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

M. Mendez et al.

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Main comments of referee #3

The authors thank the reviewer for the constructive remarks and suggestions.

Q1) The manuscript should be read carefully and checked for grammatical and other language mistakes. I list some below but this list is likely not complete.

Answer: We have read carefully the manuscript and mistakes have been corrected.

Q2) Several studies have been conducted previously by other authors that looked at

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the similar chemical systems. While these studies are properly cited (Liu et al., 2011; Hearn et al., 2007), a more detailed discussion of discrepancies of the present work should be added. - While they recorded the loss of the Cl radical, in the present study the uptake coefficient was inferred by the observed PA loss. Given the fact that in the present study multiply chlorinated products were found, shouldn't the loss of Cl be more efficient than the loss of PA? – However, comparison to the previous studies shows the opposite. - On the other hand, the Cl radical might react with products and not only with the initial reactant PA. Thus, it would be more efficiently consumed than PA. – Can you give an estimate how these two opposing effects might play out in the determined uptake coefficients and thus in the comparison of the two experimental approaches? - You use rather high Cl concentrations (as compared to atmospheric levels). What were the levels in the other studies? Could any differences in this value (or in the Cl/O₂ ratio) cause any discrepancies? - In addition, why doesn't your O₂-dependent mechanism hold for DOS particles where actually enhanced reactivity was observed in presence of high O₂? I suggest adding a subsection to Section 3 entitled 'Discussion of previous results'.

Q2.1 Given the fact that in the present study multiply chlorinated products were found, shouldn't the loss of Cl be more efficient than the loss of PA?

Answer: The reaction R2 leads to the formation of Cl. The multichlorinated products seem to be formed by the reaction of this Cl with a chlorinated palmitic acid. For this reason, the Cl loss should not be faster than the PA loss.

Q2.2 You use rather high Cl concentrations (as compared to atmospheric levels). What were the levels in the other studies? Could any differences in this value (or in the Cl/O₂ ratio) cause any discrepancies?

Answer: In the Liu et al. study the maximum chlorine exposure is $\langle \text{Cl} \rangle \cdot t \approx 1 \cdot 10^{12}$ molecule s cm⁻³ with a reaction time of $t = 33,5$ s and lead to determine a maximum concentration of Cl of $3.0 \cdot 10^{10}$ molecule cm⁻³. For the Smith et al. study the maximum

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exposure is $\langle \text{Cl} \rangle \cdot t \approx 7 \cdot 10^{11} \text{ molecule s cm}^3$ with a reaction time of $t = 3 \text{ s}$ and lead to determine a maximum concentration of Cl of $2,3 \cdot 10^{11} \text{ molecule cm}^{-3}$. In our study, the maximum exposure is $\langle \text{Cl} \rangle \cdot t \approx 1,35 \cdot 10^{12} \text{ molecule s cm}^3$ with a reaction time of $t = 180 \text{ s}$ and lead to determine a maximum concentration of Cl of $7,5 \cdot 10^9 \text{ molecule cm}^{-3}$.

So the chlorine concentration used in this study is in the range of those previously reported. And in all cases, the $[\text{Cl}]/[\text{O}_2]$ ratio is extremely low and should not causes major disparity in the measurements of the uptake coefficient for measurements done with oxygen. But we have to keep in mind that concentration and time are not always independent parameters. So in principle these experiments have also to be done by varying the contact time between organic particles and oxidants as suggested by L. H. Renbaum and G. D. Smith in *Atmos. Chem. Phys.*, 11, 6881-6893, 2011.

Q2.3 why doesn't your O₂-dependent mechanism hold for DOS particles where actually enhanced reactivity was observed in presence of high O₂?

Answer: The chemical formula of the molecules are quite different and the phase also. In the case of palmitic acid (PA), the molecule exhibits a linear carbon chain with a terminal acid function contrary to DOS. So the rate constant for the H-abstraction reaction (R1) must be likely different for each species due to the nature of the carbon chain (linear for PA or branched for Sq) and also the functional group (ether for DOS and acid for PA). As secondary chemistry was also highlighted for each heterogeneous reaction, the rate of propagation of these chemical reactions should also be strongly dependent on the chemical formula and the phase of the compound. A summarize of these answers have been added in a new subsection 3.2.4 entitled 'Discussion of previous results' together with the Table1.

Q3) Only in the conclusion section, some discussion is added on possibilities of chemical reactions in solid particles. Is this really a conclusion? I think this part should be discussed in Section 3.

Answer: This discussion has been moved to a more adequate location i.e. in section

3.

Q4) The description of the chemical mechanism is very qualitative and vague. While the authors say that it is based on the mechanism as suggested by George and Abbatt (2010), only very little detail is given about the reactions shown in Figure 8. - Section 3.2.3. should be extended and more background on the feasibility and exact reaction mechanism should be given. - While I understand that a detailed kinetic analysis of the individual reaction products might be difficult, I think that some estimates of major reaction pathways can be performed. E.g., based on bond dissociation energies, it could be estimated which branch of R12 is more feasible. In addition, rate constants for the different steps are available and can be compared (cf e.g. NIST data base for gas kinetics). If data are not available for the exact compounds in the present study, those for similar compounds might be useful.

Answer: Based on this comment and others from referee 1, we have entirely reformulated our proposal for the reaction mechanism. In this new version, we have chosen not to show minor pathways such as $\text{RO}_2^\circ + \text{R}'\text{H}$. Instead of a general mechanism with R-COOH as a generic formula, we have used the explicit chemical structure of the palmitic acid molecule and made the assumption of a chlorine attack to the beta position of the COOH function. This choice is only for a better understanding of the mechanism and does not mean that this specific H abstraction is predominant. We have clearly highlighted this point in the main text of the article. The paper from Georges et al (ACP 7, 1487-4201, 2007) already provides some clues for branching ratio and the feasibility of reaction for the RO_2 radical chemistry. We don't have enough quantitative materials to provide further information on our specific chemical system than the one already published.

Minor comments

p. 16925, l. 18: Given the rather qualitative character of the mechanism, I think saying reaction products are EXPLAINED' is a bit strong here. Since you can neither compare

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to temporal evolution nor to the relative abundance of products, a more careful wording might be more appropriate.

Answer: The sentence has been changed to “A reaction pathway for the main reaction products and more functionalized products is proposed.”

p. 16931, l. 24: Why do you assume liquid phase density here? Under what conditions has this density been determined? Are these conditions very different to those where you have solid PA particles?

Answer: The solid phase density of palmitic acid is 0.852 g cm⁻³ (Sigma Aldrich). We have switched to this value in the paper and the reference to liquid phase was indeed wrong and has been removed.

p. 16934, l. 14: Do the SMPS and the GC/MS 'see' the same particles? What is their size range? – Could some discrepancy of this lead to the incomplete mass sampling?

Answer: The discrepancy could arise from the uncertainties due to the calculating mass via the SMPS (spherical particle shape assumption for example). Incomplete solvent extraction of palmitic acid for GC/MS should also explain these discrepancies. However, regarding the totally different techniques used for the mass determination, the value of 80% has to be considered as a satisfactory result.

p. 16935, Equations 4 and 5: What are the units for the fluxes?

Answer: The unit (molecule s⁻¹ cm⁻²) has been added.

p. 16936, l. 16: Unless I misunderstand something here, doesn't Figure 4 clearly show that this assumption is not applicable since the diameter substantially decreases?

Answer: This is right, the diameter decreased of ~30%. The initial value has been chosen for two main reasons: (1) we measure initial uptake coefficient and (2) aged particle real diameter cannot be derived from SPMS data as their density is not known. There is a discussion on that choice in paragraph 3.1.3.

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p. 16937, l. 1: What is the value for k_{PA} you derive? How does it compare to other values of Cl + similar organic compounds or previously determined Cl + PA data (if available) in other phases?

Answer: From our knowledge, no kinetic data are available for this $PA+Cl^\circ$ reaction whatever the phase of the PA compound (solid or gas). The rate constant of the reaction ($PA + Cl^\circ$) can be derived from our measurements: $k_{PA} = 0.7 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the O_2 -free study and $k_{PA} = 2.2 \cdot 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ when O_2 is added in the AFT. These values are not provided in the previous studies for similar particulate organic matter ($Sq+Cl^\circ$, Liu et al. 2011 and $DOS + Cl^\circ$, Hearn et al. 2007). For comparison with the gas phase, the following rate constants be found from IUPAC : Acetic acid + Cl° $k = 2.8 \cdot 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ n-butane + Cl° $k = 2 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ showing that the rate constant is extremely dependant on the chemical formula: long carbon chain for n-butane, acid function for acetic acid. However it seems likely difficult to transfer values coming from the gas phase to the condensed phase as already suggested by the literature.

p. 16937, l. 5: Be more specific and show the correction.

Answer: The sentence as been rephrased : “Using the model developed by Fuchs and Sutugin (Fuchs and Sutugin, 1970), the calculation of the gas-phase diffusion limitation leads to a correction of 10% for γ which is smaller than the total error from the experiment setup”.

p. 16938, l. 10: R2 shows that Cl_p is formed, not Cl_g . I suppose it does not make a difference as Cl can be transferred between the phases but at least text and reaction should be consistent.

Answer: The text has been changed : $Cl(g)$ to $Cl(p)$

p. 16938, l. 118: Do you mean 'chlorine radical concentration'?

Answer: That is correct

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p. 16939, l. 14: What do you mean by 'For this reason'?

Answer: This expression has been changed to "Consequently"

p. 16939, l. 26: Do you mean 'formation of different constitutional isomers'?

Answer: Yes, it has been corrected in the article.

p. 16941, l. 5 and 6: Oxocarboxylic and ketocarboxylic acids are the same. Just use one of the names in order to be consistent.

Amended

p. 16941, l. 14: Add some details on how the yields were obtained.

Amended.

p. 16941, l. 20: Did you actually detect hydroxyl compounds? If not, why?

Answer: Those products were detected but the identification was difficult. The text was improved to be clearly specific that those identification were unclear : "Products with hydroxyl functions were also detected but their formal identification cannot be guaranteed without doubt. Those products are: hydroxyethanoic acid, hydroxypropanoic acid and several diols."

p. 16942, l. 20: 'recombination' usually refers to a radical-radical reaction. Is this what you mean here or simply the reaction of RO₂ with RH?

Answer: The term 'recombination' referred to an internal reaction. It has been removed.

p. 16944, l. l. 11/12: Not clear what you mean by 'both cases'. In the case of the experiments by Hearn and Smith, you say that O₂ is accelerating the reaction.

Answer: The text has been improved to make it more clear.

p. 16944, l. 14: Not clear. Do you mean that only the experiments with O₂ are relevant to the atmosphere?

Answer: The sentence was removed as this particular point is developed in the following paragraph.

p. 16944, l. 18: In general, these are also possible formation pathways for diacids.

p. 16944, l. 29/ p. 16945, l. 1: This sentence should be reworded. Several words are redundant.

Amended

p. 16945, l. 12: Typically only a small fraction of organic particulate matter is speciated on a molecular basis. Thus, it would be more correct to say 'most abundant identified organic compounds'.

Amended

p. 16945, l. 14: The effects of sea spray organics on cloud properties described by Westervelt et al., are rather small (< 5%). However, I do agree that in general ageing processes as described in your study might change the properties of aerosol particles relevant to radiative properties, (e.g. size, chemical composition, morphology, : : :).

Figure 6: Can you ascribe chemical structures (or at least sum formulas) to the individual peaks?

Answer: The name of the main products identified has been added to the figure 6.

Technical comments Title: ': : : product identification' Amended p. 16925, l. 10: remove comma after 'Although' Amended p. 16927, l. 5: 'the ratio of' can be omitted Amended p. 16929, l. 28: studies of: : : Amended p. 16930, l. 16: remove 'of' after 'here' Amended p. 16934, l. 12: define 'SIM' Amended p. 16936, l. 20: remove 'atom' or 'molec' Amended p. 16937, l. 3: 'formalism' does not seem the right word here Amended p. 16937, l. 5: 'from' (not 'form') Amended p. 16939, l. 11: indicate Amended p. 16939, l. 12: increased Amended p. 16940, l. 17: as a function: : : Amended p. 16941, l. 1 and 2: product identification Amended p.

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16942, l. 16: leads to the formation of monocarboxylic acids Amended p. 16943, l. 6: as a function of the : : : Amended p. 16943, l. 6: we have performed these: : : Amended p. 16943, l. 11: why not simply 'exposure to chlorine atoms'? See response to major comment 2. p. 16943, l. 22: PACl1, PACl4 have not been defined. Better: 'with up to four chlorine atoms' Amended p. 16944, l. 15: remove 'the' before 'atmospheric particles' Amended p. 16944, l. 22: under : : :conditions Amended

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/13/C7663/2013/acpd-13-C7663-2013-supplement.pdf>

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

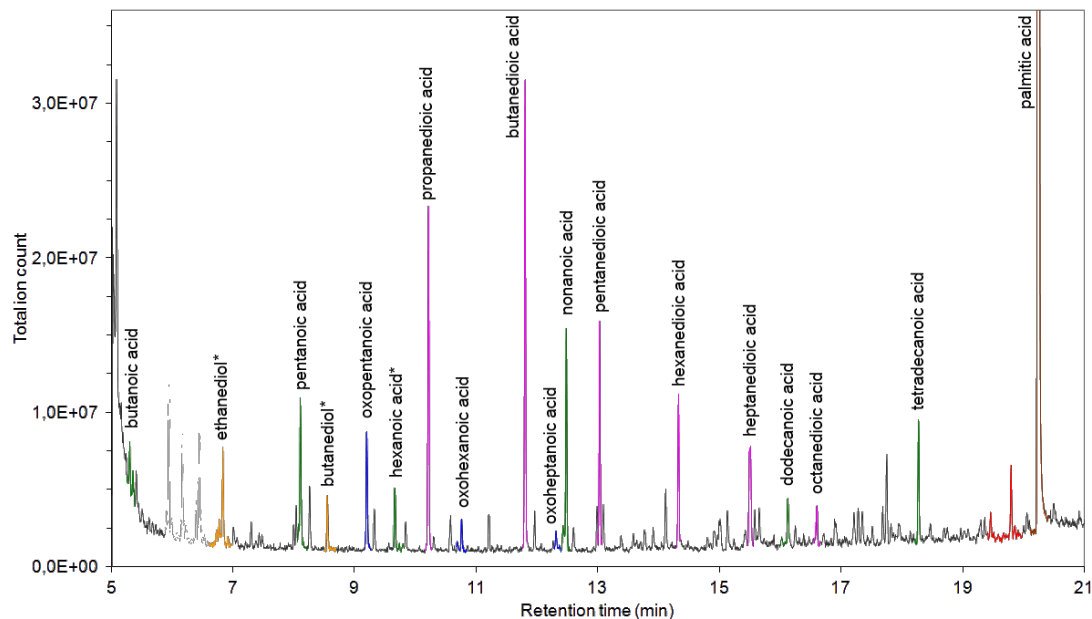
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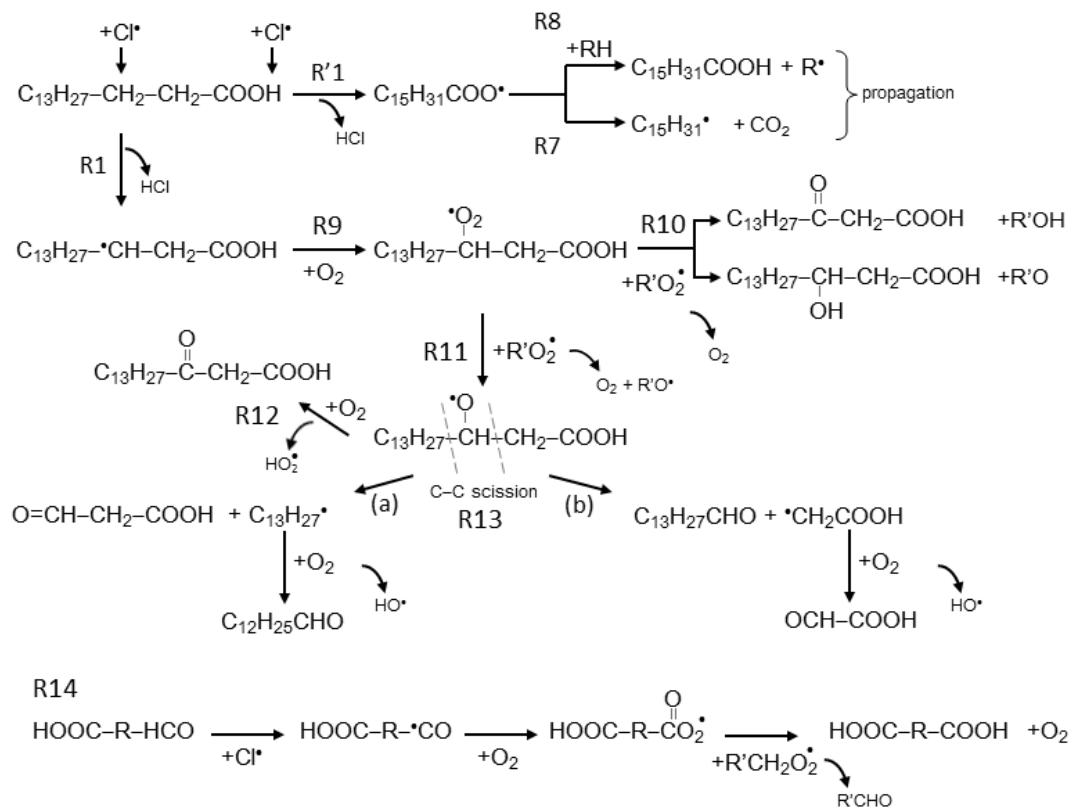


Fig. 2.