

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

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The authors thank the reviewer for the constructive remarks and suggestions

Q1. 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

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reconcile their results with previous measurements. If there is really a discrepancy with previous measurements a clear statement to indicate this is necessary.

Answer : We compare our uptake measurements with similar previous studies done with organic particles : Squalane + Cl[•], (Liu et al. 2011) and DOS + Cl[•] (Hearn et al., 2007). These studies were also performed in an AFT and Cl[•] atoms were produced by the photolysis of molecular chlorine (Cl₂). However this comparison has to be made while keeping in mind these following aspects: - the chemical formula of the molecules are quite different. In the case of palmitic acid (PA), the molecule exhibits a linear carbon chain with a terminal acid function contrary to DOS and Squalane. 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. - PA is a solid while Squalane and DOS are liquid. It is suspected that radical chain reactions may be enhanced in condensed phase due to high molecular density. Even if detailed chemical mechanisms in the condensed phase are still unclear, the rate of elementary processes might be different for solid and liquid. - the experimental determination of the uptake coefficient was not exactly performed with the same methodology. In previous studies the chlorine exposure, (<Cl> t), was measured using reference kinetics by introducing the reference compound (2-butanone or acetone) in the mixed-phase. For this, it is assumed that the atomic chlorine produced by the reaction R2 (R[•] + Cl₂ → RCl + Cl[•]) stays in the particulate phase and never returns in the gas phase. This is probably possible in the case of liquid particles like squalane or DOS. So the loss of the reference compound is only due to reaction with Cl[•] produced by the photolysis of Cl₂. However this elementary process is quite difficult to verify experimentally, especially in the case of solid particle (like palmitic acid). If a fraction of Cl[•], produced by the reaction R2, returns in the gas phase, then reaction with the reference compound can not be excluded. For this reason, we decide to measure the chlorine exposure during an

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independent experiment where only acetone and Cl₂ are introduced in the AFT, so the atomic chlorine exposure determination is chlorine only generated by the photolysis of Cl₂. - Finally while chlorine exposure used in our study are in the range of the previous cited works, the contact time in the AFT is significantly different, 3 s for Cl^o + DOS system and 180 s for our work. But recent results (L. H. Renbaum and G. D. Smith in Atmos. Chem. Phys., 11, 6881-6893, 2011) show that radical concentration and time are interchangeable parameters only if the precursor concentrations are the same. All this may explain the different values of the uptake determined for the 3 chemical systems: PA+Cl^o, Sq+Cl^o, DOS+Cl^o, with and without oxygen. From our point of view, it is not unreasonable to get disparate values for such different chemical systems. However the ratio between the uptake for PA measured in a N₂/O₂ mixture and in an O₂-free environment is in a good agreement with the same ratio measured for Squalane particles. A summarize of these answers have been added in a new subsection 3.2.4 entitled 'Discussion of previous results' together with the Table1.

Q2. 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. Answer : These measurements have been performed without UV radiations so without Cl^o radicals in the AFT. The volatility of the reaction products cannot be referring to explain the difference between masses determined by GC-MS and SMPS techniques. The authors wish to point out that the two measurements arise from two totally different techniques. Among the causes that can explain these differences, we can surely mention: - efficiency of the extraction of palmitic acid before GC/MS analyses, - errors from the SMPS which is a non-absolute technique for mass determination due to many assumptions introduce in the SMPS data process (shape and density of the particles) and other error sources as the calibration of the particles counter. These explanations

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have been added at the end of the section 2.5.1. Regarding GC analysis, the internal standards used are tetradecane and hexadecane (16933 L14). The details regarding the quantification are given on page 16934, L9 to L12.

Q3.1 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.

Answer : Unfortunately, we are not able to provide more quantitative information on the diacids distribution. It is absolutely correct that detection and extraction efficiencies are different. However, adding one carbon atom will unlikely change dramatically those values. Also, C3 and C4 were probably produced with higher yields as suggested by their much higher signals than C5 to C8. For C5 to C8, it is indeed very difficult to state for small variations.

Q3.2 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 peroxy radical H abstraction to form a hydroperoxide and an alkyl radical? The authors should clarify this part of the mechanism.

Answer : The Figure 8 has been revised with the explicit chemical structure of PA and, now, shows clearly how the small diacids are formed. The Figure 8 now shows, as an example, the H-abstraction from the β -carbon. The reaction R10 of the former mechanism has been removed because the reaction RO₂ and RH seems to be a minor

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reaction pathway of RO₂ in the atmosphere.

Q4. 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.

Answer : Alcohols, as well as other reaction products, were not quantified in this work. The extraction procedure and the silylation step have been specifically optimized for palmitic acid. As a matter of consequence, we are not able to estimate the products yields. So, we have removed from the text the term 'minor' which was only based on the peak relative size.

Q5. 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.

Answer : We do agree with this comment, such information will be very useful to validate the chemical mechanism and determine the major reaction pathways. Unfortunately, the quantification of products was not possible under our chromatographic conditions. We want to study more deeply the carbon balance of the Cl[•] + palmitic acid reaction and the quantification of the products, both in gas phase and particulate phase, will be improved in our future work.

Q6. 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.

Answer : IRTF spectrometer has been mainly used to determine the chlorine exposure by measuring the decay of acetone in the AFT. Some spectra have been recorded dur-

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ing Cl[•] uptake experiment on palmitic acid particles. HCl, CO and CO₂ were clearly identified due to their characteristic and well-known IR spectra. However the measurement of the integrated area of each band, with enough precision to perform quantification were only possible in the case of maximum exposure (i.e. 8 UV lamp and maximum flux of Cl₂ in the AFT). For lower Cl[•] exposure the signal to noise ratio was not sufficient even when spectra were co-added during 10 minutes. So we agree that the formation kinetic of HCl but also of CO and CO₂ would be an important result but due to poor confidence in the results we can't derive any kinetic information.

Q7. 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.

Answer : The same comment and response given for Question 6 can be also valid for this Question 7

Q8. 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.

Answer : The chemical mechanism has been revised. In the new mechanism, reactions R7 and R8 leads to the formation of R[•] radicals. Moreover, OH and HO₂ radicals are formed after R11 occurs. Those radicals can also react with PA or another hydrocarbon molecule.

Q9. 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.

Answer : The chromatogram shown in figure 6 has been obtained with different ex-

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traction conditions than the quantitative analysis (5 time more concentrated solutions; see 16933 L23). Products peaks were simply too small in our quantitative conditions to be properly integrated. The quantification would have also required to check for the quantitative extraction of the products from the filter and of course, to inject standards for calibration purpose. As already mentioned on answer to comment 5, further work will be done in the future on that topic by our group.

Q10. 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 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.

Answer : Following this comment the mechanism was entirely revised showing the explicit chemical structure of the palmitic acid. The formation of shorter chain carboxylic acid is now more clearly shown.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/13/C7654/2013/acpd-13-C7654-2013-supplement.pdf>

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

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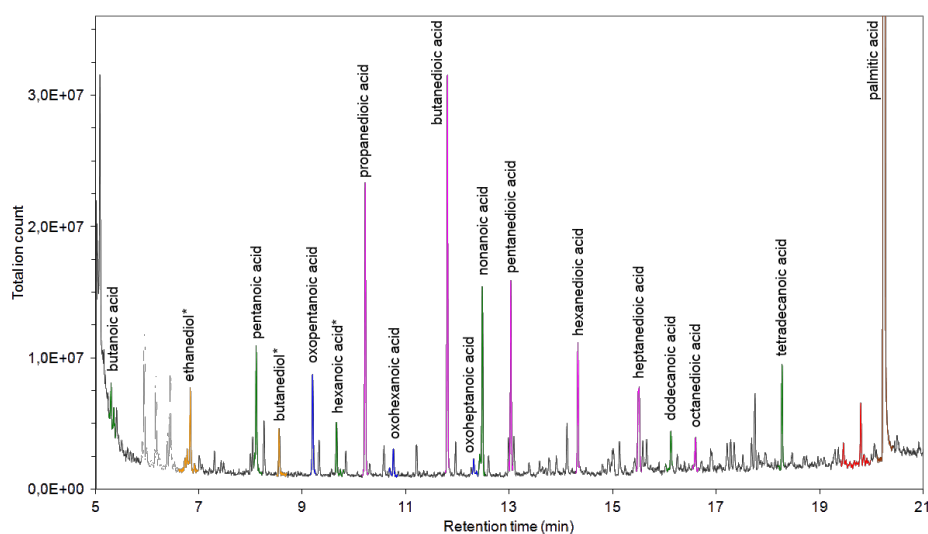


Fig. 1.

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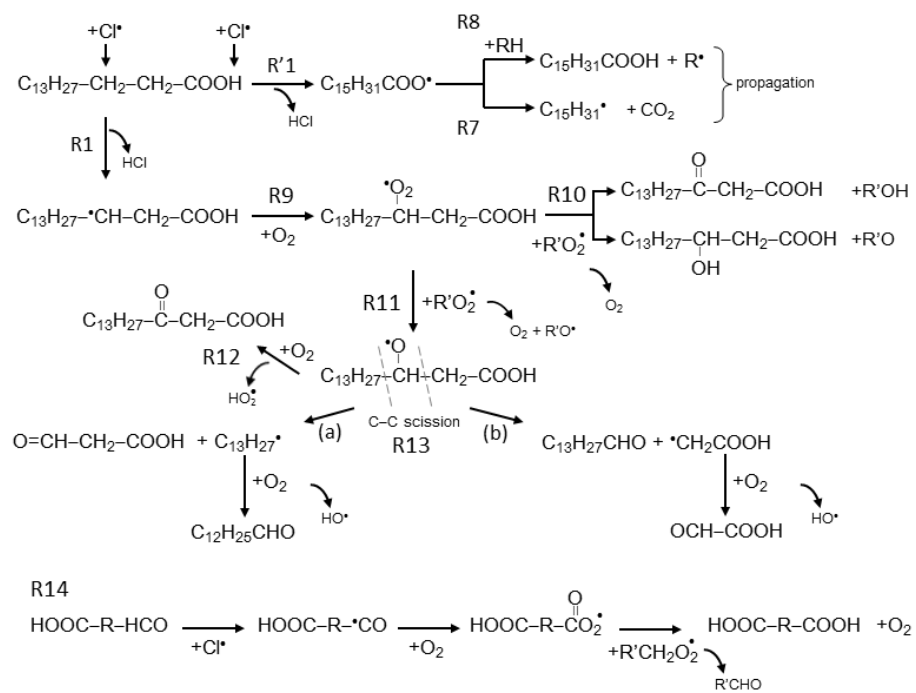


Fig. 2.