



## Secondary organic aerosol (trans)formation through aqueous phase guaiacol photonitration: a kinetic study

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It is well known that atmospheric aerosols play a crucial role in the Earth's climate and public health (Pöschl 2005). Despite a great effort invested in the studies of secondary organic aerosol (SOA) budget, composition, and its formation mechanisms, there is still a gap between field observations and atmospheric model predictions (Heald et al. 2005, Hallquist et al. 2009, and Lim et al. 2010). The insisting uncertainties surrounding SOA formation and aging thus gained an increasing interest in atmospheric aqueous phase chemistry; they call for more complex and time consuming studies at the environmentally relevant conditions allowing confident extrapolation to desired ambient conditions.

In addition to the adverse health effects of atmospheric particulate matter (PM) as such, toxicity is also attributed to nitro-aromatic and other organic compounds which have already been detected in real aerosol samples (Traversi et al. 2009). Moreover, low-volatility aromatic derivatives are believed to form at least partly in the aerosol aqueous phase and not only in the gas phase from where they partition into water droplets (Ervens et al. 2011). Two nitro derivatives of biomass burning tracer guaiacol have recently been found in winter PM<sub>10</sub> samples from the city of Ljubljana, Slovenia, and aqueous photonitration reaction was proposed as their possible production pathway (Kitanovski et al. 2012).

In this study the kinetics of guaiacol nitration in aqueous solution was investigated in the presence of H<sub>2</sub>O<sub>2</sub> and NO<sub>2</sub><sup>-</sup> upon simulated solar irradiation (Xenon lamp, 300 W). During the experiment the DURAN<sup>®</sup> flask with the reaction mixture was held in the thermostated bath and thoroughly mixed. The reaction was monitored for 44 hours at different temperatures. Guaiacol and its main nitro-products (4-nitroguaiacol, 4-NG; 6-nitroguaiacol, 6-NG; and 4,6-dinitroguaiacol, 4,6-DNG) were quantified in every aliquot, taken from the reaction mixture, by use of high pressure liquid chromatography (HPLC). The reaction kinetics was determined and the temperature dependence of pseudo-first order rate constants was described by the Arrhenius equation. The guaiacol lifetime in the atmosphere at low temperature was predicted afterwards. Last but not least, the long-term reaction monitoring explained the absence of 6-NG in real aerosol samples analyzed by Kitanovski et al. (2012).

- Pöschl, U. (2005) *Angew. Chem. Int. Ed.* 44, 7520–7540.  
Heald, C.L. et al. (2005) *Geophys. Res. Lett.* 32, L18809–L18812.  
Hallquist, M. et al. (2009) *Atmos. Chem. Phys.* 9, 5155–5236.  
Lim Y.B. et al. (2010) *Atmos. Chem. Phys.* 10, 10521–10539.  
Traversi, D. et al. (2009) *Environ. Int.* 35, 905–910.  
Ervens, B. et al. (2011) *Atmos. Chem. Phys.* 11, 11069–11102.  
Kitanovski, Z. et al. (2012) *J. Chromatogr. A* 1268, 35–43.