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Evaluation of prediction methods for aqueous phase rate constants of organics and CAPRAM mechanism development

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Organic compounds are a ubiquitous constituent of the troposphere. With either biogenic or anthropogenic sources, they have a major influence on the atmospheric multiphase system and thus have become a main research topic within the last decades.
Modelling can provide a useful tool to explore the tropospheric multiphase chemistry. While in the gas phase several detailed oxidation schemes exist, in the aqueous phase those chemical mechanism are very limited. The currently most comprehensive aqueous phase chemistry mechanism CAPRAM 3.0i (Tilgner and Herrmann, 2010) provides 777 processes for 380 species up to C4 organics. While the C1 and C2 chemistry is nearly complete, the C3 and C4 chemistry is not. The extension of the C3 chemistry in CAPRAM as the aim of the current study demands the oxidation of a large number of further organics and their intermediates. However, it is impossible to cover the whole mechanism with experimentally derived kinetic data. Especially, for larger compounds experimental data becomes rare. Therefore, estimation methods become necessary to predict missing kinetic data. To fulfil the aim of the current study and extend the C3 organic chemistry in CAPRAM 3.0i an evaluation of available experimental data from literature has been carried out. Within this process a database with over 700 reactions of hydroxyl and nitrate radicals with organics was created. For missing kinetic data prediction methods are essential and have therefore been compared and tested for their usefulness in atmospheric chemistry modelling. Among those methods are the structure-activity relationships of Monod and Doussin (2008) and Minakata et al. (2009) as well as Evans-Polanyi-type correlations (Benson, 1976). With the results of the evaluation process, the C3 chemistry of CAPRAM 3.0i has been further extended and the aqueous phase mechanism has then been coupled to the gas phase mechanism MCMv3.1 (Saunders et al., 2003). First test simulations have been performed to study the influence of the organic C3 tropospheric multiphase chemistry in more detail.

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