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Comment

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

RC C4754: 'Review of interesting and novel study by Renard et al.', Anonymous Referee #2, 12 Jul 2014

The authors appreciate many important comments raised by Reviewer 2 which have been considered in the new version of the manuscript. The authors' answers to the questions/comments of Reviewer 2 are presented below.

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Question: 1. The language in the manuscript is sometimes awkward and there are numerous errors in English language grammar and syntax. These include singular/plural disagreements between nouns and verbs, improper choice of prepositions, missing subjects, etc.... The manuscript should be edited for language before acceptance for publication.

Answer: Done.

Question: 2. p. 15287, line 12: change "ionic" to "ion"

Answer: Done.

Question: 3. p. 15288, line 13: define "UPLC"

Answer: Done.

Question: 4. p. 15288, line 4: The authors state that the experimental conditions in Table 1 were chosen to be representative of cloud droplets or wet aerosol conditions. While the lowest MVK concentration ($200 \mu\text{M}$) might represent total WSOC concentrations in some clouds or fogs, it is unlikely to find such high concentrations of a single ketone. The minimum concentration of H_2O_2 ($4000 \mu\text{M}$) is also much higher than seen in ambient clouds or fogs, where reported observations are generally at least 10x lower. Based on these discrepancies, I would conclude that the lowest MVK and H_2O_2 concentrations are perhaps an order of magnitude or so higher than in ambient clouds and fogs. This should be clarified for the reader.

Answer: In the comparison between our experimental concentrations with atmospheric ones, MVK is considered a proxy for UWSOC. We do not intend to compare the H_2O_2 concentrations with the atmospheric ones (as H_2O_2 is not the only source of atmospheric HO_2OH), but we compare the estimated HO_2OH concentrations with the atmospheric ones. We modified the text accordingly, it now reads:

"Tan et al. (2010) and Renard et al. (2013) have shown the important impact of initial concentrations on oligomer formation. The experiments were thus carried out with var-

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ious 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 initial H₂O₂ concentrations were chosen in order to obtain a ratio ($\frac{[H_2O_2]_0}{[MVK]_0} = 20$), in order to favor $\dot{A}OH$ reaction with MVK rather than with H₂O₂ by more than 90 %. Under these conditions, $\dot{A}OH$ concentrations were estimated in the range $(2 - 6) \times 10^{-14}$ M (Supplementary information SI3), which falls in the range of the estimated values for $\dot{A}OH$ concentrations in cloud and fog droplets (Herrmann et al., 2010; Ervens and Volkamer, 2010 and Arakaki et al., 2013)."

Question: 5. p. 12588, line 14: How were OH concentrations estimated? Were they measured in solution, e.g., by adding a "clock" species with a known OH-rxn rate?

Answer: $\dot{A}OH$ concentrations were calculated by means of two different methods (methods a) and b) below), which gave similar results, as shown hereafter. These calculations were added in the supplementary information of the new version of the manuscript.

a) Considering reactions R1 to R3, $\dot{A}OH$ concentrations were calculated assuming the steady state approximation at time 0: $[OH] = \frac{(2 \times J_{H_2O_2} \times [H_2O_2])}{(k_3 \times [MVK] + k_2 \times [H_2O_2])}$ H₂O₂ + h ν $\dot{A}OH$ ($\rightarrow \dot{A}OH$ + JH₂O₂) R1 JH₂O₂ was determined by fitting H₂O₂ concentration decay H₂O₂ + $\dot{A}OH$ $\dot{A}OH$ ($\rightarrow \dot{A}OH$ + k₂) HO₂ + $\dot{A}OH$ + H₂O R2 k₂ = 2,95.107 M⁻¹ s⁻¹ at 25° C (Christensen et al., 1982) MVK + $\dot{A}OH$ $\dot{A}OH$ ($\rightarrow \dot{A}OH$ + k₃) Products R3 k₃ = 7.3.(± 0,5) 10⁹ M⁻¹ s⁻¹ at 25°C (Schöne et al., 2014)

The obtained values are $[\dot{A}OH] = (5 - 6) \times 10^{-14}$ M for pH 3 - 6

b) Fitting the initial MVK decay with an exponential decay: $[MVK]_t = [MVK]_0 \times e^{-k_3 [\dot{A}OH] t}$ With k₃ = 7.3 (± 0,5) 10⁹ M⁻¹ s⁻¹ at 25°C (Schöne et al., 2014), we obtain similar values for $\dot{A}OH$ steady state concentrations ($[\dot{A}OH] =$

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2 x 10⁻¹⁴ M) as for the previous estimation.

Question: 6. p. 15288, line 23: change "its resolution mode" to "its high resolution mode" 7. p. 15289: What mass accuracy was achieved for the instrument?

Answer: The term "resolution mode" is used by the instrument constructor to specify V-mode acquisition, corresponding to a resolution of 18,000 FWHM (Full width at half maximum) at m/z 400. The term "high resolution mode" corresponds to the W-mode acquisition, with a resolution of 40,000 FWHM at m/z 400. We only used the first mode. The mass accuracy was < 5 ppm. The text has been modified to make these explanations clearer. The text now reads:

"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)."

Question: 8. p. 15290, lines 1-3: Given that the 211 nm absorption is proportional to the sum of the H₂O₂ and MVK concentrations, it is unclear to me how measuring at this wavelength defines the MVK oxidation rate. Please clarify. Presumably you need the combination of the K and R bands to separate changes in MVK and H₂O₂ concentrations.

Answer: The instrument described in the paragraph (UHPLC-UV) allows for a chromatographic separation of MVK and H₂O₂ prior detection by UV absorbance: H₂O₂ has a retention time of 0.5 minutes and is chromatographically separated from MVK which has a retention time of 1.8 minutes. We modified the text to clarify this point. Furthermore, some Tables and Figures (Table 1, Figure 2a, Figure 6) have been slightly modified using more appropriate calibrations of H₂O₂ and MVK concentrations by UHPLC-UV analysis. The chromatograms were monitored at 270, 229 nm and 211 nm and the peak areas were found to be directly proportional to both the H₂O₂ and the MVK concentrations in the range of the studied concentrations: at 211 nm for low

MVK concentrations ($[MVK] \leq 2$ mM), at 229 nm for low H₂O₂ concentrations and for high concentrations of MVK ($[H_2O_2] < 40$ mM and $2 < [MVK] \leq 20$ mM), and at 270 nm for higher concentrations of H₂O₂ (up to 400 mM). The whole paragraph 2.2.2 now reads:

“An ultra-high performance liquid chromatographic (UHPLC) system (ThermoScientific, Accela 600 auto sampler and Accela 600 pump) coupled to a diode array detector (ThermoScientific, Accela 600 PDA detector) was used to monitor the concentrations of MVK and H₂O₂ sampled from the photoreactor. The chromatographic separation was performed using a column (ThermoScientific, Hypersil GOLD, 100 x 2.1 mm - 1.9 μ m) at 40°C and a flow rate of 300 μ L min⁻¹. The mobile phase was water/acetonitrile (98:2) (v/v) and the injection volume was set to 2 μ L. The spectra were recorded from 200 to 360 nm. Under these conditions, H₂O₂ has a retention time of 0.5 min and is chromatographically separated from MVK which has a retention time of 1.8 minutes. The UV spectrum of aqueous H₂O₂ exponentially increases with decreasing wavelength, it becomes intense below 300 nm. Aqueous solutions of MVK show an intense absorption band (K-band; $\pi \rightarrow \pi^*$ transition) that peaks at 211 nm and a weak absorption band (R-band; $n \rightarrow \pi^*$ transition) that peaks at 308 nm. The chromatograms were monitored at 270, 229 nm and 211 nm and the peak areas were found to be directly proportional to both the H₂O₂ and the MVK concentrations in the range of the studied concentrations: at 211 nm for low MVK concentrations ($[MVK] \leq 2$ mM), at 229 nm for low H₂O₂ concentrations and for high concentrations of MVK ($[H_2O_2] < 40$ mM and $2 < [MVK] \leq 20$ mM), and at 270 nm for higher concentrations of H₂O₂ (up to 400 mM).”

Question: 9. p. 15290, line 24: Please give the manufacturer for the TOC/TN instrument.

Answer: Done: the text now reads: “A total organic carbon / total nitrogen (TOC/TN) analyzer (Analytik Jena, N/C2100S) with the non-purgeable organic carbon (NPOC) method was used to quantify the produced oligomers in our liquid samples.”

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Question: 10. p. 15291: Please clarify use of the NPOC measurement mode for TOC. Using this mode on acidified samples should eliminate small molecules, including low MW carboxylic acids. That seems useful if you want to quantify the OC that will be released as OA upon drop evaporation. Is that the intent?

Answer: Prior TOC measurements, MVK and small and/or volatile reactants and reaction products were specifically removed from the samples by preparative liquid chromatography. We modified the paragraph in order to clarify this point. The whole paragraph 2.2.4 now reads:

“TOC measurements were associated to preparative liquid chromatography to separate the oligomers from the small and/or volatile reactants and reaction products in the liquid samples, in order to measure the oligomer mass yields in experiment A (see section 3.2.3). A total organic carbon / total nitrogen (TOC/TN) analyzer (Analytik Jena, N/C2100S) with the non-purgeable organic carbon (NPOC) method was used to quantify the produced oligomers in our liquid samples. The NPOC method consists in pre-purging samples with oxygen and pre-acidifying (at pH=2 with HCl) to remove the inorganic carbon and purgeable organic carbon. TOC is measured by injecting the sample into a heated combustion tube (800°C) with an oxidation catalyst. The CO₂ produced is measured by a non-dispersive infrared (NDIR) gas analyzer. TN is measured in parallel using chemiluminescence detection (CLD).”

Question: 11. Accurate quantification of the CO₂⁺ fragment in the AMS requires good information about the CO₂ concentration in the sample air stream. How was this quantified? Indoor CO₂ concentrations can be much higher than outdoor concentrations.

Answer: The AMS samples particles more efficiently than gases by 7 orders of magnitude (Allan et al., 2003; Cubisson et al., 2011). It follows that gaseous CO₂ at a concentration of 1000 ppm (indoor air level, (Hussin et al., 2014) is expected to generate 100 ng m⁻³ of equivalent aerosol signal at m/z 44. This interference needs to be accounted for in view of the low aerosol equivalent signal measured at this specific ion

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in our experiments (Figure 3, maximum aerosol signal at CO_2^+ of $4 \mu\text{g m}^{-3}$). Accordingly, mass spectra of filtered air (using a HEPA capsule filter) were taken prior each series of nebulizing experiments in order to adjust the m/z 44 entry of the fragmentation table due to gas phase CO_2 . The text has been modified accordingly: in section 2.3, the following sentence has been added: “Mass spectra of filtered air (using a HEPA capsule filter) were taken prior each series of nebulizing experiments in order to adjust the m/z 44 entry of the fragmentation table due to gas phase CO_2 .”

Question: 12. p. 15293, lines 14-15: Why were these fragments "thought to be" $\text{C}_2\text{H}_3\text{O}^+$ and CO_2^+ ? Aren't you using the high res AMS data where these ions are distinguished from other ions with the same unit mass?

Answer: Yes, this is right. For the analysis of the HR-ToF-AMS spectra and identification of the respective ions, we used the high resolution V-mode (up to 2000 at m/z 200). Therefore, we can clearly identify $\text{C}_2\text{H}_3\text{O}^+$ and CO_2^+ ions fragments. The text has been modified accordingly in the new version of the manuscript, it now reads: In section 2.3: “The instrument was used under standard conditions (vaporizer at 600°C and electron ionization at 70 eV), in the high sensitivity V-mode (up to 2000 at m/z 200).” In section 3.1.2: “The AMS mass spectra (Figure 3) show two dominant fragments, at m/z 43 and m/z 44 (corresponding to $\text{C}_2\text{H}_3\text{O}^+$ and CO_2^+ fragments).”

Question: 13. p. 15293, line 28: the second ion listed here should be m/z 44. Answer: Done.

Question: 14. p. 15294, line 10: The AMS collection efficiencies stated (0.07 to 0.21) seem very small for organic aerosols. Please comment on these values relative to those typically reported for OA in other AMS studies.

Answer: The AMS collection efficiencies were investigated by comparing AMS to SMPS measurements. The AMS collection efficiency (CE) 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 sur-

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face (Huffman et al., 2005, Docherty et al., 2013). It is thus likely that the physical and chemical properties of our particles induced a low transmission and/or a high bouncing effect. 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 of 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 (in section 3.1.2) has been modified accordingly, it now reads: “For the quantitative study (section 3.2), we used the data provided by the SMPS analysis. 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 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).”

Question: 15. p. 15294, line 22: please change "increasing mode" to "increasing mode size"

Answer: Done.

Question: 16. p. 15296 and elsewhere: The authors need to comment on the possible role of OA concentration in altering the fraction of organic matter that partitions to the

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aerosol phase. The lower concentration experiments could have lower SOA yields, in part, because at lower OA concentrations a bigger fraction of the organic matter resides in the gas phase. This partitioning effect could also alter the relative oxygenation of the OA produced since only the lowest vapor pressure products will enter the particle phase when OA concentrations are low.

Answer: It is true that the OA concentrations certainly influence their gas/particle partitioning in our set up, even if the residence time is of the order of a minute. However, looking at the data in Tables 2 and 3, it is not possible to observe any significant evolution in the obtained SOA mass yields, due to their large uncertainties. This is the reason why a different experiment was performed using preparative chromatography and TOC analysis that gave the oligomer mass yield with a much smaller uncertainty. However, this check was done only for one experiment (exp A), so it is not possible to deduce any SOA mass yield evolution from our results. In contrast, the O/C and H/C ratios clearly show statistically stable values when the total particle mass increases from 100 to 900 $\mu\text{g}/\text{m}^3$ (Table 3). It is thus likely that the total mass loading does not influence the relative oxygenation of the OA produced under our experimental conditions. In order to make these points clearer in the manuscript, we have modified the beginning of section 3.23, it now reads: “The SOA mass yields, Y_t , were calculated at each reaction time step t from eq. 2.

$Y_t = \frac{[\text{SOA}]_t - \Delta[\text{MVK}]_t}{[\text{MVK}]_t}$ (eq. 2) Where $[\text{MVK}]_t$ is the consumed [MVK] in mg L^{-1} at reaction time t ; and $[\text{SOA}]_t$ is the formed SOA mass at reaction time t , in $\text{mg per L of evaporated water}$. This term takes into account the SOA mass (MSMPS) measured by the SMPS at time t (in $\mu\text{g m}^{-3}$), the atomizer flow (F_{atomizer} in L m^{-3}), the dilution (f_{dil}), and the transmission efficiency in our nebulizing system (T_{eff} in %) (see Table S1). $[\text{SOA}]_t = \frac{M_{\text{SMPS}} \times T_{\text{eff}}}{F_{\text{atomizer}} \times f_{\text{dil}} \times 1000}$ (eq. 3) The yields obtained at t_{max} for experiments A, B and C are shown in Table 3. Although the total SOA mass (at t_{max}) increases linearly with the initial concentration for these three experiments, the yields are statistically identical as well as their H/C and O/C ratios. Due

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to the very large uncertainties affected to our yield determinations (see below), it is not possible to use these data (Table 2 and 3) to provide any interpretation on the possible effect of initial concentrations on the yields. In contrast, the O/C and H/C ratios clearly show statistically stable values when the total particle mass increases from 100 to 900 $\mu\text{g}/\text{m}^3$ (Table 3). It is thus likely that the total mass loading does not influence the relative oxygenation of the SOA produced (at t_{max}) under our experimental conditions. Although the particle mass loadings (MSMPS) were accurately measured, our yield determinations were affected by large uncertainties due to the estimation of the transmission efficiency in our nebulizing system (see supplementary information 1).”

Question: 17. pp. 15297-15298: The authors do a nice job talking about the changes in chemistry and SOA yield as a function of oxidation time. This discussion, however, would benefit from tying it back to the ambient atmosphere. Please discuss what yield/time is most relevant for typical atmospheric conditions.

Answer: The transfer of these results to atmospheric conditions is the scope of part 2 of this study where they have been included in a multiphase atmospheric model (Ervens et al., 2014). Briefly, the model results indicate that cloud conditions would allow for the formation of very few oligomers, while in wet aerosol conditions, oligomer concentrations would increase up to 250 ng m^{-3} within 350 min. The comparison of predicted oligomer formation shows that for most model assumptions (e.g. depending on the assumed partitioning of MVK and MACR), SOA formation from isoprene in the gas phase would exceed aqueous SOA formation by a factor 3–4.

Question: 18. p. 15298, line 2: I think the percentage here should be 70 +/- 50%

Answer: Yes, this was a typo.

Question: 19. Fig. 8: The time evolution of the experiments needs to be better displayed in this figure.

Answer: Done.

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Question: 20. p. 15302, line 1: change "ones" to "compounds"

Answer: Done.

Question: 21. p. 15302, lines 2-3: This sentence is missing a subject. Latter is an adjective. Latter what...?

Answer: According to this comment and those by other reviewers, the whole paragraph has been modified. It now reads: "Considering the results obtained here on oligomer formation and aging from MVK at varying initial concentrations together with those obtained by previous studies on the identification of the low-molecular-weight compounds products of the reaction (Zhang et al., 2010), a general scheme of the potential atmospheric fate of MVK in the aqueous phase is shown on Figure 11. MVK α -OH-oxidation undergoes kinetic competition between functionalization and oligomerization, depending on the precursor initial concentration. At 2 mM of MVK and above this concentration, oligomerization dominates over functionalization. At these concentrations, α -OH-oxidation of MVK forms oligomers that are SV-OOA, with low O/C (lower than 0.50) and high f43. Oligomers are then fragmented, via unidentified intermediates that have the properties of LV-OOA (with increasing O/C and decreasing H/C, Figure 9) which then form organic diacids. For lower initial MVK concentrations (< 2 mM), oligomerization is not the major process, and functionalization dominates, ending into small carbonyls, dicarbonyls and acids that were identified by Zhang et al., (2010) (Figure 11). 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 ($K_{\text{H}} = 1 - 103$ 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

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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 *a*-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 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.”

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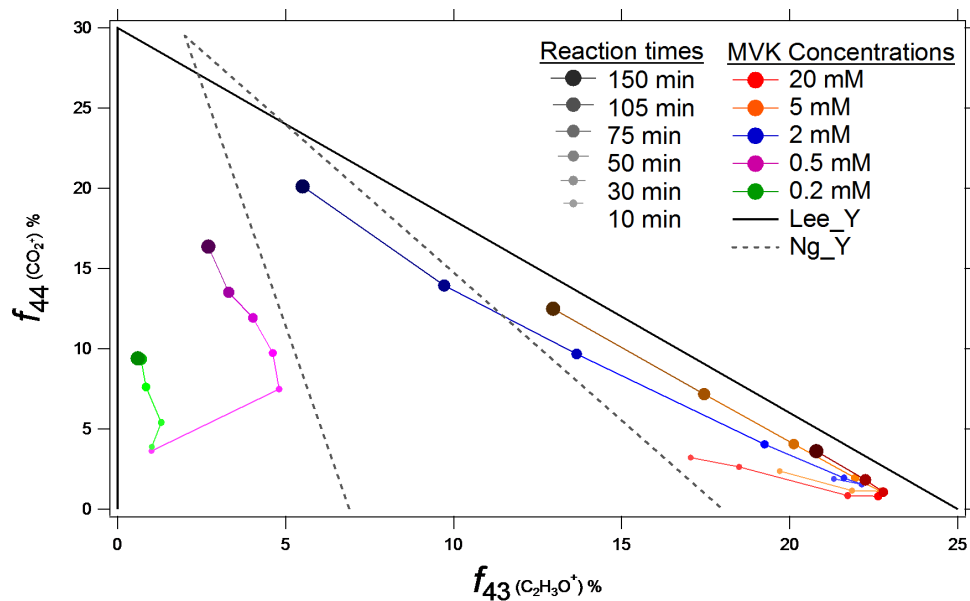
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Fig. 1. Figure 8: Fractions f_{44} versus f_{43} for the nebulized solutions from experiments A, B, C, D and E, as measured by the HR-ToF-AMS are compared to ambient air LV-OOA and SV-OOA from the compilation by Ng

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