

Current Issues in Aqueous Particle Phase Chemistry

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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 bulk 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. The various media for aqueous phase reactions in the troposphere are shown in Figure 1.

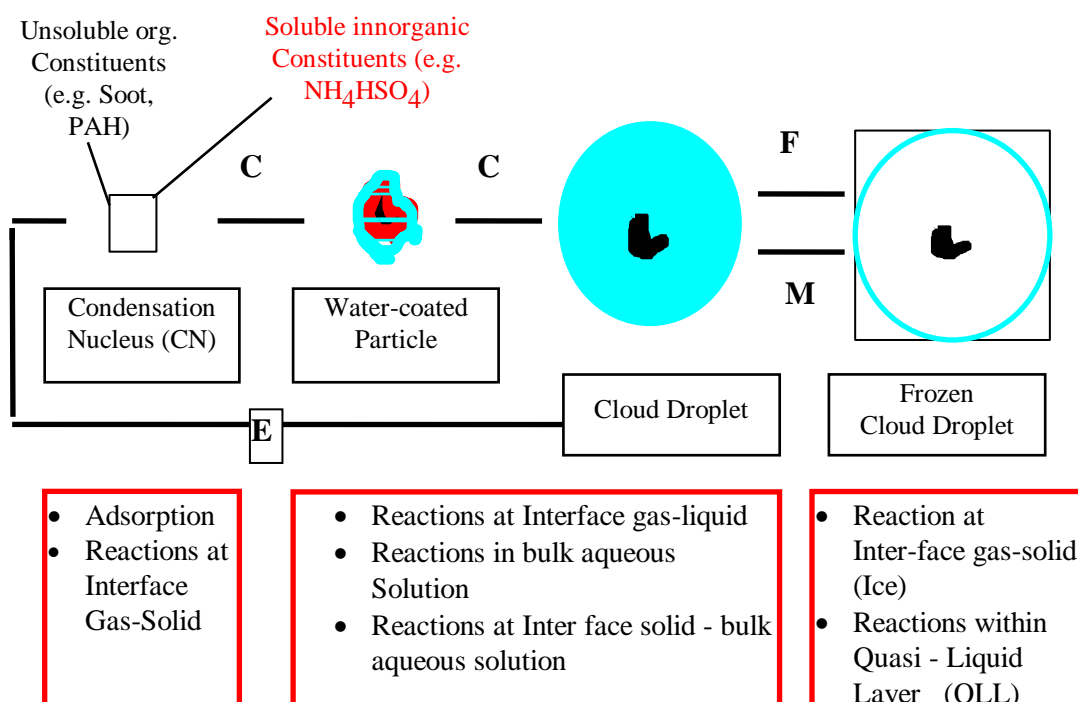


Fig. 1: Matrices for tropospheric aqueous phase chemistry

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 NO_2
- Sulfur (IV) oxidation
- Influence of transition metal ions (TMI)
- Tropospheric aqueous phase organic chemistry
- Ionic strengths effects

Finally, some result 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 NO₂ in aqueous solution has recently been investigated in our laboratory [1] and rate coefficients for both the reactions of HSO₃⁻ as well as SO₃²⁻ are now available. Results indicate, that results of HONO denuder measurements may be inferred from high SO₂ concentration ("artefacts"). However, more work has to be performed to understand these effects and the different result 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 Psiuk-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 airmasses as well as in the area of particle formation and hence for the issue of climatic change. A mayor uncertainty still lies in effects of soot on S(IV) oxidation rates.

Influence of transition metal ions (TMI's)

TMI's have been identified in aerosols, clouds and rainwater. They have the biggest potential to act as catalysts in processes such as the S(IV) oxidation (see above). Whereas many rate constants for individual reactions are now available, big uncertainties for modelling arise from estimations of TMI concentrations in tropospheric aerosols.

Tropospheric aqueous phase organic chemistry

Mayor 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 HO₂ 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 ozone may establish a chain reaction within particles leading to a decrease of ozone and aromatics in the gasphase. Whereas the removal of ozone 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.

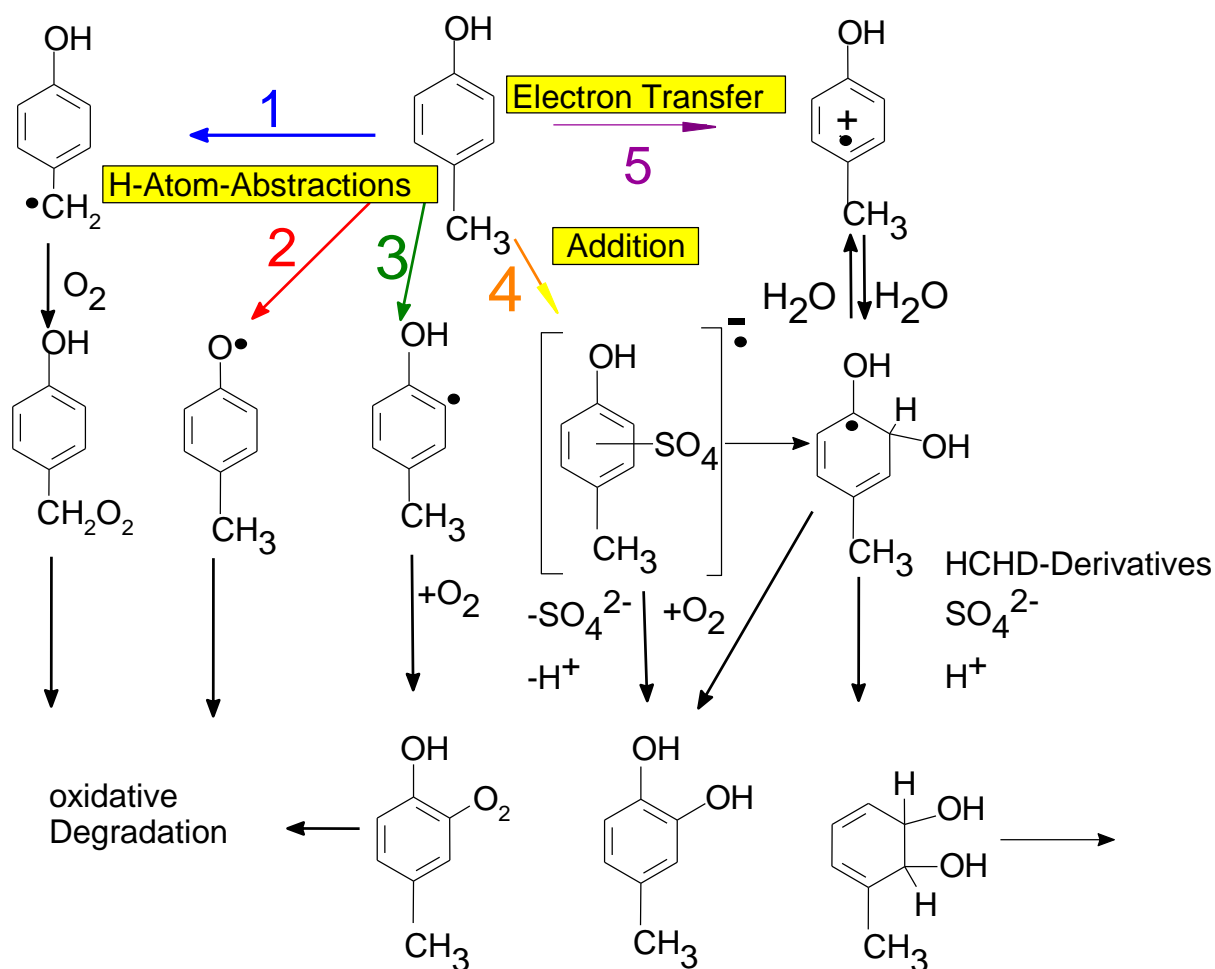


Fig.2 : Possible reaction pathways in reactions of aromatics with free radicals in aqueous solution.

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.

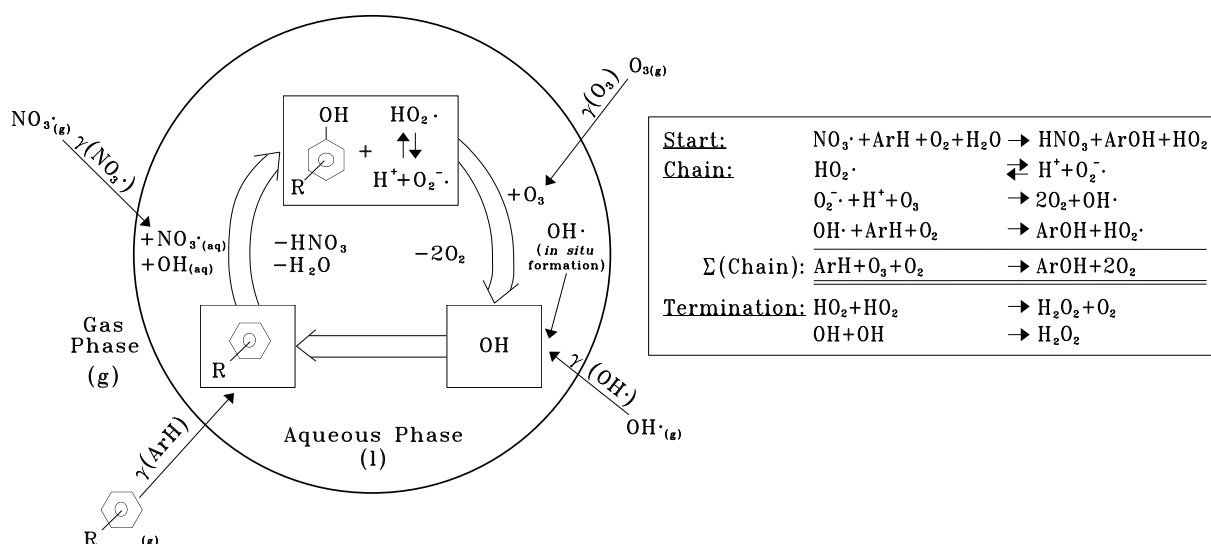


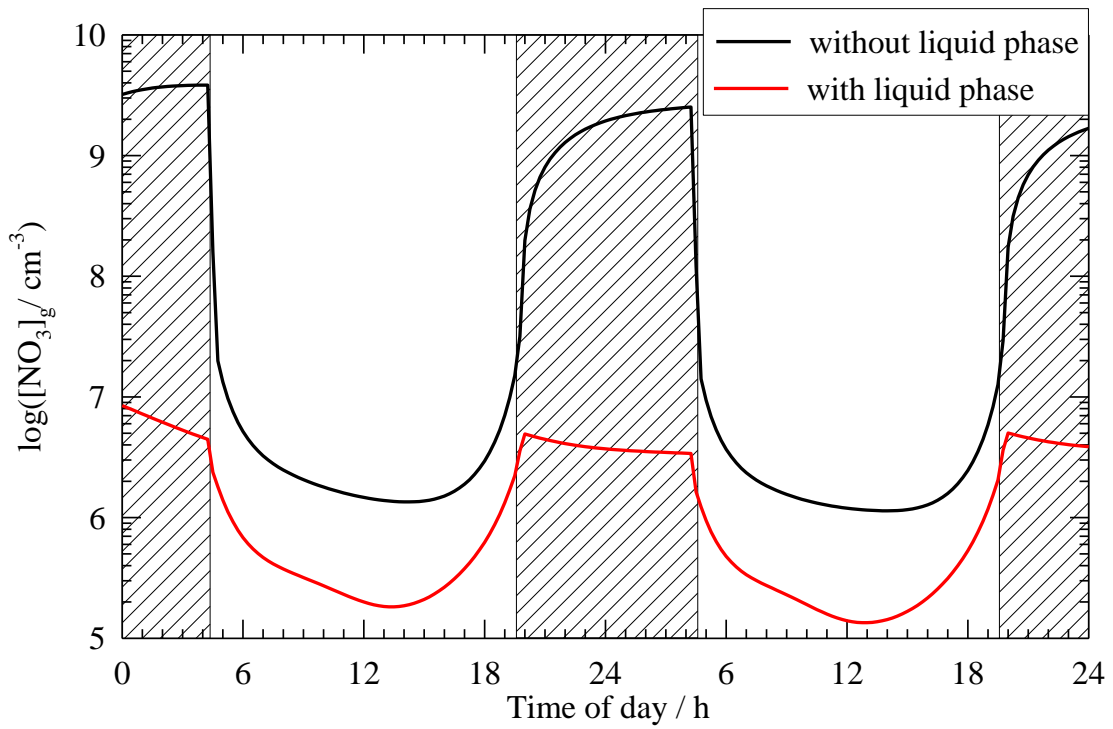
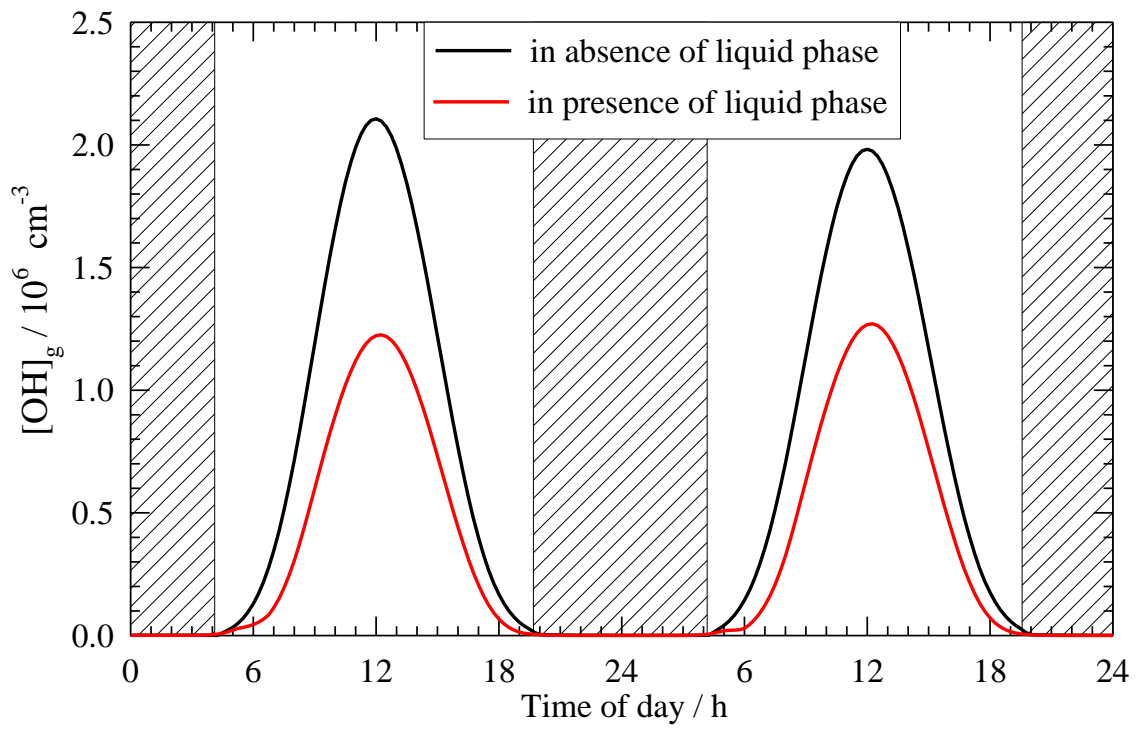
Fig.3 : A possible reaction sequence following in reactions of aromatics with free radicals in tropospheric aqueous particles.

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 current modelling results obtained with our multiphase boxmodel CAPRAM 2.3, which was coupled to the RADM 2 [4] gas phase chemistry are summarised.



Conclusions

Acknowledgements

References

- 1.: H. Herrmann, B. Ervens, P. Nowacki, R. Wolke and R. Zellner, Chemosphere **38**, 1223-1232 (1998).
- 2.: K.S. Pitzer, Activity Coefficients in Aqueous Solution", 2nd Ed., CRC Press 1991.
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