Mechanism of aqueous phase guaiacol nitration relevant for atmospheric waters

A.Kroflič[1], M. Grilc[2] and I. Grgić[1]

[1]Analytical Chemistry Laboratory, National Institute of Chemistry, Ljubljana, SI-1001, Slovenia
[2]Laboratory of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Ljubljana, SI-1001, Slovenia
Keywords: chemical mechanism, atmospheric aqueous phase aging, wet aerosols, biomass burning pollutant.
Presenting author email: irena.grgic@ki.si

One of the largest primary sources of organic aerosols in the atmosphere is biomass burning, during which many aromatic compounds are formed. It was found that particulate matter from wood smoke consists of up to 40 % phenol derivatives (Hawthorne *et al.,* 1989). Semi-volatile aromatics emitted into the troposphere undergo transformations in the gaseous and/or aqueous phase (Li *et al.,* 2014); usually more oxidized aromatics with lower volatility and higher water solubility are formed (Donahue *et al.,* 2012). Aqueous phase reactions of oxidized aromatics are also believed to be an additional source of secondary organic aerosol (Lim *et al*., 2010). Very recently it was exposed that harmful effect of low- and semi-volatile aromatics on the environment due to their tropospheric aqueous phase ageing can be especially pronounced in remote biotopes in comparison to their urban source (Kroflič *et al.*, 2015).

In the present work aqueous phase ageing of semi-volatile wood burning pollutant guaiacol (GUA) was investigated and its nitration mechanism under atmospherically relevant conditions was resolved for the first time. The investigation is based on a long-term kinetic study of GUA nitration in acidic H_2SO_4 solution, typical for the atmospheric waters (pH 4.5). Experiments were performed in the dark and under simulated sunlight conditions in the presence of mostly urban pollutants (i.e. nitrite added as $NaNO_2$ and H_2O_2). Guaiacol and its main first and second generation nitro-products, i.e. 4-nitroguaiacol, 4-NG; 6-nitroguaiacol, 6-NG; and 4,6-dinitroguaiacol, 4,6-DNG, which have been just recently chemically characterized by Kitanovski *et al.* (2014), were followed by use of a high pressure liquid chromatography (HPLC).

Based on a proposed complex mechanism of aromatic nitration in the atmospheric aqueous phase, a model function was derived and fitted simultaneously to all experimental data obtained in 1 mM $NaNO_2$ solutions. Such an approach allowed us to determine kinetic parameters of the proposed reaction pathways with a fair amount of confidence. The modelling study revealed that electrophilic nitrogen-containing reactive species (eNRS) react selectively with distinct GUA analogues. This substantially affects the time-dependent concentration profiles of eNRS in aqueous solution and further the relevant reaction rates of present aromatic compounds.

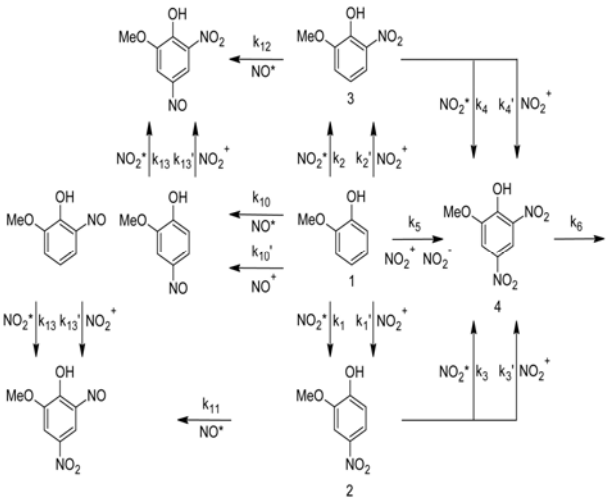

Figure 1. Proposed reaction mechanism of guaiacol nitration in acidic aqueous solution. 1 guaiacol (GUA), 2 4-nitroguaiacol (4NG), 3 6-nitroguaiacol (6NG), and 4 4,6-dinitroguaiacol (DNG). The model does not distinguish between 4- and 6-nitrosoguaiacol (NOG).

This work was supported by the Slovenian Research Agency (Contract Nos. P1-0034 and P2-0152).

Donahue, N. M., Robinson, A. L., Stanier, C. O. and Pandis, S. N. (2006) *Environ. Sci. Technol.* **40**, 2635-2643.

Hawthorne, S. B., Krieger, M. S., Miller, D. J. and Mathiason, M. B. (1989) *Environ. Sci. Technol.* **23**, 470-475.

Kitanovski, Z., Čusak, A., Grgić, I. and Claeys, M. (2014) *Atmos. Meas. Tech. 7*, 2457-2470.

Kroflič, A., Grilc, M. and Grgić, I. (2015) *Sci. Rep.* **5**, 8859-8863.

Li, Y. J., Huang, D. D., Cheung, H. Y., Lee, A. K. Y. and Chan, C. K. (2014) *Atmos. Chem. Phys.* **14**, 2871-2885.

Lim, Y. B., Tan, Y., Perri, M. J., Seitzinger, S. P. and Turpin, B. J. (2010) *Atmos. Chem. Phys. 10*, 10521-10539.