

Research proposal for “Contrats Doctoraux 2023”
Ecole Doctorale Chimie, Université Claude Bernard Lyon1.

Thesis Title: **Elaborating the formation and fate of atmospheric organic peroxy radicals**
Formation et devenir des radicaux peroxy organiques atmosphériques

Aerosol particles span roughly 1 nm – 10 μm in diameter, but only the finest particles (i.e., with particle diameters $< 1 \mu\text{m}$) have a significant impact on climate change and air quality. Therefore, the chemical components contributing to the growth of sub-micronic particles are extremely important. Atmospheric aerosol is a complex mixture of solid and liquid particles of organic and inorganic substances suspended in the air. Of specific importance, ultrafine particles ($< 100 \text{ nm}$) contribute to a major fraction of the total aerosol load. Such particles generally result from the gas-to-particle conversion of highly organic oxygenated molecules (HOMs), formed from the gas-phase oxidation of volatile organic compounds (VOCs) emitted from both biogenic and anthropogenic sources. The quantitative assessment of the impact of aerosols on climate remains poorly understood due to several factors, including an incomplete understanding of how HOMs contribute to new particle formation (NPF) and therefore to secondary organic aerosol (SOA) generation. These uncertainties lead to large errors between modeled and ambient observations of aerosol loadings.

HOM formation proceeds via autoxidation of an organic peroxy radical (RO_2), which undergoes intramolecular hydrogen abstraction (H-shift), yielding an alkyl radical (R) presenting a hydroperoxyl functional group ($-\text{OOH}$), which rapidly reacts with O_2 to produce a new $\text{R}'\text{O}_2$ radical. This process may repeat further, leading to the formation of highly oxidized RO_2 radicals, which may decompose or undergo termination/propagation reactions with nitrogen oxides (NO_x), hydroperoxy radicals (HO_2), or other RO_2 radicals to form a wide range of oxidation products, including peroxides (ROOR' or dimers). RO_2 reactions can therefore yield a plethora of multifunctional oxidation products with low or extremely low saturation vapor pressures within seconds in the atmosphere. The formation of gas-phase dimeric products (i.e., ROOR') has been reported for various VOCs, including cyclohexene, monoterpenes, and aromatics species. Among them, monoterpene-derived dimers have been observed from pristine ambient to laboratory environments and shown to be important for NPF and particle growth. Dimer yields vary depending on its precursor (VOC) structure, which determines the structure of the participating RO_2 radicals, and on the relative abundance of other reactive species in the system that competes as RO_2 sinks. The only study that estimated $(\text{RO}_2 + \text{RO}_2)$ rate constants suggested that tertiary RO_2 and less oxygenated RO_2 radicals present lower reaction rate constants, and therefore less likely to participate in ROOR' (i.e., dimers) production.

However, little is known about the molecular structures and reactivity of atmospheric relevant, i.e., (poly)functionalized, RO_2 , and ultimately of the associated HOMs and ROOR' species, making the HOM/ ROOR' formation pathways highly uncertain.

Work description

The Ph.D. work will be carried out at the *Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON, <http://www.ircelyon.univ-lyon1.fr/>)* in collaboration with the *Institut de Chimie et Biochimie Moléculaires et Supramoléculaires (ICBMS, <https://www.icbms.fr/fr/>)*.

The Ph.D. work aims at combining novel experimental and analytical strategies consisting of (i) using synthesized polyfunctionalized monoterpene-derived iodo compounds to produce specific organic radicals from the photolysis of the precursors; (2) interfacing new generation of soft ionization systems (chemical ionization source) with a highly sensitive mass spectrometry technique (i.e., Orbitrap and time-of-flight mass spectrometry). With this unique methodology, the Ph.D. student will be able to explore the chemistry of complex monoterpene derived – RO₂ to resolve their reactivity (i.e., RO₂ + RO₂, RO₂ + NO/NO_x, ...) and fate. Ultimately this will allow an accurate prediction of the chemical mechanisms leading to highly organic oxygenated molecules, especially the dimeric compounds, and ultimately to the formation of new particles produced from the oxidation of monoterpenes

PhD Candidates

Candidates with a background in chemistry, physical or analytical chemistry, or physics are encouraged to send their resumes.

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