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Interactive comment on “Secondary organic aerosol formation from acetylene (C₂H₂): seed effect on SOA yields due to organic photochemistry in the aerosol aqueous phase” by R. Volkamer et al.

R. Volkamer et al.

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General comments

We like to thank the reviewer for the detailed reading and thoughtful comments, which we feel have lead to improvements of the revised manuscript. The reviewer recommends our results for publication, though likes to see more experimental detail, and a more balanced length of the experimental and discussion section. He/She also requests more discussion of our reasoning why we conducted the experiments as we did, and not others. We have added experimental detail to Section 3, and have eliminated overlap between the discussion and conclusion sections, in an effort to reduce

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Interactive Discussion

Discussion Paper



the length of the discussion without reducing (according to the reviewer) "insightful and valuable comments". If the discussion continues to be somewhat "lengthy", we see this as a reflection of relatively simple experiments having profound implications: we demonstrate that current SOA models that parameterize the partitioning of semivolatile vapors to an organic aerosol phase are incomplete, and present an alternative pathway of SOA formation, which further holds potential to resolve a conceptual grid-lock that exists as traditional SOA models are unable to resolve the apparent contradiction between ambient C14 data and atmospheric time series data (see Section 4.4.3, among other sections). Reviewer comments are copied inbetween quotation marks first, and are followed by the response.

Response to specific comments

"1) Acronyms, especially those for various aerosol seed composition, are often used without prior definition (or the definitions are hard to find). For example, Table 1 is very difficult to understand until all the meanings of all acronyms are tracked down. The paper would be greatly improved if a table of acronyms were included."

A list of acronyms has been added at the end of the document.

"2) Pg 14844, lines to 15, What is the expected OH concentration in the chamber. This is a critical component in the chamber influencing both the gas and possibly the heterogeneous chemistry and was likely predicted by the chemical model. Comparison of expected chamber OH to typical ambient levels could also be discussed."

The OH radical concentrations predicted by our model are now included in Table 1. OH was systematically varied in our experiments; text was added that describes how this was done in greater detail in Section 2. The OH concentration actually include levels found in the atmosphere, and range up to about 10 times higher values. A separate panel B has been added to Figure 7 that now shows our data as a function of OH, and demonstrates that over the range of OH concentrations that was probed no dependence on the OH concentration is observed. A new Section 3.5 has been added,

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where OH concentrations are compared to atmospheric OH concentrations; and the sensitivity of our results to experimental conditions is discussed. This comparison supports the atmospheric relevance of our results.

"3) Pg 14846 lines 8230; and pg 14847 line 1: It is stated that aerosol is produced in the chamber via vaporizing dilute salt or salt/organic solutions. Can this be right? Is nebulizing what is meant (that is what is shown in Fig 1)."

Corrected.

"4) pg 14847 line 15, what is the "bulb""

Corrected.

"5) pg 14847 line 19, does this refer to measurement of CHOCHO in the chamber."

Yes. The text now also says so.

"6) Fig 1. The figure needs clarification. Provide labels for vacuum pumps (at least I believe that is what it is). Also the arrows representing DMA flow directions don't seem to make sense."

Figure 1 was updated.

"7) Since aerosol mass (LWC + solute) is determined via the DMA, and this is a crucial quantity in the calculated yields, some information should be given on the SMPS operation, including: 1. Are losses in the DMA and related sample lines considered 2. Was the RH monitored in the DMA to make sure particle sizes in the column did not change relative to the chamber due to heating or cooling (ie, water loss/uptake). 3. How were the DMA results inverted (eg, was multiple charging considered) 4. What is the uncertainty from these factors."

More experimental detail has been added to Section 2. Ad1: Sampling line losses have been characterized at <1% in this setup. Ad2: RH is measured in the SMPS sampling line; sheath and aerosol sampling air are both taken from the chamber and are at the

same RH. Ad3: Number and volume concentrations have been compared with a TSI 3936L72 SMPS system, and were found to agree within $\pm 10\%$. Ad4: the agreement with the TSI SMPS is taken as the uncertainty in the SMPS volume measurement. This information has been added in Section 2.

"8) One might argue that Fig 2 would be better if $dV/d\ln D_p$ were plotted instead of number concentration. Or the volumes associated with these distributions could be given on the number distribution plot."

The volumes are now given in the legend, explicitly for each sampling time shown in the Figure.

"9) Table 1. Since the composition of the aerosol formed in the chamber was not measured how sure are the authors that only CHOCHO contributed in one form or another, to increase in aerosol mass (ie, SOA). Could other C₂H₂ oxidation products be involved in some manner?"

We had addressed this point actively in the original manuscript by means of Table 2. However there was only limited text describing the Table in Section 3, and we have expanded this text. It now reads: "As is evident from Table 2, CHOCHO is the only product that partitions to the aerosol aqueous phase in appreciable amounts. Notably, our conservative estimate of $H_{eff,CHOCHO}$ results in a lower limit for the amount of CHOCHO that is expected to partition to aerosols that accounts for more than 99% of the source for aerosol growth. Higher values for H_{eff} have been reported in the presence of sulphate and from field evidence (> 109 M atm, Volkamer et al, 2007; Ip et al., 2009), and are in general agreement with the results presented here. The change in the size distribution of aqueous seed aerosols is therefore attributed to CHOCHO uptake to the seed aerosols."

"10) pg 14850 line 11 How were yields determined? It is stated that SOA mass is determined from the SPMS, but how was the mass of Delta(ROG) determined (the mass of C₂H₂ reacted). Also, in Fig 3, how were the various masses of organics in the

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particles determined (Mo). How was uncertainty in yield determined?"

The amount of C₂H₂ reacted was taken from the model. Mentioning about this was indeed missing, and is now included in Section 2, together with typical numbers for the amount of C₂H₂ reacted in our experiments. The calculation of Mom has been described in the original manuscript on page 14848, line 28ff; this text is unchanged. Text was added that describes the calculation of SOA yields, and the uncertainty in the yields at the end of Section 2. The error does not include uncertainty in the density of glyoxal SOA/oligomers, which is currently not known (see also response to question #6 by reviewer #1, and information added about density in Section 2).

"11) pg 14850 line 11, give r² or some other proof of "an excellent correlation". Also, it is stated that the Y vs LWC is linear but no proof (eg regression result) is supplied."

The linear regressions were shown in Figure 3. The equations to these fits, including the linear correlation coefficient are now also given in the text.

"12) Pg 14852, lines 5 through 10. A brief discussion providing more details on the light vs dark experiments would be helpful. It would be worthwhile including a statement that, according to my understanding, the major difference is the light experiments produce gas phase oxidants that may then participate in liquid phase reactions, whereas there are no oxidants produced in the dark expts. so no oxidation chemistry is expected in the liquid phase under dark experimental conditions (I may have this wrong, but more details of this type would make the paper clearer)."

This is correct. We have added three sentences describing the differences between photochemical and dark experiments in the first paragraph of Section 3.3.

"13) Pg 14852, line 20, how is [Gly]t determined?"

CHOCHO was measured by SPME during selected experiments. Those experiments were also used to validate an alternative approach that predicted CHOCHO from a box model constrained by CO product formation and NO-to-NO₂ conversions. Notably,

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Interactive Discussion

Discussion Paper



use of the photochemical source for CHOCHO virtually eliminates mixing times inside the chamber, and allows conducting experiments over greatly reduced times, i.e., 90 sec. This actively minimizes chamber wall effects to affect CHOCHO concentrations. The constrained model was used to predict CHOCHO in experiments where no SPME measurements were performed. This is described in Section 2.

"14) Figure 4. The explanation for panel b is not clear. There is no dashed line, as stated."

We respectfully disagree; the dashed line is shown in panel b. We liked to point out that it extends only over the 90sec when lamps were ON. The meaning of the grey area (lamps ON) is now specifically mentioned in the Figure caption.

"15) Pg 14853 line 22. The line that ends in "CHOCHO is a building block for the observed SOA formation."; I assume is based on the assumption or knowledge (which is it) that only CHOCHO, water vapor and seed particles were in the chamber during dark experiments."

Yes. We know that this experiment only contained CHOCHO, seed and water, which were added to the chamber.

"16) Generally, I have a hard time understanding Fig 4 and Section 3.3. From Fig 4 it looks like when the lights are turned on, V_{norm} jumps to some higher value (type A in Fig4b) then follows a slower growth rate (type B). But why is this, if the lights remained on why does the very high slope of type A (looks more like a step function) suddenly switch to type B. Or are the lights only on for a very short duration, as appears to be the case in Fig 5. If so, why not leave the lights on for a much longer period of time. Is the problem here that the precursor vapours are rapidly consumed? This section should be clarified by providing more details on the experiments."

Grey areas in Figs 4 and 5 indicate when lamps are ON. This has been added now to both Figure captions. Further information about how we used the lamps to control

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and vary the OH-radical concentration is now added to Section 2. We did also perform experiments over a longer time scale (several 10mins) with fewer light bulbs turned ON. This leads to lower OH concentrations, and an accordingly lower CHOCHO production rate in the chamber, but gives identical SOA yields and Heff values. See also our response to point 2). Indeed the time resolution of the SMPS system was limiting our conclusion about the rate increase in CHOCHO uptake. A more careful analysis of experiments performed at the lower CHOCHO production rate in the chamber continues to be limited by the time resolution of the SMPS system, but allowed us to quantify the rate increase as a factor 500 (previously quoted as 200), which indeed is a lower limit for the true rate increase.

"17) Page 14858 line7 and 8, Strictly, I don't see any direct proof for the statement that CHOCHO uptake is actually to the seed (AS or SucA), thus forming some compound containing both the seed and some form of the CHOCHO; could these seeds play some other indirect role (apart from liquid water formation as noted) other than direct chemical reaction with CHOCHO or its various aqueous forms."

The reviewer could have been more specific about what "indirect role" he/she is talking about here?

The dependence of SOA yields on seed chemical composition demonstrates that the chemical reactions that form SOA depend on the chemical environment provided by the seed. Other than the direct role of providing reactive functional groups, indirect roles of the seed could include any catalytic role of aerosol water, seed chromophores facilitating photolytic processes, particle pH and its influence to scavenge CHOCHO photochemistry in aerosol water. An according statement has been added at the end of Section 4.1.

"18) Page 14868, line 21, more explanation should be provided setting up the issue of double counting, the intent of this section is not clear from the first few lines."

We have added an introduction to the paragraph.

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Interactive
Comment

"19) Finally, there is a question on the use of a Henry's law constant to describe the experimental results. Maybe it should be called something else. Strictly speaking Henry's law describes the concentration of a specific chemical species in the aqueous phase relative to the gas phase, and the effective Henry's constant includes various aqueous forms of the original species. In this case Henry's law constants are given for CHOCHO based on experimental results, where, I presume, the aqueous phase concentration comes from the non-chemically specific SMPS mass measurement. Isn't it possible that other C₂H₂ oxidation products, other than CHOCHO, also contributed to the observed mass. Thus, the Henry's law constants given may depend on, for example, how the C₂H₂ was oxidized, hence on the specific experiments performed."

As for the issue of "other products" we point to our response to 2), 9) and 17) above. Our Section 3.5 was added in support of the use of Heff despite the lack of chemical specific measurements. In fact, is there any chemically specific measurement is there that could provide a quantitative mass closure measurement of all possible reaction products of CHOCHO that contribute to Heff, and would satisfy the reviewer's comment? Chemical specificity remains an experimental challenge for the detection of multifunctional reaction products as they are likely to form from CHOCHO oxidation chemistry, and were not the ambition of this paper.

As demonstrated in the added Figure 7B, the value of Heff did not depend of the OH-concentration. We have further added a discussion of the oxidation mechanism of C₂H₂, which proceeds via very short lived hydroxy peroxy radicals (lifetime on the order of 700ns). These RO₂ radicals are precursors to CHOCHO formation from C₂H₂ hence behave different from conventional RO₂ radicals for which the fate could depend on the experimental conditions (reaction with NO vs HO₂/RO₂). These results do not support the reviewers concern that changes in the experimental conditions could make a difference.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 14841, 2008.

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