Atmos. Chem. Phys. Discuss., 15, C9244–C9246, 2015
www.atmos-chem-phys-discuss.net/15/C9244/2015/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Organic peroxides gas-particle partitioning and rapid heterogeneous decomposition on secondary organic aerosol" *by* H. Li et al.

Anonymous Referee #4

Received and published: 13 November 2015

This study examines the production and gas –particle partitioning of hydrogen peroxides (H2O2), hydroxymethyl hydroperoxide (HMHP), peroxyformic acid (PFA), peroxyacetic acid (PAA) and total peroxides from dark ozonolysis of alpha-pinene. Due to the significant contribution of peroxides to the SOA mass and their role in HOx recycling this is an important question. While many studies have addressed a variety of routes of peroxide formation in the gas and particle phase, the existing knowledge on sources and decomposition is insufficient. This is especially true for the aqueous phase route of reactions of criegee intermediates with water to form hydroxyhydroperoxides which then decompose into more stable peroxides. In addition, equilibrium gas – particle partitioning is not well established for most peroxides. Therefore, the present study is of

substantial interest.

This study reports results of flow tube alpha-pinene ozonolysis experiments, with gas phase products collected into a stripping coil and particles on filters, both for offline derivatised LC-MS analysis and iodometry. The results provide molar yields of the title peroxides as well as their gas – particle partition coefficients, which is novel in terms of comprehensiveness of peroxides covered and in terms of the partition constants for most of them. Especially for PFA and PAA the partition constants are substantially higher than expected from their molecular properties. H2O2 yields were higher than expected based on known gas phase chemistry. Most of the peroxides undergo decomposition in aqueous solution enhancing the yield of H2O2, which however would still not provide sufficient H2O2 to explain the results.

The experiments appear to be well performed and analyzed. The manuscript is well written and addresses most of the detailed issues. There are a few specific comments, which could be addressed.

Specific comments

Performing this study in a flow tube brings along several advantages for most of the specific results reported but also brings along some complications:

First, due to the limited reaction time and the need to provide sufficient SOA and analyte masses within reasonable times, relatively large precursor concentrations and very large ozone excess had to be used. The authors should explicitly discuss the consequences for the SOA chemistry. While the impact of the addition of an OH scavenger on the peroxide properties was rather small overall, the large OH production may change the nature of the SOA matrix and the oxidation scheme.

Second, several recent studies have addressed the issue of partitioning between SOA and chamber walls, which must be an even more relevant issue for a flow tube. The authors should comment on the way this may impact the results of the present study,

apart from the comment on this made in the context of the H2O2 budget.

P28141: the impact of the formation of peroxyhemiacetals on the determination of peroxides by iodometry should be explained in an additional sentence for the less informed reader. This is important since hemiacetal formation is relevant for the discussion of the gas – particle partitioning.

Discussion on p28143: Is it possible that apart from wall effects, gas-particle equilibrium is not established on the relatively short flow tube residence times due to effects of high viscosity in the particle phase?

P28144/18145: decomposition and H2O2 formation in SOA solution: can the authors also speculate on the corresponding rates and life time in the native aerosol phase, i.e., in absence of dilution? Have the authors tried to let the filters sit for different times under dry or humid conditions and measure the formation of H2O2? While the experiments with the two separate flow reactors have nicely allowed to differentiate effects of humidity and the particle phase on the H2O2 yields, longer times would be required to assess peroxide stability under aerosol conditions.

Technical aspects:

There are some small language and grammar errors throughout the manuscript (not listed in detail here), which require attention. Some of it can also be taken care of in the type setting process for ACP.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 28133, 2015.