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Extension of the CAPRAM mechanism with the improved mechanism generator GECKO-A

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Organic compounds are an ubiquitous constituent of the tropospheric multiphase system. 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 comprehensive near-explicit mechanisms exist, in the aqueous phase those mechanisms are very limited. The current study aims to advance the currently most comprehensive aqueous phase mechanism CAPRAM 3.0 by means of automated mechanism construction. Therefore, the mechanism generator GECKO-A (Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere; see Aumont et al., 2005) has been advanced to the aqueous phase. A protocol has been designed for automated mechanism construction based on reviewed experimental data and evaluated prediction methods. The generator is able to describe the oxidation of aliphatic organic compounds by OH and NO_3. For the mechanism construction, mainly structure-activity relationships are used, which are completed by Evans-Polanyi-type correlations and further suitable estimates.

GECKO-A has been used to create new CAPRAM versions, where branching ratios are introduced and new chemical subsystems with species with up to 4 carbon atoms are added. The currently most comprehensive version, CAPRAM 3.7, includes about 2000 aqueous phase species and more than 3300 reactions in the aqueous phase. Box model studies have been performed using a meteorological scenario with non-permanent clouds. Besides the investigation of the concentration-time profiles, detailed time-resolved flux analyses have been performed. Several aqueous phase subsystems have been investigated, such as the formation of oxidised mono- and diacids in the aqueous phase, as well as interactions to inorganic cycles and the influence on the gas phase chemistry and composition. Results have been compared to results of previous versions and show a significant improvement in the new mechanism versions, when comparing the modelled data to field data from literature. For example, in CAPRAM 3.7 there is a malonic acid production of about 80 ng m^{-3} compared to a few ng m^{-3} in CAPRAM 3.0. The results in CAPRAM 3.7 confirm recent measurements by Bao et al. (2012), who measure up to 137 ng m^{-3}. Moreover, several attempts have been undertaken to validate the mechanisms created by GECKO-A with own field experiments, such as the HCCT-2010 campaign and chamber experiments in the LEAK chamber.

References

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