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Background and Motivation

Within the current project within the modelling cluster MODMEP work in proceeding in three directions. Firstly, the currently available complex multiphase chemistry (CAPRAM 2.4 (MODAC mechanism), Ervens et al. (2002)) is extended to more completely cover organic conversions. Secondly, the impact of the consideration of a more complex organic particle chemistry is studied both with regards to gas phase as well as of particle phase chemical composition. Thirdly, model runs will now be performed in a size-resolved manner for the treatment of aerosol and cloud chemistry and not just for monodisperse particle and droplet populations.

Mechanism development

Basic mechanism

The basic mechanism of CAPRAM2.4 (MODAC mechanism; Ervens et al., 2002) describes in detail mainly radical reactions of the species groups shown in the scheme. It represents an extended scheme of the former version CAPRAM2.3 (Herrmann et al., 2001).

The concentration levels of essential target species (NO_x, S(IV), O₃, H₂O₂, OH, NO₃ and pH) both are reproduced by the condensed mechanism in limits of ± 5% for a broad range of initial conditions (polluted/unpolluted scenarios).

CAPRAM2.4 (MODAC) reduced

Total number of processes: 438 183

HO _x / TMI 59 22	Nitrogen 32 11	Sulfur 59 18
Bromine 17 9	Chlorine 16 5	Organics (C ₁ /C ₂) 110 36
Carbonate 21 0	Equilibria 57 39	Photolysis 11 4

Organic extension

Total number of processes: 116

C ₂ organics 18	<ul style="list-style-type: none"> alcohols ketones aldehydes acids monocarboxylic ~ keto-carboxylic ~ dicarboxylic ~
C ₃ organics 59	
C ₄ organics 39	

Extension of organic chemistry

In the basic mechanism the organic chemistry is restricted to species with up to two carbon atoms. In the extension the C₂ chemistry was further completed and additionally chemical source and loss processes of mono- and difunctional C₃ and C₄ compounds are considered.

Their oxidation is initiated by the OH radical according to the finding in the reduced scheme that other radical contribute less to these conversions.

Especially formation processes of low volatile di- and keto-carboxylic acids were considered giving possibly insight about the composition of the organic content in aerosol particles after evaporation of cloud water.

Results

Composition of the particle phase

In several model and field studies it was stated that the main part of sulfur(IV) is oxidized in the particle phase. Also the oxidation of nitrogen (III) in the clouds contributes effectively (up to 30%) to the formation of nitrate.

In Figure 1a the concentrations of the main dissolved species in cloud water are shown after several hours of phase interaction time. It becomes evident that nitrate and sulfate accumulate in the particle phase explaining high amounts of them in residual particles.

About 1% of the mass are represented by water soluble organics. In Figure 1b it becomes evident that the small carboxylates, i.e. formate, glyoxylate and acetate, contribute to about 70% to the organic mass in cloud water. The further 30% are represented by di- and keto-carboxylic acids. Whereas during evaporation formate, glyoxylate and acetate will be - at least partly - transported into the gas phase, the higher acids will remain in the residual particles.

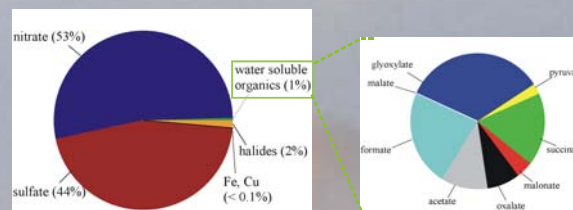


Fig. 1: Mass distribution [μg m⁻³] of dissolved species in cloud droplets (after 24 h)
a) Total mass (inorganic and organic) b) Specification of organic mass

Modification of Organic Particle Composition: Oxalate, Pyruvate

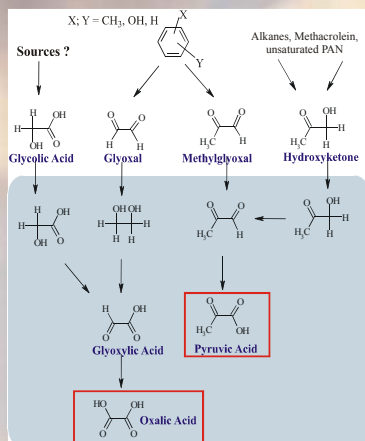


Fig. 2: Formation pathways of pyruvate and oxalate in the multiphase system

It is known that glyoxal and methyl glyoxal are ring cleavage products from the aromatic oxidation in the gas phase. The solubility, i.e. their effective Henry's Law Constants are

$$K_H^{\text{eff}}(\text{CHO})_2 = 3 \cdot 10^5 \text{ M atm}^{-1}$$

$$K_H^{\text{eff}}(\text{CH}_3\text{COCHO}) = 3 \cdot 10^4 \text{ M atm}^{-1}$$

Their oxidation in the aqueous phase leads finally to oxalic and pyruvic acid, respectively (Fig. 2).

These pathways are the most important sources of oxalate and pyruvate both in polluted and unpolluted environments. In less polluted areas also glycolic acid contributes to oxalate formation. In the mechanism the sources for this acid are restricted. Besides its formation by the recombination of the acetate peroxy radical (O₂CH₂COO) it is formed by the decay of higher carbonyl compounds.

Phase interaction times of some days leads to concentrations of

$$[\text{Oxalate}] = 7 \mu\text{M} \quad [\text{Pyruvate}] = 8 \mu\text{M}$$

Considering the liquid water content of 0.3 g m⁻³ the resulting atmospheric concentration in particles can be estimated via

$$1 \mu\text{M (in cloud water)} \approx 1 \mu\text{g m}^{-3} \text{ (in particles)}$$

Masses in this order of magnitude were found in aerosol samples (e.g., Sempere and Kawamura, 1994).

Comparing the results obtained with 1 respectively 50 size bins the biggest changes will occur in the case of marine clouds. Another observation would be that in the marine scenario some species are not affected by the size resolution in these cases the concentration in both phases will not be affected. These observations led us to the conclusion that phase transfer is primarily affected by size resolution, process which is most important in marine conditions.

Size-resolved model runs

The CAPRAM 2.4 (Ervens et al., 2002) multiphase mechanism coupled to the gas phase mechanism RACM (Stockwell et al., 1997) was applied to a size-segregated system in order to investigate the influence of size distribution and liquid water distribution on the mass transport processes and on the multiphase chemistry in cloud droplets for three different scenarios. Phase exchange had been accounted by the resistance model of Schwartz (Schwartz, 1986)

The calculations were performed with a 0-dimensional box model considering different number of size bins (1,2,3,4,5,10,20,30,50) (1 μm < rdroplet < 64 μm). For the runs time constant microphysical values (liquid water content, no liquid water fluxes between different droplet classes) were considered. For temperature (T), pressure (p) and the total liquid water content (LWC) the following values were assumed: (T=288 K, p=1 atm and LWC=3·10⁻⁷ volaq volg⁻¹) A lognormal distribution of the number concentration in function of radius was considered.

According to the results, it becomes evident that size resolution has a great effect on concentration. Interesting size effect can be observed in the case of the iron redox system, especially in the marine case. (Figure 3) While considering different size resolutions the concentrations during the day reach approximately similar values, with the concentration of Fe(II) being higher than that of Fe(III) by approx. 4·10⁻⁸ mol/l during the night the concentration of Fe(III) will be higher with approx. 2·10⁻⁸ mol/l than Fe(II) (considering 50 size bins), but considering only one size bins the concentration of Fe(II) will be over Fe(III) by approx. 2·10⁻⁸ mol/l.

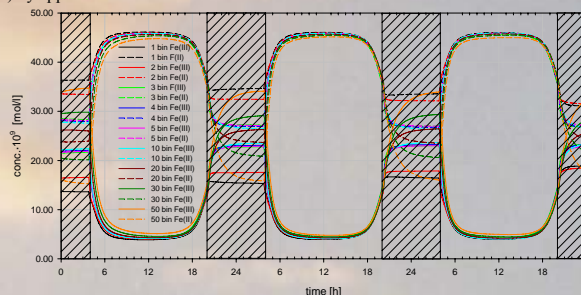


Fig. 3: Size effect during the night in the iron redox system

Conclusions

Model calculations were performed with an multiphase mechanism considering organic species in the aqueous phase with up to four carbon atoms

- => Chemical processes in clouds modify the organic content of aerosol particles
- => Dicarbonyl compounds from the gas phase can act as precursors for the formation of oxalate, pyruvate and even higher dicarboxylates in the particle phase. However, source processes of dicarboxylic acids in the gas phase are still missing
- => Size-resolved calculations indicate significant changes in the chemical system due to different conditions in the respective size bins

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Acknowledgements

The present study was supported by the European Commission under contract number EESD-ESD-3 within the project "Multiphase chemistry of Oxygenated Species in the Troposphere (MOST)" and by the Bundesministerium für Bildung und Forschung (BMBF) within the AFO2000 programme in the MODMEP project under contract 07ATF40.