Detection & Speciation of Organic Peroxy Radicals ($ROO^{\bullet}$)

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Take home message

A new experimental setup enables the direct and specific measurement of the simplest organic peroxy radicals in the laboratory ($CH_3OO^{\bullet}$, $C_2H_5OO^{\bullet}$, $C_3H_7OO^{\bullet}$, ...). Measurements demonstrated a strong uptake of organic peroxy radicals on metal, indicating redox reactions.[1]

Avoid all metal surfaces and use instead a fluoropolymer to maximize $ROO^{\bullet}$ detection!

Research Topic

We have set up an experiment to study kinetically gas-phase reactions involving radicals at room temperature and atmospheric pressure.
The kinetics reactor is simple and innovative (Fig. 1). Our method is precise, straightforward, inexpensive, and makes it possible to study surface uptakes. It can also be set up without any movable parts.
In the principle, the flow tube is here an elementary 1/4" tube. The radicals are produced continuously in a UV-C cell by the photolysis of a precursor. The radicals are then flown through a tube before their detection by proton-transfer-reaction mass spectrometry (Fig. 2). It is the residence time in the tube, by changing its length or the flows, that allows for kinetic measurements. Our laboratory approach has recently been applied to measure the uptake of small organic peroxy radicals on metallic and non-metallic surfaces (Fig. 3).

Experimental Setup

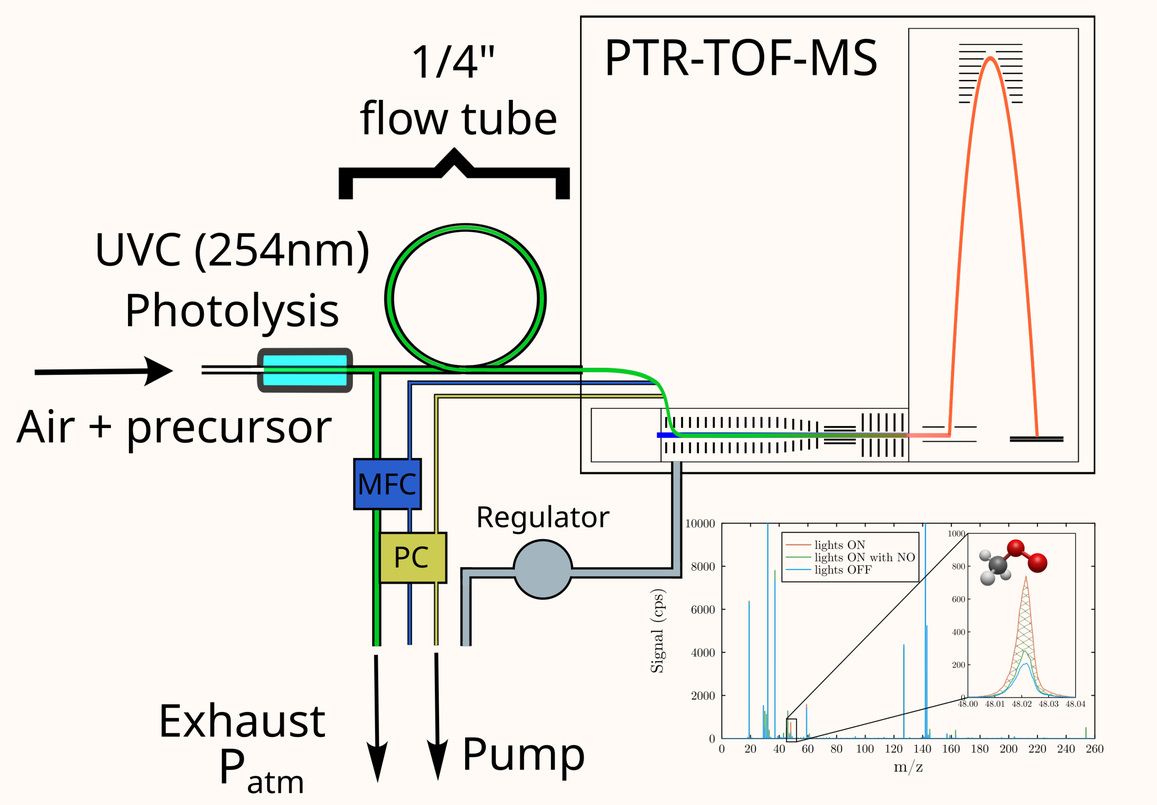

FIGURE 1 – A photolysis cell, a simple tube and a Proton-Transfer-Reaction Mass Spectrometer.

Mass Spectrometry Data

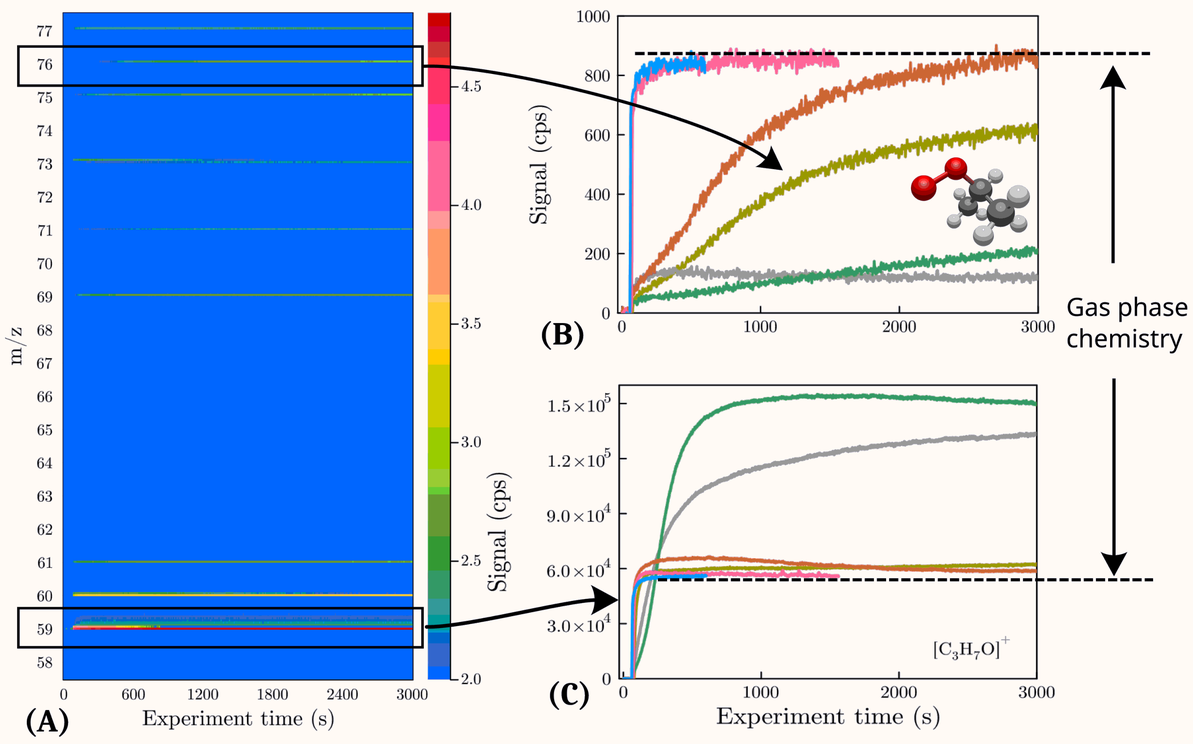

FIGURE 2 – Mass spectra acquired every second allows identification of surface reactions.

The Uptake Kinetics

Chemical system: $ROO^{\bullet} \xrightarrow{\text{Surface}} P, \quad 2\,ROO^{\bullet} \xrightarrow{\text{Gas}} P'.$

When gas-phase matter (Glass and PFA), mixte-order reaction:

$$\frac{d[ROO^{\bullet}]}{dt} = -2k_{self}[ROO^{\bullet}]^2 - k'[ROO^{\bullet}].$$

Analytical solution: $[ROO^{\bullet}](t) = \frac{k' \exp(-k't)}{\frac{k'}{[ROO^{\bullet}]_0} + 2k_{self}(1-\exp(-k't))}$.

On metals (calibration-free): $[ROO^{\bullet}](t) = [ROO^{\bullet}]_0 \exp(-k't)$.

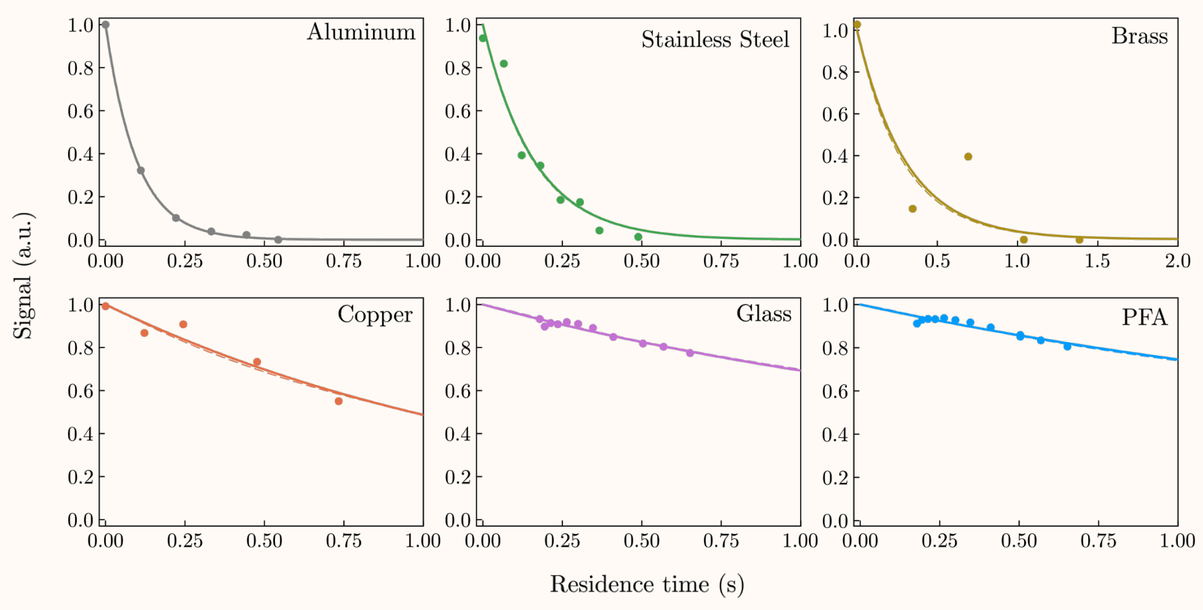

FIGURE 3 – Kinetics results demonstrated strong uptakes of organic peroxy radicals on metal, following the electropotential series.

Challenges, Present and Near Future

- Raw data and processing tools available on Zenodo: `zenodo.org/records/8250035`
- Complex data processing, GBytes of data acquired every experiment hour. A Julia package has been developed for data processing: gitlab.com/MassSpec.jl
- Impact of relative humidity on $ROO^{\bullet}$ signal ill-understood. Ongoing studies.
- An open possibility to investigate $ROO^{\bullet}$ uptake by organic and mineral surfaces.

[1] Olivier DURIF, Felix PIEL, Armin WISTHALER et Barbara NOZIÈRE. « Strong Uptake of Gas-Phase Organic Peroxy Radicals ($ROO^{\bullet}$) by Solid Surfaces Driven by Redox Reactions ». In : *JACS Au* (avr. 2024). DOI : `10.1021/jacsau.4c00060`.

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