We would like to thank referee #2 for his/her constructive comments and corrections, and for the inspiring questions. We addressed all points below. The comments are typeset in *sans serife italic*, our answers in times new roman.

Answers to Referee #2

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, 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 oxidizied 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 ! 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?

Indeed we worked at conditions somewhat different from those in the atmosphere. For example, experiments with atmospheric relevant α-pinene were performed feeding 10 ppb α-pinene into JPAC, ozone (60ppb) and RH (60%) were comparable to the atmosphere. The OH concentration, which is produced when the UV light is switched on, amounts to a few times 10^7 cm^{-3}. An intrinsic NO$_X$ source is 0.3 ppb in JPAC.

In order to extrapolate the relevance of our findings to atmospheric conditions we did some model studies for α-pinene with MCM3.2 for the boundary conditions of JPAC. For this sensitivity studies we varied (in the model!) the chamber input of α-pinene and NO$_X$ at 60 ppb O$_3$ and J(O^{1}D) = 2.9 10^{-3} s^{-1}. We then performed a set of calculations where we kept α-pinene at 0.1ppb and reduced O$_3$ (30 ppb) and J(O^{1}D) (by a factor of 20) to yield OH concentrations of a few times 10^6 cm^{-3}.

We have to consider two types of peroxy radicals: acyl radicals (see Figure 4) and functionalized secondary radicals (S2, Figure4, and S24 for α-pinene) as these types are the main players according to the analysis in our manuscript. In the model acyl radicals react about 5 times faster with other RO$_2$ (k(RO$_2$+RO$_2$) = 5x10^{-12} cm^3 molec.$^{-1}$ s^{-1}) than secondary functionalized peroxy radicals. Moreover acyl peroxy radicals react significantly with NO$_2$. In other words, we assumed that HOM peroxy radicals behave similar to other peroxy radicals and expect them to react with other RO$_2$ in this range of rate coefficients.

We performed our experiments at low rates of NO$_2$ photolysis and thus almost all NO$_X$ in the system exists in form of NO$_2$. We also considered a wall loss of radicals which we approximated by a lifetime of 120s.

The model calculations predict that at low NO$_X$ and at low J(NO$_2$), acyl peroxyradicals have a life time of about 10s. The lifetime is not changing much if we lower the α-pinene concentration to 0.1 ppb, since it is mainly determined by the reaction with NO$_2$. If OH is generated the overall lifetime remains about the same but RO$_2$+RO$_2$ gains a significant role at 10 ppb α-pinene input.

At 0.1 ppb α-pinene input RO_2+ HO_2 takes over. In the atmospheric runs the lifetime is also 10s at 0.3 ppb NO_X and drops to about 5s at 1 ppb NO_X and to less than 1s at 10 ppb NO_X. These lifetimes give the range at which autoxidation of acyl peroxyradicals must be able to compete with termination reactions.

Functionalized secondary peroxy radicals have lifetimes of about several 10s. Independent on the α-pinene input and the dominating loss (besides walls) are reactions with other RO_2 at α-pinene 10ppb and HO_2 at α–pinene 0.1 ppb. In the presence of 10 ppb NO_X and at moderate JNO_2 reaction with NO becomes dominating and is lowering the lifetime to a few seconds. For secondary peroxy radicals lifetime is much longer than 10s at most of the situations, however high NO decrease the lifetime significantly. Again autoxidation of this type of peroxy radicals must be able to compete with this range of lifetimes of 1-100s. Following from this sensitivity study we can conclude that autoxidation should be operational at almost all atmospheric conditions.

Since we are doing systematic experimental studies on the topic of atmospheric relevance of HOM/ELVOC formation we would like not to discuss that in this already very long paper.

Action:

Other minor edits:

We again thank reviewer#2 for the corrections.

Page 2792, line 14: homologous, done

line 25: cyclo, done

line 27: constrained, done

Page 2794, line 17: reactant, reactand replaced by reactant in two places

Page 2804, line 21: "found" should be "find", changed

Page 2806, line 5: not sure the accurate description is "low NOx (i.e. atmospheric) conditions", rather I think you mean typical at typical atmospherc concentrations of NO/HO2/RO2, changed as proposed

Page 2807 line 25: not sure "easy" is the correct adjective. Perhaps "H-shifts which are competitive at the experimental peroxy radical lifetimes"?, changed as suggested

Page 2808 line 6: "o" shouldn't be there, o removed

Page 2817 line 23: I think you can delete "is highly efficient" and end the sentence

there. cancelled as proposed