

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.

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We thank the reviewer 2 for the valuable comments. Below are detailed answers to the reviewer's comments.

1. As suggested by referee 2 we mention now that observed mass loss in the EDB experiments could also be due to compounds other than (hydro-)peroxides (on p.23185, line 4): “... or peroxide bond with bond strength 100 kJ mol⁻¹ or other compounds with similar bond strength e.g., secondary ozonides (Pope et al., 2010a; Hull et al., 1972).”
2. The last sentence of 3.3 is now reworded as suggested by the reviewer: “Higher
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oligomers are often detected in laboratory models systems (Kalberer et al., 2004; Reynolds et al., 2006) but less clearly observed in field samples (e.g., Samburova et al., 2005). Oleic acid, where high-mass oligomers are frequently observed and maleic acid where only dimers (but no higher oligomers) could be detected could possibly be used to represent two opposing endpoints for model systems of particle phase reactivity for less oxidized and highly oxidized organic particles, respectively.”

3. We have not found any literature data to support the proposed possible stability of the ozonide on the solid and dry particle surface. In the EDB experiments (Pope et al., 2010a) the particles were exposed to ozone for only one hour and then flushed with pure air for over 30hrs before the humidity was increased (see Figure 3, Pope et al., 2010a). This suggests that any physisorbed and unreacted ozone on the dry particle surface or in the particle bulk would have desorbed before RH was increased in the EDB.

4. We do not proposed formation or reaction of secondary ozonides in the manuscript. We added a reference (Karagulian et al., Chem. Chem. Phys., 2008) supporting our suggested reaction scheme (Figure 6) and the dominant role of water as a reactant for the primary ozonides and Criegee intermediates. A new sentence is added on p.23183, line 19: “The high reactivity of the ozonide with water is also described by Karagulian et al. (2008) where very similar water-dependent reaction routes are proposed. ” And on p.23183, line 26: “The hydroperoxide is expected to further react to form formic acid and CO₂ or GA and H₂O₂ as suggested by Karagulian et al. (2008).”

5. Decarboxylation of carboxylic acids can be observed in ESI mass spectrometry. A note of caution is now added on p. 23184, line 6: “Peaks at m/z 87.0 and 118.9 are explained in the proposed reaction scheme in Figure 6 as products of decarboxylation reactions. However, these peaks could potentially also result from decarboxylation within the mass spectrometer as it was observed for maleic acid (see Figure 2a). We assume that such mass spectrometry artifacts are minimal because we observe possible reaction products of both decarboxylation products (i.e., m/z100.9, 116.9, 133.0),

which could not be observed if these peaks would largely results from mass spectrometer artifacts.”

Figure 6, Step C: the reaction now mentioned on p.23183, line 26 (Karagulian et al., 2008) is added to the Figure (see point 4 above).

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