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Atmospheric
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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 #2

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General Comments

In this manuscript results of experimental studies of the effects of relative humidity on the aging of maleic acid particles exposed to O3 are presented. Maleic acid is a solid C4 unsaturated dicarboxylic acid that is present in atmospheric aerosol particles and O3 is an important atmospheric oxidant. Particle phase reaction products are identified by electrospray mass spectrometry and changes in particle mass are monitored in an electrodynamic balance. A reasonable chemical mechanism is presented that explains the formation of the products, and the chemical composition of the particles is used to predict hygroscopicity in good agreement with measured water uptake. The study

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is very well done. The results demonstrate enhanced O3 reactivity of the particles when exposed to high humidity, which is apparently due to formation of an aqueous maleic acid solution (sometimes as a thin film) in which maleic acid is more accessible to O3. Interestingly, water affects the extent of the maleic acid-O3 reaction even if the particles are no longer exposed to O3. The explanation for this is not entirely clear, but the results indicate that there is a need to better understand the interactions of oxidants and water with organic aerosol particles. The paper is clearly and concisely written, with appropriate figures and tables. The results of the study are sufficiently interesting and potentially important that I think the paper should be published after the following comments are addressed.

Specific Comments

1. Page 23185, first sentence: It seems reasonable that the observed activation energy for the first order loss of mass is indicative of peroxide decomposition, but probably specifically the secondary ozonides. The 100 kJ/mol value is very similar to values measured by Hull et al. [J. Phys. Chem. 76, 2659 (1972)] for gas phase thermal decomposition of monocyclic secondary ozonides, but not bicyclic secondary ozonides. Furthermore, studies of the decomposition kinetics of alkyl hydroperoxides indicate that decomposition of these compounds at room temperature is negligibly slow for periods of days [Durham et al., J. Amer. Chem. Soc. 80, 332 (1958)], and probably many months, since cumene hydroperoxide can be obtained from commercial suppliers and is quite stable for long times.

2. Page 23185, last sentence: The suggestion that MA ozonolysis is a good model for aging may not be quite justified. I would think that the reason the products are so different from most other alkenes is the absence of CH2 groups. In this regard, MA might be an outlier.

3. Page 23186, bottom paragraph: It is suggested that primary ozonides are stable and long-lived in the solid after exposure to O3 and that they then decompose when

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the particles are exposed to water. Is there any evidence in the extensive ozonolysis literature that primary ozonides are so stable at room temperature in solids? I would have thought not. Could it instead be that O3 diffuses throughout the particles during the hours of exposure, but does not react until the MA is exposed to water? This could be tested by outgassing the particles for a few hours or more before adding water.

4. What is known about the products of the reactions of water with secondary ozonides?

5. Is there any fragmentation in the mass spectrometric analysis? For example, could decarboxylation occur there for negative ions?

Technical Comments

None

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

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