

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

A. Tilgner, E. H. Hoffmann, L. Schöne, R. Wolke and H. Herrmann

Leibniz Institute for Tropospheric Research (TROPOS), Permoserstr. 15, Leipzig, 04318, Germany

Keywords: multiphase chemistry, Secondary Organic Aerosol, aerosol modelling, aerosol cloud interaction  
tilgner@tropos.de

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 are expected to proceed very efficient on short timescales and hence they are able to alter the chemical aerosol composition and the deduced physical properties on a global scale. Besides well-known radical oxidation processes, aqueous-phase non-radical reactions (e.g.  $\text{H}_2\text{O}_2/\text{O}_3$  oxidations and accretion reactions) of important organic compounds such as organic carbonyl compounds and acids are a subject of interest in the scientific community in recent years (see e.g., Ervens *et al.*, 2011). These reactions can represent a potential pathway contributing to the formation and processing of aqSOA. Moreover, these processes are partly able to form less volatile products with higher carbon numbers, thus 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 tropospheric 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 and Herrmann, 2014) and has finally coupled to the MCMv3.2/CAPRAM4.0 $\alpha$  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  $\text{NO}_3$  reactions, further  $\text{SO}_4^-$  radical reactions and firstly non-radical oxidations by  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  were considered (53 new reactions). Moreover, non-oxidative processes have been considered including oligomerisations and  $\text{NH}_4^+$  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 ( $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ) can play an important role in the aqueous oxidation of organic compounds besides key radical oxidants.  $\text{O}_3$  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  $\text{O}_3$  can be with a contribution of 75 % to the overall aqueous oxidation flux even more important than OH.  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  leading to lowered production fluxes of ketomalonic acid/oxalic acid under remote conditions. Consequently, added non-radical oxidation processes can both increase and decrease the overall aqSOA formation.

Furthermore, the simulations have investigated 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  $70 \text{ ng m}^{-3}$  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 ( $\approx 10$  times more) compared to the base case with the dimersations only. Oligomer concentration up to  $430 \text{ ng m}^{-3}$  (third day) are modelled for the extended case. The oligomer mass is dominated by GLY-oligomers. The contribution of MGLY-oligomers is substantially smaller. 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.

Ervens, B. et al. (2011) *Atmos. Chem. Phys.* **11**, 11069-11102.

Schöne, L. and Herrmann, H. (2014) *Atmos. Chem. Phys.* **14**, 4503-4514.

Wolke, R. et al. (2005) *Atmos. Environ.* **39** (23-24), 4375-4388.