

Modelling of the tropospheric non-radical aqueous phase chemistry of organic carbonyl compounds and acids

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Tropospheric clouds and deliquescent aerosol particles are a complex multiphase and multi-component environment with simultaneously occurring gas and aqueous phase chemical transformations. Aqueous phase chemical processes proceed very efficient on short timescales and thus they are able to alter the chemical composition and the deduced physical properties of tropospheric aerosols on a global scale. Besides well-known radical oxidation processes, aqueous-phase non-radical reactions (e.g. H₂O₂/O₃ oxidations and accretion reactions) of important organic compounds such as organic carbonyl compounds and acids are a subject of interest in the scientific community since recent years (see e.g., ERVENS ET AL., 2011). These reactions can represent a potential pathway contributing to the formation and processing of aqSOA. Additionally, these processes are partly able to form less volatile products with higher carbon numbers leading to an increased partitioning towards the condensed aerosol phase. The relevance of non-radical aqueous chemical processes for aqSOA is often underestimated in current multiphase models.

In order to improve the still limited understanding of non-radical aqueous phase chemical processes, detailed model studies have been performed in the present study applying a newly developed reaction module and the SPectral Aerosol Cloud Chemistry Interaction Model (SPACCIM, WOLKE ET AL., 2005). The new reaction module has been developed mainly based on recent literature data (e.g., SCHÖNE & HERRMANN, 2014) and has finally coupled to the MCMv3.2/CAPRAM4.0a mechanism with 21328 multiphase processes. The new module contains 121 additional reactions of organic carbonyl compounds and acids such as MACR, MVK, acrylic acid (AA), methacrylic acid (MAA), pyruvic acid, glyoxylic acid, glycolic acid, glycolaldehyde, glyoxal (GLY) and methylglyoxal (MGLY). Besides 22 updated OH and NO₃ reactions, further SO₄⁻ radical reactions and firstly non-radical oxidations by H₂O₂ and O₃ were considered (53 new reactions). Moreover, non-oxidative processes have been considered including oligomerisations and NH₄⁺ catalysed reactions of GLY and MGLY as well as GLY reactions with three amino acids and methylamine.

SPACCIM model simulations have been carried out for different environmental conditions (remote/urban) using a non-permanent meteorological scenario. Furthermore, sensitivity studies are performed to study the effects of the different non-radical reaction pathways on the overall aqSOA processing. The model results were analysed including time-resolved source and sinks studies. The model analyses are focused on multiphase reactions of organic compounds and particularly the role of non-radical pathways compared to radical oxidation under both cloud and deliquesced particle conditions.

The performed remote case studies have shown that non-radical oxidations (H₂O₂, O₃) can play an important role in the aqueous oxidation of organic compounds besides key radical oxidants. O₃ can be important for quite soluble unsaturated organic compounds such as MAA and AA particularly under cloud conditions. For MAA, the remote studies have shown that O₃ can be with a contribution of 75 % to the overall aqueous oxidation flux even more important than OH. H₂O₂ can be an important oxidant particularly for substituted organic acids under both cloud and deliquesced particle conditions. For example, 47% of the pyruvic acid degradation fluxes are caused by aqueous H₂O₂ leading to lowered productions of ketomalonic acid/oxalic acid in the remote case. Accordingly, added non-radical oxidation processes can both increase and decrease the overall aqSOA formation.

Moreover, the simulations have examined the importance of oligomerisations of GLY and MGLY for the aqSOA formation. The studies showed that formation of oligomers mainly appeared during the cloud evaporation. For the firstly implemented dimerization of GLY and MGLY, oligomer concentrations up to 70 ng m⁻³ are modelled. However due to the implemented equilibrium, the formed oligomers are only shortly present. Additionally considered oligomer equilibria and further OH oxidations of the formed oligomers lead to increased oligomer concentrations (≈10 times more) compared to the base case with the dimersations only. Oligomer concentration up to few hundred ng m⁻³ are modelled for the extended case. The oligomer mass is dominated by GLY-oligomers. Overall, the studies revealed that oligomer formation processes and the further oxidations of its formed oligomers in cloud entrainment/ detrainment zones might be potentially important for the aqSOA formation. However, more kinetic and mechanistic investigations are necessary to improve current model results.

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