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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 #3

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The manuscript by Li et al. investigates the formation of organic nitrogen compounds via the reaction of ammonia with acrolein in a series of laboratory experiments. The reaction products are characterized with a suite of analytical instrumentation and the possible contribution of these compounds to light-absorbing organic aerosol (brown carbon; BrC) is investigated through a series of bulk experiments characterized and UV-VIS measurements. The reaction of carbonyl species with ammonia is of interest to the community as it shows that reactions of carbonyls with ammonia may be more general than previously considered. However, I feel that there are several key issues that must be addressed before the manuscript is publishable.

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Discussion paper

Major comments

1) Gas-phase synthesis of 3-picoline from gaseous acrolein and ammonia seems highly unlikely to me. Although I have not read all of the references provided on pg 7 line 25-pg 8 line 1, those that I am familiar with do not support a gas-phase mechanism. Rather the reactions all require partitioning to some surface. I think it is more likely that this reaction occurs within the aqueous-phase and that 3-picoline then partitions to the gas-phase. On page 8 line 21-22, the authors state that 3-picoline is formed via a gas-phase reaction because no pyridinium compounds were detected in the wall washings. It would be useful to know what the detection limits were for the analytical instruments and what the expected partitioning would be for these compounds. Could it simply be a limit of detection issue?

2) The weak language ("might," "could be," etc.) and the lack of quantitative discussion make the discussion in the Atmospheric Implications section (3.4) unconvincing. The implications need to be considered in a more quantitative manner for the reader to really judge if the process is likely to have an effect. For instance, how does the typical pH of aerosol compare to the results presented in Sect. 3.3 and the implications for BrC? In the current form, this section contains multiple statements that are not supported by the current conclusions. This includes the statement that the conversion occurs in a few hours. While it occurred over the timescale of a few hours in this experiment, if the reaction involves partitioning to the aqueous or condensed phase (which it likely does) the reaction time will depend on environmental factors that have not been thoroughly investigated here. Additionally, the last paragraph of the section is overly simplistic. The last two sentences of the section (reactive oxygen species generation and climate/health effects) should be expanded upon or removed as they are currently not supported by the results.

Other comments

Sect 2.1: Please include the aerosol loading of the experiments.

Sect 2.1: It would be helpful to state the total ammonia (NH3 + NH4) in each experiment.

Page 5 lines 5-6: What exactly is meant by “more than enough water”? How much liquid water is estimated to be in the chamber?

Page 5 lines 7-8: If the aerosol deposited to the wall, this would be observed in the APS data. Was that the case?

Page 5 lines 9-11: “. . .in order to investigate the gas-phase reaction and liquid-phase reaction respectively.” The measurement of a compound in the gas-phase does not necessarily imply that it was formed via a gas-phase mechanism. It could be formed in the condensed-phase and repartition.

Page 7 line 19: Do the authors have a suggestion for why pyran aldehyde was no longer observed?

Page 10 line 22: I would think that the neutral species rather than the cation would be more reactive.

Sect 3.3: This section should include a description of how one expects the chemistry to differ in bulk vs aerosol reactions (i.e., with regards to partitioning of compounds).

Page 11 line 6: I believe the Jang et al. (2003) reference looked at acid-catalyzed reactions of carbonyls. I don’t think that reactions of the carbonyls with ammonia were considered.

Page 12 lines 4-6: I don’t necessarily see from the figure the decreasing signal intensity at 4.8 min. It appears that it decreases relative to the other peaks, but without a scale I don’t know how it relates in terms of absolute signal.

Page 12 line 10: Why not compare to pH 5?

Figure 5: It would be helpful to label the peaks (e.g., label the peak at 1.2 min as propylene imines).

Page 14 line 3-4: "...potential to form light-absorbing..." the pH of aerosols and droplets needs to be discussed before this conclusion can be made.

Page 14 line 12: Please see major comment 1.

Page 15 line 16-17: This sentence is currently unsupported by the atmospheric implications section. It should be removed or the atmospheric implications section should be substantially expanded and made more quantitative.

Figure 9: I don't find this figure particularly helpful. The reaction pathways have already been discussed.

General: There are numerous grammatical errors, many dealing with use of definite articles and subject-verb agreement. Correction of these errors would improve readability of the paper.

General: The resolution of the figures should be improved.

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