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Interactive Comment

Interactive comment on "Formation of gas-phase carbonyls from heterogeneous oxidation of polyunsaturated fatty acids at the air–water interface and of the sea surface microlayer" *by* S. Zhou et al.

Anonymous Referee #2

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This paper presents an interesting laboratory study that I'm sure is an attempt to address the unusual field observations of Sinreich et al. (Sinreich et 2010 is referenced but does not appear in the list of references) who observed very high levels of glyoxal in the remote marine boundary layer.

The paper reports work on the reaction of ozone with a linoleic acid (LA) monolayer on seawater that is well performed and shows consistent results between two different experimental approaches. These experiments give confidence in the yields and the preference for the formation of n-hexanal over 3-nonenal in contrast to studies of ozone reactivity on the pure LA liquid. What is confusing to me is the big difference in the total yield of aldehyde. I.e. on the pure liquid only 50% of the reaction produces aldehydes whereas on the seawater film essentially the production is 100%. My(perhaps incorrect) assumption is that in the pure liquid film experiments the primary ozonide has a 50:50 chance of producing the Criegee biradical on either side of the double bond, and attack on either bond is equally probable. For the seawater layer experiments reported here I can accept that the "outer" bond is more susceptible to attack, hence the enhancement in hexanal. However I cannot understand why the Criegee is exclusively formed on the hydrophilic side that is bound to the water.

The authors state that " Hence, further oxidation of 3-nonenal by ozone may produce n-hexanal leading to the higher ratio of n-hexanal to 3-nonenal, i.e. it is possible that both are formed initially at roughly 50 % yield and secondary reactions give rise to the observed enhancement of n-hexanal to 3-nonenal. While it is unlikely that the gas phase kinetics is fast enough to drive this oxidation pathway, it is possible that 3-nonenal is heterogeneously oxidized to n-hexanal. While speculative, it is for this reason that we indicate the branching ratios in Fig. 6 to the two primary ozonides to be 50 to 70 % and 30 to 50 %." However Thornberry and Abbatt examined the reactivity of ozone with a nonenal film and found reaction but no gas phase products. From Thornberry and Abbatt "To test this hypothesis, we performed a coated-wall kinetics experiment where ozone was exposed to a nonenal film. Ozone loss was observed in a similar manner to that over the fatty acid films and a reactive uptake coefficient was measured at 263 K of 3 x 10-4. No gas-phase products were observed with proton transfer. This is somewhat surprising since hexanal would be an expected product, but might be an indication that the mechanism of the reaction is affected by the proximity of the double bond to the carbonyl group." The authors performed a chamber study to examine the reaction of 3-hexanal (a surrogate for 3-nonenal) with ozone and found production of propanol, MDA and glyoxal and conclude that the observation of MDA and glyoxal in the LA experiments is due to secondary oxidation of the 3-nonenal product. However they do not discuss propanal production. If this mechanism is correct then propanal should also be formed. Is this the signal at $\sim$60 in Fig 2a. It also appears that the issue of secondary production whether it is conversion off nonenal to hexanal or of secondary conversion of aldehyde to MDA glyoxal could have been addressed by varying the residence time in the flow tube.

The value of the studies on the natural seawater samples is not clear to me because of the complexity of dissolved organic matter in seawater. What is striking, given the subject of the manuscript, is the failure to observe any signature of LA. Surely this is worthy of comment?

I wrote this without looking at any other comments so I apologize if some of these issues have already been addressed. I think the paper certainly merits publication in ACP.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 17545, 2013.