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Interactive comment on “Modelling non-equilibrium secondary organic aerosol formation and evaporation with the aerosol dynamics, gas- and particle-phase chemistry kinetic multi-layer model ADCHAM” *by* P. Roldin et al.

Anonymous Referee #3

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The manuscript of Roldin et al. represents an ambitious effort to develop and test a model capable of representing organic aerosol formation and loss under laboratory conditions. The model, ADCHAM, considers a number of poorly understood/constrained phenomena, including multiphase dimer formation, particle phase diffusion limitations, and gas and particle partitioning to chamber walls. The work builds on previous work by the authors, as well as many others in the field, yet represents one

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of few efforts to combine so many processes in a single model. The authors are to be commended for the efforts and it is likely that ADCHAM will become a very useful tool for the community. There are some clarifications and corrections that need to be made prior to publication in ACP. Some of the suggestions below echo those made by the other reviewers.

In the introduction and conclusion the authors promote the utility of ADCHAM for better understanding poorly constrained processes and their influence on SOA formation, and ultimately the representation of SOA formation in three-dimensional models. There is a generally recognized sentiment in the field that with advanced measurement and modeling techniques, we've moved beyond the need to accurately represent SOA mass concentrations and now need to accurately represent SOA mass concentrations, temporal behavior, and properties (and we need to "get it right for the right reasons"). While with each model application there was an effort to test sensitivity to various assumptions, given the significant uncertainty associated with so many of the model parameters, further sensitivity analyses is highly desired. While model validation is important, beyond being able to represent observations, a model such as ADCHAM could really provide insight into which of the model parameters need to be better constrained (and which processes need to be better understood). It is strongly suggested that the authors consider splitting this manuscript into one or more parts: one in which the model is generally described and sensitivity is assessed, and one or more describing application and validation. Given that this is the first publication on this complete version of ADCHAM, there were places where the more general and broader description of ADCHAM was confused with the specific applications described. Three examples: 1) p. 777, line 15 the authors describe the ADCHAM schematic and oxidation of SOA by O3. It isn't clear here why heterogeneous/bulk oxidation by only O3 is considered and not OH for example. After reading further it is clear that ADCHAM could consider particle-phase OH reactions, but for the specific applications this is not relevant. And, 2) While the ADCHAM model can treat oligomerization, in this application only dimerization was considered. The authors need to clarify this point and remove discussion of oligomerization in discussion of results as necessary (e.g., p. 795, lines 13-14). The blurring between model capabilities and the specific applications could be remedied by separating the publication into one or more parts. It is the opinion of this reviewer that doing so would increase distribution and citations, and greatly enhance the contribution of this work to the field.

pp. 773-774, discussion of equilibrium: While the authors note on p. 774, line 7-10 that there are a number of possible reasons why predicted evaporation does not agree with measured evaporation, the preceding discussion emphasizes (perhaps erroneously) only the mass transfer limitations. It is important to clarify that the Dzepina et al. (2009) and Vaden et al. (2011) predictions are for some specific assumed product distribution, which both lack a significant fraction of low-volatility material. The authors suggest that particles will never be in equilibrium with the gas phase. . .doesn't this depend on the temporal and spatial scale of interest? What about the findings of Saleh et al., ES&T, 2013?

pp. 775-776, discussion of development of ADCHEM from ADCHAM should be moved to the conclusion.

p. 776, the list of model applications here does not match the list provided in the abstract. 4 applications should be listed in the abstract, and mentioned first sentence last paragraph?

Model description: ADCHAM "consists of", add "s"

Section 2.2.1, are the molar growth rates calculated iteratively? If not, how does this affect predictions?

In section 2.2.1 and throughout the paper the discussion of the surface layer is somewhat confusing. On p. 780, lines 7-8 the authors state that compound i "partitions into (dissolves)" in the surface layer. However, on lines 12-13 the authors discuss the adsorption of oligomers at the surface. This is confusing throughout. Is the surface layer

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an absorption matrix for monomers but a solid for dimers?

p. 780, line 16: does setting a volatility limit on the saturation vapor pressures preclude consideration of more volatile species as reactants in dimerization? Please clarify.

p. 781, lines 18-24: the discussion of the particle wall effects corrections and their influence on predicted mass seems reversed (or needs further clarification). With method 1, particles deposit onto wall and can continue to take up gas-phase species. Give that both particles and gas-phase constituents move to the walls, it seems like this would give a lower-bound estimate of mass formed (assuming mass formed is the total suspended in the bag, and does not consider that formed on walls). Maybe the authors are considering mass formed to be the total suspended+walls. A note here about terminology: technically, “aerosols” refers to the gas+particle phase. While “aerosols” is often used to refer to the particles themselves, it can be quite confusing (and in this case the authors appear to be using it to refer to the gas phase). The authors state that the particles “take up SOA” (line 15). I think the authors mean that the particles take up volatile/semivolatile gas-phase compounds (and not both particles+gases). See also p. 783, line 6.

p. 782, line 15: sensitivity. . .how sensitive is the model to these uncertain parameters?

p. 786, line 22: “is” should be “are”

p. 787, line 18-19: why are Henry’s law constants used for the carboxylic acids? I can see how partitioning coefficients might be difficult to obtain for the inorganic compounds. However, even for those compounds it is important to consider the implications on modeling predictions. For example, it seems that NH3 would be much more soluble in water than in an organic+water phase (at low RH), and thus the influence of the NH3 uptake overestimated in the model applications. (e.g., as described on p. 802).

p. 789, line 11: Monomers restricted to of or below a specified volatility?

p. 789-790, discussion of oligomerization: What is the difference between the generic dimer formation (R7, R8) and the specified dimerization reactions (R1-R6)? Are R7 and R8 additional dimerization pathways? And if so, what is the justification of the additional pathways? If all dimer reactions are represented by R7 and R8, maybe it is better to list the specific reactions in a table? There have been a number of studies reporting on the thermodynamics and kinetics of the specific dimerization reactions considered and/or oligomer formation (e.g., Barsanti et al., AE, 2006; Walser et al., PCCP, 2008; Atkinson and Ziemann, Chem. Soc. Rev., 2012; DePalma et al., PCCP, 2013) that suggest that the kinetics/thermodynamics are not equally favorable. Thus the assumption that the dimers revert to monomers based on the relative abundance of the monomers (p. 791, line 15) does not seem justified (and is not necessarily "reasonable" as noted by the authors). At a minimum, some discussion or investigation of this assumption on the model results is needed.

p. 791, line 20-27: sensitivity…how sensitive is the model to each of these factors? Which are the most certain/uncertain? Which of these need be better constrained?

p. 799, line 19: "or" should be "and"

p. 801, line 20-25: It is not clear what the authors are trying to convey by the description of the observed RH effects by Kuwata and Martin, particularly starting with "However".

p. 803, line 14-16: What is the difference between ignoring the activity effects of the ammonium salt on the organic compounds and treating it as a separate phase?

p. 807, lines 1-15: Could these results also be explained or be sensitive to characterization of wall effects?

p. 808, lines 1-8: Could the over-/underprediction be due to uncertainties in input parameters, missing compounds rather than suggestive of some non-ideal mixing? (not sure incomplete phase separation happens)

p. 809, line 1-2: Why weren't simulations with lower input concentrations performed? Isn't this the benefit of having a model?

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p. 813-814: Are the model assumptions and parameters (e.g., assumptions about oligomer coated surface, dimer formation/decomposition rates) consistent with chamber studies/reported values (e.g., previously listed references for dimerization/oligomerization reactions)? The dimers considered in this work seem to be about the size/polarity of sesquiterpene oxidation monomers. Do such chamber studies provide support for the assumptions about dimers in the current work?

p. 832, line 17: “on” should be “of”

Figure 4: Does the skill of model performance as a function of particle size give any insight into processes or model assumptions/parameters?

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