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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Reactions of $H^+(pyridine)_m(H_2O)_n$ and $H^+(NH_3)_1(pyridine)_1(H_2O)_n$ with NH_3: experiments and kinetic modelling under tropospheric conditions" *by* M. J. Ryding et al.

Anonymous Referee #3

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The authors present experiments of positively charged pyridine-water -clusters reacting with ammonia, and modelled concentrations of positive ion clusters formed from ammonia, pyridine, alkyl substituted pyridine compounds and water. This study is apparently the first to describe the laboratory experiments on these specific reactions. The measurements are well-planned and the results seem reliable. However, as stated by the other referees, the authors fail to express a substantial atmospheric relevance for their study. Furthermore, the results from the modelling part of this study do not, at least in the way presented currently, give significant new information: some of the

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modelling results are presumable and do not differ from the previous modelling studies, whereas the rest are based on assumptions that may not be relevant and the applicability of these results is thus questionable. I find that in order to make this manuscript worth to be published in ACP, the authors should continue measurements with related clusters and include the new results in the applied model. However, if the authors can substantially improve the manuscript by removing some of the below mentioned dubious assumptions and by clarifying and justifying the remaining assumptions as well as the motivation of the study, the manuscript may be published without conducting more experiments.

Specific comments

The motivation of the study should be more clearly expressed. If the main interest on the pyridine related ion clusters, shown in previous studies to be abundant or even dominant in tropospheric concentrations, is related to the ion-induced nucleation, it should be more accurately expressed and discussed.

In addition to the motivation of the study, I was concerned with the relevance of the applied kinetic model. The results are based on assumptions that should be expressed more clearly because their reliability is, in my understanding, dubious. In model A the applicability of Reaction (R1b) with all the possible values of m is not confirmed or discussed. Viggiano et al. have reported that the reaction rates are fast (I have not read the whole article but only the abstract) while $m + n$ is 5 or smaller. However, with NH_3 concentration of 2.5*10^{10} cm^{-3} the ion clusters may be attached to significantly more than 5 ammonias: if the evaporation is totally ignored the clusters gain tens of NH_3 molecules per second. The authors seem to point out indirectly (in pages 24547-24548), by discussing the basicity and proton affinity of the molecules, that the exchange of NH_3 to Py is not self-evident. If it does not happen, the abundance of the positive Py-NH_3 -clusters diminishes greatly. In my understanding these clusters have not been reported in the field studies.

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I agree with the other referees that neglecting the evaporation rates of Py from all the clusters in model B is not justified. It should be noted that as long as the evaporation is not taken into account, the clusters will end up in the largest cluster included in the model: Figures 8 a)-d) could as well have $H^+(NH_3)_mPy_{10}(H_2O)_n$ as the largest clusters, and they would look the same in steady state, the Py_5 -cluster would be replaced by Py_{10} and $Py_{1...9}$ would appear as $Py_{1..4}$ do now. In Fig. 8d) I also wonder, why concentration of $H^+(NH_3)_m(H_2O)_n$ is two orders of magnitude higher than the sum of $H^+(Py)_m(H_2O)_n$ at pyridine concentration equal to NH_3 concentration. The related reaction rates given are basically equal and I do not see what else could here affect the concentrations.

The authors state repeatedly that the evaporation of pyridine was not observed. However, in page 24545 (lines 14-23) they determine the maximum rate coefficient for loss of pyridine. I find that the authors should add in Fig. 3 a panel and depict the mass spectrum of $H^+Py_2(H_2O)_{11}$ in which the loss of pyridine should be seen, because the peaks in Fig. 3b) at m/z -116 and -98 are apparently taken as not statistically significant.

In consequence to the comments above I find that the authors should make some remarkable changes to the manuscript before reconsidering the publication in ACP. I suggest adding more measurements including i) testing of whether Py really replaces the NH_3 in ion clusters with large number of NH_3 molecules (or if this is shown by Viggiano et al. or by somebody else, clearly stating it), and ii) evaluation of the evaporation rate of cluster including 3(-4) Py-molecules. Expansion to other directions instead is also possible, of course. I find that with the current measured data set, there is no reason to present modelling results, because they are either very similar to previously published results, which can be expected because of only minor modifications to the previous studies, or too hypothetical.

If the manuscript is published in ACP with only the current measurement data, the authors should present and discuss the evaporations of the bases both in measurement

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data and in the model much more thoroughly.

Minor comments

- notation needs unification, now m sometimes stands for number of NH_3, sometimes of Py. In some figures there are U, V, W etc., whereas in other and in text Py, Pic, and Lu. I would also replace the notation $(pyridine)_{1,2}$ in page 24541, on line 18, e.g. with $(pyridine)_{1...2}$. In the abstract the values for m (on line 5) should be given.

- picoline and lutidine should be somehow described in abstract, if mentioned.

- p. 24536, line 23: should be N_2^+, not NO^+

- the similarity of the reaction rates with the molecule collision rate in atmosphere should be mentioned in the end of p. 24539

- p. 24540, line 9: abbreviation QTOF should be opened

- p. 24540, line 25: “number of collisions below 10

- p. 24541, line 12: production of protonated water clusters from O_2^+ and N_2^+ should be explained in few words

- p. 24542, line 25 and thereafter: “m/z -18 relative the parent ion” should be expressed perhaps as “m/z 18 u smaller than parent ion”

- p. 24548, lines 14-17: this should be mentioned in Methods and/or Results

- p. 24550, lines 5-18: these are results and should be moved at least partly to Results section

- p. 24550. lines 27-28: how significant was the difference in rate coefficient to that assumed by Beig and Brasseur?

- Table 1: notations, there are some m:s appearing (e.g. in the third and 18^{th} reaction), some m:s are changing to x (e.g. 7^{th} reaction)

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- Table 1: rate coefficients for “cluster + aerosol” and “recombination” seem to be in wrong order, recombination coefficient should be higher

- Table 2: are there any negative ions to recombinate with?

- Fig. 4: Why is there no curve for -H_2O in 4a) ?

- Fig 6.: Some value is needed for the rate coefficient with which the rates are normalized.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 24535, 2011.

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