

# Tropospheric Aqueous Phase Chemistry Laboratory and Modelling Studies

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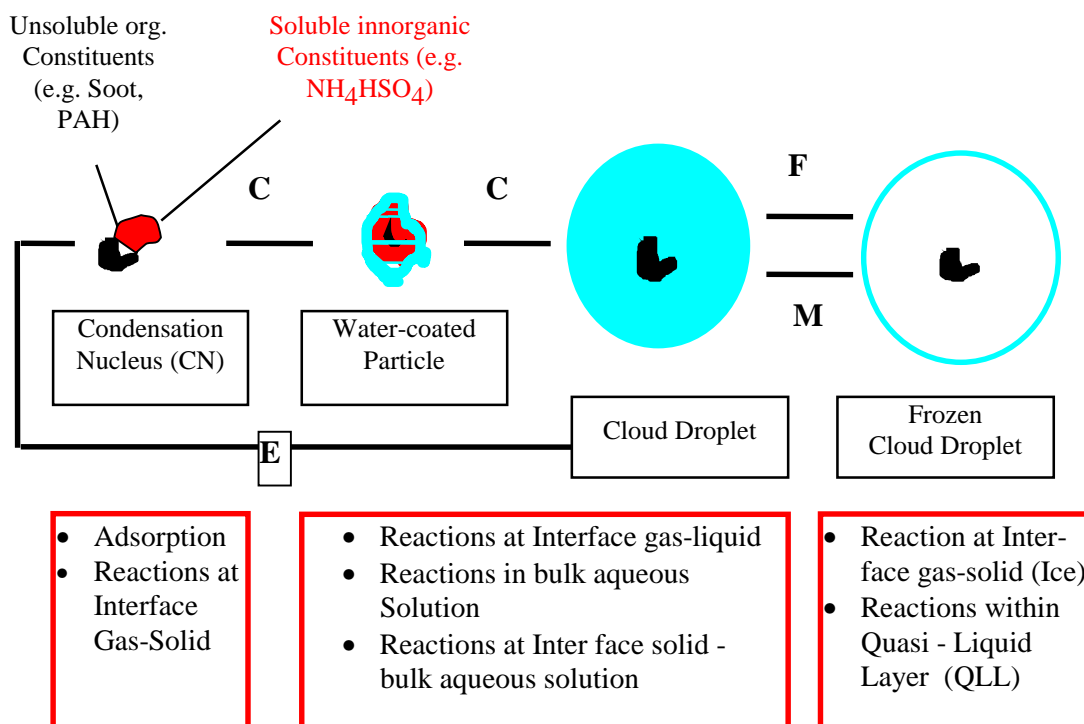
## Overview

Results from recent photochemical and kinetic laboratory and modelling studies of the formation and reactivity of aqueous phase free radicals such as OH, NO<sub>3</sub>, and Cl/Cl<sub>2</sub><sup>-</sup> will be presented. Laser-based methods have been applied for the specific generation and time-resolved detection of the above transient species in systematic studies. Photolytic radical generation in solution, radical phase transfer, radical interconversion reactions and the influence of organic compounds on the chemistry within the aqueous tropospheric phase will be discussed. Results indicate that solution reactions of the above radicals may significantly influence the net effects of chemistry within droplets and aerosols dispersed in air.

A multiphase box model coupling an advanced aqueous phase mechanism (CAPRAM 2.4) to RADM2/RACM is applied to quantify effects of multiphase conversions. It will be discussed how aqueous phase processes alter the oxidation capacity of the tropospheric gas phase by uptake and release of trace gases and radicals. Current restrictions of models will be outlined.

## Introduction

In this presentation an overview of some current issues in aqueous phase chemical processes of importance for the understanding of tropospheric chemistry was given. The systems discussed here may be referred to as multiphase chemical systems as differentiated from heterogeneous systems, where bulks solution chemistry can be neglected and which is described as a chemical processes involving reactands in different phases, e.g. in a process where one reaction partner exists in the gas phase and the other one is adsorbed on a solid.



**Fig. 1:** Matrices for tropospheric aqueous phase chemistry

The various matrices for aqueous phase reactions in the troposphere are shown in Figure 1. It will be an important task to really specify the surface and composition of particles of the aqueous aerosol for different compositions.

After the background for the occurrence, physical parameters describing tropospheric multiphase systems and the essentials of phase transfer were outlined, the following chemical sub-systems were discussed:

- HONO formation via solution phase single electron transfer to  $\text{NO}_2$
- Sulfur (IV) oxidation
- Tropospheric aqueous phase organic chemistry
- Ionic strengths effects

Finally, some results on multiphase modelling using the chemical aqueous phase radical mechanism (CAPRAM, Vs. 2.3., [1]) were presented and discussed.

## **Results and Discussion**

### *HONO-formation*

HONO-formation may involve electron transfer processes from dissolved reductants such as S(IV) or by organic systems such as substituted aromatics which are commonly found in soot. This latter issue has been discussed by M. Amman in his contribution (this volume). The reaction of S(IV) with  $\text{NO}_2$  in aqueous solution has recently been investigated in our laboratory [1] and rate coefficients for both the reactions of  $\text{HSO}_3^-$  as well as  $\text{SO}_3^{2-}$  are now available. Results indicate, that results of HONO denuder measurements may be inferred from high  $\text{SO}_2$  concentration ("artefacts"). However, more work has to be performed to understand these effects and the different results often found when HONO denuder measurements are compared with direct optical (DOAS) HONO determinations in the field.

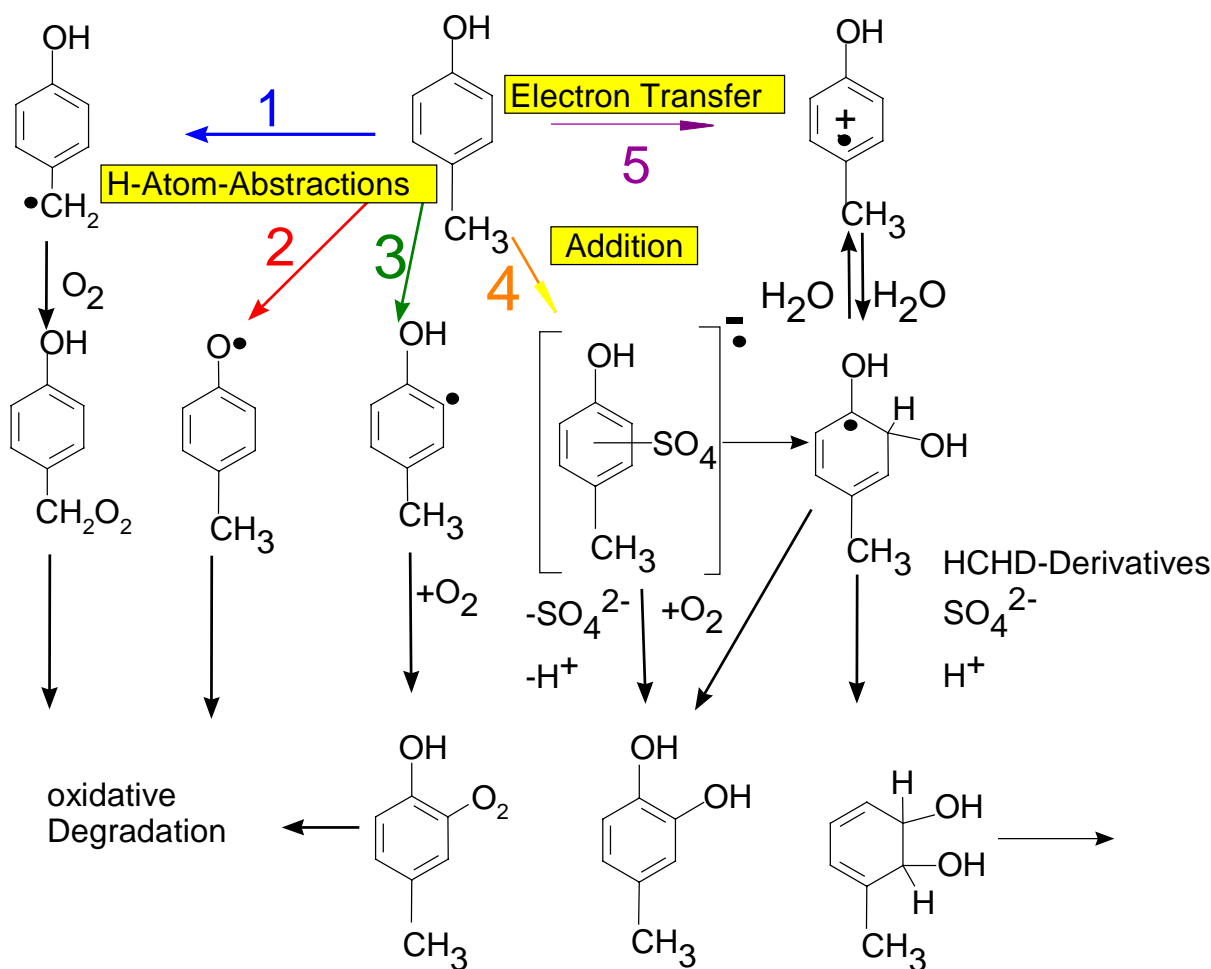
### *S(IV) oxidation*

The oxidation of S(IV) is very lively investigated throughout the atmospheric aqueous phase community including contributors to CMD-APP. A significant fraction of contributions to the Karlsruhe CMD-workshop (cp. contributions by Grgic et al., Rudzinski and Pasiuk-Bronikowska, Buxton et al, Pasiuk--Bronikowska et al, Ziajka and Pasiuk-Bronikowska) has been dealing with this topic. Open questions include the influence of TMI's, the role of organics and the proper determination of reaction rate coefficients for individual elementary reactions. The multiphase S(IV) oxidation is still far from being completely described and yet has the biggest implications for understanding multiphase processes within heavily polluted air masses as well as in the area of particle formation and hence for the issue of climatic change. A major uncertainty still lies in effects of soot on S(IV) oxidation rates.

### *Tropospheric aqueous phase organic chemistry*

Major uncertainties exist in the area of the influence of organics other than C1 or C2 aliphatics in tropospheric aqueous phase chemistry. A problem of special interest is that

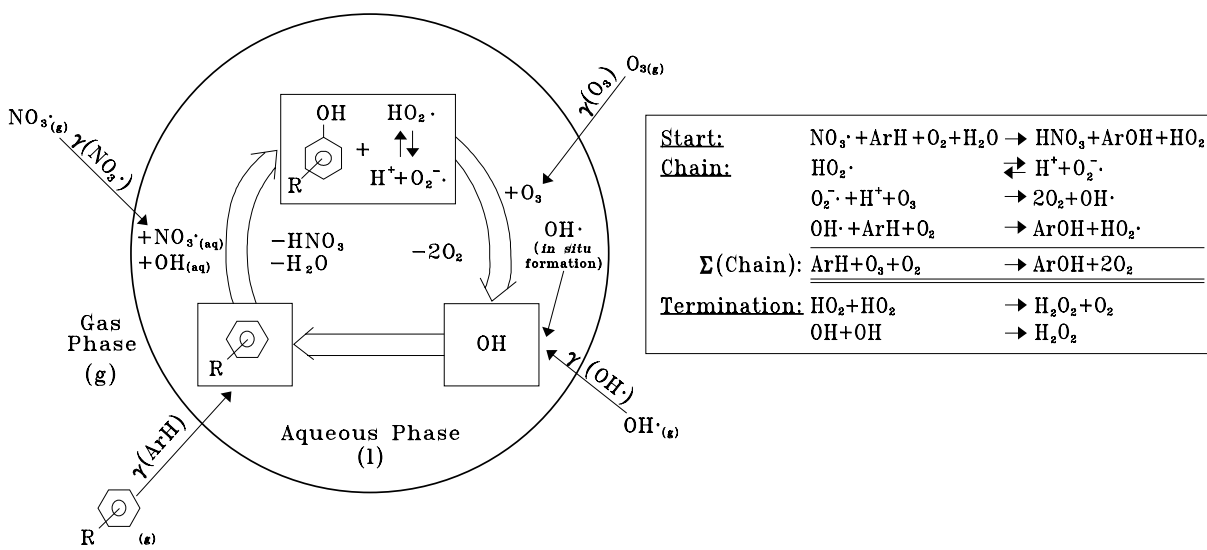
numerous aromatics which carry polar substituents have been identified in cloud- and rainwater, but it is currently unclear for most cases whether these compound result from gas phase or particle phase oxidation. This especially applies to polar substituted aromatics which might undergo a variety of different reaction pathways in aqueous solution including single-electron transfer, cp. Figure 2. The formation of HO<sub>2</sub> together with phenols might lead to the re-formation of OH which may subsequently undergo further solution phase oxidations. This may lead to a possible chain process as it is shown schematically in Figure 3. The uptake of polar aromatics, radicals and ozon may establish a chain reaction within particles leading to a decrease of ozone and aromatics in the gasphase. Whereas the removal of ozon would tend to decrease the gas phase oxidation capacity, the removal of aromatics will increase this entity. The exact effects of such complicated coupling in multiphase VOC oxidation can only be assessed by adequate models for a given set of boundary conditions.



**Fig.2 :** Possible reaction pathways in reactions of aromatics with free radicals in aqueous solution.

Reactions of free radicals with aromatics in aqueous solution have been investigated in the workshop contributions by Bolzacchini et al., Umschlag et al. and Wicktor et al.. Open questions currently investigated in the area of aqueous particle phase include the formation of harmful compounds such as nitrophenols.

As in the gas phase, product investigations are currently needed to include full aromatics degradation schemes in tropospheric multiphase mechanisms.



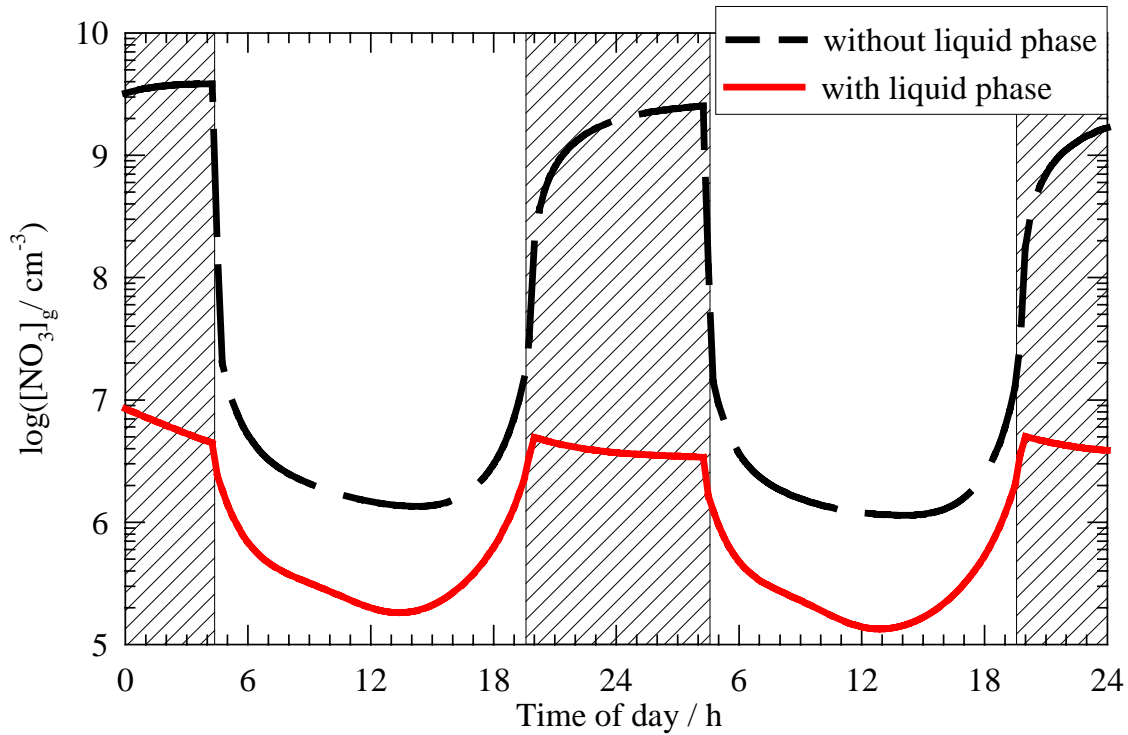
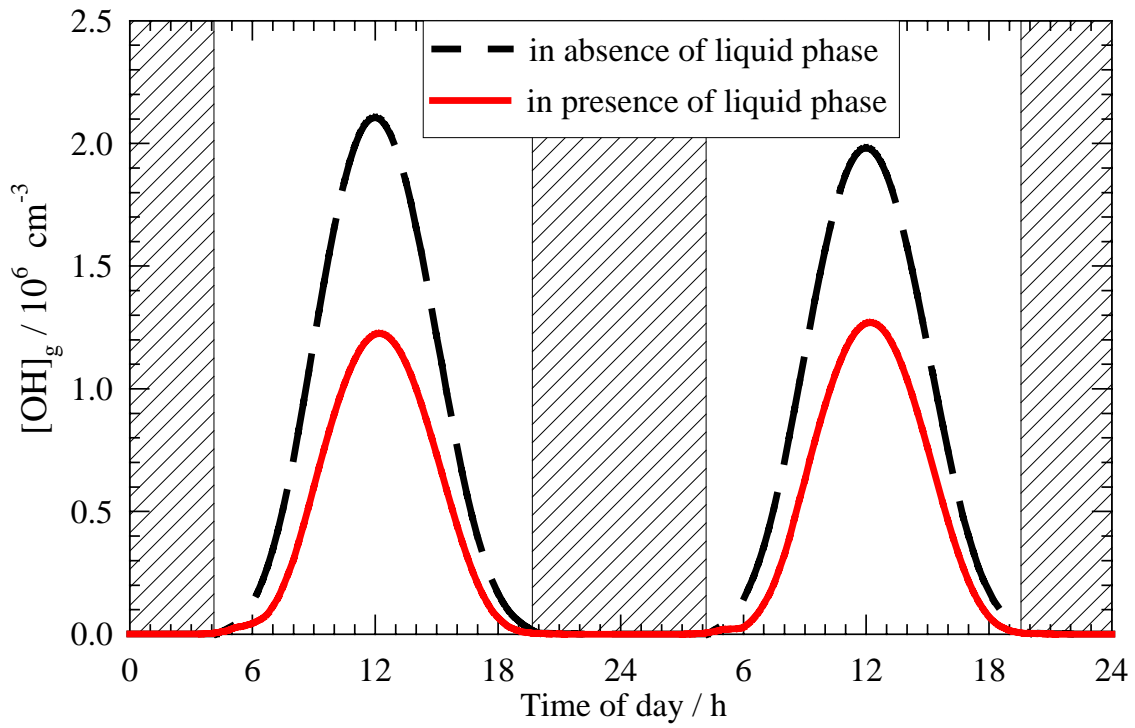
**Fig.3:** A possible reaction sequence following in reactions of aromatics with free radicals in tropospheric aqueous particles.

### Ionic strengths effects

Whereas in the field of cloud chemistry many uncertainties exist, the understanding of deliquescent aqueous aerosol particle chemistry in the troposphere is even less developed. It is suggested to base models for the high ionic strengths in such systems on a combination of the use of activity coefficients estimated by the method apparatus provided by Pitzer [2] or, in cases where estimates of activity coefficients are not possible because of too little experimental input parameters apply an ion-pairing model as it may be described by the formalism of Olson and Simonson [3]. Following this treatment, many of the experimentally determined primary kinetic salt effects may be explained and, later, be incorporated into combined multiphase cloud and aerosol models.

### Modelling results

In the following Figure 4 the modelling results for the concentration levels of  $\text{OH}_{(g)}$  and  $\text{NO}_3_{(g)}$  obtained with our multiphase boxmodel CAPRAM 2.3. which was coupled to the RADM 2 [4] gas phase chemistry are summarised. As can be seen, the gas phase OH-concentration is decreased by about a factor of two in the presence of the aqueous phase ( $\text{LWC} = 0.3 \text{ cm}^3 \text{ m}^{-3}$ , urban scenario). Such a difference will be very difficult to detect in field verification measurements. On the other hand, the nighttime  $\text{NO}_3$  concentration is diminished much more drastically, as can be seen from the bottom part of Figure 4. It is interesting to note that first experimental findings for a direct loss of OH to cloud droplets exist since recently in the literature, cp. [5] for the experiment and [6] for the very recent interpretation. Further interpretation of these and other similar experiments will be of high interest.



**Fig. 4:**  $\text{OH}_{(\text{g})}$  (top) and  $\text{NO}_{3(\text{g})}$  (bottom) concentration/time profiles for the pure gas phase system and in the presence of aqueous droplets ( $\text{LWC} = 0.3 \text{ cm}^3 \text{ m}^{-3}$ ).

Whereas the maximum pure gas phase concentration of  $\text{NO}_3$  under urban model conditions reaches  $3 \cdot 10^9 \text{ cm}^{-3}$ , this level is decreased by about three orders of magnitude in the presence of aqueous droplets, reaching a maximum concentration of  $4 \cdot 10^6 \text{ cm}^{-3}$ . When the solution droplets are considered, the maximum concentration of the  $\cdot\text{OH}$  radical at noon is nearly  $2 \cdot 10^{12} \text{ M}$ . The main source is transfer from the gas phase and in-situ generation by Fenton-type processes.  $\cdot\text{OH}$  loss mainly occurs by reactions with organic species such as formic acid and formaldehyde. At night-time  $\text{NO}_3\cdot$  reaches concentrations of  $2 \cdot 10^{13} \text{ M}$ . Its only source is transfer from the gas phase. The main sinks of this species are the reactions with chloride and bromide.

### **Conclusions**

Chemical conversions within aqueous particles (i.e. the deliquescent aerosol and cloud droplets) are subject to various laboratory investigations. Process data obtained from such studies are incorporated into chemical mechanism such as CAPRAM 2.3.. By box model runs it is demonstrated that solution phase reactions may significantly influence gas phase radical levels. Further laboratory studies, field measurements as well as advanced multiphase models are required, however, to obtain deeper insights into the multiphase chemical system 'troposphere'.

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