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# ***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 #3**

Received and published: 21 February 2015

The formation of highly oxidized multifunctional compounds (HOMs) is investigated in a systematic series of steady-state flow experiments in the Juelich Plant Atmospheric Chamber. The experiments consider the ozonolysis of a set of eight cyclic monoalkenes (including two monoterpenes), an acyclic alkene and three acyclic oxygenated alkenes (an enal, an enol and an enone). API-TOF-MS is used to determine the molecular formulae of the suite of HOMs formed in each system, and their formation is interpreted in terms of an auto-oxidation mechanism involving sequential peroxy radical H atom migration reactions.

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This is an excellent and well-conceived piece of work, building upon previous studies from the same laboratory. The systematic series of precursor compounds were well chosen, and the results provide compelling evidence for the proposed “autooxidation” mechanism. Although the paper is quite long and detailed, it is well written and carefully guides the reader through the rationale for the work, the proposed mechanism(s) and the interpretation of the results for each set of precursor compounds. I recommend that this work should be published (essentially in its present form), although the authors may wish to consider the points given below.

The only area where I felt that more attention could have been given was the systematic scavenging of OH radicals in the system. As stated in Sect. 2, some experiments were carried out with CO present to scavenge OH, although most had no scavenger present with OH presumably reacting exclusively with the parent alkene. Throughout the account of the work, I was thinking that addition of CO would increase  $[HO_2]/[RO_2]$  and therefore the balance of some of the reactions, i.e. increasing R4 relative to R5a, R5b, R6a and R8, as considered particularly by Ziemann and co-workers (e.g. Tobias and Ziemann, 2000; Docherty et al., 2005). This is only briefly mentioned at the end of Sect. 5.4. Whilst I am not suggesting that the authors need to carry out more experiments for the current paper, the possible effect of the systematic change in  $[HO_2]/[RO_2]$  could be discussed a little more than it currently is. Future experiments could look at this further by using other contrasting scavengers (e.g. cyclohexane).

Related to the above point, Ziemann and co-workers have previously detected peroxyhemiacetals, formed from the reaction of hydroperoxide groups with carbonyl groups (particularly aldehydes), which are formed in abundance in the proposed termination products. In Sect. 5.4, the current authors propose a role for “dimer” formation via the peroxide path of the peroxy radical permutation reactions (R8), with support from the distribution of products in Table 15. The use of CO to scavenge OH radicals might be expected to increase  $[HO_2]/[RO_2]$  and therefore decrease the importance of R8 relative to R4, although the authors report an increase in abundance of those formed

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from the ozonolysis chemistry (page 2813, line 18). The authors may wish to check whether the distribution of a set of peroxyhemiacetals could also account for the series of products shown in Table 15. For example, I believe that a hydroperoxide C<sub>5</sub>H<sub>8</sub>O<sub>8</sub> (which might be formed from R4 of C<sub>5</sub>H<sub>7</sub>O<sub>8</sub>) and a carbonyl C<sub>5</sub>H<sub>6</sub>O<sub>7</sub> (which might be formed from R5a of C<sub>5</sub>H<sub>7</sub>O<sub>8</sub>) would form the peroxyhemiacetal C<sub>10</sub>H<sub>14</sub>O<sub>15</sub>, i.e. the species might all be shifted by one “O” from the peroxides formed from R8. Of course, the authors understand their system better than I do, and may be able to dismiss this possibility immediately – but I think it is worthy of consideration given the prior literature in this area.

#### Minor comments

Abstract, line 5: The statement “ELVOC are highly oxidized multifunctional molecules (HOM), formed by sequential rearrangement of peroxy radicals and subsequent O<sub>2</sub> addition” refers specifically to the mechanism of interest to the present work (and the previous related studies). Presumably the definitions of ELVOCs and HOMs should not automatically preclude species that might be formed by alternative mechanisms? (i.e. it is vapour pressure or composition that defines them, not the mechanism by which they are formed).

Page 2795, starting on line 12; and page 2799, starting on line 28: The authors comment on previous work that supports the operation of H atom migration to peroxy radical groups, indicating that a role for such reactions has only been recognised recently for atmospheric conditions.

There are actually several other experimental studies that have demonstrated a role for H-atom shifts in peroxy radicals at ambient temperatures, prior to the recent theoretical and experimental studies on isoprene and terpenes – and which therefore also provide a precedent for the mechanisms proposed in the present study. Of most relevance to the current work are the studies of Perrin et al. (1998) and Jorand et al. (2003) which characterized the T-dependence of 1,6 H atom shift isomerizations of peroxy radicals

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during pentane and hexane oxidation at slightly elevated temperatures, and proposed a role for these reactions under atmospheric conditions. These are analogous to those reactions suggested for the isoprene system by Peeters et al. (2009). The earlier work of Perrin et al. (1998) and Jorand et al. (2003) is therefore also of direct relevance and should be cited.

There are also other instances of H-migration to peroxy radicals in atmospheric mechanisms. The studies of Jenkin et al. (1993) and Sehested et al. (1996) showed that  $\text{CH}_3\text{OCH}_2\text{OO}$  isomerizes to  $\text{CH}_2\text{OCH}_2\text{OOH}$  prior to decomposition to  $\text{HCHO} + \text{HCHO} + \text{OH}$  (albeit more important at reduced pressure and probably not involving a stabilized peroxy radical). The reactions of  $\alpha$ -hydroxyalkyl radicals with  $\text{O}_2$  involve isomerisation of  $\text{RR}'\text{C}(\text{OH})\text{O}_2$  to  $\text{RR}'\text{C}(\text{O})\text{OOH}$  prior to decomposition to  $\text{RR}'\text{C}=\text{O} + \text{HO}_2$ . For larger R (or R') groups,  $\text{RR}'\text{C}(\text{OH})\text{O}_2$  is (at least partially) a stabilized peroxy radical (Capouet et al., 2004) and a competition between isomerization/decomposition and NO reaction has been observed for specific examples at elevated [NO] (Orlando et al., 2000; Jenkin et al., 2005; Aschmann et al., 2010).

Sequence 2, page 2849: I think the carbonyl species denoted “R=O” (and “R'=O”) need to be represented as something like “R-H=O” (where “-H” is a subscript).

#### Typographical comments

Page 2803, line 11: “scavenge” rather than “quench”?

Page 2803, line 20 “an acetyl group”

Page 2806, line 10: “making” should be “make”.

Page 2808, line 6: “o”?

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

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15, C343–C348, 2015

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