

POSSIBLE FORMATION PATHWAYS OF DICARBOXYLIC ACIDS WITHIN THE TROPOSPHERIC AQUEOUS PHASE - A MODELING STUDY

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A wide variety of organics is identified both in the tropospheric gas, aqueous and solid phase. It is evident that with increasing oxidation state of the carbon their solubility increases so that the aqueous phase gains in importance as a possible sink. At the current state of mechanism development organic chemistry within clouds is quite restricted; the most explicit mechanism represents CAPRAM2.4 (MODAC-mechanism) [1] considering at least C₁ and C₂ organics in its basic form.

Dicarboxylic acids represent the most abundant contributors to the organic material in solid aerosol particles. Not only oxalic acid but also the higher homologues malonic and succinic acid were identified in the solid phase [2]. If such particles act as cloud condensation nuclei (CCN) it can be expected that the acids are dissolved in the resulting cloud droplets leading to concentrations in the range of 10⁻⁶ M. Field studies show that such concentrations represent a mayor fraction to the total tropospheric budget of such species: It was found that the concentration ratio between gas and particle phase amounts to 0.46 for oxalic acid and even 0.7 for pyruvic acid [3].

Whereas in several studies it is stated that these compounds are formed in the gas phase by reactions of alkenes with ozone [4], corresponding aqueous phase processes are not considered in models. Therefore an extension to CAPRAM2.4 (MODAC-mechanism) was developed considering higher (\geq C₂) organics such as aldehydes, ketones and (di-)carboxylic acids. In the present study possible formation pathways of dicarboxylic acids (and their precursors) within tropospheric cloud droplets will be discussed.

Oxalic acid is formed via the oxidation of glyoxylic acid which represents an oxidation product of glyoxal. If a similar oxidation pathway for methylglyoxal is implied it leads to pyruvic acid. In several gas phase laboratory studies that both glyoxal and methylglyoxal are ring cleavage products of aromatics [5]. Therefore aromatics may act possibly as indirect precursors for oxalic and pyruvic acid within the tropospheric particle phase. Even further oxidation of dicarboxylic and keto acids may lead to higher oxygenated products such as malic acid or tartronic acid which were also identified in aerosol particle samples [1].

Model results from the multiphase mechanism CAPRAM2.4 (MODAC-mechanism) linked to the gas phase mechanism RACM [6] show that the efficiency of the formation processes of (di-)carboxylic acids can contribute significantly to the total amount of these species identified in solid residual particles: The resulting masses of the carboxylic acids are in the same order of magnitude as the total organic masses found in the particles. These results indicate that not only the inorganic composition of the tropospheric particle phase (sulfate, nitrate) but also the organic matter could be significantly modified by chemical cloud processes.

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