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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Carboxylic acids from limonene oxidation by ozone and OH radicals: Insights into mechanisms derived using a FIGAERO-CIMS" *by* Julia Hammes et al.

Anonymous Referee #1

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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 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 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. 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 unexplained...) 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.

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?).

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.

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.

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.

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

3. I think a discussion on the selectivity of the reagent ion (acetate) is needed some-

where. 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?

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.

Technical corrections

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

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”?

p.1 l.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”

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”?

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

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

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

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

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

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

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

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

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

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

p.6 l.9: Should “carbon number >= 10” be replaced with ““carbon number <= 10”?

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

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

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

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

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

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