

Reactivity of chlorine radical on palmitic acid particles: kinetic measurements and products identification

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Recent studies have revealed that the concentration of organic matter in marine environments exhibits a seasonal behaviour, dominating the chemical composition of ultrafine particulate matter (PM₁) during periods of high biological activity. Chemical analyses of organic compounds sampled from this interfacial layer have allowed to identify mostly fatty acid (C12-C18) compounds (Marty, Saliot et al. 1979). Heterogeneous chemistry involving particulate matter is mainly initiated by surface reactions with gas-phase radicals thus playing a significant role in the chemical evolution of such species. Therefore heterogeneous reactions of this kind should also be considered along with radical reactions in the homogeneous gas-phase, in order to gain an accurate description of the key chemical pathways of the atmosphere and the global oxidant budget. Although the OH radical is the primary daytime oxidant, halogen atoms may also significantly participate in oxidation processes, especially in the marine boundary layer where Cl atoms are mainly generated from the photolysis of active chlorine species and their concentrations can be up to 10⁶ atom.cm⁻³ (Spicer, Chapman et al. 1998)

In an attempt to better understand the heterogeneous oxidation of particulate organic compounds, reactions between Cl atoms and palmitic acid (PA) have been performed in our laboratory within an Aerosol Flow Tube (AFT) where fine particles are introduced with Cl₂ as an oxidant precursor. Cl atoms are generated by photolysis of the molecular chlorine using UV lamps surrounding the reactor. Uptake coefficient has been determined by monitoring the decay of PA by GC/MS analysis as a function of the chlorine exposure. Experiments have been conducted with and without O₂. Identification of the reaction products in the condensed phase have been performed by GC/MS analyses.

The heterogeneous reactivity experiments performed without O₂ lead to the determination of $\gamma = 14 \pm 5$ and reveal that: (1) an important secondary chemistry involves Cl₂; (2) monochlorinated and polychlorinated compounds are formed (from PACl₁ to PACl₄ detected). Although, the PA particles are solid, the whole PA matter can notwithstanding be consumed. In the presence of oxygen, the reaction is still led by secondary chemistry but the propagation chain length is smaller than in absence of O₂ because there is no regeneration of Cl[•] and lead to an uptake coefficient $\gamma = 3 \pm 1$ obtained from the figure 1.

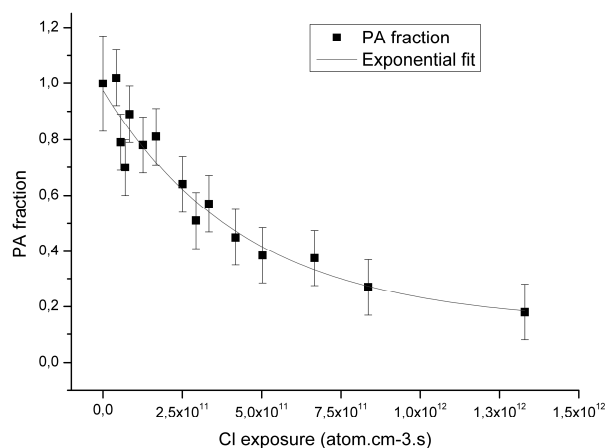


Figure 1. Experimental data (squares) and exponential fit (line) of PA decay as function of chlorine exposure in presence of O₂.

Results coming from experiments realized with O₂ allow us to observe products relevant with the detected compounds in the tropospheric particulate matter. We have observed the formation of HCl, CO and CO₂ in the gas-phase, while, in the particulate phase, oxocarboxylic acids (OXA) and dicarboxylic acids (DCA) are identified by GC/MS. Formation of alcohols and monocarboxylic acids are also suspected.

Finally, we have highlighted that there is a significant fragmentation and functionalization of the fatty acids by oxidation initiated by radicals. This leads to the volatilization of oxygenated low-molecular weighted organic compounds in the atmosphere and the formation of OXA and DCA in the condensed phase, species which have been identified in particulate matter sampled in a large number of environmental conditions (urban, coastal, remote marine, remote continental) (Mkoma and Kawamura 2013). Further research is needed to evaluate whether the functionalization of the primary organic matter and the formation of more polar compounds in the particle lead to the modification of the hygroscopicity of the particle.

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Mkoma, S. L. and K. Kawamura (2013). *Atmos. Chem. Phys.* **13**(4): 2235-2251.

Spicer, C. W., E. G. Chapman, et al. (1998). *Nature* **394**(6691): 353-356.