Borchers et al. "Retention of a-pinene oxidation products and nitro-aromatic compounds during riming"

General comments

This is an interesting and important experimental study of retention during riming that supports, refines, and expands the existing knowledge on the phenomenon. It further contributes to understanding and parameterization of the fate of a variety of compounds in freezing clouds, with potential implications for understanding of particle formation and other chemistry of the troposphere. The experimental approach is clever and carefully includes measurement of conditions and properties that have been hypothesized to affect retention, but for which more experimental data are needed. However, some of the calculation methods are unclear and need to be more rigorously explained (or applied), particularly regarding the use of the desorption/absorption correction and its extrapolation. Additionally, the conclusions somewhat overstate and generalize the results and their contrast with previous literature. These need to be more nuanced and more carefully placed within the existing knowledge base.

Specific comments

1) The overall results statements (and conclusions) on retention based on effective Henry's constant values are too broad and overstate the results. The statements should be less sweeping and be more nuanced. Reference to specific lines and discussion is provided below.

L390-391. "retention of compounds with an H*<10^3 is close to 0, i.e. *the entire amount* of the compound dissolved in water is released to the gas phase during riming." And L443 "is negligible" overstate the results seen in the graph. The graph shows retention of about 20% for H* of 10^3, and about 10% for H* of 100. This results statement (and conclusions) should be corrected to not overstate the results, such as by replacing "the entire amount" with "most" .

L395. "For compounds with H values above 10^8, a retention of 1 is expected and the compound *remains completely* in the ice phase during freezing". Due to the variability of values found in this study (and expected from theory), this also is too broad a statement. Saying something like "retention of about 1 is expected with most of the compound remaining in the ice phase" would be more appropriate.

Additionally, this threshold value is consistent with that suggested by Stuart and Jacobson (2004) for dry growth riming, who stated "A better parameterization for species with high effective Henry's law constants (the cut-off being somewhere in the range of 10^6 and 10^{10} M/atm) would be to assume complete retention." Providing a comparison to thresholds in the existing literature would be helpful.

L26-27. “retention is negligible for molecules with H* below 10^3, while unity retention can be expected for compounds with H* above 10^8”. Again this should be less definitive.

2) The conclusion of no difference in dependencies between the dry and wet growth conditions (L427 “this study shows that there appears to be no difference between dry and wet growth conditions ...”) should be more clearly limited by the conditions considered. This is particularly needed regarding the implied disagreement with the conclusions of Michael and Stuart (2009) (L429 “This is in contrast to the modelling study of Michael and Stuart ...).
In the current study, wet growth of graupel with supercooled drop/air surface temperatures (-0.8 to -2.2ºC) and no water shedding was considered whereas Michael and Stuart (2009) considered wet growth of hail, liquid air surface at 0ºC, and shedding of water. The authors do acknowledge there is a difference between the studies’ conditions (earlier, in the introduction), but then use language here in the conclusions sections that suggests a generally applicable conclusion that is too broad (no difference in dry and wet growth conditions), and also imply a disagreement in conclusions between the studies. Due to the difference in conditions, there is no clear contrast between the studies’ results. The results here are consistent with those from an earlier study (Stuart and Jacobson, 2004), which considered more similar conditions (supercooled drop surface temperatures). It remains experimentally untested which factors affect retention for conditions with little to no surface supercooling, liquid water remaining at the surface, and water shedding. I also don’t think it can yet be unequivocally stated that Henry’s law constant is the most important under all conditions. It would be more helpful to put these results in the context of the continuum of studies under different conditions, for which the results here refine and extend the understanding to a larger variety of compounds and conditions using rigorous experimental measurements.

Additionally, the substantial unexplained variation in retention in the results here (even for the high H* compounds), are consistent with the potential importance of small variations of freezing conditions on retention, also supporting the existing literature. This should be discussed.

L113. The term ‘instantaneous’ is not really appropriate. There is expected to be a finite (albeit very short) freezing time, allowing escape of some chemicals (those with lower effective Henry’s constants). It would be more appropriate to say ‘quick’.

3) There are problems with the description (and potentially the use) of the desorption correction that need to be clarified (or corrected).
P9. Section 2.4

a. It is confusing to not provide the calculation of the desorption correction coefficient here. I suggest moving the content defining the desorption correction coefficient (including current Equation 2) to here.
b. The experiment to determine the correction for desorption during flight was apparently only performed on the lowest H* compound. One would expect the amount of

desorption/adsorption during flight to be dependent on H*. Was the desorption correction adjusted for more soluble/less volatile compounds? If so, how was it adjusted? If not, a justification for why it is not expected to matter much is needed.

c. How did the droplet flight time differ between the desorption correction experiments and the retention experiments? If they are substantially different, the correction coefficient would not be valid to correct retention, so this should be provided/discussed.

L195. How does the residence time (2s) of drops in the experiment to determine the desorption correction coefficient compare with that of drops in the retention experiments? (Additionally, what was the time frame of the retention experiment and was it at steady state?)

P9. Two different approaches appear to be used to calculate the retention coefficient (R). In the second approach (Equation 3), the standard ratio (Equation 1) is adjusted by dividing by the desorption coefficient (D) for "compounds with lower retention coefficient" to correct for the possibility of <u>absorption</u> of excess amounts from air during flight or freezing. If absorption occurs, D will be greater than 1 and R will be adjusted down from the uncorrected value. This correction makes sense, but it is not clear why Equation 3 cannot be applied to all compounds, rather than deciding to apply a different method to different compounds. If absorption is small, the adjustment still works, and if desorption occurs during flight instead, R will be adjusted up, which is also appropriate. So why not use Equation 3 for all compounds? Additionally, what was the cutoff for when to use it and when not and why? Further, the statement that the correction was used for "compounds with lower retention coefficient" suggests that retention is primarily dependent on the compound itself, and not the freezing conditions. That has yet to be established, so it would be better to just clarify the conditions for which it was applied and why, rather than this vague description of the choice being compound dependent. Overall, a comparison and discussion of results for D and R with and without 'correcting' for D should be included. Finally, it is confusing to call D a desorption coefficient, but then use it to adjust for absorption, not desorption (and not use it to correct for desorption at all?).

P9. Equations 1 and 2 use the same variables for different entities, which is very confusing and results in it looking like R will always be 1 (if you assume the same variables mean the same thing and substitute into Equation 3, everything cancels out and you get 1?). However, variables that look the same actually have different definitions in these equations. E.g., c^sample_compound means the concentration of the compound in the sampled graupel for equation 1, but it means the concentration of the compound in the sampled droplets for equation 2. Please use variable definitions that are distinct to clarify.

P11. Section 3.1. The section presents the desorption coefficients determined from the experiments with droplet flight. D is less than 1, suggesting desorption occurred during the experiment, which is not surprising because this is the lowest H* compound. However, based on the methods presented in section 2.6, it doesn't seem like these Ds are used in the retention calculations because only absorption seems to be corrected for with Equation 3. Something doesn't correspond. The methods need to be clarified regarding the correction for desorption and absorption.

4) The discussion of pH dependence could be improved.
Table 4. Theoretically, we would only expect pH dependence for compounds with low enough Kh and with pKas near the range of pH studied. Looking at Table 4, the results seem pretty consistent with this. Only retention of 2-nitrophenol was found to depend on pH; it has the lowest Kh and a pKa that is somewhat close to the range of pHs studied. cis-pinic and cis-pinonic acid have pKas in the range of pHs studied, but have much larger Khs. This is interesting and worth noting.

L362. Clarify that no pH dependence was found within the range studied here (4-5.6).

L72-73. As written, this seems to imply that the dependence of retention on the dimensionless effective Henry's law solubility constant (H*) and the dependence on pH of the droplet are independent. However, for chemicals that dissociate (and for pH that are in the range of the pKs), the H* depends on pH. This is minor, but should be clarified.

5) L258. The linearity of the trend is not clear. There are only 2 series of 3 points each and the trend looks curved. Further, the extrapolation from the experimental range of temperatures to the predicted range of temperatures is substantial. It is not clear that the Ds predicted by this extrapolation are meaningful. A theory-based justification for the assumed curve shape and more data are really needed here. (However, if D is not used for desorption, these results could just be eliminated.)

6) L438. What method was used to determine the distinct Henry's law constants of 4-nitrophenol and 2-nitrophenol in Table 4 if the HENRYWIN software predicts the same values?

Technical corrections

L120. "Michael and Stuart (2009) found in their theoretical study that during wet growth conditions H* is not a dominant factor and low retention values were also found for compounds like HCl". This is a bit misleading. We found H* to be important, with retention increasing as H* increased from 300 to 3x10^6, and then leveling off. We also did not study HCl (or any chemical) directly. Rather we studied impact of specific chemical parameters.

L123. Michael and Stuart (2009) did not find the "supercooling of the liquid surface water" was a major determinant, but rather the ice-liquid interface supercooling (and liquid water content) were most important.

L81-82. The sentence "The organic compounds show a dependence on temperature and ventilation" is unclear. I suggest "Retention of the organics compounds shows ..."

L191. A “l” is missing at the end of “nitropheno”.

L347. There is a spelling error in the same word.

L370. “insert version used” should be corrected.