Review of "Chemistry of Riming: The Retention of Organic and Inorganic Atmospheric Trace Constituents" by Jost et al.

Summary

This article describes wind tunnel experiments to measure the retention factor of several soluble trace gases. When cloud drops freeze due to the riming of cloud drops by ice or snow particles, the dissolved trace gases in the cloud drops can degas, partially degas, or be retained in the frozen cloud particle. The retention factor is the fraction of the dissolved trace gas that remains in the frozen cloud particle. The authors conducted several experiments to determine the retention factor of several organic compounds using the Mainz wind tunnel. The experiments were restricted to temperatures between -16°C and -7°C, addressing only dry growth riming. The retention factors for formic, acetic, oxalic, and malonic acids as well as formaldehyde are reported. The results, combined with previous experimental data for inorganic compounds, show a nice relationship with the Henry's Law constant such that the authors provide an equation to describe the dependency. Two compounds, formaldehyde and ammonia, do not follow the Henry's Law relationship. Formaldehyde has a much higher retention factor than expected because it is unable to dehydrate before the drop freezes, while ammonia has a higher retention factor than expected because CO_2 reacts with ammonia's dissociated product, OH^-, consequently reducing the ability of molecular ammonia to be reformed and degassed. This paper is an important contribution to our science understanding of the fate of soluble trace gases in clouds.

The paper provides a nice analysis and is well written. However, there are a few discussion points to be addressed before it is ready to be published. I would like to see discussion on retention factors from previous studies other than the Stuart and Jacobson (2003; 2004) and Michael and Stuart (2009) papers. There should also be discussion of expected results for changes in environmental factors, such as pH. Lastly, some clarification of the information in Figure 3, showing results as a function of retention indicator and of Henry's Law constant, needs to be provided.

Major Points

1. The experiments done in the Mainz vertical wind tunnel were carefully controlled for several parameters, including the pH of the droplets. How would the results change if the pH of the droplets changed? This may implicitly be answered by the two data points for SO_2, where lower retention is found for a high SO_2 concentration and higher retention is found for a low SO_2 concentration. Would these same trends be the same for the organic acids?

2. The results presented here are very helpful for cloud chemistry model simulations. Leriche et al. (2013) list retention coefficients used in their model study that are based on experimental results and estimates, and Bela et al. (2016) also use these values. Although formaldehyde, formic acid, and acetic acid retention coefficients are simply estimates in their studies, it would be useful to discuss that the current results differ from these estimates (or not).

3. Bela et al. (2016) and Fried et al. (2016) use aircraft observations and modeling simulations to estimate retention coefficients for thunderstorms ranging from severe to weak in nature. Their findings are that the formaldehyde and hydrogen peroxide retention coefficients must be near zero in order to obtain the best match between model and observations. On the other hand, the methyl hydrogen peroxide retention coefficient must be greater than 0.5. Could the discrepancies between the results reported here and these previous studies be explained by wet growth riming? Could there be other processes causing such substantial differences between the experimental studies and the field observations?

Another study to include in the discussion is Bozem et al. (2017) who derive scavenging efficiencies of various trace gases based on aircraft observations of a mesoscale convective system in Europe.

4. Figure 3 is a key figure for the conclusions of this paper. It contains a lot of information and some aspects are not clear.

a) First, there are some symbols that are not easy to see. Malonic acid is faint (being so close to the dark oxalic acid symbol, one hardly see the light gray diamond). I suggest a darker color and/or a wider symbol. The yellow is always hard to read easily. Can it be changed to gold or orange?

b) Second, the faint pink open symbols for HCHO and NH_3 (i.e. the "fine lined symbols") are difficult to read. I appreciate the desire to have them similar in color to the wind tunnel results, but perhaps a color like magenta would work better. In addition, these symbols need to be explained better. Are the faint pink symbols the results where retention coefficient is from equation 6 where RI is based on all the terms in equation 2, while the red symbols use equation 6 where RI is based on the first 3 terms of equation 2 (i.e. $\tau_r=0$)?

Are all the other trace gases using equation 6 where $\tau_r=0$ in equation 2?

c) The acetic acid results are shown for different temperatures. Could the formic acid results at different temperatures also be shown since Figure 2 shows a correlation between temperature and retention coefficient?

d) Could the retention coefficient using the low SO_2 concentration be marked? It may be best to state its value in the text (e.g. line 5 on page 14, "… and one at a low concentration of 86 μmol l^{-1} (LC), which has a retention coefficient of 0.5.")

Specific Comments

1. Is equation 8 applicable to all temperatures studied? It appears from the symbols on the graph that only the T = -11°C data were used.

Technical Comments

P. 11, L19-21, I think k_1 and k_{-1} should be k_{R1} and k_{-R1}

P. 15, L. 16. Change “bases” to “is based”.

P. 16, L. 28. I suggest saying that R2 and R3 are in the text below.

P. 20. Note 15 is not listed below the table, nor is it on P. 21.

References

Bela, M., M. C. Barth, O. B. Toon, A. Fried, C. R. Homeyer, H. Morrison, K. A. Cummings, Y. Li, K. E. Pickering, D. Allen, Q. Yang, P. O. Wennberg, J. D. Crounse, J. M. St. Clair, A. P. Teng, D. O’Sullivan, L. G. Huey, D. Chen, X. Liu, D. Blake, N. Blake, E. Apel, R. S. Hornbrock, F. Flocke, T. Campos, G. Diskin, 2016: Wet Scavenging of Soluble Gases in DC3 Deep Convective Storms Using WRF-Chem Simulations and Aircraft Observations. J. Geophys. Res. Atmos., 121, doi:10.1002/2015JD024623.

Bozem, Heiko, Andrea Pozzer, Hartwig Harder, Monica Martinez, Jonathan Williams, Jos Lelieveld, and Horst Fischer, 2017: The influence of deep convection on HCHO and H_2O_2 in the upper troposphere over Europe, Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-154, 2017

Leriche, M., J.-P. Pinty, C. Mari, *and* D. Gazen *(*2013*),* A cloud chemistry module for the 3-D cloud-resolving mesoscale model Meso-NH with application to idealized cases, Geosci. Model Dev., 6, 1275–1298, *doi:10.5194/gmd-6-1275-2013.*

Fried, A., M. C. Barth, M. Bela, P. Weibring, D. Richter, J. Walega, Y. Li, K. Pickering, E. Apel, R. Hornbrook, A. Hills, D. D. Riemer, N. Blake, D. R. Blake, J. R. Schroeder, Z. J. Luo, J. H. Crawford, J. Olson, S. Rutledge, D. Betten, M. I. Biggerstaff, G. S. Diskin, G. Sachse, T. Campos, F. Flocke, A. Weinheimer, C. Cantrell, I. Pollack, J. Peischl, K. Froyd, A. Wisthaler, T. Mikoviny, and S. Woods (2016), Convective Transport of Formaldehyde to the Upper Troposphere and Lower Stratosphere and Associated Scavenging in Thunderstorms over the Central United States during the 2012 DC3 Study. J. Geophys. Res. Atmos., 121, doi: 10.1002/2015JD024477.