

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

Received and published: 3 June 2015

General This is a very interesting contribution by the group of Jon Abbatt which identifies OH formation from SOA, apparently for the first time. The photolytic OH production appears logical as SOA contains organic hydroperoxides and particle containing SOA as well contain H₂O₂. It is deduced that rather ROOH than H₂O₂ causes the OH production. An absolute quantum yield of OH production is provided. A very interesting and substantial contribution which clearly merits publication in ACP.

Response: We thank the reviewer for their comments.

Details Page 7, line 15ff: It would be great if the authors could explain why they decided for the chosen technique for peroxide determination as literature describes different
C3185

methods, cf. page 4, lines 18/19.

Response: The iodide method for peroxide detection (e.g. as used by Docherty et al. (2005)) measures both ROOR and ROOH species, as well as H₂O₂. And so, it was not viewed as being as useful because much of the response would be due to ROOR, especially at the high mixing ratios used in the chamber to generate SOA. On the other hand, as described in the paper, the HRP-DCF assay responds to only H₂O₂ and to some unknown degree to ROOH species also. This is a relatively easy assay to run and provides an overall measure of hydroperoxide formation (albeit with uncertainties related to ROOH response). Another approach would have been to use chromatographic separation and derivitization to try to identify some specific small ROOH species, but the analytical methods for detection of high molecular weight species, as would have formed in this case, have not been developed. In general, the standard analytical methods for peroxide detection are poor and this is a serious limitation for firm conclusions that can be made in this field. This point is now made in the paper (section 4.1, paragraph 1).

Page 8, line 2.4.: Apparently, BA as a OH scavenger together with the detection of PHBA seems to be a good choice when this product can only be formed when OH reacts with OH. Are there any additional pathways which can lead to the formation of PHBA? What can happen if a one-electron oxidation of the aromatic forms a radical cation which then reacts with water? Can alternative pathways for the formation of PHBA be excluded? Maybe this can be discussed to some extent.

Response: We are only aware of the formation route of PHBA via addition of OH to aromatic ring. A one-electron oxidation of BA seems unlikely to occur given the electron-withdrawing properties of the carboxylic acid group. In addition, this would require a very strong oxidizing agent in solution, different from OH, which seems unlikely. We did control experiments with only light and BA, but no SOA, and we do not see any PBHA formation.

Page 10, line 21ff: Doesn't this discussion call for an alternative technique of peroxide determination with a method which does not show such a strong sensitivity for H₂O₂ compared to ROOH ?

Response: Absolutely, as mentioned above, this study would have been greatly strengthened by a characterization of the different ROOH species present.

Page 14, line 13ff: The deduction of an absolute quantum yield is great and very helpful for future modelling.

Response: Thanks. Note that we have described the important assumptions that go into arriving at this value, of which modelers should be aware.

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