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Atmospheric
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Discussions

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

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We wish to thank the reviewer for these well thought out comments and suggestions. We provide our responses below:

Point 1) We will expand section 1.1 to include more on primary emissions of unsaturated fatty acids. The main biogenic primary emission appears to be from bubble bursting in the marine environment. We will add any quantitative data we can find in these regards. Also in this section we will incorporate some of the references suggested by A. Tuck that deal with surfaces coated with fatty acids.

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Point 2) Oleic acid is ubiquitous in the environment and has both biogenic and anthropogenic sources. It has one degree of unsaturation, making it susceptible to ozonolysis but still tractable in terms of mass spectrometric analysis. These factors make it a logical choice of a good model system to investigate the ozonolysis of unsaturated particle-phase organics. However, we view this system, or probably any one-component organic aerosol, as a gross oversimplification of real tropospheric organic aerosol. The data that has been generated on this system has the greatest potential merit if it is used as the foundation of more progressive studies that investigate the oxidation of multicomponent aerosols. Of course these future models should try to capture the essential features of the type of organic aerosol that is representative of a given troposphere. More work has to be done with aerosols akin to the coated flow reactor experiments done by Knopf et al. [1] that employed multicomponent coatings as proxies for meat-cooking aerosols.

Additionally, this simple model system is well suited to develop and test the capacity of some of the analytical methods (mainly based on mass spectrometry) for studying heterogeneous reactivity.

In this review we have intentionally maintained what some may consider a relatively tight focus -for example, we do not discuss oxidation via OH and NO_3 radical abstraction of hydrogen atoms. Even with oleic acid, the products of reaction with these important oxidants are quite different than the products of ozonolysis, as demonstrated by the recent work by Docherty and Ziemann [2]. We will make note of such differences in the edited version of our review. Similar models, such as long-chain alkanes that simulate waxes need to be developed and investigated with the aforementioned oxidants by some of the more recently developed aerosol mass spectrometric methods. Of course, reiterating the sentiments we previously stated, mixed particle proxies that capture the key features of tropospheric particulate, have to be developed, and tested not only with one of these gases but in realistic mixtures of the oxidants.

Point 3) We are going to delete “and similar hydroperoxides”; this referred to the interconversion products described by Pryde et al. [3] that were observed only to occur in ozonolysis with water as the solvent *only* under acid catalysis. In their terminology, these hydroperoxides included: methoxy and acetoxy hydroperoxides and hydroxy hydroperoxides.

Point 4) Many works that have addressed the product yields from ozonolysis of oleic acid considered the *possibility* of the formation of acids via isomerization of the Criegee intermediates that were formed from decomposition of the primary ozonide [4, 5-10]. In that case, assuming no preferential breaking of the O-O bond of the primary ozonide and no secondary reactions, one would anticipate one equivalent of oleic acid to yield one equivalent of nonanal, 9-oxononaoic acid, azelaic acid and nonanoic acid upon ozonolysis. This was not the case as the measured product yields of these species were not equal. This was one of the first major indicators that hinted at secondary chemistry and that the heterogeneous ozonolysis of OL was more akin to the liquid phase reaction as opposed to the gas phase in terms of the fate of the Criegee intermediate. For example, as noted by Katrib et al. [11] "Rearrangements to (azelaic acid) and (nonanoic acid) are minor pathways: this condensed-phase behavior contrasts to gas-phase reactions because the high density of double bonds in the condensed phase intercepts the Criegee biradicals before significant (azelaic acid) and (nonanoic acid) can form". This is most likely due to secondary chemistry, namely that the secondary ozonides are formed then decomposed back to the acids. As noted by Scot Martin, the rearrangement of the CI to an acid is a mechanism we inherited from gas phase chemistry, and is probably not what is happening in these liquid phase aerosols. However, early in this research some of us were still considering the possibility that the chemistry would have similarities to that of the gas phase, for example Thornberry and Abbatt [10] in regards to the ozonolysis of OL coatings stated: "If this is a surface reaction, it is important to access the degree to which secondary ozonide formation occurs relative to the formation of two separate products. It is for this reason that we have so carefully focused on the product yields of this study."

We will change the wording in the appropriate sections in this regard; noting that many of us, including our own group, considered the possibility of reactivity akin to what occurs in gas-phase chemistry. It will also be noted that the results indicate that the heterogeneous ozonolysis of OL proceeds in a manner akin to liquid phase chemistry as opposed to gas phase chemistry.

Point 5) We will correct this by adding the appropriate discussion regarding Ziemann's measured yields and amending Table 1.

Point 6) This concern was answered in part in our response to Point 4. The review will be revised to place emphasis on the fact that yields of nonanoic and azelaic acid more likely arise from decomposition of the secondary ozonides, in accord with liquid phase chemistry, as opposed to the isomerization of Criegee intermediates. We still believe that the early experimental considerations were correct - kinetic studies indicated this was a near surface or surface reaction: considering other reaction pathways besides the liquid phase pathways seemed logical. We made some of the first direct assignments of peroxides produced in the ozonolysis of oleic acid aerosols [7]- and our discussion of consideration of possible rearrangement Criegee intermediates to the corresponding acid in solution was not out of insufficient familiarity with synthetic organic chemistry, but rather based on a good review of the literature that showed we still have a long way to go in descrying the behavior of high molecular weight Criegee intermediates in solution. (Please see our comments to Referee 2, Response 1, for further discussion).

Point 7) In terms of the types of products formed by the ozonolysis of OL, there are very few new types of liquid phase mechanisms and products. However, that does not mean that we have not learned a great deal and do not have a great deal more to learn from this simple reaction system. The greatest merit of studying the ozonolysis of oleic acid is in three areas: a) kinetics, b) methodology development, c) (most importantly) implications to physical properties of organic aerosol in the troposphere.

a) We have tried to discuss many of the nuances of the reactive uptake of ozone by this system. For example, we discuss in section 4.4.2.2 the experimental implication that high molecular weight products that form from the ozonolysis of oleic acid can affect reactive uptake, causing γ to have an unanticipated dependency on radius [12]. If the products have an effect on reactive uptake it seems appropriate to try to establish the chemical identity of these products, even if they are in accord with established synthetic organic chemistry.

b) Many of the methods that are described in this work, such as our own method, PERCI-AMS, are recently developed [13]. This model system, ozone + oleic acid, has proven to be a great boon in facilitating the optimization of this and other methods applicable to the analysis of organic aerosol. The fact that many of our results, and those of others, are in accord with established liquid phase chemistry is *beneficial* in helping hone the capacity of PERC-AMS and other analytical methodologies. These analytical methods are presently being used to investigate more complex multicomponent proxies that better represent actual tropospheric aerosol. We try to place emphasis on this towards the end of the review, in section 4.4.3.

c) In this review, especially section 5.2, we have tried to place emphasis on the need to consider further the role of organic aerosol as CCN based on some of the results we discuss. Substantiating the nature of the chemical mechanism and products formed, even if in accord with established solution phase organic chemistry, is important in the larger scheme of atmospheric processes: a better description of the role of oxidative processing in the enhancement of CCN ability of organic aerosol. Reiterating what was stated previously, these studies have their main merit in being the foundation for future progressive experiments with multicomponent organic aerosol reactions with multiple oxidants.

We *doubt* that as more realistic multicomponent proxies are developed and assayed that a plethora of new mechanisms or product types will be found that do not exist in the literature of synthetic organic chemistry. Rather, what we anticipate are complicated competing reactions that hopefully we will begin to unravel to begin to better understand many inadequately explained aspects of organic chemistry in tropospheric aerosol (e.g. the formation of HULIS in tropospheric organic aerosol [14]).

Point 8) We will note this mechanism described by Bailey.

Point 9) We will modify sections 5.3 and 5.4 to deemphasize our hypothesis. Unfortunately, we are not aware of any reports in the literature detailing concentrations of alkenes on/in tropospheric particles. One concern that we have is in the current state of what is known about the degree of unsaturation of OA in oceanic regions of high biological activity, particularly in light of suggestions that chlorophyll (a highly unsaturated hydrocarbon) may be significant contributor to OA [15, 16]. However, from what is known at present, alkenes most likely make only a minor contribution to the *overall* hydrocarbon load in the rural and urban troposphere, and their subsequent aldehyde products probably have a concomitant smaller role in radiative forcing and increasing the oxidative capacity of troposphere. The revised sections 5.3 and 5.4 will reflect these sentiments.

Point 10) The point is well taken and these sections are being revised accordingly to soften our hypothesis while still suggesting that some significant, albeit small, contribution may be possible.

Technical Comments

TC 1) This change will be made.

TC 2) This change will be made.

TC 3) This change will be made.

TC 4) That is correct. We will also note that both of these classes of peroxides along with α-acyloxyalkyl hydroperoxides are categorized under the heading as α-oxyalky hydroperoxides by Bailey [17].

1. Knopf, D.A., L.M. Anthony, and A.K. Bertram, Reactive uptake of O3 by multicomponent and multiphase mixtures containing oleic acid. J. Phys. Chem. A, 2005. 109(25): p. 5579-5589.

2. Docherty, K.S. and P.J. Ziemann, Reaction of oleic acid particles with NO3 radicals: Products, mechanism, and implications for radical-initiated organic aerosol oxidation. J. Phys. Chem. A, 2006. 110(10): p. 3567-3577.

3. Pryde, E.H., D.J. Moore, and J.C. Cowan, Hydrolytic, reductive and pyrolytic decomposition of selected ozonolysis products. Water as an ozonization medium. JAOCS, 1968. 45: p. 888-894.

4. 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.

5. Katrib, Y., et al., Ozonolysis of mixed oleic-acid/stearic-acid particles: Reaction kinetics and chemical morphology. J. Phys. Chem. A, 2005. 109(48): p. 10910-10919.

6. Moise, T. and Y. Rudich, Reactive uptake of ozone by aerosol-associated fatty acids: kinetics, mechanism, and products. J. Phys. Chem. A, 2002. 106(27): p. 6469-6476.

7. LaFranchi, B.W., J. Zahardis, and G.A. Petrucci, Photoelectron resonance capture ionization mass spectrometry: a soft ionization source for mass spectrometry of particle-phase organic compounds. Rapid Commun. Mass Spectrom., 2004. 18: p. 2517-2521.

8. Zahardis, J., B.W. LaFranchi, and G.A. Petrucci, Photoelectron resonance capture ionization-aerosol mass spectrometry of the ozonolysis products of oleic acid particles: Direct measure of higher molecular weight oxygenates. J. Geophys. Res., 2005. 110: p. D08307.

9. 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.

10. Thornberry, T. and J.P.D. Abbatt, Heterogeneous reaction of ozone with liquid unsaturated fatty acids: detailed kinetics and gas-phase product studies. Phys. Chem.

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Chem. Phys., 2004. 6: p. 84-93.
11. 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.
12. Smith, G.D., et al., Reactive uptake of ozone by oleic acid aerosol particles: Application of single-particle mass spectrometry to heterogeneous reaction kinetics. J. Phys. Chem. A, 2002. 106(35): p. 8085-8095.
13. LaFranchi, B.W. and G.A. Petrucci, Photoelectron resonance capture ionization (PERCI): A novel technique for the soft-ionization of organic compounds. J. Am. Soc. Mass Spectrom., 2004. 15: p. 424 - 430.
14. Graber, E.R. and Y. Rudich, Atmospheric HULIS: how humic-like are they? A comprehensive and critical review. Atmos. Chem. Phys. Discuss., 2005. 5: p. 9801-9860.
15. O'Dowd, C.D., et al., Biogenically driven organic contribution to marine aerosol. Nature, 2004. 431(7): p. 676-680.
16. Coe, H., et al., Chemical and physical characteristics of aerosol particles at a remote coastal location, Mace Head. Ireland, during NAMBLEX. Atmos. Chem. Phys. , 2006. 6: p. 3289-3301.
17. Bailey, P.S., Ozonation in Organic Chemistry. 1978. 1: Olefinic Compounds.

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