

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

Anonymous Referee #1

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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 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 pho-

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tochemical reactor. The OH formation rates, which are similar for both α -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?

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?

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 μ M of SOA, 1% yield of hydroperoxide, 10-4 s-1 J values) would led to ca. 10-20% of the OH precursors being consumed, so that I would expected 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 may 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?

Finally, the author concluded that these processes may be important for cloud chemistry by comparing the in-cloud H₂O₂ 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?

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

Minor comments

Page 4119: line 23, isn't a word missing in this sentence? Page 4122: the indications of the "MFC" number could be somehow confusing to the reader and could be removed.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 4117, 2015.