

Detection & Speciation of Organic Peroxy Radicals (ROO[•])

ERCA Winter School 14 January - 3 February 2024, Grenoble

Olivier Durif¹, Lauren Cork¹, Barbara Nozière¹

¹ Kungliga Tekniska Högskolan, Department of Chemistry, Stockholm, Sweden

Keywords : Organic Peroxy Radical, Proton-Transfer-Reaction Mass Spectrometry, Flow Tube, Gas-Phase, Chemical Kinetics

Research Topic

We have set up an experiment to study kinetically gas-phase reactions involving radicals.

The method is straightforward (Fig. 1): radicals are produced in a UV-C cell by the photolysis of a precursor (for example, CH₃I to produce CH₃OO[•]). 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 that allows for kinetic measurements.

Our laboratory approach has recently been applied to measure the uptake of organic peroxy radicals (CH₃OO[•], C₂H₅OO[•], *i*-C₃H₇OO[•]) on metallic and non-metallic surfaces (Fig. 3).

One of the long-term goals of this project is to refine the spectrometer for direct field measurements of the organic peroxy radicals.

Raw Data

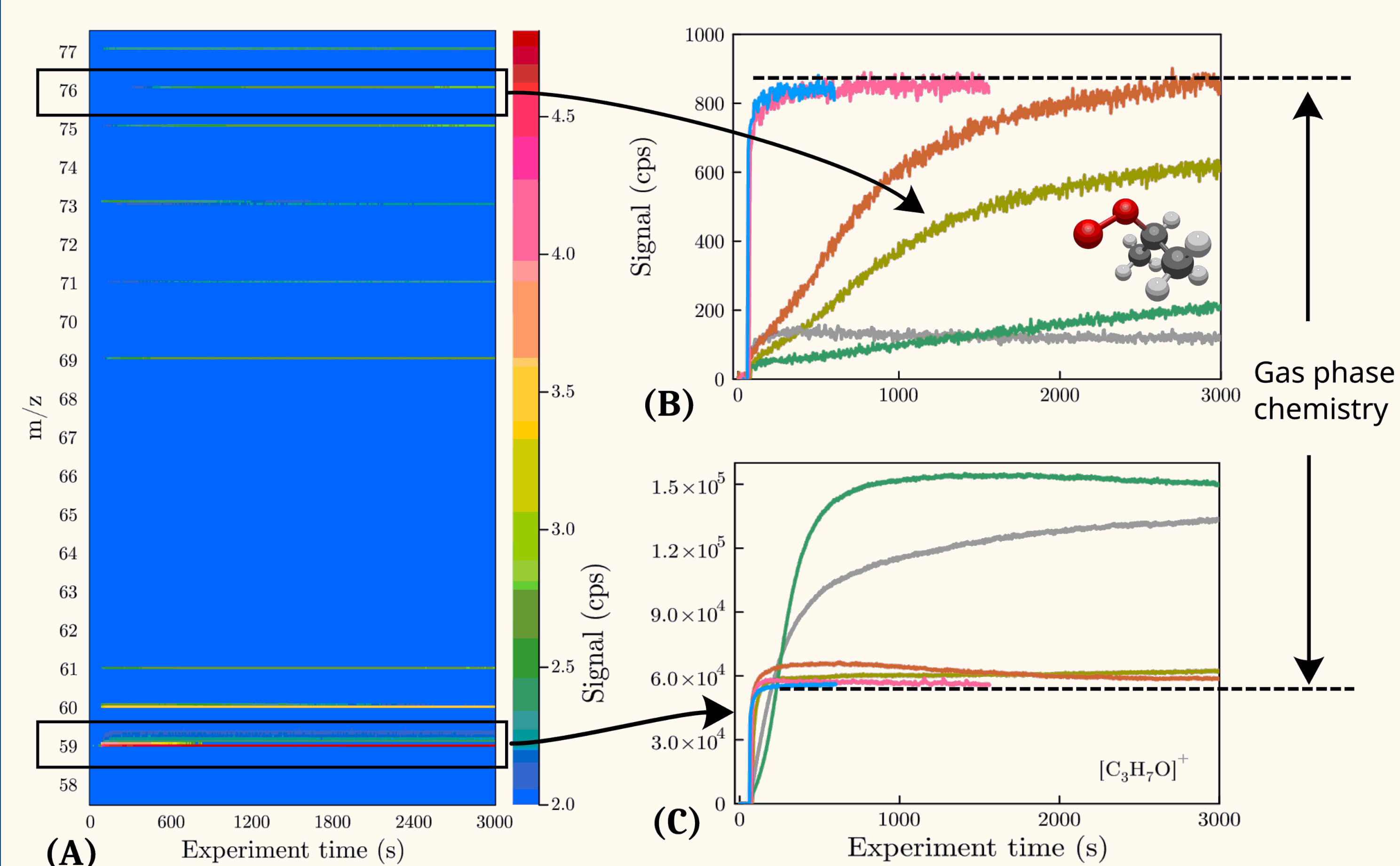


FIGURE 2 – Mass spectra acquired every second allows identification of surface reactions.

Challenges, Present and Near Future

- Complex data processing, GBytes of data acquired every experiment hour
- Impact of relative humidity on ROO[•] signal misunderstood
- An open possibility to investigate ROO[•] uptake by organic and mineral surfaces

Experimental Setup

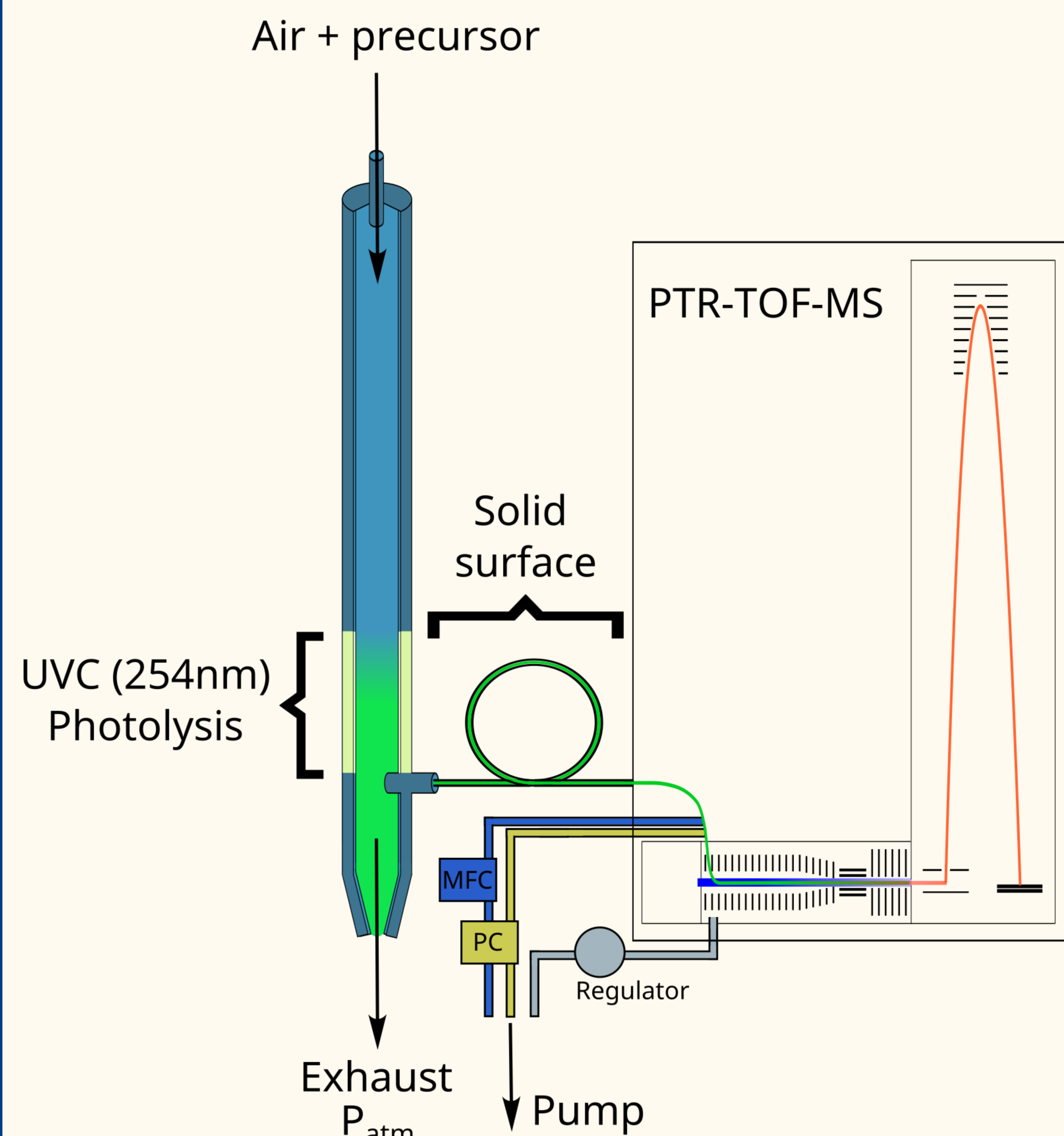


FIGURE 1 – A photolysis cell, a simple tube and a Proton-Transfer-Reaction Mass Spectrometer.

The Uptake Kinetics

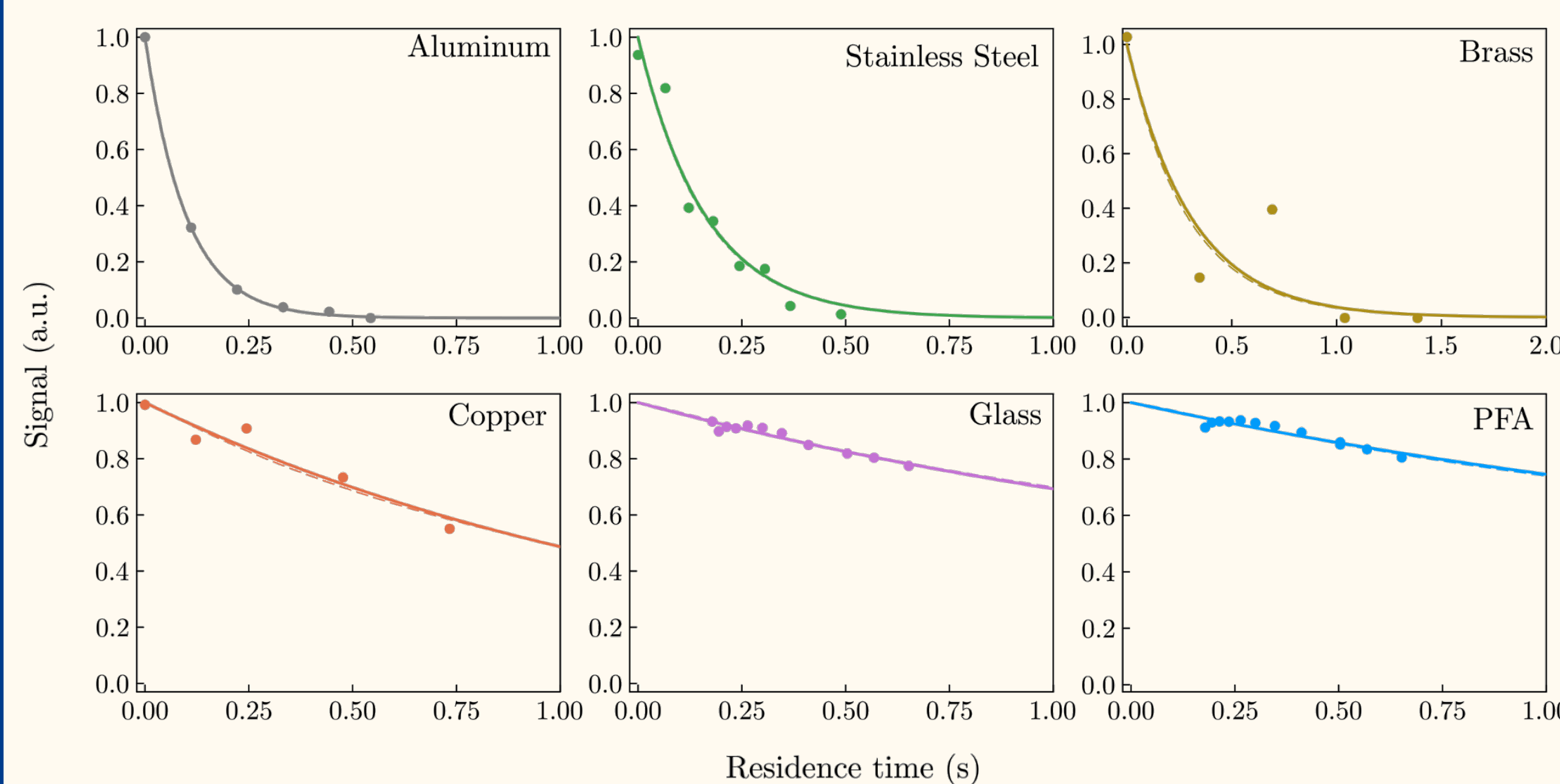


FIGURE 3 – Kinetics results demonstrated strong uptakes of organic peroxy radicals on metal, following the electrochemical series.

Take home message

A new experimental setup enables the direct and specific measurement of the simplest organic peroxy radicals in the laboratory (CH₃OO[•], C₂H₅OO[•], C₃H₇OO[•], ...).

Laboratory measurements demonstrated a strong uptake of organic peroxy radicals on metal, indicating redox reactions.