Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-284-RC1, 2016

Atmospheric Chemistry and Physics Discussions

Interactive comment on "The effect of viscosity on the HO_2 uptake by sucrose and secondary organic aerosol particles" *by* Pascale S. J. Lakey et al.

Anonymous Referee #2

Received and published: 22 May 2016

This manuscript provides an important step towards understanding the uptake of HO2 by secondary organic aerosol (SOA) and the influence of the viscous/glassy nature of the SOA on the reactive uptake kinetics. The manuscript is well-written, concise, and the data are clearly presented. I have only minor suggestions for the authors to consider before the manuscript can be accepted for publication.

Line 269: "There is good agreement between the model and the measurements suggesting that the change in HO2 uptake over the range of humidities is indeed due to a change in the HO2 diffusion coefficient which is in turn due to a change in the viscosity of the aerosol particles." Given that the viscosity of aqueous/sucrose aerosol changes by more than >8 orders of magnitude over this experimental RH range (10 Pa s to >109 Pa s), things are clearly more complex than this sentence suggests with uptake coefficients only changing by a little over 1 order of magnitude. The authors do go on to

Printer-friendly version

Discussion paper

discuss this more fully and they seem to attributed it to a combination of increasing viscosity, which suppresses diffusion rates into the particle bulk, coupled with an efficient surface reaction. In effect, the surface reaction means the uptake coefficient doesn't decreases as much as it might based on the increase in viscosity (see the dashed and solid lines in Figure 5). The near-surface chemistry is attributed to the presence of catalysing Cu2+ ions near the surface.

It would be helpful to the reader to compare directly the relative change in viscosity expected over this range to the change in the uptake coefficient (see for example the recent paper by Marshall et al., Diffusion and Reactivity in Ultraviscous Aerosol and the Correlation with Particle Viscosity, Chem. Sci., 7, 1298–1308, doi:10.1039/C5SC03223G, 2016 where they do something similar for previous measurements). Indeed, many of the studies referenced in the introduction have shown that the uptake coefficients for OH, O3 and N2O5 etc do not vary nearly as strongly with viscosity as would be expected and do infact only decrease by an order of magnitude, even though the viscosity/diffusivity changes by many more orders of magnitude.

In these earlier studies, it is not clear that there is any special surface enhanced chemistry that keeps the uptake coefficient larger than would be expected. Further clarification/discussion is needed. How can the authors be sure that that the inclusion of a surface reaction is what is needed to "correct" for a diminishing bulk diffusion inferred from water diffusion constants and does anything other than provide an additional parameter (degree of freedom) with which to ensure good agreement between the measurements and model? How legitimate do the authors believe it is to use of the diffusion constant for water (a stable molecule forming 2 hydrogen bonds etc) to represent the much more reactive, less strongly interacting HO2 in viscous sucrose? In the other measurements of reactive uptake coefficients, must similar enhancements in surface reaction rates be included to explain why the uptake coefficients do not fall as much as would be expected based on viscosity and water diffusivity?

Line 293: "Bones et al. (2012) measured that for 100 nm diameter sucrose aerosol

Printer-friendly version

Discussion paper

particles. . .” – to my knowledge, this paper does not report measurements of these timescales for size change for such small particles, it only inferred them from measurements on larger particles.

Line 309: The two bulk concentrations of copper sulfate were chosen to span the expected range based on RH. Does this mean the concentration is expected to be 0.1 M at 17 % RH? How might the pH be expected to vary for supersaturated solutions of sucrose containing copper sulfate at such low water activity?

Line 366: “. . .effect of aerosol viscosity upon HO2 uptake coefficients was systematically investigated with a combination of HO2 uptake coefficient measurements. . .” – as suggested, it might be helpful to show the dependence of uptake coefficient on viscosity explicitly.

Minor Points for Clarification/Additional Information

Line 188: What is the timescale for HO2 concentration to stabilise once mercury lamp turned on?

Line 210: Magnitude of RO2 interference signal in HO2 detection is shown to be significant for TMB SOA measurements but not a-pinene – this is different from expectations based on box model simulations. Why is this the case? Some more detailed discussion would be helpful.

Line 219: Discussion of correction for wall loss and non-plug flow would benefit from indicating directly the level of correction typically required beyond what can be inferred from Figure 3.

Line 238: “which is only slightly larger than the diameter of HO2 (0.4 nm).” – is there any significance to this?

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-284, 2016.

Printer-friendly version

Discussion paper