

***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 thank the reviewer for these insightful comments and give our responses below.

Point 1) We are going to incorporate a statement on the stabilization of the CI after the three step mechanism, which is meant to be quite general. This stabilization will be noted as being one of the key differences in gas and liquid phase ozonolysis of alkenes.

We are going to add some more possibilities to the source and identity (of the signals commonly assigned to azelaic acid and nonanoic acid. We are not going to discount

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the possibility that these signals could arise from:

- a) CI that rearrange to acids
- b) CI that rearrange to another isomer, such as an epoxide
- c) Stabilized CI
- d) An experimental artifact, such as in the ion forming process, that fragments peroxidic products that lead to these mass-to-charge products (e.g. 187 and 157 m/z in the negative ion spectra), or reactions with the products of ozonolysis with residual solvent, etc
- e) Third, or higher, generation products arising from reactions of peroxidic products of ozonolysis (e.g. the decomposition of secondary ozonides due to protic species).
- f) A combination of factors a-e

We have searched but have not been able to find any data on CI lifetime in an organic liquid phase. Additionally, we not found any relevant data on the stereochemistry (syn vs. anti) of these large CI in organic media, which is important in the fate of the CI in gas phase chemistry. The suggested route to azelaic acid and nonanoic acid via decomposition of peroxidic products as noted by Scot Martin, “the observed small yields of NA and AA come from the break down of some fraction of the SOZ’s, i.e., third-generation products” seems reasonable and will be incorporated in accord with your suggestion. Moreover, many of the very recent results of Mochida et al. [1] that show pathway preference regarding peroxide formation (secondary ozonides vs.  $\alpha$ -acyloxyalkyl hydroperoxides), which may contribute to yields of azelaic acid and nonanoic acid via decomposition, will be noted in appropriate sections of the review.

Point 2) Owing to the chemical complexity of atmospheric particles, it is not possible at this point to predict the chemical products. Nonetheless, as has been shown in the very recent studies [1,2], CI seem to react with high efficiency with acidic groups of added acids and probably form  $\alpha$ -acyloxyalkyl hydroperoxides. Natural aerosols are rich in

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smaller acids and will probably be very efficient in forming a variety of  $\alpha$ -acyloxyalkyl hydroperoxides and other peroxidic products. However, reflecting the sentiments of Scot Martin, due to the acidity of most tropospheric particulate, we anticipate most of the peroxidic species will decompose back to organic acids- hence we anticipate the greatest enhancement to CCN ability afforded to OA in the troposphere will come more from the concomitant conversion towards more acidic, oxygenated species over time, rather than conversion to high molecular species. We make this statement with great caution however - due to the variability in the stability and lifetime of peroxides and hydroperoxides, it is possible that some of the peroxidic products formed in these particles may have a relatively long lifetime.

Point 3) The resistor model for the uptake of ozone by OL currently does not account for secondary chemistry at all in the formulation of the model - corrections to this simple model are added via multiplicative adjustments to  $\gamma$ , not in reformulation of the model to account for secondary chemistry. We will add a statement regarding this after equation (4) and reiterate this in the conclusion as well.

Point 4) We will modify the text in regard to the referee's suggestion.

Point 5) Yes, that will be corrected; we meant the latter: wetting (zero contact angle) indicates activation.

Point 6) We agree with the reviewer that a quantitative estimate of the importance of absorption of solar radiation by ozone-alkene derived aldehydes would be beneficial. However, with the present state of knowledge, we are not able to make even a semi-quantitative estimate, nor are we aware of such estimates in the literature. We felt it important to at least raise this issue in the review, especially in light of the recent findings [3,4] about the degree of unsaturation of marine OA. There is insufficient data to imply or suggest that these particle-phase aldehydes could make more than a minor contribution to radiative forcing and/or the oxidative capacity of the troposphere. Nonetheless, we can appreciate the reviewer's comment and have edited these sec-

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tions of the review to present a more subdued argument.

Point 7) In regards to OA probably not being a significant sink of ozone, as we stated in our response to Scot Martin, we believe that our statement is fair, especially in light of the relatively recent findings that organics, especially in the marine environment, may make a significant contribution to the particulate load [3,4]. The recent results of O'Dowd and coworkers [3] comes to mind - where the authors showed that in times of high biological activity in the North Atlantic Ocean that the organic fraction constitutes up to over 60% of the submicron aerosol mass. These marine organic aerosols may be very high in unsaturation, with one of the main constituents likely being the multiply unsaturated porphyrins, chlorophyll [3] and chlorophyll-derived products [5]. We will clarify our statement however, changing the noted statement to:

“In regions of high organic content in the total particulate load, OA may be a significant sink for ozone as are other classes of tropospheric particulate.”

Our statement on page 11139: “Smith et al. [6] using an organic aerosol density of  $1.5 \times 10^5$  particles  $\text{cm}^{-3}$  typical of an urban setting [7], estimated that for particles with radii of 25 nm and an average OL content of 1%, the OL lifetime with respect to ozonolysis is 36 hrs” is incorrectly worded and in the wrong place and will be corrected. What Smith et al. stated was “the reaction of  $\text{O}_3$  with organic particle constituents may also affect the lifetime of  $\text{O}_3$  in the troposphere” [6]. Smith et al. continue on to calculate (using a value of  $\gamma = 7.3 \times 10^{-3}$ ) a rate of  $8 \times 10^{-6} \text{ s}^{-1}$  “corresponding to an  $\text{O}_3$  lifetime (with respect to reaction with the aerosol) of 36 h”. Note: The statement in parenthesis is in the original text by Smith et al [6].

The value for the lifetime of OL reported by Ziemann [8] will be corrected - this error stems from our reporting the value from an early version of his manuscript, which was later corrected in publication.

Point 8) This paper came out as we completed the manuscript, nonetheless many of the results of this recent paper deserve to be incorporated into this review and we shall

do so.

Point 9) We agree with the referee and will cite these references in the revised manuscript.

Technical Correction 1) This statement will be omitted.

Technical Correction 2) We will remove this reference [9] from the statement regarding formal derivations of the uptake expressions as suggested by the referee.

#### References:

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