

Interactive
Comment

Interactive comment on “Solubility and reactivity of HNCO in water: insights into HNCO’s fate in the atmosphere” by N. Borduas et al.

Anonymous Referee #2

Received and published: 6 October 2015

This paper discusses the measurements of the effective Henry’s law constant and true Henry’s law constant for HNCO by acetate ion CIMS, as well as the hydrolysis rate constants for the three decomposition pathways of HNCO using ion chromatography. Additionally, they determine the pH dependence and temperature dependence of these parameters and use this information to determine the likely lifetime of HNCO over a range of atmospherically-relevant temperatures, pH values, and aerosol/fog/cloud liquid water contents. They find that based on their measurements, the lifetime of HNCO will likely be a longer-lived species than previously thought and exposure might be higher than previously predicted. I found this to be a nicely-written, very thorough paper and recommend that it be published in ACP after addressing the minor comments below.

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Comments:

Abstract: The effective Henry's law constant is more atmospherically-relevant than the true Henry's law constant because it encompasses any additional solubility due to the ability of HNCO to possibly hydrate, and to dissociate in the aqueous phase. Therefore, $K_{H_{eff}}$ should be given in the abstract either instead or in addition to K_H .

Equation 1: The effective Henry's law constants for small aldehydes such as glyoxal and methylglyoxal incorporate the fact that the carbonyl groups can hydrate to diol groups. HNCO also has such a carbonyl group so the authors may wish to consider that there may be additional processes beyond just pH dependence that determine $K_{H_{eff}}$.

Section 2.1: A very brief overview paragraph with an overview of the experimental work should be added here prior to section 2.1.1. This will provide some context for the "The CIMS was built in house..." sentence of section 2.1.1.

Section 2.1.1: Are the detection limits and sensitivity of HNCO known for acetate CIMS? Why was the acetic anhydride flow passed through a Po-210 radioactive source? You mention that the CIMS monitored 10 m/z values, and then later say that NCO^- is detected at m/z 42. Were other m/z values monitored, and if so which ones and why?

Section 2.1.2: What was the disodium phosphate concentration in your buffer? There is recent evidence that the solubility of organic molecules is modulated by salt concentration (e.g. Kampf et al. 2013, Endo et al. 2012, Wang et al. 2014, and Waxman et al. 2015). These effects are more pronounced at the higher salt concentrations typically found in aerosols. Is your phosphate concentration high enough to impact the solubility of HNCO?

Page 24223, lines 8-10: You state that the absolute gas phase concentration of HNCO is not required. This statement makes perfect sense once one has read the Results

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and Discussion section, but is confusing here as the reader will likely be assuming that you measure aqueous phase concentration and gas phase concentration to calculate M/atm . You could consider adding an additional sentence or two to elaborate on your analysis method to explain why this value is not necessary.

Figures 3 and 4: Why show all measurements rather than average the measurements and propagate the error bars where you have multiple measurements?

References cited: Kampf, C. J.; Waxman, E. M.; Slowik, J. G.; Dommen, J.; Pfaffenberger, L.; Praplan, A. P.; Prevot, A. S. H.; Baltensperger, U.; Hoffmann, T.; Volkamer, R. Effective Henry's Law Partitioning and the Salting Constant of Glyoxal in Aerosols Containing Sulfate Environ. Sci. Technol. 2013, 47 (9) 4236– 4244, DOI: 10.1021/es400083d

Wang, C.; Lei, Y. D.; Endo, S.; Wania, F. Measuring and Modeling the Salting-out Effect in Ammonium Sulfate Solutions Environ. Sci. Technol. 2014, 48 (22) 13238– 13245, DOI: 10.1021/es5035602

Endo, S.; Pfennigsdorff, A.; Goss, K. U. Salting-Out Effect in Aqueous NaCl Solutions Increases with Size and Decreases with Polarities of Solute Molecule Environ. Sci. Technol. 2012, 46 (3) 1496– 1503, DOI: 10.1021/es203183z

Waxman, E. M.; Elm, J.; Kurten, T.; Mikkelsen, K. V.; Ziemann, P. J.; Volkamer, R. Glyoxal and Methylglyoxal Setschenow Salting Constants in Sulfate, Nitrate, and Chloride Solutions: Measurements and Gibbs Energies Environ. Sci. Technol. 2015, 49 (19), 11500–11508, DOI: 10.1021/acs.est.5b02782

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 24217, 2015.

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