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Interactive comment on “Aqueous phase oligomerization of methyl vinyl ketone through photooxidation – Part 1: Aging processes of oligomers” by P. Renard et al.

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Received and published: 24 November 2014

Interactive comment on “Aqueous phase oligomerization of methyl vinyl ketone through photooxidation – Part 1: Aging processes of oligomers” by P. Renard et al.

RC C4228: 'Review of Renard et al.', Anonymous Referee #1, 27 Jun 2014

The authors appreciate the 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:

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Question 1 In SOA formation and aging there is competition between oligomerization and oxidation into smaller/volatile species. The discussion of the latter process is missing in the introduction as there is nearly exclusive discussion of oligomerization. So this should be enhanced by mentioning also the generation of volatile species.

Answer We modified the introduction in order to consider this comment, it now reads:

“ In particular, Renard et al. (2013) showed that $\text{HO}\ddot{\text{C}}\text{OH}$ oxidation of MVK in the aqueous phase proceeds via a radical mechanism leading to oligomers which molecular masses increase (up to m/z 1200) with the precursor initial concentration from 2 to 20 mM. At lower precursor initial concentrations (e.g. 0.2 mM of MVK), Renard et al. (2013) observed lower weight molecular compounds (up to m/z 300), and Zhang et al., (2010) observed the formation of small oxidized compounds (such as acetic, formic, pyruvic acids, methylglyoxal, formaldehyde), thus suggesting a competition between functionalization and oligomerization at these low initial concentrations.” (. . .) “The aim of the present study is to investigate the aging of the oligomers formed through aqueous phase photooxidation of MVK. We determine the SOA chemical composition during the formation and aging of the aqueous phase oligomers and we revisit the corresponding SOA mass yields. A large range of initial precursor concentrations (from 0.2 to 20 mM) is investigated in order to study the competition between functionalization and oligomerization.”

Question 2 In terms of atmospheric relevance, the authors mention wet aerosols and polluted fogs. The concentrations tested here for MVK are in the mM range. Observations in fogs and clouds tend to be in the μM range for the most abundant carbonyls found, so that relevance should be more discussed. The present results appear to suggest (as other studies) that oligomerization does not actually occur in cloud or fog droplets but only in “wet aerosol” where sufficiently high concentrations can be achieved. In regards to the concentrations used, it would be interesting if the authors would discuss how these compare to the solubility/volatility of MVK and hence the possibility of MVK losses to the gas phase in their experiments and in actual cloud/aerosol

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situations.

Answer: In the comparison between our experimental concentrations with atmospheric ones, MVK is considered a proxy for unsaturated water soluble organic compounds (UWSOC). We modified the text accordingly, it now reads: - In the experimental section: “Tan et al. (2010) and Renard et al. (2013) have shown the important impact of initial precursor concentrations on oligomer formation. The experiments were thus carried out with various MVK initial concentrations (Table 1), i.e., 0.2, 0.5, 2, 5 and 20 mM (corresponding to 9.6 to 960 mgC L⁻¹). Considering MVK as a proxy for UWSOC, this concentration range is comprised in the range of the estimated total UWSOC concentrations from fog droplets to wet aerosol (Renard et al., 2013). The 50 cm³ gas phase head space of the photoreactor was opened to ambient air for a few seconds during each sampling. We verified in control experiments that this procedure induced insignificant losses of MVK from the solution”

- In the section “atmospheric implications”: “Among the atmospherically relevant alkenoic alcohols, acids, ketones and aldehydes (i.e. UWSOC), although MVK is one of the most abundant species, it is one of the most volatile ($P_{\text{sat}} = 10^{-5} - 0.1$ atm, with $P_{\text{sat}}(\text{MVK}) = 0.1$ atm at 25°C; Asher and Pankow 2006), and one of the least soluble compounds ($K_{\text{H}} = 1 - 10^3$ M atm⁻¹, with $K_{\text{H}}(\text{MVK}) = 41$ M atm⁻¹ at 25°C; Iraci et al., 1999). The atmospheric impacts of the processes shown here should thus be very limited for MVK alone. However, the oligomerization mechanism undergone by MVK occurs via saturation of the vinyl group (Renard et al., 2013), and the resulting radical monomer is stabilized by the resonance effect with the adjacent carbonyl group thus decreasing the enthalpy of polymerization facilitating the oligomerization in the aqueous phase compared to other molecules. More generally, conjugation of the C=C with substituents such as the benzene ring (styrene and α -methylstyrene), and alkene double bond (butadiene and isoprene), the carbonyl linkage (acrylic acid, methyl acrylate, methyl methacrylate), and the nitrile group (acrylonitrile) similarly leads to stabilization of the monomer and decreases enthalpies of polymerization (O'dian 2004). It is thus

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likely that a large number of atmospherically relevant molecules can follow the same process either in the bulk or at the wet aerosol interface (Kameel et al., 2013; Kameel et al., 2014). In this context, our results suggest that this class of compounds can impact the aerosol composition, and contribute to aqSOA formation upon water evaporation. The corresponding aqSOA mass yields seem to depend on the spectral irradiance of the light used to initiate the photochemistry, but further studies are needed to confirm this point. Finally, the aging of the oligomers formed could be an explanation (at least in part) for the presence the diacids (such as oxalic, malonic and succinic acids) observed in the ambient aerosol (Legrand et al., 2007; Kawamura et al., 2010). In Part 2 of this study, the atmospheric relevance of these processes is explored by means of multiphase box model studies.”

Question 3a The manuscript should be able to stand-alone and can be. So please no reference to Renard et al in the abstract (references in abstracts are not common).

Answer: The abstract was modified according to the reviewer’s comment as well as those of other reviewers, it now reads: “It has recently been established that unsaturated water soluble organic compounds (UWSOC) might efficiently form oligomers in polluted fogs and wet aerosol particles, even for weakly soluble ones like methyl vinyl ketone (MVK). The atmospheric relevance of these processes is explored by means of multiphase process model studies (in a companion paper). In the present study, we investigate the aging of these aqueous phase MVK-oligomers formed via OH-oxidation, as well as their ability to form secondary organic aerosol (SOA) upon water evaporation. The comparison between aqueous phase composition and aerosol composition after nebulization of the corresponding solutions shows similar trends for oligomer formation and aging. The measurements reveal that oligomer aging leads to the formation of organic diacids. Quantification of the SOA mass formed after nebulization is performed, and the obtained SOA mass yields seem to depend on the spectral irradiance of the light used to initiate the photochemistry. Investigating a large range of initial MVK concentrations (0.2 – 20 mM), the results show that its α -OH-oxidation under-

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goes competition between functionalization and oligomerization that is dependent on the precursor concentration. At high initial MVK concentrations ($\geq 2\text{mM}$), oligomerization prevails over functionalization, while at lower initial concentrations, oligomerization is not the major process, and functionalization dominates, resulting in small carbonyls, dicarbonyls and monoacids. The atmospheric implications of these processes are discussed.”

Question 3b: Then in your discussion, please present first your results and then discuss them relative to your group’s earlier work and not start by saying e.g. 15292L16 “In good agreement with our previous results (Renard et al., 2013), after 5 min of reaction (experiment B),”: Please first your results, then comparisons otherwise the text does not stand on its own.

Answer: The text has been modified according to this comment, it now reads:

“During experiment B (i.e. $[\text{MVK}]_0 = 5\text{mM}$), after 5 minutes of reaction, no significant formation of high molecular weight compounds (HMWC) was observed (Figure 2b), whereas after 10 minutes of reaction, mass spectra show that oligomer systems were formed on the whole range of the investigated m/z (50-1200), with a regular pattern of 70.042 amu, which corresponds to the exact mass of MVK. At 50 minutes of reaction, the maximum of oligomerization was reached (Figure 2c). At this time, we observed several series of MVK-oligomers, corresponding to several initiator radicals identified by Renard et al. (2013) under the same conditions.”

Question 4 The lamp characterization is excessively vague in the experimental section and then in the comparison with Liu. As this seems to matter please provide the actual values you measured as you use a 1000W lamp you get only twice ambient irradiation when many investigators (including Liu et al., 2012) use 300W lamps to get ambient irradiation fluxes. The irradiation and its realism should also be mentioned in the section on atmospheric relevance

Answer: The different irradiation Xe lamp intensities used: 300 W in Liu et al. (2012),

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and 1000 W in the present study, have been measured using a spectroradiometer (SR-501, LOT-Oriel). The same spectroradiometer has been used to measure the direct solar irradiance intensity at sea level, for a 48.3° zenith angle and is given as a comparison and these data are now shown in Figure S1.

We modified the text to be more precise on the lamp spectral irradiance: - In the experimental section: “The photoreactor set-up used was based on the one described by Renard et al., (2013). It was a 450 cm³ Pyrex thermostated photoreactor, equipped with a 1000 Watt Xenon arc lamp (LOT-Oriel, LSH 601) and a glass filter (ASTM 490 AM 0). The resulting spectral irradiance into the reactor is compared to that of the sun at sea level for a 48.3° zenith angle in Figure S1.”

- in section 3.2.3: “The different yields obtained here as compared to the study by Liu et al. (2012) may be due to the different irradiation Xe lamp used: 300 W (with a pyrex filter) in Liu et al. (2012), and 1000 W (with a ASTM 490 AM 0 filter) in the present study. The influence of the lamp spectra on SOA mass yields of other systems (gas phase photooxidation of biogenic and anthropogenic precursors) have been previously observed in atmospheric simulation chambers (Bregonzio-Rozier et al., 2014). We verified, using a spectroradiometer (SR-501, LOT-Oriel), that the spectral irradiance of the 300W and the 1000W Xe lamps at $\lambda \geq 400$ nm represent respectively half and twice the solar irradiance intensity at sea level, for a 48.3° zenith angle (Figure S1). Due to the high variability of the irradiance in the atmosphere at $\lambda \geq 400$ nm (as shown by the Tropospheric Ultraviolet and Visible Radiation Model http://cprm.acd.ucar.edu/Models/TUV/Interactive_TUV/), both lamps can be seen as representative of the natural irradiance in this wavelength range. However at 300 nm, the spectral irradiance of the 1000W Xe lamp is 7 and 9 times higher than that of the direct solar irradiance (for a 48.3° zenith angle) and the 300W Xe lamp respectively (Figure S1). This part of the spectrum is essential for photochemistry, and may induce different photochemical processes: we verified that we observed the same series of oligomers as in Liu et al. (2012), but with different relative intensities. The different

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spectral irradiance of the lights used at 300 nm may be the reason for the different yields obtained, but it needs to be confirmed by a thorough study of the influence of the spectral irradiance (in the UV) on the oligomer mass yields.”

Details:

Question 5: Abstract and text: Not everybody is familiar with AMS language, OOA etc: : : would need to be explained at first use, not only later on in the discussion. You use the terms in the abstract and you don't define but you define UWSOC but do not use the abbreviation in the abstract.

Answer: This remark was taken into account: see the new abstract reported in our answer to question 3.

Question 6: The experimental section looks a little sloppy. Please homogenize language and explanations. In some instances instruments are mentioned without the manufacturer, while others have manufacturer and location given in parentheses. Idem for the chemicals used.

Answer: Done

Question 7: 15289L13 shouldn't deprotonated molecules be $[M]^-$ or $[M(-H)]^+$ or something different as it looks too similar to $[M-H]^+$.

Answer: We used the IUPAC (2013) recommendations (Murray et al., 2013): $[M+H]^+$ for protonated molecules $[M - H]^+$ for deprotonated molecules

Question 8: Some text is bizarre in regard to how numbers/ranges are presented: “A yield of 595% (in mass) was obtained with this method at 90 min of reaction, thus statistically similar from the one obtained by the nebulizing method (750 %) at t_{max} .” 7 +-50%? I assume it is 50+-7%?

Answer: Yes, this was a typo that was corrected in the new version of the manuscript

Question 9: 15298L24 again bizarre, please write “50-120%” not 120-50%

Answer: Done

Question 10: 15295 first paragraph: use the same notation in the explanation of the terms than in the formula and in the next lines C/O not C:O

Answer: Done

Question 11: 15294L9 for the non AMS community it would be good to explain or mention what the correction factors are used for? Please explain its reason of being.

Answer: The AMS collection efficiencies (CE) were investigated by comparing AMS to SMPS measurements. The AMS collection efficiency represents the efficiency with which particles are transmitted through the aerodynamic lens system and the particle time-of-flight (PToF) chamber, as well as the bouncing effect on the vaporizer surface (Huffman et al., 2005, Docherty et al., 2013; Miyakawa et al., 2013). In addition to these effects, it is possible that our low CE values (compared to chamber studies or ambient aerosols) were also due to the particle size range (50 nm - 150 nm mass distribution), as the lowest part of this size range corresponds to the region where the AMS transmission curve varies greatly (Liu et al., 2007). This effect is confirmed by the fact that our lowest values for CE (0.07) were obtained for the lowest MVK initial concentrations (0.2 – 2 mM) where the smallest particles were formed (50 nm mass distribution). The text was modified, it now reads:

“Note that the overall collection efficiencies (CE) of the AMS in our experiments varied from 0.07 to 0.21 (related to the SMPS signal). These low CE values (compared to chamber studies or ambient aerosols) can be due to particle bounce at the vaporizer surface before volatilization and to the shape and size-dependent transmission of the aerodynamic lens. As a result, the studied compounds did not volatilize sufficiently fast at standard AMS vaporizer temperatures to be fully detected (Liu et al., 2007; Docherty et al., 2013; Miyakawa et al., 2013). In addition to these effects, it is possible that our low CE values were also due to the particle size range (50 nm - 150 nm mass distribution), as the lowest part of this size range corresponds to the region where the

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AMS transmission curve varies greatly (Liu et al., 2007). This effect is confirmed by the fact that our lowest values for CE (0.07) were obtained for the lowest MVK initial concentrations (0.2 – 2 mM) where the smallest particles were formed (50 nm mass distribution).”

Language:

The manuscript could benefit from English editing.

Answer: Done

Figures: Figure 1: panels b,c and d do not have the same scale so I see no reason why to have panel b with a scale such that one can hardly see the mass spectrum. Idem panel d. the small peaks would only make sense if all panels had same scale on the y axis Panel c: hard to see the underlying spectrum with the red over it. Why not prepare a figure like figure 4 or stagger the spectra. Figure 3: the panels and legends are very small and will end up being hard to read Figure 5: legend of 5a partly covered by fig 5b Figure 5: are the units on y axis right? Figure 6: show MVK consumed in % or mention in the legend how much MVK was present initially? 5mM?

Answer: All these modifications were done in the new version of the manuscript In figure 5 the units on Y axis are right.

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Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/14/C9497/2014/acpd-14-C9497-2014-supplement.pdf>

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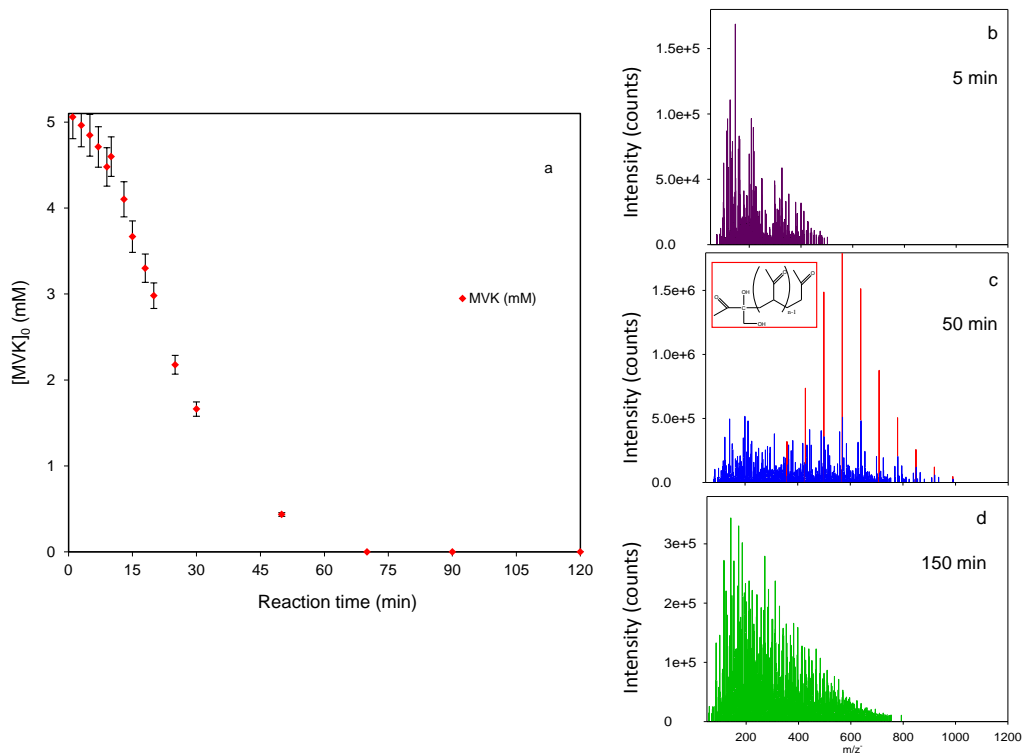


Fig. 1. Figure 2: (a): Time profiles of MVK concentrations during the reaction (experiment B); and the corresponding evolution of ESI-MS- spectra for m/z 50 - 1200 at (b): 5 min, (c): 50 min and (d): 150 min.

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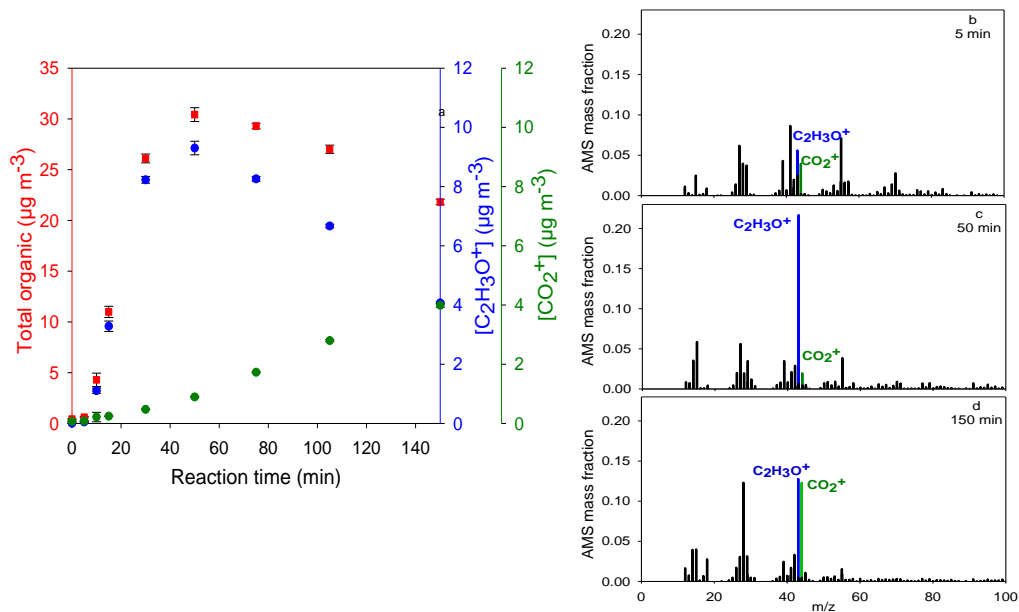
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Fig. 2. Figure 3: Time profiles of the HR-ToF-AMS total organic mass (red), ion fragments $C_2H_3O^+$ at m/z 43 (blue) and CO_2^+ m/z 44 (green) for nebulized solutions from experiment B (a), and the corresponding

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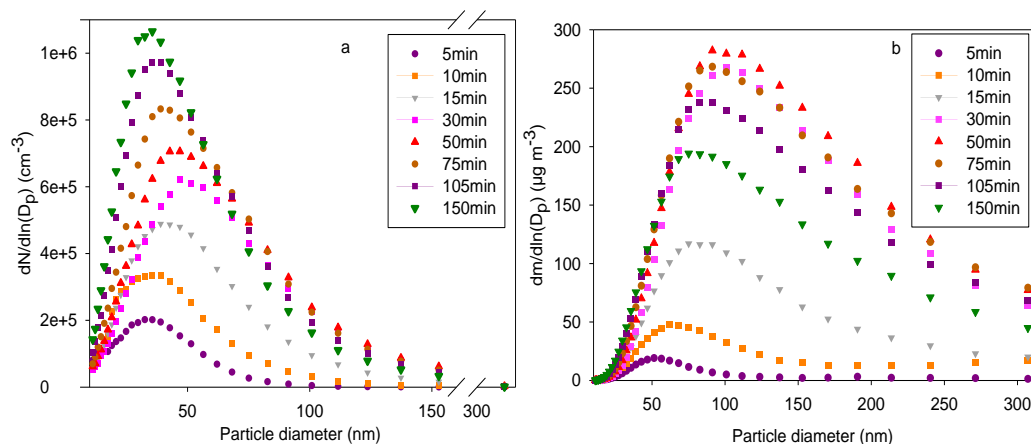
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Fig. 3. Figure 5: Evolution of particle number (a) and mass (b) size distributions for nebulized solutions sampled at different reaction times for experiment B, measured by means of SMPS. The standard deviat

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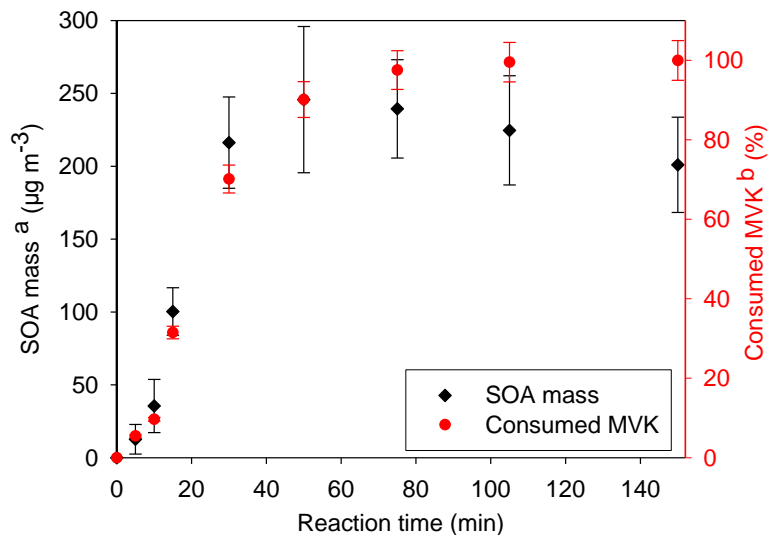


Fig. 4. Figure 6: Time profiles of the total aerosol mass (black diamonds) from the nebulized solutions, and consumed MVK in the aqueous phase (red circles) for experiment B. a Values represent averages of th

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