Atmos. Chem. Phys. Discuss., 8, S8467–S8470, 2008
www.atmos-chem-phys-discuss.net/8/S8467/2008/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Secondary organic aerosol formation from primary aliphatic amines with NO_3 radical" *by* Q. G. J. Malloy et al.

Anonymous Referee #3

Received and published: 22 October 2008

The atmospheric fate of amines has recently got attention in a series of interesting paper. The present paper is focused on night-time chemistry of four amines (primary aliphatic) and their potential to form secondary organic aerosol. The understanding of the chemistry investigated has potential to be of great value in order to establish the reaction mechanism for amines and to elucidate their role in atmospheric chemistry. Consequently, these types of studies are within the scope of ACP. Furthermore, the experimental part has been done in a good and controlled way using a suit of high quality/advanced instrumentation for this type of study (PTR-MS and HR-ToF-MS). Unfortunately, I will add to the criticism pointed out by Referee 1 in the lack of proper data evaluation and interpretations. For my concern this paper needs to be revised considerable and some key aspect being addressed. In addition, I noticed another paper with

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

an overlapping set of co-authors treating a similar system. (tertiary amines-by Erupe et al, ACPD). Rather unconventionally, I would encourage the co-authors to read the ACPD comments on that paper as well since it clearly addresses the method an evaluation as such. Even thought I encourage a full revision of the paper I have selected a few topics that I think could be useful to address specifically in addition to some minor items:

Selected topics:

Mechanism. A good proposed mechanism (such as the attempts in Figure 1 and 12) is essential for the success of this paper but in the present state this is poorly described and not well assigned to the observations and the open literature. Here the authors have a major and important task to more clearly being able to present a useful and plausible mechanism that can be tested against models, field studies or future experiments. Is there any possibility to be more quantitative? 1) Use of the measurements and standards for compound/compound class can at least give a hint on the magnitude of the yield for respectively compound. 2) From fundament knowledge in kinetics, like use of bond strength etc, one can help the reader by addressing the major partway(s) for a specific reaction. E.g. the NO3 abstraction (if this is the mechanism) should be very sensitive to the bond strength and will predominately abstract hydrogen from the carbon skeleton, i.e. C-H weaker than N-H. For the amines with long carbon chain an abstraction of secondary hydrogen is preferable to primary hydrogen. These statements can be brought forward already in the introduction when discussing Figure 1. (the missing night-time aspect of that figure has already been pointed out by referee 1, e.g. no NO present and NO3 initiating the reaction). Figure 12: Interesting thoughts that in addition could explain any molecular yield higher that one. The figure caption should state something about "surface reaction" if that is a pre-request for the protonation. The "alcohol" reacting with the amine needs something more, i.e. is it charged?/radical?). It would be beneficial if this statement be proven by time traces of carbonyl products disappearing as a result of this reaction.

ACPD

8, S8467–S8470, 2008

Interactive Comment

Evidence of NO3 reaction. Here it is unfortunate that the amines could not be directly measured in the chamber. Again looking at the "sister" paper for tertiary amines where all amines are disappearing by reaction with ozone it is not clear that NO3 is the initiating oxidazing agent for amines. However, old kinetic data (Tuazon et al., 1994) reveals that primary amines are much slower with ozone than tertiary amines which may give hope for the NO3 radical reaction in the second phase of the experiment, but this need to be established! Another caveat is that there is clearly something happening when adding just the amine to the chamber. Is there any amine left when NO3 is produced? The last concern for NO3 being the primary oxidant for the amines is to put forward evidence for NO3 being produced in significant concentration in the chamber. The reaction between NO2 and ozone is a rather slow reaction and since there is no time trends on O3, NO and NO2 one can not judge how much of amines that can react with NO3.

Influence of HONO from the chamber walls. Sometimes large chambers have difficulties to maintain low levels of HONO, depending on history of the chamber. HONO is well known to react with amines and may influence e.g the initial aerosol production. This will obvious have an influence on the interpretation of the results. Can one conclude that HONO was not present and did not influence the result at any stage of the experiment?

Reproducibility. The paper is based on four experiment (one for each amine). In order to be conclusive on the findings at least one experiment should be reproduced using the same condition. This is very high priority since the results are rather unexpected and consequently ruling out variation in smog chamber conditions would certainly add to credibility.

Minor recommendations/comments:

Title: The title should be revised forming a complete sentence. E.g. "SOA formation from oxidation of primary aliphastic under nighttme conditions". I would avoid NO3

ACPD

8, S8467–S8470, 2008

since I am not convinced the fate of the amines and subsequent SOA formation are influenced by NO3 radical chemistry (but that depends on the outcome of re-evaluation as described above).

Abstract: Row 8 "by extension NO3" needs to be revised depending on the findings of the re-evaluation.

Page 12697: row 7-9: A certain oxidation product will by definition have a specific vapour pressure. rephrase.

Its not very common nowadays to use units such as: "psig"

Presence of water. was the experiment dry experiments?

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 12695, 2008.