Reviewer Comments to Li et al.

Summary

The manuscript by Li et al. used both experimental techniques and different mode simulations (including a viscosity model and a reaction kinetics model) to systematically understand the influence of temperature on the multiphase reactive process of O_3, NO_3, and OH on levoglucosan, xylitol, glucose, 1,2,3-hexanetriol, and canola oil mixtures. The authors carefully designed a flow tube reactor to measure the reactive uptake coefficient, γ, of these three gas phase species with organic thin films from 213 to 293 K. The results suggest that the phase state of the organic compounds at cooler temperatures in the upper troposphere could heavily impact the multiphase reactions and the lifetime of the organic aerosols.

The experimental section and the kinetic model sections of the manuscript are well done. The results are very important to help understand the multiphase process under low temperature regimes. The interpretation of the experimental data is a little bit unclear and overstated and should be corrected in the revision. With the following points being addressed, this manuscript is suitable to be published in Atmospheric Chemistry and Physics.

Major Comment

1. The author measured the reactive uptake coefficients of several species for residence times between 2 ms to 100 ms. Is the residence time safe to extrapolate the experimentally derived reactive uptake coefficients to ambient conditions where the residence time of the particles can be much longer? Shiraiwa et al. (2011) shows that the reactive uptake coefficients of ozone can vary significantly depending on the residence time. Can the author discuss about the potentially effects of short residence times in the manuscript?

2. The trends of the γ values as a function of temperature are really interesting and it shows strong heterogeneity among different species. The authors seem to imply in the manuscript that phase state change is the dominant reason for γ values to change (line 18, line 484-485, line 496-497). However, Shiraiwa et al. (2011&2012) demonstrate that if the organic species change their phase state from liquid to glass, the mass accommodation coefficients will change by orders of magnitude rather than just 34 times. Could the authors comment on the discrepancy between previous modeling results showing the uptake could change by orders of magnitude vs. the current experimental data showing the γ values only change up to a factor of 34?

With carefully designed experiments, I do believe the γ values the authors presented are accurate, but I think the data interpretation part is a little bit overstated to conclude phase state is the main reason for γ to change. The authors need to discuss more why γ values did not decrease as fast as previous modeling results (Shiraiwa et al., 2011&2012) shown when the viscosity changes. For instance, could the desorption lifetime (line 331) help increase γ values as temperature decreases? I think it is important to discuss these aspects in the paper to show that maybe both phase state and the desorption kinetics play important, but counter roles, with the role of the phase state dominating the γ value during this process.

3. The authors performed the poke-flow technique that was used in other papers to determine the glass transition temperatures of organic species. However, past literature on poke-flow technique were mostly used to determine the viscosity of the organic species and glass shattering phenomenon can indicate the viscosity is anywhere >10^{12} Pa s (Lindsay et al. 2013), but does not necessarily mean the viscosity is exactly near 10^{12} Pa s when the compound is right around glass transition. The accuracy of the glass transition temperature derived from this technique will heavily impact data interpretation in Fig. 7-9. Given that the T_g values shown in Table 1 do not match the T_g values from literature (and the author also mentioned these compounds may have water in them, so it is difficult to compare the T_g values with pure compounds from the literature), can the author provide any evidence to consistently show that the poke-flow technique can be used to derived accurate T_g values? Given there hasn't been studies before using observation on glass shattering to solely determine the glass transition temperature, maybe the author can cross compare with previous data to validate this technique (such as Koop et al. 2010, Dette et al. 2015).

4. What is the relative humidity of the flow tube when the experiments were performed? Given the author performed the flow experiments under a variety of low temperatures, even small partial pressure of water could potential lead to relatively high humidity and alter the phase state of the organic film and increase the error bar range of the estimated viscosity. Another related question is that the poke flow measurement also was performed under "sealed room air" (line 190). The water vapor in the room air may lead to near high relative humidity at cooler temperatures. How would the authors ensure the RH levels in the flow tube and the poke flow cooling state are the same and don't lead to errors in estimating the phase state?

5. The author used "slight changes in viscosity" (line 330) and "small changes in viscosity" (line 491) multiple times in the manuscript to describe viscosity change as temperature drops. However, the changes in viscosity during semi-solid phase state spans over several orders of magnitude (Figure 4) and I would not consider these changes small. In fact, these changes coule be even larger than the phase state transition from liquid to semi-solid. This leads to my question when viscosity changes a few orders of magnitude from liquid to semi-solid, it seems the uptake coefficients are still the same.

6. The logical deductions of how phase state alters γ values are a bit confusing and somewhat contradictory in multiple parts of the manuscript. For instance, line 339 shows the largest change of γ is observed around the expected T_g for LEV/XYL film, showing a transition from semi-solid to glass regime has the maximum influence of γ. However, in the next sentence, the author made a contradictory comment (line 340-341), saying "significant change in NO_3 uptake reactivity in the investigated temperature range can be attributed to the transition of a liquid to a highly viscous or solid substrate film". The similar statement appeared in line 351-352 saying that "the lower sensitivity of γ on temperature may be due to the generally higher viscosity" of the compound studied. Again, in line 358-400 the authors state that the γ is less sensitive to temperature change when canola is in semi-solid/glass phase states. If the γ change is less obvious, then why would the author observe the largest change of γ around T_g for LEV/XYL film?

The authors also compared the γ change with the same amount of temperature change (25 K) at higher temperature regimes (liquid) and lower temperature regimes (semi-solid/solid) in the manuscript. Results show that that γ changes more significantly at higher temperature regimes (liquid). My question is, would the statement still be correct when comparing viscosity change instead of temperature change? I.e., will γ still change more significantly when viscosity changes the same orders of magnitude from liquid to semi-solid vs. semi-solid to glass?

7. The reactive uptake data as a function of temperature from this manuscript is very insightful since there have not been such data available at low temperature. Results also show that change of γ as a function of temperature is drastically different when it comes to different organic species. For instance, OH oxidation of GLU/HEX mix and NO_3 oxidation of LEV is not sensitive to temperature while OH and O_3 oxidation oxidations of canola oil are more sensitive to temperature change. Can the author discuss further in the manuscript why different species exhibit difference in γ value changes? Given the strong heterogeneity of how the γ values of different compounds respond to temperature change, can the author still make the conclusions that "chemical reactivity of organic matter towards atmospheric oxidants can vary significantly in response to ambient temperature", as the ambient OA may have a different response of γ towards temperature than the organic surrogate compounds used in this study?

Minor Comments

1. Line 287: The equation doesn't seem to be right. Why would the diffusion coefficient to the left side of the equation be in the numerator, but the diffusion coefficients to the right side of the equation be in the denominator? Could the authors please double check?

2. The literature citation in the introduction part is good overall, but missed some recent important publications that are highly relevant to this study. Please include those citations for a more comprehensive introduction.

Line 40: please add the following two papers that are relevant.
Murray, B. J., T. W. Wilson, S. Dobbie, Z. Cui, S. M. R. K. Al-Jumur, O. Mohler, M. Schnaiter, R. Wagner, S. Benz, M. Niemand, H. Saathoff, V. Ebert, S. Wagner and B. Karcher (2010). "Heterogeneous nucleation of ice particles on glassy aerosols under cirrus conditions." Nature Geosci **3**(4): 233-237.

Pöschl, U. and M. Shiraiwa (2015). "Multiphase Chemistry at the Atmosphere–Biosphere Interface Influencing Climate and Public Health in the Anthropocene." Chemical Reviews **115**(10): 4440-4475.

Line 42: please add the following two papers that are relevant.
Renbaum-Wolff, L., J. W. Grayson, A. P. Bateman, M. Kuwata, M. Sellier, B. J. Murray, J. E. Shilling, S. T. Martin and A. K. Bertram (2013). "Viscosity of α-pinene secondary organic material and implications for particle growth and reactivity." Proceedings of the National Academy of Sciences **110**(20): 8014-8019.

Kidd, C., V. Perraud, L. M. Wingen and B. J. Finlayson-Pitts (2014). "Integrating phase and composition of secondary organic aerosol from the ozonolysis of α-pinene." Proceedings of the National Academy of Sciences **111**(21): 7552-7557.

Line 44-45: please include the following two papers that are relevant.
Dette, H. P. and T. Koop (2015). "Glass Formation Processes in Mixed Inorganic/Organic Aerosol Particles." The Journal of Physical Chemistry A **119**(19): 4552-4561.

Zhang, Y., L. Nichman, P. Spencer, J. I. Jung, A. Lee, B. K. Heffernan, A. Gold, Z. Zhang, Y. Chen, M. R. Canagaratna, J. T. Jayne, D. R. Worsnop, T. B. Onasch, J. D. Surratt, D. Chandler, P. Davidovits and C. E. Kolb (2019). "The Cooling Rate- and Volatility-Dependent Glass-Forming Properties of Organic Aerosols Measured by Broadband Dielectric Spectroscopy." Environmental Science & Technology **53**(21): 12366-12378.

Line 47: please include the following three papers that are relevant
Rothfuss, N. E. and M. D. Petters (2016). "Coalescence-based assessment of aerosol phase state using dimers prepared through a dual-differential mobility analyzer technique." Aerosol Science and Technology **50**(12): 1294-1305.

Zhang, Y., M. S. Sanchez, C. Douet, Y. Wang, A. P. Bateman, Z. Gong, M. Kuwata, L. Renbaum-Wolff, B. B. Sato, P. F. Liu, A. K. Bertram, F. M. Geiger and S. T. Martin (2015). "Changing shapes and implied viscosities of suspended submicron particles." Atmos. Chem. Phys. **15**(14): 7819-7829.

Järvinen, E., K. Ignatius, L. Nichman, T. B. Kristensen, C. Fuchs, C. R. Hoyle, N. Höppel, J. C. Corbin, J. Craven, J. Duplissy, S. Ehrhart, I. El Haddad, C. Frege, H. Gordon, T. Jokinen, P. Kallinger, J. Kirkby, A. Kiselev, K. H. Naumann, T. Petäjä, T. Pinterich, A. S. H. Prevot, H. Saathoff, T. Schiebel, K. Sengupta, M. Simon, J. G. Slowik, J. Tröstl, A. Virtanen, P. Vochezer, S. Vogt, A. C. Wagner, R. Wagner, C. Williamson, P. M. Winkler, C. Yan, U. Baltensperger, N. M. Donahue, R. C. Flagan, M. Gallagher, A. Hansel, M. Kulmala, F. Stratmann, D. R. Worsnop, O. Möhler, T. Leisner and M. Schnaiter (2016). "Observation of viscosity transition in α-pinene secondary organic aerosol." Atmos. Chem. Phys. **16**(7): 4423-4438.

Line 51: please add the following two relevant papers:
Shiraiwa, M. and J. H. Seinfeld (2012). "Equilibration timescale of atmospheric secondary organic aerosol partitioning." Geophysical Research Letters **39**(24): L24801.

Renbaum-Wolff, L., J. W. Grayson, A. P. Bateman, M. Kuwata, M. Sellier, B. J. Murray, J. E. Shilling, S. T. Martin and A. K. Bertram (2013). "Viscosity of α-pinene secondary organic material and implications for particle growth and reactivity." Proceedings of the National Academy of Sciences **110**(20): 8014-8019.

Line 53: please include the following two papers that are relevant:
Gaston, C. J., J. A. Thornton and N. L. Ng (2014). "Reactive uptake of N2O5 to internally mixed inorganic and organic particles: the role of organic carbon oxidation state and inferred organic phase separations." Atmos. Chem. Phys. **14**(11): 5693-5707.

Zhang, Y., Y. Chen, A. T. Lambe, N. E. Olson, Z. Lei, R. L. Craig, Z. Zhang, A. Gold, T. B. Onasch, J. T. Jayne, D. R. Worsnop, C. J. Gaston, J. A. Thornton, W. Vizuete, A. P. Ault and J. D. Surratt (2018). "Effect of Aerosol-Phase State on Secondary Organic Aerosol Formation from the Reactive Uptake of Isoprene-Derived Epoxydiols (IEPOX)." Environmental Science & Technology Letters **5**(3): 167-174.

Line 55: Please add the following paper that is relevant:
Riedel, T. P., Y.-H. Lin, S. H. Budisulistiorini, C. J. Gaston, J. A. Thornton, Z. Zhang, W. Vizuete, A. Gold and J. D. Surratt (2015). "Heterogeneous Reactions of Isoprene-Derived Epoxides: Reaction Probabilities and Molar Secondary Organic Aerosol Yield Estimates." Environmental Science & Technology Letters **2**(2): 38-42.

Line 61: please include the following citations that are highly relevant to the paper:
Pajunoja, A., W. Hu, Y. J. Leong, N. F. Taylor, P. Miettinen, B. B. Palm, S. Mikkonen, D. R. Collins, J. L. Jimenez and A. Virtanen (2016). "Phase state of ambient aerosol linked with water uptake and chemical aging in the southeastern US." Atmos. Chem. Phys. **16**(17): 11163-11176.

Gaston, C. J., J. A. Thornton and N. L. Ng (2014). "Reactive uptake of N2O5 to internally mixed inorganic and organic particles: the role of organic carbon oxidation state and inferred organic phase separations." Atmos. Chem. Phys. **14**(11): 5693-5707.

Houle, F. A., A. A. Wiegel and K. R. Wilson (2018). "Predicting Aerosol Reactivity Across Scales: from the Laboratory to the Atmosphere." Environmental Science & Technology **52**(23): 13774-13781.

Zhang, Y., Y. Chen, A. T. Lambe, N. E. Olson, Z. Lei, R. L. Craig, Z. Zhang, A. Gold, T. B. Onasch, J. T. Jayne, D. R. Worsnop, C. J. Gaston, J. A. Thornton, W. Vizuete, A. P. Ault and J. D. Surratt (2018). "Effect of Aerosol-Phase State on Secondary Organic Aerosol Formation from the Reactive Uptake of Isoprene-Derived Epoxydiols (IEPOX)." Environmental Science & Technology Letters **5**(3): 167-174.

Riva, M., et al. (2019). "Increasing Isoprene Epoxydiol-to-Inorganic Sulfate Aerosol (IEPOX:Sulfinorg) Ratio Results in Extensive Conversion of Inorganic Sulfate to Organosulfur Forms: Implications for Aerosol Physicochemical Properties." Environmental Science & Technology **53**(15): 8682-8694.

Zhang, Y., Y. Chen, Z. Lei, N. E. Olson, M. Riva, A. R. Koss, Z. Zhang, A. Gold, J. T. Jayne, D. R. Worsnop, T. B. Onasch, J. H. Kroll, B. J. Turpin, A. P. Ault and J. D. Surratt (2019). "Joint Impacts of Acidity and Viscosity on the Formation of Secondary Organic Aerosol from Isoprene Epoxydiols (IEPOX) in Phase Separated Particles." ACS Earth and Space Chemistry **3**(12): 2646-2658.

DeRieux, W.-S. W., P. S. J. Lakey, Y. Chu, C. K. Chan, H. S. Glicker, J. N. Smith, A. Zuend and M. Shiraiwa (2019). "Effects of Phase State and Phase Separation on Dimethylamine Uptake of

Ammonium Sulfate and Ammonium Sulfate–Sucrose Mixed Particles." ACS Earth and Space Chemistry **3**(7): 1268-1278.

Line 64: please include the following citation that is relevant:
Arangio, A. M., J. H. Slade, T. Berkemeier, U. Pöschl, D. A. Knopf and M. Shiraiwa (2015). "Multiphase chemical kinetics of OH radical uptake by molecular organic markers of biomass burning aerosols: humidity and temperature dependence, surface reaction, and bulk diffusion." The Journal of Physical Chemistry A **119**(19): 4533-4544.

Line 70-73: there are other works that also analyzed the effects of phase states on OH oxidation that should be included:
Houle, F. A., A. A. Wiegel and K. R. Wilson (2018). "Predicting Aerosol Reactivity Across Scales: from the Laboratory to the Atmosphere." Environmental Science & Technology **52**(23): 13774-13781.
Houle, F. A., A. A. Wiegel and K. R. Wilson (2018). "Changes in Reactivity as Chemistry Becomes Confined to an Interface. The Case of Free Radical Oxidation of C30H62 Alkane by OH." The Journal of Physical Chemistry Letters **9**(5): 1053-1057.

3. The measured T_g values of a few species listed in Table 1 are lower than the value measured by other literature. The author explains that was due to water remaining in the organic compound which lowers the glass transition temperature. If that is the case, it is a bit misleading to still associate the experimentally derived glass transition temperatures with the name of the pure compounds. Maybe the author should add information to highlight that the experimental derived T_g values in Table 1 refers to the mixture of water and organic species.

4. n-Hexadecane in Table 2 was never mentioned in the main text. Please call out the name. Also, in Table 2, a comma should be added between reference number and the γ values

Additional References:

Shiraiwa, M., M. Ammann, T. Koop and U. Pöschl (2011). "Gas uptake and chemical aging of semisolid organic aerosol particles." Proceedings of the National Academy of Sciences **108**(27): 11003-11008.

Koop, T., J. Bookhold, M. Shiraiwa and U. Poschl (2011). "Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere." Physical Chemistry Chemical Physics **13**(43): 19238-19255.

Shiraiwa, M. and J. H. Seinfeld (2012). "Equilibration timescale of atmospheric secondary organic aerosol partitioning." Geophysical Research Letters **39**(24): L24801.

Renbaum-Wolff, L., J. W. Grayson, A. P. Bateman, M. Kuwata, M. Sellier, B. J. Murray, J. E. Shilling, S. T. Martin and A. K. Bertram (2013). "Viscosity of α-pinene secondary organic material and implications for particle growth and reactivity." Proceedings of the National Academy of Sciences **110**(20): 8014-8019.

Dette, H. P., M. Qi, D. C. Schröder, A. Godt and T. Koop (2014). "Glass-Forming Properties of 3-Methylbutane-1,2,3-tricarboxylic Acid and Its Mixtures with Water and Pinonic Acid." The Journal of Physical Chemistry A **118**(34): 7024-7033.