

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 #2

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General Comments

The authors have put together a comprehensive review of an important reaction which has become a model system for understanding the oxidative processing of organic aerosol in the troposphere. This ozone + oleic acid (OL) system has been studied with a variety of analytical techniques by a number of researchers. The authors do a good job of placing these varied measurements in context with one another, drawing significant conclusions from them and identifying significant questions still remaining. The paper is clearly written, the presentation is well-structured and it is appropriate for

publication in ACP. The use of bullets throughout is particularly helpful in such a long paper and makes it easier to locate important conclusions and findings. This review will serve as a good reference for those already in this field and as a good introduction for those entering it.

Specific Comments

1. Page 11,104 - The three-step process for ozonolysis appears to neglect the stabilization of the Criegee intermediates (CI) which can be especially important in condensed phases. Echoing the on-line comments of Scot Martin, it is unlikely that the CI will have sufficiently long lifetimes in the particles to be observed on the timescales of the aerosol flow tube (AFT) experiments (i.e. several seconds).

Along those same lines, could the signals that are attributed to azelaic acid as a product of the CI rearrangement originate from the decomposition of some of the secondary products (e.g. secondary ozonides, organic peroxides, oligomers)? It would be appropriate to address this possibility in the discussion of azelaic acid (end of page 11,108) and nonanoic acid (top of page 11,111).

2. Pages 11,112-5 - How are the yields of secondary ozonides (SO) and peroxides expected to be different in particles in the atmosphere? Specifically, the particles will contain many other molecules which could react with the CI. Also, there will be much less ozone than is typically used in the laboratory experiments resulting in a lower steady-state concentration of CI. This could also reduce the rate of polymer formation in ambient particles.

3. Page 11,119 - Equation 4 is true only if the stoichiometry of ozone loss and OL loss is the same. In this system, as the authors point out later, this is not true because of secondary reactions of OL. Please correct this.

4. Page 11,120 - The assumption that OL diffusion is fast is made to ensure that the OL concentration can be assumed to be uniform throughout the particle (especially near

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the surface, as the authors point out). Making this assumption allows the pseudo-first order approximation ($k = k_2 [OL]$) to be made. Please clarify this.

5. Page 11,142 - Activation isn't defined by a contact angle being finite. The contact angle will be 0-180 degrees. Perhaps the authors meant to say that activation is indicated by wetting (contact angle of 0 degrees).

6. Page 11,144 - An estimate should be made as to how important absorption of solar radiation by aldehydes formed from ozonolysis might be.

7. Page 11,147 - Tropospheric organic aerosol (OA) is probably NOT a significant sink for ozone (see on-line comment by Scot Martin). The lifetime of 36 hours cited from Smith et al. (2002) (page 11,139) is for OL, not ozone. Also, Ziemann estimated the OL lifetime to be 30 minutes (not 15 minutes) in Ziemann (2005).

8. A recently-published paper relevant to this review is not cited:

Nash, D.G., M.P. Tolocka, and T. Baer, The uptake of O₃ by myristic acid-oleic acid mixed particles: evidence for solid surface layers. *Physical Chemistry Chemical Physics*, 2006. 8(38): p. 4468-4475.

9. While one paper by Inoue et al. is cited, Inoue et al. (2004), there are others which are of relevance to the mixed particle discussion in this review. For example:

Inoue, T., et al., Solid-liquid phase behavior of binary fatty acid mixtures 2. Mixtures of oleic acid with lauric acid, myristic acid, and palmitic acid. *Chemistry and Physics of Lipids*, 2004. 127(2): p. 161-173.

Inoue, T., et al., Solid-liquid phase behavior of binary fatty acid mixtures 3. Mixtures of oleic acid with capric acid (decanoic acid) and caprylic acid (octanoic acid). *Chemistry and Physics of Lipids*, 2004. 132(2): p. 225-234.

Technical Corrections

1. Page 11,118 - Statement "The aim of this review is to provided consolidated infor-

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mation \ddot{E} ” seems out of place at this point in the paper. It appears in the introduction to Section 4 (Reactive uptake of ozone: overview”), yet it mentions products and secondary chemistry. This entire statement could be omitted without detracting from the section.

2. Page 11,118 - Hearn et al. (2005) did not derive the uptake expressions and probably should not be cited here.

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