Atmos. Chem. Phys. Discuss., 11, C9675–C9678, 2011
www.atmos-chem-phys-discuss.net/11/C9675/2011/

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 #1

Received and published: 2 October 2011

The authors present measurements and modeling of the reactions of positively charged pyridine-containing water clusters with ammonia. The methods and results are presented clearly and the manuscript is well-structured. The presentation quality is high, but my concern lies in the scientific significance of the manuscript. I do not feel that the authors have motivated why this research is of importance for the atmospheric research community and thus would motivate publication in ACP. The introduction mentions aerosol formation, but the authors do not relate their results to aerosols. Furthermore, the conclusion of the paper is that atmospheric positive ions should contain

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

several pyridine molecules (Py) and ammonia, and then suggests that the fact that this is not in agreement with atmospheric measurements is due to problems with the atmospheric measurements. Although evaporation/fragmentation may have been of importance in the atmospheric measurements, I think a larger problem with the comparison is the overly simplified model used in this paper. Nevertheless, I will recommend publication in ACP if the authors can address the specific comments below, as the improvement of ion cluster models is of certain interest, although the manuscript only presents an incremental improvement of a previous model.

Specific comments

Model limitation. The model produces water clusters that then can react with pyridines, NH3, acetone and acetonitrile. When looking at ambient positive ion spectra published by Eisele, Junninen or Ehn, there are a great number of peaks around that are not related to Py. Additionally, the authors suggest that major evaporation/fragmentation may have influenced the ambient measurements, and if correct, the real ambient spectra would be even more complex. The obvious molecules that are missing in the model are at least alkyl amines and quinolones which have been observed in most ambient measurements, but a large part of the ambient ions are still completely unidentified. The last sentence in the abstract states "...cluster ions containing ammonia and more than one pyridine, picoline or lutidine molecule should dominate at ground level under typical conditions." I do not know if this should be interpreted as clusters with Py will contain more than one Py, or that the positive ion spectrum is typically dominated by clusters with several Py. If the former, this should be stated clearly. If the latter, ambient observations do not agree with this, and the limitations of the model should be discussed. Overall, the limited number of molecules included in the model, and the effect of this on the results should be discussed in more detail.

Motivation of study. To warrant publication in ACP, the reason for conducting this research, and how this benefits atmospheric science should be made clear in the introduction. Further, if the introduction is to be started with aerosols, they should be dis-

ACPD

11, C9675–C9678, 2011

cussed and related to the current study in more detail. If this is not possible, then the text about aerosols should be shortened and rewritten. Ions may enhance nucleation rates, but are the authors aware of papers claiming Py to be specifically important?

Experimental conditions. The title of the manuscript suggests experiments at atmospheric conditions, but as the reactions are made in vacuum, I would not call the conditions atmospheric. The authors could consider modification of the title. Another concern I have relates to the large water clusters used in this study. Do the authors suggest that water cluster ions with 10 or more water molecules are abundant in the atmosphere? The amount of water molecules attached to cluster ions should also be a function of RH. What was the RH of the sample entering the QTOF? If the ESI does not produce atmospherically relevant clusters to begin with, the reaction rate coefficients derived from the experiments are also not relevant.

Fig 2. Is there no loss of U1-U4 clusters, or is this only missing in the figure? If this truly is lacking in the model, then this could cause major errors in the resulting cluster distributions.

Minor comments

Introduction: - The authors state that ion clusters are more stable than neutral clusters, but this is not correct for all clusters. Adding a charge to some clusters will cause them to become much less stable, e.g. small clusters of one strong base and one strong acid. This statement should be reformulated.

- The ion formation process description only talks about cluster formation, but charge transfer should also be discussed.

- 24537, row 18. Should be Eisele 1983?

- Please also define the range of n in H+(Py)_m(H2O)_n

Results: - 24543, rows 8-24 are hard to follow, and the authors might consider adding a diagram to make the reactions more clear.

ACPD

11, C9675–C9678, 2011

- 24546, row 14. Including this reaction in a model that also includes reaction R1b does not make sense to me. In practice these are opposite reactions, exchanging between Py and NH3 in the clusters. What is the net effect of these reactions, and how are the rate coefficients determined in the situation where both are used compared to when only one is used?

- 24550, row 27: “give loss of” should be reformulated.

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