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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Enhanced uptake of water by oxidatively processed oleic acid" *by* A. Asad et al.

Anonymous Referee #1

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General comments:

This manuscript describes the use of a quartz crystal microbalance to measure mass change on an organic film over a wide range of relative humidities. Water uptake is measured from the mass changes on both pure films and films which have been exposed to O_3/O_2 for a length of time. From such comparisons, the authors are able to estimate a 3-4 fold increase in the amount of water taken up by the oxidized films (at RH near 100

Specific comments:

1. Page 5. Since the O_3 was continuously generated and flowed through the reaction flask, it is possible that radicals such as OH or HO_2 could also have been generated even in the presence of small amounts of water. These radicals could also oxidize

the organic films and lead to enhanced water uptake. Were any precautions taken to eliminate this possibility or were there any indications that this was not significant in these experiments?

2. Page 7. In Figure 1 it appears as if the use of methanol as a solvent for depositing the oleic acid drastically affects the water uptake. Is it valid to compare the current results to the uptake curves of the authors' previous study (Demou et al., 2003) in which a solvent was used in preparing the organic coating on the crystal?

3. Page 8. The absence of a mass change does not necessarily imply that no chemical changes occurred when the film was exposed to O_2. Though unlikely, a volatile product might remove mass at the same rate that O_2 adds mass. Also, some O_2 would adsorb to the film, so one would expect to see a mass increase after it is placed in the QCM apparatus even in the absence of chemical reactions. Was such an increase observed?

4. Figure 3a. It appears as if the amount of water taken up (per mole of oleic acid) reaches a plateau near five minutes for all of the O_3 concentrations (spanning a range from about 1x10^{14} molecules/cm^3 to 9x10^{15} molecules/cm^3). This behavior seems to contradict the conclusion that the O_3 exposure ($[O_3]$*t) governs how much water is taken up.

5. Page 9 and Figure 3b. It is not clear how the mass of the film remaining (massfilm) is calculated. I assume that it is estimated by measuring the mass of the film before and after exposure to O_3 but before addition of water, but it would be helpful to state this explicitly. The curve in Figure 3b does not necessarily indicate an increased amount of water taken up since $mass_{H2O}/mass_{film}$ could increase if the mass of the film is reduced. For example, assuming a yield of 0.5 for the nonanal product, complete evaporation of it would result in a net mass loss of 23 amu (+48 amu for O_3, -0.5*142 amu for nonanal). Thus, $mass_{H2O}/mass_{film}$ would increase even if no additional water was taken up. The discussion of the parameter plotted in this figure would benefit from additional clarification.

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6. Page 9 and Figure 3b. The claim that the hydrophilicity of the condensed-phase products does not increase after all of the oleic acid supposedly reacts is not corroborated by the figure. In particular, the mass$_{H2O}$/mass$_{film}$ is still increasing from exposures of 10^{17}-10^{19} molec cm^{-3} sec. The rate at which the hydrophilicity increases might be slower than at smaller exposures, but it should not be implied that it stops increasing altogether. Precise interpretation of these results is critical as they may indicate that the ozonolysis products are reacting with O_3 even after all of the oleic acid is reacted away. The inclusion of error bars would also help the reader to interpret the data.

Also, in doing a rough calculation of how fast a 100 microgram oleic acid film should react, I estimate that an exposure of 1.4 x 10^{15} molec cm^{-3} sec should be sufficient (assuming gamma = 10^{-3}). This is a factor of 35 smaller than the exposure indicated by the arrow in the figure and would substantially change the conclusions correlating the change in water uptake with the extent of reaction. Admittedly, my calculation is approximate, but please provide more information about how the exposure for completion of the reaction (i.e. the position of the arrow) was calculated. This point is critical to the interpretation of the data. If a smaller exposure was sufficient to react all of the oleic acid, then a smaller enhancement in water uptake would be estimated for the reaction products, but a larger enhancement would be calculated for the additional oxidation (after oleic is reacted away).

7. Page 10 and Figure 4. It is not clear how the spectrum in Figure 4b shows that the reacted oleic acid is much more highly oxidized than azelaic acid (Figure 4c) as indicated in the text. Please clarify.

8. Page 11. Again, it is not clear that a plateau in water uptake is reached when the oleic acid has reacted away. Please see comments above for Page 9 and Figure 3b.

9. Page 11. Formation of secondary ozonides will not change the O:C ratio as implied. The secondary ozonides result from reaction of aldehyde products (1-nonanal or 9-

oxononanoic acid) and one of the Criegee intermediates, so the numbers of O atoms and C atoms will be conserved when the secondary ozonides are formed.

Also, it is surmised that there could be an increase in oxidation resulting from reaction at the carboxylic acid group, presumably of oleic acid (as opposed to one of the acid products). I am not aware of any significant reactions between O_3 and a carboxylic acid. Are there any precedents for such a reaction that the authors could cite?

Technical comments:

Page 2. The ozone uptake work of Eliason et al. (2003) is incorrectly identified as preceding earlier work. In particular, the paper by Morris et al. was published in 2002 as was the paper by Smith et al.

Page 7: “typre” should be “type”

References: Citation for Broekhuizen is missing

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