

## ***Interactive comment on “Formation of hydroxyl radicals from photolysis of secondary organic aerosol material” by K. M. Badali et al.***

**K. M. Badali et al.**

kmbadali@gmail.com

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Reviewer Number 1

It is obvious that most chemical transformations occurring in the troposphere are induced by photochemically produced radicals. This paper demonstrates that OH radicals are formed by photolysis of secondary organic aerosol (SOA) material formed by terpene ozonolysis. This is an interesting contribution and points toward the potential importance of the photochemistry of hydroperoxide produced during the ozonolysis process as source of OH radicals in the particles. Similar processes have been discussed for cloud and fog conditions. However, due to the potentially higher mass loadings of such functionalized products, such pathways maybe have an increased

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importance in SOA. The experiments have been performed according to the best available standards. Basically, SOA particles were collected on filters, dissolved in water containing a radical trap (benzoic acid), and then exposed to ultraviolet light in a photochemical reactor. The OH formation rates, which are similar for both  $\alpha$ -pinene and limonene SOA, were measured from the formation rate of p-hydroxybenzoic acid as measured using offline HPLC analysis.

Did the authors vary the ozone concentration in the chamber, or more exactly the ozone/terpene ratio, which could impact on the ROOH/ROOR ration, in order to check whether that could alter the OH production rates in SOA?

Response: We did not systematically vary the ozone-to-terpene ratio in the chamber, but this would be an interesting experiment to try in future experiments.

Figure 2 presents the photon flux inside the reactor and the SOA absorption cross section. However, I'm wondering how informative this is. In fact, wouldn't the hydroperoxide absorption be blue shifted (compared to SOA) and therefore with a quite reduced overlap with the photon flux?

Response: This is a useful point, which we now elaborate upon in the paper. We agree that the tail in the SOA absorption spectrum to long wavelengths may not arise from peroxides. However, much of the overlap between the light intensity and the cross-section is at lower wavelengths (e.g. from 300 to roughly 340 nm) where contribution from peroxides is possible. Given that carbonyls may contribute to this absorption to an unknown degree, we now add a caveat to the paper that the product yield calculation explicitly assumes that hydroperoxides represent the major adsorbing functional group but that others may also be important (section 4.2, paragraph 3).

Figure 3 presents a nicely linear behavior of the PHBA concentration as a function of time (or OH production rate), up to one hour. But what happens at longer times? In fact, a back-of-the-envelope calculation (250  $\mu$ M of SOA, 1% yield of hydroperoxide, 10-4 s<sup>-1</sup> J values) would led to ca. 10-20% of the OH precursors being consumed, so that

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I would expect a levelling-off of the OH production rate. Has this been observed? If this production rate is sustained over longer times, could it be that other processes are involved such as photochemistry of carbonyls (as recently discussed for pyruvic acid, SOA formation, etc.)? This would also explain a red shifted absorption spectrum. In the same vein, could a chain reaction be initiated where 1,4 isomerization steps are taking place in the condensed phase (similarly to those occurring during the formation of ELVOVs), leading to steady-state ROOH concentrations. Maybe the authors could comment on that?

Response: This is an excellent point. We did not extend the measurements beyond 1 hour observation time. However, the reviewer is entirely correct that even for one hour and for the inferred initial first-order formation rate of OH, we should have observed levelling off of the OH production rate if the primary photolysis of the peroxides was the only OH production route. As we described in detail in the original version of the paper (see Section 4.2), we cannot assess how much of the OH formation is primary and how much from secondary processes (such as carbonyl photolysis). We now stress that the linearity of the OH production rate over the one hour time scale may indeed be evidence for some component of the OH formation being secondary (section 4.2, paragraph 7). We also add the possibility that 1,4-isomerizations leading to ELVOC-like compounds may be leading to hydroperoxide formation.

Finally, the author concluded that these processes may be important for cloud chemistry by comparing the in-cloud H<sub>2</sub>O<sub>2</sub> and SOA concentrations. However, the mass fluxes from the gas phase to the cloud droplets are then also quite important and potentially dominating the overall OH production flux. Maybe the authors could comment on that too?

Response: Yes, the reviewer is correct that OH mass transfer from the gas phase may be important too, increasingly so for smaller cloud droplets. The importance of this process is now mentioned in the manuscript (section 4.2, last paragraph).

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I like very much that study and would recommend its publication with minor comments.

Response: We would like to thank the reviewer for their useful comments.

Minor comments Page 4119: line 23, isn't a word missing in this sentence?

Response: We think the sentence is ok as written.

Page 4122: the indications of the "MFC" number could be somehow confusing to the reader and could be removed.

Response: We would prefer to leave the MFC number labelling, to help orient the reader to the different MFCs used in the experiment, i.e. as indicated in the upper half of Figure 1.

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