Atmos. Chem. Phys. Discuss., 15, 2791–2851, 2015
www.atmos-chem-phys-discuss.net/15/2791/2015/
doi:10.5194/acpd-15-2791-2015

Mentel et al.,
Formation of highly oxidized multifunctional compounds: Autoxidation of peroxy radicals formed in the ozonolysis of alkenes – deduced from structure-product relationships

We would like to thank referee #3 for his/her constructive comments and corrections, and for the inspiring questions. We addressed all points below. The referee comments are typeset in *sans serife italic*, our answers in times new roman.

Answers to Referee #3

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.

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 [HO2]/[RO2] 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 [HO2]/[RO2] 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).

We agree with the reviewer and want to state here clearly that role of OH and scavenging OH is an open question which needs further investigation.

Ziemann and coworkers observed that different OH-scavengers influenced the SOA yield in different ways. For endocyclic compounds - the case which here applies - they postulated that HO_2/RO_2 ratio is changed in a systematic way depending on the OH-scavenger. According to Ziemann and coworkers, higher fraction of HO_2 leads to a larger importance of HO_2+RO_2 reactions (reaction R4 in the manuscript) and thus to a higher fraction of "monomeric" hydroperoxides on cost of dimers from RO_2+RO_2 reactions (Docherty and Ziemann, 2005). The monomer hydroperoxides supposedly have higher vapor pressures and thus lower "SOA formation potential" than the dimers. As shown in the Ehn et al. 2014, we also find a specific role of dimeric ELVOC/HOM for SOA formation but more in early stages of particle formation. Nevertheless the point is well taken as also in our case increasing HO_2/RO_2 ratios will reduce the rates of RO_2+RO_2 reactions, thus the chance to form dimers from these reactions. (Note that we have a different conception what dimers could be compared to Ziemann and coworkers, see below).

In order to estimate the potential effect of changing HO_2/RO_2 ratios we performed some model studies with MCM3.2 for the boundary conditions of JPAC for α-pinene. For these sensitivity studies we varied (in the model!) the chamber input of α-pinene and NO_X and added 50 ppm CO to the reaction system with α-pinene ozonolysis. In our case acyl radicals (compare Figure 4) and functionalized secondary radicals (S2, Figure 4, and S24 for α-pinene) likely are important. According MCM3.2, the two classes of peroxy radicals have different reaction rates in permutation reactions with other RO_2 and we assumed 5×10^{-12} and 1×10^{-12} cm^3 $molec^{-1}$ s^{-1}, respectively, for the following analysis. 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 also this range of rate coefficients.

A fraction of the RO_2-RO_2 reactions should lead to dimers. So lowering the branching ratio of RO_2+RO_2 reactions by increasing HO_2 concentrations will indeed lower the yield of such dimers.

However, the branching ratio into RO_2+RO_2 reactions is not only dependent on HO_2, but also on all other loss processes. And these - according to our model calculations - are significant.

For example, model runs for a typical ozonolysis experiment at 10 ppb VOC input showed that about 60% of acyl peroxy radicals may react with the NO_2 arising from a minor source of 0.3 ppb of NO_X which we have inherently in JPAC. About 25% of the acyl peroxys react with other RO_2 and only 2% with HO_2. The latter is low if we have only the "dark OH" produced during ozonolysis.

If we actively produce OH (in the model) to levels of several 10^7 cm^{-3} OH radicals, the branching ratio of the reaction of acyl peroxy radicals with other RO_2 increases to about 60%, thus also the potential to form dimers. The branching ratio for HO_2 reactions increases to about 6%, that of reactions with NO_2 drops to about 25%.

In the same context we model the OH scavenging by CO for a typical experiment, low NO_X and 10 ppb VOC (here α-pinene). Starting the model run with ozonolysis and then adding 50 ppm CO, the relative importance of termination switches from RO_2+RO_2 to HO_2+RO_2. Although the ratio $[HO_2]/[RO_2]$ remains less than one, the reaction HO_2+RO_2 dominates in the model because of the higher rate coefficient $k(RO_2+HO_2)$ compared to $k(RO_2+RO_2)$ used in the model calculation. In scavenging experiments with CO we have seen the drop of dimers, however weaker. Switching on the OH production should enhance the role HO_2+RO_2 on cost of the importance of the reaction RO_2+RO_2.

Action:

We will refer to earlier results by the Ziemann group and add the following sentence at the end of the CO quenching discussion, page 20 the modified manuscript:

Docherty and Ziemann (2005) discussed such an effect of increasing HO_2 concentration by scavenching OH in the dark on the formation of hydroperoxides (R4) in competition to dimer formation by RO_2+RO_2 reactions.

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 [HO2]/[RO2] and therefore decrease the importance of R8 relative to R4, although the authors report an increase in abundance of those formed 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 C5H8O8 (which might be formed from R4 of C5H7O8) and a carbonyl C5H6O7 (which might be formed from R5a of C5H7O8) would form the peroxyhemiacetal C10H14O15, 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.

We found no strong peaks in our mass spectra that could be attributed to peroxyhemiacetals analogous to the ones postulated by Tobias and Ziemann (2000) but we cannot exclude that such compounds are present in small amounts in the gas-phase of our reaction system. These could condense very effectively on particulate matter. According to Ziemann and Tobias peroxyhemiacetals are likely formed preferably on the surface of particles or in the particulate phase and would then not be observable by our analytics. We prefer not further to discuss this point within this manuscript.

Action:
We added one remark and give reference to the work of Tobias and Ziemann on page 18 in the changed manuscript:

The molecular compositions discussed here are not commensurable with peroxyhemiacetals (proposed by Tobias and Ziemann, 2000) that would have been formed by reaction of HOM peroxy radicals and HOM carbonyl compounds and should have an odd number of O-atoms but 14 H-atoms.

Minor comments

Abstract, line 5: The statement "ELVOC are highly oxidized multifunctional molecules (HOM), formed by sequential rearrangement of peroxy radicals and subsequent O2 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).

This is correct.

Action:

The two sentences in the abstract were reformulated accordingly:

The sequential rearrangement of peroxy radicals and subsequent O2 addition results in ELVOC which are highly oxidized multifunctional molecules (HOM). Key for efficiency of such HOM in early particle growth is that their formation is induced by one attack of the oxidant (here O3), followed by an autoxidation process involving molecular oxygen.

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 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.

Thank you for the hints, we were not aware of this work.

Action:

We read through the material and quoted now the missing references of Jorand et al. and Perrin et al..

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 CH3OCH2OO isomerizes to CH2OCH2OOH prior to decomposition to HCHO + HCHO + OH (albeit more important at reduced pressure and probably not involving a stabilized peroxy radical). The *reactions of a-hydroxyalkyl radicals with O2 involve isomerization of RR'C(OH)O2 to RR'C(O)OOH prior to decomposition to RR'C=O + HO2. For larger R (or R') groups, RR'C(OH)O2 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).*

Thank you for making us aware of that work. We read through the papers and of course these are all interesting and important studies. They are related to presented work, however, not immediately. The referee stated already himself that rearrangement of CH_3OCH_2OO is not involving a stabilized peroxy radical. Jenkin 2005 pointed out that larger energy-rich peroxy radical could stabilize, mentions but does not discuss H-shifts. In Capouet et al., Orlando et al., Aschmann et al. discussions of isomerization of alkoxy radicals are more in focus. And that is now well established. We tried to cover that aspect by referencing to the overview paper by Vereecken and Francisco. From this point of view we would like not to add these references to our paper.
Action:
We checked the material. Changes, none.

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).

The R=O look a little strange, we agree to use $R_HC=O$.
Action:
Modified sequence 2 accordingly

Typographical comments
Thank you for the corrections.
Page 2803, line 11: "scavenge" rather than "quench"?, done
Page 2803, line 20 "an acetyl group", done
Page 2806, line 10: "making" should be "make". done
Page 2808, line 6: "o"?, o deleted

References

Aschmann, S. M., Arey, J. and Atkinson, R: Kinetics and products of the reactions of OK radicals with 4,4-dimethyl-1-pentene and 3,3-dimethylbutanal at 296 (+/-2) K, J. Phys. Chem. A 114, 5810–5816, 2010.

Capouet, M., Peeters, J., Noziere, B., and Mueller, J.-F.: Alpha-pinene oxidation by OH: simulations of laboratory experiments, Atmos. Chem. Phys., 4, 2285-2311, doi:10.5194/acp-4-2285-2004, 2004.

Docherty, K. S., Wu, W., Lim, Y. B. and Ziemann, P. J.: Contributions of organic peroxides to secondary aerosol formed from reactions of monoterpenes with O3, Environ. Sci. Technol., 39, 4049–4059, 2005.

Jenkin, M. E., Hayman, G. D., Wallington, T. J., Hurley, M. D., Ball, J. C., Nielsen, O. J., and Ellermann, T.: Kinetic and mechanistic study of the self reaction of CH3OCH2O2 radicals at room temperature, J. Phys. Chem., 97, 11 712–11 723, 1993.

Jenkin, M. E., Andersen, M. P. S., Hurley, M. D., Wallington, T. J., Taketani, F., and Matsumi, Y.: A kinetics and mechanistic study of the OH and NO2 initiated oxidation of cyclohexa-1,3-diene in the gas phase, Phys. Chem. Chem. Phys., 7, 1194–1204, 2005.

Jorand, F., Heiss, A., Perrin, O., Sahetchian, K., Kerhoas, L., and Einhorn, J.: Isomeric hexyl-ketohydroperoxides formed by reactions of hexoxy and hexylperoxy radicals in oxygen, Int. J. Chem. Kinet., 35(8), 354–366, 2003.

Orlando, J. J., Noziere, B., Tyndall, G. S., Orzechowska, G. E.: Paulson, S.E., and Rudich, Y., Product studies of the OH- and ozone-initiated oxidation of some monoterpenes, J. Geophys. Res., 105, 11561–11572, 2000.

Perrin, O., Heiss, A., Doumenc, F., and Sahetchian, K.: Determination of the isomerization rate constant HOCH2CH2CH2CH(OO.)CH3 -> HOC.HCH2CH2CH(OOH)CH3. Importance of intramolecular hydroperoxy isomerization in tropospheric chemistry. J. Chem. Soc. Faraday Trans., 94, 2323–2335, 1998.

Sehested, J., Mogelberg, T., Wallington, T. J., Kaiser, E.W. and Nielsen, O. J.: Dimethyl ether oxidation: Kinetics and mechanism of the CH3OCH2 + O2 reaction at 296 K and 0.38-940 Torr total pressure, J. Phys. Chem, 100, 43, 17218-17225, 1996.

Tobias, H. J. and Ziemann, P. J.: Thermal desorption mass spectrometric analysis of organic aerosol formed from reactions of 1-tetradecene and O3 in the presence of alcohols and carboxylic acids, Environ. Sci. Technol., 34, 2105–2115, 2000.