REVIEWER #1:

Remarks by the authors: We thank the reviewer for the detailed comments and thoughts on our paper. We have carefully revised the manuscript and added sensitivity studies and further discussion on the most sensitive parameters in the mechanism. In order to better constrain the mechanism by more accurate laboratory results, additional experiments were performed. Because of this, a coauthor was added and several figures were replotted.
In addition, we fully revised and shortened the section of multiphase simulations since we agree with the reviewer that these model studies include many quite uncertain parameters and at this point only a very approximate initial estimate of the potential role of oligomerization in the atmosphere can be given.
In the following response, our comments are marked with 'Response' (Courier New font); all reviewer comments are in 'Times New Roman' font. Line and figure numbers refer to the revised manuscript without annotations.

This is a study on the oligomer formation originating from MVK. It is undertaken at an early point in time as only limited process information on all the steps involved is available. Clearly stated, it might be too early to try to model this system. Some process information, which is now available from the literature, is not used and there is a wrong treatment of the branching ratio of the OH initiation reaction.

I would advise the authors to clearly mark the very explorative nature of this contribution from its beginning and throughout. Clearly, all results will be strongly dependent on the chosen input and one possible variant to be added to the manuscript would be a sensitivity study which variation of input parameter would lead to which change in the results. To some extend this has been done for oxygen concentration but there are many more variables, which are critical to the results of the model. The possible depletion of oxygen in tropospheric particles seems to be a non - proven hypothesis, the fulfillment of which, however, is required, as otherwise, the calculated oligomer formation will be much below its possible maximum.

In my view, the results obtained with a non - depleted oxygen concentration are most realistic and this should be clearly stressed within the manuscript. The paper contains plain errors. Overall, the manuscript needs revision at many points and should generally be seen as an explorative study.

Response: We thank the reviewer for these general comments. We make it now clearer throughout the revised manuscript that the study is indeed rather exploratory and that the mechanism still contains numerous uncertainties. However, we still think that the study can be regarded as an initial step towards a better understanding of oligomerization reactions and there potential role as SOA source in the atmosphere.

We have also corrected the OH initiation reactions in Table 1, which contained typos.

We agree on the fact that the results obtained with a non-depleted oxygen concentration are most realistic. To our knowledge, this is one of the first studies that actually monitors oxygen in the aqueous phase during lab experiments while most studies simply assume that oxygen is not depleted. The goal of the multiphase model is to test whether the oligomerization reactions are still of importance under realistic non-depleted oxygen conditions.

Details

1) Introduction: ‘gasSOA’ is a strange acronym

Response: In agreement with the article by Ervens et al. (2011) where this term was introduced, we explained "termed 'gasSOA' by Ervens et al. (2011) as the chemical reactions leading to condensable species occur in the gas phase" (p. 2, l. 14). The term 'gasSOA' has been also used in more recent literature in the same context by the same and other authors, e.g. (Ervens et al., 2014; van Pinxteren et al., 2014).

2) Pages 21567, 21568: The selection of references in this part seems somewhat arbitrary. I feel the author should give a better coverage of work related to the presented study. Recent studies are missing.

Response: We added and replaced some references to cover also more recent work on SOA formation and oligomerization:
p. 2, l. 4: The references to Tolocka et al, 2004 and Kalberer et al., 2004 were removed and added later (l. 23) as the first studies that identified oligomers in particles;
p. 2, l. 30: Kuwata et al., 2015 was added;
p. 3, l. 10: Kampf et al., 2013, Healy et al., 2008 were added
p. 3, l. 21: Mead et al., 2015 was added
Please, note that these changes are not marked in the annotated manuscript

3) Page 21568, line 15: Great care has to be taken following this approach: By just fitting observables to a mechanism without detailed knowledge of the chemical steps involved, a detailed process model cannot be deduced. The fitted mechanistic scheme is a parameterization. Whether the parameterization is valid for environmental conditions has to be proven independently. It cannot be only postulated that such parameterization can be applied direct to environmental systems. This, even though this approach has been followed recently quite often, might potentially represent a strong systematic error in the work described here.

Response: The reviewer is right that we cannot say for sure that all reactions occur as described in Figure 1. However, unlike many other recent studies, the mechanism presented here is relatively well constrained by experiments that identified intermediates and products. We performed a set of sensitivity studies on the least constrained rate constants and summarized these results in a new Section S4 in the supplemental information. These studies show that the combination of rate constants we have chosen (and call 'Base Case' there) gives the most robust and consistent results for different initial MVK concentrations and experimental conditions. We added text
In the abstract (p. 1, l. 19-22)
Upon model sensitivity studies, in which unconstrained rate constants were varied over several orders of magnitude, a set of reaction parameters was found that could reproduce laboratory data over a wide range of experimental conditions.
and at the end of Section 2.1.1 (p. 7, l. 2-12)

We performed sensitivity studies on the most uncertain and least constrained rate constants. Results are summarized in Section S4 of the supplemental information. They show that the simulation results are insensitive to the choice of k_{arr} ***and*** k_{recomb}***; even a change of ± five orders of magnitude for each of the constants gives the same results as the base case (black line in***

Figure S3; results of the sensitivity studies are not displayed but would be on top of the base case results) with less than 1% difference. Simultaneous changes of k_{O2}, k^{1st} or k_{olig} can reproduce similar results for selected experimental conditions; however, the most robust results for all concentration ranges and experimental conditions were obtained for the set of rate constants as summarized in Table 1. While this agreement does not necessarily prove that indeed these are the exact rate constants, they reveal important sensitivities and suggest which rate constants should warrant future laboratory experiments.

4) Page 21569, section2:

a) As for the processes listed in Table 1:JH2O2: A value derived from actinometry should be given and compared to this maximum value. Why is just a maximum value given?

Response: To answer this question, and also, in order to better constrain the model, we have performed several additional experiments. The results are shown hereafter. This text (in rephrased and slightly shortened form) is now included in Section 2.2.2 of the revised manuscript (p. 10, l. 29 – p. 12, l. 14).

The direct photolysis of H_2O_2 provides $^{\bullet}OH$ radicals, *via* reaction 1

$$H_2O_2 + h\nu \rightarrow 2\ {}^{\bullet}OH \qquad (1)$$

The corresponding photodissociation coefficient J_{H2O2} (s^{-1}) is defined in equation 1

$$J_{H2O2} = \int I_{0,\lambda} \times \varepsilon_\lambda \times \phi_\lambda \times d\lambda \qquad \text{(eq. 1)}$$

Where:

- ε_λ is H_2O_2 extinction coefficient ($cm^3\ molec^{-1}\ cm^{-1}$): it was determined experimentally at the nm resolution up to 350 nm (as it is of negligible importance above this wavelength). We verified that the obtained extinction coefficients were in good agreement with previous works (e.g. Kwon and Kwon, 2010).
- ϕ_λ is H_2O_2 quantum yield: quantum yield values for $^{\bullet}OH$ production recommended by the review of Herrmann et al. (2010) were used up to 350 nm.
- $I_{0\lambda}$ is the spectral irradiance (Photons $cm^{-2}\ s^{-1}\ nm^{-1}$): the average spectral irradiance of our 1000 Watt Xe arc lamp over our photoreactor's water surface was measured every 1.4 nm (up to 350 nm) using a laboratory spectroradiometer (modified SR-500 from Spectral evolution)

The resulting photodissociation coefficient J_{H2O2} (s^{-1}) obtained by this actinometry calculation is compared to the experimental one in the following Table R1:

J_{H2O2} (s^{-1}) actinometry calculation	J_{H2O2} (s^{-1}) Experimental values
5.1 (±2.0)x 10^{-6}	9.5 (±1.4)x 10^{-6}

Table R1: H_2O_2 photodissociation coefficient values: comparison between experimental determinations and actinometry calculations.

This comparison shows that the experimental determination of J_{H2O2} and the actinometry calculation are in the same order of magnitude. The slightly lower value obtained by the actinometry calculation may be due to light reflections in the vessel, that have not been taken into account in the calculation. However, this comparison is done for the direct photolysis of H_2O_2 alone in pure water.

When MVK is introduced in the vessel, its absorbance spectrum around 300 nm partly filters the light available for H_2O_2 photolysis, thus inducing a reduction of the rate of H_2O_2 photolysis. This is why the value for J_{H2O2} indicated in Table 1 of the previous manuscript was given as a maximum value.

Knowing the absorbance spectrum of MVK ($A_{MVK,\lambda}$), one can calculate the resulting irradiance spectrum $I'_{0\lambda}$ available for H_2O_2 photolysis (eq. 2).

$$I'_{0,\lambda} = I_{0,\lambda} \times 10^{-A_{MVK,\lambda}} \qquad \text{(eq. 2)}$$

Using this new irradiance spectrum, one can calculate the corresponding photodissociation coefficient J'_{H2O2} (s^{-1}) (equation 3).

$$J'_{H2O2} = \int I'_{0,\lambda} \times \varepsilon_\lambda \times \phi_\lambda \times d\lambda \qquad \text{(eq. 3)}$$

Using the values of $A_{MVK,\lambda}$ experimentally determined at different concentrations of MVK, the resulting values of J'_{H2O2} are compared (Figure R1 = Figure in the manuscript) to the experimental values, where the kinetics of H_2O_2 decomposition have been monitored during MVK reactivity initiated at different MVK concentrations.

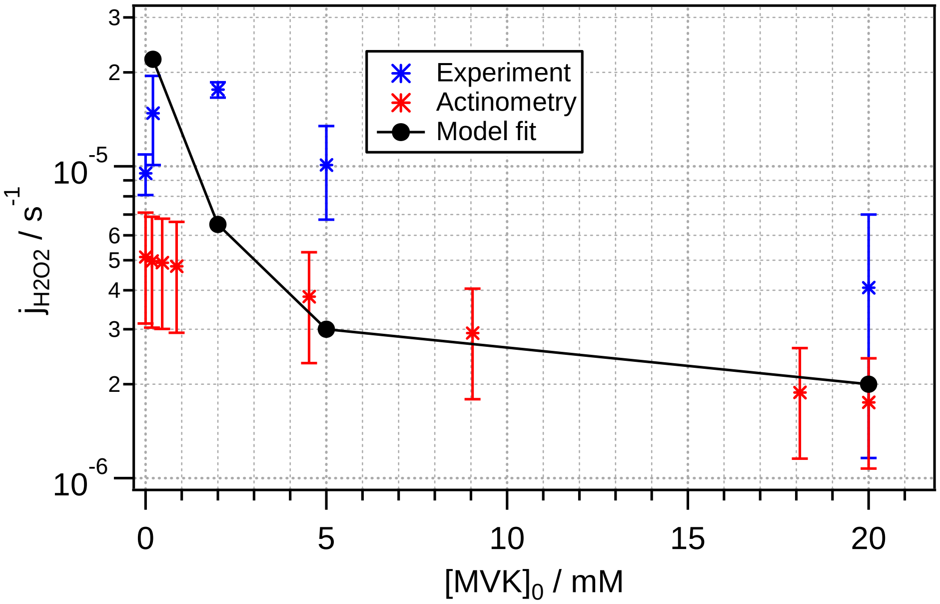

Figure R1-1 (= Figure 3 in the revised manuscript): H_2O_2 photodissociation coefficient values: comparison between experimental determinations and actinometry calculations in absence and in presence of MVK, at different initial MVK concentrations.

The results show the same trend of $J(H_2O_2)$ with increasing MVK concentrations for both experimental and actinometry determinations. The actinometry calculations give slightly smaller values, but this can be due to light reflections in the vessel, that have not been taken into account in the calculation.

In addition to these theoretical and experimental data, Figure 3 includes photolysis rates as used in the model calculations that were adjusted to match the initial MVK loss in the experiments. This loss is solely ascribed to the reaction of MVK with OH, and the only fitting parameter in this reaction rate is the OH concentration that depends directly on j_{H2O2}. It should be noted that the actinometry-derived data are based on the assumption of a constant (initial) MVK concentration while the model and experimental data take into account decreasing MVK concentrations. For example, at the highest initial MVK concentration (20 mM) where MVK complete decay takes more than 100 min, model, experimental and actinometry-derived data are in good agreement. Globally, one would expect the model to agree with the experimental data rather than with the actinometry ones, which is the case for low and high initial concentrations of MVK, but it is not clear why the model better matches actinometry data at intermediate MVK concentrations.

4b) Page 21569, section2:
(i) k MVKOH(a) and k MVKOH(b) ‘ abstraction from allyl group ’ is wrong and must be replaced by “addition reaction ...” or something similar .

(ii) As the abstraction from the allyl group is wrongly mentioned here: What will be the branching ratio considering addition and H - abstraction via both pathways, i.e. at the methyl group and at the allylic H abstraction at the allylic H is not considered, but only the first pathway being treated in analogy to acetone. Splitting the measured rate constant just between addition and methyl group H -abstraction does not make sense.

(iii) In the OH addition pathway (MVKOH(a)), all formed organic radical products react with O2 to form a peroxy radical. In the other pathway (MVKOH(b)), the RO2· formation is not included for all formed organic radical products (see e.g., Mgly(MVK)i , MVK(MVK)i , HAc(MVK)i). This inconsistency has to be revised.

Response: (i) The reviewer is right that the wording 'abstraction from allyl group' has been wrong. We replaced it by "(3) it might abstract a hydrogen atom from either the vinyl group or from the saturated end of the molecule " (p. 4, l. 26).

(ii)The answer to this question is in section 2.1.1 of the manuscript where we describe specific electron paramagnetic resonance (EPR) experiments dedicated to detect and quantify the first step organic radicals formed from the reaction. In order to make it clearer and also in order to answer to question c), we have modified the text in section 2.1.1, it now reads (new text in bold) (p. 4, l. 23ff).

“as an ~-unsaturated carbonyl, MVK bears highly reactive ~~functional groups, i.e.,~~ conjugated carbon-carbon and carbon-oxygen double bonds. Therefore, its oxidation by OH might occur via three reaction channels: OH might add to the vinyl group of the MVK molecule either on (1) the ~-carbon atom or on (2) the -carbon atom, or (3) ***it might abstract a hydrogen atom from either the vinyl group or from the saturated end of the molecule****. Pathways (1) and (2) lead to isomeric hydroxyalkyl radicals with identical molecular weights and, thus, neither the initiator radicals nor the resulting oligomers, respectively, are distinguishable with the analytical techniques (mass spectrometry) applied here.* ***In a thorough study of reaction products, Schöne et al. (2014) have***

identified oxidation products formed on both reaction pathways, and no branching ratio could be determined either.

Theoretically, OH addition on the ~ -carbon atom (pathway 1) is favored on both steric and resonance grounds; the propagating radical formed by this pathway (1) is the more stable one (Odian, 2004; **Schöne et al., 2014***). An attempt to distinguish between the three pathways was performed by direct observation* ***and quantification*** *of the resulting alkyl radicals using continuous-flow electron paramagnetic resonance (EPR) experiments with MVK concentrations from 1 to 25mM (Sect. S1 in the Supplement). The obtained highly complex spectra were the result of superimposition of various EPR signals. Using spectral simulations, the signal of* $HO\text{-}CH_2\text{–}CH\text{–}C(O)CH_3$ *radical adduct resulting from pathway (1) was clearly distinguished (dots in Fig. S1). The proportions of another transient radical was found to depend on the initial MVK concentration (compare the spectra in Figs. S1.1 and S1.2 in the Supplement). A very similar behavior of concentration-dependenc**e** of radical species was previously observed in experiments performed on acrylic acid by Gilbert et al. (1994), and they attributed this behavior to the formation of dimer radicals. Therefore, our concentration-dependent radical was attributed to a dimer radical such as* $HO\text{-}CH_2\text{-}CH(C(O)CH_3)\text{-}CH_2\text{-}CH\text{-}C(O)CH_3$*, thus confirming ~~the~~* ***a*** *very fast ~~oligomerization (~~recombination~~)~~ pathway (Gilbert et al., 1994). More than two different radical species were present in our experiments, but their respective signals remained unidentified due to overlapping EPR signals in the spectra. Although it was not possible to identify these other radical species, the occurrence of radicals resulting from pathways (2) and (3) was expected, and the EPR experiments showed that their relative importance was much lower than that of pathway (1). In the model, we lump pathways (1) and (2) to the more likely radical from pathway (1) (kMVKOH(a), Fig. 1). H-abstraction (pathway 3) might occur most likely on the most weakly bonded H atoms, which are the ones in the methyl group (bond energy _ 94 kcal* mol^{-1}*, as opposed to _ 111 kcal* mol^{-1} *for the other H-atoms of the molecule, (Blanksby and Ellison, 2003)) and stabilization of the resulting radical due to the adjacent carbonyl group. The rate constant for the reaction of MVK with OH has been recently determined as* $k_{MVKOH} = 7.3\times10^{9}\ M^{-1}\ s^{-1}$ *(Schöne et al., 2014). ~~Since the branching ratios for the various reaction pathways are not well constrained for the different branching reactions~~* ***Since the branching ratios for the various reaction pathways are not known****, we assume that pathway (3) might occur with a similar rate constant as* ***H-abstraction from the structurally-similar acetone (*** $k_{OH,Acetone} = 1.2\times10^{8}\ M^{-1}\ s^{-1}$***, Ervens et al., 2003; Monod et al., 2005). The ratio between the overall rate constants*** $k_{OH,Acetone}/k_{MVKOH}$ ***~ 1.6% is in qualitatively good agreement with i) our EPR results and ii) the calculation of the possible amounts of H abstraction reaction by Schöne et al. (2014)that both suggest a minor contribution of the H-abstraction pathway."***

(iii) In Figure 1, we had only included the O2 reactions of oligomer1 since this was the only pathway that led to a detected oligomer series (oligomer II). The equivalent peroxide compounds from the other series were not detected and are, therefore, not depicted in the mechanism (Figure 1).
In the simulations, all oligomer radicals are considered to react with O2. These pathways were indeed omitted in the original Figure 1 and are added now. However, since no products of these pathways were detected, the arrows lead only to not further specified 'products' in the same way as denoted before for the monomer species MGly, HAc etc.

4c) Page 21569, section2:

As for the kinetics: The overall rate constant measured by Schöne et al. (2014) covers all occurring pathways but they are not all discussed in the present manuscript. Any branching ratio must cover all of the three occurring pathways. Schöne et al. (2014) are discussing mechanisms for the reaction of OH with MVK which are not reflected at all in this contribution. This needs to be fully revised. The revision of this includes the possibility that any model calculation must be repeated with corrected values.

Response: We added the discussion of findings by Schöne et al. (2014) to Section 2.1.1 (p. 5, l. 1). For a detailed response to the reviewers comment, please, see our answer to comment b) (ii)

4d) J ROOH : How valid is the applied approximation ? Please please put „estimated " into the comment column

Response: The reviewer is right that this value is estimated. Due to the lack of appropriate data, we chose this approximation, similar to estimates as done in other aqueous phase mechanisms, such as CAPRAM. We added 'estimated' to the table. In addition, this estimate is based on experimental observations that have shown similar j values (within experimental uncertainties) between j(H_2O_2), j(CH_3OOH) and j(C_2H_5OOH) under the same experimental conditions (Monod et al., 2000; Monod et al., 2007).
We also noted that j_{H2O2} was included twice in Table 1. We removed the first entry.

4e) k 1st for the conversion of oligomer products to stable products. Is this just an estimate? Give a sound reason for the order of magnitude of this conversion rate constant.

Response: k1st is an estimate and it was adjusted such that the net formation of the oligomer mass as observed in the experiments (Renard et al., 2013; 2015) could be matched. For simplicity, we assume the same rate constant for all oligomer series as we do not have basis to assume different rate constants for different initiator molecules or oligomer chain lengths. We clarified this in the text in Section 2.1.2 (p. 8, l. 21ff)

"Since these are second-order rate constants, this range is not directly comparable to the fitted value of $k^{1st} = 6 \cdot 10^4$ s^{-1}, but implies that the total radical concentrations might be on the order of ~10^{-5} – 10^{-3} M, which ~~seems reasonable~~ ***might seem high even*** *in the relatively highly concentrated solutions used here.* ***It should be noted that depending on chain length and/or initiator radical the rate constants for the termination steps might differ. However, in order to keep the number of reactions manageable within the mechanism but yet to reproduce empirically the increase in oligomer mass as observed in the experiments by Renard et al. (2015) was matched, for simplicity and due to the lack of detailed theoretical or experimental data we assumed the same k^{1st} constants for all oligomer series."***

4f) k recomb : This value appears way too low. Give a justification.

Response: We'd like to point out that this value is a first-order rate constant [s^{-1}].Therefore, we do not think that it is too low. Despite the fact that recombination reactions occur with second order kinetics, we chose the parameterized representation of the loss of the radicals by recombination being 30% of the pathway we termed 'rearrangement'. This branching ratio was

estimated such that the observed relative differences in the abundance of Oligomers III vs Oligomers V + VI could be reproduced by the model.
We added a discussion and references that support the choice of this value (Gilbert et al., 1976; Schuchmann and von Sonntag, 1981, 1984; von Sonntag and Schuchmann, 1997) to Section 2.1.1. (p. 6, l. 27-29)
Please, see also our more detailed discussion of the choice of k_{recomb} and k_{arr} in our response to the reviewer comment #6 below.

4g) k HAcOH : Is this the best available value ? compare with others and justify choice.

Response: In the NIST solution data base, there are four values for the reaction of acetic acid (1.7e7 M^{-1} s^{-1}; 1.5e7 M^{-1} s^{-1}; 9.2e6 M^{-1} s^{-1}; 2.3e7 M^{-1} s^{-1}) and five for acetate (6.5e7 M^{-1} s^{-1}; 7.4e7 M^{-1} s^{-1}; 1e8 M^{-1} s^{-1}; 7.9e7 M^{-1} s^{-1}; 8.5e7 M^{-1} s^{-1}). None of these values has been marked as 'recommended' there, so there is no preference for a 'best value'. However, the values we have chosen (1.5e7 and 1e8 M-1 s-1 are those that are used in the mechanism CAPRAM whose development was accompanied by a thorough data evaluation and review in the framework of a European project (Ervens et al., JGR 2003). Therefore, we think that the choice of these values is justified, also given that the other values are at most 50% different.

4h) Could you please explain the basis of the estimation of the rate constants of the recombination of RO2 with HO2 /O2 - radicals.

Response: Due to the lack of systematic experimental data, we assumed that RO2 + HO2 reactions occur with the same rate constants as the recombination reactions of HO2. We are aware that this is a crude approximation; however, at this point we do not know how to perform a more sophisticated estimate.

4i) In the WSOC reactions: WSOC + OH → R· + HO2 . Please discuss the approximated HO2 formation. How realistic is a 1:1 stochiometry ?

Response: The reviewer is right that the overall stoichiometry might not be 1:1 but the HO_2 yield might be smaller. As pointed out below by the reviewer, HO2 recombination might affect the O2 levels in the aqueous phase. Since in the revised version of the manuscript, we point out that O_2(aq) is always in equilibrium with the gas phase, any assumption of HO_2 production in the aqueous phase does not affect the O_2 levels there.
During revision, we have shortened Section 3 of the manuscript and do not include the sensitivity to OH anymore. Therefore, the discussion of the reaction of WSOC with OH was also omitted.

5) k MVK is not listed in Table1.

Response: We are not sure which k the reviewer is referring to. The rate constant of the reaction of MVK with OH is denoted as k_{MVKOH} and is included in the table, split into the pathways a and b ($k_{MVKOH(a)}$, $k_{MVKOH(b)}$). Following up on the reviewer comments regarding the different branching ratios of the overall reaction, the table has been revised (typos corrected) but the nomenclature k_{MVKOH} in the table and text has not been changed.

6) Overall, the applied mechanism appears very uncertain and includes a huge number of tuning parameters. What would the meaning of the result be if, in the end, the mechanism reproduces measurements? It would only show that this is one possible solution. The authors should scan the parameter space and search for other solutions (see the above general comment) – include a sensitivity study. Is the one given by the listed set of parameters an absolutely best solution? Rank different solution sets. Discuss all the uncertainties of the parameters in detail. Give ranges of possible values.

Response: The reviewer is right that many of the rate constants are estimated based on similar compounds or analogies and are therefore uncertain. However, the experimental data give good constraints on the main processes that control MVK decay and overall oligomer formation and loss and to the relative distribution of the various oligomer series (Figure 5). The rate constant of the MVK + OH reaction has been measured in lab measurements and therefore constrains well the initial decay of MVK (Figure 2). The following MVK consumption has to occur due to oligomerization and therefore this rate constant (k_{olig}) is constrained, too. While it might be possible that oligomerization and termination (k^{1st}) occurs with different constants for different initiator radicals and/or chain lengths (k^{1st}), we cannot make any sophisticated guess about such differences. The same is true for the loss of the oligomers that can be only adjusted based on the loss of the total oligomer mass (Figure 3 in Part I, Renard et al., 2015).
To our knowledge, there is no available literature value for the exact same molecules as inferred in our mechanism. However, several studies suggest that rates of the rearrangement reactions (k_{arr}) are on the same order as we have estimated (Gilbert et al., 1976; Schuchmann and von Sonntag, 1981, 1984). While – again – no data are available for the ratio k_{arr}/k_{recomb} for the molecules as in our mechanism, we assumed the ratio to be the same as for primary ethers (von Sonntag and Schuchmann, 1997).
In additional sensitivity simulations (Section S4 in the supplemental information), we show that the model results are insensitive to the choice of k_{arr} and k_{recomb} (< 1% change in simulated MVK and oligomer concentration for a change of 10 orders of magnitude in these rate constants). In the same section other combinations of estimated rate constants are explored and it is shown that only the set of rate constants in Table 1 is in agreement with both literature values for similar compounds and with the laboratory experiments over a wide range of conditions.

7) p.21570, l 28: Please rephrase the sentence. Replace “There is a lack of exact reaction rate constants for the different branching reactions” by “There is a lack of branching ratios for the...”.

Response: We changed the wording to "Since the branching ratios for the various reaction pathways are not well constrained…" (p. 5, l. 30)

8) Section 2.2. How is the concentration of oxygen in aqueous solution treated in the model?

Response: For the simulation of the laboratory experiments, the concentration of oxygen is not calculated, but the measured concentration profiles from each experiment are used as an input (cf. Section 2.2.1). These profiles are provided in the Supplemental Information Figure S2), together with the numerical fits describing them. This approach was necessary since the solutions were constantly stirred, a process that cannot be represented in our box model. Note that we replaced the figures in the revised version. The new figures display the oxygen concentration in mg/L whereas the previous ones showed them in microM. Therefore, the empirical coefficients in the fit equations have changed.

In the multiphase simulations, the concentration of oxygen is calculated based on its uptake rates (i.e. mass accommodation coefficient, Henry's law constant and gas phase diffusion coefficient), and chemical production and loss processes. We added the reference by Lang et al. (1996) that shows that most organic salts actually lead to a slight salting-out effect of oxygen (cf. p. 16, l. 13ff, and Section 3.3.4).

9a) P 21579, 21580: The estimates about the phase partitioning are chosen in such a way to lead to maximum uptake. How are they justified? This is adding additional uncertainty to the results of the study. The authors assume an effective Henry's law constant of 2.1·10^6 for the uptake of MVK. Please, specify how this value has been derived! Is there any evidence from laboratory or field measurements for such high Henry's law constants of MVK or represents the chosen value just a tool to tune the results?

Response: We admit that the choice of the effective Henry's law constant was done such that a (unrealistic?) maximum effect of the oligomerization was shown. Following also comments by Reviewer #2, we carefully revised the discussion of this value and make it clear that a lower effective K_H (i.e a much weaker salting-in effect) might be more likely. Section 3 has been completely revised and $K_H^* = 0.01 \cdot K_H$ has been estimated as a reasonable value for the solubility reduction of MVK and MACR in aerosol water as compared to pure water (K_H).
Additional model studies take now into account the possibility that additional oligomer precursors are present in aerosol water (Sections 3.1.2 and 3.3.3). We perform estimates of the concentration limits that might be required to induce efficient oligomer formation.

9b) Moreover, an effective Henry's law constant means that certain processes shift the phase partitioning towards the aqueous phase. But in this case, MVK might not necessarily be present in its monomer form. It might be hydrated or in its dimer form or in other forms. However, this might have effects on the reaction mechanism. In the present work, the authors consider an effective Henry's law constant, but consider all of the dissolved MVK in its monomer form. This might be incorrect and questionable with regards to the proposed chemical mechanism. Can you, e.g., exclude to have dimers to be present in you system? Please provide proper answers to the questions and discuss them in the paper.

Response: The reviewer is right that in some cases a shift in the observed partitioning as compared to the physical K_H might be caused due to additional chemical reactions, such as hydration, oligomerization. However, as discussed now in Section 3.1, salting-in and –out effects are usually caused by thermodynamic effects that change the solubility of organics in salt solutions. For example, for glyoxal, it has been shown that physical effects, e.g. the interaction of the carbonyl group with surrounding ions such as sulfate trap more glyoxal in the aqueous phase as compared to pure water (Yu et al., 2011).
We cannot exclude that, in general, chemical reactions such as hydration or oligomerization might change the chemical nature of the dissolved organics. To our knowledge, the hydration constant of MVK has not been experimentally determined to date. However, several studies point to the fact that it is likely very small: In the aqueous phase, carbonyl groups absorb UV light in

the region 200–350 nm. Carbonyl compounds that are known to be totally hydrated in the aqueous phase, such as formaldehyde and glyoxal, do not absorb in this region (Fig 6 in by Liu et al.(2009)). MVK shows a strong absorption with a maximum at 296 nm, comparable to that of acetone, which hydration constant is as low as 0.0014 (Guthrie and Pitchko, 2000). Compared to isobutyraldehyde (K_{hyd} = 0.5–0.6 (Bell, 1966; Guthrie and Pitchko, 2000)(Bell et al., 1966; Guthrie et al., 2000), the absorbance of MVK is more intense. This may be due to a mesomeric effect between the C=C and C=O bonds in MVK, which prevents hydration.

Instead, we focus here on the modification of thermodynamic solubility equilibria that can be described by the Setchenov coefficients. We have added a discussion of Setchenov coefficients for atmospherically relevant carbonyl compounds (Section 3.1.1) and discuss the possible reductions of Henry's law constants in salt solutions (cf. also response to comments by Reviewer #2).

10) p.21580 , line 13: What do the authors want to say with the sentence "... an aqueous phase concentration of 2 mM, that can be considered as being typical for organics in aerosol water (Lim et al., 2010)"? The work of Lim et al. (2010) is mostly related to glyoxal and does not present data related to MVK. Why do the authors use the data given in Lim et al. (2010) for MVK? Do the authors think that MVK and glyoxal behave similar? The authors should keep in mind that the physico - chemical properties of MVK and glyoxal are not identical such as the different effective Henry's law constants which have been measured for both compounds .

Response: We revised the text. We referred to the paper by Lim et al. because they state that millimolar levels might be considered an approximate concentration of all potential aqSOA precursors (e.g. small carbonyl compounds) in aerosol water. An aerosol liquid water content (LWC) of ~20 μg m^{-3} is a reasonable average estimate for ambient conditions. Several studies suggest that water might exceed all other condensed matter by a factor of 2-3 (Meng et al., 1995) and ambient concentrations of particulate matter range from <1μg m^{-3} to >10 μg m^{-3} (Jimenez et al., 2009).

Using these numbers, one obtains

$$LWC\left(\frac{20\cdot10^{-6}\,\mathrm{g_{H2O}}}{\mathrm{m_g^3}}\right)\cdot c_{aq}\left(\frac{10^{-3}\mathrm{mol_{org}}}{\mathrm{L_{H2O}}}\right)\cdot M_{org}\left(\frac{150\,\mathrm{g_{org}}}{\mathrm{mol_{org}}}\right)\cdot\frac{\mathrm{L_{H2O}}}{1000\mathrm{g_{H2O}}}=3\ \mathrm{ng\ m^{-3}}$$

If one assumes an average molecular weight of 150 g mol^{-1} for organics and a water density of 1 g cm^{-3}.

This calculation shows that only a very small fraction of carbonyl compounds as determined in particulate matter (e.g. (Kawamura et al., 2013)) makes up already a concentration that initiates significant oligomerization.

In the revised manuscript, we simulate now three different cases with respect to the solubility/abundance of oligomer precursors: (i) using K_H(MVK)·0.01 = K_H*(MVK), based on Figure 6, and (ii) a case where we assume that typical aerosol particles comprise a few ng m^{-3} potential oligomer precursors with MVK being a proxy. In addition a third case is discussed where we assume oligomer precursors as in case (ii) but reduced oxygen solubility.

These cases are now explained at the end of Sections 3.1.2. and 3.3.2.

11) p.21581/9: Please add "+ H2O" to the right hand side of (R1).

Response: In the revised manuscript, we omitted the discussion of the sensitivity to OH; therefore the reaction is not included in the manuscript anymore.

12) p.21581/11 - 13: The authors consider (R 1 - 2) to account for additional OH and O2 sinks. However, the authors should keep in mind that O2 is at least partly recycled during peroxy - peroxy radical recombination's (see , e.g. Alfassi, 1997). In case of a chemical system, where the amount of dissolved O2 might be important, this recycling should be considered in a proper mechanism

Response: We revised the mechanism and consider now the recombination reactions (HO2 + RO2, RO2 + RO2) as an oxygen source. Please, note that we also revised the discussion on oxygen saturation in the atmospheric multiphase system and point out now such conditions are not met in the atmosphere as opposed to experimental conditions.

13) p. 21585, line 27: Table 4:

13a) There is no uptake data given for H2O2 and O2 in the manuscript. However, in the manuscript it is mentioned: "However, instead of initializing MVK, H2O2 and O2 in the aqueous phase, gas phase species are initialized, and their uptake into the aqueous phase of aerosol particles is described by the resistance model (Schwartz, 1986)".

Response: We added the uptake parameters of OH, H_2O_2 and O_2 to Table 2.

13b) Please, put the used KH values in the Table and not the measured data of Iraci et al. (1999) since they were not really applied in the mechanism. This is misleading and the small comment below is not sufficient enough.

Response: We removed the K_H values from the table (now Table 3) and only include gas phase reactions there. In Table 2, it is now clarified that we estimate the solubility of MVK as $K_H^* = 0.01 \cdot K_H$ based on Figure 6.

14) Figure 1:

13a) From the reviewer's point of view, it might be better, for the sake of clarity, to provide both Figure1 and a detailed revised Table 1 with all single reactions considered in the mechanism.

Response: Given that we assumed the same rate constants for reactions of many species for the sake of simplicity and limited knowledge, we think that the abbreviated table as we have provided, is sufficient. We increased the font in Figure 1 for better readability.

14b) For the compound (CH(=CH2)C(O)C·H(OH)) the RO2· formation and subsequent HO2 elimination reaction is missing.

Response: The reviewer is right that the RO_2 formation was missing in the Figure, but the reaction was actually taken into account in the model, as previously mentioned in our answer to question on Page 21569, section2, b) (iii). The reaction has been added to the revised Figure 1.

14c) Moreover, the mechanism in its current version does include RO2· recombinations for all formed RO2· radicals. For some single species, only the reaction with HO2 is considered. However, also the RO2· recombination should be considered as potential sink as well as source of O2 . Without this recycling process of O2, the presented result in Figure 6b is inadequate. Moreover, it is mentioned that the formation of some end-products given in Figure 1 (for example: Products, small molecular weight compounds, ..) represents an artificial loss of O2 . This issue needs at least to be mentioned.

`Response: We revised the discussion of a potential oxygen limitation (Section 3). We state more clearly now that under atmospheric conditions oxygen limitation might only occur if the oxygen solubility were decreased by a factor of ~10 due to a decrease of solubility on salt solutions (Section 3.3.3).`

14d) The oxygen addition reactions for the alkyl radicals formed after the MVK addition (Pathway leading to oligomer III, IV, V, VI, VII) are missing. Could you please explain why the RO2 reaction with HO2 radicals in one pathway forms the oligomer II and in a second pathway a thermodynamic unfavorable hydroperoxid, which undergoes a subsequent photolysis reaction. It is more likely that this reaction produce an alkoxy radical, a hydroxyl radical and molecular oxygen. Can you please elaborate the possibility of the addition reaction of peroxyl radical with double bond of MVK.

`Response: We agree that these possibilities seem likely. However, the oligomer with a hydroperoxid group (Oligomer II) was analytically identified (see Tab 2 in Renard et al., 2013). If the peroxy radical added to the double bond of MVK, the resulting products would have been observed and distinguished by the analytical techniques applied by Renard et al., 2013 and 2015. Since the corresponding signals were absent, we did not include the reactions leading to these products. Discussion has been added on p. 6, l. 2-5.`

15) Figure 4: The right part of the Figure (4b) needs a legend.

`Response: We added a legend to Figure 4b.`

16) Supplement:
The page numbers of the supplement are not in the correct order

`Response: We thank the reviewer for noticing this. We corrected the page numbers in the supplemental information.`

17) On page S1, Line 11 there is a typo. The space between (Figure S1.2) obtained is missing. Also in line 13: mL.min - 1 instead of m L ·min - 1 and on page S2, Line 4: mL.min - 1 instead of m L ·min - 1 The layout of equation e) on page S5 is different in comparison with equation d)

`Response: We corrected these typos.`

References

Bell, R. P.: The reversible hydration of carbonyl compounds, Adv. Phys. Org. Chem., 4,1-29, 1966.

Blanksby, S. J., and Ellison, G. B.: Bond dissociation energies of organic molecules, Acc. Chem. Res., 36, 4,255-263, 10.1021/ar020230d, 2003.

Ervens, B., Sorooshian, A., Lim, Y. B., and Turpin, B. J.: Key parameters controlling OH-initiated formation of secondary organic aerosol in the aqueous phase (aqSOA), J. Geophys. Res. - Atmos., 119, 7,3997-4016, 10.1002/2013JD021021, 2014.

Gilbert, B. C., Holmes, R. G. G., Laue, H. A. H., and Norman, R. O. C.: Electron spin resonance studies. Part L. Reactions of alkoxyl radicals generated from alkyl hydroperoxides and titanium(III) ion in aqueous solution, Journal of the Chemical Society, Perkin Transactions 2, 9,1047-1052, 10.1039/p29760001047, 1976.

Guthrie, J. P., and Pitchko, V.: Hydration of Carbonyl Compounds, an Analysis in Terms of No Barrier Theory: Prediction of Rates from Equilibrium Constants and Distortion Energies, Journal of the American Chemical Society, 122, 23,5520-5528, 10.1021/ja992991q, 2000.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of organic aerosols in the atmosphere, Science, 326, 5959,1525-1529, 10.1126/science.1180353, 2009.

Kawamura, K., Okuzawa, K., Aggarwal, S. G., Irie, H., Kanaya, Y., and Wang, Z.: Determination of gaseous and particulate carbonyls (glycolaldehyde, hydroxyacetone, glyoxal, methylglyoxal, nonanal and decanal) in the atmosphere at Mt. Tai, Atmos. Chem. Phys., 13, 10,5369-5380, 10.5194/acp-13-5369-2013, 2013.

Liu, Y., ElHaddad, I., Scarfogliero, M., Nieto-Gligorovski, L., Temime-Roussel, B., Quivet, E., Marchand, N., Picquet-Varrault, B., and Monod, A.: In-cloud processes of methacrolein under simulated conditions - Part 1: Aqueous phase photooxidation, Atmos. Chem . Phys., 9,5093-5105, 2009.

Meng, Z., Seinfeld, J. H., Saxena, P., and Kim, Y. P.: Contribution of Water to Particulate Mass in the South Coast Air Basin, Aeros. Sci. Technol., 22, 1,111 - 123, 1995.

Schuchmann, H.-P., and von Sonntag, C.: Photolysis at 185 nm of dimethyl ether in aqueous solution: involvement of the hydroxymethyl radical, Journal of Photochemistry, 16, 4,289-295, http://dx.doi.org/10.1016/0047-2670(81)80051-2, 1981.

Schuchmann, H.-P., and Von Sonntag, C.: Methylperoxyl Radicals: A Study of the y-Radiolysis of Methane in Oxygenated Aqueous Solutions, Z. Naturforschung, 39b,217-221, 1984.

van Pinxteren, D., Neusüß, C., and Herrmann, H.: On the abundance and source contributions of dicarboxylic acids in size-resolved aerosol particles at continental sites in central Europe, Atmos. Chem. Phys., 14, 8,3913-3928, 10.5194/acp-14-3913-2014, 2014.

von Sonntag, C., and Schuchmann, H.-P.: Peroxyl radicals in aqueous solution, in: Peroxyl Radicals, edited by: Alfassi, Z. B., Wiley, Chichester, 173–234, 1997.

Yu, G., Bayer, A. R., Galloway, M. M., Korshavn, K. J., Fry, C. G., and Keutsch, F. N.: Glyoxal in aqueous ammonium sulfate solutions: Products, kinetics and hydration effects, Environ. Sci. Tech., 45, 15,6336–6342, 10.1021/es200989n, 2011.