

Interactive comment on “Reactivity of chlorine radical with submicron palmitic acid particles: kinetic measurements and products identification” by M. Mendez et al.

Anonymous Referee #1

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General Comments: The manuscript entitled, “Reactivity of chlorine radical with submicron palmitic acid particles: kinetic measurements and products identification,” by Mendez et al., describes a series of experiments examining the heterogeneous reactivity of chlorine atoms and palmitic acid aerosol. The chemistry explored in this manuscript has relevance to the marine boundary layer in which Cl atoms and fatty acids are important chemical constituents. Overall the paper reports kinetic measurements (with and without oxygen) as well as detailed product identification. The paper is well written and data analysis is carefully conducted. The conclusions drawn by the authors follow logically from their measurements. Overall the paper is suitable for pub-

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lication only after the authors address some specific comments outlined below.

Specific Comments:

1. The authors report an uptake coefficient (with oxygen) that is larger than 1; indicating chain propagation chemistry. This value, as the authors point out, is larger than previously measured by Liu et al. 2011 and Hearn et al., 2007. The authors say on page 16937 (line 9) that strictly speaking these values cannot be compared. While they imply the reason for this is due to some experimental differences, I simply do not follow their arguments. The authors should clarify this discussion and endeavor to reconcile their results with previous measurements. If there is really a discrepancy with previous measurements a clear statement to indicate this is necessary.
2. They report a mass closure for the GC-MS of 80% relative to SMPS measurements. Is this due to volatile products not detected by the GC or uncertainty due to computing mass via SMPS for non-spherical particles? Otherwise the reader is left to conclude that 20% of the reaction products are in the gas phase? Is this correct? What internal standards were used for quantification in the GC? The authors should provide a few more details regarding how the GC measurements are quantified.
3. It is indeed very interesting that the authors detected smaller carbon number diacids, which has potential implications for the budget of these species in the atmosphere. In Figure 7 the distribution of these diacids peaks at C3 and decays toward C8. Can the authors provide more evidence that this is the nascent population in the particle and that this distribution is not simply a product of GC detection or transmission efficiencies? These are commonly available compounds; were internal standards run from quantification. Furthermore, it is not clear to me that the authors have presented a plausible reaction mechanism for the production of these small acids? Fig. 8 shows a partial reaction mechanism, which shows a diacid being produced by R10. However, I don't see how this works. R10 shows a peroxy radical reacting with RH to form a stable alkane, alkyl radical and a diacid. How does this work? To me R10 implies as written

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peroxy radical H abstraction to form a hydroperoxide and an alkyl radical? The authors should clarify this part of the mechanism.

4. It is not clear to me why alcohols would be formed as minor products given the importance of the Russell mechanism observed in many previous studies (liquid particles) of similar reactions. The authors should address this since this might indicate an important difference in the chemistry of liquid vs. solid particles.

5. The authors don't show product formation kinetics. It would be useful here or in the future to show how the products evolve relative to the decay of PA. These kinds of data are extremely important to have and use to determine whether a proposed mechanism is viable or not.

6. By measuring the formation kinetics of HCl, via FTIR, can the authors measure directly the primary uptake coefficient for Cl in the absence of secondary chemistry. Such a number would be extremely important to have to constrain the chain propagation length.

7. The formation kinetics of CO₂ should also be shown to evaluate the relative rates of H abstraction from the acid site vs. the rest of the molecule. Typically this acid H is considered somewhat unreactive compared with those of secondary carbon sites.

8. It is unclear to me from the mechanism how in the presence of O₂ the uptake coefficient can be 3. Perhaps this will be clarified when R10 is edited. In any case, the authors should clearly point out the places in the mechanism (with O₂) where chain cycling can occur. 9. The results shown in Figure 6 should be presented in a quantitative form (table, histogram). For example, the relative yield of various oxidation products. This kind of quantitative data would be most useful for the community. If this kind of quantification is not possible the authors should say why.

10. On page 16942 (line 15), the authors say, "On the other hand, if an internal recombination occurs, it leads to a monocarboxylic acid with a carbon chain length smaller

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than palmitic acid..." I really don't understand how this works. The authors need to revise the mechanism (and this sentence) in Fig. 8 to show explicitly how changes in carbon number occur with oxidation. The authors should write out the explicit chemical structure of PA and the various transformations to make changes in carbon number more transparent in their reaction mechanism.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 16925, 2013.

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