



Influence of the coating level on the heterogeneous ozonolysis kinetics and product yields of chlorpyrifos ethyl adsorbed on sand particles



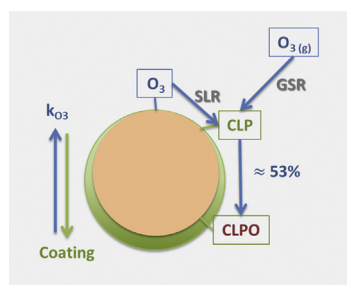
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HIGHLIGHTS

- The coating level strongly impacts the atmospheric lifetime of CLP adsorbed on sand particles towards ozone.
- The O_3 equilibrium constant between the gas and the coated sand is independent of the pesticide particulate concentration.
- The pesticide-coating level does not influence the heterogeneous ozonolysis mechanism of CLP.

GRAPHICAL ABSTRACT



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ABSTRACT

Heterogeneous oxidation of chlorpyrifos ethyl (CLP) coated sand particles by gaseous ozone was studied. Mono-size sand was coated with CLP at different coating levels between 10 and 100 $\mu\text{g g}^{-1}$ and exposed to ozone. Results were analyzed thanks to Gas Surface Reaction and Surface Layer Reaction Models. Kinetic parameters derived from these models were analyzed and led to several conclusions. The equilibrium constant of O_3 between the gas phase and the CLP-coated sand was independent of the sand contamination level. Ozone seems to have similar affinity for coated or uncoated sand surface. Meanwhile, the kinetic parameters decreased with an increasing coating level. Chlorpyrifos Oxon, (CLPO) has been identified and quantified as an ozonolysis product. The product yield of CLPO remains constant ($53 \pm 10\%$) for the different coating level.

The key parameter influencing the CLP reactivity towards ozone was the CLP-coating level. This dependence had a great influence on the lifetime of the CLP coated on sand particles, with respect to ozone, which could reach several years at high contamination level.

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1. Introduction

Because of their low vapor pressure (between 10^{-6} – 10 Pa), semi

volatile organic compounds (SVOC) can be found in gas phase but also in particulate phase of the atmosphere (Bidleman, 1988). Particulate SVOC are thus submitted to atmospheric oxidants. To understand their atmospheric fate and estimate their lifetime, heterogeneous kinetic determinations towards atmospheric oxidants have to be carried out. Several heterogeneous ozonolysis studies have been conducted on different supports (carboneous,

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silica, quartz, organics) for various SVOC like pesticides, PAH, fatty acids (Yang et al., 2010; Kahan et al., 2006; Kwamena et al., 2004, 2007; Pöschl et al., 2001; Pflieger et al., 2011; Socorro et al., 2015; El Masri et al., 2014). The surface nature could be a determining factor for the reactivity as observed for PAH (Kwamena et al., 2004) and for pesticides (Socorro et al., 2015).

A kinetic model framework for aerosols has been developed and helps the understanding of kinetic heterogeneous reactivity (Pöschl et al., 2007; Berkemeier et al., 2013). However, to our knowledge, the influence of the particle coverage with solid deposit on the kinetic of the surface reaction is poorly investigated. Heterogeneous studies were usually performed for one value of coverage and often in submonolayer conditions 0.4% (Socorro et al., 2015), 10% (Perraudin et al., 2007); ~60% (Bouya et al., 2015; Al Rashidi et al., 2014). Few studies have determined the influence of surface coverage on the solid/gas heterogeneous ozonolysis rate constant. For PAH, studies were conducted on various type of particles: silica particles (Pflieger et al., 2012), soot particles (Kamens et al., 1988; Pöschl et al., 2001; Kwamena et al., 2004) as well as organic and salt particles (Kwamena et al., 2007). The amount of PAH on the surface seems to influence reaction rates (Alebic-Juretic et al., 1990, 2000). Pöschl et al. (2001) showed that PAH reaction toward ozone is 30% slower for double layer than submonolayer coverage.

We propose to study the influence of pesticide coating level on sand particles over the heterogeneous ozonolysis and to give a phenomenological interpretation of the rate constant variation. The pesticide targeted in this study is the chlorpyrifos ethyl (CLP), also known as chlorpyrifos (CAS: 2921-88-2). It is a widely used chlorinated organo-phosphorous insecticide (Giese and Solomon, 2014). It has been detected in atmospheric particles at levels between 1.3 pg m^{-3} and 2.66 ng m^{-3} (Hart et al., 2012; Borrás et al., 2011). Trichloropyridinol (TCP) and Chlorpyrifos oxon (CLPO) have been assigned as CLP degradation products in several media (El Masri et al., 2014; Maya et al., 2012). LeNoir et al. (1999) found CLP and CLPO concentrations in dry deposition up to 24 and $80 \text{ ng m}^{-2} \text{ day}^{-1}$, respectively and always higher levels of CLPO.

Gas phase fate of CLP and CLPO toward atmospheric oxidants or photolysis has been explored (Hebert et al., 2000; Muñoz et al., 2014) leading to the conclusion that CLP and CLPO are principally removed by OH-radicals with lifetimes of 2 h and 11 h (Muñoz et al., 2014), respectively considering an average OH concentration of $2 \times 10^6 \text{ cm}^{-3}$. Two studies have investigated the mechanism and kinetics of ozonolysis of CLP in the particulate phase on azelaic acid particles (Meng et al., 2010) and on quartz plaques (El Masri et al., 2014) leading to quite different lifetimes with respect to ozone: 8 days against 3.3 months, respectively. If the nature of the support on the lifetime has been discussed previously, few studies exist about the influence of the particle contamination level with pesticides (Socorro et al., 2015). There is a need to assess whether the initial contamination level of the particle with CLP has an influence on the reactivity and the products formation yield. Thus, in this work we report rate constants of the heterogeneous ozonolysis of CLP-coated sand particles for different surface contamination levels and discuss the related lifetimes. The CLPO formation yield is measured for the different coating levels and compared to the one determined for another solid support (El Masri et al., 2014).

2. Materials and methods

2.1. Sand properties and coating procedure

The sand (reference NE34) was provided by SIBELCO - France. It has an average size distribution of $103 \pm 7 \text{ }\mu\text{m}$ diameter and a mass density of 2.65. It is mainly composed of SiO_2 (99.86%) and trace of other minerals (Al_2O_3 , Fe_2O_3 , ...). Its BET specific surface is

$0.573 \pm 0.003 \text{ m}^2/\text{g}$. These particles mimic the sand particles present in the atmosphere.

Considering that atmospheric PM10 have an average European atmospheric concentration (Putaud et al., 2010) of $40 \text{ }\mu\text{g m}^{-3}$ in order to be in the same range of CLP atmospheric concentrations (Hart et al., 2012), we have coated sand particles with 10–100 μg CLP by gram of sand leading to 0.4–4 ng CLP m^{-3} . Sand contamination by CLP was obtained by dissolution of the pesticide in dichloromethane, immersion of sand in the CLP solution and evaporation of dichloromethane: five sand coating levels were prepared: 10.0 ± 0.2 , 25.0 ± 0.6 , 50.0 ± 1.1 , 75.0 ± 1.6 and $100.0 \pm 2.2 \text{ }\mu\text{g CLP per gram of sand}$. The surface of one molecule of CLP was found to be $405 \text{ }\text{Å}^2$ (data provided by Marvin Suite, ChemAxon). Assuming that only one half of the pesticide surface is in contact with the sand surface and knowing the sand specific area, the surface coverage related to the coating levels were calculated (Table 1). Error on the surface coverage was estimated using the propagation of error. This value takes into account uncertainties on the sand coating level and on sand specific area.

2.2. Residual CLP extraction on sand particles

One gram of CLP coated sand was transferred in a gauged vial and extracted by 10 mL of dichloromethane in an ultrasonic bath Bandelin Sonorex at ambient temperature for 15 min. Extraction time and mass to be extracted were optimized to provide a near to 100% extraction. The extraction recovery of CLP and CLPO were found to be $97.4 \pm 7.2\%$ and $95.7 \pm 8.1\%$.

2.3. CLP and CLPO analysis

CLP and CLPO analysis were performed by Trace Ultra GC-FID provided by Thermoelectron. Separation was achieved with a $15 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$ Agilent DB-5ms column. Helium Alpha gas 2 provided by Air Liquid was used as a carrier gas with a constant flow of 1.2 mL min^{-1} . $2 \text{ }\mu\text{L}$ aliquots of the extracted residue were injected in the splitless mode at 230°C . Oven temperature was programmed to start at 80°C and increased up to 200°C at $40^\circ\text{C min}^{-1}$, then increased again up to 230°C at $20^\circ\text{C min}^{-1}$. A Flame Ionization Detector (FID) was kept at 230°C .

2.4. Experimental device and experimental conditions

In order to ensure a good exposure of the coated sand particles to the gaseous oxidant, particles were introduced in a rotary evaporator (Heidolph 94200) used as a reactor. 10–15 g of CLP-coated sand were introduced in a 250 mL round bottom flask connected to the rotary evaporator with a rotation speed of 90 rpm (Fig. 1). Similar experimental setup was previously used by Pflieger et al. (2011) to investigate reactivity of Trifluralin.

Ozone was introduced in the flask thanks to a constant gaseous flow of a mixture O_3/air conducted into the flask through a glass tube. Oxygen and synthetic dry air were of quality alphasgaz 1 (99.999%) from Air Liquid.

Ozone was generated from oxygen using an ozoniser. The O_3/O_2 mixture was diluted with air before being introduced into the reactor at an adjusted pressure of 400 Torr. The ozone concentration was controlled by varying the discharge voltage of the ozoniser. Ozone was introduced in a Pyrex cell, 100 cm in length and 5 cm in diameter, equipped with quartz windows at both extremities. An UV beam issued from a deuterium lamp detected by an Avaspec CCD camera provided by Avantes was used to measure the optical density at 254 nm. Ozone concentration was deduced from Beer Lambert law knowing $\sigma_{\text{O}_3}(254 \text{ nm}) = 1.13 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ (Malicet et al., 1995). To minimize CLP volatilization and

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