Geophysical Research Abstracts
Vol. 13, EGU2011-5607, 2011
EGU General Assembly 2011
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The role of long-lived reactive oxygen intermediates in the reaction of ozone with aerosol particles

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Heterogeneous reactions of ozone with aerosol particles have been studied extensively, but the molecular mechanism and kinetics remained unresolved. Among the organic aerosol components readily reacting with ozone, polycyclic aromatic hydrocarbons (PAHs) are one of the most prominent groups related to health effects. Chemical transformation can change the toxicity of PAHs and modify the hygroscopic properties and climate effects of combustion aerosol particles. Several studies have shown that ozone can also promote the nitration of protein molecules contained in primary biological aerosol particles like pollen and fungal spores [1]. This posttranslational modification can enhance the allergenic potential of proteins. It provides a molecular rationale for the enhancement of allergic diseases by traffic-related air pollution in urban and rural environments, which has been observed in epidemiological studies but remains to be elucidated on a molecular level [2].

Based on new experimental data and model calculations, here we show that long-lived reactive oxygen intermediates (ROIs) are formed upon oxidation of PAH and nitration of protein [3]. The chemical lifetime of these intermediates exceeds 10^2 s, which is much longer than the surface residence time of molecular O_3 ($\sim 10^{-9}$ s). The ROIs explain and resolve apparent discrepancies between earlier quantum mechanical calculations and kinetic experiments. They play a key role in the chemical transformation and adverse health effects of toxic and allergenic air particulate matter, such as soot, polycyclic aromatic hydrocarbons and proteins. Moreover, ROIs may contribute to the coupling of atmospheric and biospheric multiphase processes.

Apart from chemical aging of air particulate matter, long-lived ROIs might also participate in the formation and growth of secondary organic aerosols. In particular, surface interactions of long-lived ROIs may lead to the formation of multifunctional organic substances (acids, nitrates, sulfates, dimers/oligomers, etc.) with high molecular mass and low vapor pressure that are required for the nucleation and growth of new particles and may also influence their phase state [4]. The experimental and theoretical information currently available suggests that long-lived ozone-generated ROIs play a central role in the multiphase chemistry of atmospheric aerosols.

Acknowledgements.

This work was funded by the Max Planck Society (MPG), the Swiss National Science Foundation (grant no. 130175), and the European Integrated Project on Aerosol, Cloud, Climate and Air Quality Interactions (No 036833-2 EUCAARI). We thank M. Birrer, T. Bartels-Rausch and M. Kerbrat for support. The staffs of the PSI accelerator facilities are acknowledged for providing stable proton beams used to produce ^{13}N.

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