

Dear Editor,

We thank the reviewers for the helpful comments! We have now taken the benefit from those in improving the manuscript. A point by point response by a reply or/and actions (in black) to the reviewers' comments (in blue) will follow. New texts added or removed are shown in italics. The aim was to reply on each comment separately even if it creates some repetitions in replies (several comments solved by similar change). However, due to the number of comments there are a few that become obsolete due to changes from others. Then that are described by a reply. At the end is the full manuscript with changes in "track changes mode".

Response to Anonymous Referee #1

General comments

The manuscript presents the study of carboxylic acid formation from limonene ozonolysis. Experiments have been performed in a laminar- flow reactor in the dark under NO_x-free conditions at 20°C, using various conditions of humidity, initial ozone and precursor concentrations, and with or without the use of an OH scavenger. The gas and particle phases were analyzed using an acetate HR-ToF-CIMS for the measurement of carboxylic acids. Around 100 molecular formulas of carboxylic acid have been identified, the chemical structures have been suggested for the major detected carboxylic acids, and their contribution to the total carboxylic acid signal has been calculated. Spearman correlation analysis and comparisons with the MCM have been performed.

Reaction pathways have been suggested to explain the formation of some carboxylic acids not present in the MCM. The work performed here provides a large and original experimental dataset on carboxylic acid formation from limonene ozonolysis. From my point of view, the manuscript still need large improvements to provide a clear message and an argued discussion. The following points have to be considered before publication.

Major comments:

1. The discussions in section 3 and 4 of the manuscript should (1) be supported by the experimental/modeling work performed here showing appropriated figures, (2) presented in a quantitative way and (3) compared to recent bibliographic references (especially from other research teams). These two sections of the manuscript should according to me be rewritten in this way. If not, the discussions appear subjective. Here is only one example among others in the manuscript on the sensitivity of carboxylic acid formation to humidity, initial ozone and precursor concentrations, with or without the use of an OH scavenger. Currently, the authors discuss the sensitivity in term of signal intensity, diversity of products... but the discussion remains qualitative (increase or decrease, considerable or slight, higher or lower, opposite effects, explained or un- explained...) and is not directly supported by figure 3 (showing only in percent the total contribution of the 10 major carboxylic acids to the detected signal for dry and humid, and with and without the OH scavenger). A quantitative discussion, supported by a figure that summarizes all of the 33 experiments, showing the measured carboxylic acid signal intensity, and the individual contribution of the major

carboxylic acid molecular formulas could be of large interest here. The authors could for example present a figure showing for each experiment, as cumulated bar plots, the total signal intensity of the detected carboxylic acids and the contribution of the individual top 10 (or 20, ...) to the total signal intensity (in intensity not in %) (or to the total signal intensity divided by the reacted precursor quantity, as yields, to be able to compare more easily the different experiments?) (a) for the gas phase and (b) for the particulate phase.

Reply: Thanks for the suggestions to clarify the presentation and discussion. The focus on relative intensities/concentrations is related to the aim to understand which acids are dominating under what conditions. Since there is always from laminar flow reactor studies hard to extract absolute yields we avoid explicit statements related to that and prefer to still a focus on relative intensities and correlations. Obviously, one can derive average yields/concentrations as measured at the end of the flow reactor, from the intensities presented in table s7 and s8 bearing in mind the residence time distribution.

Action: We have added a new Figure (now figure 4) where we present cumulated bar plots with the molar yield of the detected carboxylic acids (focus on the 8 most important acids with individually categories). We have added some quantitative information discussing some aspects of this figures and the overall molar yield from the experiments. Now these are presented in Table 1.

Text added:

“This experiment was done at medium ozone and high limonene concentration with an estimated 8 % molar yield of large carboxylic acids.”

“Typically, these acids stand for 2-23% of reacted limonene on a molar basis assuming an average reaction time and CIMS sensitivity (Table 1). The distribution between gas and particle phase varied between compounds where the average particle fraction was between 5 and 80% depending on experimental conditions.”

” Figure 3 shows for the comparable data to Fig. 2 (medium ozone, high limonene) the fraction of the 10 most prevalent ions. This was the most complete sub-step (dry-humid, with and without scavenger) of the total matrix and the illustrated pairwise features (e.g. dry vs humid) that was common also among other concentrations (e.g. for other condition we had missing particle phase data, see table 1). For these four selected experiments the estimated total yield of larger carboxylic acids (c7-c10) were very similar 6% (dry, scavenger), 8% (humid, scavenger), 6% (dry, no scavenger) and 7 % (humid, no scavenger).”

“Figure 4 shows the total molar yield of the acids identified in this study. One may note that the absolute yield presented here has significant uncertainties while the relative important of an acid can guide us in our mechanistic interpretation.”

2. The authors state at several places in the manuscript that a large amount of carboxylic acids is formed during limonene ozonolysis but the contribution of the detected carboxylic acids is never compared to the total amount of secondary organic species formed during the experiments. Would it be possible to quantify this? This quantification is indeed difficult on a concentration basis but could maybe be done on a carbon basis, i.e. carbon concentration in the detected carboxylic acids divided by the carbon concentration in reacted limonene amount (considering that the intensity of the signal is directly proportional to the concentration with the same proportional factor used for all the acids if possible?).

Reply: Yes, using estimated limonene consumed, the intensities from Table S7 and S8 (now Table S2 and S3), and general sensitivity (from calibrations of standard acids) carbon yields can be estimated.

Action: To indicate the amount of c7-c10 acid produced the total molar yields estimated from experiments and modelling are now given.

*Beginning of abstract:

“The experiment and model providing yield of large (c7-c10) carboxylic acid in the order of 10% (2-23 and 10-15%, respectively)”

*Last sentence in abstract:

“Using the additional mechanisms proposed in this work nearly 75% of the observed gas-phase signal in our lowest concentration experiment (8.4 ppb converted, ca 23% acid yield) done at humid conditions can be understood.”

*Discussion/result section a sentence was added:

“Generally, the model provides small variation in the total molar yield for the large carboxylic acids (c7-c10) of 10-15% while the experiments shows larger variability (2-23% molar yield) plausible due to the complication of aerosol formation not covered by the model.”

3. Spearman correlation analysis have been performed to interpret the results. I am personally not familiar with this analysis. At the reading of the manuscript, I am not convinced by the relevance of such a statistical criterion for the purpose of this study (for an experimental work or a modeling study) nor by the substantial interest provided in the interpretation of the spearman correlations (the conclusions being mainly that two variables have a positive or negative correlation). Could the authors explain their objectives prior showing the spearman correlations? Have the spearman correlations been used previously for nonlinear / multigenerational / atmospheric chemistry? Also, I find these figures rather complex so could the authors discuss in general what we learn for a few selected points (what does it mean and what do we learn for example if the correlation is -1, 0 or 1?) Can we talk about a correlation between two variables if the spearman correlation is close to 0? If the results from these spearman correlations and rank correlations analysis is of largest interest for the manuscript,

figures should be shown in the manuscript and not in supplementary, and they should be clearly presented and longer discussed.

Reply: The Spearman correlation analysis was done as a tool to achieve a pattern on correlation that was used to extract selective compounds for more detailed analysis/description-maybe more as a guideline for our interpretation and as such we decided to give the full matrix. One could elaborate more on this but it will not be the main point of the paper.

Action:

*To reduce the focus on the spearman correlation we removed one sentence from the abstract:

“Spearman correlation analysis of the produced carboxylic acid species and experimental parameters were helpful in interpreting the results.”

*To describe why we used spearman compared to normal correlation we added the following in the method section:

“A spearman correlation analysis was done based on of major products, experimental conditions and calculated radical concentrations. Compared to standard correlation the spearman correlation is more robust to outliers and independent of any assumptions about the distribution of the data. It was therefore preferred to assess the degree of association between each dominant acid and experimental parameters. The evaluation using spearman correlation is similar to other correlation methods giving 0, -1 and 1 for no correlation, perfect negative and positive correlation, respectively.”

4. For the comparisons performed between the MCM and the experiments, more information and justifications should be provided in the manuscript. In particular, could the authors explain how the model has been set to represent the experiments (box- model used, representation of the gas/particle partitioning, estimation of the vapor pressures, initialization...)? Could a simulated temporal evolution be shown in the manuscript for a typical experiment? Also, I would have expected a comparison between model/measurement rather than a spearman correlation between MCM species. Could a figure summarizing quantitatively the MCM/experiment comparisons for the carboxylic acids be provided (for all experiments) in the manuscript and discussed in detail? One detail, the MCM is not a “model” as written several time in the manuscript but a chemical mechanism.

Reply: We use the existing chemical mechanism (MCM) to probe the effects on the formation of compounds due to changes in experimental conditions via gas-phase chemistry and the mechanism does not cover the particle phase. However, in comparison we use experimental data from both gas and particle phase. We do not show any temporal evolution since all measurements were done after the same residence time. However, one could use the model to illustrate formation of key compounds and e.g. radical distribution (RO_2/HO_2). Yes, the statement of MCM as a model is wrong and should be replaced by mechanism.

Action:

*We have added a sentence:

“The model did only consider gas-phase scheme of MCM.”

*A section describing the model were moved from the first part of R&D to the model results and comparison section.

*We present the calculated integrated HO₂/RO₂ ratio (normalised to respective rate coefficient with RO₂) in the experimental condition table (Table 1) as an example on variation in chemistry.

We have added another reference to this table to emphasis the modelling results.

“However, the variation of radical distribution between experiments is illustrated in Table 1. Here the values of radicals are given as the integral concentration over the reaction time (unit pbb × s).”

* We also added a discussion on Table 1- the text now reads:

“The model results show that the HO₂/RO₂ ratio in experiments employing the OH scavenger 2-butanol is approximately one order of magnitude higher than that of the mixed oxidant experiments. This higher ratio results from the HO₂ radicals generated by the reaction of 2-butanol with OH and will provide more influence of the HO₂ + RO₂ reaction in the experiment with scavenger. However, the RO₂ self-reaction are still the major pathway also in these experiment, twice the normalised rate of the HO₂ reaction. One may note that the RO₂ reaction rates are very much structural dependent and might be faster or slower that the assumed rates, see Jenkin et al. (2019) for a recent review on RO₂ chemistry.”

*We added a comparison of the total acid yield:

“Generally, the model provides small variation in the total molar yield for the large carboxylic acids (c7-c10) of 10-15% while the experiments shows larger variability (2-23% molar yield) plausible due to the complication of aerosol formation not covered by the model.”

*The MCM is now referred to as a mechanism rather than a model.

Minor comments:

1. This paper focus on limonene ozonolysis and the experiments are performed in the dark under NO_x-free conditions. I think this should be explicitly written somewhere in the manuscript.

Reply: We agree

Action: This is now included.

*The first sentence in the abstract:

“This work presents the results from a flow reactor study on the formation of carboxylic acids from limonene oxidation in the presence of ozone under NO_x free conditions in the dark.”

*The last sentence in introduction:

“This work (i) considers ozonolysis under dark condition and NO_x free conditions (for various limonene concentrations) the effect of humidity, OH scavenging and ozone level on carboxylic acid formation,…”

2. To clarify the discussions (1) figures/tables should be presented and discussed once, before presenting the conclusions and comparisons to other studies and (2) the legend of the figures and the tables should be clearer / more precise. Here are a few examples only:

- p.5 l.5... “The general effect of parameters on SOA formation concurs with our previous results” but the results of this study have not been presented yet.
- p.5 l.16, p.5 l.19, p.7 l.12... qualitative conclusions are provided with references to figures in parenthesis but figures have not been presented and discussed yet in the manuscript
- figure 4: please show which carbon of R1, R2 and R3 is connected to – C(CH₃)=CH₂
- the legend of Figure 8 is not clear (ex: compound previously described?)
- table S2: are the structure proposed by the authors or in literature?
- The legend of figure S3, S4 and especially S5 should provide more information

Reply: 1) Yes, this is a valid point and should be implemented as far as possible. However, the two examples on this would rather reflect subjective ways of writing? Maybe we do not understand the points/examples correctly. The first point relates to a statement that the SOA behavior is in line with our previous study and we don't want to spend too much effort in repeating our old findings. Alternatively, we could remove this but then one would be criticised for not including any results on SOA formation behaviour. The second point is our way of writing a statement and then referring to a figure (in the same sentence) to support that statement. However, one could do it an opposite way saying “Figure x shows this and that”. Maybe that would be clearer for the reader (as we interpret is the suggestion from the reviewer). 2). Yes, we should be more careful on doing this.

Action:

- 1) We removed the statements on SOA properties since that is not the focus on our paper. We have now rewritten part of the wording ensuring we introduce the figures more clearly.
- 2) The legend to the figures has been scrutinized and improved-especially for the points raised by the reviewer.

3. I think a discussion on the selectivity of the reagent ion (acetate) is needed somewhere. Are all the carboxylic acids detected and are all the detected species carboxylic acids, as suggested by the authors? Could some interferences occur with other species (such as organic peroxy acids formed in low-NO_x conditions)? What is the possible impact of these interferences on the results of this study?

Reply: The acetate ionization is primarily sensitive for acids. However, the ionisation is also able to e.g. deprotonate nitrophenols as shown by Mohr et al. (2013); and Lopez-Hilfiker et al.

(2015) measured peroxy acids as their corresponding carboxylate anion in their study. In our study the detection of peroxy acids cannot be ruled out. So yes, the formation of peroxy acids would be an important interference and we do mention this as a possibility in the mechanism discussion but it should be more clearly written in e.g. materials and methods section.

Action: A statement on selectivity and potential interference from peroxy acids is given in the materials and methods section. We now use a sensitivity of 5.5×10^{-3} Hz ppt⁻¹ (Le Breton et al, 2019) to calculate the total molar yield of the large carboxylic acids detected. This is now stated in the experimental section. Text read:

” One may note that also peroxy acids has high sensitivities (Lopez-Hilfiker et al., 2015) and that the acetate ionisation has previously been used to detect nitro phenols (Mohr et al., 2013; Le Breton et al., 2019) and organic sulphates (Le Breton et al., 2019). However, here we assume carboxylic acids and peroxy acids to be the primarily compounds being observed with current set-up the CIMS. The used sensitivity for larger carboxylic acid was 5.5×10^{-3} Hz ppt⁻¹ (Le Breton et al., 2019). This sensitivity was used to estimate molar yields; even if one should be precautious to provide absolute yields from this type of studies it provides indications on the product contribution.”

4. p.5 l.26 “the proposed structures of these acids are also shown” On which criteria are the structure proposed? Based on the “common” gaseous chemical pathways? On literature? A table with the carboxylic acid structures proposed by the authors should be included in the manuscript.

Reply: The structures presented in the literature overview Table S1 were proposed by the authors for the paper referred to in that table.

Action: We more clearly direct the readers to Table S1:

“Table S1 also illustrate the proposed structures of these acids based on the current literature.”

Technical corrections:

p.1 l4: What “profile” are we talking about? Remove the word?

Action: The word “profile” was removed

p.1 l.9: Should “The measured concentrations of dimers” be changed by “The measured concentration of dimers bearing at least one carboxylic acid function”?

Action: The beginning of the sentence was changed to

“The measured concentration of dimers bearing at least one carboxylic acid functional group”.

p.1l.15: I don’t understand the meaning of this sentence (and not fully figure 8) “Based on the mechanisms proposed in this work, nearly 75% of the qualitative gas-phase signal of the low concentration (ppb converted), humid, mixed oxidant experiment can be explained”

Action: The sentence was changed to:

“Using the additional mechanisms proposed in this work nearly 75% of the observed gas-phase signal in our lowest concentration experiment (8.4 ppb converted, ca 23% acid yield) done at humid conditions can be understood.”

p.2 l.4: Is this sentence used to justify why limonene is studied: “The emission rates of limonene are lower than those of other monoterpenes (e.g. α -pinene), and limonene is doubly unsaturated and exhibits high reactivity in the presence of ozone”?

Action: The text now reads:

“..and elevated indoor concentrations can be expected (Brown et al., 1994;Langer et al., 2008) with subsequent SOA formation (Youssefi and Waring, 2014). The total global forest emission of limonene has been estimated to 11.4 Tg year⁻¹, placing it on the top four among monoterpenes (Guenther et al., 2012). A high aerosol yield and the two chemically different double bonds, an endocyclic and an exocyclic double bond makes limonene ozonolysis of specific interest (Koch et al., 2000;Saathoff et al., 2009;Chen and Hopke, 2010;Gong et al., 2018)..”

p.2 l.7: Does “primary” in “However, the primary products may be unsaturated” mean emitted? “primary” be replaced by “first generation product”?

Reply: The word “primary” means first generation products in this context.

Action: The word “primary” was replaced by “first generation products”

p.2 l.10: Please remove “basic” in “basic reaction mechanisms”

Action: The word “basic” was removed

p.2l.17: The sentence “The 10 carbon skeleton is retained during this process” is not right if O₃ addition occurs on the exocyclic double bond

Reply: The referee’s comment is correct, but in this case we refer to the attack on the endocyclic double bond.

Action: We clarified:

“The 10 carbon skeleton is retained during this process, if an endocyclic double bond is attacked.”

p.3 l.15: “The OH scavenger reduces the OH concentration but leads to an increase in the HO₂ concentration” and also in the RO₂ concentration

Action: The sentence was changed to

“The OH scavenger reduces the OH concentration but leads to an increase in the HO₂ and RO₂ concentrations”.

p.4 l.14: Please refer to “table S1” after “A summary of experimental conditions is provided in”

Action: The cross reference was added

p.4 l.16: A reference is needed here “The reagent ion acetate is especially susceptible to acidic organic compounds such as carboxylic acids”

Action: The reference to Bertram et al. 2011 was added

p.4 l.19: Change “The gas-phase chemistry” into “The gas phase composition”?

Action: “The gas-phase chemistry” was changed into “The gas phase composition”

p.5 l.6: Something is missing here “(for e.g.)”

Action: The sentence was removed based on another comment.

p.5 l.31 to p.6 l.5: These sentences refer to the model and should be moved after the discussions on the experimental results

Action: The sentences were moved

p.6 l.5: If the species are of low volatility they are not VOC (volatile organic compound)

Action: The text was changed accordingly: “..fraction of low-volatility and often very oxygenated organic compounds”

p.6 l.9: Should “carbon number ≥ 10 ” be replaced with ““carbon number ≤ 10 ”?”

Action: The text was changed from “carbon number ≥ 10 ” to “carbon number ≤ 10 ”?

p.6 l.13 Something is missing in “(e.g.)”

Action: (e.g) was removed. “However, the relative signals are significantly lower than those reported for dimer formation in a study on limonene with nitrate radicals (Faxon et al., 2018) or the ozonolysis of other terpenes such as α -pinene (Kristensen et al., 2016)”

p.8 l.7 to p.8 l.13 The discussion on the HO₂/RO₂ ratio is not clear

Action: The discussion has been clarified and Table 1 now also includes a row of modelled HO₂/ratios. the text now reads:

“The model results show that the HO₂/RO₂ ratio in experiments employing the OH scavenger 2-butanol is approximately one order of magnitude higher than that of the mixed oxidant experiments. This higher ratio results from the HO₂ radicals generated by the reaction of 2-butanol with OH and will provide more influence of the HO₂ + RO₂ reaction in the experiment with scavenger. However, the RO₂ self-reaction are still the major pathway also in these experiment, twice the normalised rate of the HO₂ reaction. One may note that the RO₂ reaction rates are very much structural dependent and might be faster or slower than the assumed rates, see Jenkin et al. (2019) for a recent review on RO₂ chemistry.”

p.9 l.23: Fig. 11 does not exist

Action: The cross reference was changed to Fig. 1

p.17: Please, provide the of the experiment and explicit “OH-S”

Reply: The comment appears to be incomplete. We interpreted it as missing experimental number and writing clearly what OH-S stands for.

Action: Actions according to our interpretation but extended with more info in the caption:

“Example of derived mass spectra of condensed phase taken from the experiment (#21) with medium-ozone and high-limonene conditions with added OH scavenger. Indicated are the regions with identified monomers (orange region) and selected dimers (blue region). The peaks at 319, 344 and 363 are associated with the used mass calibrant HPFA. The complexity of this mass spectra is described using the fraction of 10 dominated product ions and are compared to other experiments with similar conditions in Fig. 3.”

p.18: Does the figure show the “explained and unexplained fraction” (see title) or the “top 10 and other than top 10” (see labels)?

Reply: The figure shows the contribution of the highest 10 compounds to the total signal.

Action: The caption was changed and are now reading:

“Contribution of the highest 10 compounds (blue) to the total signal in the gas and particle phase. The red fraction shows the signal not explained by the 10 highest compounds. A larger red fraction would indicate a more complex composition. Data shown for selected experiments with 1000 ppb ozone and 150 ppb limonene under different conditions. The estimated total yield of larger carboxylic acids (c7-c10) for these four experiments were very similar 6% (dry, scavenger), 8% (humid, scavenger), 6% (dry, no scavenger) and 7% (humid, no scavenger).”

Response to Anonymous Referee #2

General Comments:

1. The motivation of the study could be carved out better. The authors introduce limonene as an important indoor VOC, but do not further go into detail about quantities etc. They then switch immediately to limonene in ambient air, but it is not clear at all whether indoor or outdoor limonene was the motivation for the study, and whether precursor conditions were tuned to simulate indoor or outdoor conditions (I assume, outdoor). In addition, the authors do not discuss any numbers, and only make qualitative statements in the introduction. This makes it hard to gauge the significance of the results presented here in the context of previous research.

Reply: Yes, one could elaborate more in the introduction. However, the general scientific motivation on studies of limonene ozonolysis cannot be divided by indoor or outdoor boundaries, but rather the difference in chemical regimes. Here e.g. the influence on RO2 chemistry could be important e.g. if the peroxy radical reacts with HO2 or via selfreaction (or in presence of NOx via NO).

Action:

*The introduction has been elaborated and now includes a quantitative motivation (we also added a point in method-see below). Text reads.

“...and elevated indoor concentrations can be expected (Brown et al., 1994;Langer et al., 2008) with subsequent SOA formation (Youssefi and Waring, 2014). The total global forest emission of limonene has been estimated to 11.4 Tg year⁻¹, placing it on the top four among monoterpenes (Guenther et al., 2012). A high aerosol yield and the two chemically different double bonds, an endocyclic and an exocyclic double bond makes limonene ozonolysis of specific interest (Koch et al., 2000;Saathoff et al., 2009;Chen and Hopke, 2010;Gong et al., 2018).”

*We have added the environmental condition (dark without NOx) in the abstract:

“This work presents the results from a flow reactor study on the formation of carboxylic acids from limonene oxidation in the presence of ozone under NOx free conditions in the dark.”

In the last sentence of the introduction where we also state our aim on ambient atmospheric application:

“This work (i) considers ozonolysis under dark condition and NO_x free conditions (for various limonene concentrations) the effect of humidity, OH scavenging and ozone level on carboxylic acid formation, and (ii) provides an outlook and suggestions for mechanistic gaps with the aim of eventually describing major acidic products found in the gas and particle phases under realistic atmospheric conditions, i.e. ozonolysis is performed in the absence of an OH scavenger under low concentration and humidity conditions.”

2. A related point is to be made for the materials and methods section. A short discussion on precursor concentrations, and how they compare to atmospheric conditions, or other lab studies, would help placing the study in context within previous/ongoing research.

Action: Material and methods has been extended with a motivation on using this specific set-up and these conditions.

Text added:

“The experimental matrix was chosen to understand ozonolysis of limonene under dark NO_x free conditions. The laminar flow reactor approach is well suited for investigating changes in experimental condition, e.g. dry vs humid, high vs low concentration. Due to short residence time the absolute concentration is higher than ambient even if the amount limonene converted (few ppb and higher) is similar to larger simulation chamber studies. The conversion of any RO₂ radicals is biased towards self-reaction; of importance in VOC dominated rural forest conditions and in the indoor environment.”

3. Generally, choices for both analysis and figures should be better motivated (scientifically). Why was this particular mass spectrum chosen in Figure 2? Why is the analysis focused on acids with 7 – 9 carbon atoms? Why were experiments with 1000 ppb of ozone and 150 ppb limonene only chosen for Figure 3? Again, the importance of the results presented here is hard to gauge without a clear scientific reasoning. In addition, e.g. Figure 2 and Figure 3 would be more interesting if they represented average and diversity of mass spectra for different experiments, and not examples.

Action: Motivations have been added to put the work/selected illustrations in context.

“Figure 3 **Error! Reference source not found.** shows for the comparable data to Fig. 2 (medium ozone, high limonene) the fraction of the 10 most prevalent ions. This was the most complete sub-step (dry-humid, with and without scavenger) of the total matrix and the illustrated pairwise features (e.g. dry vs humid) that was common also among other concentrations (e.g. for other condition we had missing particle phase data, see table 1). For these four selected experiments the estimated total yield of larger carboxylic acids (C₇-C₁₀) were very similar 6% (dry, scavenger), 8% (humid, scavenger), 6% (dry, no scavenger) and 7 % (humid, no scavenger).”

4. The discussion on the different effects on observed spectra is interesting, but somewhat hard to follow. It would be beneficial if the authors could provide figures that support their claims, and visualize the most important statements/relationships.

Reply: Yes, the text could be complemented with a Figure.

Action: We have added a new Figure (now figure 4) where we present cumulated bar plots with the molar yield of the detected carboxylic acids (focus on the 8 most important acids with individually categories). We have added some quantitative information discussing some aspects of this figures and the overall molar yield from the experiments. Now these are presented in Table 1.

Specific comments

P. 1, l. 19: This reference is used rather often throughout the manuscript. It is with out any doubt an important reference for the study. However, there might be certain subtopics of SOA that have seen some progress and update in the last decade, and it might be worth finding these.

Action: We have complemented this with more recent citations.

P. 1, l. 19: Are number, size, and chemical composition “particle properties”? This sentence should be clarified.

Action: The sentence was clarified: “Atmospheric aerosol particles have an impact on climate and human health and the respective effects depend on particle properties determined by the size and its chemical composition”

P.2, l. 16: Why was only the anti – Cl* pathway chosen for Figure 1, and not the syn – Cl* pathway? Please motivate.

Reply: The anti – Cl* pathway was chosen for Figure 1 because it shows the formation of carboxylic acids via the two pathways A and B. The syn-pathway would preferably decompose via the vinyl hydroperoxide channel

P. 2, l. 29: The switch to RO₂ radicals is rather sudden. Try to better introduce that paragraph.

Action: A sentence was added to improve the transition:

“The decomposition of Cl* can lead to the formation of alkyl radicals. They rapidly react with oxygen to form alkylperoxy radicals (RO₂) which are an important intermediate in the gas phase oxidation of organic compounds.”

P. 4, l. 2: Table S1 should be moved into the main manuscript. It would greatly help in following the results.

Reply: We agree with the referee

Action: Table S1 was moved to the main manuscript (now Table 1)

P. 4, l. 17: Is it possible that dilution may have influenced the gas-particle equilibrium as resulting from G-FROST in your sampling line? From Figure S1 it looks like the flow to the SMPS was diluted as well (same inlet)?

Reply: Due to instrumental limitations dilution was necessary. An impact of dilution cannot be ruled out even if the residence time is rather short (<1 s). Most of the analysis was done by looking at sum of the compounds specified and not necessarily the partitioning.

Action: We have added a point regarding this potential interference for the most volatile compounds in the particulate phase.:

“The dilution was necessary for analytical reason and might evaporate some of the most volatile compounds from the condensed phase. However, the time between dilution and analysis was short (< 1s), exactly the same for all conditions and a possible effect would somewhat mimic atmospheric conditions.”

P. 4, l. 32: Please motivate why you used Spearman correlation for your analysis.

Reply: Spearman correlation determines the strength and direction of the monotonic relationship between two variables. As a non-parametric rank correlation, Spearman analysis is independent of the assumption of any underlying distribution and was therefore chosen over Pearson correlation.

Action: To describe why we used spearman compared to normal correlation we added the following in the method section:

“A spearman correlation analysis was done based on of major products, experimental conditions and calculated radical concentrations. Compared to standard correlation the spearman correlation is more robust to outliers and independent of any assumptions about the distribution of the data. It was therefore preferred to assess the degree of association between each dominant acid and experimental parameters. The evaluation using spearman correlation is similar to other correlation methods giving 0, -1 and 1 for no correlation, perfect negative and positive correlation, respectively.”

P. 5, l. 16 – 17: Is the statement of the influence of water based on the numbers in Fig. 3? Are the differences significant?

Reply: The statement is based on Fig. 3 as well as Table 1, which shows that the % contribution of the highest 10 compounds is lower in all humid experiment, which is interpreted as having a higher diversity

Action: We more clearly refer to Figure 3 and Table 1. The sentence now reads

“The presence of water in the system also increases the diversity of the product distribution in both the gas and particle phases, i.e. a small effect in Fig. 3 but consistent for all pairwise dry/humid experiments shown in Table 1.”

P. 5, l. 23 – 24: Can the authors explain why the product distribution of the gas phase in pure ozonolysis experiments is more diverse?

Reply: This statement is an over simplification since there is a scatter in the diversity between different experiment. The sentence should be removed or more elaborated.

Action: The sentence was removed.

Technical corrections

P. 1, l. 18 – p. 3, l. 32: The introduction should be divided into paragraphs, separated by line breaks.

Action: The introduction was divided for better readability.

P. 2, l. 16 – 17: “[...] where the oxygen atoms contribute to the formation of [. . .]”

Action: The sentence was changed to

“The POZ will undergo decomposition where the oxygen atoms contribute to the formation of a carbonyl and a carbonyl oxide group, the so-called excited Criegee intermediate (CI*).

P. 4, l. 4: Unfinished sentence

Reply: The sentence

“G-FROST consists of a laminar-flow reactor (vertical Pyrex glass cylinder, length 191 cm, inner diameter 10 cm, with a halocarbon wax coating) in a temperature-controlled housing (see fig. S1).” stretches over 2 rows. We cannot see an obvious unfinished sentence here

Action: No action

Carboxylic acids from limonene oxidation by ozone and OH radicals: Insights into mechanisms derived using a FIGAERO-CIMS

Julia Hammes^{1*}, Anna Lutz¹, Thomas Mentel^{1,2}, Cameron Faxon¹, Mattias Hallquist^{1*}

¹ Department of Chemistry and Molecular Biology, University of Gothenburg, Gothenburg, Sweden

² Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany

Correspondence to: [Julia Hammes \(julia.hammes@gu.se\)](mailto:julia.hammes@gu.se) [Mattias Hallquist \(hallq@chemgu.se\)](mailto:Mattias.Hallquist@chemgu.se)

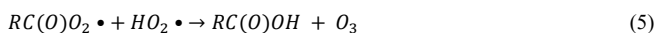
Abstract. This work presents the results from a flow reactor ~~studies~~ study on the formation of carboxylic acids from limonene oxidation ~~in the presence of ozone~~ under ~~various~~ NO_x free conditions ~~in the dark~~. A High Resolution Time Of Flight acetate Chemical Ionisation Mass Spectrometer (HR – TOF – CIMS) was used in combination with the Filter Inlet for Gases and AEROSols (FIGAERO) to measure the carboxylic ~~acid-profile~~ acids in the gas and particle phases. The results revealed that limonene oxidation produced large amounts of carboxylic acids which are important contributors to secondary organic aerosol (SOA) formation. The highest 10 acids contributed 56–91% to the total gas-phase signal and the dominant gas-phase species in most experiments were C₈H₁₂O₄, C₉H₁₄O₄, C₇H₁₀O₄ and C₁₀H₁₆O₃. The particle-phase composition was generally more complex than the gas-phase composition and the highest 10 acids contributed 47–92% to the total signal. The dominant species in the particle phase were C₈H₁₂O₅, C₉H₁₄O₅, C₉H₁₂O₅ and C₁₀H₁₆O₄. The measured ~~concentrations~~ concentration of dimers ~~bearing at least one carboxylic acid function~~ in the particle phase ~~were~~ was very low, indicating that acidic dimers play a minor role in SOA formation via ozone/OH oxidation of limonene. ~~Spearman correlation analysis of the produced carboxylic acid species and experimental parameters were helpful in interpreting the results.~~ Based on the various experimental conditions, the acidic composition for all experiments were modelled using the ~~descriptions from the Master Chemical Mechanisms (MCM).~~ ~~The experiment and model providing yield of large (c7-c10) carboxylic acid in the order of 10% (2-23 and 10-15%, respectively).~~ Significant concentrations of 11 acids, from a total of 16 acids, included in MCM were measured with the CIMS. However, the model predictions were, in some cases, inconsistent with the measurement results, especially in the case of the OH dependence. Reaction mechanisms are suggested to fill-in the knowledge gaps. ~~Based on~~ Using the ~~additional~~ mechanisms proposed in this work, nearly 75% of the ~~qualitative~~ observed gas-phase signal ~~of the low in our lowest concentration (experiment (8.4 ppb converted), ca 23% acid yield) done at humid, mixed oxidant experiment conditions~~ can be ~~explained~~ understood.

1 Introduction

Atmospheric aerosol particles have an impact on climate and human health and the respective effects depend on particle properties, ~~number, determined by the~~ size and ~~its~~ chemical composition (~~Hallquist et al., 2009~~). ~~Of~~, Among the many constituents of atmospheric aerosol particles, organic aerosol particles are the least understood. (~~Glasius and Goldstein, 2016~~). Secondary organic aerosol (SOA) is the major component of organic aerosols. Identifying the chemical pathways of condensable products is essential for predicting SOA formation. (~~Hallquist et al., 2009; Ziemann and Atkinson, 2012; Ehn et al., 2014; Shrivastava et al., 2017; McFiggans et al., 2019~~). However, this identification is inherently difficult as such products often reside in both the gas and particulate phases and continuous partitioning occurs between these two phases. Low vapour pressure products from radical- (i.e. OH) initiated oxidation or ozonolysis of volatile organic compounds (VOCs), such as monoterpenes ($C_{10}H_{16}$), contribute significantly to atmospheric aerosol particle formation and growth (~~Hallquist et al., 2009~~)(~~Hallquist et al., 2009~~). Limonene, the main constituent of the essential oil from citrus plants, is a widely used chemical in personal care and household-related consumer products (owing to its pleasant smell) and elevated indoor concentrations can be expected (Brown et al., 1994; Langer et al., 2008). ~~The emission rates of limonene are lower than those of other monoterpenes (e.g. α -pinene), and limonene is doubly unsaturated and exhibits high reactivity in the presence of ozone. Limonene has two chemically different double bonds, an endocyclic and an exocyclic double bond. The initial reaction will occur predominantly at the endocyclic double bond. However, the primary with subsequent SOA formation (Youssefi and Waring, 2014). The total global forest emission of limonene has been estimated to $11.4 \text{ Tg year}^{-1}$, placing it on the top four among monoterpenes (Guenther et al., 2012). A high aerosol yield and the two chemically different double bonds, an endocyclic and an exocyclic double bond makes limonene ozonolysis of specific interest (Koch et al., 2000; Saathoff et al., 2009; Chen and Hopke, 2010; Gong et al., 2018). The initial reaction will occur predominantly at the endocyclic double bond. However, the first generation~~ products may be unsaturated and exhibit high reactivity for further oxidation. The oxidation of limonene will eventually lead to the formation of SOA in both the atmosphere and indoor environments. The oxidation of monoterpenes and, specifically, limonene has been previously reported (Leungsakul et al., 2005a; Walser et al., 2008; Leungsakul et al., 2005b; Maksymiuk et al., 2009) and ~~basic~~ reaction mechanisms that describe first- and second-generation oxidation products have been proposed. (~~Carslaw, 2013; Chen and Griffin, 2005~~). Due to their low vapour pressure, carboxylic acids, a major class of limonene-oxidation products can play an important role in SOA formation (Salo et al., 2010). The relative contribution of carboxylic acids from limonene oxidation to SOA formation has been assessed via a model (Pathak et al., 2012). According to that study, limonene-ozonolysis produces significant amounts of carboxylic acids and the distribution of these acids is affected by the OH and ozone concentrations.

During ozonolysis, limonene is attacked by ozone and forms an unstable and energy-rich primary ozonide (POZ), see Figure 1. The POZ will undergo decomposition where ~~each~~the oxygen ~~contributes~~atoms contribute to the formation of a carbonyl and a carbonyl oxide group, the so-called excited Criegee intermediate (CI*). The 10 carbon skeleton is retained during this process, if an endocyclic double bond is attacked. The CI* has a planar structure and the orientation of the outer oxygen will determine its chemical fate. The dominant reaction pathway (86% (Atkinson et al., 1992)) for limonene syn – CI* is the vinyl hydroperoxide channel (VHP) which generates an alkyl radical under loss of an OH radical. This pathway provides a source for night-time OH in the atmosphere. The VHP requires an alkyl group in the syn position and is, hence, inaccessible to anti – CI*. The dominant fate of the anti – CI* is decomposition via the ester or the “hot acid” channel where an energy-rich ester or acid formed will undergo decomposition thereby resulting in various products. Two possible products, i.e. OH and an acyl radical (RC(O)•) (Vereecken and Francisco, 2012), which can react with O₂ and subsequently HO₂ to form a carboxylic acid and ozone. Furthermore, the CI* can, to some extent, become collisionally stabilised (sCI) and exocyclic CI* are stabilised more efficiently than endocyclic CI*. The formed sCI will undergo further reactions and the reaction sCI + water will produce a carbonyl, an alkyl or an alkoxy radical. If the sCI contains an α-hydrogen, a carboxylic acid can be produced directly from the water reaction. Although the sCI + water reaction is likely the most dominant in the atmosphere, sCI may also react with carboxylic acids forming stable adducts which have been identified as dimer esters (Kristensen et al., 2016). The decomposition of CI* can lead to the formation of alkyl radicals. They rapidly react with oxygen to form alkylperoxy radicals (RO₂) which are an important intermediate in the gas phase oxidation of organic compounds.

The atmospheric fate of RO₂ radicals in the absence of NO_x includes a self-reaction (reaction (1) – (3)), isomerisation via an internal H-shift (reaction (4)), and a reaction with HO₂ (reaction (5)) (Ehn et al., 2014). If RO₂ is an acylperoxy radical, a carboxylic acid can be formed.



These reactions lead to further functionalisation, e.g. formation of acids, alcohols, carbonyls or peroxides and may in addition produce alkoxy radicals. Subsequently, alkoxy radicals can be converted by oxygen to a carbonyl, if an

α -hydrogen is present. Alkoxy radicals that lack this hydrogen will undergo isomerisation or decomposition via β -scission.

During ozonolysis experiments, OH radicals are produced and react with the precursor as well as the reaction products. This process occurs in the laboratory as well as in the actual atmosphere and increases the complexity of the degradation mechanisms. In the laboratory, one can scavenge the produced OH radicals by adding a compound, e.g. 2-butanol, that reacts rapidly with OH, thereby reducing OH. The OH scavenger reduces the OH concentration but leads to an increase in the HO₂ and RO₂ concentration. This yields changes in the distribution of radicals and subsequently the radical-dependent chemistry (Keywood et al., 2004)(Keywood et al., 2004;Jonsson et al., 2008b).

For example, the reaction of 2-butanol with OH produces HO₂ radicals with a yield of 64% (MCM v 3.3.1) thereby increasing the HO₂/RO₂ ratio. In laboratory experiments, these features can be employed in investigating the importance of various radicals/pathways for product distribution and subsequent SOA formation.

The Gothenburg Flow Reactor for Oxidation Studies at Low Temperatures (G-FROST) has been used in previous studies (Jonsson et al., 2006;Faxon et al., 2018;Jonsson et al., 2008a;Jonsson et al., 2008b;Kristensen et al., 2014)(Jonsson et al., 2006;Faxon et al., 2018;Jonsson et al., 2008a;Jonsson et al., 2008b;Kristensen et al., 2014) to investigate the dependence of aerosol properties on different parameters (e.g. humidity and radical conditions). The G-FROST setup has now been extended with a High-Resolution Time-of-Flight Chemical Ionization Mass Spectrometer (HR-ToF-CIMS) that will provide insight into the chemical composition of the gas and particle phase through connection to the Filter Inlet for Gases and AEROsols (FIGAERO). These new techniques allow for sensitive simultaneous detection in the gas and particle phases. Herein, an ionisation using acetate allows investigation of carboxylic acid formation. In the following, we analyse the carboxylic acid product spectrum of limonene. The goal is to detect major pathways and to compare the results with ~~existing mechanisms~~ a model using the existing master chemical mechanism (MCM) that was primarily developed for gas-phase chemistry related to the impact on tropospheric ozone formation, but now frequently are used as a link to particle formation. This work (i) considers ozonolysis under dark condition and NOx free conditions (for various limonene concentrations) the effect of humidity, OH scavenging and ozone level on carboxylic acid formation, and (ii) provides an outlook and suggestions for mechanistic gaps with the aim of eventually describing major acidic products found in the gas and particle phases under realistic atmospheric conditions (i.e. ozonolysis is performed in the absence of an OH scavenger under low concentration and humidity conditions).

2 Materials and methods

Oxidation studies of limonene in the presence of ozone have been performed under a variety of experimental conditions (see [SI Table 1](#); [Table 1](#)). The experimental matrix was chosen to understand ozonolysis of limonene under dark NO_x free conditions. The laminar flow reactor approach is well suited for investigating changes in experimental condition, e.g. dry vs humid, high vs low concentration. Due to short residence time the absolute concentration is higher than ambient even if the amount limonene converted (few ppb and higher) is similar to larger simulation chamber studies. The conversion of any RO₂ radicals is biased towards self-reaction: of importance in VOC dominated rural forest conditions and in the indoor environment. The G-FROST system employed has been described in detail elsewhere ([Jonsson et al., 2008b](#); [Jonsson et al., 2008a](#)) ([Jonsson et al., 2008b](#); [Jonsson et al., 2008a](#)) and will only be presented briefly here. G-FROST consists of a laminar-flow reactor (vertical Pyrex glass cylinder, length 191 cm, inner diameter 10 cm, with a halocarbon wax coating) in a temperature-controlled housing (see [SI Figure 1](#); [Figure S1](#)). The total inflow into the system was 1.6 LPM and the sample outflow was 0.94 LPM, yielding an average residence time of 240 s. The aerosol was sampled with a funnel system from the centre part of the laminar flow, to minimise wall effects. Limonene (Alfa Aesar, (R)-(+)-Limonene, 97%) was added by passing synthetic air (Laboratory Zero Air Generator, N-GC-6000, Linde Gas) through a characteristic diffusion source. Limonene was then pre-mixed with a dry or humidified bulk flow, with or without 2-butanol (Merck, p.a. >99%) as an OH scavenger. During each experiment, limonene concentrations were increased stepwise (15, 40, 150 ppb), while the temperature inside G-FROST was kept constant at 20°C for either dry (relative humidity (RH) <2%) or 40% RH conditions. Ozone (400, 1000, 5000 ppb) was generated by passing oxygen gas through a set of Pen-Ray® mercury lamps (UVP, λ 254 nm) and added through a separate 6-mm Teflon line to G-FROST. The ozone level was kept constant during each experimental run.

A summary of experimental conditions is provided in [Table 1](#). The product distribution in the gas and particle phases was analysed with an acetate HR-ToF-CIMS (Aerodyne) (Bertram et al., 2011) coupled to the FIGAERO inlet ([Lopez-Hilfiker et al., 2014](#)) ([Lopez-Hilfiker et al., 2014](#)). The reagent ion acetate is especially susceptible to acidic organic compounds such as carboxylic acids. (Bertram et al., 2011). One may note that also peroxy acids has high sensitivities (Lopez-Hilfiker et al., 2015) and that the acetate ionisation has previously been used to detect nitro phenols (Mohr et al., 2013; Le Breton et al., 2019) and organic sulphates (Le Breton et al., 2019). However, here we assume carboxylic acids and peroxy acids to be the primarily compounds being observed with current set-

up the CIMS. The used sensitivity for larger carboxylic acid was 5.5×10^{-3} Hz ppt⁻¹ (Le Breton et al., 2019). This sensitivity was used to estimate molar yields; even if one should be precautious to provide absolute yields from this type of studies it provides indications on the product contribution. The sample flow from G-FROST was diluted with ultra-high purity (UHP) nitrogen gas and pumped at 2×4 LPM by two diaphragm pumps (KNF, N816.3KN.18) through the FIGAERO inlet. The dilution was necessary for analytical reason and might evaporate some of the most volatile compounds from the condensed phase. However, the time between dilution and analysis was short (< 1s), exactly the same for all conditions and a possible effect would somewhat mimic atmospheric conditions. Perfluoroheptanoic acid (Sigma Aldrich, 99%) was used as the internal mass calibration standard. The gas-phase chemistry composition was determined via 60 min measurements and particles were collected simultaneously on a 1 μ m 24 mm Zefluor® PTFE filter (Pall Corp.). During desorption, the temperature was increased from 25°C to 200°C in 50 min (3.5°C min⁻¹) and kept constant at 200°C for 10 min. Subsequently, UHP nitrogen gas was bubbled (flow rate: 0.02 LPM) through acetic anhydride (Sigma Aldrich, puriss p.a. $\geq 99\%$) and diluted with a bulk flow of UHP nitrogen to 2.2 LPM. This flow was reduced to 2 LPM using a critical orifice (O'Keefe Controls Co) and passed through a commercial ²¹⁰Po alpha emitter (NDR, P-2021) to produce acetate reagent ions. A Scanning Mobility Particle Sizer (SMPS; CPC 3775 and DMA 3081, TSI Inc.) was used to measure the particle size distribution. The mass of the produced aerosol was determined, assuming a particle density of 1.4 g cm⁻³ (Hallquist et al., 2009)(Hallquist et al., 2009). The CIMS data were analysed using the Tofware package (Tofwerk/Aerodyne) for IGOR Pro (WaveMetrics). The data were acquired at 1 Hz and pre-averaged to 0.0167 Hz (1 min) for further analysis. To account for thermal decomposition (double or triple peaks in desorption profile), the average (four desorption cycles per reaction condition) FIGAERO desorption profiles (thermograms) were analysed in Python 3.6.0 using the NumPy (v 1.11.3), SciPy library (v 0.18.1) and pandas (v 0.19.2) packages. The exponentially modified Gaussian function (Foley and Dorsey, 1984) was used as a peak shape function for peak fitting of the thermograms (SI Figure 2)(Fig. S2). The area of the fitted peaks was calculated by integrating along the given axis using the composite trapezoidal rule. SpearmanA spearman correlation plots were analysis was done based on of major products, experimental conditions and calculated radical concentrations. Compared to standard correlation the spearman correlation is more robust to outliers and independent of any assumptions about the distribution of the data. It was therefore preferred to assess the correlation degree of association between each dominant acid with the respective response to changes in the and experimental parameters. The evaluation using spearman correlation is similar to other correlation methods giving 0, -1 and 1 for no correlation, perfect negative and positive correlation, respectively. All experiments have been modelled utilizing the an open access mechanism (MCM (v3.3.1) (see SI Table 4 Table 1 for the initial conditions). The initial

concentration of 2-butanol was set to $3 \times 10^5 \mu\text{g m}^{-3}$ in the case of OH scavenger experiments (Pathak et al., 2012). Based on the calculations, the amount of reacted limonene was derived. The OH, HO₂ and RO₂ levels enabling calculation of the corresponding values integrated over a reaction time of 240 s were used in the spearman correlation analysis.

5 3 Results and discussion

A total of 33 different experiments have been performed under various reaction conditions (~~SI Table 1~~). ~~The general effect of parameters on SOA formation concurs with our previous results, where (for e.g.) an increase in SOA formation with increasing RH was observed (Jonsson et al., 2006)(Table 1).~~ In the following, we will characterise the distribution of gas- and particle-phase organic acid. Figure 2 shows an example of a mass spectrum from one of the experiments.

~~Over~~This experiment was done at medium ozone and high limonene concentration with an estimated 8 % molar yield of large carboxylic acids. Still over 100 different molecular formulas for acids have been identified, far exceeding the number of acids reported in previous studies (Leungsakul et al., 2005a;Jaoui et al., ~~2005a~~2005;Jaoui et al., 2006;Rossignol et al., 2012;Rossignol et al., 2013;Walser et al., 2008;Marianne Glasius et al., 2000). Here we will focus on the analysis of acids with carbon numbers ranging from seven to ten (and the dimers formed from these acids). Typically, these acids stand for 2-23% of reacted limonene on a molar basis assuming an average reaction time and CIMS sensitivity (Table 1). The distribution between gas and particle phase varied between compounds where the average particle fraction was between 5 and 80% depending on experimental conditions.

The contribution of each acid to the total signal is calculated and the highest 10 ion signals are selected from each experiment. This ~~yields~~gave a total of 32 different molecular compositions, representing the greatest fraction (47%–91%) of the total signal.

The fraction corresponding to the sum of ~~identified~~10 highest ions to the total signal can reveal the diversity of the product distribution for each condition. A low coverage indicates an experiment where several compounds with the same intensities are generated. Figure 3 shows for the comparable data to Fig. 2 (medium ozone, high limonene) the fraction of the 10 most prevalent ions. This was the most complete sub-step (dry-humid, with and without scavenger) of the total matrix and the illustrated pairwise features (e.g. dry vs humid) that was common also among other concentrations (e.g. for other condition we had missing particle phase data, see table 1). For these four selected experiments the estimated total yield of larger carboxylic acids (c7-c10) were very similar 6% (dry, scavenger), 8% (humid, scavenger), 6% (dry, no scavenger) and 7 % (humid, no scavenger).

In general, the particle-phase composition is more diverse, less dominated by the 10 top compounds, than the gas-phase composition (Figure 3). The presence of water in the system also increases the diversity of the product distribution in both the gas and particle phases, i.e. a small effect in Fig. 3 but consistent for all pairwise dry/humid experiments shown in Table 1. Compared with lower ozone concentrations, higher concentrations generally yielded larger product diversity, owing to greater possibility for exocyclic double-bond oxidation or unsaturated-acid oxidation that yields a wider variety of products (SI Figure 3–4). The OH reaction pathways are suppressed in experiments with an OH scavenger and the oxidation can then occur only via ozonolysis. This apparently reduces the oxidation product diversity of the particle phase, consistent with the findings of Watne et al. (Watne et al., 2017). In that study, the volatility of limonene SOA produced via ozonolysis only was found to be more homogeneous than that of limonene produced via other/additional processes. However, the product distribution of the gas phase obtained via ozonolysis only is more diverse than the distribution obtained via other/additional processes. Figure 4 shows the total molar yield of the acids identified in this study. One may note that the absolute yield presented here has significant uncertainties while the relative importance of an acid can guide us in our mechanistic interpretation. Generally, the most important acids (averaged over all experiments) are C₇H₁₀O₃, C₇H₁₀O₄, C₈H₁₂O₄, C₈H₁₂O₅, C₉H₁₄O₄, C₉H₁₄O₅, C₁₀H₁₆O₃ and C₁₀H₁₆O₄. These are compared with the overview (see SI Table 2) of previously reported carboxylic acids (C₇–C₁₀) resulting from limonene ozonolysis. The proposed structures of these acids are also shown with yields at or below 1% which is in line with the yield of major acids in the study of Glasius et al. (2000). The most important acid in the present study are compared with an overview (Table S1) of previously reported carboxylic acids (C₇–C₁₀) resulting from limonene ozonolysis. Table S1 also illustrate the proposed structures of these acids based on the current literature. Ten of the previously reported acid formulas are found in this study while three acids, C₇H₁₀O₆, C₈H₁₂O₆ and C₈H₁₄O₄, lie outside the ten highest corresponding ions identified in any of our 33 experiments. Leungsakul et al. (Leungsakul et al., 2005a) and Walser et al. (Walser et al., 2008) reported that C₉H₁₄O₄ and C₁₀H₁₆O₃ were the most and second-most dominant particle-phase compounds, respectively. However, in our study, the more oxidised (compared with C₉H₁₄O₄ and C₁₀H₁₆O₃) C₉H₁₄O₅ and C₁₀H₁₆O₄ are the most dominant particle-phase compounds. Most of the previously reported molecular formulas are included in the master chemical mechanism (MCM, <http://mem.leeds.ac.uk/MCM/>). The MCM was originally developed to provide accurate, robust and current information regarding the role of specific organic compounds in ground-level ozone formation, in relation to air-quality policy development in Europe. Over the years, MCM has been employed in studies linked to SOA formation (Jenkin, 2004), although this mechanism is still under development to capturing descriptions on the fraction of low-volatility and often very oxygenated fraction of VOCs (Barley et al., 2011).

In the present study, we employ a wider range of experimental conditions (than the range of conditions typically considered) to further assess the influence of different parameters on the formation of the observed carboxylic acid products. In SI Figure 4, we show the ~~However~~. However, in our study, the more oxidised (compared with $C_9H_{14}O_4$ and $C_{10}H_{16}O_3$) compounds $C_9H_{14}O_5$ and $C_{10}H_{16}O_4$ are the dominant in the particle-phase. From Fig. 4 it is evident that the composition of acids is very complex and many compounds contributes to the total signal. Also among the most prominent acids there is no acid that clearly dominate in any of the experiments. We should also remember that in addition to the acids there are many more product categories contributing to the product distribution, e.g. recently, Gong et al. (2018) did a similar study focusing on peroxides and carbonyls. Utilising the complexity to further understand the mechanism requires some strategy. Here we decide to start with the 10 most prominent ions for each experiment creating a correlation matrix of 32 different molecular compositions, where each composition might include several isomers. The intensities measured for each compounds are presented in the supplemental, Table S2 and S3. In Fig. S3-S4, we show the corresponding correlations, using Spearman ranking, for each of the 32 different molecular compositions representing the majority of the ion signals: ~~divided in with and without OH scavenger (Fig S3) and for humid and dry conditions (Fig S4)~~. The results for the eight most important acid formulas, i.e. $C_7H_{10}O_3$, $C_7H_{10}O_4$, $C_8H_{12}O_4$, $C_8H_{12}O_5$, $C_9H_{14}O_4$, $C_9H_{14}O_5$, $C_{10}H_{16}O_3$ and $C_{10}H_{16}O_4$, are presented and discussed. These are all oxidation products with mass ranging from 130 m/z to 250 m/z and are identified as carboxylic acids with carbon numbers ≤ 10 . Based on other studies (Kristensen et al., 2014; Mohr et al., 2017; Kristensen et al., 2012; Kristensen et al., 2016; Witkowski and Gierczak, 2014), dimer formation is expected. These dimers are expected to contribute significantly to the particle phase. For the particle-phase data, compounds with mass above 300 m/z are detected and are ~~identified~~ classified as dimer species ~~withif they have a~~ carbon numbers > 10 . These compounds occur only in the particle phase. However, the relative signals are significantly lower than those reported ~~(e.g.)~~ for dimer formation in a study on limonene with nitrate radicals (Faxon et al., 2018) or the ozonolysis of other terpenes such as α -pinene (Kristensen et al., 2016). In the present study the identified products must be acids, since we apply CI using the acetate ion. We conclude that, although dimer formation may occur (in general), no important acidic dimers are formed in the system. Consequently, we will focus on the formation of the monomer acids.

Water effect. Generally, most of the 32 top ions have higher signals in humidity experiments than in other environments. ~~Table S2 and S3 and correlation matrix in Fig. S4~~. The opposite is true for the 400 ppb ozonolysis-only (OH-scavenged) cases (gas and particle phases). For experiments with OH scavenger, the importance of water is evidenced by the prominent formation of gas-phase $C_{10}H_{16}O_3$, $C_9H_{16}O_3$, $C_9H_{14}O_3$ and $C_8H_{14}O_3$ (SI Figure 3)-(4). The water dependence of these acids is less pronounced in the mixed oxidation cases (except for $C_8H_{14}O_3$), than in

other cases, but water seems to be favourable for the formation of other acids, such as $C_8H_{10}O_{4-5}$ and $C_7H_{10}O_{2-3}$. In general, water enhances the formation of the particle-phase acids. This concurs with the findings of Jonsson et al. (Jonsson et al., 2006) who reported an increase in the SOA number and mass under humid conditions. The authors attributed (i) this result to an increase in the number of low-volatility products with increasing water concentration during the ozonolysis of limonene, and (ii) the water effect on SOA formation to $C_{10}H_{16}O_3$ formation. For humidity experiments considered in the present study, we observe a considerable increase and a slight increase in the formation of gas-phase $C_{10}H_{16}O_3$ and particle-phase $C_{10}H_{16}O_3$, respectively. Assuming that the humidity effect on $C_{10}H_{16}O_3$ production is responsible for the SOA dependence on humidity, subsequent transformation of condensed material is required as the particulate phase is deficient in $C_{10}H_{16}O_3$.

Radical effect. Consistent with previously reported results on the SOA mass (Jonsson et al., 2008b; Pathak et al., 2012)(Jonsson et al., 2008b; Pathak et al., 2012), the intensities of most acids in the low- and medium-ozone cases are higher for experiments employing mixed oxidation than for experiments employing an OH scavenger. For low-ozone and low-VOC experiments, the scavenger-provided SOA mass decreases with 2-butanol addition, as previously reported (Jonsson et al., 2008a)(Jonsson et al., 2008a), although the effect observed here is weaker than the effect reported in that work. However, for relatively high concentrations of limonene, the opposite effect is observed, i.e. the SOA mass increases with the use of a scavenger. Notably, this effect occurs independently of the acid-intensity behaviour, and may have resulted from the fact that (i) the SOAs associated with mixed oxidation are quite volatile and (ii) increased oxidation in the presence of OH, rather than converting semi volatiles to low/extremely low volatiles, converts volatiles/intermediate volatiles to semi volatile species, as suggested by Pathak et al. (Pathak et al., 2012); these are then lost during the dilution process. Another possibility is that changes in the chemistry affect nucleation, as indicated by a size-distribution shift to smaller sizes which (compared with larger sizes) are more susceptible to evaporative losses in the dilution step. Separation of these effects during the experiments is impossible and, hence, the SOA formation potential associated with mixed oxidation may have been underestimated in this study. Owing to the sufficiently low ozone levels employed in the low and medium experiments, OH has an influence on the reaction pathways. At the highest ozone level, however, the intensities of acids associated with mixed oxidation are lower than those resulting from the use of an OH scavenger. To investigate the effect of radical chemistry on the reaction pathways leading to the observed carboxylic acids, the OH, HO_2 and RO_2 concentrations are calculated and integrated using MCM(the model) for each experiment (SI Figure 3)-(Table 1). Regarding correlation, Fig. S3, a comparison of the mixed oxidation cases reveals that the formation of most gas-phase acids (e.g. $C_{10}H_{16}O_3$, $C_9H_{14}O_4$ and $C_7H_{10}O_3$) decreases with increasing amount of OH radicals in the system. The HO_2/RO_2 ratio has only a small influence on the mixed oxidation. However, when an OH scavenger

is used, the amount of gas-phase products ($C_{10}H_{16}O_3$, $C_{10}H_{16}O_4$, $C_9H_{14}O_4$ and $C_8H_{14}O_3$) decreases considerably with increasing HO_2/RO_2 . The general influence of OH on acid formation is most pronounced for experiments performed under dry conditions. Under these conditions, OH and HO_2/RO_2 have a significant effect on the formation of $C_{10}H_{16}O_3$, $C_9H_{14}O_3$ and $C_7H_{10}O_4$. For example, $C_{10}H_{16}O_3$ and $C_9H_{14}O_3$ formation increases with increasing OH and decreasing HO_2/RO_2 . The opposite is true for $C_7H_{10}O_4$ formation which decreases with increasing OH and decreasing HO_2/RO_2 .

Effect of excess ozone. Experiments with high ozone levels are performed to assess the effect of excess ozone on acidic oxidation products. The aim is to oxidise, with ozone, the remaining double bond of the produced unsaturated carboxylic acids. The results show that ozone has a distinct negative impact on $C_7H_{10}O_{2-3}$ in the pure ozonolysis cases (see [SI-Figure 4](#) correlation matrix in [Fig. S3](#)) and, hence, we conclude that those compounds are unsaturated.

5 Furthermore, the levels of gas-phase $C_{10}H_{16}O_3$, $C_9H_{16}O_3$, $C_9H_{14}O_{3-4}$ and $C_8H_{14}O_3$ are positively correlated with ozone in the absence of OH. For $C_{10}H_{16}O_3$, this is surprising as this compound is assumed to be limonic acid, an unsaturated compound. This positive correlation may have resulted from the fact that the production of $C_{10}H_{16}O_3$ dominates over the removal (via ozonolysis) of the remaining double bond. The correlation with ozone is negative for most acids in the presence of OH and is most pronounced for gas-phase $C_{10}H_{16}O_3$, $C_9H_{14}O_3$ and $C_8H_{12}O_3$. The
10 negative ozone correlation observed for mixed oxidation cases considering $C_{10}H_{16}O_3$ and $C_9H_{14}O_3$ concurs with the modelling results of a previous study that assessed the influence of ozone on limonene oxidation (Pathak et al., 2012). A positive (albeit slightly) correlation with ozone is observed only for particle-phase $C_8H_{14}O_3$. The acid-ozone correlation obtained for humid conditions differs significantly from that obtained for dry conditions. The negative acid-ozone correlation is quite pronounced in the dry experiment cases and becomes increasingly negative
15 (in general) for acids with relatively low carbon numbers, a trend unique to these experiments. The level of $C_{10}H_{16}O_3$ (especially the particle-phase) is positively correlated with ozone levels in the dry experiments. Generally, the amount of gas-phase acids ~~have~~ has a stronger positive correlation with the limonene consumption (Δ limonene) under humid conditions compared to dry experiments. In the dry experiments, $C_{10}H_{16}O_5$ and $C_9H_{14}O_4$ are the only acids with a strong positive correlation to Δ limonene. Compared with the occurrence of gas-phase acids, the
20 occurrence of particle-phase acids is (in general) more strongly correlated with Δ limonene.

Model results and comparison with experiments. Model calculations ~~with~~ using the [scheme presented by the master chemical mechanism \(MCM v3, <http://mcm.leeds.ac.uk/MCM/>, v3.3.1\)](#) have been performed for all 33 experimental conditions, in order to calculate Δ limonene and radical concentrations as well as product distributions, based on the experimental conditions. ~~The~~ The model did only consider gas-phase scheme of MCM.
25 [Most of the previously reported carboxylic acid molecular formulas \(see Table S1\) are included in the MCM which was originally developed to provide accurate, robust and current information regarding the role of specific organic compounds in ground-level ozone formation, in relation to air-quality policy development in Europe. Over the years, MCM has been employed for models in studies linked to SOA formation \(Jenkin, 2004\), although this mechanism is still under development to capturing descriptions on the fraction of low-volatility and often very](#)
30 [oxygenated organic compounds \(Barley et al., 2011\).](#)

Generally, the model provides small variation in the total molar yield for the large carboxylic acids (c7-c10) of 10-15% while the experiments shows larger variability (2-23% molar yield) plausible due to the complication of aerosol formation not covered by the model. A key for understanding the chemical mechanism leading to various products is the radical distribution. The experiments set-up where product distribution was measured at the end of the flow reactor restrict dynamic information. However, the variation of radical distribution between experiments is illustrated in Table 1. Here the values of radicals are given as the integral concentration over the reaction time (unit $\text{pbb} \times \text{s}$). Furthermore, the integral HO_2/RO_2 ratio is presented together with a rate normalised ratio of these reaction, i.e., the modelled OH levels decrease with the initial limonene concentration, except for the highest ozone cases. High-ozone experiments yield the highest OH dose. The model results show that the HO_2/RO_2 ratio in experiments employing the OH scavenger 2-butanol is approximately one order of magnitude higher than that of the mixed oxidant experiments. This higher ratio results from the HO_2 radicals generated by the reaction of 2-butanol with OH. According to the model calculations, RO_2 levels are generally 10 times higher than HO_2 levels when 2-butanol is included in the model. The $\text{HO}_2 + \text{RO}_2$ reaction is rapid and the typical rate constant is one order of magnitude larger than that of the $\text{RO}_2 + \text{RO}_2$ self-reaction (Orlando and Tyndall, 2012).

Regarding oxidant/radical variation the modelled OH levels decrease with the initial limonene concentration, except for the highest ozone cases. High-ozone experiments yield the highest OH dose. The model results show that the HO_2/RO_2 ratio in experiments employing the OH scavenger 2-butanol is approximately one order of magnitude higher than that of the mixed oxidant experiments. This higher ratio results from the HO_2 radicals generated by the reaction of 2-butanol with OH and will provide more influence of the $\text{HO}_2 + \text{RO}_2$ reaction in the experiment with scavenger. However, the RO_2 self-reaction are still the major pathway also in these experiment, twice the normalised rate of the HO_2 reaction. One may note that the RO_2 reaction rates are very much structural dependent and might be faster or slower than the assumed rates, see Jenkin et al. (2019) for a recent review on RO_2 chemistry.

In the MCMv3.3.1, 25 closed-shell carboxylic acids with 16 different chemical formulas are included for limonene. We identify 11 of the 16 acids (SI Table 3; See SI Table 5 for the model results of the MCM species)(Table S4 and S5; all MCM species used in the model are presented in Table S6). $\text{C}_9\text{H}_{14}\text{O}_3$ and $\text{C}_9\text{H}_{14}\text{O}_4$ are the most dominant and second-most dominant acids in all 33 modelled experiments. $\text{C}_{10}\text{H}_{16}\text{O}_3$ (LIMONONIC), formed by the reaction of sCI + water, is the only acid that exhibits an overall positive water dependence. The model calculations predict that water should also have a positive influence on KLIMONONIC and $\text{CO}_2\text{SC}_6\text{CO}_2\text{H}$. However, this influence is undetectable in our experiments, owing to the extremely low concentrations of these compounds and the stronger influence exerted on other compounds with the same molecular mass.

The model predicts that, compared with the presence of water, the presence of OH radicals has a greater influence on the product distribution. Most individual ~~MCM~~-species from the MCM exert a strong positive OH-chemistry effect in the model, except for LIMONONIC ($C_{10}H_{16}O_3$), C823CO3H ($C_9H_{14}O_5$), C823OOH ($C_8H_{14}O_4$) and C825OOH ($C_8H_{12}O_5$). In all cases, the concentrations estimated with the model of the last three compounds are highest when the OH chemistry is “turned off” (2-butanol added in model). C82CO2H ($C_9H_{14}O_3$) is produced to a lesser extent under humid and high ozone and for the highest OH conditions. It was produced to a higher extent under medium and low ozone and for the medium and lowest OH conditions. In the presence of OH chemistry, the LIMONONIC concentration is lower under humid conditions than under dry conditions. The presence of OH is essential for the formation of numerous compounds (see SI Table 5) and yields significant concentration only in the absence of 2-butanol, i.e. the modelled concentrations are close to zero in the presence of 2-butanol. For example, C731CO2H, KLIMONIC and KLIMONONIC are formed by ozone attack on the limona ketone which, in the model, is formed by the initial OH attack on the exocyclic double bond of limonene. Owing to the presence of 2-butanol, this attack on the double bond is reduced thereby minimizing the amount of products generated. The correlation results for the humid and dry cases show that C823CO3H, C823OOH and C825OOH are negatively correlated with OH levels in the model. The reaction with OH represents the only destruction pathway of the produced acids in the model (even if unsaturated). This negative correlation indicates that, as the OH levels increase, the OH-induced destruction of the respective acid dominates over acid production. However, the reactions of unsaturated acids with ozone are ~~neglected by~~ not included in the MCM.

The experimental results reveal that the four dominant compounds are $C_8H_{12}O_4$, $C_8H_{12}O_5$, $C_9H_{14}O_4$ and $C_9H_{14}O_5$. However, $C_9H_{14}O_3$ which plays only a minor role in the experiments, represents the dominant compound in the modelling results. $C_8H_{12}O_4$ which contributes significantly to the experimental results, is characterised by medium-level contribution to the model. $C_8H_{12}O_4$ and $C_8H_{12}O_5$ exhibit a positive OH-dependence in the model consistent with the gas-phase results obtained for $C_8H_{12}O_4$ under humid low-ozone and all medium-ozone experiments. The estimated concentration of $C_8H_{12}O_5$ is lower in the presence of OH chemistry for most conditions except for humid low ozone experiments. The model reveals a positive OH dependence and a negative OH dependence for $C_9H_{14}O_4$ and $C_9H_{14}O_5$, respectively. The behaviour of the $C_9H_{14}O_4$ gas phase concurs with the model results for low- and medium-ozone experiments. For the highest ozone-level experiments, the levels observed for mixed oxidation are lower than those observed for oxidation in the presence of an OH scavenger. The OH dependence of $C_9H_{14}O_5$ in the experimental results differs from the overall negative OH dependence of modelled $C_9H_{14}O_5$. In contrast to the model predictions, the C7 acids $C_7H_{10}O_4$ and $C_7H_{12}O_3$ contribute significantly to the gas-phase results and exhibit only a weak OH dependency. The model predicts a weak OH dependence for $C_{10}H_{16}O_3$ which is in stark contrast

to the strong dependence revealed by the experimental results. Overall, most acids exhibit a positive RH dependence in the medium-ozone and humid low-ozone cases, a behaviour that is lacking from the modelling results. However, consistent with the modelling results, water in the system increases the concentration of $C_{10}H_{16}O_3$ by a factor of two. This holds true for all cases, except for the highest ozone cases where the concentrations observed in the experiments are higher than the values predicted for dry conditions. In conclusion, significant concentrations of 11 acids (from a total of 16) included in MCM are measured with the CIMS. The model predictions are, in some cases, inconsistent with the measurement results, with the most notable inconsistencies occurring for the OH dependence.

4 Mechanism interpretation and outlook

10 The formation and the dependence of the eight most prominent ions in the experiments are only partly explained by the [MCMv3.3.4 model](#) and reaction pathways that form compounds with the molecular formulas $C_7H_{10}O_3$ and $C_{10}H_{16}O_4$ are absent. In the following, we propose reaction pathways for explaining the formation of some ions not accounted for in the model and propose additional pathways for compounds already included in MCM. Examples include reactions of unsaturated acid products with ozone or the formation of C10 acyl radicals via the hot acid channel (see pathway A in Figure 1). The largest discrepancy between model and experimental results is -observed for the formation of compounds, such as the group of C7 acids or ketolimononic, -limonic or -limonic acid which are OH-dependent in the model but are OH-independent in the observations. The dominance of $C_9H_{14}O_4$ and positive correlation with ozone can be explained by the additional formation of ketolimononic acid via reaction pathways as seen in [Figure](#). Here, ozone attacks the double bond of the primary product limononic acid thereby forming a CI. In the case of exocyclic CI, sCI can be formed directly and the remaining CI* are usually more effectively stabilised than endocyclic CI* and therefore a larger yield of sCI can be expected. The produced sCI can produce ketolimononic acid via the water channel ([see Figure 4](#);[see figure 5](#)). Ketolimononic ($C_8H_{12}O_4$) and ketolimononic ($C_8H_{12}O_5$) acid may be formed via the reaction of limononic (R2, $C_9H_{14}O_3$) and limonic acid (R3, $C_9H_{14}O_4$), respectively, with ozone. The formation of a vinyl hydro peroxide (VHP) and subsequent decomposition via OH elimination and oxygen addition to the alkyl radical yields an alkyl peroxy radical. The bimolecular reaction of the alkyl peroxy with other RO_2 can lead to an alkoxy radical which then can form a carbonyl and HO_2 upon reacting with oxygen. This reaction chain may explain the formation of $C_9H_{12}O_5$ and $C_8H_{10}O_{5,6}$. The model predictions for cases with and without the scavenger differ only slightly but the reaction pathway involving OH is an important contributor to $C_{10}H_{16}O_3$ formation in the experiments. This becomes especially clear

when dry experiments with/without OH (with no possibility for the water pathway) are compared. The pathway leading to the formation of $C_{10}H_{16}O_3$ via the hot acid channel from the anti - Cl^* (see Figure 1) is also neglected by the model. ~~The Figure 6 illustrate how the~~ remaining double bond can also be attacked by OH which would lead to the formation of an alkyl radical and subsequent addition of O_2 . The reaction pathways shown in ~~Figure 5 figure~~ 6 lead to the observed acid formation and may explain the formation of $C_7H_{10}O_4$, $C_9H_{14}O_5$ and $C_9H_{14}O_4$. The produced alkoxy radical will probably follow pathway A which produces the most stable radical and subsequently $C_7H_{10}O_4$. This pathway involves two bimolecular steps and is positively correlated with RO_2 levels in the system. Saturated compounds, although non-reactive with ozone, are susceptible to secondary chemical reactions induced by OH. ~~The Figure 6ii illustrate how the~~ fate of the saturated compounds will depend on the relative reactivity of different sites to OH, and may include the abstraction of the acidic hydrogen followed by splitting off of CO_2 ; the subsequent bimolecular reactions will produce $C_7H_{10}O_4$. This reaction competes with the abstraction of the tertiary hydrogen, but will lead to products that are inconsequential to the present experimental results. The formation of $C_{10}H_{16}O_4$ results from processes other than ozonolysis or OH attack on the exocyclic double bond of an acid product due to the fragmentation of the produced POZ and excessively high resulting O numbers. $C_{10}H_{16}O_4$ may have resulted from the reaction of an acylperoxy radical with HO_2 (see Figure 1) and the formation of a peroxy acid. However, the pathway for $C_7H_{10}O_3$ formation remains unclear. For the particle phase, $C_8H_{12}O_5$ and $C_9H_{14}O_5$ are the dominating compounds in most experiments performed in this study, whereas $C_{10}H_{16}O_3$ (a major gas-phase compound) represents only a minor contributor to this phase. $C_{10}H_{16}O_4$ is excluded ~~from MCM in the model~~, but plays a role in the particle-phase results. The formation of $C_{10}H_{16}O_4$ is positively correlated with the presence of RO_2 and HO_2 . $C_9H_{14}O_3$ and $C_9H_{14}O_4$ are the dominant acids in the model calculations, but are only minor compounds in the particle phase. $C_9H_{14}O_4$ formation seems to occur only in experiments with the highest limonene content. Rapid autoxidation for the formation of highly oxidised molecules (HOMs) has recently gained significant attention (Ehn et al., 2014). This autoxidation proceeds via intramolecular H abstraction of RO_2 and subsequent formation of -hydroperoxide groups. RO_2 lifetimes in low NO_x environments are usually sufficient for the occurrence of this process (Orlando and Tyndall, 2012). During this process, large amounts of oxygen are rapidly introduced into the molecules, leading to a decrease in their vapour pressure. Most of the RO_2 will originate from the VHP channel, in the case of limonene ozonolysis, and products will probably be non-identifiable unless the radical termination reaction yields a carboxylic acid. Even if the formed compounds contain one or more carboxylic acid groups, the corresponding low vapour pressure may be undetectable by the used FIGAERO inlet. ~~Jokinen et al.~~ (Jokinen et al., (2014) investigated the formation of HOM from limonene and found that highly oxygenated monomers (C10) and dimers (C20) with oxygen numbers ranging from 5 to 11 and 7 to 18, respectively, play a

crucial role in this formation. Only one compound with the same chemical formula ($C_9H_{14}O_5$) has been found in this study but it is unclear if the chemical structure is the same.

In this study, dimers have exclusively been detected in the particle phase and are absent from the gas phase, owing to their potentially low vapour pressure. The formation of dimer esters from α -pinene ozonolysis has recently been investigated (Kristensen et al., 2016). In that work, the reaction of sCI with carboxylic acids, suggested as the formation pathway in the gas phase, was followed by partitioning into the particle phase. Consequently, the carboxylic acid group is lost in the esterification process which may explain the relatively low signals observed for acidic dimers in the present study. A potential acidic dimer ester will only be detectable if the dimer has a carboxylic acid group, as in the case of a di or tri carboxylic acid, or if the sCI carries a carboxylic acid group. Unsaturated dimers may react with ozone. The $C_{18}H_{28}O_8$ and $C_{19}H_{30}O_7$ can form via the reaction of the endocyclic limonene sCI with ketolimonic ($C_8H_{12}O_5$) or limonic ($C_9H_{14}O_4$) acid, respectively (see [Figure 7](#); [Fig. 7](#)). In addition, $C_{19}H_{30}O_8$ may be formed from the dimerization reaction of limononic acid and the limononic-sCI. Gas-phase dimerization reactions of dominating C7–C10 acids with sCI account for only some of the dimer formulas. Reactions of acids with relatively small carbon numbers (<C7), RO₂ dimerization reactions or condensed-phase reactions may account for the other formulas.

5 Conclusion

[Figure 8A](#) provides an overview of the most important acidic compounds found in this study. These are identified by comparing the average contribution of each compound to all 33 experiments. Explicit formation pathways for the compounds $C_{10}H_{16}O_4$ and $C_9H_{12}O_5$ implemented in the [MCM model](#) and additional reaction pathways for $C_7H_{10}O_4$, $C_8H_{12}O_{4.5}$, $C_9H_{14}O_{4.5}$ and $C_{10}H_{16}O_3$ are proposed. Structures for $C_{10}H_{14}O_5$ and $C_{10}H_{16}O_4$ have been proposed in previous studies (Jaoui et al., 2006; Rossignol et al., 2012; Leungsakul et al., 2005a; Walser et al., 2008; Marianne Glasius et al., 2000) but the current mechanistic understanding is inadequate for explaining the formation of compounds with the proposed structures. In [Figure 8A](#), we show that the mechanisms proposed in this work can improve the qualitative understanding of the formation characterising (on average) 65% of the dominant gas-phase compounds and 50% of the particle-phase compounds. Notably, the particle-phase data correspond partly to compounds with low oxygen content (2–3 Oxygen) and their formation and negative correlation with ozone remain unclear and require further study. However, only a few acidic dimers are detected. This may have resulted from lack of evaporation of these dimers (i.e. as acidic dimers) or loss of the acid functional

group from potential acid monomer precursors during the dimer formation, as suggested in previous studies (Kristensen et al., 2016; Witkowski and Gierczak, 2014; Wang et al., 2016). Experiment #1, performed at low concentrations, for mixed oxidants and under humid conditions, should best represent atmospheric conditions. The summarised signal of the highest 10 acids in experiment #1 can be qualitatively attributed to 89% of the gas phase and the proposed mechanisms in this study account for 74% of the total signal (see [Figure 8B](#)-[Fig. 8B](#)). The particle-phase composition can be qualitatively explained (by up to 42%) by the mechanisms proposed in this work. The relatively large percentage of unexplained signal in the atmospheric case will result in large uncertainties when the acidic-particle phase composition of limonene SOA is modelled based on existing mechanisms (e.g. MCM) and partitioning theory.

10 For a more quantitative mechanism (compared with the mechanism considered), inclusion of non-acidic products is required for a complete picture of the oxidation products. Furthermore, secondary and tertiary chemistry must be considered when the oxidation of compounds is modelled. Subsequent aerosol formation as well as dimerization and condensed-phase reactions must also be evaluated.

15

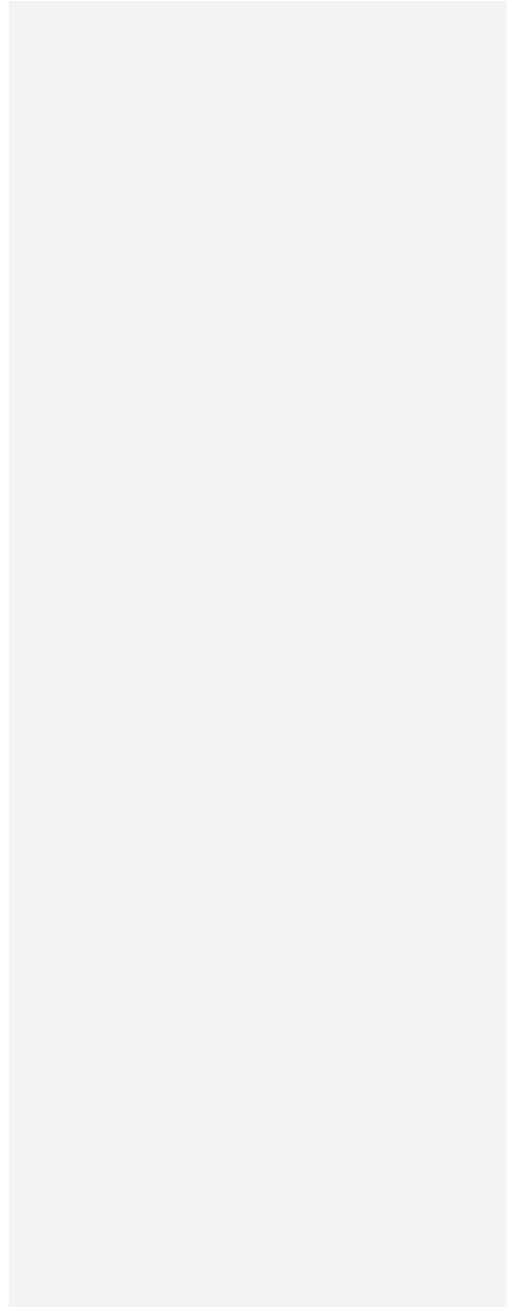


Table 4-1: Summary of experimental conditions and overview of the selected results. **Units for O₃, OH, HO₂ and RO₂ are integrated concentrations (ppb and the last three are ×s) as calculated with the model using the MCM.** Water in the system increases the SOA mass and yield in the system whereas the presence of 2-butanol decreases the SOA mass and yield. **The contribution of the highest 10 compounds is linked to complexity of the product distribution, i.e. if 10 compounds dominate then any minor product is less important and the composition appears less complex.** The rate normalised HO₂/RO₂ ratio assumed rate coefficients of 8.8 × 10⁻¹³ and 9.1 × 10⁻¹² for RO₂ and HO₂ reaction respectively (MCM v3.3.1)

#	O ₃ (ppb)	limonene initial [Δreacted] (ppb)	RH	OH - S	OH (ppb×s)	HO ₂ (ppb×s)	RO ₂ (ppb×s)	Rate normalised* [HO ₂]/[RO ₂]	SOA Mass (μg m ⁻³)	% Contribution of highest 10 compounds gas phase Yield of C ₇ -C ₁₀ carboxylic acids	% Contribution of highest 10 compounds in gas [particle] phase [†]
1	400	15 [8,4]	40%	-	0.085	1	400	0.03	2.6	7323%	73 [54]
2	400	40 [22]	40%	-	0.083	3	710	0.04	4.2	7318%	73 [57]
3	400	150 [81]	40%	-	0.079	5	1500	0.03	32	7220%	72 [51]
4	400	15 [8,4]	Dry	-	0.086	2	400	0.05	0.04	7911%	-79 ^a
5	400	40 [22]	Dry	-	0.084	3	710	0.04	0.8	804%	-80 ^a
6	400	150 [81]	Dry	-	0.079	5	1500	0.03	12	782%	-78 ^a
7	400	15 [5,7]	40%	✓	0	10	190	0.55	2.3	6913%	69 [61]
8	400	40 [15]	40%	✓	0	16	330	0.50	6	727%	72 [60]
9	400	150 [54]	40%	✓	0	29	640	0.47	40	706%	70 [58]
10	400	15 [5,7]	Dry	✓	0	10	190	0.55	0.2	91 ^a	9291 ^a
11	400	40 [15]	Dry	✓	0	19	330	0.60	2.3	90 ^a	8790 ^a
12	400	150 [54]	Dry	✓	0	29	640	0.47	57	87 ^a	5487 ^a
13	1000	15 [13]	40%	-	0.160	2	530	0.04	4.7	7418%	74 [53]
14	1000	40 [34]	40%	-	0.157	4	930	0.04	7.3	759%	75 [54]
15	1000	150 [124]	40%	-	0.152	7	1900	0.04	25	747%	71 [49]
16	1000	15 [13]	Dry	-	0.162	2	530	0.04	750.04	8%	75 [63]
17	1000	40 [34]	Dry	-	0.160	4	9200	0.00	1.4	774%	77 [51]

Inserted Cells

Inserted Cells

Inserted Cells

18	1000	150 [125]	Dry	-	0.154	7	1800	<u>0.04</u>	19	737%	<u>73 [51]</u>
19	1000	15 [10]	40%	✓	0	13	280	<u>0.48</u>	13	6318%	<u>63 [51]</u>
20	1000	40 [28]	40%	✓	0	20	460	<u>0.45</u>	18	6410%	<u>64 [55]</u>
21	1000	150 [101]	40%	✓	0	38	890	<u>0.44</u>	94	648%	<u>61 [55]</u>
22	1000	15 [10]	Dry	✓	0	13	280	<u>0.48</u>	0.9	706%	<u>70 [61]</u>
23	1000	40 [28]	Dry	✓	0	21	460	<u>0.47</u>	6.3	724%	<u>72 [58]</u>
24	1000	150 [101]	Dry	✓	0	33	890	<u>0.39</u>	66	696%	<u>69 [55]</u>
25	5000	15 [15]	40%	-	0.242	3	570	<u>0.05</u>	4	608%	<u>60 [52]</u>
26	5000	40 [40]	40%	-	0.254	4	1000	<u>0.04</u>	10	604%	<u>60 [47]</u>
27	5000	150 [150]	40%	-	0.253	8	2000	560.04	56	2%	<u>56 [49]</u>
28	5000	15 [15]	Dry	-	0.248	3	550	<u>0.06</u>	4	78^a	-78^a
29	5000	40 [40]	Dry	-	0.260	4	980	<u>0.04</u>	5.7	78^a	-78^a
30	5000	150 [150]	Dry	-	0.259	8	1900	<u>0.04</u>	22	75^a	-75^a
31	5000	15 [15]	40%	✓	0	12	340	<u>0.37</u>	23	6223%	<u>62 [51]</u>
32	5000	40 [40]	40%	✓	0	19	530	<u>0.37</u>	35	6510%	<u>65 [52]</u>
33	5000	150 [150]	40%	✓	0	37	1000	<u>0.38</u>	186	647%	<u>64 [58]</u>

Inserted Cells

Inserted Cells

^a Some data for experiments 4-6, 10-12 and 28-29 are unavailable due to no/low particle concentrations or malfunctioning of the FIGAERO unit.

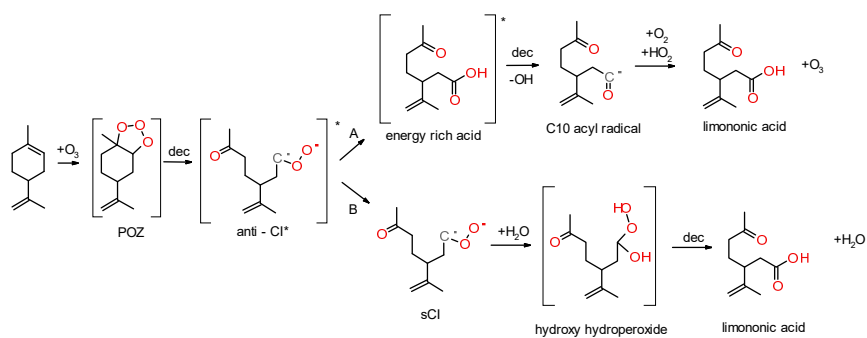


Figure 1. (A) Example of initial reactions of limonene with ozone to form limonic acid from the anti – Cl* via the hot acid channel and (B) the collisional stabilisation channel (Vereecken and Francisco, 2012) .

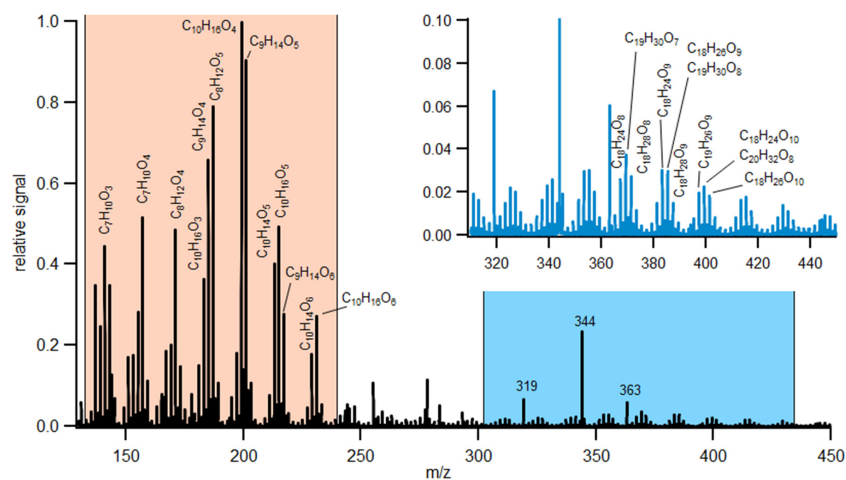


Figure 2. Example **MS for** of derived mass spectra of condensed phase taken from the experiment (#21) with medium-ozone and high-limonene conditions with **OH-S for particle-phase data** added OH scavenger. Indicated are the regions with identified monomers (orange region) and selected dimers (blue region). The peaks at 319, 344 and 363 are associated with the **mass calibrant HPFA** used mass calibrant HPFA. The complexity of this mass spectra is described using the fraction of 10 dominated product ions and are compared to other experiments with similar conditions in Fig. 3.

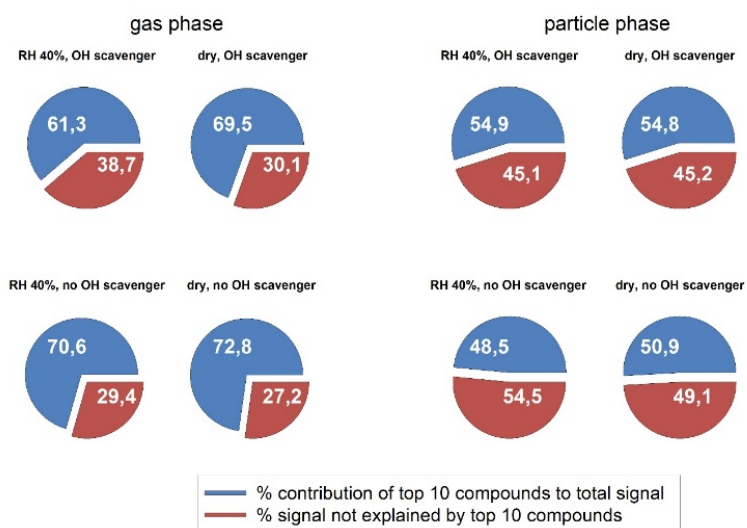


Figure 3. Explained and unexplained fractions Contribution of the highest 10 compounds (blue) to the total signal in the gas and particle phase. The red fraction shows the signal not explained by the 10 highest compounds. A larger red fraction would indicate a more complex composition. Data shown for selected experiments with 1000 ppb ozone and 150 ppb limonene under different conditions. The estimated total yield of larger carboxylic acids (c7-c10) for these four experiments were very similar 6% (dry, scavenger), 8% (humid, scavenger), 6% (dry, no scavenger) and 7% (humid, no scavenger).

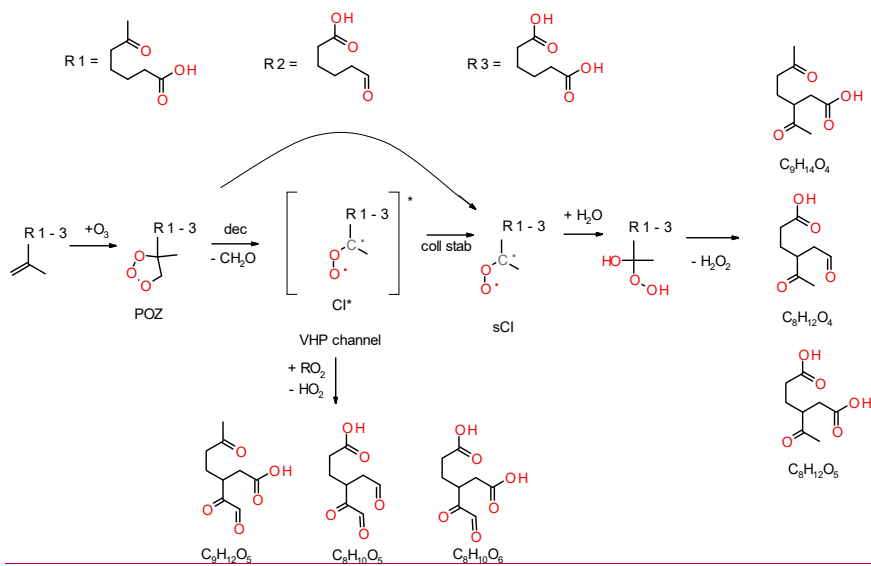


Figure 4.

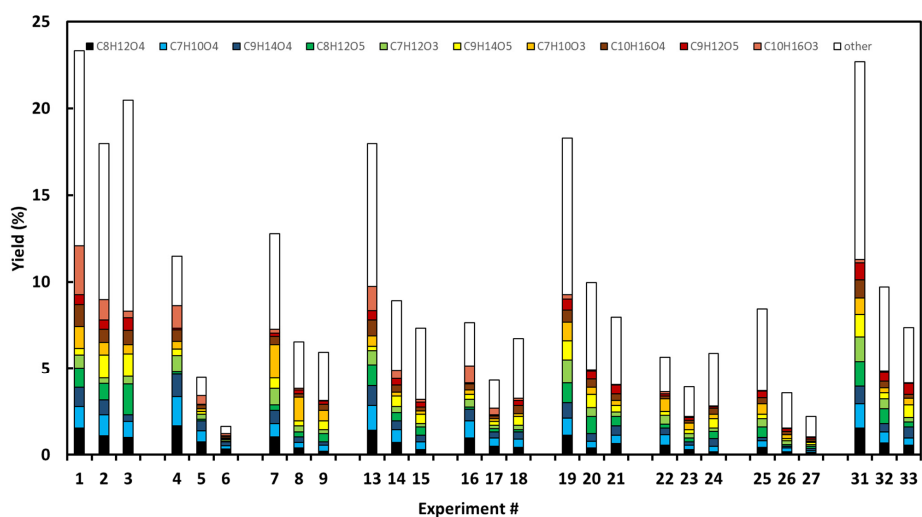


Figure 4. The molar yields of identified c7-c10 acids. The most important acids (averaged over all experiments) are $C_7H_{10}O_3$, $C_7H_{10}O_4$, $C_8H_{12}O_4$, $C_8H_{12}O_5$, $C_9H_{14}O_4$, $C_9H_{14}O_5$, $C_{10}H_{16}O_3$ and $C_{10}H_{16}O_4$ and are illustrated by individual colours. Exp. 10-12 and 28-30 were removed due to uncompleted particle phase characterisation.

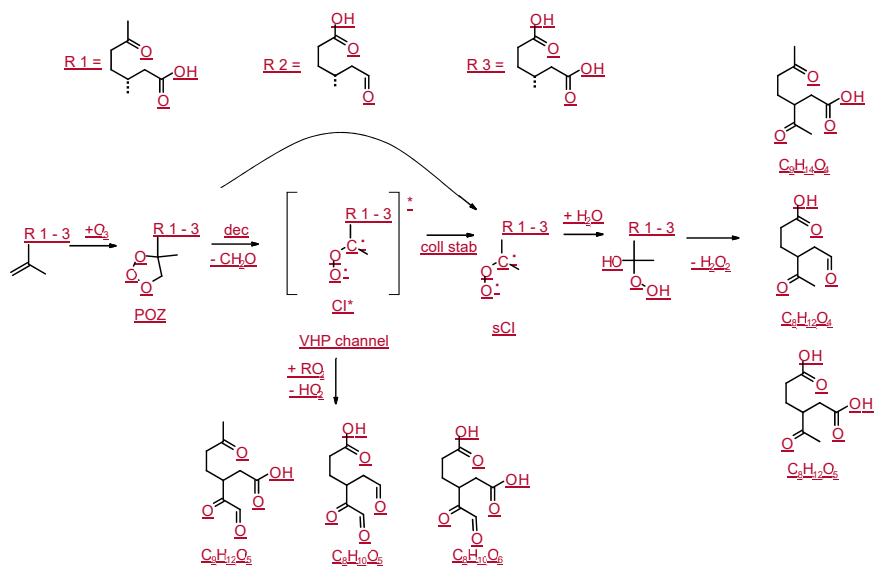
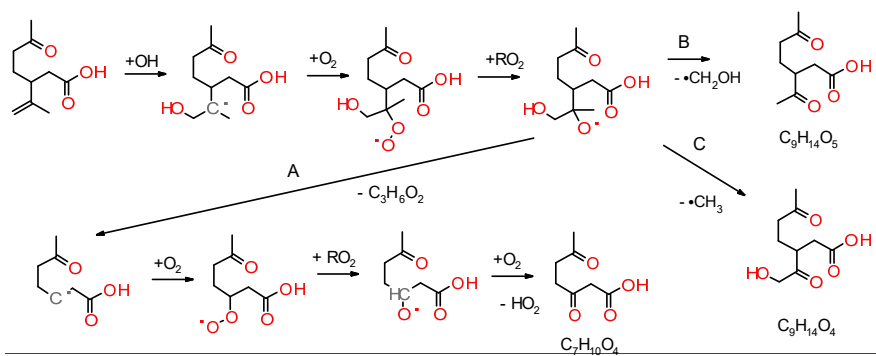


Figure 5. Proposed reaction mechanisms for secondary ozone chemistry of limononic (R1), limonic (R2) and limonalic (R3) acid. The dotted bond shows where R1-3 is connected to the 2-methyl-etenyl group (i.e. -C(CH₃)=CH₂) in the parent compounds.



5

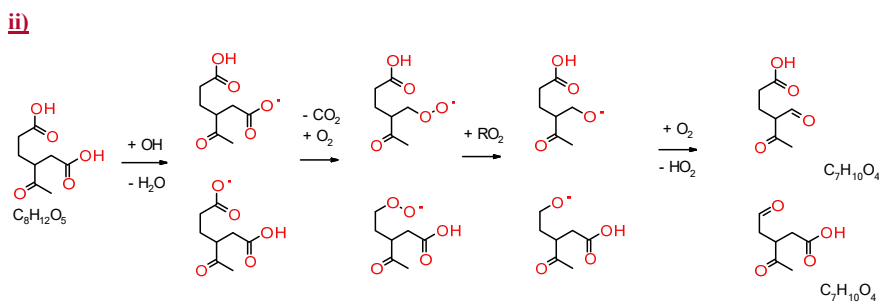
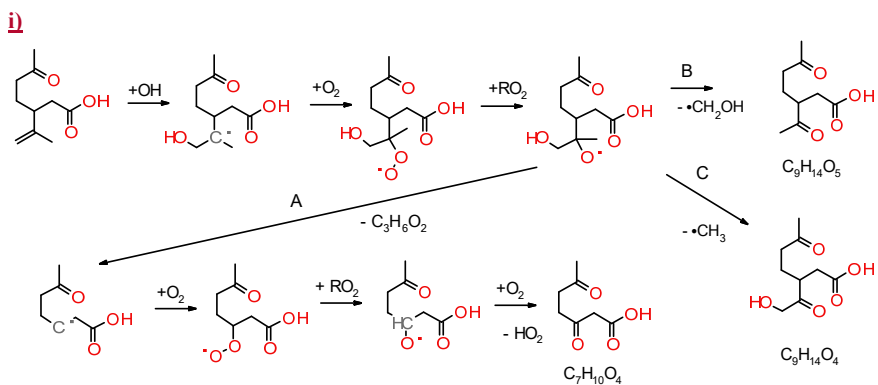


Figure 5.6. Secondary chemistry i) Addition of OH to the remaining unsaturated double bond of the primary product limonic acid and the subsequent formation of $C_7H_{10}O_4$, $C_9H_{14}O_5$ and $C_9H_{14}O_4$.

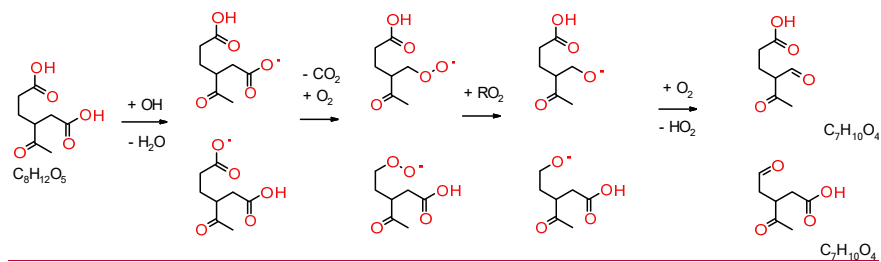


Figure 6.ii) Secondary chemistry of a selected saturated carboxylic acid product. ($C_8H_{12}O_5$) giving observed C_7 products

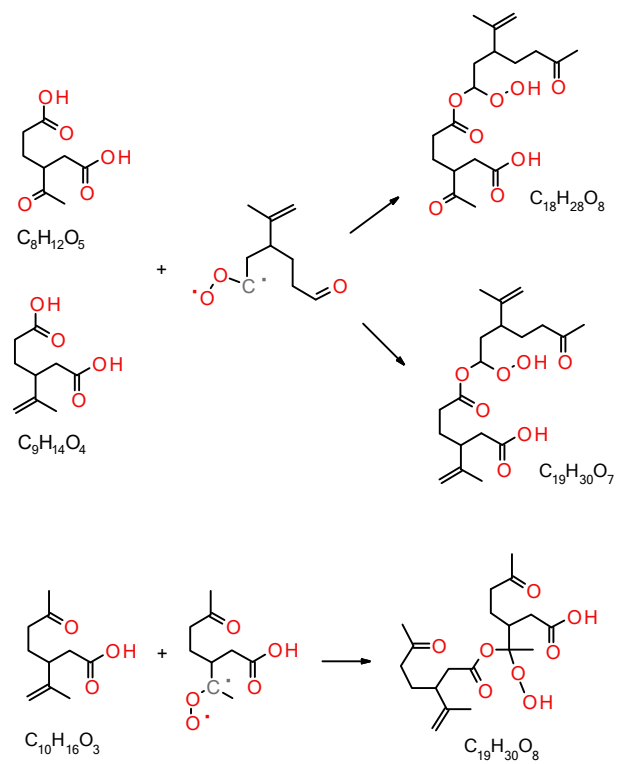


Figure 4. Proposed formation of observed dimers ($C_{18}H_{28}O_8$, $C_{19}H_{20}O_7$ and $C_{19}H_{30}O_8$) from monomer-crige reactions.

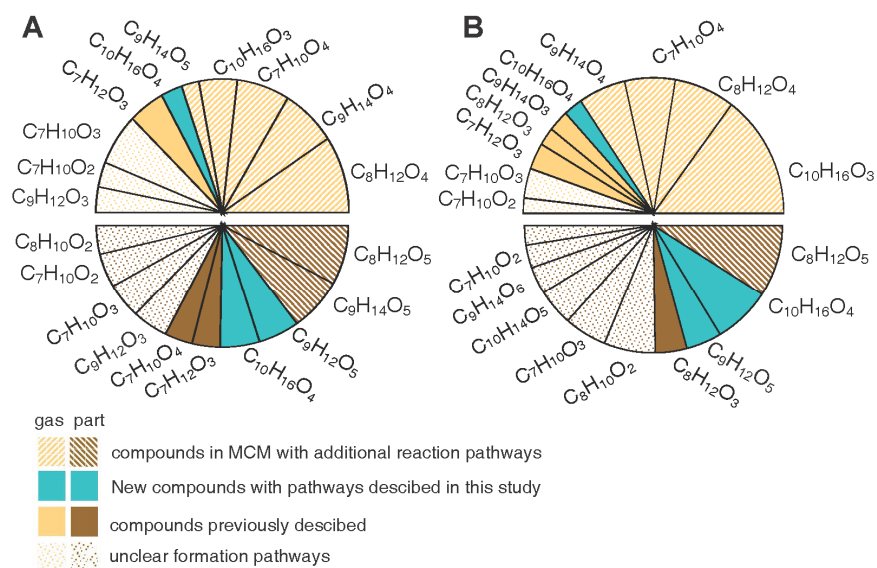


Figure 8. A) Averaged 10 highest contributors to all experiments. B) Highest 10 contributors to experiment 1. Figure 8. Pie charts showing the percentage contribution of each compound to for the top major 10 compounds observed. Top half wheel shows the gas-phase data and the bottom wheel shows the particle-phase data. The compounds are classified according to current knowledge, i.e. previous described reaction mechanism, mechanism suggested in this study and unclear formation pathways. A) Averaged contribution for all experiments. B) Specific contributions for experiment 1 that had the lowest concentrations of reactants, with mixed oxidants and humid conditions.

References

- 10 Atkinson, R., Aschmann, S. M., Arey, J., and Shorees, B.: Formation of OH radicals in the gas phase reactions of O₃ with a series of terpenes, *Journal of Geophysical Research*, 97, 10.1029/92jd00062, 1992.
- Barley, M. H., Topping, D., Lowe, D., Utembe, S., and McFiggans, G.: The sensitivity of secondary organic aerosol (SOA) component partitioning to the predictions of component properties - Part 3: Investigation of condensed compounds generated by a near-explicit model of VOC oxidation, *Atmospheric Chemistry and Physics*, 11, 13145-13159, 10.5194/acp-11-13145-2011, 2011.
- 15 Bertram, T. H., Kimmel, J. R., Crisp, T. A., Ryder, O. S., Yatavelli, R. L. N., Thornton, J. A., Cubison, M. J., Gonin, M., and Worsnop, D. R.: A field-deployable, chemical ionization time-of-flight mass spectrometer, *Atmos Meas Tech*, 4, 1471-1479, 10.5194/amt-4-1471-2011, 2011.

- Brown, S. K., Sim, M. R., Abramson, M. J., and Gray, C. N.: Concentrations of Volatile Organic-Compounds in Indoor Air - a Review, *Indoor Air-International Journal of Indoor Air Quality and Climate*, 4, 123-134, DOI 10.1111/j.1600-0668.1994.t01-2-00007.x, 1994.
- 5 [Carslaw, N.: A mechanistic study of limonene oxidation products and pathways following cleaning activities, *Atmos. Environ.*, 80, 507-513, 10.1016/j.atmosenv.2013.08.034, 2013.](#)
- [Chen, J. J., and Griffin, R. J.: Modeling secondary organic aerosol formation from oxidation of alpha-pinene, beta-pinene, and d-limonene, *Atmos. Environ.*, 39, 7731-7744, 10.1016/j.atmosenv.2005.05.049, 2005.](#)
- [Chen, X., and Hopke, P. K.: A chamber study of secondary organic aerosol formation by limonene ozonolysis, *Indoor Air*, 20, 320-328, 10.1111/j.1600-0668.2010.00656.x, 2010.](#)
- 10 Ehn, M., Thornton, J. A., Kleist, E., Sipila, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I. H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurten, T., Nielsen, L. B., Jorgensen, S., Kjaergaard, H. G., Canagaratna, M., Maso, M. D., Berndt, T., Petaja, T., Wahner, A., Kerminen, V. M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-volatility secondary organic aerosol, *Nature*, 506,
- 15 476-479, 10.1038/nature13032, 2014.
- Faxon, C., Hammes, J., Le Breton, M., Pathak, R. K., and Hallquist, M.: Characterization of organic nitrate constituents of secondary organic aerosol (SOA) from nitrate-radical-initiated oxidation of limonene using high-resolution chemical ionization mass spectrometry, *Atmospheric Chemistry and Physics*, 18, 5467-5481, 10.5194/acp-18-5467-2018, 2018.
- 20 Foley, J. P., and Dorsey, J. G.: A Review of the Exponentially Modified Gaussian (Emg) Function - Evaluation and Subsequent Calculation of Universal Data, *Journal of Chromatographic Science*, 22, 40-46, DOI 10.1093/chromsci/22.1.40, 1984.
- Glasius, M., Lahaniati, M., Calogirou, A., Di Bella, D., Jensen, N. R., Hjorth, J., Kotzias, D., and Larsen, B. R.: Carboxylic Acids in Secondary Aerosols from Oxidation of Cyclic Monoterpenes by Ozone, ~~*Environmental science & technology*, 34, 1001-1010, 10.1021/es990445r, 6, 2000.~~
- 25 [Glasius, M., and Goldstein, A. H.: Recent Discoveries and Future Challenges in Atmospheric Organic Chemistry, *Environ. Sci. Technol.*, 50, 2754-2764, 10.1021/acs.est.5b05105, 2016.](#)
- [Gong, Y. W., Chen, Z. M., and Li, H.: The oxidation regime and SOA composition in limonene ozonolysis: roles of different double bonds, radicals, and water, *Atmos. Chem. Phys.*, 18, 15105-15123, 10.5194/acp-18-15105-2018, 2018.](#)
- 30 [Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 \(MEGAN2.1\): an extended and updated framework for modeling biogenic emissions, *Geoscientific Model Development*, 5, 1471-1492, 10.5194/gmd-5-1471-2012, 2012.](#)
- 35 Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, ~~*Atmospheric Chemistry and Physics*, 9, 5155-5236, DOI 10.5194/acp-9-5155-2009, 2009.~~
- 40 [Jaoui, M., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., and Edney, E. O.: Identification and quantification of aerosol polar oxygenated compounds bearing carboxylic or hydroxyl groups. 2. Organic tracer compounds from monoterpenes, *Environ. Sci. Technol.*, 39, 5661-5673, 2005a2005.](#)
- 45 [Jaoui, M., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., and Edney, E. O.: Identification and quantification of aerosol polar oxygenated compounds bearing carboxylic or hydroxyl groups. 2. Organic](#)

- [tracer compounds from monoterpenes, Environmental science & technology, 39, 5661-5673, 10.1021/es048111b, 2005b.](#)
- 5 Jaoui, M., Corse, E., Kleindienst, T. E., Offenberg, J. H., Lewandowski, M., and Edney, E. O.: Analysis of Secondary Organic Aerosol Compounds from the Photooxidation of Limonene in the Presence of NO_x and their Detection in Ambient PM_{2.5}, *Environmental science & technology*, 40, 3819-3828, 10.1021/es052566z, 2006.
- Jenkin, M. E.: Modelling the formation and composition of secondary organic aerosol from α - and β -pinene ozonolysis using MCM v3, *Atmospheric Chemistry and Physics*, 4, 1741-1757, 10.5194/acp-4-1741-2004, 2004.
- 10 [Jenkin, M. E., Valorso, R., Aumont, B., and Rickard, A. R.: Estimation of rate coefficients and branching ratios for reactions of organic peroxy radicals for use in automated mechanism construction, Atmos. Chem. Phys., 19, 7691-7717, 10.5194/acp-19-7691-2019, 2019.](#)
- Jokinen, T., Sipila, M., Richters, S., Kerminen, V. M., Paasonen, P., Stratmann, F., Worsnop, D., Kulmala, M., Ehn, M., Herrmann, H., and Berndt, T.: Rapid autoxidation forms highly oxidized RO₂ radicals in the atmosphere, *Angewandte Chemie (International ed. in English)*, 53, 14596-14600, 10.1002/anie.201408566, 2014.
- 15 [Jonsson, A. M., Hallquist, M., and Ljungstrom, E.: The effect of temperature and water on secondary organic aerosol formation from ozonolysis of limonene, Delta\(3\)-carene and alpha-pinene, Atmospheric Chemistry and Physics, 8, 6541-6549, DOI 10.5194/acp-8-6541-2008, 2008a.](#)
- 20 [Jonsson, A. M., Hallquist, M., and Ljungström, E.: Impact of Humidity on the Ozone Initiated Oxidation of Limonene, \$\Delta\$ 3-Carene, and \$\alpha\$ -Pinene, Environmental science & technology, 40, 188-194, 10.1021/es051163w, 2006.](#)
- 25 [Jonsson, A. M., Hallquist, M., and Ljungstrom, E.: The effect of temperature and water on secondary organic aerosol formation from ozonolysis of limonene, Delta\(3\)-carene and alpha-pinene, Atmos. Chem. Phys., 8, 6541-6549, 2008a.](#)
- [Jonsson, A. M., Hallquist, M., and Ljungström, E.: Influence of OH Scavenger on the Water Effect on Secondary Organic Aerosol Formation from Ozonolysis of Limonene, \$\Delta\$ 3-Carene, and \$\alpha\$ -Pinene, Environmental science & technology, 42, 5938-5944, 10.1021/es702508y, 2008b.](#)
- 30 Keywood, M. D., Kroll, J. H., Varutbangkul, V., Bahreini, R., Flagan, R. C., and Seinfeld, J. H.: Secondary Organic Aerosol Formation from Cyclohexene Ozonolysis: Effect of OH Scavenger and the Role of Radical Chemistry, *Environmental science & technology*, 38, 3343-3350, 10.1021/es049725j, 2004.
- [Koch, S., Winterhalter, R., Uherek, E., Kolloff, A., Neeb, P., and Moortgat, G. K.: Formation of new particles in the gas-phase ozonolysis of monoterpenes, Atmos. Environ., 34, 4031-4042, 2000.](#)
- 35 Kristensen, K., Enggrob, K. L., King, S. M., Worton, D. R., Platt, S. M., Mortensen, R., Rosenoern, T., Surratt, J. D., Bilde, M., Goldstein, A. H., and Glasius, M.: Formation and occurrence of dimer esters of pinene oxidation products in atmospheric aerosols, *Atmospheric Chemistry and Physics Discussions*, 12, 22103-22137, 10.5194/acpd-12-22103-2012, 2012.
- 40 Kristensen, K., Cui, T., Zhang, H., Gold, A., Glasius, M., and Surratt, J. D.: Dimers in α -pinene secondary organic aerosol: effect of hydroxyl radical, ozone, relative humidity and aerosol acidity, *Atmospheric Chemistry and Physics*, 14, 4201-4218, 10.5194/acp-14-4201-2014, 2014.
- Kristensen, K., Watne, A. K., Hammes, J., Lutz, A., Petäjä, T., Hallquist, M., Bilde, M., and Glasius, M.: High-Molecular Weight Dimer Esters Are Major Products in Aerosols from α -Pinene Ozonolysis and the Boreal Forest, *Environmental Science & Technology Letters*, 3, 280-285, 10.1021/acs.estlett.6b00152, 2016.
- 45 Langer, S., Moldanova, J., Arrhenius, K., Ljungstrom, E., and Ekberg, L.: Ultrafine particles produced by ozone/limonene reactions in indoor air under low/closed ventilation conditions, *Atmospheric Environment*, 42, 4149-4159, 10.1016/j.atmosenv.2008.01.034, 2008.

- [Le Breton, M., Psichoudaki, M., Hallquist, M., Watne, A. K., Lutz, A., and Hallquist, A. M.: Application of a FIGAERO ToF CIMS for on-line characterization of real-world fresh and aged particle emissions from buses, *Aerosol Sci. Technol.*, 53, 244-259, 10.1080/02786826.2019.1566592, 2019.](#)
- 5 Leungsakul, S., Jaoui, M., and Kamens, R. M.: Kinetic mechanism for predicting secondary organic aerosol formation from the reaction of d-limonene with ozone, *Environmental science & technology*, 39, 9583-9594, 2005a.
- Leungsakul, S., Jeffries, H. E., and Kamens, R. M.: A kinetic mechanism for predicting secondary aerosol formation from the reactions of d-limonene in the presence of oxides of nitrogen and natural sunlight, *Atmospheric Environment*, *Atmos. Environ.*, 39, 7063-7082, [10.1016/j.atmosenv.2005.08.024](#), 2005b.
- 10 Lopez-Hilfiker, F. D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T. F., Lutz, A., Hallquist, M., Worsnop, D., and Thornton, J. A.: A novel method for online analysis of gas and particle composition: description and evaluation of a Filter Inlet for Gases and AEROSols (FIGAERO), *Atmos. Meas. Tech.*, 7, 983-1001, [10.5194/amt-7-983-2014](#), 2014.
- [Lopez-Hilfiker, F. D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T. F., Carrasquillo, A. J., Daumit, K. E., Hunter, J. F., Kroll, J. H., Worsnop, D. R., and Thornton, J. A.: Phase partitioning and volatility of secondary organic aerosol components formed from \$\alpha\$ -pinene ozonolysis and OH oxidation: the importance of accretion products and other low volatility compounds. *Atmos. Chem. Phys.*, 15, 7765-7776, \[10.5194/acp-15-7765-2015\]\(#\), 2015.](#)
- 15 Maksymiuk, C. S., Gayahtri, C., Gil, R. R., and Donahue, N. M.: Secondary organic aerosol formation from multiphase oxidation of limonene by ozone: mechanistic constraints via two-dimensional heteronuclear NMR spectroscopy, *Physical chemistry chemical physics : PCCP*, 11, 7810-7818, [10.1039/b820005j](#), 2009.
- Marianne Glasius, Maria Lahaniati, Aggelos Calogirou, Dario Di Bella, Niels R. Jensen, Jens Hjorth, Dimitrios Kotzias, a., and Larsen*, B. R.: Carboxylic Acids in Secondary Aerosols from Oxidation of Cyclic Monoterpenes by Ozone, *S0013-936X(99)00445-9*, 2000.
- 25 [McFiggans, G., Mentel, T. F., Wildt, J., Pullinen, I., Kang, S., Kleist, E., Schmitt, S., Springer, M., Tillmann, R., Wu, C., Zhao, D., Hallquist, M., Faxon, C., Le Breton, M., Hallquist, A. M., Simpson, D., Bergström, R., Jenkin, M. E., Ehn, M., Thornton, J. A., Alfarra, M. R., Bannan, T. J., Percival, C. J., Priestley, M., Topping, D., and Kiendler-Scharr, A.: Secondary organic aerosol reduced by mixture of atmospheric vapours. *Nature*, 565, 587-593, \[10.1038/s41586-018-0871-y\]\(#\), 2019.](#)
- 30 [Mohr, C., Lopez-Hilfiker, F. D., Zotter, P., Prévôt, A. S. H., Xu, L., Ng, N. L., Herndon, S. C., Williams, L. R., Franklin, J. P., Zahniser, M. S., Worsnop, D. R., Knighton, W. B., Aiken, A. C., Gorkowski, K. J., Dubey, M. K., Allan, J. D., and Thornton, J. A.: Contribution of Nitrated Phenols to Wood Burning Brown Carbon Light Absorption in Detling, United Kingdom during Winter Time. *Environ. Sci. Technol.*, 47, 6316-6324, \[10.1021/es400683v\]\(#\), 2013.](#)
- 35 Mohr, C., Lopez-Hilfiker, F. D., Yli-Juuti, T., Heitto, A., Lutz, A., Hallquist, M., D'Ambro, E. L., Rissanen, M. P., Hao, L. Q., Schobesberger, S., Kulmala, M., Mauldin, R. L., Makkonen, U., Sipila, M., Petaja, T., and Thornton, J. A.: Ambient observations of dimers from terpene oxidation in the gas phase: Implications for new particle formation and growth, *Geophysical Research Letters*, *Geophys. Res. Lett.*, 44, 2958-2966, [10.1002/2017gl072718](#), 2017.
- 40 Orlando, J. J., and Tyndall, G. S.: Laboratory studies of organic peroxy radical chemistry: an overview with emphasis on recent issues of atmospheric significance, *Chemical Society reviews*, 41, 6294-6317, [10.1039/c2cs35166h](#), 2012.
- Pathak, R. K., Salo, K., Emanuelsson, E. U., Cai, C., Lutz, A., Hallquist, A. M., and Hallquist, M.: Influence of ozone and radical chemistry on limonene organic aerosol production and thermal characteristics, *Environmental science & technology*, 46, 11660-11669, [10.1021/es301750r](#), 2012.
- 45

- Rossignol, S., Chiappini, L., Perraudin, E., Rio, C., Fable, S., Valorso, R., and Doussin, J. F.: Development of a parallel sampling and analysis method for the elucidation of gas/particle partitioning of oxygenated semi-volatile organics: a limonene ozonolysis study, *Atmos. Meas. Tech.*, **5**, 1459-1489, 10.5194/amt-5-1459-2012, 2012.
- 5 Rossignol, S., Rio, C., Ustache, A., Fable, S., Nicolle, J., Meme, A., D'Anna, B., Nicolas, M., Leoz, E., and Chiappini, L.: The use of a housecleaning product in an indoor environment leading to oxygenated polar compounds and SOA formation: Gas and particulate phase chemical characterization, *Atmospheric Environment*, **75**, 196-205, 10.1016/j.atmosenv.2013.03.045, 2013.
- 10 [Saathoff, H., Naumann, K. H., Mohler, O., Jonsson, A. M., Hallquist, M., Kiendler-Scharr, A., Mentel, T. F., Tillmann, R., and Schurath, U.: Temperature dependence of yields of secondary organic aerosols from the ozonolysis of alpha-pinene and limonene, *Atmos. Chem. Phys.*, **9**, 1551-1577, 2009.](#)
- Salo, K., Jonsson, A. M., Andersson, P. U., and Hallquist, M.: Aerosol volatility and enthalpy of sublimation of carboxylic acids, *The journal of physical chemistry. A*, **114**, 4586-4594, 10.1021/jp910105h, 2010.
- 15 [Shrivastava, M., Cappa, C. D., Fan, J. W., Goldstein, A. H., Guenther, A. B., Jimenez, J. L., Kuang, C., Laskin, A., Martin, S. T., Ng, N. L., Petaja, T., Pierce, J. R., Rasch, P. J., Roldin, P., Seinfeld, J. H., Shilling, J., Smith, J. N., Thornton, J. A., Volkamer, R., Wang, J., Worsnop, D. R., Zaveri, R. A., Zelenyuk, A., and Zhang, Q.: Recent advances in understanding secondary organic aerosol: Implications for global climate forcing, *Reviews of Geophysics*, **55**, 509-559, 10.1002/2016rg000540, 2017.](#)
- 20 Walser, M. L., Desyaterik, Y., Laskin, J., Laskin, A., and Nizkorodov, S. A.: High-resolution mass spectrometric analysis of secondary organic aerosol produced by ozonation of limonene, *Physical chemistry chemical physics : PCCP*, **10**, 1009-1022, 10.1039/b712620d, 2008.
- Wang, M., Yao, L., Zheng, J., Wang, X., Chen, J., Yang, X., Worsnop, D. R., Donahue, N. M., and Wang, L.: Reactions of Atmospheric Particulate Stabilized Criegee Intermediates Lead to High-Molecular-Weight Aerosol Components, *Environmental science & technology*, **50**, 5702-5710, 10.1021/acs.est.6b02114, 2016.
- 25 Watne, A. K., Westerlund, J., Hallquist, A. M., Brune, W. H., and Hallquist, M.: Ozone and OH-induced oxidation of monoterpenes: Changes in the thermal properties of secondary organic aerosol (SOA), *Journal of Aerosol Science*, **114**, 31-41, 10.1016/j.jaerosci.2017.08.011, 2017.
- Vereecken, L., and Francisco, J. S.: Theoretical studies of atmospheric reaction mechanisms in the troposphere, *Chemical Society reviews*, **41**, 6259-6293, 10.1039/c2cs35070j, 2012.
- 30 Witkowski, B., and Gierczak, T.: Early stage composition of SOA produced by α -pinene/ozone reaction: α -Acyloxyhydroperoxy aldehydes and acidic dimers, *Atmospheric Environment*, **95**, 59-70, 10.1016/j.atmosenv.2014.06.018, 2014.
- [Youssefi, S., and Waring, M. S.: Transient Secondary Organic Aerosol Formation from Limonene Ozonolysis in Indoor Environments: Impacts of Air Exchange Rates and Initial Concentration Ratios, *Environ. Sci. Technol.*, **48**, 7899-7908, 10.1021/es5009906, 2014.](#)
- 35 [Ziemann, P. J., and Atkinson, R.: Kinetics, products, and mechanisms of secondary organic aerosol formation, *Chem. Soc. Rev.*, **41**, 6582-6605, 2012.](#)