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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Nitrogen-containing Secondary Organic Aerosols Formation by Acrolein Reaction with Ammonia/Ammonium" *by* Zhijian Li et al.

Anonymous Referee #1

Received and published: 21 October 2018

This manuscript describes laboratory studies of the aqueous aerosol-phase and bulk-phase reactions between acrolein and ammonia / ammonium salts as a function of pH. This work represents a significant advance, as it identifies acrolein for the first time as a precursor for atmospheric brown carbon formation. Furthermore, this work shows that aldehyde + reduced nitrogen reactions appear to be a more general path to brown carbon products than aerosol chemists may currently suppose. This work is publishable after revisions in consideration of the following comments:

One of the conclusions of the paper (repeated in the abstract) is that 3-methylpyrazine may be produced via gas-phase reactions. Both gas-only and aerosol studies were

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performed at high humidity in a Tedlar bag, such that condensed water formed on the surface of the bag. As a result, it is challenging to confidently attribute any reaction to gas-phase chemistry alone. In addition, the o-chem literature cited in the paper does not support this, and the authors already provide what seems a more plausible mechanism. It seems that 3-methylpyrazine could be produced in the aqueous phase and then partition to the gas phase if the aqueous phase is alkaline (in non-bulk experiments where this is a possibility).

p. 4 line 4: The authors should also mention here what is known about acrolein photolysis. This might help (or refute) their later argument that reaction with ammonia / ammonium salts is an important sink for acrolein.

p. 5 line 2: How did the RH in the acrolein / ammonia experiment reach 90-100% if dry N2 and no aerosol were added?

Several of the statements made about 3-picoline (for example, p. 8 line 4) would be obvious if the authors would refer to it by its standard name (3-methylpyrazine).

p. 8 last paragraph. The logic of this paragraph is difficult to follow because of the multiple contrasting hypothetical statements (e.g. “should be formed”, “should occur”, “ought to result”). This is one point where pH and protonation effects would seem to explain the partitioning of 3-methylpyrazine.

p. 11: It should be noted that bulk experiments, by preventing opportunities for volatile compounds to evaporate as quickly as they would in aerosol particles, could result in unrealistic over-reactivity of volatile compounds.

p. 12 line 6: The effects described here are similar to how pH influences imidazole formation. Making this connection might assist the reader in developing a general chemical understanding of N-heterocycle formation in clouds.

Bottom of p. 14: It would be helpful to the field if the authors could spell out what additional information, beyond what they have provided, will be necessary in order to

take these reactions into account when evaluating climate or health effects of SOA.

The last two sentences of the conclusion seem premature based on evidence available at this point. In order to demonstrate that reactive uptake into aerosols is an important sink for acrolein, the authors would have to consider all other sinks. As noted earlier, they have not yet considered photolysis, and it is unclear whether they can realistically estimate the uptake rate into aerosol with the information gained in this study in order to compare it with OH oxidation. The last sentence also requires at least semi-quantitative comparison with other sources of N-heterocyclic brown carbon in order to determine if acrolein is "one of the important building blocks." Thus, these two sentences are not strongly supported by the evidence presented in this work.

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