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 NOx-free conditions at 20◦C, using various conditions of humidity, initial ozone and pre- cursor 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 no 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. 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. Obviously, one can derive average yields/concentrations as measured at the end of the flow reactor bearing in mind the residence time distribution. However, one can always directly present signal intensity and even using our calibrations to derive estimation on concentrations.

Action: The discussion now contains more quantitative information like signal intensities and concentrations.

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 and an general sensitivity (from calibrations of some standard acids) carbon yields can be calculated.

Action: The carbon yield of some selected acids are now presented.

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: The description of the Spearman correlation analysis and outcome was extended and specified.

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: Selective model runs are shown to illustrate the temporal evolution. The model description is updated and MCM is now referred to as a mechanism.

Minor comments:

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

Reply: We agree

Action: This is now included.

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, p7 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.

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-NOx 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 .

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 S2 were proposed by the authors for the paper referred to in that table.
Action: We more clearly direct the readers to Table S2

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 has been divided and is now included in a section more clearly describing Figure 8.

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. a-pinene), and limonene is doubly unsaturated and exhibits high reactivity in the presence of ozone"?
Action: The sentence has been changed to more clearly motivate the study of limonene oxidation.

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: The section was clarified
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 HO_2 and RO_2 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 changed accordingly

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

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: The text was changed accordingly

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 now also includes a Figure of modelled ratios.

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

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 accordingly

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. However, our last statement in the introduction is clearly aiming at an ambient atmospheric application.
Action: The introduction has been elaborated and now includes more quantitative motivations.

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.

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. Figure2 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.

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 should be complemented with some Figures.
Action: The discussion has been facilitated by addition of a Figure.

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.

P.2, l. 16: Why was only the anti – CI* pathway chosen for Figure 1, and not the syn – CI* pathway? Please motivate.
Reply: The anti – CI* 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: The text was changed to improve the transition of the paragraphs
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

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 (approx. 2 – 3 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.

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.

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 the particle phase, which is interpreted as having a higher diversity

Action: We more clearly refer to Figure 3 and 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