Oxidation of substituted aromatic hydrocarbons in the tropospheric aqueous phase: Kinetic mechanism development and modelling

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Aromatic compounds are an important anthropogenic emitted family of VOCs. They are ubiquitously present in the troposphere and are very important for the formation of anthropogenic secondary organic aerosol, brown carbon, and ozone. Due to their generally small water solubility, previous studies dealing their atmospheric effect focused mainly on gas-phase oxidation of benzene, toluene, and xylene. However, oxidised aromatic compounds such as phenol, catechol or cresol are much more soluble compared to their precursors and can more efficiently partition effectively into cloud droplets. Therefore, their aqueous-phase oxidation can be very effective in clouds or even deliquescent aerosols. Up to now, no detailed studies are available investigating the impact of multiphase chemistry on oxidation of these aromatic compounds. To examine this issue, a detailed aqueous-phase oxidation mechanism of substituted aromatic compounds is developed and applied. The developed mechanism contains 296 processes considering the oxidation of aromatic oxidation products from benzene and toluene oxidation, such as phenol and cresol by different oxidants down to the formation of non-cyclic compounds. The developed mechanism has been coupled to the existing gas-phase mechanism MCMv3.2 linked with the aqueous-phase mechanism CAPRAM4.0. Detailed model studies were carried out using the air parcel model SPACCIM. The simulations revealed the high importance of in-cloud oxidations for substituted aromatics. Aqueous-phase chemistry of aromatic compounds in clouds leads to more than 6% increase in total organic aerosol mass, significant amounts of brown carbon, and is important for oxidation of nitrated aromatic compounds.