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Comment

***Interactive comment on* “Formation of highly oxidized multifunctional compounds: autoxidation of peroxy radicals formed in the ozonolysis of alkenes – deduced from structure–product relationships” by T. F. Mentel et al.**

Anonymous Referee #2

Received and published: 13 March 2015

The paper by Mentel et al reports on steady state flow reactor chamber experiments to understand the effect of structure on the formation of highly oxidized multifunctional molecules (HOM) in the ozonolysis of alkenes. Eleven monoalkenes are studied (eight endocyclic monoalkenes including two atmospherically important monoterpenes, and four acyclic monoalkenes with varied functional groups) in the Juelich Plant Atmospheric Chamber. The study includes experiments with CO as an OH scavenger to explore the effect of reducing OH on the overall formation of HOM. Evidence is presented for the measurement by the APi-TOF-MS of elemental composition of HOM,

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as well as their precursor peroxy radicals. The data presented provides mechanistic insight into autoxidation mechanisms involved in the sequential addition of molecular oxygen after one oxidation step by ozone.

The study is well conceived and significantly builds on previous research on the importance of autoxidation in the atmosphere. The comparison between the products studied provides compelling evidence for the importance of aldehydic hydrogens in the initial H-shifts responsible for the formation of highly oxidized multifunctional compounds. The paper does a good job guiding the reader through the thoroughly detailed experimental results and chemical framework used to interpret the results. I recommend this work be published.

One point the authors might consider: I did feel that more discussion could have been given to interpreting the current experimental results in terms of the conditions found in the real atmosphere, and discussing where the oxidation mechanism might differ dramatically from the real atmosphere. The study presents evidence for the aldehydic hydrogen as being important for the efficient HOM formation, as those molecules lacking an aldehyde at the ω C-atom do not form significant amounts of HOM. It is clear then that in the experiments, only an aldehydic H-shift is able to compete with the bimolecular reactions of the peroxy radicals with HO₂ or RO₂ levels in the chamber. Do the authors have any sense of how similar the peroxy radical lifetimes in the chamber compare to the real atmosphere, and therefore whether or not the real atmosphere might allow less favorable H-shifts to still occur to form HOM?

Other minor edits:

Page 2792, line 14: homologous

line 25: cyclo

line 27: constrained

Page 2794, line 17: reactant

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Page 2804, line 21: “found” should be “find”

Page 2806, line 5: not sure the accurate description is “low NO_x (i.e. atmospheric) conditions”, rather I think you mean typical at typical atmospheric concentrations of NO/HO₂/RO₂

Page 2807 line 25: not sure “easy” is the correct adjective. Perhaps “H-shifts which are competitive at the experimental peroxy radical lifetimes”?

Page 2808 line 6: “o” shouldn’t be there

Page 2817 line 23: I think you can delete “is highly efficient” and end the sentence there.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 2791, 2015.

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