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Atmospheric
Chemistry
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Discussions

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 #3

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Mochida et al. address an important emerging topic in atmospheric chemistry, namely the secondary reactivity of Criegee intermediates (CI) from the ozonolysis of unsaturated organic particle phase species. Recent work has emphasized the unsaturated fatty acid, oleic acid (OL), and a host of high molecular weight (HMW) products, many peroxides, are observed. These low volatility, HMW products have atmospheric implications such as transforming the particulate into more efficient CCN. We need a better quantitative description of the peroxides that form under specific conditions and of the importance of the reaction channels. These topics are addressed in the current work of Mochida et al. using a derivative of OL, methyl oleate (MO). MO presents a logical choice for a model compound to explore the secondary chemistry of the CI in that it

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does not have the carboxyl group as does its fatty acid congener, which is associated with reactivity with CI. Hence the authors are able to interrogate two product routes, one going to secondary ozonides (SOZ) and the other to alpha-acyloxyalkyl alkyl peroxides (alpha-AAHP-type compounds), via the respective addition of an ester (dioctyl adipate) vs. an alkanoic acid (myristic acid).

This work is timely, original and in accord with the scope of ACP. There are some points that I feel should be addressed or clarified by the authors which are listed below.

Questions and Issues

1) Page 7138, line 9: Reference to specific companies should not be made in the Abstract, unless central to the science, which is not the case here. The specific reference to “Aerodyne” should be removed. 2) Page 7138, lines 23-25: the last sentence is misleading, giving the impression that these are the first results to suggest that HMW organic peroxides could result from ozonolysis of unsaturated organic molecules in the atmosphere. This has already been shown by several groups previously, as acknowledged by the authors. The focus of this report is on a quantitative measure of these organic peroxides. I would suggest that this last sentence be removed. 3) Page 7142, line 6: The term “atomizing” in the second line of Sec. 2.1 is a misnomer (although commonly used). There is no atom formation taking place. The correct terminology is “nebulizing.” 4) Page 7143, line 4: Was the interaction time of 6 s determined experimentally, or estimated from simple flow considerations? This should be clarified. 5) Page 7143, line 24: Again, the interaction time of “0 s” with the injector tube fully inserted is a “reference zero” for this particular study. Was this measured experimentally or is it simply the shortest interaction time that serves as the “0 point?” 6) Page 7145, line 16: A difference of up to 507) Page 7146, lines 22-24: The authors discuss bis(acyloxy-1-alkyl) peroxides (BAAP’s , see lines 233-237) and reference older works by Rebrovic and Nishikawa. Ziemann [1] has a much more recent observation and discussion of these types of peroxides and should be referenced and possibly this work should be discussed. Moreover, Ziemann’s observation is based on the ozonol-

ysis of aerosols, as compared to the works of Rebrovic and Nishikawa. These latter reports were for solution-based bulk chemistry and might be considered less relevant that Ziemann's work. 8) Page 7147, line 20: The value of the uptake coefficient has an associated error, but no error bars are evident in Figure 3. 9) Page 7147, line 20: Is the reference to Katrib et al 2005 a) or b) or both 10) Page 7148, line 13: How was the evaporation rate of reacted particles determined? Since the particles were "reacted to completion," what served as the zero evaporation time? This should be clearly detailed. 11) Page 7148, line 24: What is the justification for inference that the sum of the volume fractions of the four LMW products has an upper limit of 512) Page 7149: This entire discussion should be clarified extensively. Try as I might, I was not able to reproduce the numbers with the data provided in Table 1. In fact, the authors appear to have used data that is not reported in the Table. For example, the authors calculate a ratio of particle masses before and after ozone exposure, but in order to calculate this ratio, the mobility diameter of the reacted particles is needed; however, only the aerodynamic diameters (as determined with the Aerodyne instrument) are given in the Table. 13) Page 7149, lines 10-11: The authors state that a correction could be applied for evaporative losses of the products but that they did not apply the correction. Why not? 14) Page 7149, lines 14-15: The authors are making a second inference based on a first, unsubstantiated inference (see item "i.") 15) Page 7166, Table 1: First line should read "increasing reaction time" 16) Page 7166, Table 1: The caption is not clear, especially regarding the longer residence times of 27 and 45 seconds. Do the authors physically change the tubing between the flow tube and the DMA? If so, what tubing length was used for the "0" and "6" s measures? I assume that there was always some connecting tubing present. Are the "2" and "20" seconds in addition to the tubing used typically? Assuming that there was always some tubing connecting the flow tube to the DMA, then "0" and "6" second residence times were actually longer. How much? This should all be clarified. 17) Figure 2: The products observed should be indicated with underlining. For example, the authors observe SOZ2/3 but not SOZ1, which they discuss in the text, yet are not clear on the figure. 18) Figure 3: Error bars should be included. If smaller than the data symbols (which I don't think is the case), it should be stated. 19) The authors focus on secondary chemistry that forms peroxide particles but a mechanism for oxygenation by ketone formation has been proposed for OL [2], observed for the ozonolysis of OL[3, 4], and in unsaturated methyl esters[5]. This route should be discussed. If it is an unimportant route in these MO based systems that should noted and justified. 20) Kinetic analysis: In general, more details are needed on the reactive uptake calculations: Is the calculation of the uptake coefficient data driven or model driven? If the calculation is (resistor) model driven, what is the limiting case regime used? This regime should be discussed in context of not only other findings for MO, but OL as well since there are still questions about the reactive uptake of ozone by the OL system being a surface reaction or limited by the diffusion of ozone within the particle - did the reactive uptake of measurements using MO provide additional insight about the reactive uptake by OL, which has been adopted as a model heterogeneous reaction system? 21) In the spirit of ACP some of the implications of these HMW oxygenated products towards CCN ability and subsequently radiation effects (indirect aerosol effects, etc) should be included.

1. Ziemann, P.J., Aerosol products, mechanisms, and kinetics of heterogeneous reactions with oleic acid in pure and mixed particles. Faraday Discuss., 2005. 130(25): p. 469-490. 2. Katrib, Y., et al., Products and mechanisms of ozone reactions with oleic acid for aerosol particles having core-shell morphologies. J. Phys. Chem. A, 2004. 108(32): p. 6686-6695. 3. Hearn, J.D. and G.D. Smith, Kinetics and product studies for the ozonolysis reactions of organic particles using aerosol CIMS. J. Phys. Chem. A, 2004. 108(45): p. 1019 -1029. 4. Zahardis, J., B.W. LaFranchi, and G.A. Petrucci, Direct observation of polymerization in the oleic acid - ozone heterogeneous reaction system by photoelectron resonance capture ionization aerosol mass spectrometry. Atmos. Environ., 2006. 40(9): p. 1661-1670. 5. Zahardis, J., B.W. LaFranchi, and G.A. Petrucci, The heterogeneous reaction of particle-phase methyl esters and ozone elucidation by photoelectron resonance capture ionization: Direct products of ozonolysis and secondary reactions leading to the formation of ketones. Int. J. Mass Spectrom.,

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