Atmos. Chem. Phys. Discuss., 8, S9981–S9985, 2008
www.atmos-chem-phys-discuss.net/8/S9981/2008/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Glyoxal uptake on ammonium sulphate seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions" *by* M. M. Galloway et al.

Anonymous Referee #1

Received and published: 17 December 2008

General comments:

In this paper a relatively small number of experiments are described that add significantly to our understanding of the processes involved in the direct uptake of glyoxal by aerosol. The authors expose ammonium sulfate (AS) aerosol to glyoxal in the dark and under irradiated conditions and then compare the results with each other and with previous studies. Several significant conclusions are mined from these comparisons, and a few as-yet unexplainable differences in experimental results are flagged. For the most part the discussion is very clear.

In the dark, the major products detected by AMS are glyoxal oligomer peaks. These

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

peaks slowly disappear when the aerosol is diluted, which directly demonstrates for the first time that glyoxal oligomer formation is reversible in aqueous aerosol at 50% RH. This is not unexpected because NMR studies of concentrated aqueous glyoxal solutions have shown that the formation of glyoxal oligomers is a reversible process. Since a dilution experiment performed on solid aerosol did not detect a reversal of particle growth due to glyoxal uptake (1), it appears that reversible glyoxal uptake may be a function of particle phase.

Using high-resolution time-of-flight AMS, the authors unequivocally show that organosulfate compounds are not formed when glyoxal is taken up in the dark by non-acidic aerosol. However, when the lights are turned on, acidic products of glyoxal oxidation are observed, and these acids are enough to catalyze the production of organosulfates, which are also observed. This result is consistent with previous studies where organosulfates were formed on acidic aerosol.

Unlike in a previous study where oxidants were supplied to the system (2), in this study the total SOA formed did not increase with irradiation. The authors note that the first generation oxidation products of glyoxal are likely to repartition to the gas phase, and that irradiation increase the chamber temperature, also favoring vaporization. The implication, never quite spelled out, is that oxidant concentrations were probably too low to produce significant amounts of oxalic acid or even to catalyze oligomer formation through other pathways (3).

The most surprising result is the AMS detection of the irreversible production of small amounts of C-N-containing molecules. The only nitrogen source in the experiment is the AS aerosol itself, suggesting a direct reaction between glyoxal and particle-phase ammonia. The authors do not directly address whether the rate of this reaction is enhanced by irradiation, but note that the C-N products are seen both in the dark and during irradiation. The authors hypothesize that an imidazole derivative has formed based on a similar, known glyoxal + ammonia + formaldehyde reaction. While the product exact mass (and therefore formula) is confirmed by HR-ToF-AMS, the fragmentation pattern, which is often not structurally specific, is the only direct experimental evidence presented in support of this particular product structure. A bit more evidence would nail it.

The applicability of Henry's law constants to describe glyoxal uptake by aerosol has been the subject of recent debate. The data analysis in this work, showing a constant ratio between glyoxal concentrations in the gas phase and in the aqueous aerosol phase (as measured by aerosol growth), provides strong support for the usefulness of Henry's law constants in describing the uptake of glyoxal by aqueous-phase aerosol. While the authors make a convincing argument that glyoxal oligomerization should make the relationship non-linear at high concentrations, it is in fact surprisingly linear, as they show.

Specific comments and questions:

There are two issues with the calculation of the Henry's law constant. The calculated glyoxal aerosol-phase density is far higher than the MSDS-reported density of the commercially available trimer, biasing the calculated Henry's law constants upward by almost a factor of 2. Secondly, the authors treat the entire aerosol volume as the aqueous phase. While this is likely the correct approach, the authors could report the water content of the aerosol (before glyoxal uptake, using Chak Chan's data, for example) in support.

On page 20815 line 21, the authors make the odd claim that the difference between the Henry's law constants measured in water and in AS aerosol is due to the low amount of water in AS aerosol. Doesn't Henry's law by definition normalize for the amount of water?

While the authors call the imidazole product non-volatile, they estimate the vapor pressure using an on-line calculator to be 1.43 x 10^{-3} Torr. This is at the high end of the "semi-volatile" range, certainly high for a particle-phase compound. Wouldn't partitioning theory predict that most of this imidazole would evaporate?

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

It is not clear what additional information is provided by Figure 9b. Since 9a and 9b are graphical expressions of two different forms of the same equation, why wouldn't they produce similar values for K_H?

Technical corrections:

P20808 line 6: Figure 4b can,t really be called a blank experiment.

Line 21: typo ”wass”

P20811: The peak at m/z 96 is referred to as a molecular ion, but how do the authors know that it is not a fragment of a larger molecule?

P20819 line 20. Without warning the text suddenly switches from discussing glyoxal reactions to discussing other aldehyde reactions with ammonia. The switch is confusing.

Table 3 should include the control experiments. Many more experiments seem to be described in the Experimental section than are listed here. This table should also show which experiments were irradiated.

The Fig 5 caption has a typo: the authors meant to refer to m/z 68 behaving differently than the others, not m/z 58, it appears.

References cited:

1. Hastings, W. P., et al., Secondary organic aerosol formation by glyoxal hydration and oligomer formation: humidity effects and equilibrium shifts during analysis. Environ. Sci. Technol. 2005, 39, 8728-8735.

2. Volkamer, R., et al., Secondary organic aerosol formation from acetylene (C2H2): seed effect on SOA yields due to organic photochemistry in the aerosol aqueous phase. Atmos. Chem. Phys. Discuss. 2008, 8, 1-52.

3. Altieri, K. E., et al., Evidence for oligomer formation in clouds: reactions of isoprene

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

oxidation products. Environ. Sci. Technol. 2006, 40, 4956-4960.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 20799, 2008.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper