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Introduction and Motivation

Motivation: Recent detailed 0-D multiphase chemistry model studies [e.g. Tilgner et al. 2008] have implicated the necessity of more complex aqueous phase processes to be considered in future higher scale chemistry transport models (CTMs). Important chemical cloud effects are mainly not yet considered or less represented in currently available regional scale CTMs because of both the restricted knowledge in the past and the high computational costs of detailed aqueous phase chemistry mechanisms such as CAPRAM 3.0i (Chemical Aqueous Phase RADical Mechanism, Herrmann et al. [2005]). In this context, mechanism reductions using manual methods and automatic techniques have been already carried out to develop simplified chemical mechanisms.

Objective: The objective of the present work was to develop a reduced aqueous phase CAPRAM mechanism which is operational in higher scale CTMs. The aim of a reduction was to develop a chemical mechanism with a manageable size which accurately represents the main chemical processes viz. without a loss of key information. This will allow chemical investigations of a wider range of conditions in shorter time periods and in higher scales together with transport and microphysical processes. Due to the CTM restrictions concerning an aqueous phase chemical interaction description, the aim of the reduction was to develop a mechanism with less than 250 processes including chemical reactions, equilibria and mass transfer processes of soluble compounds. The application of this reduced mechanism should allow further investigations of the multiphase chemical processes in future regional CTMs.



Table 1: Selected target compounds for the CAPRAM reduction.

Target compounds	
Key inorganics	
Oxidants	OH, NO ₃ , HO ₂ , O ₂ ⁻ and H ₂ O ₂
Transition metal ions (TMI)	Cu(I), Cu(II), Fe(II) and Fe(III) species
Acidity and inorganic acids/bases	H ⁺ , SO ₄ ²⁻ , HSO ₄ ⁻ , NO ₃ ⁻ , NH ₄ ⁺ and Cl ⁻
Key organics	
Aldehydes (considering substitutes)	formaldehyde, acetaldehyde, glycolaldehyde, etc.
Dialcohols	ethylene glycol
Dialdehydes	glyoxal, methylglyoxal, 1,4-butanediol
Monoacids (considering substitutes)	acetic acid, pyruvic acid, glyoxylic acid, etc.
Diacyls (considering substitutes)	oxalic acid, ketomalonic acid, tartaric acid, etc.

Reduction: The mechanism reduction has been performed by means of a manual method including detailed chemical flux investigations and automatic method. Both methods have been focused on the identification and depletion of less important chemical processes to provide a less computationally intensive mechanism. Finally, the results of the two reductions have been compared. Based on the limitations of both reduction methods, the reduced CAPRAM mechanism was finally derived.

1. Automatic reduction (AR):

The ISSA-method (Iterative Screening and Structure Analysis, Mauersberger [2005]) was used to determine unimportant chemical processes and species in CAPRAM 3.0i mechanism. The reduction has been done by G. Mauersberger in the same manner as presented in Mauersberger [2005] for the former CAPRAM version 2.4 using a permanent cloud model scenario.

2. Manual reduction (MR):

The manual reduction was performed similarly to the studies of Ervens et al. [2003] based on detailed chemical flux analyses for pre-selected key species (see Table 1) and was mainly focused on the organic chemistry. Thus, the condensed CAPRAM 2.4 mechanisms (Ervens et al. [2003]; Mauersberger [2005]) have been used as initial start-up for the manual CAPRAM reduction. The mechanism reduction studies have been carried out with the Spectral Aerosol Cloud Chemistry Interaction Model (SPACCIM, Wolke et al. [2005]). In this parcel model, a non-permanent meteorological cloud scenario was applied including an extended cloud passage of about 26 hours within 48 hours modelling time. The target species have been chosen relative to their roles in tropospheric chemistry. For the identification of unimportant reaction paths and species, detailed chemical flux analyses have been performed mainly for the target species in different atmospheric scenarios.

Mechanism Reduction

• Detection of reaction rate-determining steps in the reaction chains of the organic chemistry (MR)

- Initial OH and NO₃ radical reactions
- Peroxy radical (RO₂) formation
- Bimolecular RO₂ decomposition
- Unimolecular RO₂ decomposition

The studies have shown that for the majority of the organic oxidations the peroxy radical formation and the uni- or bimolecular RO₂ decomposition are not reaction rate-determining steps. Consequently, these processes have been deleted and the linear step by step reaction pathways were linked together by reducing the number of reaction steps and species considering only the rate limiting reaction steps (mostly only the initial radical reactions, see Figure 1).

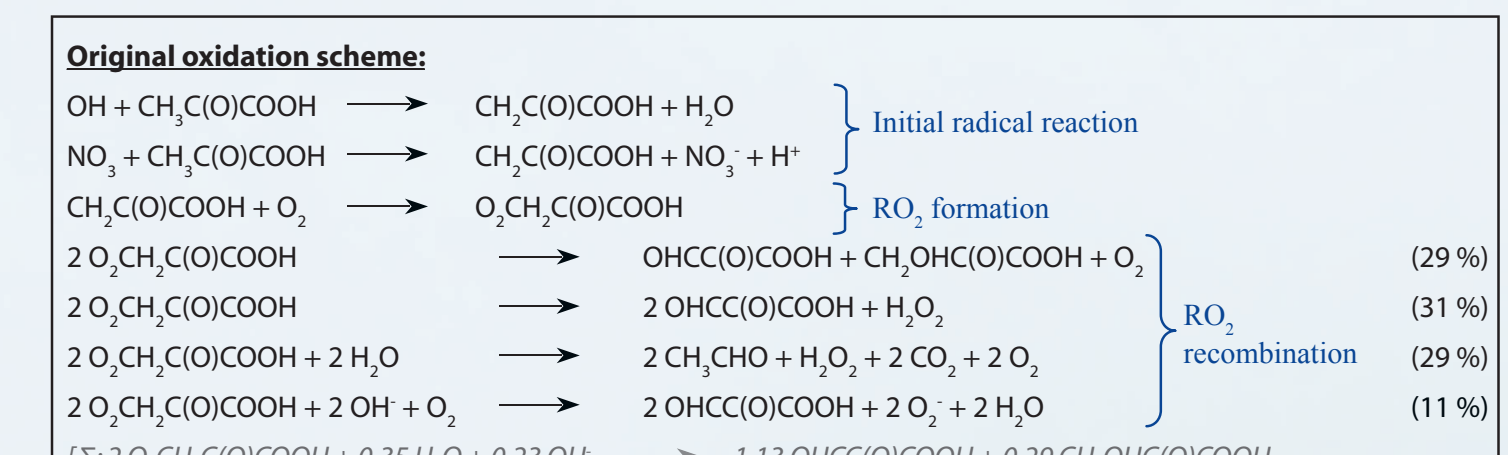
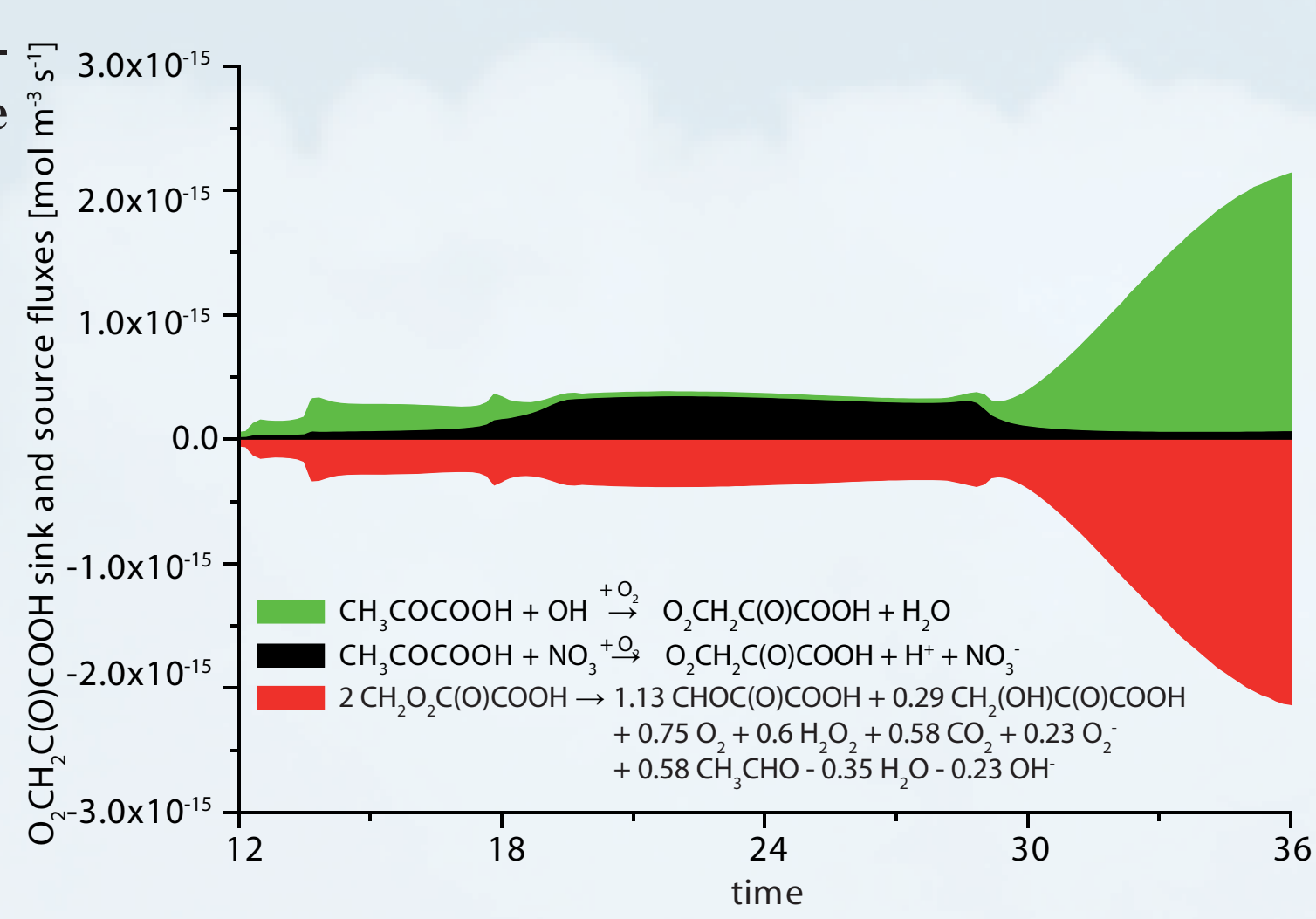


Figure 1: Modelled in-cloud sink and source fluxes of the pyruvic acid peroxy radical [CH₃C(O)C(O)OOH] for urban conditions (top) and schematic depiction of the performed reduction of the aqueous pyruvic acid oxidation (down).

• Further chemical investigations and reductions (MR)

- Analysis of important chemical sub-systems regarding their reduction potential
 - Deletion of effective hydrate formation in the aqueous phase
 - Deletion of the hydroxy methane sulfonate oxidation scheme
 - Simplification of the sulphur radical subsystem
 - Reduction of less important NO₃ radical oxidations of organic compounds (see Figure 2)
 - Reduction of the aqueous chemical processing of acetic, propanoic and butyric acid
- Deletion of less important organic sub-systems (see Figure 3)

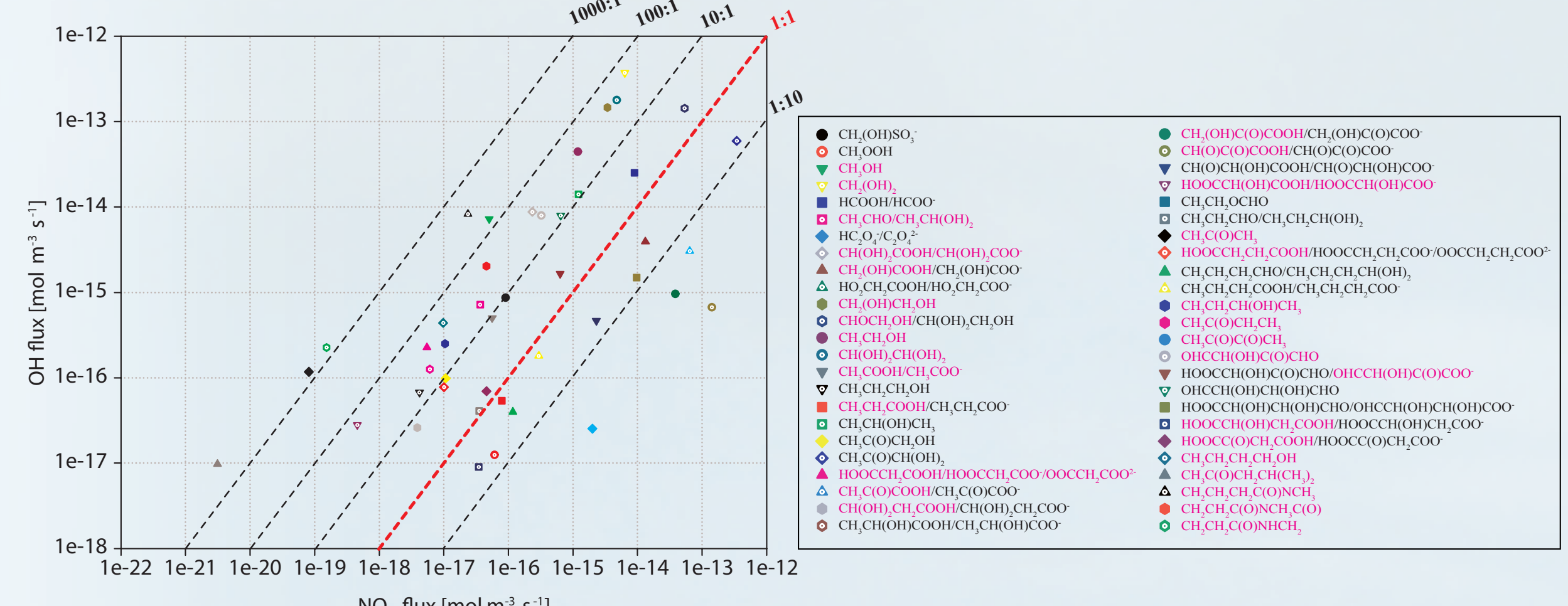


Figure 2: Comparison of the mean modelled in-cloud NO₃ and OH degradation fluxes of organic compounds under urban conditions [Tilgner et al., 2008]. For magenta-marked chemical compounds the percentage contribution of the NO₃ reaction to their total degradation is less than 5%. These NO₃ oxidations were removed from the mechanism.

• Comparison of the AR and MR results

- Comparison of the manual and MR automatic reduction shows a good agreement with minor differences in the organic chemistry.
- Inorganic chemical mechanism part almost the same than obtained in previous studies (Mauersberger [2005]).
- Based on the limitations of both used methods a postprocessing of generated mechanisms was done to merge the reduction results and to derive adequate and feasible reduced mechanism
- The automatic ISSA screening method not able to detect rate-limiting steps in reaction chains (unimportant processes such as unimolecular and bimolecular RO₂ decays as well as hydrations not removed from the mechanism)
- ISSA program not able to reformulate chemical processes, therefore the number of processes differs considerably between the two reduction schemes.
- AR removed more NO₃ radical oxidations caused by the performed permanent cloud modelling which presumably tends to underestimate the NO₃ radical importance (see Tilgner et al. [2008]).

Based on the obtained mechanism differences, the inorganic chemical processes in the final reduced mechanism have been mainly considered according to the AR results and the organic chemistry is implemented in the final mechanism following the manual reduction results (including the lumping and reformulation of the oxidation chains).

Reduced aqueous phase mechanism: CAPRAM 3.0i-red

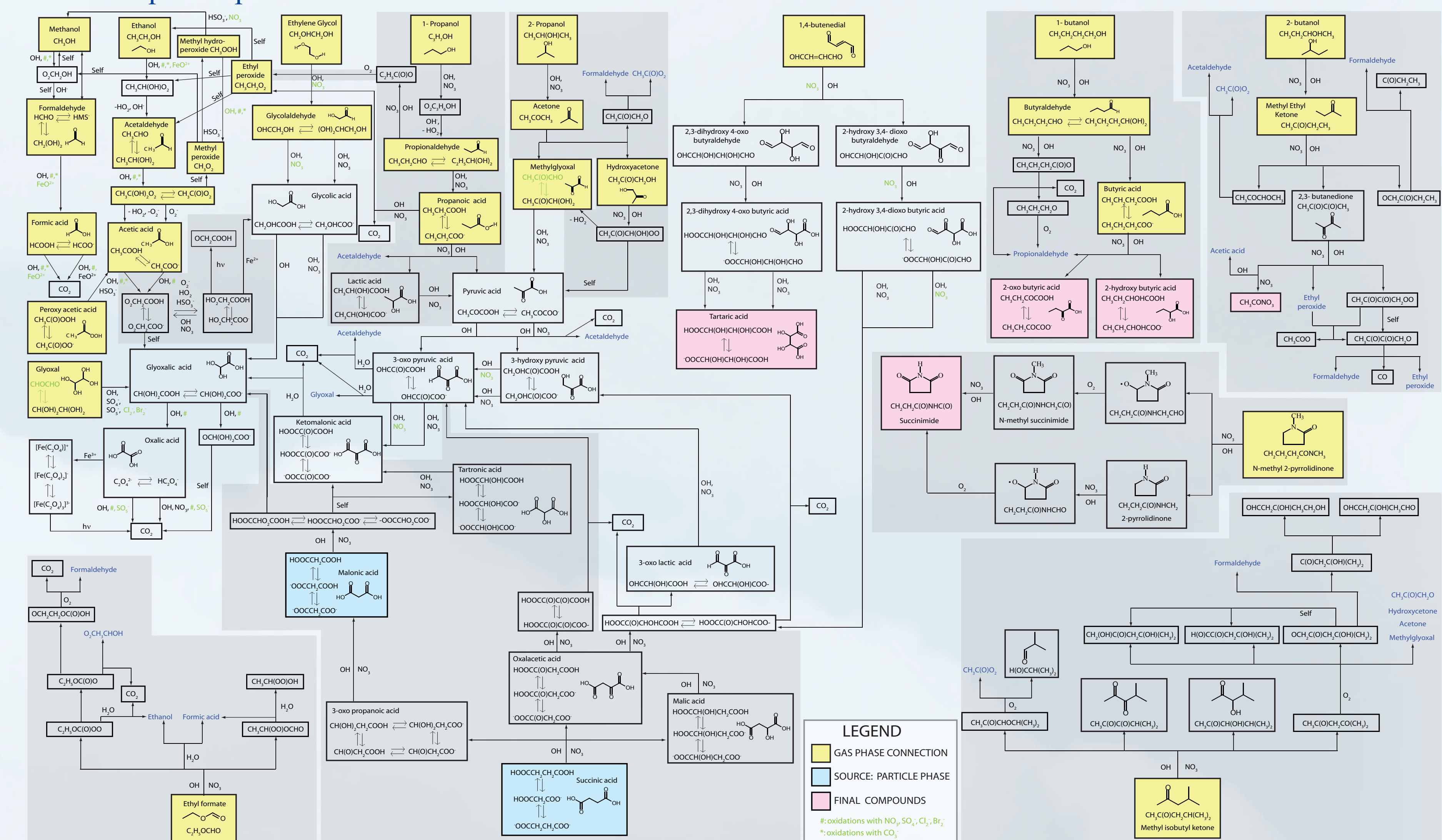


Figure 3: Schematic depiction of the organic chemistry in CAPRAM 3.0i-red. The reduced chemical organic subsystems compared to the full CAPRAM 3.0i mechanism are indicated by a grey background and marked in green. (For purpose of clarity, the explicit oxidation scheme of the full aqueous phase mechanism including peroxy radical formation and recombination reactions is not displayed as far as these processes are not considered in the reduced mechanism.)

CAPRAM 3.0i-red		CAPRAM 3.0i	
Total number of processes:			
HO ₂ / TMI	30	59	777
Bromine	2	17	
Chlorine	6	16	
Carbonate	0	21	
Nitrogen	7	32	
Sulphur	19	59	
Organics (C1-C4)	73	472	
Equilibria	55	89	
Photolysis	5	12	

Figure 4: Comparison of the full CAPRAM 3.0i and the reduced CAPRAM3.0i-red mechanism.

Aqueous phase mechanism	C3.0i	C3.0i-red
Number of aqueous reactions	676	137
Number of photolysis reactions	12	5
Mass transfer processes	51	37
Equilibria	89	55
Total number of chemical processes	777	197
Number of aqueous species	380	129

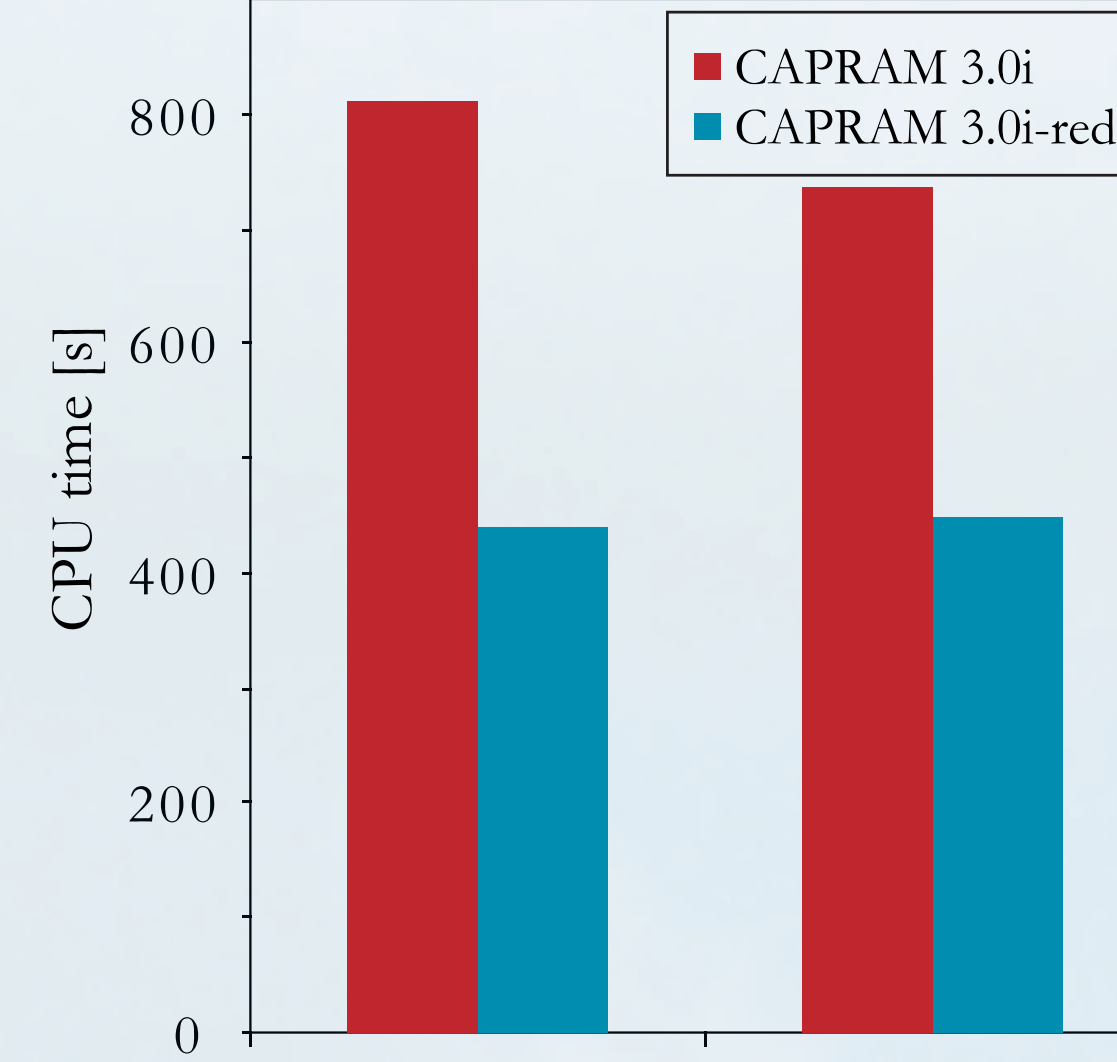


Figure 5: Comparison of the required CPU time of the full CAPRAM 3.0i mechanism (blue bars) and the reduced CAPRAM3.0i mechanism (orange bars) for the urban and remote model run.

- Percentage deviations between the two mechanisms are mostly below 5% for the most important target compounds (see Table 2)
- Reduction of the total required CPU time by approximately 40% (see Figure 5)

Table 2: Mean percentage deviations [%] of some inorganic and organic target compounds between full and reduced RACM-MIM2ext/CAPRAM 3.0i mechanism (deviations calculated from the last 12 hours of the SPACCIM simulation).

Species	Remote scenario	Urban scenario
H ₂ O ₂	5.2%	7.4%
OH	4.5%	11.5%
HO ₂ O ₂	2.2%	2.1%
NO ₃	6.2%	2.1%
NO ₂	3.8%	0.1%
HSO ₄ ⁻ /SO ₄ ²⁻	0.0%	3.2%
H ⁺	1.7%	3.4%
CH ₃ (OH)	1.3%	1.4%
CH ₂ (OH)CH ₂ (OH)	1.3%	3.7%
CH(OH)CH(OH)	3.4%	0.2%
CH ₂ (O)OH/CH ₂ (O)OO	0.1%	7.1%
CH(OH)CH(OH)CH ₂ (OH)	1.6%	2.2%
CH(OH)COOH/CH(OH)COO	8.4%	12.4%
CH ₂ (O)C(OH)	0.2%	1.1%
CH ₂ C(O)OH/CH ₂ C(O)OO	1.6%	3.2%
CH(O)C(O)OH/CH(O)C(O)OO	7.4%	5.6%
OHCC(O)COOH	4.1%	4.0%
OHCC(O)CH(O)CH(O)CHO	0.9%	2.3%
OHCC(O)CH(O)C(O)CHO	1.0%	2.6%
Average deviation	2.8%	4.0%

Summary and Outlook

A manual and automatic chemical mechanism reduction was performed in order to develop a reduced CAPRAM 3.0i mechanism which describes the main characteristics of inorganic and organic aqueous phase processes occurring in tropospheric warm clouds. The developed reduced mechanism with less than 200 reactions is nearly a factor of 4 smaller than the full CAPRAM 3.0i. Most of the chemical reduction potential has been realised in the organic chemistry with 393 minor important reactions. Moreover, the number of aqueous phase species decreased from 380 in the full CAPRAM 3.0i mechanism to 129 in the final reduced version. The calculated percentage deviations between the two mechanisms are mostly below 5% for the most important target compounds. Comparisons of the required CPU times between the full and final reduced mechanism showed reductions of approximately 40%. Hence, the mechanism should be applicable in regional scale chemistry transport models. Numerical sensitivity tests showed the relevance of both the relative and absolute integration error tolerances for an accurate and efficient modelling. The sensitivity studies have shown that particularly evaporation periods have shown to be circa three times more computationally intensive than the in-cloud conditions. This has indicated the requirement for sufficiently accurate tolerance levels particularly there. Prospectively, the final reduced aqueous phase mechanism represents the basis for studying cloud effects on regional scale with CTMs such as the COSMO-MUSCAT [Wolke et al., 2006]. Finally, the application of this new mechanism in various model studies will be essential for a better understanding of multiphase aerosol cloud processing effects on regional scale and will allow a better interpretation of field measurements.

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