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Atmospheric
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Interactive comment on "The relative importance of competing pathways for the formation of high-molecular-weight peroxides in the ozonolysis of organic aerosol particles" *by* M. Mochida et al.

Anonymous Referee #2

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Mochida et al. make a significant contribution to our understanding of stabilized Criegee intermediate (SCI) reactions to secondary organic aerosol (SOA) by quantifying the relative importance of secondary ozonide and peroxide channels. Previous studies have been inconclusive as some have implicated the ozonide channel (e.g. Lee and Kamens, Atmospheric Environment (2005) 39, 6822) and others the peroxide channel (e.g. Docherty, Wu, Lim and Ziemann, Environmental Science and Technology (2005) 39, 4049) as the major route. Mochida et al. show for the methyl oleate system that the relative rates of the two channels are comparable, which is consistent with a recent study by Tolocka, Heaton, Dreyfus, Wang, Zordan and Johnston, Environmental Science and Technology (2006) 40, 1843.

This review is being written with the benefit of Reviewer 1 and 3 comments already posted. This reviewer concurs with the previous comments, particularly those of reviewer 3 regarding the kinetic analysis. Three additional comments are given below.

Both reviewers highlight the impact of high molecular weight (HMW) products for CCN activity. An equally important impact is gas particle partitioning: The primary products in Fig. 2 (NN, OAME, NA, AAME) are volatile or semivolatile. If HMW products did not form, most of the aerosol mass would be lost upon reaction. The possibility of a significant loss of aerosol mass owing to oxidation has been suggested in the literature (Molina, Ivanov, Trakhtenberg, Molina, Geophysical Research letters (2004) 31(22), Art. No. L22104). Mochida et al. show that aerosol mass loss for the MO system is relatively small. It would be very interesting to study how the competition between primary product evaporation and HMW product formation changes as the particle size decreases. An increasing surface to volume ratio should favor evaporation. The authors performed this experiment with relatively large particles (500 nm dia.) which favors volume processes such as HMW formation over surface processes such as evaporation. Can the experiment be repeated, for example, with 100 nm dia. particles to probe this effect?

It is well known from the authors' previous work and from the work of others (e.g. Baer) that the kinetics of oleic acid ozonolysis is complex. However, the discussion in section 3.1 avoids this topic. Since the main motivation for using MO over oleic acid is the potential for a simplified product distribution, it is important to understand how the kinetics mechanisms compare as well. For example, is there evidence for surface shell polymerization during MO ozonolysis as is observed with oleic acid? How well do the data in Fig. 3 fit an exponential vs. square root time dependence? Please comment on the mechanism in some detail.

Finally, the reproducibility (repeat measurements at a given time) and repeatability (repeat measurements on different days/weeks) should be addressed. Is the product distribution (relative signal intensities) stable over time? Or is there an inherent instability associated with the cascade of reactions leading to the formation of specific HMW products?

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7137, 2006.

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