

Mechanism Development for Tropospheric Multiphase Chemistry with CAPRAM

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Several studies in recent years have shown the influence of aqueous phase processes on tropospheric chemistry (e. g. Jacob, 1986, 2000; Chameides, 1984). Chemical mechanisms currently used for the description of tropospheric multiphase processes contain detailed descriptions of inorganic processes (before all sulphur oxidation), but mostly the organic chemistry is restricted to C₁ species (e. g. Jacob *et al.*, 1986, 1989; Walcek *et al.*, 1997). In the Chemical Aqueous Phase Radical Mechanism the description of the organic chemistry was extended to species with two carbon atoms (CAPRAM2.3, Herrmann *et al.*, 2000).

At the current state of multiphase model development the mechanism CAPRAM (version 2.3: Herrmann *et al.*, 2000) includes one of the most detailed extended description of organic chemistry and radical processes within clouds. In particular are considered (1) a detailed presentation of the oxidation of organic compounds, in the basic form restricted to organics with one and two carbon atoms, (2) an explicit description of S(IV)-oxidation by radicals and iron(III), as well as by peroxides and ozone, (3) the reactions of OH, NO₃, Cl₂⁻, Br₂⁻, and CO₃⁻ radicals, as well as reactions of the transition metal ions (TMI) iron, manganese and copper. The updated version, called CAPRAM2.4 (MODAC mechanism) represents a model containing very recent findings on reaction patterns and kinetic data in the liquid phase (Ervens *et al.*, 2000). In the comparison to the former version changes occur in the chemistry of transition metal ions (TMI), considering reactions of iron, manganese and copper ions. In the update of the oxidation of organic species the C₂ chemistry was completed including the oxidation of difunctional species glyoxal, glyoxylic acid and oxalate/oxalic acid and a detailed formulation including peroxy radical chemistry throughout the scheme.

This overall aqueous phase mechanism including now 710 processes (before: 526) is coupled with the existing gas phase chemical scheme RACM (Stockwell *et al.*, 1997). The model calculations are performed with constant values for the liquid water content (0.3 g m⁻³), temperature (288.15 K) and pressure (1 atm) to be able to distinguish clearly between influences of chemical and physical processes. Initial concentrations of gas and aqueous phase species and also emissions/ depositions are chosen for three different scenarios (continental polluted, continental unpolluted and marine). Recent results clarifying the influence of clouds

to the gas phase obtained by the application of CAPRAM2.4 (MODAC mechanism) in (i) its extended and (ii) a condensed version are presented.

A further extension of CAPRAM 2.4. (MODAC mechanism) based on new data from aqueous phase laboratory studies is outlined. The background for this is that it is known from analytical studies of field measurements that within tropospheric clouds and aerosols a lot of higher hydrocarbons beyond C₂ from biogenic and anthropogenic sources exist: Beside of the class of dicarboxylic acids (oxalic, malonic and succinic acid) found in cloud water or aerosol samples gas phase measurements of water soluble C₃ species are available (e. g. ketones, aldehydes). These species are not treated in aqueous phase models up to now because of the lack of kinetic input parameter. To obtain these parameter for the further extension of the reaction scheme laboratory studies have been performed to gain better insight into chemical conversions in clouds and the wet tropospheric aerosol. Specifically, OH radical reactions studied focus on C₃ and C₄ compound which have been identified in tropospheric aerosols and clouds. With the combination of lab studies and the direct implementation in the multiphase system statements can be given about the importance of reactions added in different scenarios. Implications will be discussed and an outlook on further activities with regards to organic tropospheric multiphase chemistry will be given.

References

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