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

Anonymous Referee #3

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This manuscript presents new measurements for the yields of peroxides (hydrogen peroxide, an organic hydroperoxide, peroxy acids, and total peroxides) formed when a-pinene is oxidized by ozone. The individual species were measured using an HPLC-derivitization method, whereas the total peroxides were measured using the conventional approach involving iodine. Measurements were made of both the gas phase and aerosol peroxides, where the SOA was formed in a flow tube. Yields of the species in both phases are reported, from which partitioning coefficients are derived. As well, the aqueous phase decomposition rates of both total peroxides from SOA, as well as individual pure species were measured.

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Interactive Discussion

Discussion Paper

The value of this work is that these are new measurements, particularly the speciated nature of the results and the measurements of peroxides in both the gas and aerosol states. Most past measurements of this type have used a general assay without speciation. Peroxides are an important, very poorly characterized component of VOC oxidation systems, especially those that form SOA. Thus, it is not too surprising that some of the experimental results are not well matched by models. In particular, the paper reports much higher gas phase yields of hydrogen peroxide than anticipated and much higher partitioning coefficients than calculated with a simple partitioning model. The authors do an extensive job of trying, unsuccessfully, to explain the gas phase yields. They suggest that the high partition coefficients are due to reactions of the peroxides in the condensed phase, perhaps forming peroxyhemiacetals. This seems like a reasonable suggestion. Also, there is value to the measurements of the relatively fast decay rates of individual peroxide species in solution, although the mechanism (likely heterogeneous) is not established. Measurements of this type (again, with less speciation) have been reported by Badali et al.

There are three aspects of the paper which are weaker. One, the mixing ratios of both a-pinene and ozone are very high, hundreds of ppbv for the terpene and tens of ppm for ozone. I understand why these conditions were chosen, i.e. high ozone to react all the a-pinene away, and high a-pinene to get sufficient signal (I assume). However, the conditions do bring up the questions of how representative are the results of behavior in the atmosphere. Indeed, for this reason, I would weaken the relationships as stated in the paper to the GABRIEL field measurements, given that the field conditions are quite different from those in the lab. It would have been nice to seen similar experiments performed at longer times and lower mixing ratios in a chamber (although, chambers themselves have their own experimental issues, I admit). For example, does the very high ozone affect the SOA when passing through the filter upon which the SOA is collecting for many hours? Two, I would like to see some discussion of how the gas and aerosol constituents are experimentally separated. In particular, how are the gases stripped (and analyzed) without affecting the SOA? Could re-partitioning of species between the two phases occur when the separation process is being performed? Three, I found some sections of the paper really quite hard to read – especially those dealing with discussion of results (Sections 3.3 and 3.4). I recommend that these discussion sections be shortened and clarified, focusing on just the main points.

Overall, while this paper opens up many questions and could have been written more tidily, its new measurements are valuable and so it should probably be published, after the above points are addressed.

Small wording issues: Line 11, page 28134 – mention the type of SOA Line 20, page 28134 – perhaps "explain" instead of "interpret" Line 22, page 28134 – perhaps "preserves" instead of saves Line 28, page 28136 – Criegee Line 19, page 28146 – unclear instead of unclearly

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