

Heterogeneous chemistry and nanometer particle growth: Laboratory studies of particle size dependent aerosol chemistry

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Currently, the formation of extremely low-volatile organic compounds required for nanometer particle growth is mainly discussed based on the formation of HOMs by gas-phase chemistry (autoxidation). However, the nanometer particles themselves provide a unique nanoscale chemical environment that can influence the chemical reactions within the newly formed condensed phase. Beyond pure gas-phase reactions, several formation pathways of very low-volatility organic compounds exist. One is heterogeneous oxidation reactions, e.g. at the particle surface, another is the formation of organic salts and finally oligomerization reactions in the condensed phase. Of particular interest are reactions that preferentially occur in the smallest particles, since it is these particles that require matter for their growth into size ranges where they are not rapidly lost by coagulation. In these cases, particle size-dependent chemical reactions may play a critical role in the life cycle of atmospheric aerosols by bridging the gap between the initial formation of particle embryos and their growth into size ranges where their survival probability is greater and on which cloud droplets can eventually form. Here we report the results of laboratory experiments on particle size-dependent reactions, e.g., model reactions on the influence of pressure on oligomerization reactions (Diels-Alder reactions), heterogeneous oxidation processes, and condensation reactions in which volatile products are formed. All of these reactions could or should be influenced by the curvature of the surface of organic aerosol particles and accordingly can show a size dependency. The studies were carried out in laboratory-scale flow reactors at the University of Mainz. In particular, mass spectrometric analytical techniques such as UHPLC-ESI-Orbitrap MS and GC-Orbitrap MS measurements as well as on-line CI-Orbitrap-MS studies were used. Size-dependent chemical reactions are shown to play a role in the size range between 30 and 100 nm, and thus could be important for the growth of freshly formed particles up to a size where they can act as cloud condensation nuclei (CCNs).