Short comment on Berkemeier et al. “Kinetic modelling of formation and evaporation of SOA from NO_3 oxidation of pure and mixed monoterpenes”.
https://www.atmos-chem-phys-discuss.net/acp-2020-55/

I offer some suggestions to improve the modeling in this study, as a few of the kinetic model input parameters and output results do not appear to be consistent with the state of the science.

1) Accommodation coefficient.

In the model description (Sect. 2.2), it is stated that an accommodation coefficient (alpha) of 0.1 for organic species was assumed for this study and references the paper Julin et al. (2013), which is a molecular dynamics simulation study of water vapor accommodation coefficients (and reports alpha of unity). Recent isothermal chamber (Krechmer et al., 2017; Liu et al., 2019) and flow reactor (Palm et al., 2016) studies, as well as molecular dynamics simulations (Julin et al., 2014) of accommodations coefficients for SOA-forming organic compounds into organic aerosols show values near unity for a wide range of compound functionalities, structures and volatility, as well as organic aerosol types. Therefore, I suggest that the authors use a more-relevant alpha value of unity (or near unity) for the modeling presented here. While other studies have shown lower values of alpha for organic molecules (e.g., references included in Fig. 3 in Liu et al. (2019)), those methods tended to be less direct, in many cases involve substantial heating, and/or contain limited information about the volatility of the compounds changing phase state, as compared to the Krechmer et al. (2017) and Liu et al. (2019) studies. If the authors feel that a range of alpha values should be considered for these modeling studies, then an approach that tests the sensitivity to the different values (including alpha=1) could be implemented.

2) Irreversible loss of gas products to chamber walls.

It appears that reaction product gases are assumed to be irreversibly lost to the Teflon chamber walls (Sect. 3.1.2, lines 295, 304, 315). This aspect is only mentioned in the results sections, and not earlier in the model description, so it is not clear why the authors made this assumption. However, several studies over the past decade have show that gases partition reversibly to and from Teflon chamber walls, with a strong dependance on compound volatility (e.g., Matsunaga and Ziemann, 2010; Yeh and Ziemann, 2014, 2015; Zhang et al., 2015; Krechmer et al., 2016). The volatility basis sets shown in this manuscript in Figs 2 and 3 show that a substantial fraction of compounds that participate in aerosol formation are at c* = 10,100,1000 $\mu g/m^{-3}$. Figure 4 in Krechmer et al. (2016) summarizes measured values of Fp (fraction of compound in gas-phase vs wall+gas) vs compound volatility, and shows that for c* = 10-1000, large fractions, up to 20-100% (that are not in the aerosol) remain in the gas-phase. Therefore, I suggest that the authors consider implementing a more realistic parameterization of the gas-wall interactions based on current literature, or otherwise demonstrate that the assumption does not significantly affect their results.

3) Gas-to-wall loss rate.

In Sect. 3.1.2 (lines 313-322), it is stated that a loss coefficient of gas-phase molecules to the chamber wall was determined to be equivalent to a loss timescale of 3.0 x 10^4 seconds (8.3 hours). This is an output of the modeling, it appears. The authors state that it falls in the range of values in the literature, citing the studies by Ziemann and colleagues (Yeh and Ziemann, 2015; Krechmer et al., 2016) who measured values of 1 x 10^3 s (0.27 hours) and those done in the CalTech chamber (3 x 10^4 to 5 x 10^5 s; 8.3-140 hours). However, a more recent experimental and modeling study by the CalTech group (Huang et al., 2018) concluded that the timescale relevant to the bulk equilibrium of gases with the surface layer of the chamber walls is rapid (1 x 10^3 s), in accordance with the Ziemann and colleagues studies — while the long time constants measured by the earlier CalTech studies, such as in Zhang et al. (2015), were more likely due to slower inner layer diffusion processes in the Teflon film (as the experimental timescales in those earlier CalTech studies were too slow to capture the fast bulk partitioning to the surface layer of the chamber walls). Such diffusion through the bulk Teflon is very slow and has little effect on typical chamber experiments.

Additionally, another group has reported gas-to-wall rates similar to Ziemann and colleagues for a similar sized chamber (10 m^3), as described in Ye et al. (2016) who reported a timescale of 0.26 hours (rate coefficient: 3.8 ± 0.3 h^{-1}), as did Ziemann and colleagues in a somewhat larger chamber (20 m^3) reported in Liu et al (2019) (rate coeff: 1.0 x 10^{-3} ± 20% s^{-1} => timescale 0.26 hours). Therefore it would be expected that for this experiment, where temperatures are changed relatively rapidly, effects of gas-wall partitioning on the bulk SOA measured would be dominated by the fast time ~10-minute time constant. Therefore, it is concerning that the model results support a timescale that is 30 times slower for that process — and suggests that there is at least one other aspect of the modeling, related to some kinetic framework or input, that is very inconsistent with the system being modeled. I suggest that the authors constrain the wall loss timescale to be consistent with the literature, in order to improve the model representation of these experiments.

Generally, as the manuscript is presented, it is difficult to predict (beyond some qualitative speculation) what the effects of these inputs / assumptions / and outputs have on or indicate about the main results presented for this study. Therefore, it would be very useful if sensitivity studies were conducted to help understand the dependencies and assess the robustness of the results presented (i.e. oligomerization rate constants and their contributions to the SOA, effects of particle diffusivity, volatility basis sets and organic nitrate evolution vs time).

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