Environmentally Relevant Organic Compounds at the Air-Ice Interface

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The compartments of the Earth's system are firmly interconnected. Alteration in one component can produce strong impact on the state of other compartments. Therefore, the physical and chemical processes undergoing in the cryosphere have a strong impact on the biogeochemical cycles and fates of the organic contaminants in the global scale. The chemical processes are significant in terms of removal of the contaminants or often generation of reaction products which are more toxic and more bioaccumulative than the original contaminants. Hence worldwide current research on snow chemistry is aimed to a better understanding about the location of contaminants in snow/ice, the reaction mechanism followed and the effects of environmental parameters, such as temperature, on the chemical processes.

We investigated the applicability of artificial snow as an alternative of natural snow to be utilized in the laboratory. The apparent specific surface area was determined using valerophenone photochemistry and ozonolysis of 1,1-diphenylethylene (DPE). The calculated specific surface area of artificially produced snow grains (80–150 cm^2g^{-1}) and that of natural snow grains (125 cm^2g^{-1}) were comparable and in good agreement with the values determined by other physical methods. The cage effect values were obtained to confirm that impurities, which are mostly ejected to the surface of snow during the freezing of the aqueous solutions, form a two-dimensional layer at the air-ice interface. We found that the heterogeneous reaction of ozone and snow-surface adsorbed DPE follows a Langmuir-Hinshelwood type of reaction kinetics at 258K. Also the temperature dependence of DPE ozonation was studied in the temperature range of 268 to 188K. A remarkable and unexpected increase in the apparent ozonation rates with decreasing temperature was evaluated using the Langmuir–Hinshelwood and Eley-Rideal kinetic models, and by estimating the apparent specific surface area of ice grains. We propose that an increase of the number of surface reactive sites and possibly higher ozone uptake coefficients are responsible for apparent rate acceleration of DPE ozonation at the air–ice interface at lower temperatures. Our results can be beneficial for understanding heterogeneous reactivity of volatile and semi-volatile organic compounds on the natural ice surface.

Keywords: artificial snow, photochemistry, cage effect, ozonolysis, specific surface area, Langmuir-Hinshelwood kinetics and Eley-Rideal kinetics.

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