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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The link between organic aerosol mass loading and degree of oxygenation: an α-pinene photooxidation study" *by* L. Pfaffenberger et al.

Anonymous Referee #3

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Synopsis of the paper: The paper describes a set of smog chamber experiments to test the concept of aerosol aging with the research question being "How can secondary organic aerosol produced in a smog chamber be more representative of ambient aerosol". The main analytical tool for evaluating the aerosol in this way is specific masses produced in the Aerodyne Aerosol Mass Spectrometer (AMS) m/z 43 and m/z 44. The ratio is then compare to the work of Ng et al. (2010; 2011) to compare the degree of oxidation in the chamber produced aerosol to that of oxidized ambient aerosol.

General comments: The paper appears to include carefully performed experiments using a unique experimental protocol. The authors have produced their aerosol from the

OH-oxidation of HONO and subsequently by the standard NOx-cycling. One metric that they focus on is the so-called OH-exposure in molec cm-3 h-1, which is related back to the level of oxidation in the atmosphere, thus, an OH concentration of 1x10^6 molec cm-3 for 24 h is representative the same oxidation processes for an OH concentration of 2.4x10^7 molec cm-3 for 1 h. In this work the assumption is not tested but relies on previous findings. A number of the findings appear to be dependent on the exact means of conducting the experiment and many of these will be considered below. However, a number of experimental aspects are poorly described and these flaws should be addressed before considering uncertainties in interpretation.

In general, I believe that there are an insufficient number of experiments with only a single precursor to come to the broad conclusions reached in the paper. The authors need to be more reserved in their statements about the role of organic mass in the aging of the aerosol. In addition, the manuscript uses a considerable amount of jargon (triangle, aging scale, etc.) that makes the writing suitable for only a small insider class of scientists.

Specific comments:

Much of the interpretation relies on the work of Ng and coworkers (2010; 2011). I would suggest the Introduction as a place to discuss the background and findings of Ng et al. (2010; 2011) and to provide the basis for the "triangle" frequently referred to in the Results section of the paper.

With respect to the Experimental part of the paper, some topics are handled in far more detail than needed (p.24741, l.9-29; detail on flushing and other items in that paragraph). In the same paragraph, it seem quite incredible that one can get to 85% RH in a 27 m^3 bag. What was the chamber temperature in this test.

Black carbon is injected into the chamber as part of the seed aerosol composition from a liquid suspension. Is there any information as to how reproducible this injection is?

The use of the word “chemical composition” (p24742, l. 5) is a bit of a misnomer with respect to the conventional use of the word chemical composition.

Give the diameter and length of the sampling lines as described on p.24742, l. 8. This is a factor of 30 dilution for wall-loss corrected aerosol

As I understand the basic experimental method. a-Pinene and NO, NO2, and HONO were added to the chamber a combination of Xe arc and blacklights photolyzed the mixture to create SOA. After 5 hours and accounting for the wall loss, ozone was added to the chamber. At that point, the Xe arc photolyzed ozone to give O(1D) which reacted at least partially with water to give high concentrations of OH which could then undergo heterogeneous reactions to age the particles thereby increasing the O:C ratio which is then reflected in the f43/f44 ratio. Perhaps this is correct, perhaps incorrect but it is clear that the description needs to be improved so that the reader know exactly the experiment being conducted.

One question that arises from the experimental method is the disposition of the OH radicals produced at high concentration. I’m curious about your evidence for whether the radicals are undergoing surface reactions in the particle or oxygenated products still in the gas phase.

According to a simple calculation, the 4 Xe arcs and 80 blacklights produce 24 KW of energy that needed to be dissipated for seven of the nine experiments. Please say a word (more than just giving a reference) as to how this energy was removed without there being some increase in the chamber temperature. Was the reported temperature range of 21-24 C, the initial temperature, the temperature during the irradiation, or both? I find it hard to believe that the chamber could be operated at 85% RH with full lights and not have condensed water somewhere in the chambers (p.24741, l. 18-19). Presumably some level of air conditioning is used to keep the chamber between 21-24 C, which would generate local cold spots and sites for condensation.

From the OH tracer method using the loss of butanol-d9, give the maximum absolute

OH concentration determined during the individual experiments, needed for the OH exposure determination. Does the concentration ever get as high as 1x10^8 molec. cm-3?

Discuss the possibility that products of the butanol tracer could sufficiently oxidize to generate condensible products on the aerosol, especially after the addition of ozone and the generation of high levels of OH radicals.

Discuss the likelihood of the hydrocarbons present in the reaction mixture photolyzing due to the presence of short wavelength radiation from the Xe arc. What is the lowest wavelength UV likely in the chamber.

What is the magnitude of the wall loss correction. What is the factor increase of the aerosol mass concentration due to the correction. Do both f43 and f44 use the same correction factor?

At least a cursory explanation to the “triangle” (p24747, l. 2) needs to be given either in the Introduction or in the Results section itself.

Some definition for the “aging scale” (p.24747, l. 26) needs to be give. It is not self evident.

What is the implication of the sentence starting on p.24747, l. 6. The authors imply that this is a significant scientific finding. What is the implication for chamber measurements conducted by other research groups.

The authors need to be more specific in stating on p.24747, l. 22 that the data clearly shows. . .

The conclusions of the authors on p.24751 at the present time pertain only to a single monoterpene and without additional precursor measurements should not be generalized presently.

Copy edits:

p24740, l. 14. A rogue question mark is present.

p24740, l. 27. Some product information is needed for Tokai black printer ink.

p.24746, l. 16-20. This is a repetition of text presented earlier

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 24735, 2012.