Atmos. Chem. Phys. Discuss., 13, C8614–C8618, 2013
www.atmos-chem-phys-discuss.net/13/C8614/2013/

Atmospheric Chemistry and Physics Discussions
Open Access

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.

S. Zhou et al.

szhou@chem.utoronto.ca

Received and published: 31 October 2013

Referee #1: This is a nice piece of work focusing on the potential heterogeneous chemistry occurring at the ocean surface when exposed to ozone. Gas-phase products were observed combining state-of-the-art tools such as online proton-transfer-reaction mass spectrometry (PTR-MS) and light-emitting diode cavity enhanced differential optical absorption spectroscopy (LED-CE-DOAS). When a reactive sea surface microlayer (SML) component, in this case linoleic acid (LA) or some authentic samples, was exposed to gaseous ozone oxygenated gas-phase products (mainly aldehydes) were observed, including two highly reactive di-carbonyls i.e. malondialdehyde (MDA) and glyoxal. This paper is interesting, well written and illustrated and conveys new information. I would favor publication of this manuscript in ACP.

Thanks for the positive comments. The responses to the comments are following.

I have just a few minor comments. It is stated that the type 1 experiments involves a “uniform” monolayer of LA. Conclusion drawn from the experiment described in section 3.1, where a drop a pure LA was deposited into the boat leading to lower amount of products. To be really convincing, the difference in the signal should match the difference in ozone exposed surface. Is it the case? On page 17555, line 24, it is stated that the monolayer is replenished by the excess LA droplet. This is confusing and some incoherent with section 3.1. Are the few μL of added LA spreading over the surface or just making some phase separation, exhibiting some island of fatty acids?

We assume that the LA forms a monolayer in type 1 experiments where 2 μL LA was added onto the seawater in the boat based on a previous study of Rouviere and Ammann (2010) who investigated the phase properties of fatty acids on KI aqueous particles. The authors reported that if more than a monolayer of fatty acid was deposited on the aqueous particles, the fatty acid formed a monolayer and the residual material remained as an excess droplet on the particles. We believe that this is the case in the present work, i.e. a monolayer of LA was formed on the seawater and the excess LA resulted in a phase separation forming an oily droplet (Section 2.1, page 17550 line 18-20) rather than forming some islands of the LA. Moreover, a control experiment was conducted by adding the same amount (2 μL) of LA into a dry boat without sea water presence and exposing it to the same level of ozone. As mentioned in Section 3.1 the product signals obtained in the control were found to be much lower than the type 1 experiment. As the Reviewer pointed out such a difference in product signals between the control and type 1 experiment should be due to the different LA surface areas available for ozone to react. The much larger LA surface in type 1 experiment should be a

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

result of the LA spreading across the seawater surface forming a monolayer that does not happen when LA was sitting in a dry boat in the control.

Another observation made in the type 1 experiment is that the product signals quickly reached steady-state levels and remained stable during the experiment (Fig. 4). It is very likely that after the LA monolayer is consumed by heterogeneous reaction with ozone, it is promptly replenished by the excess of LA droplet, resulting in the sustained production of gas-phase products. Otherwise, the LA surface area should have decreased and lower product signals should have been observed.

The argumentation developed on lines 5-8 on page 17556 appears to be not fully convincing to me. Nonanoic is a long chain acid, quite insoluble in water and will certainly be surface active. Logically part of it (if produced at all) will stay at the surface. On line 6 (p.17557), it is stated that the ozone net-collision rate in the presence of a thin organic layer (butanol, on NaI(aq)) is virtually identical to that in the absence of the organic layer (D. Tobias, personal communication, 2013). Does this means that the incoming flux of ozone is not disturbed? Is so, you may see the same amount of products even if nonanoic acid stays at the surface?

The reviewer brings up a good point, and it is hard to predict precisely the behavior that will happen. Our argument on page 17556 was that the nonanoic acid product would simply dilute the surface LA coating and make the reaction go more slowly. Even if the ozone flux remains the same (as argued on p 17557), it is thus possible that the ozone-LA reaction goes more slowly under such conditions.

Some yield calculations have been made based on the consumption of ozone, but how much ozone is consumed by sea water? In fact, the ozone reaction with iodide is quite fast and depending on the exact composition of your Sigma-Aldrich seawater. You may have been affected by such an additional loss. Is it the case?

This is a very good point. Using the similar set-up with the type 1 experiment, test experiments were conducted by measuring ozone consumption by the Sigma-Aldrich seawater we used. The results suggest that only ~2 ppb of ozone reacted with the seawater. Compared to the total ozone loss due to reaction with LA in type 1 experiments (85-150 ppb) its loss due to reaction with seawater is negligible. We have added this point in the manuscript (Page 9 line 26).

Also, this chemistry (if occurring at all during your experiments) may produce other compounds (XO-) which may potentially interact with the unsaturated bounds from the other side of the air/water interface (aqueous bulk phase chemistry). Do you suspect that this may be the case?

This is an interesting suggestion. However, as mentioned above since the ozone consumption with commercial Sigma-Aldrich seawater is far less important than what arises with the reaction with LA, the consequences arising from the aqueous or gas-phase products from the halogen chemistry will not affect the product distributions at a significant level. Of course, we cannot rule out that a small amount of this chemistry is occurring, which we now state in the paper. Note however that the XO- compounds are likely to rapidly form HOX species, which will then react with more halides to then form X2, which will degas from solution.

At the end, seawater is used but the role of the halides never mentioned. Why? Are they simply inert? Which I doubt just having in mind all the literature about the O3+X reactions... Do you expect having the same chemistry occurring on pure water?

As discussed above, the halides chemistry is likely less important than (or, at least, independent from) the ozone-organic reactions. In particular, since the present work focuses on the gas-phase organic carbonyls production we believe the halide chemistry is not of major direct relevance.

On page 17557 – line 9, you report that glyoxal is lost with unit efficiency which is somehow in disagreement with the fact that it needs to react with water to get really soluble (low physical solubility but high effective Henry's law constant). This leads to pH dependent hydration kinetics and the uptake may range from low to high depending of the pH of your solution. Maybe the argumentation on page 17557 can be more elaborated.

We agree with the Reviewer that the loss of glyoxal in the flow tube is complex and may not be simplified by a unit collisional loss in the aqueous sub-phase. This complexity in glyoxal uptake and hydration kinetics impedes our full understanding of its loss processes. This paragraph has been modified based on the Reviewer's comments (Page 10 line 20-23).

Also, glyoxal may also be produced from the interaction of ozone with the enol form of MDA. However, based on the time series of the MDA and glyoxal in Fig. 7 the contribution of further oxidation of MDA to glyoxal formation is concluded to be of minor importance. But could this gas phase observations be directly transferred to the air/water interface, which is the focus of this work? Especially water (liquid or gaseous), may affect the enol reactions. . . Any thought on that?

This is a good point. Due to the similar chemical structures of MDA and glyoxal, it is expected that the MDA has similar behavior at the air/water interface as does glyoxal, i.e. MDA may be readily hydrated and may dissolve in water rather than remain at the air/water interface. As a result, its hydrated form may dominate in the aqueous-phase rather than its reactive enol form. This may lead to different reaction mechanisms for MDA in the gas- and aqueous-phases.

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

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper