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Atmospheric
Chemistry
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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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Firstly, we wish to express our thanks to S. Martin for his constructive and insightful comments and suggestions. Our responses and points for further discussion follow:

Point 1) In sections 3.3.1 and 3.3.3 we do address the ambiguity in the (commonly referred to as) azelaic acid and nonanoic acid assignments that have been made. In fact, it has not been conclusively shown that these signals do 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

Your recent paper, coauthored with Mochida et al [1], suggests factors (d and e) may be significant to consider before making assignments. In regards to (d), the work of Mochida et al. discussed the formation of alkoxy hydroperoxides with ozonolysis of methyl oleate in the presence of methanol. This experimental observation should be noted in that many investigators in this field, including our own group, use alcohols in the aerosol forming process. This recent and significant result will be incorporated into our discussion. We will also add a statement regarding the possibility of the azelaic acid and nonanoic acid arising from the decomposition of secondary ozonides as you note in your addendum.

We believe that all these experimental nuances highlight the general lack of experimental and theoretical data on liquid phase CI. Initially this review had a considerable subsection dedicated towards work detailing what is known about the CI. We consolidated this into what is currently section 3.2 because most of what is known about CI comes from small gas phase molecules. This general problem of limited information on liquid phase carbonyl oxides (i.e. Criegee intermediates) is described by Bunnelle [2] in his review, and interested readers should refer to section IV C “Isomerization of Carbonyl Oxides” in the original article. This section places a lot of emphasis of syn and anti stereoisomers of CI, and discusses the difficulties associated with solution measure of the isomers. We have referred readers to Bunnelle’s review in our work and have found little experimental or theoretical data on large CI in organic solution at ambient temperature that answer the following questions:

a) What is the lifetime of a large stabilized CI (SCI) in an organic medium? b) What is the preferred resonance form of these SCI and how does this affect their reactivity in these mediums? c) To what extent, if any, do stabilized CI rearrange to carboxylic

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acids or other species (e.g. epoxides) in the aforementioned solutions?

We would appreciate knowing if there is any work reported in the literature that we may have overlooked.

Point 2) We agree that we should note the need for studies at elevated humidity to further simulate the fate of more realistic particles. The crux of processing in the OL-O_3 HRS is the fate of the CI, which may be influenced by water. We allude to the significance of the presence of water as well as other protic species in section 3.4.4, highlighting some studies that have been, for the most part, done on gas and liquid phase alkenes. Detailed work with fatty acid aerosols and coatings akin to what has been done with 1-tetradecene [3, 4] needs to be done for fatty acid based heterogeneous reaction systems. We will incorporate a statement about the need for detailed studies in the presence of water in the Conclusions section of this report.

Point 3) We are paraphrasing Hearn and Smith [5] here, specifically from page 10027 in that work: “We conclude from the results of our experiments and those of Moise and Rudich [6], Morris et al. [7], and Thornberry and Abbatt [8] that the reactive uptake coefficient for O_3 by oleic acid is on the order of 10^{-3}. Thus, approximately one in a thousand collisions results in reactive loss of oleic acid, whereas analogous reactions of ozone with alkenes in the gas phase typically proceed with rate constants of 10^{-15} - 10^{-17} cm^3/molecule/s [9], equivalent to one reaction per 10^5 -10^7 collisions. Such an enhancement in the reaction rate has been pointed out before [7, 8, 10, 11], but is still an open question to what causes it and to what extent it affects the processing of atmospheric particles.”

We are in agreement with this statement; however we do not wish to be misleading - the reactive uptake coefficient, γ, as you correctly point out, is composed of multiple terms, including D and k. Enhanced uptake of ozone to the condensed phase does not explicitly imply an enhanced bimolecular rate constant, it implies an enhanced rate of loss of gas phase ozone - which can come from diffusion into or reaction with the condensed phase medium. We will change “enhanced reaction rate” to a more general “enhanced rate of loss” in the first paragraph of section 5.1.

Point 4) The recently published work by Mochida et al. [1] came into press at about the same time we submitted this work for publication in ACP. Nonetheless, we will state some of the key results and implications of this work, especially noting the efficiency with which the stabilized Criegee intermediates attack carboxylic acids in mixed particles of methyl oleate and myristic acid, forming α-acyloxyalkyl hydroperoxides type compounds.

Point 5) We describe many of the results from that specific work by Katrib et al. [12] in the review although we do not discuss this work in section 3.4.2 “Peroxides and Hydroperoxides”. In that work, Katrib et al. reported high mass fragments, denoted CHO_T, with yields greater than 25%, in their mass spectra of ozonized OL. This, and other factors noted in their work, led to them to hypothesize “the formation of CHO_T molecules is hypothesized by us to involve reactions of the Criegee biradical in the condensed phase.” They describe several reaction mechanisms, including the addition of Criegee biradicals to oleic acid, forming peroxides. In section 3.4.2 (pages 11112-11113) we emphasized recent observations of peroxides, with emphasis on works that made specific assignments of these high MW products. Although Katrib et al. discuss the possibility of peroxides, no definitive assignments in this regard are made in that work; moreover emphasis is placed on the C27 products leading to ketones: “The key point in our proposed mechanism in our proposed mechanism is that the resulting Criegee biradicals add to the double bond of oleic acid.” In the accompanying figure (Figure 8 in that work) two major pathways are indicated: a) leading to a C18 ketone and 9-oxononanoic acid via decomposition of the C27 product, and b) another path that simply indicates the formation of C27 products and their decomposition. Notice the depicted condensed phase reaction pathway (see Figure 8 in their cited work) emphasizes the formation of novel ketones from the decomposition of addition products that arose from the reactivity of the Criegee intermediate with the double bond of OL.

We will incorporate a brief statement stating that the results of Katrib et al. could support peroxide formation - this is particularly relevant as of late, with the recent results of Mochida et al. [1] and others that seem to indicate the route to peroxides, namely secondary ozonides and α-acyloxyalkyl hydroperoxides type compounds is probably more significant than the route to ketones.

In section 3.4.4 (beginning page 11115) we place emphasis on “classic” gas and liquid phase reactions that support peroxide formation in ozonolysis of alkenes. We also include information on the 1- tetradecene - ozone system since there exist some similarities between this system and OL-ozone in terms of the types of peroxidic products formed. Moreover, we wanted to show some of the nuances of the chemistry of how water and other protic species could affect the products of a model heterogeneous reaction system that is probably a lot simpler than OL-ozone. There was no discussion of the results or inferences of OL, other fatty acids, or their derivatives in this section - we reserved that for other sections that covered specific types of products. In light of this, we do not feel the results of Katrib et al. belong in that section.

Point 6) We agree with the comment that some sort of commonality should be used with language denoting these peroxides. We will change ACOAH to AAHP for α-acyloxyalkyl hydroperoxides. The abbreviation ALOAH for α-alkyloxyalkyl hydroperoxides is probably not needed in this work; we only mention this type of compound several times in the text and we refer to it by its full name in these cases.

Point 7) The coated wall experiments bear a long, established tradition in the field of heterogeneous processing and they measure the loss of ozone directly. This method will not suffer from artificially large values of γ arising from secondary reactions of the condensed phase species as we are seeing in the aerosol based measurements. As we discuss, the aerosol based methods all monitor the loss of the condensed phase species, which is then used to calculate γ. The secondary reactions these condensed phase species can undergo and can lead to an artificially large value of and are the reason that corrections have been applied to the values of the reactive uptake coefficient.

Therefore, at least initially, we feel the value γ obtained from an aerosol based mass spectrometric method should be compared (i.e., referenced) to values in the literature obtained from coated-wall experiments.

Point 8) We hold by our statement that tropospheric OA may be a significant sink of ozone, especially in light of the relatively recent findings that organics, especially in the marine environment, may make a significant contribution to the particulate load [13, 14]. The recent results of O'Dowd and coworkers [13] come to mind - where they showed that in times of high biological activity in the North Atlantic Ocean, the organic fraction constitutes up to over 60% of the submicron aerosol mass. These marine organic aerosols are probably very high in unsaturation, with one of the main constituents being the multiply unsaturated porphyrins, chlorophyll [13] and chlorophyll-derived products [15]. 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.”

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