under atmospherically relevant conditions. Done

p 2916, line 16: HULIS is not defined before use. Done: HUmic-LIke Substances (HULIS)

p. 2917, line 1: mechanisms Done

p. 2917, line 20: "more intense (less than an order of magnitude)" is confusing.

Answer: We replaced this by “approximately twice more intense” (see comments on Figure A)

p. 2920, line 6: "to evidence" -> "to demonstrate" Done

p. 2920, line 12: organics -> organic Done

p. 2951, Fig. 8: MVK concentration not indicated. Done

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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).

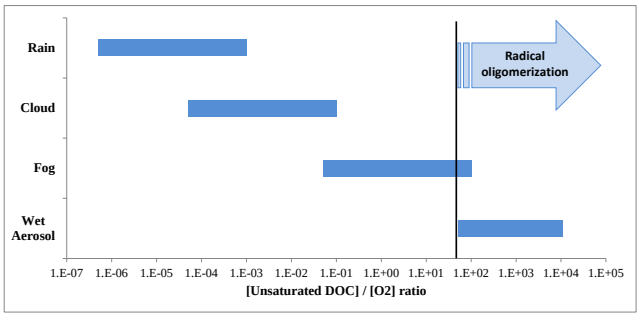

Fig. 1. Figure 12

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	2.5×10^{-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] $k_{oligo} = 8 \times 10^{-4}\ s^{-1}$; [b] Iraci et al., 1999; [c] Nozière et al., 2006.

Fig. 2. Table 3