Comment on acp-2021-571

Anonymous Referee #2

Referee comment on "Effects of oligomerization and decomposition on the nanoparticle growth: a model study" by Arto Heitto et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-571-RC2, 2021

In the study at hand, Heitto et al. investigate the effect of condensed-phase oligomerization and decomposition reactions on the growth of atmospheric nanoparticles. The study consists of two parts. In the first part, an explorative sensitivity study is performed to determine model parameters that affect particle size/growth rate as primary model output. In the second part, atmospheric observations of particle growth rates are compared to model simulations using best guesses of these parameters. Using literature data of gas phase concentrations of organic molecules, the authors show that agreement between previously measured and modeled particle growth rates can only be achieved by including oligomerization. The authors also admit that this result depends on which parametrization for the saturation vapor pressure C* of the product bins is used, so a definite answer is not possible at this stage.

The presented model seems quite well behaved and all parameters seem to affect the model result in certain sensitive ranges. The authors derive the parameter ranges for which oligomerization rate, oligomer decomposition rate, monomer volatility, and oligomer volatility are sensitive from the systematic sensitivity study. This is very technical work and no major conclusions can be drawn given the uncertainty in many input parameters. However, this study might proof helpful as a compass for future investigations. The manuscript fits overall well within the scope of ACP. The manuscript is well-written from a technical perspective and easy to understand, though, it will benefit from copy editing to improve grammar and punctuation and increase overall readability. I can thus recommend publication after a few comments are addressed as detailed below.

General Comments

l. 130, "The particle is assumed to be liquid like and have no particle phase diffusional limitations." – But particle-phase diffusivities are defined (Table 1) and evaluated (l. 256)? How is diffusion treated here?

l. 152, please indicate where the ranges for upper and lower limits of oligomerization rate coefficients stem from, same for decomposition rates in l. 159.

l. 176. "In addition, we have 280 product compounds (group IV)" – This comes surprising as groups I-III were already defined further above. What is this and what is it for? What diffusivity is mentioned here (l. 177), gas-phase diffusivity?

l. 216-221 "In some simulations the growth rate is decreased also by oligomerization" - This result is interesting; can you comment on whether you think it is relevant for the atmosphere?

Figure 2 - It is an interesting result in panel e/f that the 3rd highest (1 µg/m3) and highest volatility (100 µg/m3) bin have the largest potential for enhancing growth. This was seen previously for particles in the accumulation mode, even for higher volatility bins of more than 10^4 µg/m3, and was needed to explain the slow growth of SOA in an environmental chamber after an initial rapid growth phase (Berkemeier et al. 2020). Overall, the authors seem to have missed this recent study in which the effects of oligomerization and viscosity on the growth and evaporation of SOA was investigated in a similar process model. How would higher volatility bins > 100 µg/m3 behave here, are they relevant for Hyytiälä?

The observation that oligomerization is not so efficient when the 2nd highest (10 µg/m3) volatility bin is chosen was curious to me at first, but after reading l. 240, I understand that the calculations are set up such that only half of the total mass can oligomerize if $C^*\_O1 = C^*\_O2$. I genuinely wonder if something can be changed in the model setup to avoid this curiosity, e.g. allowing 2/3 of the bin to react instead of 1/3 in that specific case. Otherwise, it would be helpful to put another disclaimer somewhere so reader does not spend too much time trying to understand Fig. 2f when looking at figures first.

l. 257 "particle phase concentrations, which are very low in the small particles" – Is this because you initialize the calculations with pure sulfuric acid particles?

Fig. 5 – I would suggest to use the same color scaling as in Fig. 4, or use a color-scaling that is not as incremental as the one used here. Otherwise Fig. 5 might give the impression that k_dec is more sensitive than it really is.

Figure 7 – I wonder if plotting a line of a single particle size versus time through an image plot depicting particle number density and the evolution of many particles at the same time is a fair comparison. The reader's eye follows the upper and lower contours of the "banana" in the image plot and assumes that the line for a single particle size must follow

the same trend and slope. Can the authors expand more on this process and what potential pitfalls might be? Would it be possible to create a similar image plot by running a full particle size distribution through the model? Would this model result also show the spots of darker red color that seem to appear at ~13-14 h?

l. 449 "For instance, survival probability of particles from 3 nm to 20 nm calculated for the 450 NPF event presented in Fig. 7 were 15 %, 25 % and 44 %, respectively" – Were these calculations performed for this paper? How is this calculated? This is not described in the methods section.

Technical Comments

In many places "gas phase" needs to be replaced with "gas-phase" (l. 16, l. 37, l. 40, l. 43, l. 45 …)

The mentions of what the model can theoretically do (l.125, l. 136) are irrelevant for this work and confuse the reader more than help the presentation of this study.

l. 171, it would probably help the understanding when the cases where named / introduced earlier, e.g. line 64.

Figure 2: C*_O2 was somewhat confusing at first as it suggests to mean molecular oxygen. It would have been clearer what the "2" stands for if C*_O1 and C*_O2 would have been introduced around l. 233.

Fig. 4 - Should the subplot x and y axes be labelled C*_O1 and C*_O2?

l. 305 "oligomerization happens so fast that even these higher volatility molecules will oligomerize before evaporation" – This sounds like these molecules were placed in the particle phase at the beginning of the simulation. Should this be "… these higher volatility molecules will oligomerize significantly despite their small equilibrium particle-phase concentrations"?

l. 336 "ELVOC" – was not yet introduced.

l. 374 "Ehn et al. (2007) observations behind a thermodenuder determined size

distributions showed that the growth rate was one-third of the GR measured with a normal DMPS-system." – I think the meaning of this sentence would be very difficult to understand if the original paper is not known.

References

Berkemeier, T., Takeuchi, M., Eris, G., and Ng, N. L.: Kinetic modeling of formation and evaporation of secondary organic aerosol from NO3 oxidation of pure and mixed monoterpenes, Atmos. Chem. Phys., 20, 15513–15535, https://doi.org/10.5194/acp-20-15513-2020, 2020.