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Atmospheric Measurement Techniques Discussions

Interactive comment on "Production of highly oxygenated organic molecules (HOMs) from trace contaminants during isoprene oxidation" *by* Anne-Kathrin Bernhammer et al.

Anonymous Referee #1

Received and published: 30 January 2018

This paper reports on ion signals at m/z 137.133 (C10H17+) and m/z 81.070 (C6H9+) measured by the proton transfer reaction time-of flight mass spectrometer (PTR3-TOF, Ionicon) during isoprene oxidation experiments in the CLOUD chamber at CERN. These ions correspond to protonated monoterpenes and their fragments and are therefore unexpected / unwanted for pure isoprene oxidation experiments. Authors explain the origin of these compounds by the reactions inside the PTR3 reaction chamber and by cycloaddition of isoprene in the gas bottle itself. Placing cryogenic trap between the gas bottle and the CLOUD chamber shows clear decrease of the signal for these ions and therefore their successful removal. It points out and identifies the source of monoterpene contaminants and the way how to remove them which is important and

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Discussion paper

valuable information for future experiments involving isoprene. The manuscript itself needs minor revisions prior to being published, at the moment it is clumsy and needs to be more straight-forward. The main point of the paper should revolve around the possible misinterpretation of data when conducting experiments with isoprene, which is why this journal is appropriate for this paper. The biggest issue with the paper comes from stating that the presence of contaminants impacts the gas phase reactions of isoprene. The final sentence of the paper says "This clearly indicates a significant change in the observed oxidation products, and shows how strongly trace contaminations, even at low concentrations, can impact gas phase oxidation processes and the formation of HOMs from isoprene ozonolysis." The first part is true, contaminants can affect the observed oxidation products, but there is no evidence for the later point that contaminants can "impact gas phase oxidation processes and the formation of HOMs from isoprene." How will contaminants stop gas phase processes occurring with isoprene? This could only occur if all of the ozone present is being consumed by reactions with monoterpenes prior to reacting with isoprene. In these experiments this is likely not true. You could argue that dimers formed between an isoprene oxidized product and an alpha-pinene oxidized product impact the gas phase distribution of isoprene oxidation products, but that is not done here. The first point is the important aspect of the paper, contaminants change the observed oxidation products which is remarkably important for possible misinterpretation of the data. The paper as a whole should be geared more towards these efforts, including the introduction. Further, in the introduction it is mentioned the lack of knowledge about the role of isoprene in new particle formation as well as the importance of the ratio of isoprene to alpha-pinene, however it is not discussed in the paper to what extent the monoterpene contaminants would influence the general results from the CLOUD experiments. In Figure 5. you show quite dramatic change in the gas phase composition with/without cryotrap. I assume the nucleation/growth rates must also differ. If so, could you please comment on this even if it lies slightly behind the scope of Atmospheric Measurement Techniques, it might highlight the relevance of your findings.

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Minor Comments:

1. Page 1 line 19. Please define New Particle Formation before simply mentioning NPF

2. Page 2 line 3. references are needed since extensive studies are referenced

3. Page 2 line 3-5. references are needed since studies are referenced.

4. Page 2 line 5 "can occur in the presence of sulfuric acid, as well as in its absence" this is a bit weird formulation

5. Page 2 line 8-9. reference studies on NPF of monoterpenes.

6. Page 2 line 13. Epoxide growth on acidic particles

7. Page 2 line 16. explain the concentration ratio (R) and its impact on the NPF because its value is used later on page 2, but no figure of merit is offered. For instance, how does the suppression depend on R? A brief explanation here will help the reader understand the implication of R discussed below.

8. Page 2, line 19. "numerous field studies" yet you mention only one

9. Page 3 line 7. add a sentence that distills the message of the paper.

10. Page 3 line 11. reword to "... a novel proton transfer reaction-time-of-flight mass spectrometer (PTR-MS), called the PTR3-TOF, that utilizes a. . ." Also, stick to a normal naming convention for the PTR3 it is either called the PTR3 or PTR3-TOF throughout the manuscript.

11. Page 3 line 13. the abbreviation RF is not defined and should be capitalized.

12. Page 3 line 16. see above

13. Page 7 line 6. why not mention how old the bottle was in 2016?

14. Figure 4a and 4b: changes these plots so the legend is not obscuring the traces.

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15. Figure 4a: why does the C4H7O+ signal increase prior to O3 addition?

16. Figure 5a: what is the series of points that sits above the C10H18Ox? Is that a C15?

17. Page 7 line 14-28. This section is clumsily put together. It would be clearer to introduce what you want to show prior to showing the figures. This section is all about the effect of the cyrotrap on the oxidation products after the precursor(s) are exposed to ozone.

Set the stage for this at the beginning of the section, and then talk about each figure. The discussion about the rates of reaction of different precursors probably isn't necessary without more discussion about its importance. What point is trying to be made about the rates of reactions with ozone?

18. Page 8 line 6-7: what is the predominant compound after freeze-out?

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