Heterogeneous reaction kinetics and mechanism of the nitration of aerosolized protein by O3 and NO2

Manabu Shiraiwa (1), Yulia Sosedova (2), Aurélie Rouvière (2), Markus Ammann (2), and Ulrich Pöschl (1)

(1) Max Planck Institute for Chemistry, Biogeochemitsrty, Mainz, Germany (m.shiraiwa@mpic.de, +49-6131-305-487), (2) Paul Scherrer Institute, Villigen, Switzerland

The effects of air pollution on allergic diseases are not yet well-understood. Proteins contained in biogenic aerosol particles (pollen, spores, bacteria, etc.), which accounts for up to 5% of urban air particulate matter, are efficiently nitrated in polluted environments before inhalation and deposition in the human respiratory tract [1], which is likely to trigger immune reactions for allergies. Proteins undergo a nitration reaction that leads to the formation of 3-nitrotyrosine residues. The kinetics and reaction mechanism of protein nitration are still largely unknown.

The kinetics of nitration of protein particles by O3 and NO2 was measured using the short-lived radioactive tracer 13N. The routine for the online production of 13N-labeled nitrogen dioxide and the main experimental setup were reported previously [2]. Bovine serum albumin (BSA) was used as a model protein compound. Deliquesced NaCl particles were also used as a reference. Particles generated by an ultrasonic nebulizer were mixed with O3 (0 – 150 ppb) and NO2 (5 – 100 ppb) in a flow tube reactor under humid conditions (30 – 75 % RH), which lead to gel-like swelling of the protein [3, 4]. The reaction time was varied in the range of 4 -10 min by changing the position of the inlet of the reactor. The surface concentration of particles was monitored by a scanning mobility particle sizer (SMPS). After passing through the flow tube reactor, the gas and aerosol flow entered a narrow parallel-plate diffusion denuder coated to selectively absorb gas phase NO2, followed by a particle filter collecting the particles. The detectors were attached to each denuders and the filter to count the amount of gamma quanta, which are emitted in the decay of 13N. From the count-rate, the concentration of the corresponding species was derived, which was used for the calculation of uptake coefficients of NO2 (NO2).

In absence of O3 in the flow tube reactor, NO2 uptake by both BSA and deliquesced NaCl were below the detection limit (NO2 < ~10-6). The NO2 by BSA is of the order of 10-5, strongly depending on gas phase ozone concentration, which indicates that O3 plays an important role in NO2 uptake. The NO2 by deliquesced NaCl is one order of magnitude smaller, which is likely to be attributed to the formation of gas phase NO3 and N2O5, as neither O3 nor NO2 is expected to rapidly react with deliquesced NaCl. This amount of uptake is considered to be maximum contribution of gas phase NO3 radicals and N2O5 to uptake of 13N-labeled species by protein particles. The possible mechanisms of high NO2 uptake by protein particles are: 1) surface reaction between adsorbed O3 and NO2 forming NO3 radicals on the surface which react with protein [5], 2) O3 first reacts with protein forming intermediates, followed by reaction with NO2. Further experiments and modelling are under way.

REFERENCES
[1] Franze et al., Environ. Sci. Tech., 39, 1673 (2005).
[2] Sosedova et al., J. Phys. Chem A., 113, 10979 (2009).
[3] Mikhailov et al., Atmos. Chem. Phys., 4, 323 (2004).
[4] Mikhailov et al., Atmos. Chem. Phys., 9, 9491 (2009).
[5] Shiraiwa et al., Atmos. Chem. Phys., 9, 9571 (2009)