HO2 REACTIVE UPTAKE ON ORGANIC AEROSOLS: A MOLECULAR LEVEL STUDY

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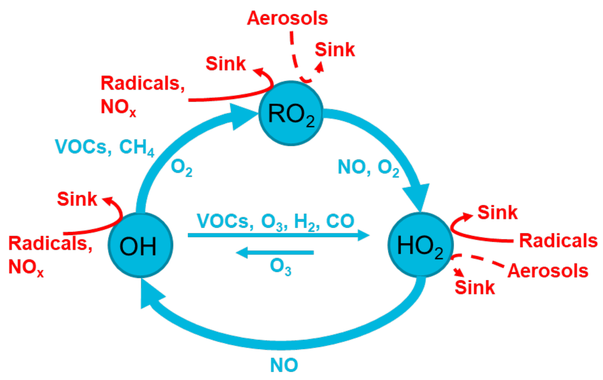
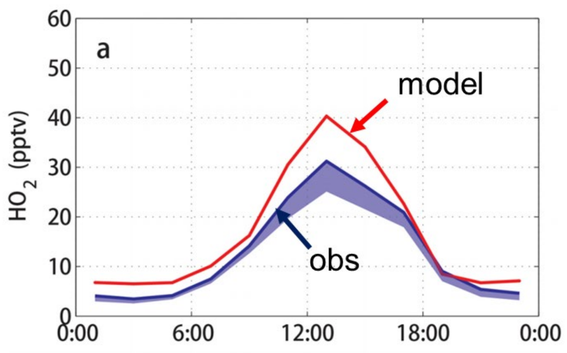
RO_X CHEMISTRY

OH initiates the degradation of atmospheric pollutants / RO_2 & HO_2 propagate to OH and sustain the tropospheric oxidizing capacity.



Some discrepancies between HO_2 concentration in the atmospheric model and the HO_2 concentration measured during field campaign have been observed



Measured RO_x radicals are usually not well reproduced by atmospheric models in forested areas according to Heard et al. (2006) and Dusanter et al. (2017).

Impact of missing radical uptakes on aerosols in models?

Mao et al. (2013) also observed by Griffiths et al. (2013)

UPTAKE PROCESS

Uptake coefficient is a some of several processes such as:

- Gas diffusion (Γ_g)
- Surface accommodation (S)
- Surface reaction (Γ_{surf})
- Dilution (K) and bulk diffusion (Γ_{sat})
- Bulk reaction (Γ_{rxn})

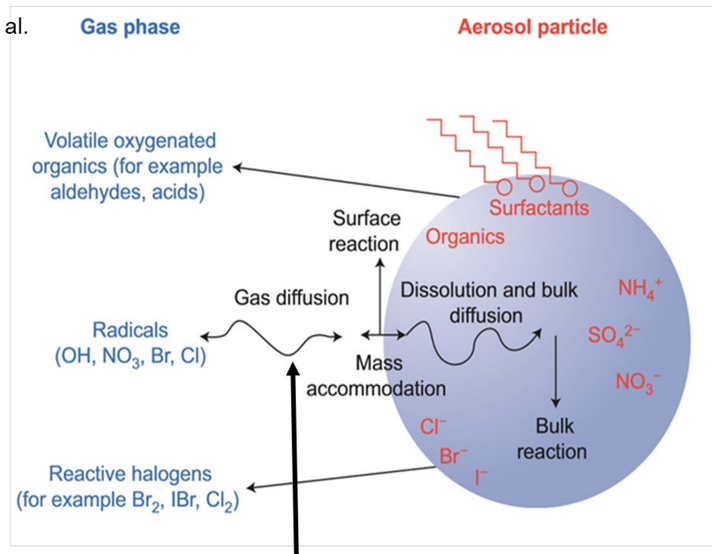
Mass accommodation coefficient :

$$\frac{1}{\alpha} = \frac{1}{S} + \frac{1}{SK}$$

Uptake coefficient :

$$\frac{1}{\gamma} = \frac{1}{\Gamma_g} + \frac{1}{S} + \frac{1}{\frac{1}{SK} + \frac{1}{\Gamma_{sat} + \Gamma_{rxn}} + \frac{1}{\Gamma_{surf}}}$$

George et al. (2010)



$$\frac{1}{\Gamma_g} = \lambda(r) = \frac{0.75 + 0.283K_n}{K_n(1 + K_n)}$$

according to Fuchs & Sutugin 1971

OBJECTIVES AND METHODS

Objectives: Investigate the importance of HO_2 uptake onto organic aerosols in the lower troposphere

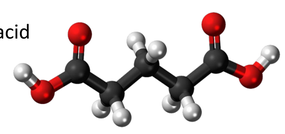
Classical Molecular dynamics (MD)

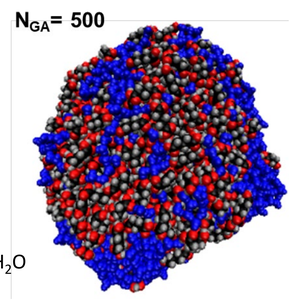
Method:

Generation and characterization of glutaric acid aerosol using GROMACS software with AMBER GAFF Force field and SPC/E water model (T = 300 K, Δt = 2fs)

Computation of HO_2 mass accommodation coefficient (parameters from Vacha et al., 2004 and Chalmet and Ruiz Lopez 2006)

Glutaric acid (GA)





Aerosol of 500 GA and 1000 H_2O generated by classcial MD

Quantum Mechanics (QM)

Method:

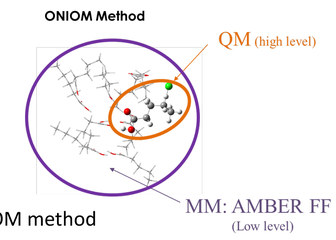
Reactivity treatment in gas phase using density functional theory (DFT) ωB97X-D/def2-TZVP (recommended by Goerigk et al. 2017). Software: Gaussian 16

Quantum mechanics/Molecular mechanics (QM/MM)

Method:

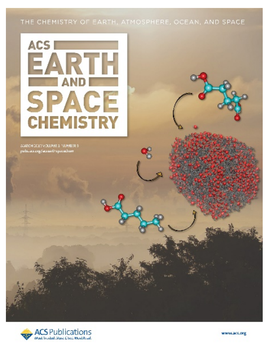
Treatment of the reactivity in aerosol phase using ONIOM method (ωB97X-D/def2-TZVP:Amber). Software: Gaussian 16

$$E_{QM/MM} = E_{MM}(QM+MM) + E_{QM}(QM) - E_{MM}(QM)$$



Schematics of the ONIOM method

HO_2 MASS ACCOMMODATION COMPUTATION



The generated aerosols have been characterized. Main results can be found in Roose et al. *ACS Earth Space Chem.* 2019, 3, 3, 380-389

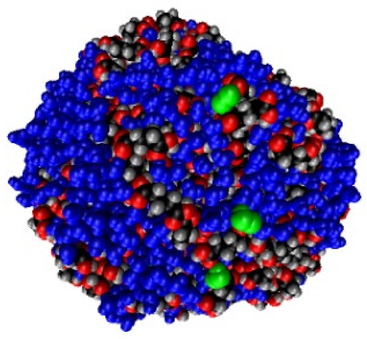
Two methods have been used in order to determine the mass accommodation coefficient

All in one method (20 HO_2 on 1 aerosol):

This method consists in the random addition of 20 HO_2 in one trajectory. Then the computation run until an equilibrium is reached. The mass accommodation coefficient is computed using :

$$\alpha = \frac{N_{gas,0} - N_{gas,eq}}{N_{gas,0}}$$

The mass accommodation coefficients computed for dry aggregates were ~0.99, ~1.00 and ~0.99 for the aggregate $(GLU)_{100}$, $(GLU)_{200}$ and $(GLU)_{500}$ respectively. For wetted aggregates, mass accommodation was also close to unity.



Statistical approach (2500 trajectories of 1 HO_2 on 1 aerosol):

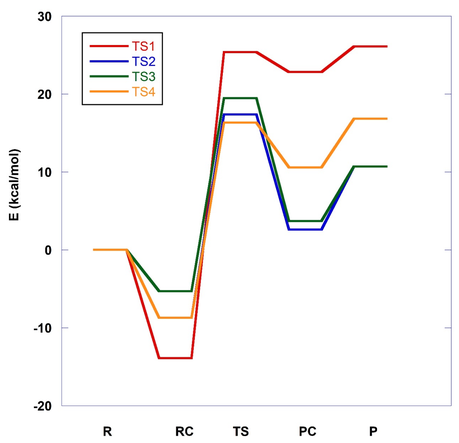
This method consists in the addition of one HO_2 on the particles. Several hundreds of trajectories are lunched to compute the mass accommodation using the statistical approach:

$$\alpha = \frac{n_{adsorb} + n_{absorb}}{n_{total}}$$

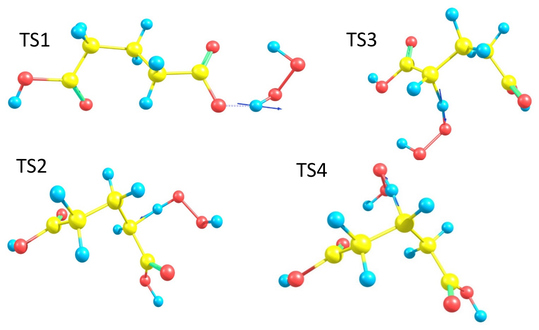
A mass accommodation coefficient close to unity was also found for wetted aggregate.

HO_2 REACTIVITY COMPUTATION

- Reactivity with glutaric acid is explored. .
- Tunneling is taken into account (Eckart)
- Rate constant computed using TST with Kishtelp
- Very low rate constant compared to HO_2 self-reaction (1.25×10^{-12} $cm^3 molecule^{-1} s^{-1}$) which is in accordance with experimental observation.
- The aerosol phase has no impact on the barrier height (less than 1 kcal/mol difference).
- Reactivity of HO_2 with water and/or itself on the aerosol are in progress.



	Γ	k_{TST} (cm^3 molecule^{-1} s^{-1})	k (cm^3 molecule^{-1} s^{-1})
1	1.72	6.99×10^{-33}	1.22×10^{-32}
2	379.58	1.05×10^{-27}	2.96×10^{-25}
3	662.01	3.64×10^{-29}	1.95×10^{-26}
4	24.61	2.73×10^{-27}	7.07×10^{-26}
k_{tot}		7.63×10^{-27}	7.73×10^{-25}

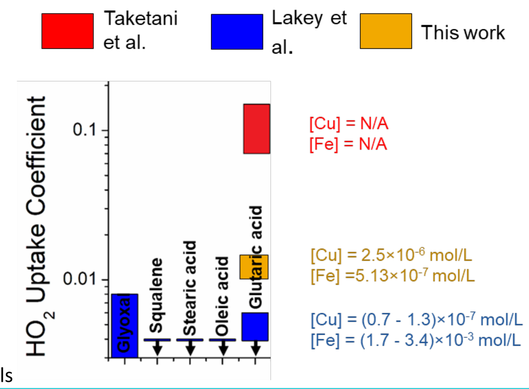


CONCLUSION

Nanoscale glutaric acid aerosols have been generated with different amounts of water. HO_2 mass accommodation coefficient has been computed on these model particles using classical molecular dynamics. The mass accommodation coefficient is close to unity in presence or not of water. The reaction of HO_2 with the diacid is not favored at the aerosol surface, the calculated rate constant being really small. The heterogenous reactivity will be completed with the reactivity of HO_2 with water and/or itself. Other parameters like diffusion into the bulk are currently investigated as well. Compiling the different calculated data, a theoretical uptake coefficient may be deduced and compared with experimental values.

PERSPECTIVE

HO_2 uptake coefficient has been measured experimentally using an aerosol flow tube at IMT Laboratory (Lille-Douai). The differences between the measured values and the values reported in the literature may be explained by different amounts of copper. Once the reactivity computation will be finished, the theoretical reactive uptake coefficient will be compared to the experimental one.



Experimental HO_2 uptake coefficient on some organic aerosols

ACKNOWLEDGMENTS

The present work was funded by the French ANR Labex CaPPA through the PIA under Contract No. ANR-11- LABX-0005-01, by the Regional Council Hauts-de-France, by the European Funds for Regional Economic Development (FEDER), and by the contract CPER CLIMIBIO. This work was performed using HPC resources from GENCI-TGCC (Grant 2020-A0010806820).

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