

CAPRAM2.4 (MODAC mechanism): The current state

A contribution to subproject CMD-MPM

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Summary

Model studies were performed to investigate the importance of chemical processes in the tropospheric aqueous phase. Whereas the formation of sulfate and nitrate as main contributors to the total aerosol particle mass was often investigated, very few studies were performed with regards to the organic content. These ratios between organic and inorganic fractions can be reproduced by the multiphase model. In the interpretation of the model results the main focus was set to formation pathways of organic compounds ($\leq C_4$). The chemical aqueous phase radical mechanism (CAPRAM) used here is represented by CAPRAM2.4 (MODAC mechanism)-condensed linked to an additional module considering processes of C_3 and C_4 organic compounds. There the formation and decay processes of monofunctional and difunctional compounds, such as oxalic, malonic, succinic, pyruvic and malic acid are considered. These compounds are of interest because they remain in the particle phase after evaporation of cloud water and represent compounds found in aerosol particle samples in field campaigns.

In an urban scenario the main fraction of mass in cloud water is represented by nitrate and sulfate (> 90%). The fraction of mono-, di- and ketocarboxylic acids of the total mass is about 1%. The remaining mass fractions are represented by further inorganic species, such as halides and transition metal ions.

The formation of oxalic and pyruvic acid is closely linked to the aromatic oxidation in the gas phase. There glyoxal and methylglyoxal are formed being essential precursors for oxalic and pyruvic acid, respectively, in the aqueous phase. Other soluble species formed in the gas phase, such as unsaturated dicarbonyl compounds and hydroxyketones, do not have a large influence to the formation of oxygenated organics in the particle phase. It becomes evident that for higher acids, such as succinic and malic acid, source strengths are underestimated by the model because much lower concentrations are predicted by the model as found in field studies.

Introduction

In several model studies it was shown that the main part of sulfate and also an essential fraction of nitrate is formed in tropospheric clouds (Warneck, 1999; Langner and Rodhe, 1991). After evaporation of the cloud water these species remain in residual aerosol particles. The mass of soluble organic carbon in aerosol samples contributes to up to 10% of the total aerosol mass but mostly fractions of 1-2% are found (Sempere and Kawamura, 1994). The source processes of the inorganic species can be described properly by models due to many laboratory and field studies. But up to now less attention was paid to the composition of the organic fraction in the particles due to many lacks of knowledge about their source and sink strengths. At the current state of mechanism development for multiphase models the organic chemistry within the tropospheric particle phase is quite restricted. The most explicit mechanism is represented by CAPRAM2.4 (MODAC-mechanism, Ervens *et al.*, 2002) considering in its basic form C_1 and C_2 organics and inorganic chemistry (radicals/radical anions (OH , NO_3 , SO_4^- , Cl_2^- , Br_2^- , CO_3^- and SO_5^-), transition metal ions and sulfur oxidation.

In the widely used gas phase mechanism RACM (Stockwell *et al.*, 1997) organic species groups are lumped in different groups based on their reactivity, concentration and emissions. In CAPRAM2.4 (MODAC-mechanism) all processes are formulated explicitly considering all reactive intermediates such as alkyl and peroxy radicals. The advantage of this explicit formulation is that source and sink processes of every single compound can be followed, the disadvantage is a higher complexity of the mechanism.

In the present study it will be clarified that in tropospheric clouds chemical conversions can take place effectively leading to oxygenated organic species, i.e. acids, which can finally contribute to the organic mass of aerosol particles. The vapor pressure of organic species decreases with increasing oxidation state of carbon and therefore the solubility of such compounds increases enhancing the importance of the aqueous phase as a possible sink.

Dicarboxylic and ketocarboxylic acids represent the most abundant contributors to the organic material in solid aerosol particles. Not only oxalic acid but also the higher homologues malonic and succinic acid were identified in the solid phase (Neusüß, 2000). A cloud water concentration of few μM correspond to atmospheric concentrations of some $\mu\text{g mg}^{-3}$. Also monocarboxylic acids were identified in the particle phase but due to their lower vapor pressure it can be expected that their fraction in the gas phase is higher after evaporation of the cloud.

The box model

The calculations were performed with a 0-dimensional box model considering a monodisperse droplet distribution in clouds ($r_{\text{droplet}} = 10 \mu\text{m}$). In the present study an urban scenario is considered characterized by high concentrations and emissions of trace gases such as NO_x , SO_2 , VOC and O_3 . Emissions and depositions of trace gases are constant fluxes into or out of the box, respectively, allowing a continuous renewal and loss of gas species in the box. For the whole simulation period the parameters temperature (T), pressure (p) and liquid water content (LWC) were assumed to be constant ($T = 288 \text{ K}$, $p = 1 \text{ atm}$ and $\text{LWC} = 3 \cdot 10^{-7} \text{ vol vol}^{-1}$, respectively). This simplification was made to clarify exclusively the influence of chemical effects without any possible overlapping of meteorological or microphysical effects.

Chemical mechanism

CAPRAM2.4 (MODAC-mechanism) (**C**hemical **A**queous **P**hase **R**adical **M**echanism) in its extended version includes 147 species and 438 processes including 34 phase transfer processes (Ervens *et al.*, 2002). The mechanism is based on the former version of CAPRAM (CAPRAM2.3, Herrmann *et al.*, 2000). For the current study a condensed version of this mechanism was applied with 185 reactions characterized among other points by the fact that organic oxidation is exclusively initiated by the OH radical; the contributions of other radicals/ radical anions, such as NO_3 , SO_4^- , Cl_2^- and Br_2^- are neglected. Both mechanisms are available in the internet (<http://www.tropos.de/CHEMIE/multimod/CAPRAM/capram.html>). The mechanism was coupled to the gas phase mechanism RACM (Stockwell *et al.* 1997). The phase transfer processes were described using the the resistance model of Schwartz (1986) considering Henry's law constants, mass accommodation and gas phase diffusion coefficients.

In the basic version of CAPRAM2.4 (MODAC mechanism) the formation of oxalic acid is described via the reaction chain of the oxidation of glyoxal followed by that of glyoxylic acid (Karpel vel Leitner and Doré, 1997). But furthermore it can be expected that also glycolic acid can act as an precursor of glyoxylic acid. On the one hand this acid is formed by recombination of the acetate peroxy radical (Schuchmann *et al.*, 1985). On the other hand hydroxy acetaldehyde could possibly act as precursor. The latter species is not treated explicitly in the gas phase mechanism. Therefore, currently its source strength as an indirect

oxalate precursor cannot be rated and is not included in CAPRAM.

Not only glyoxal but also methylglyoxal was identified as a ring cleavage product in the aromatic oxidation in the gas phase. Its effective Henry's Law constant ($3.71 \cdot 10^3 \text{ M atm}^{-1}$, Betterton and Hoffmann, 1988) shows that in presence of clouds the aqueous phase can act as an important sink. The oxidation in the aqueous phase leads to pyruvic acid, corresponding to the conversion from glyoxal to glyoxylic acid.

Corresponding to the recombination of the acetate peroxy radical anion leading to glyoxylic and glycolic acid it is assumed that similar pathways take place also with the peroxy radical anions of more complex carboxylates, such as those of malonate and succinate. Such pathways would lead to the hydroxy and oxo dicarboxylic acids, mesoxalic, tartronic, oxalacetic and malic acid, respectively. However, both small oxo and hydroxy dicarboxylic acids are unstable; they decarboxylate resulting in an alcohol and an aldehyde with a smaller carbon chain, respectively. These considerations show that decarboxylation steps of highly functionalized organics can be essential pathways in which smaller difunctional compounds are formed.

Results

In Figure 1 the composition of the mass is shown obtained from the model after one simulation day. It becomes evident that the organic mass (i.e. the mass of low volatile organics which can be expected to remain in the residual particle) contributes to about 1% to the total mass. In the right figure this bar is further resolved into single compounds showing that oxalate, pyruvate and malonate are the main contributors. Obviously sources of malic acid are underestimated in the model. In field studies its concentration is comparable to those of the smaller dicarboxylic acids.

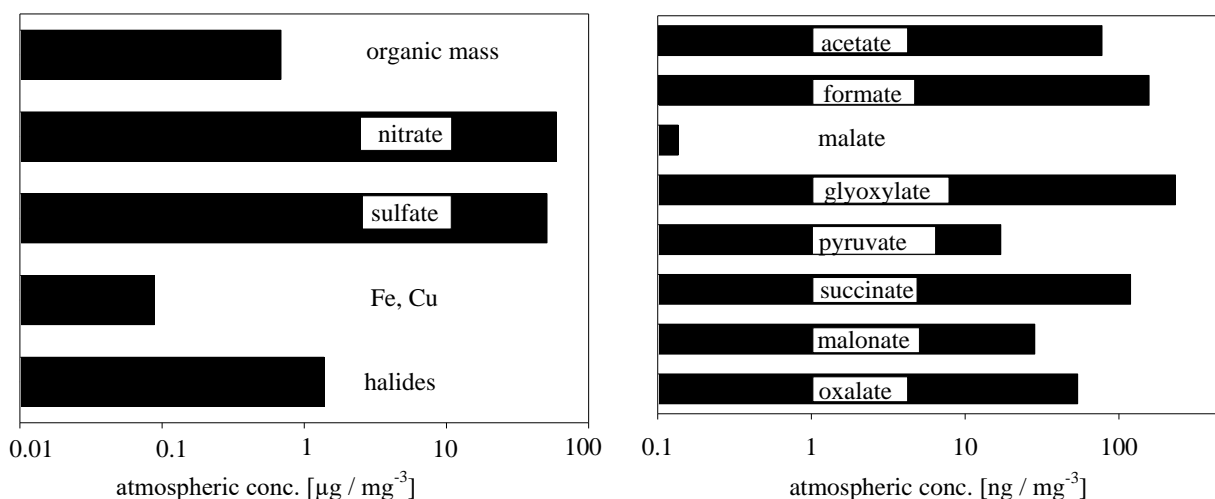


Figure 1: Mass distribution in a cloud droplet (after 24 h simulation time); left: total mass [$\mu\text{g m}^{-3}$], right: distribution of organic mass [ng m^{-3}]

The analysis of formation pathways makes evident that, in fact, the formation both of oxalic and pyruvic acid is connected strongly to the amount of aromatics in the gas phase. More than 90% of glyoxal and methylglyoxal are produced by aromatics. Other pathways such as the oxidation of glycolic acid as oxalate precursor are much less important maybe due to the fact that currently no sources of hydroxyacetaldehyde are implemented in the model. However, the oxidation of hydroxy ketones, which are mainly formed in the gas phase in the oxidation of alkanes and methacrolein, contributes only less than 5% to the methylglyoxal formation. In general, the formation of oxygenated compounds, e.g. acetone, hydroxy ketone and

methylglyoxal takes mainly place in the gas phase, but they are further oxidized in clouds. In the literature (e.g. Baboukas *et al.*, 2000) it is suggested that the high amount of oxalic acid in aerosol particles can be partly explained by decay processes from higher acids. The intermediate products in the succinate decay such as oxalacetic or mesoxalic acid are stabilized by decarboxylation so that the carbon chain becomes shorter. It seems reasonable that finally glyoxylic acid is formed. Therefore, the presented reaction scheme shows such correlations between long and small dicarboxylic acids.

Currently gas phase processes leading to di- or ketocarboxylic acids are not included in the gas phase mechanism used here. E.g. it is known that gas phase reactions between ozone and alkenes can lead to the formation of dicarboxylic acids. But also sink processes are omitted in the mechanism such as the photolysis of pyruvic acid being very efficient in the gas phase. Furthermore, the C₄ chemistry is not complete because the highly abundant unsaturated acids, fumaric and maleic acid, are not included in the mechanism although they are found in the same concentration range as e.g. pyruvic acid.

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