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Comment

Interactive comment on “The oleic acid-ozone heterogeneous reaction system: products, kinetics, secondary chemistry, and atmospheric implications of a model system – a review” by J. Zahardis and G. A. Petrucci

Anonymous Referee #1

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General Comments

The authors have written a very thorough and valuable review of recent research carried out by atmospheric chemists on the ozonolysis of oleic acid and related compounds. This is an important model system for studies of organic aerosol oxidation, and the review covers all the important areas and does a nice job of summarizing major findings and future research needs. The manuscript represents a large amount of time and effort and the community will be indebted to the authors for this contribution. The manuscript is well written and includes the important references (with the addi-

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tion of those mentioned in the comment by Adrian Tuck). It is certainly appropriate for publication in ACP, but I have some comments that should first be addressed.

Specific Comments

1. Section 1.1: This is a nice review of the literature on organic/fatty acids. Considering that the focus of this manuscript is oleic acid, however, I suggest the authors include specific information on what is known about the contributions of unsaturated organic acids to primary organic aerosol emissions and atmosphere organic aerosol concentrations. My sense is that unsaturated organic acids (and unsaturated compounds in general) are a small fraction of the mass. This has a significant impact on the comments made throughout the manuscript on the potential importance of the ozonolysis of oleic acid (and other alkenes) aerosol on atmospheric chemistry and processes such as CCN activation.

2. In what respects is oleic acid-O₃ chemistry a good model for organic aerosol oxidation? Since most organic aerosol compounds are saturated, the major oxidation reactions are initiated by OH and NO₃ radical abstraction of H-atoms. The products of such reactions are in many ways quite different from those obtained from ozonolysis.

3. Page 11105, lines 9-10: What is meant by "and similar hydroperoxides"?

4. Page 11105, lines 13-15: What are the predictions based on? See Specific Comments #6 and #7.

5. Table 1 and discussion of the table: The product yields given in Ziemann (2005) are mentioned on page 11113, but are not shown in Table 1 or referred to in the discussion of primary products.

6. One concern I have with the manuscript is that the authors format much of their discussion of the reaction products around the expectation that nonanal, 9-oxo-nonanoic acid, azelaic acid, and nonanoic acid should be the major products and that their yields should be approximately the same. Significant discrepancies from this composition are

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considered to be "anomalous" or "unexpected". I am afraid that in taking this approach the authors perpetuate errors made by some previous investigators who were not sufficiently familiar with the synthetic organic chemistry literature on ozonolysis to know that the isomerization of CI to acids is a minor pathway in solution (this is also true in the gas phase) and that CI solution chemistry is dominated by bimolecular not unimolecular reactions. As a result, the reader is led to believe that the low yields of azelaic and nonanoic acids and the high yields of peroxides (secondary reaction products) are surprising, when according to decades of literature on solution phase ozonolysis it is what one should expect. Please note that Scot Martin has made essentially the same comment.

7. As an addendum to Specific Comment #6, I think it would be useful for the authors to make some comments with regards to what has been learned from the many recent studies of oleic acid (and related unsaturated compounds) ozonolysis chemistry that was not known or expected from previous solution phase studies. A synthetic organic chemist might reasonably wonder why so much effort was made on a class of reaction that has already been so well studied. Aerosol drops are not the same as a bulk solution, but they have much in common. Enhanced surface reactions and evaporation of volatiles can potentially alter aerosol products relative to a bulk solution, but it seems to me that for the most part the products and mechanisms of this reaction are the same as those established previously for bulk solutions [See the excellent review by Bailey (1978)]. This observation may help to guide future studies of other aerosol reactions.

8. Section 3.4.1: The ketone products discussed here can also be formed by "partial cleavage" of the primary ozonide (Bailey (1978), Chapter 11). According to Bailey, this is the most likely mechanism.

9. Sections 5.3 and 5.4: The discussions in both these sections appear to be predicated on the assumption that particulate alkenes are a significant fraction of the total (gas and particle phase) atmospheric alkene loading. This is certainly not the case in rural regions where terpenes such as isoprene and monoterpenes dominate the

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hydrocarbon loading. It is probably also not the case in urban areas, where primary particulate alkene emissions/concentrations are likely to be highest. For example, from the book by Calvert et al. (2000) "The Mechanisms of Atmospheric Oxidation of the Alkenes", the alkene concentration in a typical urban area is ~27 ppbv C. If one considers a relatively high organic aerosol loading of $10 \mu\text{g m}^{-3}$, this is equivalent to 17 ppbv C (assuming a composition of $(\text{CH}_2)_x$). Unless alkenes make up a large fraction of the organic PM, which I do not think is the case, it is difficult to argue that particulate alkenes could play an important role in either radiative forcing or the oxidative capacity of the atmosphere.

10. Sections 5.3 and 5.4: The emphasis on carbonyls in these sections assumes that the contributions of carbonyls to the atmosphere from particulate alkene ozonolysis are significant relative to other sources, which include the oxidation of gas phase alkenes and gas and particle phase alkanes and aromatics. Considering that particulate alkenes make up such a small fraction of the possible sources of atmospheric carbonyls, I don't see how this can be possible. Please note that the other reviewer has made a similar comment.

Technical Comments

1. Page 11100, lines 15-16: I suggest this sentence be changed to: "AMS to measure the loss of oleic acid due to O₃ uptake and reaction (Katrib)".
2. Page 11102, line 1: The sentence should probably be "coupled with time-of-flight mass spectrometry (TOF-MS) are"
3. Page 11103, line 3: See Technical Comment #1.
4. Page 11105, line 9: I believe "a-alkoxyalkyl" should be "a-hydroxyalkyl".

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 11093, 2006.