Atmos. Chem. Phys. Discuss., 11, C9838–C9840, 2011
www.atmos-chem-phys-discuss.net/11/C9838/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Importance of relative humidity in the oxidative ageing of organic aerosols: case study of the ozonolysis of maleic acid aerosol" *by* P. J. Gallimore et al.

Anonymous Referee #1

Received and published: 5 October 2011

This study reports analysis of products of ozonolysis of maleic acid as a function of relative humidity. Several hygroscopic products are identified that explain the hygroscopicity of the product particles. Several other products or structures as suggested based on high resolution mass spectrometry form the basis to suggest an ozonolysis mechanism. In contrast to longer chain unsaturated compounds such as oleic acid, reactivity of the Criegee is dominated by its reaction with water leading to a number of highly oxygenated peroxides, acids and aldehydes; notably, no oligomerisation is observed. The authors also demonstrate that using water as an extraction medium leads to further reactions continuing in absence of ozone, further highlighting water as an important reactant.

Mainly for reasons of relatively low reactivity of maleic acid, the work was performed at very high ozone concentration to achieve appreciable product masses for analysis. This somewhat reduces the relevance of the experiment to the real atmosphere. However, at close inspection, secondary chemistry of products with ozone is quite unlikely, since the rate of first generation product formation remained comparable to those in other studies with lower ozone concentration but more reactive species. Nevertheless, the authors could have demonstrated that product formation scaled with time and/or concentration. The high concentration caveat should therefore also be mentioned in the abstract.

Overall this is an interesting and well done analytical study with significant implications for aging of atmospheric particles, and I recommend publication in ACP after the comments below have been addressed.

1. General comments: The manscript is overall well written and structured. However, it remains unclear about the precise role of the EDB experiments. If new EDB experiments have been performed beyond those published earlier by the same group, they should be described in the experimental part. If not, this should be clearly stated in the results section.

2. P23171, line 2: Earth uppercase

3. P23172, top lines: Vesna et al. (2008) explicitly showed that ozonolysis of oleic acid particles did not (!) lead to an increase in hygroscopicity, because the products (C9 acids and aldehydes) though are more hygrophilic, but not soluble! The increased hygroscopicity was observed with arachidonic acid, a polyunsaturated compound that breaks up into smaller chained, e.g., C3-C5 carboxylic acids, which are soluble.

4. P23174, line 25: rotameter: measurement of flow rate or pressure? How does this device 'ensure' atmospheric pressure? Is it a regulator?

5. P23175, top paragraph: was the residence time in the reaction barrel characterized?

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How?

6. P23175, middle paragraph: do the authors think that the particles were trapped in the filter in the form of individual particles, or was it rather a maleic acid film covering the majority of the filter structure?

7. P23178: discussion of volatility of some of the products? Since denuders were used to remove volatile products, the relative proportion of products may have been different. This might enter the discussion at various places.

8. P23180, line 27: the authors could also cite Shiraiwa et al. (2011) that establishes a direct link between ozone uptake and diffusivity.

9. P23186, section 3.4 and also discussion of hygroscopicity of products further above: deliquescence points of mixture may often not be the ‘average’ of DRHs of the pure compounds. This in mind, an oxidized layer could also lead to solvation of the maleic acid core.

References:

Shiraiwa, M., Ammann, M., Koop, T., and Pöschl, U.: Gas uptake and chemical aging of semisolid organic aerosol particles, Proceedings of the National Academy of Sciences, 108, 11003-11008, 10.1073/pnas.1103045108, 2011.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 23169, 2011.