

Reactivity of chlorine radical with submicron palmitic acid particles: kinetic measurements and product identification

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Abstract

The heterogeneous reaction of Cl^\bullet radicals with sub-micron palmitic acid (PA) particles was studied in an aerosol flow tube in the presence or in the absence of O_2 . Fine particles were generated by homogeneous condensation of PA vapours and introduced in the reactor where chlorine atoms were produced by photolysis of Cl_2 using UV lamps surrounding the reactor. The effective reactive uptake coefficient (γ) has been determined from the rate loss of PA measured by GC/MS analysis of reacted particles as a function of the chlorine exposure. In the absence of O_2 , $\gamma = 14 \pm 5$ indicates efficient secondary chemistry involving Cl_2 . GC/MS analysis have shown the formation of monochlorinated and polychlorinated compounds in the oxidized particles. Although the PA particles are solid, the complete mass can be consumed. In the presence of oxygen, the reaction is still dominated by secondary chemistry but the propagation chain length is smaller than in the absence of O_2 which leads to an uptake coefficient $\gamma = 3 \pm 1$. In the particulate phase, oxocarboxylic acids and dicarboxylic acids were identified by GC/MS. Formation of alcohols and monocarboxylic acids is also suspected. A reaction pathway for the main products and more functionalized species is proposed. All these results show that solid organic particles could be efficiently oxidized by gas-phase radicals not only on their surface, but also in bulk by mechanisms which are still unclear. They help to understand the aging of primary tropospheric aerosol containing fatty acids.

1 Introduction

The concentration of organic matter in marine environments exhibits a seasonal behaviour, which dominates the chemical composition of fine particulate matter during periods of high biological activity (Yoon *et al.*, 2007; O'Dowd *et al.*, 2004; Cavalli *et al.*, 2004; Sciare *et al.*, 2008). Cells of living organisms in the oceans decompose after their death and the hydrophobic cellular constituents accumulate on the water surface forming a sea-surface micro-layer of 1 to 1,000 μm thickness (Hardy, 1982). When sea-salt aerosols (SSA) are generated by the mechanical ejection of droplets from waves and winds, these organic compounds are also ejected, thus becoming a component of the newly formed particles (Barger and Garrett, 1976; Gogou *et al.*, 1998; Marty *et al.*, 1979). Recent laboratory and field measurements have shown that the organic mass fraction of SSA increases from 0.1 to near 1 when the ambient aerosol aerodynamic diameter decreases from 1 to 0.1 μm (Keene *et al.*, 2007; Facchini *et al.*, 2008). The exact mechanism for such large organic mass fraction of submicron SSA is not well understood.

Chemical analysis of organic compounds sampled in SSA have allowed to identify fatty acid (C12-C18) compounds (Marty *et al.*, 1979), contributing to up to 10% in mass of the total organic content of the particles (Mochida *et al.*, 2002).

Molecular characterizations of sea-salt aerosols collected in marine air masses have shown that fatty acids (FA) consist of relatively short carbon chains (Tervahattu *et al.*, 2002b; Tervahattu *et al.*, 2002a; Mochida *et al.*, 2002; Oros and Simoneit, 2001). Due to the hydrophobic properties of surfactants, the fatty acids are thought to form an organic coating around the inorganic core of the particles (Ellison *et al.*, 1999; Rudich, 2003). When considering a monolayer coating, the surface coverage by FA is estimated to be on the order of 0.3 to 14% (Tervahattu *et al.*, 2005; Mochida *et al.*, 2002).

Fatty acids are also ubiquitous in airborne particles sampled in urban atmospheres (Oliveira *et al.*, 2007). They were found to contribute to up to 50% of identified organic compounds from emission sources such as biomass burning (Nolte *et al.*, 2001; Schauer *et al.*, 2001; Fine *et al.*, 2001), cooking (Schauer *et al.*, 2002; He *et al.*, 2004), and automobiles (He *et al.*, 2006). Among the fatty acids, palmitic acid ($\text{C}_{16}\text{H}_{32}\text{O}_2$) is the most abundant one (Mochida *et al.*, 2002).

Recent literature reviews have presented the physical and chemical processes which occur at the interface of airborne organic particles (Donaldson and Vaida, 2006; Rudich, 2003; George and Abbatt, 2010). Many heterogeneous reactions of atmospheric particles involve the main oxidant of the atmosphere (*i.e.* the hydroxyl radical OH[•]) which chemically alters their surfaces thus aging them. The intensity of this aging depends on various parameters such as meteorological conditions, size of the particle, and the chemical composition of the particle surface and bulk. Consequently, variability of these parameters leads to the observed spatial and temporal variability of the physical and chemical properties of atmospheric aerosols. These heterogeneous processes affect the optical, hygroscopic and reactive properties of airborne particles thereby making uncertain the prediction of their global and regional atmospheric impact. Although the OH[•] radical is the primary daytime oxidant, halogen atoms (Cl, Br and I) may also significantly participate in oxidation processes, especially in the marine boundary layer (MBL). Halogen species are emitted from anthropogenic sources, but important sources are also represented by the halogen-release from sea-salt aerosols and associated heterogeneous reactions. Cl[•] atoms are mainly generated from the photolysis of active chlorine species and their concentrations can be up to 10⁶ atom.cm⁻³ (Spicer *et al.*, 1998; Pechtl and von Glasow, 2007).

Recent atmospheric measurements (Osthoff *et al.*, 2008) have shown that nitryl chloride (ClNO₂) is produced by heterogeneous reactions on sea-salt particles and accumulates during the night. At dawn, the photolysis of nitryl chloride produces a peak of Cl[•] with an estimated rate of formation of 1×10⁶ atom cm⁻³ s⁻¹.

This Cl[•] atom source seems modest relative to other oxidants. However, it has been reported that Cl[•] reacts faster than OH[•] radicals with hydrocarbon compounds (Spicer *et al.*, 1998) and may represent the major oxidant of the troposphere in coastal and industrialized areas, especially at dawn, when concentrations of OH[•] radicals are low. While sources of reactive halogen species and halogen chemistry in the troposphere are relatively well studied, detailed chemical processes are still unknown (George and Abbatt, 2010).

Given the high reactivity of Cl[•] atoms with organic compounds and the ubiquity of Cl[•] and fatty acids in the troposphere, especially in the MBL, it is obvious that this heterogeneous reactivity must be considered. However, only a few experimental studies between gas-phase radicals (Cl[•] or OH[•]) with condensed-phase organic compounds, including model organic surfaces, are reported.

Uptake coefficients of OH[•] on pure palmitic acid (PA) particles between 0.8 and 1 have been reported by McNeill *et al.* (McNeill *et al.*, 2008). The authors also measured uptake coefficients for thin PA film coatings on solid and liquid NaCl particles, obtaining lower values than for pure PA experiments (solid, $\gamma^{\text{OH}} \approx 0.3$ and liquid, $\gamma^{\text{OH}} \approx 0.05$). Experiments with chlorine atoms, generated from Cl₂ photolysis, have also been considered as a model for radical-initiated oxidation chemistry which avoids the presence of reactive precursors or side-products during generation of OH[•]. The reactive uptake of Cl[•] atoms on self-assembled organic monolayers was studied by Moise and Rudich (Moise and Rudich, 2001) using a flow reactor coupled to a chemical ionization mass spectrometer. The uptake coefficient, measured by recording the rate of loss of Cl[•] radicals, was estimated to be in the range ($0.1 < \gamma < 1$), close to the diffusion-limited loss rate.

Reactions of Cl[•] radicals in the presence of O₂ have been studied using an aerosol flow tube to stand as a model of the radical-initiated oxidation of liquid phase organic aerosols. In the case of reactions of Cl[•] radicals with dioctyl sebacate (DOS) particles (Hearn *et al.*, 2007), in the presence of O₂, uptake coefficient has been determined by monitoring the rate of loss of DOS species. The uptake coefficient exhibits a value greater than unity ($\gamma_{\text{DOS-OH}} = 1.7 \pm 0.3$) indicating a radical chain chemistry. Products were mainly identified in the particles, showing an inefficient volatilization process.

More recently, heterogeneous reactions between Cl[•] atoms and submicron squalane particles have been investigated in a photochemical aerosol flow tube (Liu *et al.*, 2011). Secondary chain chemistry occurring in the liquid phase has also been demonstrated during this study. The measured uptake coefficient decreases from a value of ~ 3 for experiments performed without O₂ to a value of 0.65 for experiments in the presence of O₂. Product formation in condensed phase is controlled by competitive reaction rates of O₂ and Cl₂ with alkyl radicals.

All of these studies of heterogeneous reaction between radical species and organic surfaces or particles as a model for the oxidation of organic aerosols clearly emphasize the role of OH[•] or Cl[•] in initiating oxidation processes *via* an H-abstraction pathway. This is followed by a chain reaction which can accelerate the overall rate of particle transformation. Concerning experiments with Cl[•] radicals, it was shown that more than 60% of the initial condensed matter can be consumed by the reactions. Several hypotheses have been put forth to explain these surprising observations: (1) a quite rapid surface renewal process, (2) an efficient secondary chain chemistry in the bulk. These processes might readily occur in the case of

liquid droplets (DOS or squalane) but are limited by the diffusion of the species in the liquid phase for both reactants and products. In the case of solid particles, surface renewal can be induced by volatilization. Trapping of species within the particle or phase change of the surface layer cannot be excluded.

Chemical mechanisms adapted from the homogeneous phase have been proposed to interpret the formation of products mainly in the particulate phase but reaction pathways still remain unclear due to the specificity of the condensed phase (microscopic arrangement of the molecules, diffusion process in liquid/solid phase, for example).

We present here the experimental results of heterogeneous reactivity between Cl^\cdot and PA within an Aerosol Flow Tube (AFT) where fine particles generated by homogeneous condensation of PA vapours are introduced with Cl_2 as a radical precursor. Cl^\cdot atoms are generated by photolysis of the molecular chlorine using UV lamps surrounding the reactor. Experiments have been conducted with and without O_2 . For both cases, uptake coefficients have been determined by monitoring the decay of PA by GC/MS analyses of collected particles on filters at the exit of the reactor. Identification of the reaction products in the condensed phase have been performed by GC/MS analyses and has led to the proposal of a detailed chemical mechanism for oxidation of carboxylic acids in particulate matter.

2 Experimental section

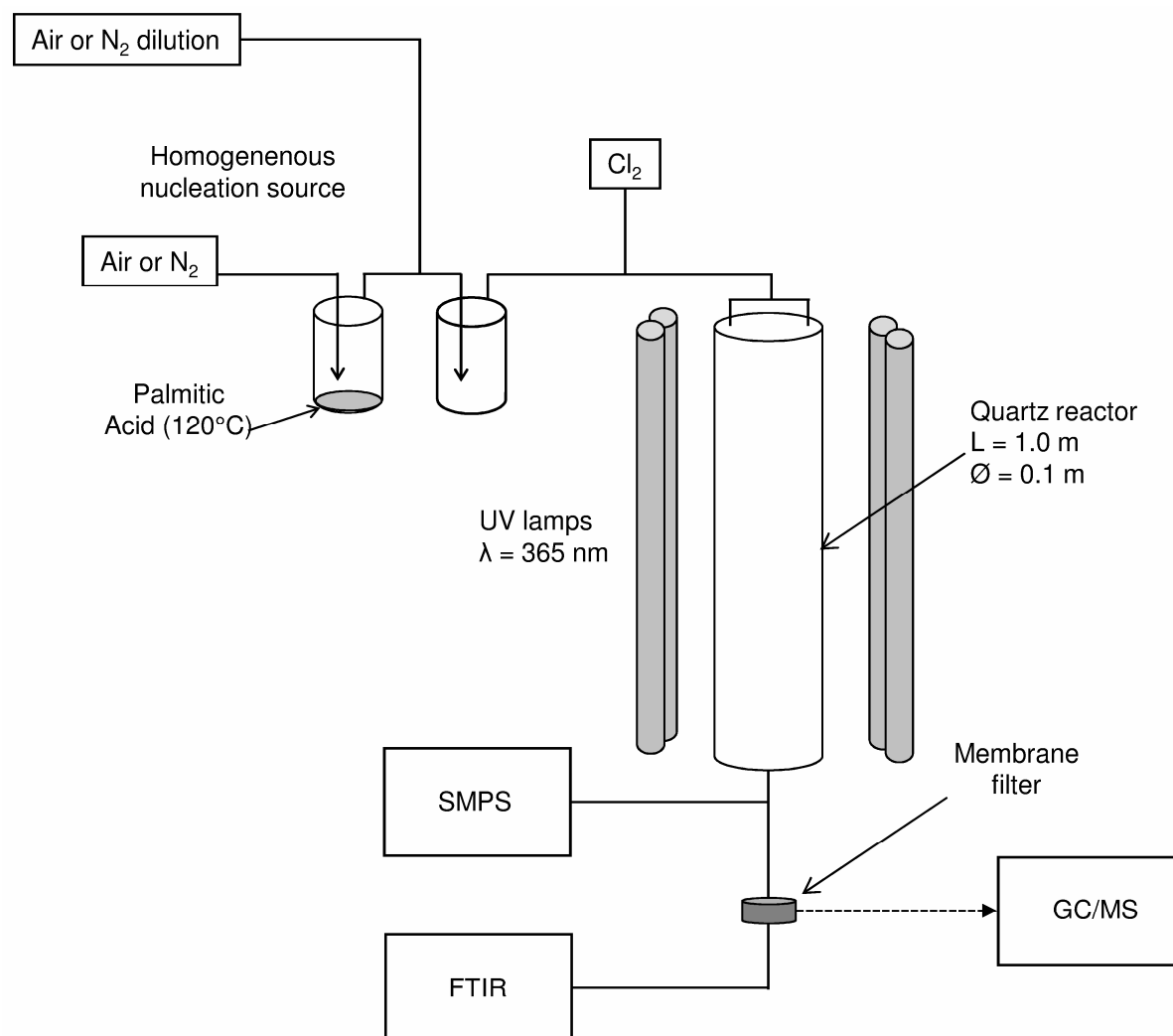
2.1 Aerosol flow tube

An atmospheric pressure aerosol flow tube (AFT) is used to investigate the heterogeneous reactivity of PA particles with chlorine atoms (Fig. 1). The AFT is a 1 m long and 10 cm inner diameter quartz tube surrounded by 8 UV lamps (UVP, 365 BLB, $\lambda_{\text{mean}} = 365 \text{ nm}$). The particles and the gas-phase oxidant precursor are introduced into the upper flange of the reactor through two $\frac{1}{4}$ " stainless steel connectors. The total flow, monitored by mass flow meters, is fixed at 4.0 L min^{-1} which corresponds to a mean residence path time of 180 s in the AFT.

2.2 Reactant generation

Palmitic acid ($\geq 98\%$) is purchased from Roth. Chemical purchased from Aldrich is: dichloromethane (99.8%). Chemicals from Fluka are: tetradecane ($\geq 98\%$), hexadecane (\geq

1 98%). N,O-Bis (trimethylsilyl) trifluoroacetamide, $C_8H_{18}F_3NOSi_2$ - Trimethylchlorosilane
 2 (BSTFA-TMCS) (99%-1%) solution is purchased from Supelco. Gases are purchased from
 3 Praxair: Synthetic air 3.0, Nitrogen 4.6. Chlorine (1% of Cl_2 in Helium) is purchased from Air
 4 Liquide (99.6%).



5
 6 Figure 1. Experimental setup, SMPS (Scanning Mobility Particle Sizer), FTIR (Fourier
 7 Transform InfraRed spectrometer), GC/MS (Gas Chromatography, Mass Spectrometer)

8 **2.3 Particle generation**

9 Palmitic acid particles are generated by homogeneous nucleation in a stream of 1 L min⁻¹ N₂
 10 or N₂/O₂ flowing through a glass vessel containing 5 grams of PA. A heating wire wraps the
 11 glass vessel and the PA temperature is kept constant (+/- 1°C) using a temperature controller.
 12 The flow is diluted with 1 L min⁻¹ of N₂ or N₂/O₂ and sent to a condensation tube of 1.5 L
 13 volume at room temperature. The size distribution of the particles is continuously recorded by

a SMPS (model TSI 3080L) every 2 minutes. Palmitic acid particle density was assumed to be the solid phase density ($d=0.852 \text{ g cm}^{-3}$). Depending on the heating temperature and flows, mass concentrations between 500 and 1,000 $\mu\text{g m}^{-3}$ of PA particles are generated. For a temperature of around 120°C, the setup produces a log-normal particle size distribution with a mean surface-weighted diameter of $\sim 500 \text{ nm}$ and a geometric standard deviation of ~ 1.5 . Measuring the aerosol concentration before and after the AFT has revealed that the mean diameter is not modified and that at maximum a mass loss of 10% occurred while passing through the AFT.

2.4 Atomic chlorine production

The chlorine radicals are generated along the length of the AFT by powering all or some of the 8 UV lamps. The Cl concentration can also be adjusted by controlling the Cl_2 initial concentration in the AFT.

The chlorine radical concentration is measured by performing reference kinetic experiments with acetone. Molecular chlorine (3 to 20 ppm) and acetone (50 ppm) are introduced in the reactor and the reaction between acetone and Cl takes place with a second order rate constant (k_{ref}) of $2.09 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Liu *et al.*, 2011; George *et al.*, 2007). The loss of acetone is monitored by Fourier transform infrared (FTIR) spectroscopy by integration of the absorbance of the C-C stretching band at $1,217 \text{ cm}^{-1}$ (Perelygin and Klimchuk, 1974) between 1,160 and $1,260 \text{ cm}^{-1}$. The loss rate of acetone can be expressed as:

$$v = \frac{d[\text{Acet}]}{dt} = -k_{ref} [\text{Acet}][\text{Cl}] \quad (1)$$

Integration of Eq (2) leads to determination of the chlorine exposure ($\langle \text{Cl} \rangle_t$ in $\text{atom cm}^{-3} \text{ s}$) which is the product of the reaction time t with the time averaged chlorine radical concentration along the reactor $\langle \text{Cl} \rangle_t$ where $[\text{Acet}]_0$ and $[\text{Acet}]_t$ are the initial and final concentrations of acetone measured by FTIR spectroscopy respectively.

$$\frac{\ln \frac{[\text{Acet}]_t}{[\text{Acet}]_0}}{-k_{ref}} = \int_0^t [\text{Cl}] dt = \langle \text{Cl} \rangle_t \cdot t \quad (2)$$

As shown in Fig. 2, the chlorine exposure, $\langle \text{Cl} \rangle_t$, is linearly proportional to $[\text{Cl}_2]$ with a maximum time averaged chlorine concentration of $2.25 \times 10^9 \text{ atom cm}^{-3}$. The ratio $[\text{Cl}_2]/[\text{Cl}]$

expresses the photodissociation efficiency and is greater than 3,000 and means that on average one Cl_2 out of 6,000 is dissociated by photolysis and produces 2 Cl^\cdot radicals.

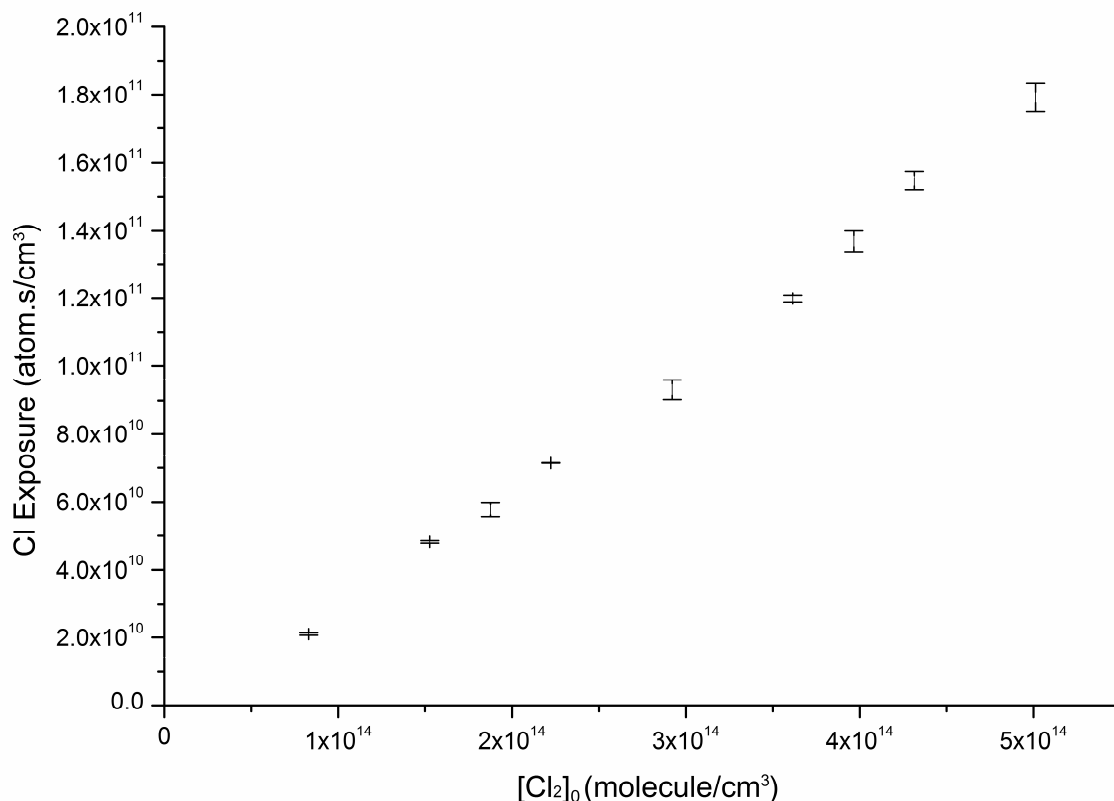


Figure 2. Chlorine exposure as function of the initial Cl_2 concentration in the reactor; $Q_{\text{tot}} = 4.0 \text{ L min}^{-1}$ and 8 UV lamps powered. Errors bars express the minimum and maximum values of 4 experiments.

2.5 Analytical procedure

2.5.1 Particle sampling and GC/MS analysis.

At the reactor outlet, the particles are sampled on a PTFE (PolyTetraFluoroEthylene) filter (Millipore FALP, 1.0 μm , diameter 47 mm) for 10 minutes in order to collect about 20 μg of PA. The filter is then placed in a 1.5 mL vial and 10 μL of a solution containing two internal standards (tetradecane and hexadecane) and 25 μL of a commercial mixture 99% BSTFA / 1% TMCS are deposited directly on the membrane. Quantitative analysis of carboxylic acids by gas chromatography requires derivatization of the $-\text{COOH}$ function. Silylation by BSTFA (N, O-Bis (trimethylsilyl) trifluoroacetamide, $\text{C}_8\text{H}_{18}\text{F}_3\text{NOSi}_2$) has been previously used for the determination of mono- and dicarboxylic acids in samples of atmospheric particles collected

on filters (Docherty and Ziemann, 2001; Wang *et al.*, 2009; Zuo *et al.*, 2007; Yu *et al.*, 1998). Trimethylchlorosilane (TMCS) acts as a catalyst by increasing the silyl donor strength of the BSTFA. After finally adding a volume of 1 mL of dichloromethane, the filter is subjected to 10 minutes of sonication. For the product identification, only a volume of 200 μL of dichloromethane is added before the sonication. NIST mass spectra database (V2.2) is used for the identification. After the extraction and silylation steps, 1 μL of the solution is injected in a Gas Chromatograph Mass Spectrometer (Perkin-Elmer GC Clarus 680). The chromatographic conditions are as follows: inlet 250°C, split mode 5 mL min⁻¹, constant column flow 1 mL min⁻¹, oven temperature: 50°C for 0.5 min, ramp +20°C min⁻¹ to the final temperature 310°C. Separation is provided by an Elite-5MS 30 meter long column (diameter 250 μm and film thickness 0.5 μm). Identification and quantification is performed on a Clarus 600C mass spectrometer in 70 eV electron impact mode with a source temperature of 180°C.

The quantification of palmitic acid is done by injecting standard solution of known concentration. The ion fragment corresponding to the silyl group $\text{Si}(\text{CH}_3)_3$ ($m/z=73$) is chosen for the quantification of silylated palmitic acid. All samples are injected in triplicates in Selected Ion Monitoring (SIM) mode for the quantification and once in scan mode for identification. The mass of PA particles collected on the filter for 10 minutes was quantified by GC/MS and compared to the mass concentration measured by the SMPS analysis during the same period. It appears that the mass derived from GC/MS represents 80 % \pm 10 % of the mass as determined by the SMPS. These measurements have been performed without UV radiations so without Cl° radicals in the AFT. 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.

2.5.2 FTIR analysis

Gas phase analysis were performed by Fourier transform infrared spectroscopy mainly for the chlorine exposure determination. The FTIR spectra are recorded with an Avatar–Thermo Scientific spectrometer equipped with a 10 m length multipath cell. Each spectrum is obtained while averaging 100 scans in the 400 – 4,000 cm⁻¹ spectral range with a spectral resolution of 1 cm⁻¹. Background spectra are taken before and after reactivity experiments to make sure that measured products are not stuck on the mirrors of the cell.

3 Results and discussion

3.1 Chlorine reactivity in N₂

3.1.1 Kinetic measurements

First, we studied the heterogeneous oxidation of palmitic acid particles by Cl radicals in an O₂-free environment. The classical parameter determined in heterogeneous kinetic measurements is the reactive uptake coefficient γ_{Cl} which is defined as the fraction of Cl collisions with the particle leading to the loss of Cl in the gas-phase. Since the loss of Cl is not measured in this experiment, the reaction is monitored through the reactive loss of palmitic acid in the particle phase γ_{PA} . The PA loss rate can be expressed as follows:

$$\frac{d[PA]}{dt} = -k_{PA} [Cl][PA] \quad (3)$$

where k_{PA} is the second order rate constant of PA with Cl (cm³ molecule⁻¹ s⁻¹). [PA] and [Cl] are the time dependent concentrations of the reactants (molecule cm⁻³). The palmitic loss ϕ_{loss} (molecule s⁻¹ cm⁻²) is defined by:

$$\phi_{loss} = \frac{V}{S_p} k_{PA} [Cl][PA] \quad (4)$$

where S_p is the particle surface density (cm² cm⁻³) and V the volume of the particle. The flux of collisions ϕ_{coll} (molecule s⁻¹ cm⁻²) occurring on the particle surface per second is expressed in the equation 5:

$$\phi_{coll} = \frac{[Cl] \cdot \omega_{Cl}}{4} \quad (5)$$

where ω_{Cl} is the mean speed of gas-phase Cl (cm s⁻¹). The integration of equation 3 leads to:

$$k_{PA} = \frac{\ln \frac{[PA]_0}{[PA]_t}}{\langle Cl \rangle_t \cdot t} \quad (6)$$

[PA]₀ and [PA]_t are the initial and final concentrations of particle-phase PA, respectively, and measured by GC/MS (molecule cm⁻³). $\langle Cl \rangle_t$ (atom cm⁻³ s) is the exposure obtained by the reference kinetics measurements and k_{PA} is experimentally determined from the decay of

palmitic acid as a function of the exposure. Moreover, $[PA]_0$ can be replaced in the uptake coefficient expression by:

$$[PA]_0 = \frac{V_P \cdot \rho_{PA} \cdot N_A}{M_{PA}} \quad (7)$$

where V_P is the particle volume density ($\text{cm}^3 \text{ cm}^{-3}$), M_{PA} is the molar mass of palmitic acid ($M_{PA} = 256 \text{ g.mol}^{-1}$), ρ_{PA} is the palmitic acid density ($\rho_{PA} = 0.852 \text{ g.cm}^{-3}$) and N_A is the Avogadro's number. Finally, the uptake coefficient γ_{PA} can be expressed as:

$$\gamma_{PA} = \frac{\phi_{loss}}{\phi_{coll}} = \frac{4 \cdot k_{PA} \cdot D_{mean} \cdot \rho_{PA} \cdot N_A}{\omega_{Cl} \cdot 6 \cdot M_{PA}} \quad (8)$$

D_{mean} is the mean surface-weighted diameter of the particle distribution and is calculated by $V_P/S_P = D_{mean}/6$ (Smith *et al.*, 2009). The mean particle diameter is determined by SMPS measurements and is assumed to be constant and equal to the initial mean particle diameter.

The normalized decay of ($[PA]_t/[PA]_0$) as a function of Cl exposure is shown in Fig. 3. The decay constant k_{PA} is obtained from an exponential fit to the experimental measurements for exposure values ranging from 0 to $4 \times 10^{11} \text{ molecule cm}^{-3} \text{ s}$.

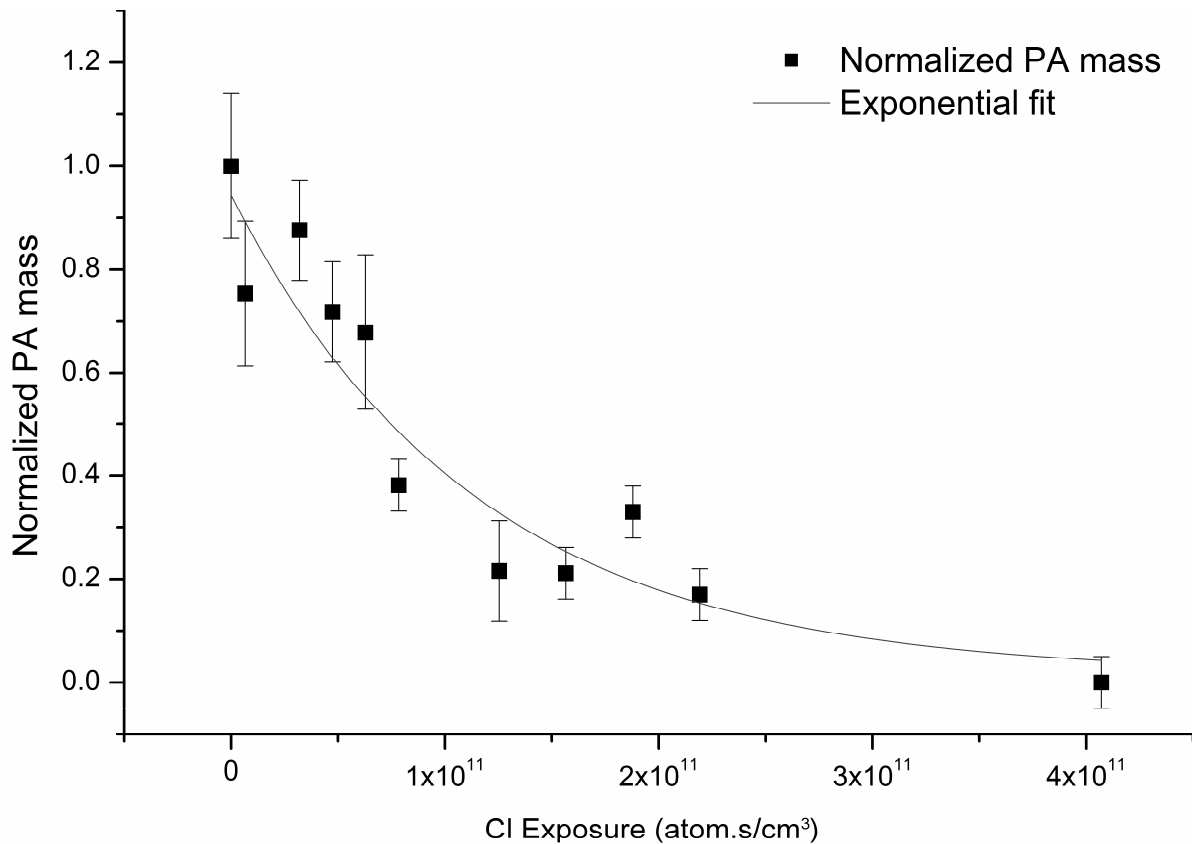


Figure 3. Normalized mass of PA remaining in particles collected on filter during 10 minutes as a function of the chlorine exposure (squares). Each data point is a mean value obtained from three GC/MS analyses of two particles samples; errors bars represent minimum and maximum values. The data have been fitted by an exponential function (solid line).

Using the rate constant k_{PA} ($k_{PA} = 1 \cdot 10^{-11} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$) obtained from the slope of the exponential fit of kinetic data in Fig. 3, the initial uptake coefficient γ_{PA} has been determined to be equal to 14 ± 5 in an oxygen-free environment. 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. The high value of γ means that: (1) the heterogeneous reaction of PA with Cl radical is very efficient; (2) the secondary chemistry is leading the overall reaction. These results are similar to those of Liu *et al.* (Liu *et al.*, 2011) who reported $\gamma = 3$ for the uptake coefficient of chlorine on squalane particles. However, Liu *et al.* determined the loss of squalane as a function of the total chlorine radical concentration while, in this study, the loss of palmitic acid is measured as a function of the chlorine radical concentration produced only from the photolysis of Cl_2 . As a result, the uptake coefficients cannot be strictly compared but both show the importance of secondary chemistry.

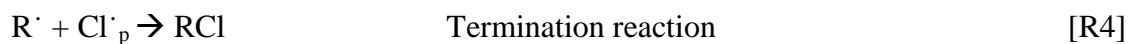
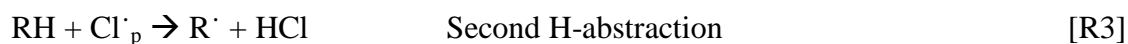
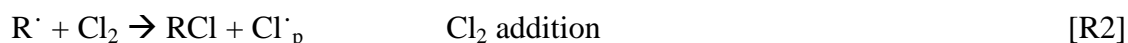
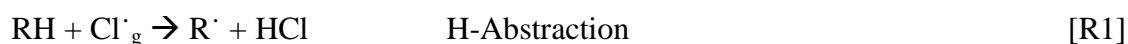
By definition, the initial uptake coefficient, when derived from the measurement of the rate loss of the gas phase oxidant Cl_g , γ_{Cl} , cannot be greater than 1. Here the uptake coefficient, determined from the rate loss of the condensed phase (γ_{PA}) is significantly greater than one ($\gamma_{PA} = 14 \pm 5$), indicating an efficient secondary heterogeneous chemistry leading the whole reaction. The chain propagation length is the ratio between the number of palmitic acid molecules lost and Cl_g atoms that react and corresponds to the ratio γ_{PA}/γ_{Cl} . The chain propagation length is at least equal to 14.

Although, the palmitic acid particles are solid, the complete palmitic acid mass can be almost completely consumed. This behavior has already been observed for heterogeneous chemistry involving liquid compounds where diffusion in the bulk can be suggested as an explanation for fast refreshing of the surface. In the case of solid particles, this surprising observation is somehow more difficult to discuss. Two hypotheses can be put forward: (1) an efficient volatilization of the products formed at the surface of the particle or, (2) a phase change of the

first layers facilitating diffusion or trapping of species within the particle (McNeill *et al.*, 2008; Marcolli *et al.*, 2004; Garton *et al.*, 2000).

3.1.2 Reaction mechanism

The high value of the uptake coefficient confirms that the PA consumption is enhanced by secondary chemistry. Liu *et al.* proposed a catalytic mechanism which can be adapted to our oxidation process.

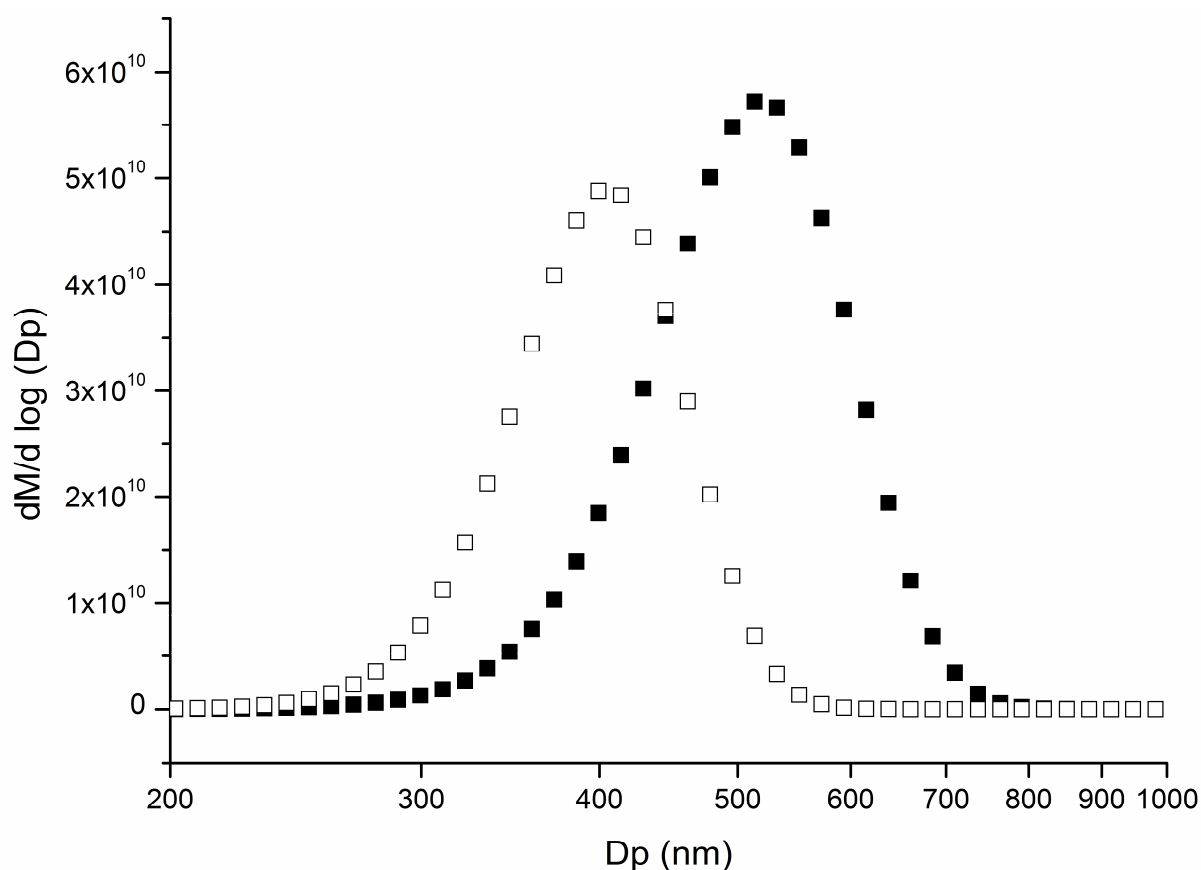


$\text{Cl}^{\cdot}_{\text{g}}$ is defined as a gas phase Cl^{\cdot} produced from Cl_2 photolysis. The initiation reaction [R1] is the heterogeneous reaction between $\text{Cl}^{\cdot}_{\text{g}}$ and particle-phase PA at the surface of the particle producing an alkyl radical R^{\cdot} . A chlorine molecule can be added on the R^{\cdot} leading to formation of a chlorinated product and atomic chlorine $\text{Cl}^{\cdot}_{\text{p}}$. This chlorine atom is released from the surface of the particle and can easily react with another hydrocarbon. R4, R5 and R6 are reactions terminating the radical chain propagation. R6 could occur heterogeneously via the collision between $\text{Cl}^{\cdot}_{\text{g}}$ and $\text{Cl}^{\cdot}_{\text{p}}$ but also can take place in the condensed phase and involve two $\text{Cl}^{\cdot}_{\text{p}}$. Such heterogeneous mechanism has already been observed in previous studies performed either on NaCl particles (Ciuraru *et al.*, 2011) or on ammonium sulphate particles (Ciuraru *et al.*, 2012). The reaction rate of [R1] is defined by the uptake coefficient of chlorine on the particle surface γ_{Cl} . R2 is a source of Cl^{\cdot} allowing the chlorine radical concentration to be renewed; moreover the $[\text{Cl}_2]$ concentration is in excess of $[\text{Cl}^{\cdot}]$ ($[\text{Cl}_2]/[\text{Cl}^{\cdot}] > 3,000$).

3.1.3 Change in the particle size distribution

The SMPS data indicate that the initial log-normal particle distribution mean diameter shifts from 520 to 405 nm after a Cl-exposure of 1.25×10^{11} molecule cm^{-3} s (see Fig. 4). For this

1 specific exposure, the aerosol mass measured by SMPS decreases by 40% whereas the
 2 GC/MS analysis shows that 80% of the particle-phase PA is lost. Chlorinated products have a
 3 higher molar mass than PA and it is assumed that they remain in the condensed phase, thus
 4 changing the density of oxidized particles compared to initial pure PA particles. The oxidized
 5 particle diameter cannot therefore be rigorously determined because the particle diameter is
 6 obtained from electrical mobility of the particle which depends on their density. Assuming
 7 that the change of the mean diameter is only due to the density variation would indicate that
 8 the particle density would have increased from 0.852 to 1.850. This value seems too high for
 9 an organic compound and suggests that the mean diameter change is also due to volatilization
 10 of products. Consequently, the initial mean surface-weighted particle diameter is considered
 11 in this following kinetic study.



12
 13 Figure 4. Mass-weighted particle distribution (normalized $\mu\text{g m}^{-3}$) of PA particles before
 14 (filled squares) and after (open squares) a chlorine exposure of $1.25 \times 10^{11} \text{ atom cm}^{-3} \text{ s}$. Each
 15 distribution is an average of eight measurements.

3.1.4 Particulate-phase product identification

Evidence of presence of monochlorinated palmitic acid is found in the mass spectra. Fragments with $m/z=362$ and 364 are detected and correspond to the parent peaks of the silylated monochlorinated palmitic acid ($C_{15}H_{30}Cl-COO-Si-(CH_3)_3$) with characteristic pattern for the $m/z=35$ and 37 isotopic relative abundances of chlorine. In those mass spectra, the presence of the peak $m/z=117$ (corresponding to $-COO-Si-(CH_3)_3$) shows that the carboxylic acid function has not been modified and the chlorine atom has not been added on the oxygen atom. Because the hydrogen abstraction by chlorine can occur at 17 different sites, several monochlorinated products are detected instead of one single product.

Dichlorinated palmitic acid molecules are also detected in the sampled particles. The formation of different constitutional isomers induces much smaller peaks than the monochlorinated ones. The mass spectra of those species shows the $m/z=396$, 398 and 400 amu, indicating the presence of the parent peak of $C_{15}H_{29}Cl_2-COO-Si-(CH_3)_3$ with the natural abundance of chlorine atoms. The mass spectra of those species indicates the presence of the silylated monochlorinated palmitic acid fragment ($m/z=362$ and 364) and also the silylated carboxylic acid function. Polychlorinated palmitic acid molecules such as trichlorinated palmitic acid molecules and more are highly suspected but the signal/noise ratios are too low to get unambiguous identifications.

3.2 Chlorine reactivity in the presence of O_2

3.2.1 Kinetic measurements

The effect of oxygen on the heterogeneous reactivity between Cl^\bullet atoms and PA particles has been explored by using a N_2/O_2 mixture (80%/20%) as a carrier gas for the aerosol flow. The particle-phase PA decay is much slower when oxygen is added in the chemical system compared to the measurements without O_2 (see Fig. 5). The uptake coefficient of $\gamma_{PA}=3$ has been determined and shows that the catalytic secondary reactions still govern the decay of PA but the propagation length of the catalytic reactions is reduced. The decrease of the uptake coefficient as a function of the oxygen concentration has been previously observed by Liu *et al.* (Liu *et al.*, 2011) in the heterogeneous oxidation of squalane (Sq) by chlorine radicals. The secondary chemistry involving Cl_2 is considered as insignificant because the ratio between O_2 and Cl_2 concentrations is greater than 1,000. In the presence of O_2 , a new reaction ($R^\bullet + O_2$)

competes with R2, leading to the formation of an alkyl peroxy radical instead of a chlorinated radical.

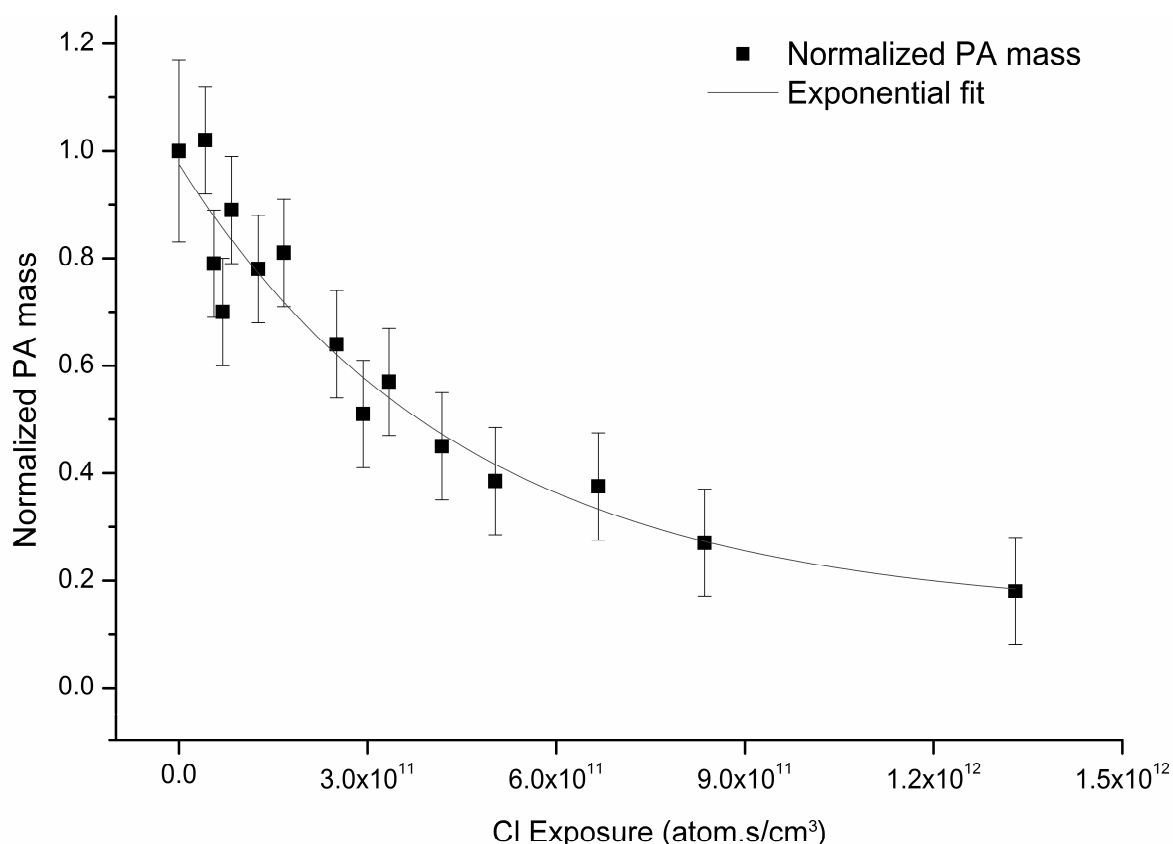


Figure 5. Normalized mass of PA remaining in the particles as a function of the chlorine exposure in the presence of oxygen (squares) and the corresponding exponential fit (solid line).

3.2.2 Particulate product identification

The products identification has been performed after the derivatization step by collecting the particles at the AFT outlet during 30 minutes (see Fig. 6). We were not able to identify any products on non-derivatized samples.

The main identified products are dicarboxylic acids and oxocarboxylic acids and confirm the observations by McNeill (McNeill *et al.*, 2008) where oxocarboxylic were detected. This new study allows to identify and speciate dicarboxylic and oxocarboxylic acids. Oxocarboxylic acids detected are oxopentanoic, oxohexanoic and oxoheptanoic acid.

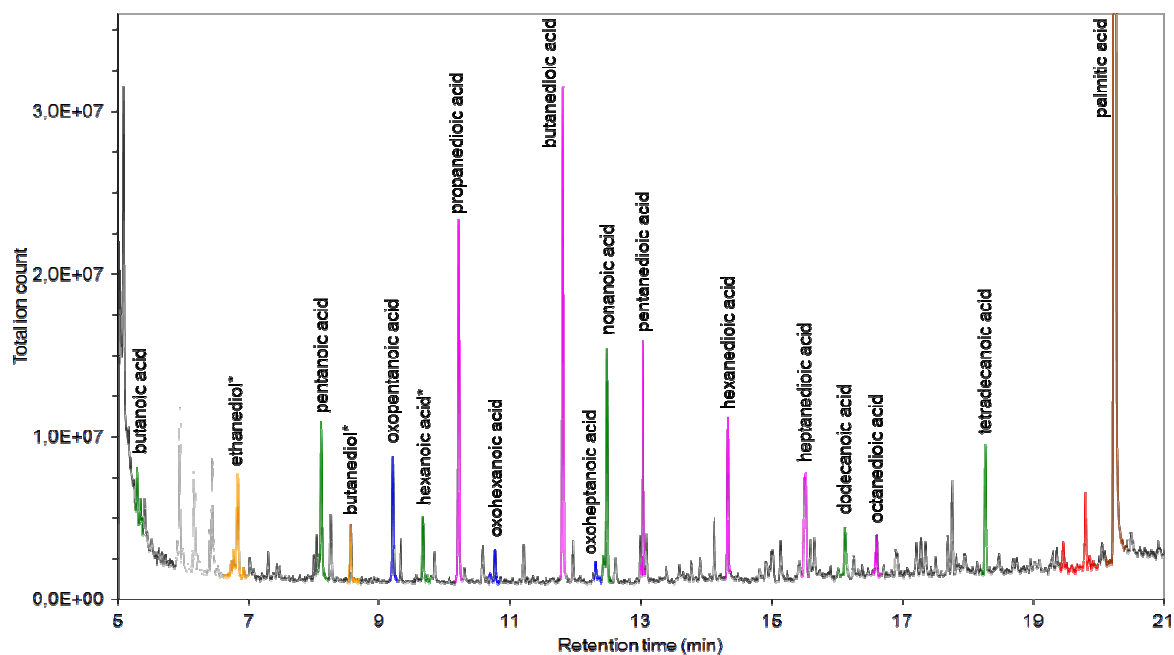


Figure 6. Chromatogram of the silylated-products from the Cl-initiated oxidation of PA in the presence of O₂ (* uncertain identification).

The identification shows that the oxocarboxylic acids are produced on shorter carbon chain length than the palmitic acid but the C=O function position could not be determined in the mass spectra. Moreover, we suppose that several isomers of oxocarboxylic acids can be produced and that they may have not been separated with the gas chromatography conditions. Dicarboxylic acids have been detected from the propanedioic acid (C3) to octanedioic acid (C8). The normalized yields (Fig. 7) are calculated from the ratio of a specific dicarboxylic acid chromatographic peak area over the C3 dicarboxylic acid peak area. Those ratios are only for a comparison purpose and assume that the response coefficients are equals. The normalized yields are much higher for C3 and C4 dicarboxylic acids (Fig. 7). For that reason, oxalic acid is suspected to be produced but it has not been detected under our analytical conditions.

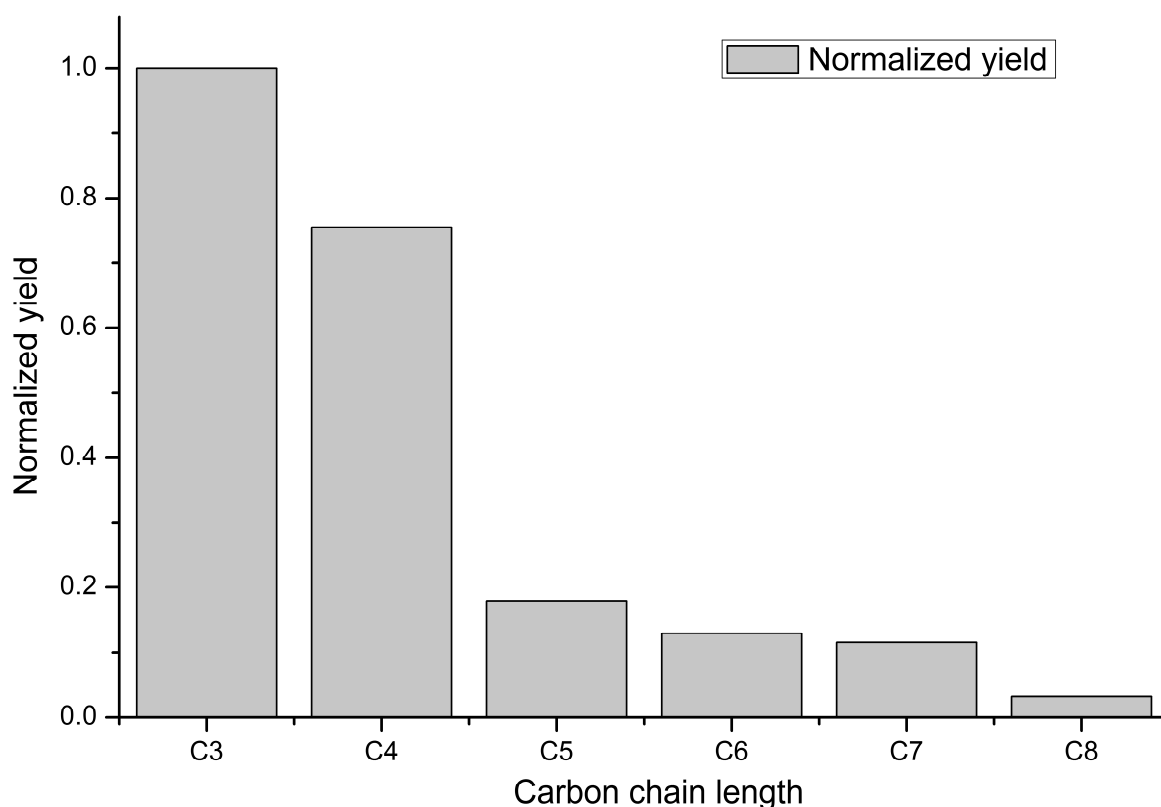


Figure 7. Normalized yields of the detected dicarboxylic acids as a function of the carbon chain length.

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 which are consistent with the formation of hydroxyacid proposed by McNeill *et al.* (McNeill *et al.*, 2008). Monocarboxylic acids have also been detected in much lower quantities. Moreover, the gas-phase products HCl, CO₂ and CO have been clearly identified by FTIR spectroscopy by means of their characteristic fundamental bands in the case of the maximum chlorine exposure. For lower Cl^o exposure the signal to noise ratio was not sufficient even when spectra were co-added during 10 minutes.

3.2.3 Chemical mechanism

We propose a reaction mechanism (see Fig. 8) for the radical initiated oxidation of PA particles adapted from the mechanism presented by George and Abbatt (George and Abbatt, 2010). We have intentionally reduced the reaction mechanism to the observed pathways based on the products identified by GC/MS. Because no relative carbon yields are suggested in our study, we cannot determine which reaction path dominates. We have chosen to show the

mechanism with an H-abstraction on the β position of the carboxylic function. This is for a better understanding of the mechanism and does not necessarily correspond to a preferential site of H-abstraction.

As in the case of the experiments without O_2 , the first step leads to the abstraction of a hydrogen atom by a Cl^\bullet radical from the aliphatic chain (R1) or from the carboxylic acid group (R'1) (Smith and Ravishankara, 2002; Singleton *et al.*, 1989). R7 is the internal recombination of $RCOO^\bullet$ to form CO_2 and the R^\bullet radical. R8 leads to the regeneration of palmitic acid. The radical $C_{15}H_{31}^\bullet$ formed on R7 will be oxidized to an alcohol, aldehyde or ultimately to a carboxylic acid.

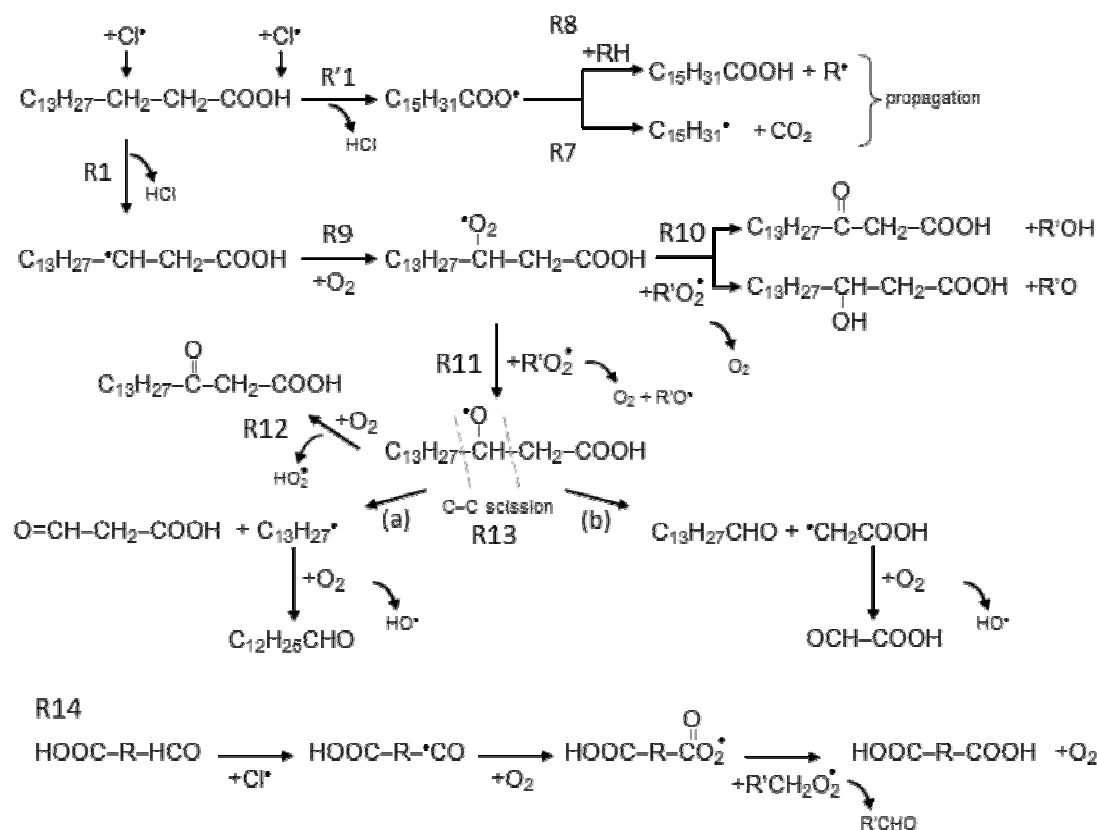


Figure 8. Proposal of a reaction mechanism for the chlorine radical initiated oxidation of palmitic acid in the presence of O_2 .

R10 shows the recombination of RO_2^\bullet with RO_2^\bullet to form an aldehyde and an alcohol. R11 leads to the formation of an alkoxy radical by recombination of two RO_2^\bullet radicals. This radical leads, via R12, to the formation of a C16 oxocarboxylic acid with the carbonyl group on the position of the initial H abstraction. The alkoxy radical recombines by C-C scission via

two pathways, R13(a) and (b), to form shorter chain oxocarboxylic acids and ketones. Formation of dicarboxylic acid is proposed on R14 to occur from an oxocarboxylic acid via H abstraction on the carbonyl group and further recombination with a second peroxy radical.

The current study suggests that the products can also be formed by any radical-initiated oxidation of carboxylic acids. Moreover, the proposed mechanism is valid independently of the radical (OH^\cdot or Cl^\cdot) that is involved in the H abstraction.

3.2.4 Discussion of previous results.

The values of γ determined in this work for $\text{Cl}^\cdot + \text{PA}$ are significantly higher than for previously published papers for the chemical system $\text{Cl}^\cdot + \text{Squalane (Sq)}$ and $\text{Cl}^\cdot + \text{DOS}$ (dioctyl sebacate) heterogeneous reactions (Table 1). In the presence of oxygen, the reaction is still dominated by secondary chemistry but the propagation chain length is smaller than in the absence of O_2 because there is no regeneration of Cl^\cdot . In our conditions, the uptake coefficient decreases by a factor of five when oxygen is added to the chemical system. This result confirms the observation made by Liu *et al.* for squalane reactivity in the presence or not of O_2 . Hearn and Smith study reports the opposite result where the rate of DOS loss is faster in the presence of oxygen.

These comparisons have 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. As secondary chemistry is highlighted for each heterogeneous reaction, the rate of propagation of these chemical reactions should be strongly dependent on the chemical formula.

- PA is a solid while Squalane and DOS are liquid. 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 performed with the same exact methodology. In previous studies the chlorine exposure, ($\langle \text{Cl}^\cdot \rangle t$), 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 ($\text{R}^\cdot + \text{Cl}_2 \rightarrow \text{RCl} + \text{Cl}^\cdot_{\text{p}}$) stays in the liquid particulate phase and never returns in the gas phase. So the loss of the reference compound is only due to reaction with Cl produced by the

photolysis of Cl_2 . However, for the case of solid particle (PA), we have made the assumption that a fraction of chlorine atoms from the reaction R2 could return in the gas phase and reacts with the reference compound (acetone). For this reason, we decide to measure the chlorine exposure during an independent experiment where only acetone and Cl_2 are introduced in the AFT, so the atomic chlorine exposure determination is chlorine only generated by the photolysis of Cl_2 . 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 $\text{Cl}^\cdot + \text{DOS}$ system and 180 s for our work. But recent results (Renbaum and Smith, 2011) show that radical concentration and time are interchangeable parameters only if the precursor concentrations are the same. These discrepancies with previous studies can explain at least part of our higher uptake values.

Table 1. Summary of measured uptake coefficients for heterogeneous reaction systems involving organic aerosol with the radical species OH^\cdot and Cl^\cdot .

Uptake coefficient	OH	Cl
Squalane ($\text{C}_{30}\text{H}_{62}$)	$\gamma_{\text{SQ}} = 0.3$ (Smith <i>et al.</i> , 2009)	$\gamma_{\text{SQ}} = 3$ in N_2 (Liu <i>et al.</i> , 2011) $\gamma_{\text{SQ}} = 0.6$ in N_2/O_2 (Liu <i>et al.</i> , 2011)
DOS ($((\text{CH}_2)_8(\text{COOC}_8\text{H}_{17})_2)$)	$\gamma_{\text{DOS}} = 2.0$ (Hearn and Smith, 2006)	$\gamma_{\text{DOS}} = 1.7$ in N_2/O_2 (Hearn <i>et al.</i> , 2007)
Palmitic acid ($\text{C}_{16}\text{H}_{32}\text{O}_2$)	$\gamma_{\text{PA}} = 0.3$ (McNeill <i>et al.</i> , 2008)	$0.1 < \gamma_{\text{Cl}} < 1$ (Ciuraru, 2010) $\gamma_{\text{PA}} = 14 \pm 5$ in N_2 $\gamma_{\text{PA}} = 3 \pm 1$ in N_2/O_2

4 Conclusions and atmospheric implications

Kinetic studies have been performed to measure the uptake coefficient of chlorine atom on palmitic acid particles as a function of chlorine exposure formed by photolysis of Cl_2 . The uptake coefficient has been derived from two experimental conditions (with and without O_2)

by measuring the palmitic acid lost from the particle phase as a function of the chlorine exposure. First, we have performed these experiments in an oxygen free environment. In this case, the uptake coefficient γ_{PA} is estimated to be $\gamma = 14 \pm 5$. Secondly, we determined the uptake coefficient in a N_2/O_2 mixture (80/20). It appears that palmitic acid loss rate as a function of the chlorine exposure is lower and $\gamma_{PA} = 3 \pm 1$. It must be considered that the chlorine exposure has been defined as the exposure to the chlorine atom formed only by photolysis of Cl_2 and measured during separate experiments. Contrariwise, in the work of Hearn *et al.* and Liu *et al.*, reference kinetics were performed simultaneously with the particle oxidation considering then the chlorine atoms formed by the photolysis but also those formed as products of Cl_2 dissociation due to reactivity with R^\cdot radicals. The uptake coefficient determined in those studies cannot be compared directly with the uptake coefficients measured in this work. Under the conditions in this study, their uptake coefficient would have been greater. However, the general behaviour is similar: (1) the uptake coefficient variation is a function of O_2 concentration; (2) the uptake coefficient greater than 1 explained by a secondary chemistry involving radicals R^\cdot .

The heterogeneous reactivity experiments we performed without O_2 reveal that: (1) an important secondary chemistry where Cl_2 is involved; (2) monochlorinated and polychlorinated compounds are formed with up to four chlorine atoms.

We have observed the formation of HCl, CO and CO_2 in the gas-phase, while, in the particle-phase, oxocarboxylic acids and dicarboxylic acids are detected. Alcohols and monocarboxylic acids were also detected but with no certain identification of molecular formula. Dicarboxylic and oxocarboxylic acids have been measured in the particulate matter by several field measurement campaigns (Kawamura and Gagosian, 1987; Kawamura and Gagosian, 1990; Kawamura and Ikushima, 1993; Mochida *et al.*, 2002; Kawamura and Yasui, 2005; Wang *et al.*, 2006; S. Kundu, 2010; Pavuluri *et al.*, 2010; Hegde and Kawamura, 2012; Mkoma and Kawamura, 2013) under various environmental conditions (urban, coastal, remote marine, remote continental). The presence of oxocarboxylic acids is generally explained by biomass combustion and the aging of primary organic matter (Kawamura and Gagosian, 1987; Kawamura and Gagosian, 1990; Kawamura and Yasui, 2005; S. Kundu, 2010; Pavuluri *et al.*, 2010; Hegde and Kawamura, 2012; Mkoma and Kawamura, 2013). In this study, we observed that the concentration of dicarboxylic acids seemed to decrease with the carbon chain length. Similar distributions of dicarboxylic acids have been observed several times in

1 ambient particulate matter during field measurements campaigns (Kawamura and Yasui,
2 2005;S. Kundu, 2010;Pavuluri *et al.*, 2010;Hegde and Kawamura, 2012;Mkoma and
3 Kawamura, 2013). Those studies correlate the presence of dicarboxylic acids with the
4 oxidation of fatty acids and show that oxalic acid is the main dicarboxylic acid whatever the
5 origin of the analyzed samples. Those conclusions suggest that a large amount of oxalic acid
6 mass could have been formed in our experimental system although it has not been detected.

7 Finally, we have highlighted that there is a significant fragmentation and functionalization of
8 the fatty acids by oxidation initiated by radicals. This leads to the volatilization of oxygenated
9 low-molecular weight organic compounds in the atmosphere. Moreover, the functionalization
10 of the primary organic matter leads to the formation of more polar compounds at the surface
11 of the particle and suggests a modification of the hygroscopic properties of the particle. As
12 fatty acids are the most abundant identified organic compounds in the marine aerosols, the
13 aging process of those particles via radical-initiated chemistry may facilitate cloud droplet
14 activation (Westervelt *et al.*, 2012).

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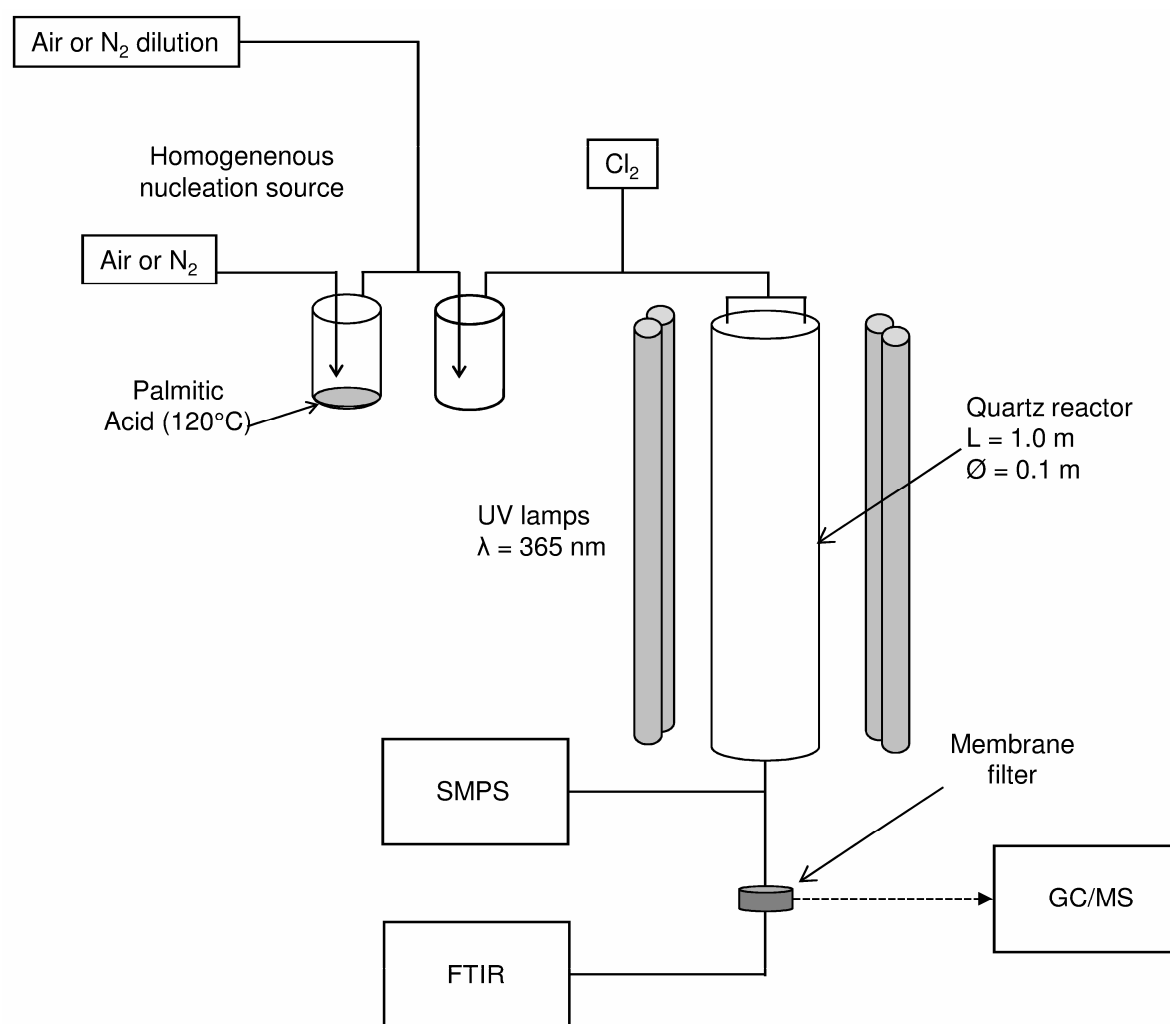
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1 Table 1. Summary of measured uptake coefficients for heterogeneous reaction systems
 2 involving organic aerosol with the radical species OH[•] and Cl[•].

Uptake coefficient	OH	Cl
Squalane (C ₃₀ H ₆₂)	$\gamma_{\text{SQ}} = 0.3$ (Smith <i>et al.</i> , 2009)	$\gamma_{\text{SQ}} = 3$ in N ₂ (Liu <i>et al.</i> , 2011) $\gamma_{\text{SQ}} = 0.6$ in N ₂ /O ₂ (Liu <i>et al.</i> , 2011)
DOS ((CH ₂) ₈ (COOC ₈ H ₁₇) ₂)	$\gamma_{\text{DOS}} = 2.0$ (Hearn and Smith, 2006)	$\gamma_{\text{DOS}} = 1.7$ in N ₂ /O ₂ (Hearn <i>et al.</i> , 2007)
Palmitic acid (C ₁₆ H ₃₂ O ₂)	$\gamma_{\text{PA}} = 0.3$ (McNeill <i>et al.</i> , 2008)	$0.1 < \gamma_{\text{Cl}} < 1$ (Ciuraru, 2010) $\gamma_{\text{PA}} = 14 \pm 5$ in N ₂ $\gamma_{\text{PA}} = 3 \pm 1$ in N ₂ /O ₂

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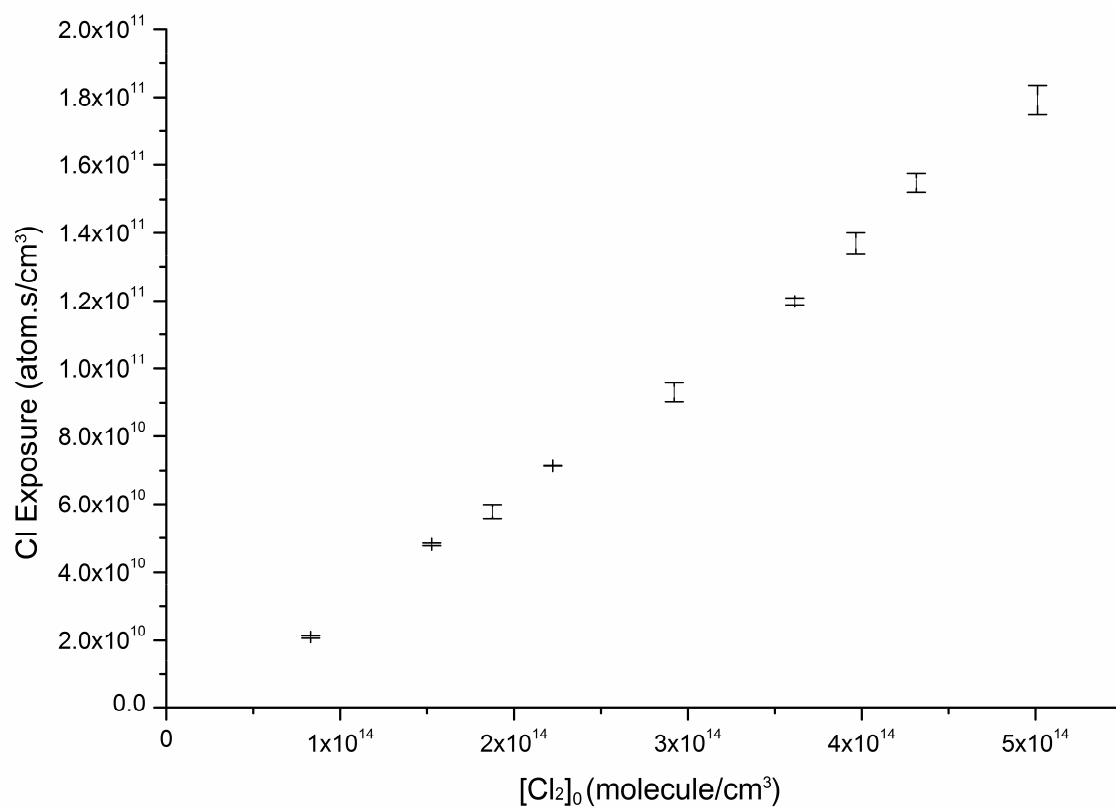
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3 Figure 1. Experimental setup, SMPS (Scanning Mobility Particle Sizer), FTIR (Fourier
4 Transform InfraRed spectrometer), GC/MS (Gas Chromatography, Mass Spectrometer)

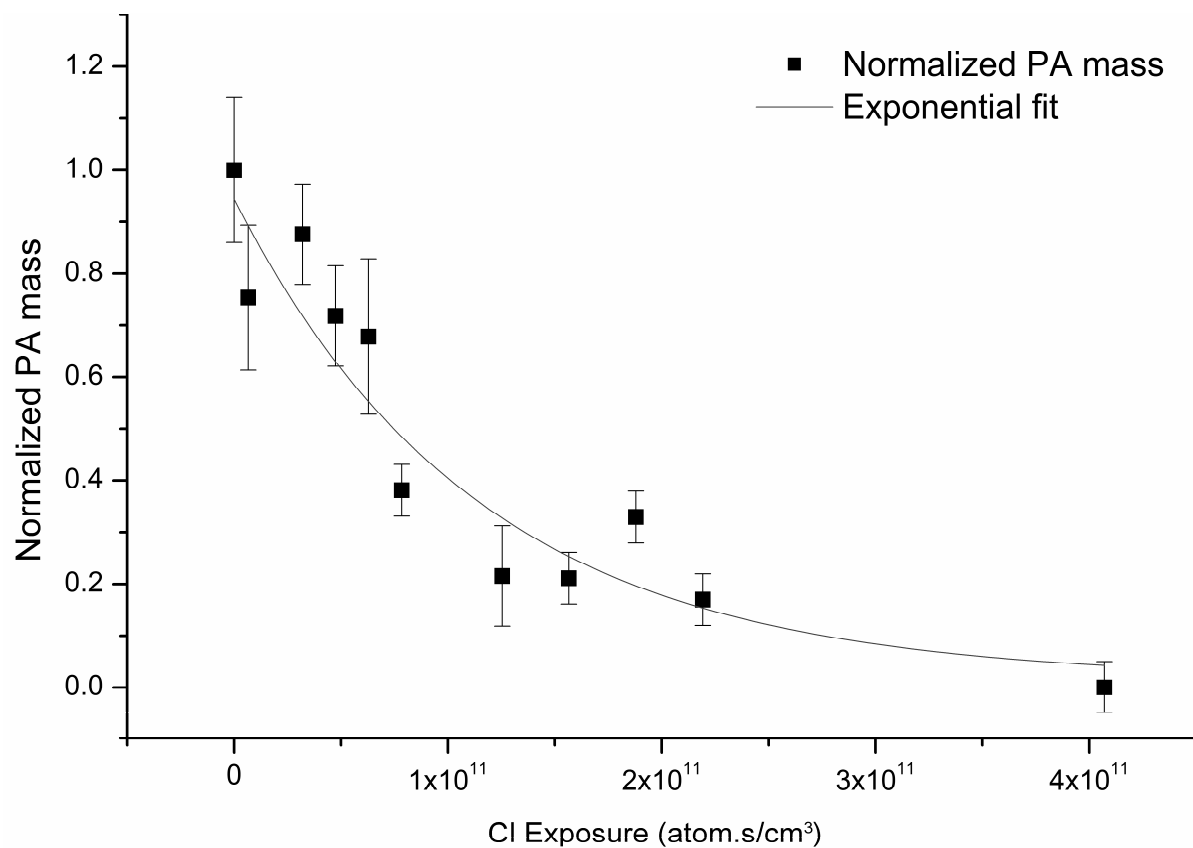
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3 Figure 2. Chlorine exposure as function of the initial Cl_2 concentration in the reactor; $Q_{\text{tot}} =$
 4 $4.0 \text{ L} \cdot \text{min}^{-1}$ and 8 UV lamps powered. Errors bars express the minimum and maximum values
 5 of 4 experiments.

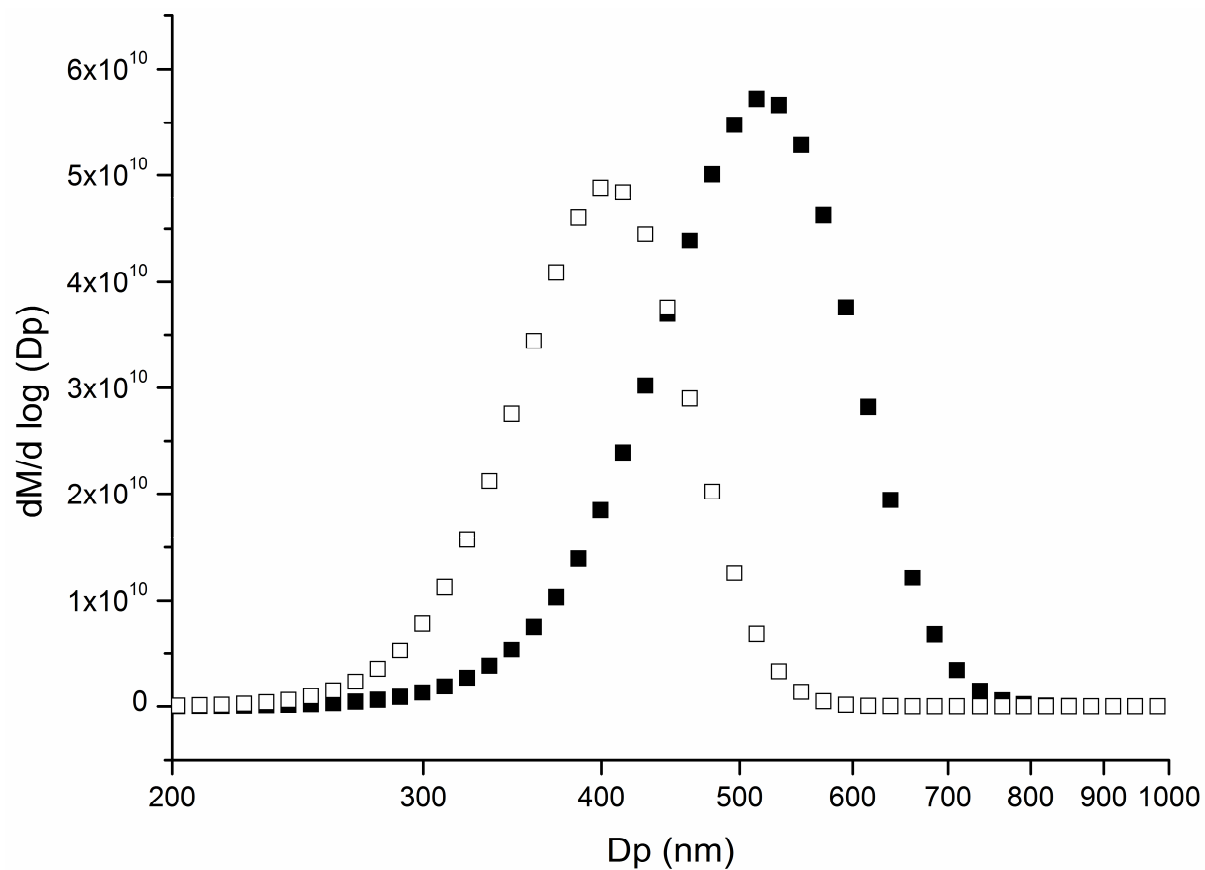
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3 Figure 3. Normalized mass of PA remaining in the particles collected on filter during 10
 4 minutes as a function of the chlorine exposure (squares). Each data point is the mean value
 5 obtained from three GC/MS analyses of two particles samples, Errors bars represent the
 6 minimum and maximum values. The data have been fitted by an exponential function (solid
 7 line).

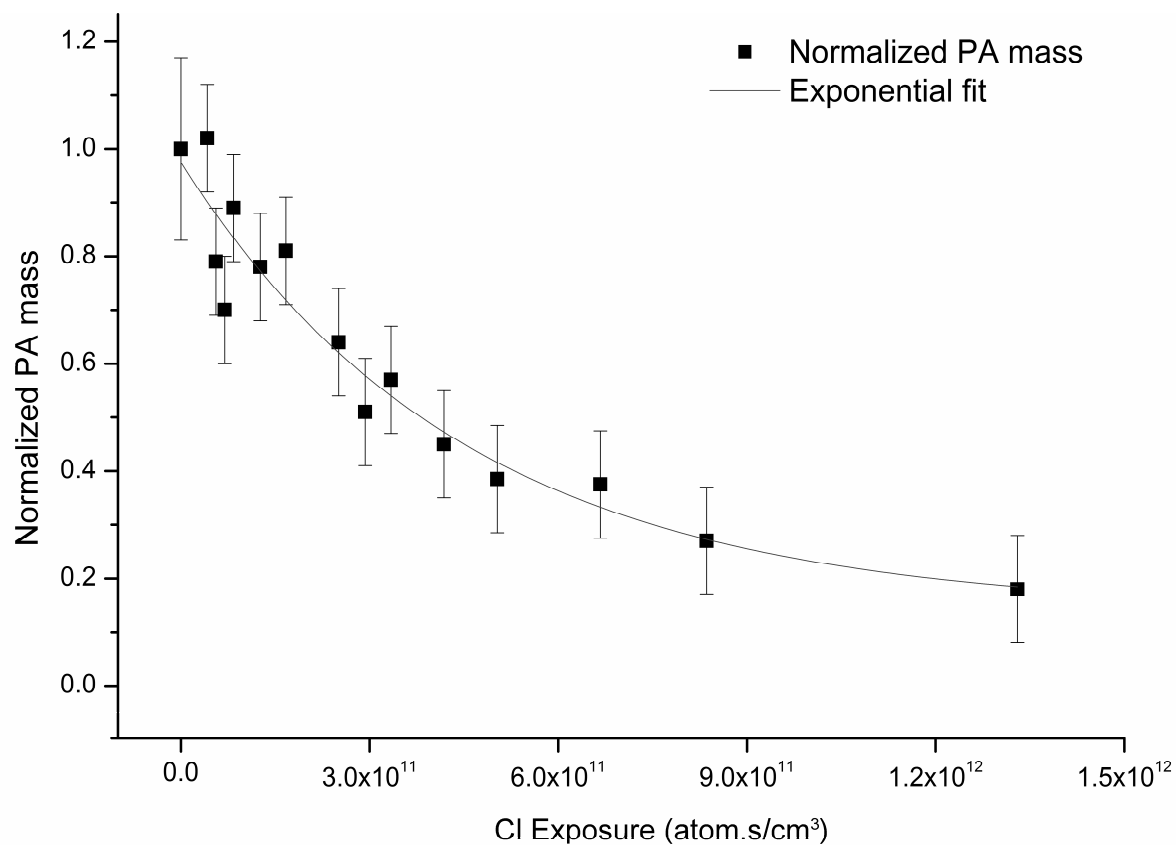
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3 Figure 4. Mass-weighted particle distribution (normalized $\mu\text{g m}^{-3}$) of PA particles before
 4 (filled squares) and after (open squares) a chlorine exposure of $1.25 \times 10^{11} \text{ atom.cm}^{-3}.\text{s}$. Each
 5 distribution is an average of eight measurements.

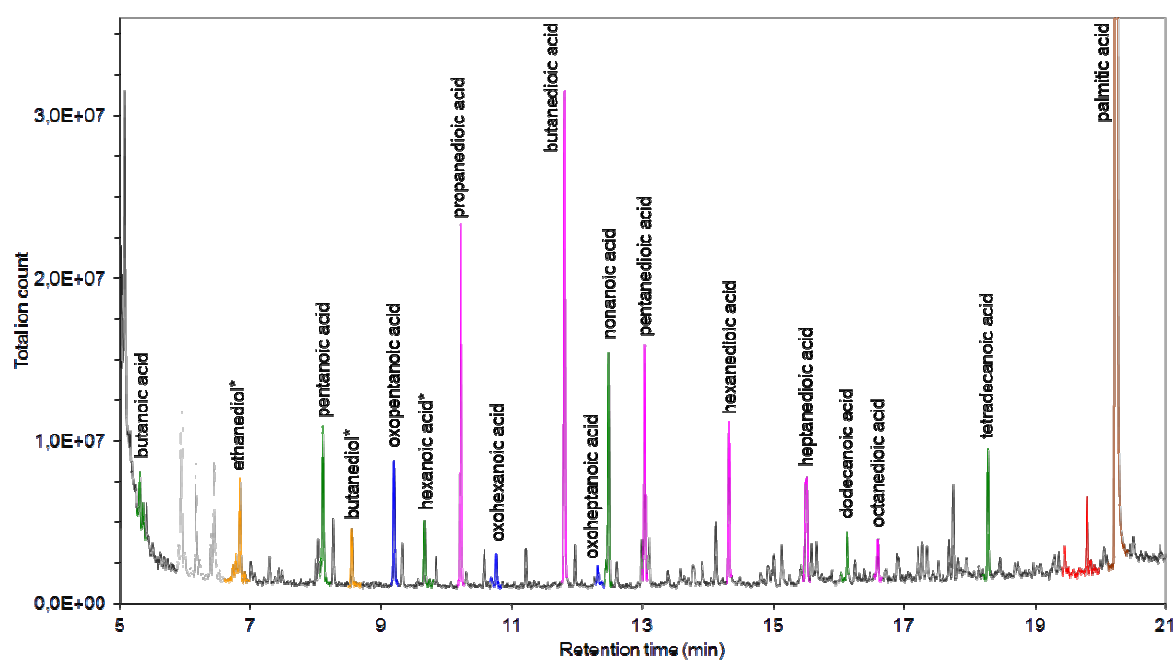
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3 Figure 5. Normalized mass of PA remaining in the particles as a function of the chlorine
4 exposure in the presence of oxygen (squares) and the corresponding exponential fit (solid
5 line).

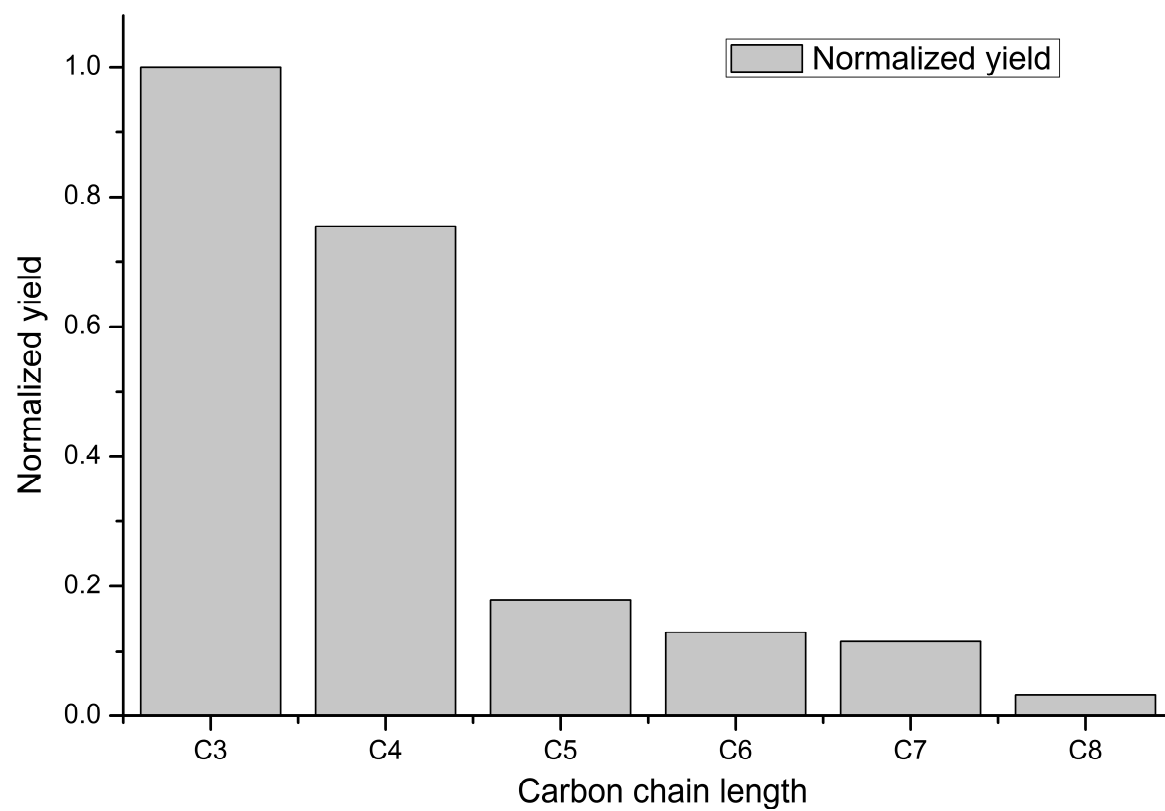
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3 Figure 6. Chromatogram of the silylated-products from the Cl-initiated oxidation of PA in the
 4 presence of O₂ (* uncertain identification).

1



2

3 Figure 7. Normalized yields of the detected dicarboxylic acids as function of the carbon chain
4 length.

$$\begin{array}{l}
 \begin{array}{c}
 \text{+Cl}^\bullet \quad \text{+Cl}^\bullet \\
 \downarrow \quad \downarrow \\
 \text{C}_{13}\text{H}_{27}\text{-CH}_2\text{-CH}_2\text{-COOH} \xrightarrow{\text{R1}} \text{C}_{13}\text{H}_{27}\text{-}\dot{\text{C}}\text{H-CH}_2\text{-COOH} \xrightarrow{\text{R9, +O}_2} \text{C}_{13}\text{H}_{27}\text{-}\dot{\text{O}}_2\text{-CH-CH}_2\text{-COOH} \xrightarrow{\text{R10}} \begin{cases} \text{C}_{13}\text{H}_{27}\text{-C(=O)-CH}_2\text{-COOH} + \text{R'OH} \\ \text{C}_{13}\text{H}_{27}\text{-CH(OH)-CH}_2\text{-COOH} + \text{R'O} \end{cases} \\
 \downarrow \text{HCl} \quad \downarrow \text{HCl} \\
 \text{C}_{13}\text{H}_{27}\text{-CH}_2\text{-CH}_2\text{-COOH} \xrightarrow{\text{R'1}} \text{C}_{15}\text{H}_{31}\text{COO}^\bullet \xrightarrow{\text{R8}} \begin{cases} \text{C}_{15}\text{H}_{31}\text{COOH} + \text{R}^\bullet \\ \text{C}_{15}\text{H}_{31}^\bullet + \text{CO}_2 \end{cases} \quad \left. \vphantom{\text{C}_{15}\text{H}_{31}\text{COO}^\bullet} \right\} \text{propagation}
 \end{array} \\
 \\
 \begin{array}{c}
 \text{C}_{13}\text{H}_{27}\text{-}\dot{\text{O}}_2\text{-CH-CH}_2\text{-COOH} \xrightarrow{\text{R11, +R'O}_2} \text{C}_{13}\text{H}_{27}\text{-}\dot{\text{O}}\text{-CH-CH}_2\text{-COOH} \xrightarrow{\text{R12, +O}_2} \text{C}_{13}\text{H}_{27}\text{-C(=O)-CH}_2\text{-COOH} \\
 \downarrow \text{O}_2 + \text{R'O}^\bullet \quad \downarrow \text{O}_2 \\
 \text{C}_{13}\text{H}_{27}\text{-}\dot{\text{O}}\text{-CH-CH}_2\text{-COOH} \xrightarrow{\text{R13, C-C scission}} \begin{cases} \text{(a) } \text{O=CH-CH}_2\text{-COOH} + \text{C}_{13}\text{H}_{27}^\bullet \xrightarrow{\text{+O}_2} \text{C}_{12}\text{H}_{25}\text{CHO} + \text{HO}^\bullet \\ \text{(b) } \text{C}_{13}\text{H}_{27}\text{CHO} + \text{}^\bullet\text{CH}_2\text{COOH} \xrightarrow{\text{+O}_2} \text{OCH-COOH} + \text{HO}^\bullet \end{cases}
 \end{array}
 \end{array}$$

Figure 8. Reaction mechanism for the chlorine radical initiated oxidation of palmitic acid in the presence of O₂.