

Atmos. Chem. Phys. Discuss., referee comment RC2
<https://doi.org/10.5194/acp-2021-919-RC2>, 2022
© Author(s) 2022. This work is distributed under
the Creative Commons Attribution 4.0 License.

Comment on acp-2021-919

Anonymous Referee #2

Referee comment on "The impact of molecular self-organisation on the atmospheric fate of a cooking aerosol proxy" by Adam Milsom et al., Atmos. Chem. Phys. Discuss.,
<https://doi.org/10.5194/acp-2021-919-RC2>, 2022

Review of "The impact of molecular self-organisation on the atmospheric fate of a cooking aerosol proxy" (Milsom et al., ACPD, 2021)

Overview

Milsom and co-workers investigate the kinetics of the decay of oleic acid (pure and "lamellar", by mixing with its sodium salt) by ozone. This system is a common proxy for heterogeneous chemistry of organic aerosol in general and cooking aerosol in particular. The study focuses on kinetic modelling and derives a set of parameters for composition-dependent diffusion of ozone and organics by inverse fitting of experimental data of double bond prevalence in the reaction system. The experimental data in this study is based on previous work using Raman spectroscopy in quartz capillaries (Milsom et al. 2021) and supplemented by a new data set. The authors find accumulation of reaction product close to the film surface, leading to formation of a surface crust, i.e. a region of decreased diffusivity. A remarkable result is the extraordinarily low ozone diffusivity in the organic matrix indicative of a semi-solid phase state of the "lamellar" oleic acid, even in the unreacted state.

The work employs state-of-the-art experimental and modelling techniques. The detailed analysis of the model results, including a comprehensive sensitivity and kinetic regime analysis, is very insightful. The paper is well-written and the conclusions are clear. I believe the topic of diffusion limitations in heterogeneous chemistry systems with relevance to the atmosphere is of great interest to readers of ACP.

While the paper makes a convincing case that the experimental system can be described reasonably well with a composition-dependent diffusion coefficient, the opposite is not proven: would it also be possible to describe the system reasonably well with simpler assumptions? Or is composition-dependent diffusivity inside the organic film and surface

crust-formation really needed to describe the system properly? A few other open questions remain as detailed below. Thus, I would suggest to reconsider this manuscript for publication in ACP after revision.

Major Comments

- A sketch of the experimental setup(s) and how the authors picture the oleic acid microstructure would be very helpful. It is difficult to picture the lamellar phase oleic acid and pure oleic acid capillary experiments without looking up other papers by the authors.
- How do C9 reaction products influence the diffusivity calculation? Are they treated as "oleic acid"?
- Figure 1 – There seems to be a general trend: thick films react quicker than simulated by the model and thin films react slower than the model predicts. What could be the reason? Is this trend stronger or less strong in a model without composition-dependent diffusivity? My initial thought was that the reacto-diffusive length of ozone and hence the "reaction zone" might be too small in the optimized model. In less bulk-diffusion limited model runs there should be less difference between thin and thick films (i.e. the reaction becoming more pseudo first-order instead of second-order).
- In general and as stated above, how good or bad is the model without the Vignes-type composition dependence of diffusion, i.e. just with single fitted diffusion coefficients D_X and D_Y ? This might help the reader understanding the necessity and effect of incorporating the surface crust formation.
- Figure 2 – Is there a delay in reaction onset? Data does not drop until more than 1 min after the experiments starts, but then drops very quickly. Also, the film thickness seems to be used as fitting parameter. Is there a way of verifying these 0.9 μm ? Reporting a possible range (e.g. with a shading) might overcome a potential arbitrariness of the fit parameter.
- Is line 154 ("the shorter spacing between fatty acid tails on a particle surface could provide steric hindrance to diffusing ozone molecules, limiting access to the double bond") at odds with line 169 ("2-D SAXS patterns obtained for these samples did not exhibit any alignment of the lamellar phase")? Would one expect a difference in diffusion between "entry" of the layer and diffusion within the layer? Instead of correcting the bulk diffusion coefficient, could or should the bulk accommodation coefficient be fitted?

Minor and Technical Comments

- I. 46 – There seems to be a word missing in or after "has been linked with particle phase".
- I. 56 – It is difficult to wrap one's head around "self-organised phase resolved model description" and what it may mean.

I. 82 – “The selected decays were from the same experiment carried out simultaneously in the same capillary under the same conditions” – It is not clear what this means.

I. 133 - Fixing the model time at which one looks for sensitivity tests can have pitfalls. A quicker initial oleic acid decay could lead here to depletion before 40 minutes and hence a lowering of the loss rate at 40 minutes. I would suggest comparing loss rates at similar reaction coordinate / progress (e.g. loss rate after 50 % has reacted).

Table 1 – Here Y stands for “oleic acid”, but previously it was also synonymous for C9 compounds. Which is true?

Table 1 – Is the dimer diffusion coefficient D_{dimer} not composition-dependent? Why? Was D_{trimer} forgotten in this table?

I. 341 – “an upper half-life estimate” – should this read “an upper estimate of half-life”?

References

Milsom, A., Squires, A. M., Woden, B., Terrill, N. J., Ward, A. D. and Pfrang, C.: The persistence of a proxy for cooking emissions in megacities: a kinetic study of the ozonolysis of self-assembled films by simultaneous small and wide angle X-ray scattering (SAXS/WAXS) and Raman microscopy, *Faraday Discuss.*, 226, 364–381, 2021.