Geophysical Research Abstracts
Vol. 12, EGU2010-1907-1, 2010
EGU General Assembly 2010

Kinetic double-layer model of aerosol surface chemistry and gas-particle interactions (K2-SURF): Degradation of polycyclic aromatic hydrocarbons exposed to O3, NO2, H2O, OH and NO3

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We present a kinetic double-layer surface model (K2-SURF) that describes the degradation of polycyclic aromatic hydrocarbons (PAHs) on aerosol particles exposed to ozone, nitrogen dioxide, water vapor, hydroxyl and nitrate radicals [1]. The model is based on multiple experimental studies of PAH degradation and on the Pöschl-Rudich-Ammann (PRA) framework [2] for aerosol and cloud surface chemistry and gas-particle interactions.

For a wide range of substrates, including solid and liquid organic and inorganic substances (soot, silica, sodium chloride, octanol/decanol, organic acids, etc.), the concentration- and time-dependence of the heterogeneous reaction between PAHs and O3 can be efficiently described with a Langmuir-Hinshelwood-type mechanism. Depending on the substrate material, the Langmuir adsorption constants for O3 vary over three orders of magnitude, and the second-order rate coefficients for the surface layer reaction of O3 with different PAH vary over two orders of magnitude. The available data indicate that the Langmuir adsorption constants for NO2 are similar to those of O3, while those of H2O are several orders of magnitude smaller. The desorption lifetimes and adsorption enthalpies suggest chemisorption of NO2 and O3 and physisorption of H2O. Note, however, that the exact reaction mechanisms, rate limiting steps and possible intermediates still remain to be resolved (e.g., surface diffusion and formation of O atoms or O3- ions at the surface).

The K2-SURF model enables the calculation of ozone uptake coefficients, O3, and of PAH concentrations in the quasi-static particle surface layer. Competitive adsorption and chemical transformation of the surface (aging) lead to a strong non-linear dependence of O3 on time and gas phase composition, with different characteristics under dilute atmospheric and concentrated laboratory conditions. Under typical ambient conditions, O3 of PAH-coated aerosol particles are expected to be in the range of 10-6 - 10-5.

At ambient temperatures, NO2 alone does not efficiently degrade PAHs, but it was found to accelerate the degradation of PAHs exposed to O3. The accelerating effect can be attributed to highly reactive NO3 radicals formed in the gas phase or on the surface. Estimated second-order rate coefficients for O3-NO2 and PAH-NO3 surface layer reactions are in the range of 10-17 – 10-16 cm2 s-1 and 10-15 – 10-12 cm2 s-1, respectively.

The chemical half-life of PAHs is expected to range from a few minutes on the surface of soot to multiple hours on organic and inorganic solid particles and days on liquid particles. On soot, the degradation of particle-bound PAHs in the atmosphere appears to be dominated by a surface layer reaction with adsorbed ozone. On other substrates, it is likely dominated by gas-surface reactions with OH or NO3 radicals (Eley-Rideal-type mechanism).

To our knowledge, K2-SURF is the first atmospheric process model describing multiple types of parallel and sequential surface reactions between multiple gaseous and particle-bound chemical species. It illustrates how the general equations of the PRA framework can be simplified and adapted for specific reaction systems.

References:
[1] Shiraiwa et al., Atmos. Chem. and Phys., 9, 9571-9586 (2009).
[2] Pöschl et al., Atmos. Chem. and Phys., 7, 5989-6023 (2007).