

# Measurement of the steady state concentration of hydroxyl radicals in cloud water

A. Lallement<sup>1</sup>, V. Vinatier<sup>1</sup>, M. Sancelme<sup>1</sup>, L. Deguillaume<sup>2</sup>, A.M. Delort<sup>1</sup> and G. Mailhot<sup>1</sup>

<sup>1</sup>Institut de chimie de Clermont-Ferrand, Université Blaise Pascal, Aubière, 632171, France.

<sup>2</sup>Laboratoire de Météorologie Physique, Université Blaise Pascal, Aubière, 632171, France

Keywords: Cloud water, Hydroxyl radical, Steady state concentration.

Audrey.LALLEMENT@univ-bpclermont.fr

In the atmosphere, clouds play a key role because they cover 50% of the globe surface. As they also have an impact on Earth's radiative balance, it is necessary to better understand their chemical reactivity.

Clouds are a multiphase compartment compounded with gaseous, aqueous and solids parts. Beside they are known to be an oxidant medium because of the presence of hydroxyl radical (HO<sup>•</sup>), hydroperoxy radical (HO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>)... Among these molecules, hydroxyl radical is the most oxidant; dubbed "detergent of the atmosphere".

Hydroxyl radical participates at the oxidation and the transformation of the organic matter. Sources of HO<sup>•</sup> are the hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), iron complexes, nitrate and nitrite ions and the uptake from the gas phase (A. Bianco *et al.*, 2015).

Until now the concentration of hydroxyl radical was estimated through their formation rates (R<sup>f</sup><sub>HO<sup>•</sup></sub>) or was simulated using atmospheric chemical models. There is a high variability in the concentration: models find a range of 10<sup>-12</sup> at 10<sup>-14</sup> M (M. Vätilingom *et al.*, 2011) and rates formation are proportional to [HO<sup>•</sup>]<sub>ES</sub> so they vary widely. Estimation of HO<sup>•</sup> concentration is difficult because its life time (less than a microsecond) and its very low concentration. However it can be assayed using a terephthalic acid probe which can react with hydroxyl radical to give 2-hydroxyterephthalic acid (TAOH), which is more stable, and fluorescent (Figure 1).

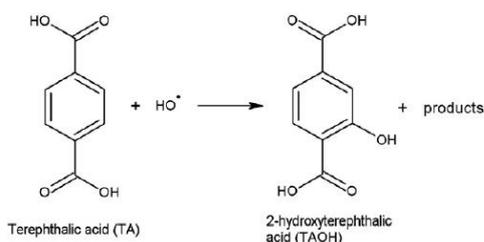


Figure 1 : Structural composition of the chemical reaction between terephthalic acid (TA) and hydroxyl radical (HO<sup>•</sup>)

Here, we propose to measure the steady state concentration of hydroxyl radical using this terephthalic acid probe. For that we use the following equation:

$$\frac{d[HO]}{dt} = V_{f_{HO}} - k_{TA} \cdot [TA] \cdot [HO] - \sum K_{Si} \cdot [Si] \cdot [HO] - k_{HO} \cdot [HO]^2$$

Where:

-  $V_{f_{HO}}$  is [HO<sup>•</sup>] formation rate

-  $k_{TA} \cdot [TA] \cdot [HO]$  is [HO<sup>•</sup>] trapping by TA (with  $k_{TA}$  the second order rate constant between TA and HO<sup>•</sup>)

-  $\sum K_{Si} \cdot [Si] \cdot [HO]$  is [HO<sup>•</sup>] trapping by scavengers (Si) (with  $K_{Si}$  the second order rate constant between chemical compounds and HO<sup>•</sup>)

-  $k_{HO} \cdot [HO]^2$  is recombination between HO<sup>•</sup>

At steady state,  $\frac{d[HO]}{dt} = 0$  and TAOH formation rate

is directly proportional to TA concentration.

The main objective of this work is thus to measure for the first time at steady state the concentration of HO<sup>•</sup> in real cloud waters. It will give realistic values to be integrated in atmospheric models. This essential parameter will allow us to better understand the real oxidizing capacity of cloud.

The second objective, using the same method, is to evaluate the impact of the presence of microorganisms on the steady state concentration of HO<sup>•</sup>. For that purpose lab experiments are performed comparing HO<sup>•</sup> concentrations under biotic (presence of microorganisms) and abiotic conditions (absence of microorganisms). Two types of microcosms simulating cloud conditions (solar light, temperature) are used:

- incubations in artificial cloud water containing or not model microbial strains isolated from clouds,
- incubations in real atmospheric cloud waters (rain, cloud) filtered or non-filtered.

## Acknowledgements:

This work was supported by the French ANR program "BIOCAP". The authors thank the scientists of OPGC for the sampling of cloud aqueous phase at the top of puy de Dôme.

Bianco, A., Passananti, M., Perroux, H., Voyard, G., Mouchel-Vallon, C., Chaumerliac, N., Mailhot, G., Deguillaume, L. and Brigante M. (2015) *Atmos. Chem. Phys.*, 15, 9191-9202.

Vätilingom, M., Charbouillot, T., Deguillaume, L., Maisonobe, R., Parazols, M., Amato, P., Sancelme, M., and Delort, A. M. (2011) *Atmos. Chem. Phys.*, 11, 8721-8733, doi:10.5194/acp-11-8721-2011.