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Interactive comment on “Reactive uptake of ammonia to secondary organic aerosols: kinetics of organonitrogen formation” *by* Y. Liu et al.

Y. Liu et al.

ycliu@rcees.ac.cn

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In this manuscript the authors report on an experimental investigation of reactive uptake of ammonia onto secondary organic aerosols (SOA), with the intends to evaluate the kinetics and mechanism leading to organonitrogen formation. Environmental chamber measurements were presented for the ozonolysis of a-pinene and the OH oxidation of m-xylene in the presence of ammonia. Organonitrogen formation from their chamber experiments was analyzed using a High Resolution Time-of- Flight Aerosol Mass Spectrometer and a Quantum Cascade Laser instrument. The uptake coefficients of NH3 to SOA leading to organonitrogen compounds were estimated, and the reaction of ammonia with carbonyl was speculated to be by liquid-phase diffusion limited heterogeneous reaction on SOA. Overall, this work represents a useful study to evaluate the role of NH3 on SOA formation. The paper was reasonably written. I recommend that this work can be publishable in ACP, provided that the following issues are adequately addressed.

Response: Thank you for your positive comments.

Their discussion on the mechanism of NH3 on SOA leading to organonitrogen formation was both qualitative and speculative. Two types of mechanism were suggested under their experimental conditions, i.e., the reactions of ammonia/ammonium with carbonyl functional groups in SOA leading to the formation of covalently bonded carbon to nitrogen and acid-base reactions between ammonia/ammonium and organic/inorganic acids in particles leading to organic ammonium salts. The authors claimed that a large diversity of nitrogen containing organic (NOC) fragments observed were consistent with the reaction of ammonia with carbonyl. However, it was uncertainty on what types of carbonyls might be relevant to their experimental conditions. It was indeed interesting that they explored two types of VOC oxidations, ozonolysis of a-pinene and OH-initiated oxidation of m-xylene. For the former type, it would be expected that organic acids are the dominant SOA component (for example, Ma et al., Geophys. Res. Lett. 40, 6293–6297, 2013). On the other hand, small a-dicarbonyls would be most dominant products from the OH-initiated oxidation of m-xylene (Zhao et al., J. Photoch. Photobio. A 176, 199-207, 2005). In fact, their measured larger NOC mass fraction for m-xylene derived SOA than that for the total a–pinene derived SOA would be indicative of the efficient reaction mechanism for a-dicarbonyls with NH3 to form imine and/or imidazole formation. Nevertheless, the authors would need to provide some quantitative assessment of the plausible mechanism leading to organonitrogen formation, in light of available literature results on the yields of organic acids and small a-dicarbonyls from VOC oxidation.

Response: Thank you for your comment and suggestion. In this work, we speculated two types of mechanisms based on previous studies (Lee et al., 2013;Bones et al., 2010;Galloway et al., 2009;Zarzana et al., 2012), namely the reactions of ammonia/ammonium with carbonyl functional groups in SOA leading to the formation of covalently bonded carbon to nitrogen, and acid-base reactions between ammonia/ammonium and organic/inorganic acids in particles. As shown in Figure 3 and 6, a larger amount of nitrogen containing organic (NOC) fragments and higher uptake coefficients were observed during uptake onto SOA from OH-initiated oxidation of m-xylene than ozonolysis of a-pinene. We agree with you that efficient reaction for a-dicarbonyls with NH3 to form imine and/or imidazole formation is likely here as carbonyls are likely the most dominant products from the OH-initiated oxidation of m-xylene (Zhao et al., 2005) compared to ozonolysis of ïĄą-pinene (Ma et al., 2013). We cannot of course, be fully quantitative in these types of experiments for a variety of reasons. Such reasons include the inability to detect specific product molecules with the AMS, and the potential for other functional groups (ie: acids) to be formed from both precursors with oxidative aging. Regardless, the possible dominance of dicarbonyls in the aromatic system is a plausible reason for the enhanced NOC observed. While this cannot be confirmed we have nonetheless modified the manuscript to reflect this possibility. In the manuscript (page 17460, line 14 and line 17), two sentences were added as “In particular, previous work has found that organic acids are the dominant SOA component (Ma et al., 2013).” and “It has been found that a-dicarbonyls are the dominant products from the OH-initiated oxidation of m-xylene (Zhao et al., 2005)”, respectively. And in page 17464, lines 21-24, the sentences “This is in contrast to recent reports that OH initiated anthropogenic SOA forms relatively less NOC than ozone oxidation of monoterpenes (Updyke et al., 2012). However this is likely dependent upon differences in a variety of conditions between experiments.” has been replaced with “As discussed in Section 3.2, a-dicarbonyls are likely the most dominant products from the OH-initiated oxidation of m-xylene (Zhao et al., 2005), while organic acids are more likely the dominant SOA component from ozonolysis of a-pinene (Ma et al., 2013). This suggests an efficient reaction for a-dicarbonyls with NH3 to form imine and/or imidazole and is consistent with the higher NOC content in the total SOA mass from OH oxidation of m-xylene.”

Two previous studies (Paciga et al., Environ. Sci. Technol. 2014, 48, 13769-13775;

Na et al., Environ. Sci. Technol. 2007, 41, 6096-6102) have assessed the effects of ammonia on SOA formation, but were not discussed in the present work. In particular, the later work examined the effects of ammonia in an environmental study of a-pinene ozonolysis in dry and humid conditions. Furthermore, a recent review article has provided a good coverage on heterogeneous reactions relevant to acid-base reactions and reactions relevant to carbonyls with basic species (Zhang et al., Chem. Rev. 115, 3803-3855, 2015). Those literature results should be carefully considered, when discussing their present results.

Response: Thank you for your suggestion. These previous studies will be considered and discussed in our revised manuscript (page 1746, line 26), as “Previous studies have observed the neutralization reaction between NH3 and organic acids in both flow reactor (Paciga et al., 2014) and environmental chambers (Na et al., 2007). In particular, high concentrations of NH3 greatly promoted SOA formation from ozonlysis of a-pinene (Na et al., 2007). This was ascribed to the formation of organic ammonium salts.”

What were the systematic and random errors in their estimated uptake coefficients? The methods for such uncertainty assessment should be discussed.

Response: As shown in equation (2), the uncertainty of the uptake coefficient results from the uncertainty of NOC mass concentration measured by the AMS, the concentration of NH3 measured by the QCL and the diameter measured by the SMPS. In chamber studies, it is very difficult to perform experiments with exactly the same conditions each time. In this study, the error bars are derived from the uncertainties of the uptake model parameters based on the measured time series of mass concentration of NOC fragments. The uncertainties of NH3 concentration and particle diameter have been considered in this model. In the titles of Figures 5 and 6, the uncertainties have been pointed out. A sentence about this has been added in page 17457, line 13, as “The uncertainty in the uptake coefficient will result from the uncertainty in NOC mass concentration measured by the AMS, the concentration of NH3 measured by the QCL and the diameter measured by the SMPS. In this study, the uncertainty is derived from the uptake model parameters based on the measured time series of mass concentration of NOC fragments."

Could they differentiate whether such an uptake was surface or bulk reaction?

Response: As discussed in the manuscript (Page 21), the measured uptake coefficients decrease with the increasing of NH3 concentration, which is consistent with surface reaction. However the observed acidity dependence argues against surface reaction. We therefore cannot rule out bulk reaction in our experiments.

In the abstract, add "respectively" after "m-xylene derived SOA,".

Response: Thanks. We have corrected the similar mistakes throughout the paper.

Reference:

Bones, D. L., Henricksen, D. K., Mang, S. A., Gonsior, M., Bateman, A. P., Nguyen, T. B., Cooper, W. J., and Nizkorodov, S. A.: Appearance of strong absorbers and fluorophores in limonene-O(3) secondary organic aerosol due to NH(4)(+)-mediated chemical aging over long time scales, J. Geophys. Res.- Atmos., 115, doi: 10.1029/2009JD012864, 2010.

Galloway, M. M., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Flagan, R. C., Seinfeld, J. H., and Keutsch, F. N.: Glyoxal uptake on ammonium sulphate seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions, Atmos. Chem. Phys., 9, 3331-3345, doi: 10.5194/acp-9-3331-2009, 2009.

Lee, H. J., Laskin, A., Laskin, J., and Nizkorodov, S. A.: Excitation Emission Spectra and Fluorescence Quantum Yields for Fresh and Aged Biogenic Secondary Organic Aerosols, Environ. Sci. Technol., 47, 5763-5770, doi: 10.1021/es400644c, 2013.

Ma, Y., Brooks, S. D., Vidaurre, G., Khalizov, A. F., Wang, L., and Zhang, R.: Rapid modification of cloud-nucleating ability of aerosols by biogenic emissions, Geophys.

Res. Lett., 40, 6293–6297, doi:10.1002/2013GL057895, 2013.

Na, K., Song, C., Switzer, C., and Cocker, D. R.: Effect of Ammonia on Secondary Organic Aerosol Formation from α-Pinene Ozonolysis in Dry and Humid Conditions, Environ. Sci. Technol., 41, 6096-6102, 10.1021/es061956y, 2007.

Paciga, A. L., Riipinen, I., and Pandis, S. N.: Effect of Ammonia on the Volatility of Organic Diacids, Environ. Sci. Technol., 48, 13769-13775, 10.1021/es5037805, 2014.

Zarzana, K. J., De Haan, D. O., Freedman, M. A., Hasenkopf, C. A., and Tolbert, M. A.: Optical Properties of the Products of α-Dicarbonyl and Amine Reactions in Simulated Cloud Droplets, Environ. Sci. Technol., 46, 4845-4851, doi: 10.1021/es2040152, 2012.

Zhao, J., Zhang, R., Misawa, K., and Shibuya, K.: Experimental product study of the OH-initiated oxidation of m-xylene, Journal of Photochemistry and Photobiology A: Chemistry, 176, 199-207, http://dx.doi.org/10.1016/j.jphotochem.2005.07.013, 2005.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/15/C7425/2015/acpd-15-C7425-2015-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 17449, 2015.

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