

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

Received and published: 30 September 2015

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.

C7412

Response: Thank you so much for your positive comments and suggestions.

GENERAL COMMENTS

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.

Response: Thank you for your suggestions. In the introduction, we shall weaken the statements about the possible role of NH₃ uptake reactions by relevant organic aerosols. For example, the word “significant” will be replaced with “possible” in line 26, page 17451. The sentence in lines 23–29, page 17452 will be revised as “Although it has not been confirmed with ambient data, the formation of light absorbing compounds has been inferred in laboratory studies during reactions between glyoxal, methylglyoxal and primary amines glycine, methylamine and ammonium (Zarzana et al., 2012; Yu et al., 2011; Powelson et al., 2014; Lee et al., 2013a; Trainic et al., 2011). Visible light absorption has also been observed from the reactions between O₃/OH initiated biogenic and anthropogenic SOA and NH₃ (Updyke et al., 2012; Nguyen et al., 2013; Lee et al., 2013b; Bones et al., 2010).” A new sentence as “Recent studies have found that BrC produced via such reactions is unstable with respect to degradation by oxidants (Sareen et al., 2013) and sunlight (Lee et al., 2014; Zhao et al., 2015). Regardless, NOC are likely have very interesting chemical properties and atmospheric implications.” will

C7413

be added in line 4, page 17453.

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.

Response: Thank you for your good suggestion. The references will be updated as you suggested. For example, "Alexander et al., 2008" will be replaced with "Laskin et al., 2015" in line 8, page 17451; "Andreae and Gelencser, 2006; Powelson et al., 2014; Alexander et al., 2008" will be replaced with "Andreae and Gelencser, 2006; Alexander et al., 2008; Moise et al., 2015" in lines 9-10, page 17451.

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.

Response: Thank again for this suggestion. As you pointed out, Flores et al. (2014) have examined the composition of NH₃-aged SOA from ozonolysis of alpha-pinene and limonene with DESI-HR-MS. In that study a significant increase in the fraction of organic constituents with one or two N atoms after ageing with NH₃ was observed. For NH₃-aged limonene SOA, they also observed products containing 1-4 units of ketolimononaldehyde and 0-2 nitrogen atoms in the m/z range of 168 - 360 with ToF-AMS. Due to the differences in the precursors and the mass range used, we cannot

C7414

directly compare their results with ours. However, in their work, 1-2 N atoms have been observed in both reaction systems. This is consistent with our results. Therefore, the following sentence will be added in our revised manuscript "Our results are consistent with the previous work that observed a significant increase in the fraction of organic constituents with one or two N atoms for NH₃-aged alpha-pinene SOA (Flores et al., 2014)." in line 10, page 17458.

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 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.

Response: While we cannot entirely rule out the possibility that some N-containing fragments might be formed in the ionization region of the AMS it is likely to be very small. Since pinonic acid contains one isolated carbonyl, Schiff-base or Mannich reactions may occur during synthesis of the ammonium salt from pinonic acid in the laboratory. Hence, here, we directly measured the mass spectrum of pure ammonium benzoate (Fig. R1). While some N-containing fragments were observed in Fig. R1B (when the mass loading of OA was around 200 μg m⁻³), the fragment pattern was very different from that observed in chamber experiments (Fig. R2 and Fig. S3), in which the signals of C_xH_yN_n and C_xH_yON_n were prominent. These fragments are not likely to be observed at the low aerosol loading levels of our chamber experiments. Hence it is highly likely that the uptake of NH₃ mainly contributed to the signals of NOC during photochemical reaction of m-xylene. We do recognize that some uncertainties might arise from the possible pyrolysis/ionization processes in the AMS. In the revised manuscript (Page 17455, line 18), we have added some discussion about this possibility as "It should also be pointed out that some NOC species may be formed through

C7415

the pyrolysis/ionization processes occurring in the ionization region. This would result in a positive uncertainty for NOC measurements in this study, although it is expected to be small”.

Fig. R1. Mass spectra of (a) non-N-containing species fragments and (b) N containing species fragments of ammonium benzoate.

Fig. R2. Mass spectra of (a) non-N-containing species fragments and (b) N-containing species fragments in the SOA formed by OH oxidation of m-xylene in the presence of 66 ppbv NH₃ (Exp. M16).

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.

Response: We agree with you that chemical uptake of one NH₃ is accompanied with a release of one or more H₂O molecules in Schiff-base reaction. If the H₂O molecules escape from the particle surface and the NOC has a similar molar volume as the initial carbonyls, the overall particle mass and size will reduce. However, if the formed H₂O remained on the particle surface, the particle size will increase after uptake of NH₃. It should be noted that uptake of an additional aldehyde in Mannich reaction will lead to an increase of particle size. In addition, the measured uptake coefficients are comparable to the similar reaction systems as discussed in page 17467. This also increases

C7416

the confidence with respect to the method used in our work.

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.

Response: Yes, the assignment of the IR band at 2195 cm⁻¹ is highly speculative. In the revised manuscript (lines 7-8, page 17459), the sentence “. . ., which was not present in the α-pinene derived SOA (Fig. 2) and was assigned to ν_s,C=C-CiCžN (Lin-Vien et al., 1991) (a nitrile).” will be revised as “. . ., which was not present in the α-pinene derived SOA (Fig. 2) and was potentially assigned to ν_s,C=C-CiCžN (Lin-Vien et al., 1991) (a nitrile).” The discussion, in lines 4-8, page 17460, will be revised as “In addition, SOA, which was formed through the ozonolysis of α-pinene and d-limonene, subsequently impacted on a polymeric plate and then exposed to gaseous NH₃, resulted in a significant enhancement in relative abundance of several NOC molecules, such as, C₉H₁₁NO₂, C₉H₁₃NO₂, C₁₉H₂₉NO₄, C₁₉CH₂₉NO₅, C₁₉H₃₃NO₅ (Laskin et al., 2014).”

Page 17464, line 12: is → are

Response: It will be corrected in the revised manuscript.

Page 17464, line 13: insert comma before “respectively”

Response: It will be corrected in the revised manuscript.

Page 17464, lines 14-17: there is a simple present - simple past tense inconsistency in this sentence.

C7417

Response: The “is” in line 15, page 17464 will be revised as “was” in the revised manuscript.

Page 17464, lines 19 and 23: upon -> on

Response: It will be corrected in the revised manuscript.

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.

Response: Thanks. The sentence “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” in lines 21-24, page 17464 will be removed.

Page 17466, line 19: insert comma before “respectively”

Response: It will be corrected in the revised manuscript.

Page 17467, line 1: at present -> at the present

Response: It will be corrected in the revised manuscript.

Page 17468, line 8: photo-chemistry -> photochemistry

Response: It will be corrected in the revised manuscript (page 17468, line 7).

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

Response: It will be corrected in the revised manuscript.

Page 17470, line 18: a value 1.4 -> a value of 1.4

Response: It will be corrected in the revised manuscript.

Page 17470, line 22: troposphere -> the troposphere

C7418

Response: It will be corrected in the revised manuscript.

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.

Response: Thanks. It will be updated as you suggested.

Page 17471, line 24: the result -> the results

Response: It will be corrected in the revised manuscript.

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.”

Response: Thanks. It will be corrected in the revised manuscript.

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

Response: It will be corrected in the revised manuscript.

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

Response: It will be corrected in the revised manuscript.

Page 17483: Where TN -> TN.

Response: “Where TN” will be replaced with “TN”.

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

C7419

Response: Thanks. Here, we decompose the observed profile into sub-bands to qualitatively demonstrate the presence of these species which have been assigned in Table S1. The IR curve was fitted based on the deconvolution curve as well as the frequencies of these products reported in the literatures. The peak centers which have been labeled in the figure were fixed and the band widths was set to vary during curve fitting. We only keep the same color for the same or similar species in panels a and b.

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.

Response: Thanks for your suggestions. This figure will be edited as you suggested and shown as follow (Fig. R3). Since the uptake reactions of NH₃ by OA should be related to Schiff-base or Mannich reactions as discussed in this work, UV light should not be necessary for these reaction. The objective of this portion of the experiment is to confirm whether the relatively aged SOA can take up NH₃. Therefore, additional NH₃ was introduced to the chamber immediately after the UV lights were turn off. Turning the lights off avoids unnecessary complicating SOA formation (of less aged organic material).

Figure R3. Concentration changes for N-containing fragments and SOA for (A) ozonolysis of a-pinene (Exp. P6) and (B) OH oxidation of m-xylene (Exp. M16), respectively; the relative fraction of each species to total NOC mass (TNOC=C_xH_yN+C_xH_yON+C_xH_yO₂N+NO_x) and TNOC to SOA fraction for (C) ozonolysis of a-pinene and (D) OH oxidation of m-xylene, respectively.

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

Response: Yes, it is and will be corrected in the revised manuscript.

C7420

Figure 7: m-myylene -> m-xylene

Response: It will be corrected in the revised manuscript.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/15/C7412/2015/acpd-15-C7412-2015-supplement.pdf>

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

C7421

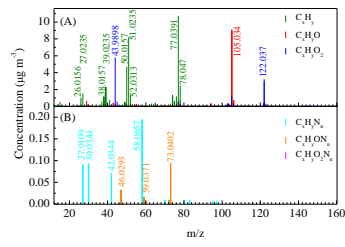


Fig. R1. Mass spectra of (a) non-N-containing species fragments and (b) N containing species fragments of ammonium benzoate.

Fig. 1.

C7422

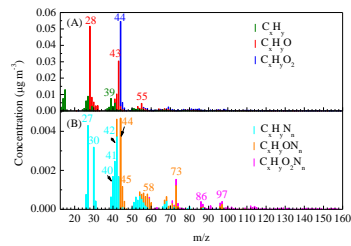


Fig. R2. Mass spectra of (a) non-N-containing species fragments and (b) N-containing species fragments in the SOA formed by OH oxidation of n-xylene in the presence of 66 ppbv NH₃ (Exp. M16).

Fig. 2.

C7423

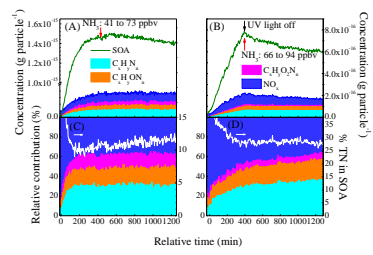


Figure R3. Concentration changes for N-containing fragments and SOA for (A) ozonolysis of α -pinene (Exp. P6) and (B) OH oxidation of m-xylene (Exp. M16), respectively; the relative fraction of each species to total NOC mass (TNOC=C₂H₃N+C₂H₃ON+C₂H₃O-N+NO_x) and TNOC to SOA fraction for (C) ozonolysis of α -pinene and (D) OH oxidation of m-xylene, respectively.

Fig. 3.

C7424