

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

Anonymous Referee #1

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This paper contains novel data on reactive uptake of ammonia (NH₃) by secondary organic aerosol (SOA) particles. Specifically, the authors describe chamber-based measurements that provide the reactive uptake coefficients of gaseous NH₃ by two very different types of SOA. An important result of this paper is the direct observation of a relatively efficient uptake resulting in the formation of a significant concentration of nitrogen organic compounds (NOC). The paper is well written, and the experiments seem to have been carried out very carefully. A few relevant recent studies were missed by the authors; the list of some of the missing references is provided at the end. Other than that I am in favor of publishing it in ACP.

GENERAL COMMENTS

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1. In my opinion, the importance of BrC resulting from the NH₃ + SOA reactions is overstated in the introduction. I would strongly recommend emphasizing that formation of BrC in reactions of NH₃ with glyoxal, methylglyoxal, and SOA compounds has been demonstrated in the lab in experiments with model systems but never actually confirmed in the field. Furthermore, the existing evidence suggests that BrC produced by such NH₃ reactions is rather unstable with respect to degradation by oxidants (Sareen et al., 2010) and sunlight (Lee et al., 2014; Zhao et al., 2015). Finally, the BrC formation by this mechanism is relatively slow and the MAC values of this type of BrC are quite small, which implies a low level of impact on the climate relative to that of primary BrC from biomass burning. I would therefore recommend shifting the stress of the introduction from the formation of BrC to the formation of NOC, which may or may not be light absorbing but likely have very interesting chemical properties.
2. The choice of references cited in support of the importance of BrC in the introduction section appears to be a little unbalanced in my opinion. Citing review articles such as the one by Andreae and Gelencser (2006) is very appropriate; however, more focused papers by Powelson (2014), Updyke et al. (2012), Alexander et al. (2008), etc., are perhaps not the best choices for the introduction of BrC as a topic. The formation of BrC from NH₃ + organics reactions has recently been reviewed in detail by Laskin et al. (2015); the authors could significantly cut down their citation list by taking advantage of this review. A related review by Moise et al. (2015) could also work very well for that purpose.
3. The authors appear to be unaware of the study by Flores et al. (2014), who examined reactive uptake of NH₃ by different types of SOA, including alpha-pinene SOA, using a ToF-AMS instrument amongst other things. The present ToF-AMS results should probably be compared to the results of Flores et al. experiments, if such a comparison makes sense to the authors.
4. One potential weakness of the AMS method is the complications from the pyrolysis/ionization processes occurring in the ionization region. Can the authors prove

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that the NOC species they are observing are not produced in that process? I would feel much more comfortable with the conclusions of the paper if the authors presented reference AMS spectra ammonium salts of several carboxylic acids (e.g., of pinonic acid and of benzoic acid) recorded under their specific AMS operating conditions and showed that they gave much different patterns in the mass spectra.

SPECIFIC COMMENTS

Equation 2 and equations in the SI section: Chemical uptake of each NH₃ molecule is probably accompanied with a release of one or more H₂O molecules as byproducts (this prediction is based on the multiple studies cited in the text, and on Scheme 1 used by the authors). Organic Carbonyl + NH₃ → NOC + x H₂O Unless the initial carbonyl and NOC have very different volatilities and molar volumes, there might not be any increase in the overall particle mass and size, or possibly even particle shrinking if x > 1. Would this consideration affect equation 2 and conclusions drawn from it? I have not analyzed this question too carefully but equation (2) does include particle size and density in it, and equations (S5) does imply that the authors assume an increase in the particle diameter during the reaction.

Page 17459, line 8: The proposed assignment of an IR band to a C=C-CN species cannot be claimed with the level of certainty currently used in the manuscript without isotopic data. This conclusion is highly speculative and it should be clearly labelled as such. Related to this, please see the comment about Figure 2 below.

Page 17460, the first paragraph on this page, and subsequent discussion: Laskin et al. (2014) actually have a paper on alpha-pinene SOA reacting with NH₃, which might be much more relevant for the discussion than some of the less relevant papers on limonene SOA +NH₃ reactions currently cited by the authors.

Page 14464, line 12: is → are

Page 14464, line 13: insert comma before “respectively”

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Page 14464, lines 14-17: there is a simple present - simple past tense inconsistency in this sentence.

Page 14464, lines 19 and 23: upon → on

Page 17464, line 24: In my opinion, there is no inconsistency here because Updyke et al. (2012) did not report any NOC amounts; they only reported absorption coefficients. More NOC does not mean more absorbing aerosol.

Page 14466, line 19: insert comma before “respectively”

Page 17467, line 1: at present → at the present

Page 17468, line 8: photo-chemistry → photochemistry

Page 17468, line 17: significant organic material (SOA) → significant amount of organic material (e.g., in the form of SOA)

Page 17470, line 18: a value 1.4 → a value of 1.4

Page 17470, line 22: troposphere → the troposphere

Page 17471, line 2: Updyke et al. (2012) is an unsuitable reference for BC absorption coefficients; a review on BC would be much better; the already quoted review by Andreae and Gelencser (2006) should work.

Page 17471, line 24: the result → the results

Reference section: I suspect that “P. Natl. Acad. Sci. USA” is not the correct abbreviation for this journal. I would guess “P.” should be “Proc.”

Page 17473: fix subscripts/superscripts in the title of Bones et al. reference.

Page 17481: fix alpha and beta in the title of Zhang and Zhang reference.

Page 17483: Where TN → TN.

Figure 2: I have a couple of issues with this figure. The first issue is related to the

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ambiguity of FTIR band assignments mentioned above. The decomposition of the observed profile into sub-bands does not look very convincing to me, especially for the “1563”, “1315”, and “1050” bands shown in panel b. The authors should explain how their peak centers and band widths were chosen in the fit. The second issue is technical: what is the significance of different colors (if any) used in this figure? This has not been explained in the caption or text.

Figure 3: I would make capitalization of panel labels uniform; the red arrow in panel (a) is not placed well; the choice of red line on blue background in panels (c) and(d) is likely to make the red line invisible in print. In terms of the experimental design, I think it was not ideal to turn the lights off and add extra ammonia at the same time, as shown in panel (b). It would have been better to wait between these two events.

Figure 6: I believe the second sentence should reference (c) and (d), not (b) and (c).

Figure 7: m-mylyene -> m-xylene

REFERENCES MENTIONED

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