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Discussions

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

Anonymous Referee #2

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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 α-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.

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 α-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 α-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 α–pinene derived SOA would be indicative of the efficient reaction mechanism for α-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 α-dicarbonyls from VOC oxidation.

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 α-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.

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

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

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

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