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Interactive comment on "Heterogeneous oxidation of amorphous organic aerosol surrogates by O_3, NO_3, and OH at typical tropospheric temperatures" *by* Jienan Li et al.

Jienan Li et al.

daniel.knopf@stonybrook.edu

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We thank the reviewer for evaluating our manuscript and giving suggestions for improvement. Following the reviewer' suggestions, we have revised our manuscript correspondingly. Listed below are our point-by-point responses given in normal font.

In this work, Li et al. investigated the reactive uptake coefficients of O3, NO3 and OH onto thin film of surrogate organic aerosols (OA) species over a troposphere-relevant temperature range. The underlying hypothesis is that the temperature induced change in phase state of the studied chemicals will impact the uptake kinetics of atmospheric oxidants onto OA and consequentially the degradation rate of OA. This was clearly shown from the measurement of uptake coefficient that took place in a temperature-controlled flow reactor with inner wall coated with the studied OA surrogate species. The phase state changes were supported by poke-flow experiments. The measured uptake coefficients onto the thin film were extended to estimate the temperature dependent particle degradation fraction (DF) for studied species/binary mixture as 200 nm particles. Atmospheric implications were drawn that the lifetimes of OA are expected to be longer against heterogeneous oxidation due to a liquid-to-solid or semi-solid to solid phase transition that slows down the reactions. The overall experimentations were well thought and designed to minimize effects that can impact the accurate determination of reaction kinetics. The results were presented in high quality and discussed in detail with appropriate reference to the literature for data interpretation and comparison. Some specific comments provided below:

1. Could authors give more background to justify the choice of canola oil, levoglucosan and glucose as OA surrogates and the choice of paired oxidant as well?

Our choices of OA surrogate compounds were motivated by the fact of examining compounds that are representative of OA and for which the phase state properties are known. The choices of gas-phase radicals and oxidants include typical species of the polluted and background atmosphere to reflect oxidation processes close to the source region and during atmospheric transport, where NO_3 is representative of nighttime oxidation processes and OH and O_3 of daytime processes.

Canola oil (CA) is a mixture of multiple saturated and unsaturated fatty acids, however, dominated by unsaturated oleic and linoleic acid. Those species are prevalent components of both marine and terrestrial organic aerosol (Limbeck et al. 1999, Schauer et al. 2002, Kawamura et al. 2003) and constitute a major anthropogenic source of OA in urban environments from cooking (Rogge et al. 1991, Zahardis et al. 2007, Allan et al. 2010, Liu et al. 2017). Daytime photochemical aging of these compounds is simulated by studying the reaction with O_3 and OH oxidants.

Levoglucosan is applied in this study to reflect OA from biomass burning stemming from the pyrolysis of cellulose and hemicellulose products (Schauer et al. 2001, Iinuma et al. 2007). This reflects OA from natural sources such as forest fires and anthropogenic sources such as from heating and cooking. Sugars, such as glucose (GLU), can serve as tracers to characterize and apportion primary biogenic organic aerosols (PBOAs) (Zhu et al. 2015, Samaké et al. 2019). Previous studies, including our own, have indicated very slow oxidation reaction kinetics against O_3 (Knopf et al. 2011). To reflect urban day- and nighttime oxidation of these OA and its chemical transformation during long-range transport, we investigated the multiphase chemical kinetics involving NO_3 and OH radicals reflecting nighttime and daytime chemistry, respectively.

We will add the following sentences to the manuscript:

Line 105: “Canola oil (CA) is a mixture of multiple saturated and unsaturated fatty acids, however, dominated by unsaturated oleic and linoleic acid, and serves as OA surrogate for both marine and terrestrial organic aerosol including anthropogenic emissions like cooking (Rogge et al. 1991, Limbeck et al. 1999, Schauer et al. 2002, Kawamura et al. 2003, Liu et al. 2017). Levoglucosan (LEV) serves as a surrogate for biomass burning aerosol (BBA) including natural sources such as forest fires and anthropogenic sources such as heating and cooking BBA (Schauer et al. 2001, Iinuma et al. 2007). Glucose (GLU) can serve as a tracer to characterize and apportion primary biogenic organic aerosols (PBOAs) (Zhu et al. 2015, Samaké et al. 2019) and. Xylitol and 1,2,6-hexanetriol are used in compounds mixtures to modify the glass transition temperature, thus, condensed-phase viscosity. O_3 and OH radicals reflect typical gas oxidants present in photochemically active regions and during long-range transport. NO_3 radicals reflect an effective oxidant participating in the nighttime chemistry of typically polluted regions (Finlayson-Pitts et al. 1999, Brown et al. 2006)."

2. There are no clear indications on the morphologies of films before being poked. Please consider adding these images to help interpret the images including those in the SI. Are the films for all individual species and mixtures supposed to be transparent

before poking?

In general, all examined films were transparent and, considering a magnification of 230, appeared to have a smooth surface. When solidifying the film substrate, we try to avoid crystallization, which would result in a poly-crystalline surface distinctly different from film images presented here. The look of the images depends on the focal point and the thickness of the substrate. We focused on the film surface (except Fig. S4, image 2) to monitor the flow of the substrate to estimate phase state. When the film is thicker than the focal depth or the focal point is further away from the film surface, the substrate holder (i.e., the surface of the silver block in the temperature-controlled cooling stage) is barely- or non-visible, e.g., Fig. 3. If the film is thinner or the focal point is further within the substrate, you may see structures which stem from scratches in the sample holder, e.g., Figs. S2 and S3. (Recall, film is on thin glass slide on top of sample holder). Hence, the morphology of the substrate before poking is the area of the substrate not affected by the poking and potential shattering. For example, in the image of Fig. 3A at 10s, the area around the dent reflects the film surface properties as imaged by the microscope. The slightly darker shades within the imaged area do not represent any surface morphology but the unfocused scratches from the silver substrate holder beneath the film. Same with figures in supplement, however, in some of those cases, one can see the scratches in the sample holder.

To clarify this issue, we add the following sentences:

Line 187: “Images of the film substrate were recorded at 230 magnification and the depth of field of the 10X objective is 15.9 μm.”

Line 192: “Images were recorded with the film surface in focus to monitor the flow of the organic substrate and to probe film viscosity. Under the applied resolution, all film substrates appeared to be smooth and transparent.”

Line 208: “The area around the dent reflects the smooth morphology of the film substrate before poking it. The slightly darker shades within the imaged area do not represent any morphology features but the unfocused scratches from the silver substrate holder beneath the film."

Supplement, line 79: "Structures in Figs. S2-S7 that are not in focus are from minor superficial scratches of the silver sample holder within the temperature-controlled cooling stage."

3. Line 224, would the T_g^{pred} agree better with T_g exp if 10%-16% residual water was accounted for in the calculation? This will help to support the argument here.

If 10%-16% residual water is considered, using Gordon-Taylor equation, the predicted $T_g^{(pred,water)}$ would be lower than our experimentally determined T_g^{exp}. Comparing values of $T_g^{(pred,water)}$ and T_g^{exp} yields for LEV 210 K and 243 K, for GLU 241 K and 273 K, for LEV/XYL 207 K and 238 K, and for GLU/HEX 216 K and 248 K, respectively. Hence, about 30 K in difference would be observed. This prediction assumes that the residual water is homogeneously distributed within the substrate. However, we suggest that this discrepancy is due to our substrate film preparation process where under slow drying (evaporation), the outermost layers of the film contain less water than the deeper layers. The outermost layers adjust quicker to the targeted phase state, potentially forming a core-shell configuration where the outer shell can display higher viscosity than the core/bulk. The focus in our poke-flow experiments is solely on the substrate surface, thus monitoring the substrate flow that is governed by the film viscosity closest representing the desired conditions. This effect will not impact the interpretation of our findings since, even in the case of a liquid substrate, the reacto-diffusive length is on the nanometer scale (George et al. 2010, Shiraiwa et al. 2011, Slade et al. 2014, Lee et al. 2016), much shorter than the overall depth of the substrate.

We add the following information to the text:

Line 224: "If 10%-16% residual water is considered while using Gordon-Taylor equation, the predicted T_g would be roughly 30 K lower than our experimentally determined T_g^{exp}, assuming the residual water is homogeneously distributed in the film. This discrepancy is very likely due to our substrate film preparation process where under slow drying (evaporation), the outermost layers of the film contain less water than the deeper layers. Thus, the substrate surface represents closer the experimental conditions. Furthermore, the microscope focus in our poke-flow experiments is on the substrate surface, thereby monitoring the substrate morphology that is governed by the film viscosity closest representing the desired conditions."

4. In Section "Atmospheric implications" and "Conclusions", author should probably note that when coupled with higher ambient relative humidity the estimated temperature dependent DF using uptake coefficient derived from dry experiments may be underestimated for hygroscopic species like levoglucosan and glucose. Some discussions in this regard and directions for future studies could be added.

The reviewer is correct. We add to the Atmospheric Implications section: Line 466: "The presence of water vapor will significantly impact the phase state, in particular, of hygroscopic species such as LEV and GLU (Zobrist et al. 2008, Mikhailov et al. 2009, Koop et al. 2011), where increasing humidity yields lower condensed-phase viscosity and, in turn, faster reaction kinetics (Slade et al. 2014, Davies et al. 2015, Slade et al. 2017). Neglecting this effect will lead to an underestimation of DF."

For the Conclusions section, we will add:

Line 495: "This study did not address the role of water vapor acting as a plasticizer concurrent to phase changes induced by temperature changes (Zobrist et al. 2008, Mikhailov et al. 2009, Koop et al. 2011). The role of humidity on amorphous phase state and resulting multiphase kinetics has been studied at room temperature (Shiraiwa et al. 2011, Slade et al. 2014, Davies et al. 2015, Li et al. 2018). Most of these studies suggest that increasing humidity leads to faster reactive uptake kinetics. However, at lower temperatures, diffusivity is slower leading to kinetically hindered adjustments of the condensed-phase state (Wang et al. 2012, Berkemeier et al. 2014, Charnawskas et al. 2017, Knopf et al. 2018). Future experimental studies should focus on how the coupled effects of ambient temperature and humidity on the amorphous phase state of OA particles modulate the multiphase oxidation kinetics.

Technical Notes: 1. Font types of header and numbers in Table S4-Table S6 are not consistent.

Corrected.

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