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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #3

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The authors present results of a laboratory study of the reactive uptake of chlorine atoms by solid palmitic acid (PA) particles. The fact that the uptake coefficient exceeds unity is explained by radical chain reactions that lead to an efficient decay of PA. Detailed product identification by FTIR and GC/MS is performed and based on these products a chemical mechanism is suggested that qualitatively explains the products. Overall, the results are clearly presented and the data are of atmospheric relevance. However, I have several comments that should be carefully addressed before the manuscript can be considered for publication in ACP.

Major comments

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Interactive Discussion
Discussion Paper

1) 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.

2) Several studies have been conducted previously by other authors that looked at 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'.

3) 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.

4) 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

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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.

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

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?

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?

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

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?

p. 16937, l. 1: What is the value for kPA 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?

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

p. 16938, l. 10: R2 shows that Clp is formed, not Clg. 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.

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

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

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

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

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

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

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?

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.

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

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.

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'.

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 individ-

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ual peaks?

Technical comments

Title: '. . . product identification'

p. 16925, l. 10: remove comma after 'Although'

p. 16927, l. 5: 'the ratio of' can be omitted

p. 16929, l. 28: studies of. . .

p. 16930, l. 16: remove 'of' after 'here'

p. 16934, l. 12: define 'SIM'

p. 16936, l. 20: remove 'atom' or 'molec'

p. 16937, l. 3: 'formalism' does not seem the right word here

p. 16937, l. 5: 'from' (not 'form')

p. 16939, l. 11: indicate

p. 16939, l. 12: increased

p. 16940, l. 17: as a function. . .

p. 16941, l. 1 and 2: product identification

p. 16942, l. 16: leads to the formation of monocarboxylic acids

p. 16943, l. 6: as a function of the . . .

p. 16943, l. 6: we have performed these. . .

p. 16943, l. 11: why not simply 'exposure to chlorine atoms'?

p. 16943, l. 22: PACl1, PACl4 have not been defined. Better: 'with up to four chlorine atoms'

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p. 16944, l. 15: remove 'the' before 'atmospheric particles'

p. 16944, l. 22: under . . .conditions

Figure 3, caption: particle samplers

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