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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.

P. Renard et al.

pascal.renard@etu.univ-amu.fr

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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.

RC C4779: ‘Review of Renard et al.’, Anonymous Referee #3, 13 Jul 2014 Printer-friendly Version

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.

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Question 1: Overall, the writing quality is not strong. As examples:

i. An Abstract should be a clear, succinct description of the experiments and results, and so the first paragraph should be removed.

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 undergoes a kinetic competition between functionalization and oligomerization that is dependent on the precursor concentration. At high initial MVK concentrations (≥ 2 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.”

ii. The Results section simply lists the results one after the other, without connecting one section to the others, i.e. helping the reader to better understand the work,

Answer: The manuscript has been modified according to this comment: each part of

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the results has been introduced by a small paragraph.

iii. The Discussion section starts immediately with some highly detailed discussion without codifying the overall results from the study.

Answer: The manuscript has been modified according to this comment:

- The discussion section is now introduced by the following paragraph: “This section discusses the results obtained on the aging of the reaction products of MVK- $\dot{\text{A}}\text{C}\text{OH}$ experiments and the related oxidation processes by two relevant ways. First, the competition between functionalization and oligomerization and the subsequent aging according to the initial concentration of MVK is discussed; and second, a Van Krevelen diagram (i.e, H/C vs O/C ratios) of the obtained SOA is presented and compared to previous studies.”

- Section 4.1 is now introduced by the following paragraph: “In order to compare our work with the aging of organic aerosol in the atmosphere compiled by Ng et al. (2010), we used the AMS data, and in particular, the development of the two dominant fragments, m/z 44 (CO_2^+) and m/z 43 (mostly $\text{C}_2\text{H}_3\text{O}^+$), observed in our study. More precisely, we focused on the ratio of m/z 44 and m/z 43 to total organic aerosol, f44 and f43, respectively.”

iv. The Figures have too small labels and axis values.

Answer: The labels and axis values have been enlarged in the new version of the manuscript.

References: Please check that all relevant studies related to oligomerization have been included. For example, the work of Aljawhary et al., AMT, 2013 describes the loss, presumably by OH oxidation, of SOA oligomers in solution.

Answer: This reference was added as well as other recent works on radical oligomerisation, such as Kameel et al. (2013); Kameel et al. (2014); Daumit et al. (2014); Tan et al. (2012); Zhao et al., (2012).

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Question 2: The authors need to address how the sensitivity of ESI to different classes of compounds affects their results. For example, in Figure 2 how much of the change in shape of the spectrum is due to the formation of polyacids that are detected easily by ESI, when starting with a precursor that does not contain an acid functionality? Are oligomers detected as efficiently as the monomers?

Answer: The ESI source used in this study is designed to operate with UPLC which requires very high column pressure (~ 104 PSI), and thus necessitates, in the ESI, high flows of desolvation gas (N_2 at 800 L h^{-1}). As a result, most of the small and/or volatile molecules are lost prior entering the mass spectrometer. For example, the instrument can barely detect MVK, oxalic and pyruvic acids (m/z 71+ 89- and 87-, respectively). Conversely, a higher signal is obtained for larger molecules, identified as MVK-oligomers (Figure 2), by means of the UPLC-ESI-MS used in its resolution mode, up to 18,000 FWHM (Full width at half maximum) at m/z 400. As a result, it is likely that oligomers are detected more efficiently than monomers, which in turn are detected more efficiently than MVK, or small carboxylic acids, but the instrument was not used for quantification. This is the reason why we have performed UHPLC-UV and ion chromatography analyses of the solutions to specifically quantify MVK, H_2O_2 and the formed carboxylic acids.

The manuscript has been modified to clarify this point, as follows: An introduction has been added to section 2.2, it reads:

“Aliquots of the solution sampled from the photoreactor were analyzed for qualitative structure elucidation of the oligomers using ultra-performance liquid chromatography mass spectrometry (UPLC-ESI-MS); and for quantitative studies of the concentrations of i) MVK and H_2O_2 by liquid chromatography coupled to UV detection (UHPLC-UV), iii) carboxylic acids by ion chromatography-mass spectrometry (IC-ESI-MS), and iv) oligomers using preparative liquid chromatography associated to total organic carbon (TOC) analyses.”

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in section 2.1.1, “The mass spectrometer was used in its resolution mode (V-mode), up to 18,000 FWHM (Full width at half maximum) at m/z 400. The mass accuracy was < 5 ppm, and allowed for the determination of elemental composition of organic species (Renard et al., 2013 and Renard et al., 2014), using the I-FIT software. The I-FIT isotope predictive filtering is a strategy to reduce the number of proposed elemental compositions using algorithms to estimate the number of carbon, oxygen (or sulfur) atoms in an unknown molecule based on the mass of the molecular ion and the relative intensity of the 1st and 2nd isotopes (Hobby, 2005).”

Question 3: For the AMS spectra in Figure 3, has high resolution mass fitting identified the composition of the different ions labelled? For example, m/z 43 may have multiple elemental compositions.

Answer: For the analysis of the AMS spectra and identification of the respective ions, we used the high resolution V-mode (up to 2000 at m/z 200). Using this mode with the adapted software PIKA 1.10H for data treatment, we can clearly distinguish between $C_2H_3O^+$ and $C_3H_7^+$ ions at m/z 43. Other ions were not observed at this mass in our experiments. The blue bar in Figure 3 only represents $C_2H_3O^+$ ions. The manuscript has been modified to clarify this point in section 3.1.2, as follows:

“The AMS mass spectra (Figure 3) show two dominant fragments, at m/z 43 and m/z 44 (corresponding to $C_2H_3O^+$ and CO_2^+ fragments).”

Question 4: When quantitatively comparing data at different times in the reaction (e.g. AMS data in Figure 4), how is it known that the nebulizer output is constant from one time to the other? Nebulizer outputs are affected by the surface tension and volatility of the solution being atomized. Indeed, the numbers of particles being formed is changing dramatically during the experiment as shown by the SMPS scans in Figure 5. Why is that occurring, for a “constant output” TSI atomizer? How does this affect the interpretation of the results? Should the authors normalize all their aerosol results to the changing number output of the atomizer? Please clarify.

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Question 5: As a related question, if the number output of the atomizer is changing I don't understand how a yield can be quantified. For example, if the number of particles being produced by the atomizer is lower at the beginning of the experiment than at the end, then the yield (using equation 2) will be calculated to be lower. This does not reflect changing chemistry, only the changing efficiency of atomization. Unless I am incorrect, this will make the stated yields invalid.

Answer (4 and 5): - The AMS mass spectra presented in Figure 4 show normalized signals, i.e. signal intensity contribution of each fragment to the total signal, (AMS-mass fractions). Therefore only a qualitative comparison is performed in this figure, showing that the spectrum contains more fragments in the mass range m/z 100-200 at 50 min than at 150 min of reaction. In the new version of the manuscript, we replaced "normalized AMS-signal" by "AMS mass fraction" in Figures 3 and 4, and we explained the term in the captions: "The AMS-mass fraction is the signal intensity contribution of each fragment to the total signal."

- Calibration experiments of our set up were performed using aqueous solutions of three different compounds (NaCl, NH_4NO_3 , and succinic acid) at various concentrations covering those of the consumed MVK during its reaction (Table S1). In these calibration experiments, for each compound, the obtained numbers of particles increase with increasing solution concentrations, and the corresponding total particle mass increases linearly with the solution concentration. This result is used to evaluate the transmission efficiency of our set up. Assuming a similar behavior for the nebulized MVK-oligomers up to t_{max} (i.e. increasing oligomer concentrations with reaction time, assuming no major change in the oligomer composition), the calibration experiments are used to determine the SOA mass yields according to equations 2 and 3 of the new version of the manuscript. However, this protocol induces very large uncertainties (e.g. $\text{YSOA} = 70 (\pm 50)\%$ at 105 minutes of reaction in exp A). A different experimental protocol, that does not use the nebulizer, has been developed (i.e. preparative chromatography followed by TOC analysis, as described in sections 2.2.4 and 3.2.3) to

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determine the SOA mass yield, and confirm the obtained numbers with narrower uncertainties ($YSOA = 59 (\pm 5)\%$ at 90 minutes of reaction in exp A). All these precisions have been added in supplementary information 1, it now reads:

“Calibration experiments of our set up were performed using aqueous solutions of three different compounds (NaCl, NH_4NO_3 , and succinic acid) at various concentrations covering those of the consumed MVK during its reaction (Table S1). In these calibration experiments, for each compound, the obtained numbers of particles increase with increasing solution concentrations, and the corresponding total particle mass (using the corresponding densities) increases linearly with the solution concentration. This result was used to evaluate the transmission efficiency of our set up. Assuming a similar behavior for the nebulized MVK-oligomers up to t_{max} (i.e. increasing oligomer concentrations with reaction time, assuming no major change in the oligomer composition), the calibration experiments were used to determine the SOA mass yields according to equations 2 and 3. The differences obtained between the three calibration experiments may be due to the different physical properties of the particles (e.g. volatility, surface tension and hygroscopicity) linked to their chemical composition. Table S1 shows that the solutions of NaCl generated a significantly higher transmission efficiency than the solutions of NH_4NO_3 and succinic acid. It is likely that the properties of the SOA generated from the nebulized solutions of oxidized MVK were closer to that of NH_4NO_3 and succinic acid than NaCl. Finally, the transmission efficiency obtained for NH_4NO_3 solutions was used to calculate the SOA mass yields according to equations 2 and 3.”

Question 6. Caption to Figure 8. I am not sure what the authors mean by the comparison to the data of Lee et al., 2001?

Answer: The aim of the comparison was to highlight the similarity of the oxidation (aging) processes evidenced here with previous studies (Lee et al., 2011; Ng et al., 2010), despite differences in conditions. We have modified the text to make this point clearer, it now reads:

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“In order to compare our work with the aging of organic aerosol in the atmosphere compiled by Ng et al. (2010), we used the AMS data, and in particular, the development of the two dominant fragments, m/z 44 (CO_2^+) and m/z 43 (mostly $\text{C}_2\text{H}_3\text{O}^+$), observed in our study. More precisely, we focused on the ratio of m/z 44 and m/z 43 to total organic aerosol, f_{44} and f_{43} , respectively. In Ng et al. (2010), low volatility oxygenated organic aerosol (LV-OOA) has higher f_{44} than semi-volatile oxygenated organic aerosol (SV-OOA) which in turn has higher f_{43} values. Despite the very different conditions, it is interesting to compare our aging data with those compiled from field studies and other aqueous phase experiments. Figure 8 compares our f_{44} versus f_{43} values to those provided in the compilation by Ng et al. (2010) as well as the nebulization data by Lee et al., (2011a). It is clear from this figure that the SOA composition and its evolution highly depend on the initial MVK concentration.

References: Daumit, K. E., Carrasquillo, A. J., Hunter, J. F. and Kroll, J. H.: Laboratory studies of the aqueous-phase oxidation of polyols: submicron particles vs. bulk aqueous solution, *Atmospheric Chemistry and Physics*, 14(19), 10773–10784, doi:10.5194/acp-14-10773-2014, 2014. Hobby, K.: A novel method of isotope prediction applied to elemental composition analysis, 2005. Kameel, F. R., Hoffmann, M. R. and Colussi, A. J.: OH Radical-Initiated Chemistry of Isoprene in Aqueous Media. Atmospheric Implications, *The Journal of Physical Chemistry A*, 117(24), 5117–5123, doi:10.1021/jp4026267, 2013. Kameel, F. R., Riboni, F., Hoffmann, M. R., Enami, S. and Colussi, A. J.: Fenton Oxidation of Gaseous Isoprene on Aqueous Surfaces, *The Journal of Physical Chemistry C*, 140725063829009, doi:10.1021/jp505010e, 2014. Lee, A. K. Y., Herckes, P., Leaitch, W. R., Macdonald, A. M. and Abbatt, J. P. D.: Aqueous OH oxidation of ambient organic aerosol and cloud water organics: Formation of highly oxidized products: AQUEOUS OXIDATION OF AMBIENT ORGANICS, *Geophysical Research Letters*, 38(11), n/a–n/a, doi:10.1029/2011GL047439, 2011a. Lee, A. K. Y., Zhao, R., Gao, S. S. and Abbatt, J. P. D.: Aqueous-Phase OH Oxidation of Glyoxal: Application of a Novel Analytical Approach Employing Aerosol Mass Spectrometry and Complementary Off-Line Techniques, *The Journal*

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Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/14/C9528/2014/acpd-14-C9528-2014-supplement.pdf>

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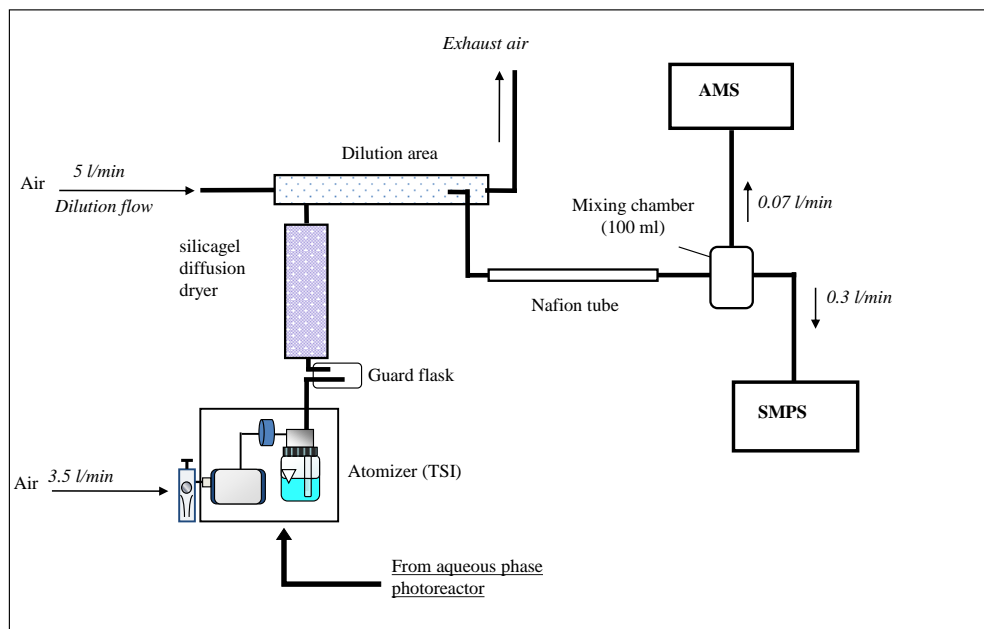
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Fig. 1. Schematic overview of the aerosol generation setup.

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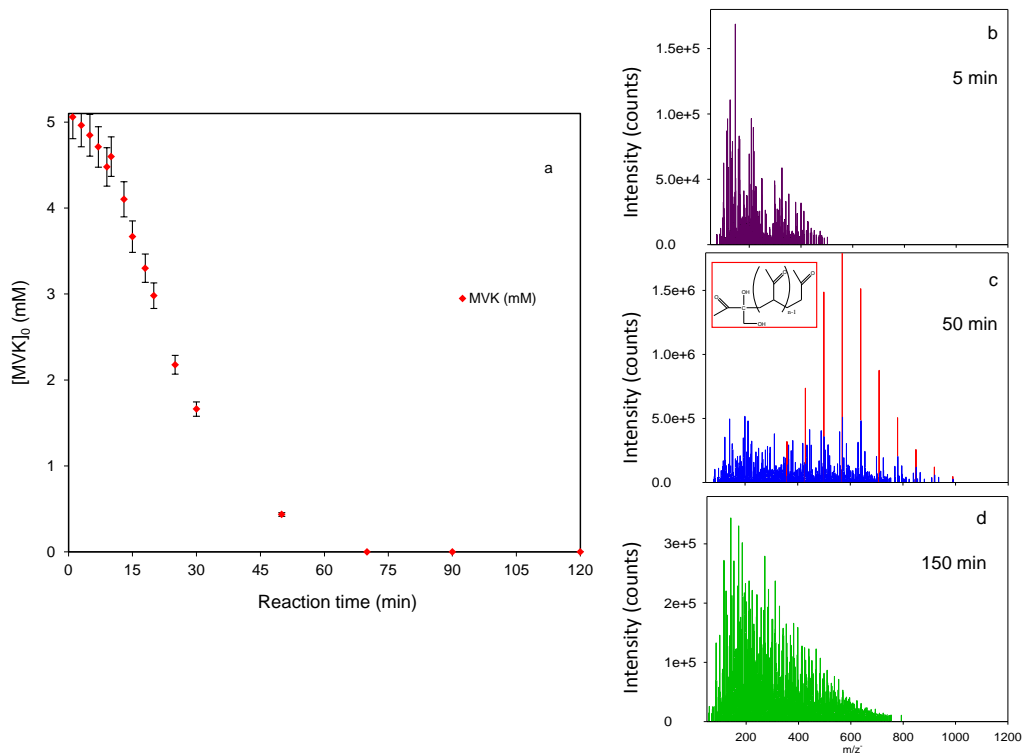


Fig. 2. Figure 2: (a): Time profiles of MVK concentrations during the reaction (experiment B); and the corresponding evolution of ESI-MS- spectra for m/z 50 - 1200 at (b): 5 min, (c): 50 min and (d): 150 min.

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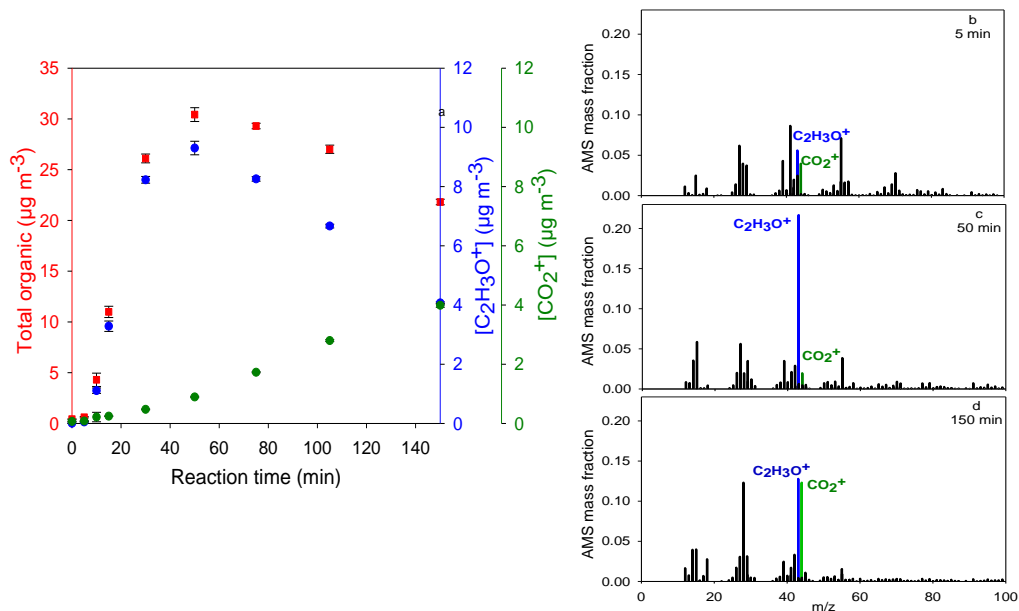
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Fig. 3. Figure 3: Time profiles of the HR-ToF-AMS total organic mass (red), ion fragments $C_2H_3O^+$ at m/z 43 (blue) and CO_2^+ m/z 44 (green) for nebulized solutions from experiment B (a), and the corresponding

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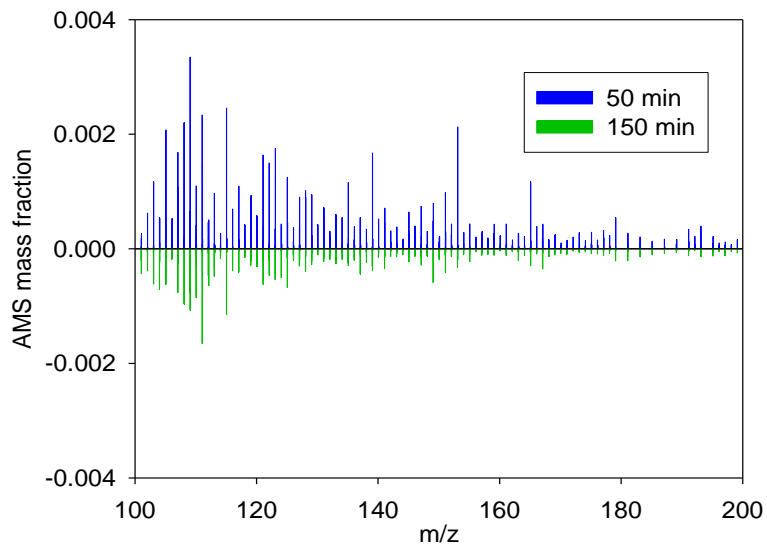
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Fig. 4. Figure 4: Comparison of HR-ToF-AMS mass spectra (in the range 100 - 200 amu) of the nebulized solutions sampled from experiment B after 50 and 150 min of reaction in the aqueous phase. The AMS-mass fr

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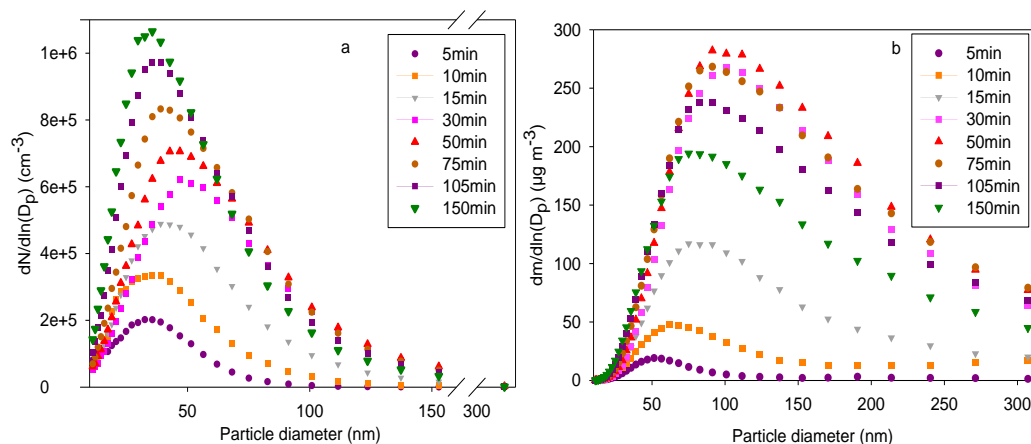
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Fig. 5. Figure 5: Evolution of particle number (a) and mass (b) size distributions for nebulized solutions sampled at different reaction times for experiment B, measured by means of SMPS. The standard deviat

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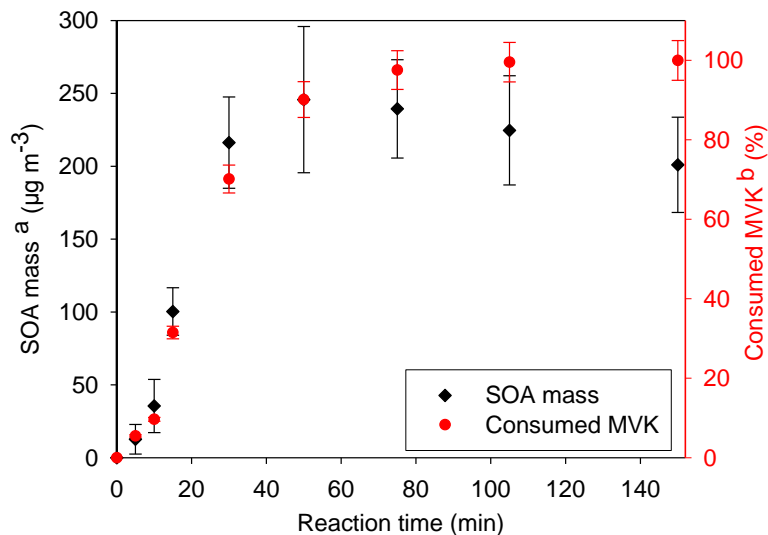


Fig. 6. Figure 6: Time profiles of the total aerosol mass (black diamonds) from the nebulized solutions, and consumed MVK in the aqueous phase (red circles) for experiment B. a Values represent averages of th

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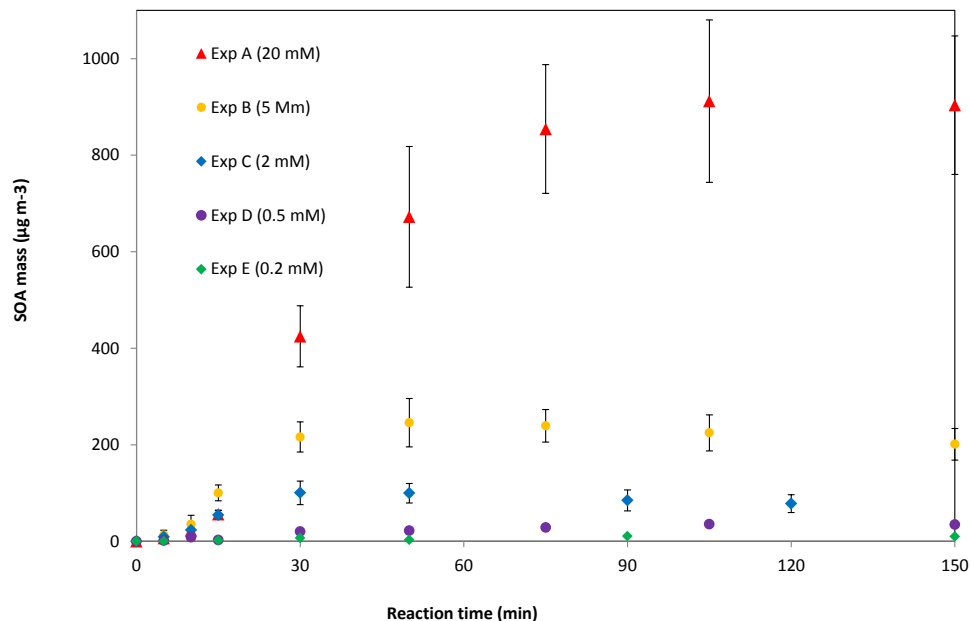
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Fig. 7. Figure 7: Influence of the initial MVK concentration on the evolution of the total SOA mass obtained from the nebulized solutions. Values represent averages of three consecutive SMPS-measurements for

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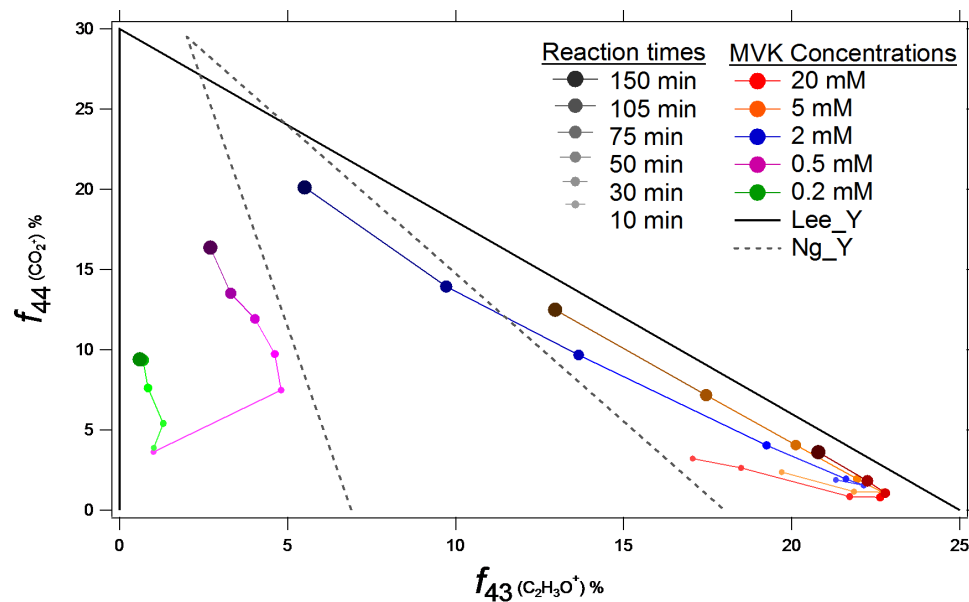
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Fig. 8. Figure 8: Fractions f_{44} versus f_{43} for the nebulized solutions from experiments A, B, C, D and E, as measured by the HR-ToF-AMS are compared to ambient air LV-OOA and SV-OOA from the compilation by Ng

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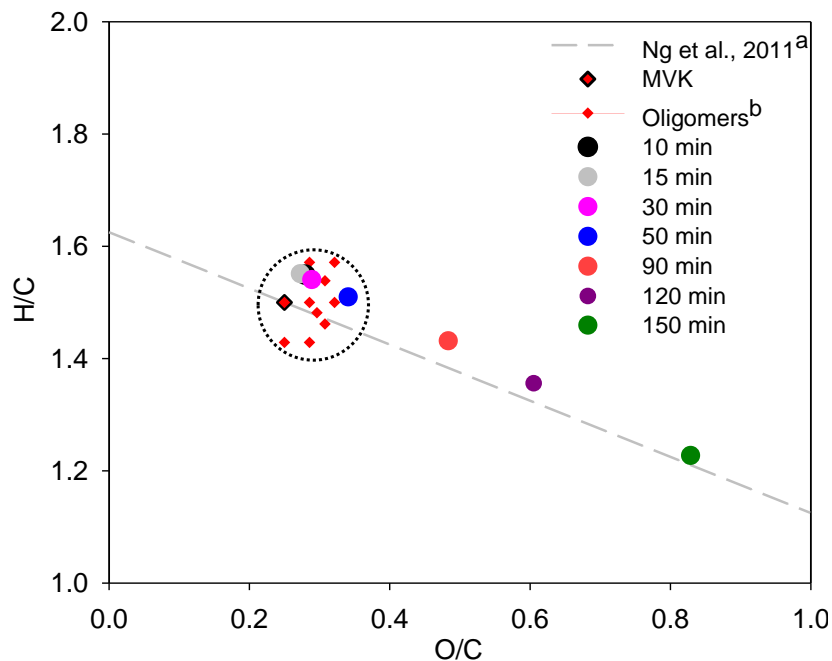
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Fig. 9. Figure 9: Van Krevelen diagram for the nebulized solutions of experiment C, as measured by the AMS. Only experiment C is shown for clarity as the data for experiments A and B are stacked together with

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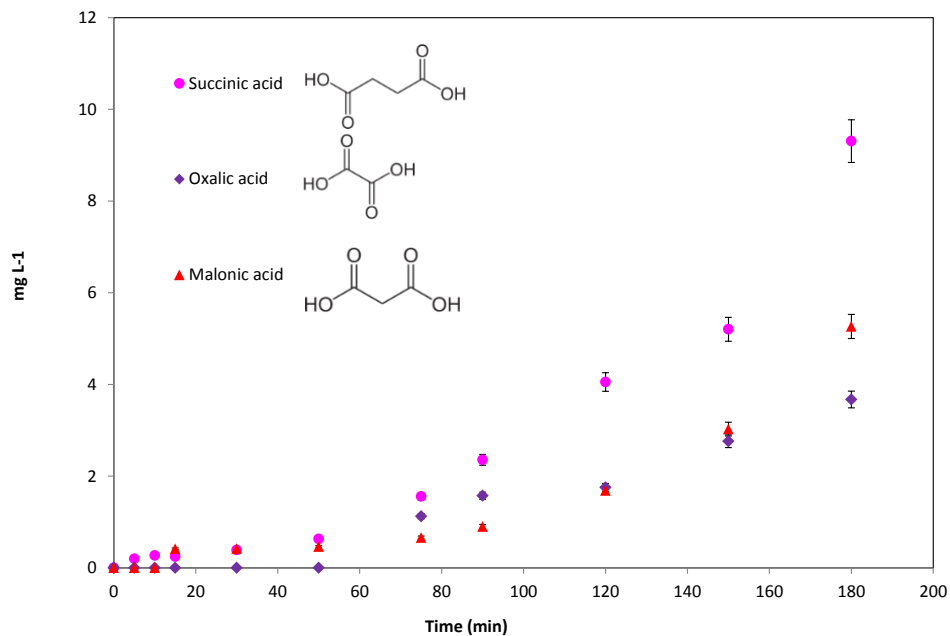
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Fig. 10. Figure 10 : Time profiles of the quantified diacids in the solutions as measured by IC-ESI-MS for experiment B ([MVK]₀ = 5 mM).

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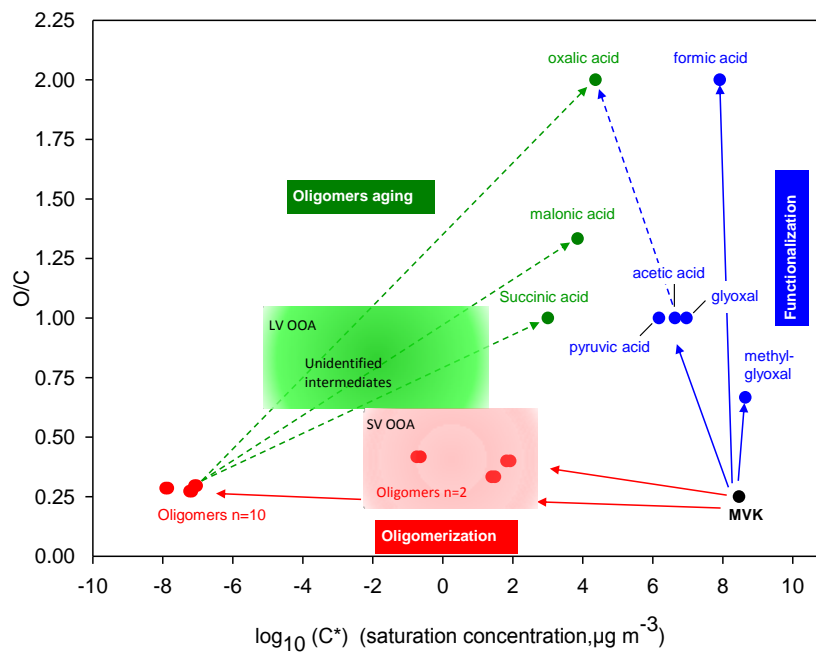
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Fig. 11. Figure 11: Potential atmospheric fate of MVK in the aqueous phase. X-Axis denotes volatility (\log_{10} of C^* at 298K), y-axis denotes oxidation state, approximated by O/C (Jimenez et al., 2009).

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