Interactive comment on "Dynamic Consideration of Smog Chamber Experiments" *by* W. K. Chuang and N. M. Donahue

Anonymous Referee #2

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Review of "Dynamic Consideration of Smog Chamber Experiments" by Wayne K. Chuang and Neil M. Donahue

The study aims to provide insights to the apparent contradiction in observations of secondary organic aerosol (SOA) formation in smog-chamber and nucleation-chamber experiments. The authors apply a dynamic volatility basis set (VBS) model to explore possible reasons for why smog-chamber experiments suggest that SOA from α-pinene is mainly semi-volatile, while recent nucleation-chamber experiments at CLOUD point to high yields of very low-volatile organics.

The study is well conducted and suits in the scope of ACP. The used methods and obtained results are clearly presented, and the conclusions are generally reasonable. There are, however, some additional aspects relevant for the interpretation of the

experimental data that are not brought up in the study. In addition, it is not clear if the model used in the study can provide a valid description of particle growth at all different conditions and throughout the studied particle size range. Publication in ACP can be considered after the authors have addressed the issues listed below. I also agree with the main comments of Referee 1.

Specific comments:

Major comments:

1) The manuscript is motivated by the fact that yields of extremely low-volatile products in the CLOUD experiment are apparently much higher than in previous smog-chamber experiments. How large are the uncertainties in the assessed volatilities? Are the saturation vapor pressures of the α-pinene oxidation products based on their O:C ratios and the SIMPOL model, as presented by Tröstl et al. (2016)? The recent study "α-pinene autoxidation products may not have extremely low saturation vapor pressures despite high O:C ratios" by Kurtén et al. (2016) shows that group-contribution methods such as SIMPOL very likely underestimate the volatility of α-pinene autoxidation products. SIMPOL predictions for the saturation vapor pressures of species studied in the work of Kurtén et al. are generally lower compared to other methods that are more suitable for describing the chemical interactions of autoxidation systems.
How would the comparison of the CLOUD and smog-chamber experiments look like if the saturation vapor pressures of the species of the CLOUD chamber were not as low as assumed by Tröstl et al.?

2) When modeling the particle size evolution at the conditions of the CLOUD experiment, the role of ions and ion-ion recombination in the growth of the particle population is not addressed at all. Kirkby et al. (2016) state that the new-particle formation

(NPF) events generated in the CLOUD chamber, from which the experimental growth rate (GR) data used in the present manuscript (as well as in the study by Tröstl et al. (2016)) are extracted, are in practice driven by ions when the ion clearing field is off. The nucleation rates presented by Kirkby et al. imply that almost all particles that appear at d_p = 1.7 nm at a HOM concentration of around 10^7 cm^{-3} are either positively or negatively charged, and "ion–ion recombination progressively neutralizes the charged particles as they grow".

I assume that at least the "constant HOM" data is from the CLOUD ion runs, as I don't see how the HOM concentration could otherwise be kept constant in the experiment while observing a NPF event. If this is so, the experimental growth rates determined from the time evolution of size-classified particle concentrations should be influenced by

-Recombination of particles of opposite polarities to form larger, electrically neutral particles.

-Possible enhancement in the condensation rate of molecules onto particles due to electrostatic interactions (charge enhancements for different compounds in the CLOUD chamber have been assessed by Lehtipalo et al. (2016)).

3) Even when ions are not involved, coagulation of molecular clusters and small particles may also play a role in the evolution of the particle distribution. In the CLOUD experiment, this was previously addressed for NPF from sulfuric acid and bases by Lehtipalo et al. (2016), who concluded that nano-particle growth can be assisted by cluster coagulation in the presence of a strong stabilizing compound. While Lehtipalo et al. studied different chemical compounds than used here, the conclusion on the role of coagulation is general: the less small particles evaporate, the more their concentrations increase and thus the more significant the effect of coagulation becomes. This should be relevant also for NPF from oxidized organics, if ELVOCs are capable of forming very stable small clusters -can the authors assess the effect of coagulation at the studied conditions?

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4) In the CLOUD experiment comparisons, the particle growth model is applied to particle sizes down to around one nanometer. However, the validity of a single-particle model at very small nano-particle sizes is questionable. The model is "deterministic" in the way that it assumes that all particles of the same size grow at the same rate. It can't thus describe the fact that while the very smallest particle sizes may be unstable against evaporation so that the evaporation rate of molecules from the particle exceeds the collision rate of molecules, these unstable particles can still grow and generate a flux of particles towards larger sizes (this is the definition of nucleation). Instead, the used model requires the condensation rate to exceed the evaporation rate for all particle sizes in order for the particles to grow, even if this might not be the case in reality.

It appears that the authors are trying to simulate the initial NPF process with a model that might not even in principle be capable of describing the phenomenon. Is it reasonable to start modeling the growth from the size of $d_p \approx 1$ nm, which corresponds to approximately a molecule or two? Is the growth rate of a single molecule even a reasonable concept?

5) Further, the evaporation of molecules from particles is described by the Kelvin approach throughout the modeled size range, and it is concluded that the Kelvin effect is important especially for the smallest sizes. On the other hand, the Kelvin approximation is based on classical macroscopic droplet thermodynamics, and is therefore not expected to be valid for small sizes of a few molecules, which instead need to be treated with more sophisticated, atomic-level methods (e.g. Merikanto et al., 2007). Evaporation rates based on the Kelvin approach are thus likely to be highly uncertain; how does this uncertainty affect the results?

Similarly, can condensed-phase oligomerization processes be expected to be similar for larger, macroscopic particles and for the smallest modeled sizes consisting of only a few molecules? Can the smallest sizes even be considered particle phase?

6) The contribution of different VOC species to particle growth is obtained by fitting the model to experimental growth rates deduced from the "appearance times" of

different particle sizes. Recent studies suggest that for the smallest, sub-3 nm sizes, the experimental appearance time-GR method can give distorted results, namely the apparent growth rates can be too high (Olenius et al., 2014; Kontkanen et al., 2016). Would the VBS fit change if the GRs of sub-3 nm sizes were lower?

Minor comments:

1) In the introduction, the expression "yield" is used in the context of both SOA mass yields and (E)LVOC yields; for easier reading, it would be good to better clarify which quantity is addressed when discussing the yields.

2) Page 12, lines 4-5: Please explain CSTR mode and batch mode, and also reformulate the expression "significantly higher than the (older) data" which is somewhat unclear.

3) Page 13, line 5: The expression "For this simulation the suspended condensation sink was a few minutes" is not all clear; please clarify what is meant by a sink being a few minutes.

4) Page 13, line 35: When discussing the nucleation rate data from Kirkby et al., are the authors referring to the neutral or ion-induced rates?

5) Page 14, lines 1-5: "The data in the log-log plot have a slope of 2, indicating that the nucleation rate is a second order reaction with respect to the ELVOC concentration": generally, the slope does not indicate something about reactions (e.g. Ehrhart and Curtius, 2013). The derived "nucleation rate constant" doesn't have an actual physical meaning, as the rate is not affected only by the vapor concentration (and cluster evaporation), but also by e.g. losses of the formed molecular clusters onto chamber walls and surfaces of larger particles. The slope of the nucleation rate, regardless of what all the dynamic processes affecting the nucleation are, also varies with the absolute vapor

concentration (as well as other factors affecting the nucleation process), and therefore applying the "nucleation rate constant" to a completely different experimental set-up is questionable.
Large sinks, i.a. large suspended particles, can efficiently suppress nucleation; could this be related to the fact that particle formation was not observed in the smog-chamber experiments? Moreover, how was the effect of temperature on the nucleation rate taken into account when assessing rates for a smog-chamber?

6) Figure 8: Why are the growth rates of specific particle sizes much higher in the "increasing HOM" case? Are the absolute vapor-phase HOM concentrations similar for the "constant HOM" and "rising HOM" experiments? Why is the particle size range different for the two experiments? Same x- and y-axis limits would make the figure easier to read. Why are some particle appearance times negative in panel c? How is $t = 0$ defined? It is stated that "the experimentally determined growth rate at 10 nm matches the model", but no experimental growth rates are presented; please show also GRs deduced from the CLOUD observations in Figure 8.

7) Are the presented particle diameters mass or mobility diameters?

Technical comments:

-Page 11, line 10: Should "$\Delta\alpha\text{-pinene}/C_{\text{OA}}$" be "$C_{\text{OA}}/\Delta\alpha\text{-pinene}$"?

-Page 12, line 4: Remove "also" from the sentence "In Figure 5 we also also show..."

-Figure 1: Explain the markings with alphas on the right-hand side of the figure frame. Also state that the figure (minus the offset bar and the green curve) is taken from Presto and Donahue (2006).

-Figure 3, figure caption: Expressions "Experiment 1 monodisperse (a) and polydisperse (b) results. Experiment 2 monodisperse (c) and polydisperse (d) results." are

somewhat clumsy; please replace them with proper sentences.

-Figure 6: The upper limit of the y-axis could be set to 1, as the white space above the value of 1 is unnecessary.

-Figure 7 a and b: A legend would be helpful. Also, an extra occurrence of the word "experiments" should be removed from the figure caption: "Vapor saturation ratios for smog-chamber experiments experiments", and "dark gray" should be "dark grey". The unit of the nucleation rate on the y-axis label should be particles cm^{-3} s^{-1}, not molec. cm^{-3} s^{-1}.

-Figure 8: A legend would be good here, too. In the caption, "oligomerizeration" should be "oligomerization".

-Figure 10: In the caption, "blue triangles" should presumably be just "blue".

-Figure 12: I don't see the discussion starting with "At a low CS ratio, fewer seeds..." belonging to a figure caption (and in any case, essentially the same information is already included in the main text, so there is no need to repeat it). Similarly for Figure 13: the explanation starting with "Given a seed concentration..." shouldn't be a part of a caption.

-For all figures that present same quantities for different experimental set-ups or simulation cases in separate panels (Figures 3-5, 7-9, and 11-13), adding titles to the panels would make the figures easier to read.

-There are quite many separate figures in the manuscript. Could some of the figures be combined together as panels of a larger figure (e.g. Figures 4 and 5), or merged into the same panel (e.g. Figure 5 and 10)?

References:

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