Light-induced multiphase chemistry of gas phase ozone on aqueous pyruvic and oxalic acids

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Multiphase reactions of atmospheric interest have been extensively studied in the last decade. The light-absorbing organic compounds present on the condensed aerosol particles interacting with trace gases such as ozone can initiate a new and potentially important photo-induced multiphase chemistry. However, the investigations of light induced multiphase processes are very scarce.

In this context we launched the idea of pyruvic acid (PA) being photosensitizer in the multiphase reactions between gas-phase ozone and aqueous oxalic acid (OA). The performed photochemical batch experiments yielded a complex suite of organic molecules which resulted primarily from the oligomerization of OA/PA and subsequent reactions, including decarboxylation and cycloadition.

We demonstrated that presence of pyruvic acid in the aqueous droplet can potentially influence the reaction mechanism of the ozone multiphase chemistry on aqueous oxalic acid. Moreover, such multiphase chemistry induces the formation of OH radical in the aqueous phase which implies that the reaction pathway of OH reaction with oxalic acid in the aqueous phase can be altered as well.

Keeping in mind that pyruvic acid is always accompanied by other carboxylic acids (and by extension with other organics) which are deposited in the aqueous droplet it is recommended that future model studies should consider the impact of pyruvic acid on the aqueous reaction mechanism under sunlight irradiation. Preferably, potential pathways should be evaluated in more advanced multiphase chemistry models such as CAPRAM.

In a very recent study we performed experiments in the aerosol chamber facility LEAK at IFT, Leipzig to verify the influence of pyruvic on the multiphase (photo)oxidation of oxalic acid. The aim of these experiments was to study the multiphase photo-induced oxidation reactions with airborne deliquescent particles to demonstrate the applicability of the reactions mentioned above under more realistic conditions than in a batch reactor. State of the art sampling and analytical tools were applied for the analysis of the ongoing chamber runs and the formed particulate products which include denuder sampling, carbonyl compound derivatisation, PTR-MS measurements, GC-MS measurements and HPLC-MS and CE-MS for the particle phase. The particle phase products were analysed using High Performance Liquid Chromatography coupled to Electrospray Ionization Mass Spectrometry (HPLC/ESI-MS) which is an ideal tool for the analysis of polar organic compounds typically found in SOA as it offers a wide range of a separation modes and selectivity.