Summary

In the manuscript at hand, Gatzsche et al. combine an established model for formation of secondary organic aerosols (SOA), SPACCIM, with a kinetic gas-particle partitioning approach following the works of Zaveri et al. (2014). Comprehensive sensitivity studies show the importance of a wide variety of model input parameters, including particle-phase diffusion coefficients, particle-phase reaction rates and particle size. A few of these parameters are tuned to fit experimental results obtained in the LEAK aerosol chamber. The manuscript is well structured and contains many useful figures. The author's however have to make a better job at explaining what (a) the model exactly does and (b) which conditions and parameters are chosen in the manifold of presented simulation results. These points are outlined in more detail in the specific comments below. The contribution of the particle phase to SOA formation via chemical reaction and impeded diffusion is a highly interesting and under-studied topic and this study fits well within the scope of ACP. The study of Gatzsche et al. makes worthwhile progress towards understanding these concepts on the level of fundamental process understanding and method development. The execution, portability and application to real world applications or chamber experiments is less convincing on the other hand. The authors assume certain mechanisms for gas-particle partitioning (absorptive partitioning, which evidently fails in the case of low diffusivity) and chemical reaction (unimolecular reaction of all reaction products, which seems like a vast simplification), but do not discuss their choices and the potential alternative mechanisms that might be at work. All parameters that are varied in this study are only loosely (D) or almost completely unconstrained (k_c and k_b) and chosen more or less arbitrarily. While this is acceptable in a rather exploratory study, there is a strong mismatch between the strong conclusions drawn (e.g. Sect. 4: "*particle-phase bulk diffusion coefficient is the key parameter for the simulation of SOA formation*") and the uncertainty in molecular processes and parameters in this study. This conclusion is obtained from fitting multiple flexible parameters to only a single experiment of SOA formation. Is there only a single combination of parameters that leads to a good fit between model and experiment? What role does the general uncertainty in the gas-phase reaction mechanism and estimated volatilities play? I hence can only recommend this manuscript for publication after major revisions. I am happy to expand on my thoughts of how I think the manuscript could be improved in three sections below: general comments, specific comments and technical comments. Quotes from the manuscript are given in italics, comments begin with a bullet point.

General Comments

- My biggest concern is how the authors justify their assumption that organic molecules must diffuse into the particle phase in order to contribute to particle growth. This assumption is crucial for all conclusions in this paper and finds too little scrutiny.

- In Sect. 2.2.2., which parts of these equations are necessary? Entrainment and outflow are not considered in this study and there is an argument for omitting it from the equations here. The authors have to add what M stands for here, is it the number of size-section? I see a term for partitioning between aqueous and organic phases, how is this utilized in this manuscript? The manuscript never mentions phase-separation, so how does this play

a role? From reading the manuscript, it is also not clear how the mass-transfer term works and when it is needed.

- Regarding the sensitivity studies (Sect. 3.1), the authors must do a better job in highlighting that some of these simulations are probably far from reality. For example, Fig. 4c interestingly shows that omitting HOMs in the mechanism leads to an increase in SOA mass. However, the SOA mass yield is so low in these simulations that I strongly doubt their usefulness for real applications. The same argument can be made for Figs. 2b and 3b. These simulations show very different reaction regimes that might not be encountered in a simulation chamber experiment. While I find it interesting to show how a system reacts under strong perturbation, the questionable practicality must be indicated more clearly in the text.

- In Sect. 3.1.2, I find it imperative to describe what the reason is that there is no particle growth at low diffusivities. I would suggest expanding on the description about what happens in the model, in words or figures.

Section 3.3

- I am not sure if I understand the purpose of Sect. 3.3. This section essentially looks at the effect of different equilibrium constants of the particle phase reaction, but it is presented as effect of different first-order reaction rates. I tend to think that an equilibrium constant is more straightforward here as the particle will most likely be in reactive equilibrium anyway. I find Fig. 5 very instructive and what happens in Fig. 6 is just that the share of r-products (orange bands) is reduced, is that correct? This is not a very exciting result given that all reaction rates are arbitrary guesses, or are the amounts of p-products and HOMs also affected? A normalized sensitivity coefficient of the mass of r-products and p-products to a reaction rate might be much more instructive. On a different note, would it be possible to connect these cases to real scenarios, e.g. by making more realistic assumptions of k_c and k_b for examples at high RH / low RH?

Sect. 3.4

In this section, it is very hard to follow what exact calculations were performed. This leads to many open questions: What are the initial conditions for these experiments, especially x_{inorg} and x_{water}? What were the diffusivties D_{inorg} and D_{water}? On which humidity is the water concentration based? What is the hygroscopicity of these particles, how is it determined? Why is it safe to assume that organic and inorganic phases are mixed? Are we seeing an effect of D_{inorg} or an effect of D_{water} here?
It would be interesting to see D_m plotted against humidity, following this framework. You could compare the humidity-dependence of your D_m for self-diffusion in SOA to the values of tracer diffusion determined in Berkemeier et al. (2014), Lienhard et al. (2015), Price et al. (2015) or Berkemeier et al. (2016).

It would be helpful if it were more explicitly explained what happens in the simulations. What does the time profile of D_m look like? I suppose it increases due to the smaller contribution of inorganics.

On, p. 17, l. 33, the wording seems suboptimal. You write that using a constant bulk diffusion coefficient lowers the total SOA mass. Along the lines of the argumentation, this should be formulated the other way around: implementing a weighted particle-phase diffusion scheme increases total SOA mass. I have to wonder though, what of this effect is due to water and what is due to inorganics? It seems very clear to me that you would need to compare the diffusivity of the equilibrium SOA-water mixture and only add in the inorganics. Otherwise, you mainly make the argument that humidity leads to more SOA mass and not so much investigate the effects of a time-dependent diffusivity coefficient.

Specific Comments

p. 12, l.27-28

"No initial organic mass OM0 is utilized for the simulations with HOMs."

- This change seems arbitrary when first reading the article and gets only clear upon further reading. I wonder how the simulations would look like if no initial organic mass would be utilized for the simulations without HOMs? I find that would be much more instructive.

p. 13, l.2

"A rapid condensation of HOMs occurs due to their low vapor pressures (Fig. 4a)."

- How can this be seen in Fig. 4a? It seems not easy to see whether the solid lines take off sooner than the dashed lines. Is also does not appear as if the solid lines separate from the dashed lines within the early moments of the experiment/simulation, but rather over the first half of the experiment. Maybe referring to Fig. 5 would be helpful here if it is showing what you mean here?

p. 13, Fig. 3

- Since particle radius is reduced down to 11 nm, are Kelvin effects considered in this study? I don't see this mentioned in the manuscript.

p. 14, l.5-7

"This may be the reason for the convergence of formed SOA mass for $k_c = 1\ s^{-1}$ combined with $D_b = 10^{-14}\ m^2\ s^{-1}$ and the overall more effective SOA formation without consideration of HOMs for semisolid particles ($D_b = 10^{-18}\ m^2\ s^{-1}$, Fig. 4c)."

- Would it be possible to give more explanation on this odd result of Fig. 4c? Should this be left out if not realistic?

p. 14, l.10

"In general the HOMs provide about 27% of the simulated final total SOA mass and introduce SOA mass formation."

- How does this compare to the molar yields in Berndt et al. (2016)? In addition, there is a comma missing after "in general".

p. 15, l. 8f

"The main benefit of the implementation of a sufficiently fast backward reaction ($k_b \geq 10^{-3}$ s^{-1}) is the asymptotic curve shape of the SOA mass for proceeding simulation times. This behavior is also observed during chamber studies, which indicate an equilibrium state of the gas and the particle phase after a proceeding oxidation time."

- This reads interesting, but is difficult to understand without practical experience with smog chambers. Could this statement be explained in more detail and justified with examples?

p. 18, l. 25

"Consideration of the weighted particle-phase bulk diffusion coefficient and additional considered HOMs lead to a faster SOA mass increase at the beginning of the simulation. The decreasing particle-phase bulk diffusion coefficient due to the uptake of further organic material and the backward reactions in the particle phase induce a flattening of the mass increase."

- Where can this be seen? Why should a weighted particle-phase diffusion coefficient generally speed up SOA formation?

p. 20, Figure 8

- In Fig. 8, it is very difficult to understand the simulation conditions of each plotted line. Am I correct that the dashed lines are showing the same results in both panels? This would be worthwhile pointing out! It would be easier to see if both panels would show the same range on the y-axis. It is also difficult to spot the line that fits the experimental data well in Fig. 8b, maybe draw these on top of the markers or highlight it in another way.

p. 21, l. 4ff

"For the preferred model setup of Fig. 8b with $k_b = 10^{-2}$ s^{-1}, the simulation is in a very good agreement with the measured concentration decrease of α-pinene (Fig. 10a)."

- Why does the α-pinene concentration depend on k_b?

p. 21, l. 7

"The depletion of ozone is slightly overestimated by the model after 1.5 hours (Fig. 10b). The measured gas-phase concentration of pinonaldehyde is underestimated by the model (Fig. 10c)."

- Do you have ideas what could be the underlying reasons here? This would add much more to the manuscript than just plotting results.

Technical Comments

Figure 6 caption

"… both combined with different fast chemical backward reactions k_b."

- This sentence is difficult to understand in general and might deserve revision, but I believe what you mean here is "differently".

"The reference simulations for the regarding k_c and no k_b are shown with dashed lines."

- Do you mean "respective" instead of "regarding"? Do you mean "without backward reaction" instead of "no k_b"?

p. 18, l. 33ff

"After 1 h simulation time, it is obvious that the simulated concentration profile agree well with the experimentally observed SOA mass with a backward reaction rate constant of $k_b = 10^{-2}$ s^{-1}."

- Do the authors mean:

   "After 1 h simulation time, it is obvious that the simulated concentration profile agree*s* well with the experimentally observed SOA mass *when using a* backward reaction rate constant of $k_b = 10^{-2}$ s^{-1}."

Figure S5b

- This figure is not discussed in the manuscript.

References

Berkemeier, T., Shiraiwa, M., Pöschl, U., and Koop, T.: Competition between water uptake and ice nucleation by glassy organic aerosol particles, Atmos. Chem. Phys., 14, 12513-12531, 10.5194/acp-14-12513-2014, 2014.

Berkemeier, T., Steimer, S. S., Krieger, U. K., Peter, T., Poschl, U., Ammann, M., and Shiraiwa, M.: Ozone uptake on glassy, semi-solid and liquid organic matter and the role of reactive oxygen intermediates in atmospheric aerosol chemistry, Phys. Chem. Chem. Phys., 18, 12662-12674, 10.1039/C6CP00634E, 2016.

Lienhard, D. M., Huisman, A. J., Krieger, U. K., Rudich, Y., Marcolli, C., Luo, B. P., Bones, D. L., Reid, J. P., Lambe, A. T., Canagaratna, M. R., Davidovits, P., Onasch, T. B., Worsnop, D. R., Steimer, S. S., Koop, T., and Peter, T.: Viscous organic aerosol particles in the upper troposphere: diffusivity-controlled water uptake and ice nucleation?, Atmos. Chem. Phys., 15, 13599-13613, 10.5194/acp-15-13599-2015, 2015.

Price, H. C., Mattsson, J., Zhang, Y., Bertram, A. K., Davies, J. F., Grayson, J. W., Martin, S. T., O'Sullivan, D., Reid, J. P., Rickards, A. M. J., and Murray, B. J.: Water diffusion in atmospherically relevant alpha-pinene secondary organic material, Chem. Sci., 6, 4876-4883, 2015.