

Investigation of nucleation thresholds in the reactions of ozone with Volatile Organic Compounds (VOCs)

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Current climate models present large uncertainties due to the evaluation of the radiative forcing of atmospheric aerosol particles (Myhre *et al.*, 2013), partially linked to the poor understanding of atmospheric new particle formation and their potential to act as cloud condensation nuclei. A major process to form new particles in the atmosphere is clustering from gas phase, which can account up to 50-90% of the total particle number, and 30-50% of the cloud condensation nuclei (Merikanto *et al.*, 2009). Sulfuric acid appears as a key species in these secondary processes although its atmospheric concentrations cannot explain alone the aerosol formation rates observed, which points out that some other compounds are playing a key role as well (Sipila *et al.*, 2010; Kirkby *et al.*, 2011).

Over the past years, many laboratory experiments have identified biogenic and aromatic compounds as the main precursors in secondary organic aerosol (SOA) formation in the atmosphere (Calvert *et al.*, 2002; Kanakidou *et al.*, 2005). However, the role played by these compounds in the formation of new particles and in the modification of the particle atmospheric burden under the real conditions of the atmosphere is still difficult to apprehend and thus, to take into account in models. One key parameter that is still unknown or uncertain for many species forming SOA is their nucleation threshold, which corresponds to the amount of organic compound reacted necessary to start forming new particles. Determining these amounts for various species will help in better understanding the formation of new particles.

A laminar flow reactor, working in stationary conditions with reaction times ranging from a few seconds to a few minutes, has been used to study ozonolysis reactions (Duncan *et al.*, 2012; Braure *et al.*, 2015). It is coupled to a GC/FID-MS which can identify and quantify organic compounds in the gas-phase after online sampling on adsorbent cartridges followed by thermodesorption. A water-based condensation particle counter upstream the reactor has a minimum detectable size of $D_{50} = 2.5$ nm.

Several biogenic VOCs have been studied. A typical experiment has investigated the number of particles formed due to an ozonolysis reaction and compared it with the amount of organic compound consumed. A scavenger of OH radicals (CO or 2-butanol) could be added to avoid additional depletion of the organic compound by OH radicals potentially formed as a secondary product. Figure 1 presents the results

obtained for d-limonene, β -pinene and γ -terpinene with and without OH scavenger.

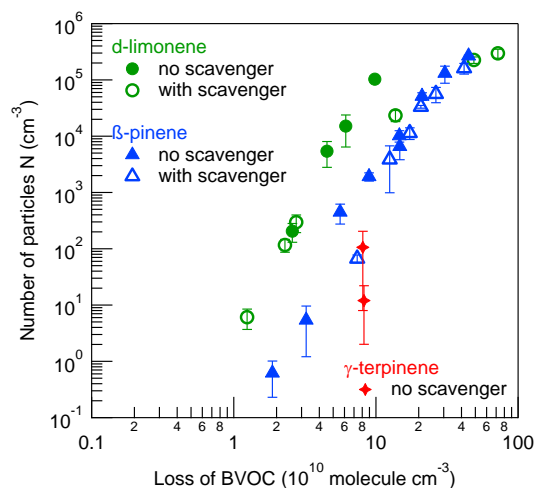


Figure 1. Number of particles as a function of the loss of VOC.

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- Braure, T., et al. (2015) *Int. J. Chem. Kinet.* **47**, 596-605.
Calvert, J.G., et al. (2002) *The Mechanisms of Atmospheric Oxidation of the Aromatic Hydrocarbons*, Oxford University Press.
Duncan, M., et al. (2012) *J. Phys. Chem. A* **116**, 6169-6179.
Kanakidou, M., et al. (2005) *Atmos. Chem. Phys.* **5**, 1053-1123.
Kirkby, J., et al. (2011) *Nature* **476**, 429-433.
Merikanto, J., et al. (2009) *Atmos. Chem. Phys.* **9**, 8601-8616.
Myhre, G., et al. (2013) *Anthropogenic and Natural Radiative Forcing, in: Climate Change 2013: The Physical Science Basis. Contribution of WG I to the 5th Assessment Report of the IPCC*, Cambridge University Press.
Sipila, M., et al. (2010) *Science* **327**, 1243-1246.