

Modelling Calculations of Tropospheric Gas Phase and Aqueous Phase Chemistry under Consideration of Halogen Activation

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A contribution to the sub-project CMD-MPM

This contribution is divided into two parts: Firstly model results were presented from the basic version of the Chemical Aqueous Phase Radical Mechanism (CAPRAM2.3). Here the influence of the aqueous phase chemistry on concentration levels of gas phase radicals was shown. The second part was ascribed to results of an extended mechanism of CAPRAM2.3 considering the halogen activation under marine conditions.

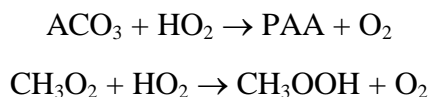
I. Model description

The basic mechanism includes in total 428 processes, 158 from that are gas phase reactions, currently the well known RADM2 by Stockwell [1]. For 34 species the phase transfer is described using the resistance model by Schwartz [2] considering mass accommodation coefficients, gas phase diffusion and Henry's Law coefficients. 236 reaction take place in the aqueous phase. To the authors knowledge is this the first aqueous phase mechanism including C1 as well as C2 organic chemistry. The chemistry of radicals such as NO₃, OH, HO₂, C1 and C2 peroxy radicals and radical anions (SO₄⁻, Cl₂⁻, Br₂⁻ and CO₃⁻) is treated in detail. The meteorological conditions are constant during the simulation with a temperature of 288 K and a pressure of 1 atm. The liquid water content is fixed at 0.3 g m⁻³ with a droplet radius of 1 μm it leads to a droplet concentration of 7·10⁴ cm⁻³. For the calculations a box model was used without emissions, depositions and horizontal and vertical transport processes.

II. Results from the basic mechanism

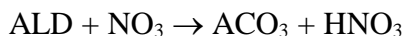
In absence of the liquid phase and phase transfers the OH radical in the gas phase reaches a maximum concentration of 2.1·10⁶ cm⁻³ at noon. In presence of droplets the concentration is reduced to 1.2·10⁶ cm⁻³. The difference can be explained with the direct phase transfer from the OH into the droplet. As can be seen diagnosis showing that only about 50% of the OH remains in the gas phase. The situation of the NO₃ radical in the gas phase is similar. Calculations without the aqueous phase chemistry show a maximum concentration at night of 2.2·10⁹ cm⁻³, with the liquid phase the concentration is decreased to 3.6·10⁶ cm⁻³. This large difference of three orders of magnitude is also caused from the direct phase transfer of the NO₃ radical. About 80% of the NO₃ are transported from the gas phase

into the droplet. The situation in the aqueous phase of the two radicals described is following: The OH accumulates and has maximum concentration at noon of $1.9 \cdot 10^{-12}$ M, the concentration of the NO_3 is smaller although more NO_3 is transported from the gas phase. Its maximum concentration at night ($1.8 \cdot 10^{-13}$ M) amounts to only a tenth of that of OH at noon. The behaviour of the peroxy radicals in the gas phase is more complicated: During daytime the concentration levels of the methylperoxy radicals (CH_3O_2) and the acetylperoxy radicals ($\text{ACO}_3 = \text{O}_2\text{CH}_2\text{C}(\text{O})\text{H}$ and $\text{CH}_3\text{C}(\text{O})\text{O}_2$) in the gas phase calculated without liquid phase are lower than in presence of droplets. With RADM2 only the acetylperoxy radical reaches its maximum concentration at noon of $6.6 \cdot 10^7 \text{ cm}^{-3}$, whereas with the whole mechanism this maximum amounts to $8.7 \cdot 10^7 \text{ cm}^{-3}$. The differences for the methylperoxy radical are smaller: Without liquid phase the maximum concentration is $2.4 \cdot 10^8 \text{ cm}^{-3}$, whereas in the presence of the aqueous phase it reaches $3.1 \cdot 10^8 \text{ cm}^{-3}$. The reason for this behaviour during daytime is the conversion of peroxy radicals with HO_2 forming peroxy acetic acid (PAA) or methyl hydroperoxide, respectively:

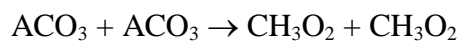


These processes form the main sink for peroxy radicals in RADM2.

In the presence of the liquid phase nearly 100 % of the $\text{HO}_{2(\text{g})}$ is transported into the droplet, so that more organic peroxy radicals remain in the gas phase. During nighttime the behaviour of the concentration levels of both peroxy radicals are comparable that one of the NO_3 . At 24:00 the concentration are $9.2 \cdot 10^7 \text{ cm}^{-3}$ for the acetylperoxy radical and $1.8 \cdot 10^8 \text{ cm}^{-3}$ for the methylperoxy radical without consideration of the aqueous phase. In the presence of the liquid phase the concentration levels are decreased to $6.1 \cdot 10^7 \text{ cm}^{-3}$ for the acetylperoxy radical and $1.1 \cdot 10^8 \text{ cm}^{-3}$ for the other radical. The most important source reaction during nighttime for the acetylperoxy radical is the reaction between aldehydes (ALD) with NO_3 .



As described earlier 80% of the gas phase NO_3 is directly transported into the aqueous phase, so that less acetyl peroxy radicals are produced in presence of the liquid phase. The concentration level of the methylperoxy radicals is influenced directly by the acetylperoxy radicals, because it is formed from the recombination of two acetylperoxy radicals.



So in presence of the liquid phase CH_3O_2 is reduced due to decreased ACO_3 formation via the nighttime NO_3 reaction. Note, that these are preliminary results because in the new gas phase mechanism (RACM) by Stockwell [3] reactions between peroxy radicals and NO_3 are now also included.

III. Results of the mechanism considering halogen activation

In the second part of the presentation the results of an extended mechanism were shown. The extension considers the halogen activation under marine conditions (CAPRAM2.3+Marine). It is based on the mechanisms by Sander and Crutzen [4] and its extension by Vogt *et al.* [5]. The essential reactions of the mechanism module added in this work can be parted into four groups:

- (1) In the aqueous phase there are *reactions yielding halogen atoms*. These are on the one hand reactions between the hypohalogenic acids HOX ($\text{X} = \text{Cl}, \text{Br}$) with HO_2/O_2^- forming directly X . On the other hand reactions are implemented between HOX and hydrogen sulfite forming firstly halogenides which react with radicals such as SO_4^- or NO_3 yielding also halogen atoms. Besides in this group the equilibria between the dihalogenide radical anions (Cl_2^- , Br_2^- and BrCl) and the corresponding halogenides X^- and halogen atoms X are included.
- (2) Moreover, aqueous phase are *reactions yielding molecular halogens* included. The pH dependent reactions of HOX with X^- forms BrCl , Cl_2 or Br_2 . Furthermore, the recombinations of the dihalogenide radical anions are implemented.
- (3) Additional to the 34 uptake processes in the basic mechanism of CAPRAM2.3 the *phase transfer* for further five more species (BrO , HOBr , ClO , HOCl and BrCl) are described.
- (4) The gas phase mechanism was extended with some reactions. The photolyses of the molecular halogens and the hypohalogenic acids are added. (Test calculations have shown that the corresponding processes in the aqueous phase can be neglected as sources for halogen atoms.) The mechanism contains also reactions between the halogen atoms and ozone forming XO radicals. These radicals react with HO_2 or O_3 forming HOX . A sink reaction for the chlorine atom is the reaction with methane forming HCl and CH_3 . The corresponding reaction for the bromine atom is not included because the reaction rate is several orders of magnitude smaller.

The results of this mechanism were compared with the halogen activation mechanism developed by Sander and Crutzen [4] without its subsequent extensions. For the comparison that aqueous phase mechanism was coupled with RADM2 and the phase transfers of CAPRAM2.3. The same initial concentrations describing cloud chemistry were applied here. The comparison of the concentration levels of the halogen atoms and ozone in the gas phase shows that in CAPRAM2.3+Marine about 1

cm⁻³ chlorine atoms are present while in the mechanism by Sander and Crutzen (coupled to RADM2 here) the concentration is six orders of magnitude lower. For the bromine atoms the ratio is inverted: the mechanism of Sander and Crutzen leads to nearly 10³ cm⁻³ Br, and only 10⁻³ cm⁻³ Br in CAPRAM2.3+Marine. The ozone concentration after three days of calculation is similar (in CAPRAM2.3+Marine: 77ppb; in the mechanism by Sander and Crutzen 74 ppb). The reason for the enhanced chlorine activation in CAPRAM2.3+Marine can be explained with the following reaction chain: HOBr is transported into the droplet where it reacts with HO₂/O₂⁻ to the Br atom. This is in equilibrium with chloride forming BrCl. The direction of the equilibrium is shifted totally to the BrCl because chloride is present in high excess. BrCl decays to bromide and chlorine atoms reacting again with chloride forming the dichloride radical anion Cl₂⁻. The main part (5.4·10⁻⁹ M s⁻¹) of the Cl₂⁻ reacts with HO₂/O₂⁻ or H₂O₂ to chloride, less than a 0.1% (1.1·10⁻¹² M s⁻¹) of the total loss flux of Cl₂⁻ is the recombination of two dichloride radical anions yielding molecular chlorine. This very small flux represents the main source for the chlorine which is transported into the gas phase. In the mechanism by Sander and Crutzen this reaction chain in the aqueous phase is missing, so that no link to the radical chemistry exists.

IV. Summary

In the first part of the presentation with CAPRAM2.3 the influence of aqueous phase chemistry to the photooxidant levels in the gas phase was shown. These are strongly affected by the aqueous particle phase. This is due to direct radical phase transfer (OH and NO₃) and phase transfer of reactands (peroxyl radicals). In the second part results of an additional sub-system, the halogen activation under marine conditions were presented. It could be shown that chlorine activation to the gas phase is mainly caused from the chemistry of BrCl and Cl₂⁻ in the aqueous phase.

V. Acknowledgements

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VI. References

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