

Structures and reactivity of peroxy radicals probed by advanced VUV photoionization mass spectrometry

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Peroxy radicals (RO₂) are key reaction intermediates in the low temperature oxidation of organic compounds and play essential roles in combustion and atmospheric chemistry. In this talk, I will present our recent research progress on the structures and reactivity of peroxy radicals by using synchrotron radiation VUV photoionization mass spectrometry (PIMS, at Hefei) and double imaging photoelectron photoion coincidence spectroscopy (i²PEPICO, at SOLEIL). Peroxy radicals are generated in a microwave discharge flow tube through the reactions of alkyl radicals with oxygen, initiated with fluorine or chlorine atoms. Two kinds of alkyl cations, originating from direct photoionization of alkyl radicals, and from dissociative photoionization of peroxy radicals whose cations are not stable, have been observed and separated through their different ion kinetic energies. The precursors of the latter, the isomers/rotamers of peroxy radicals are individually identified and assigned in photoionization spectra or mass-selected threshold photoelectron spectra (TPES) with the aid of computed adiabatic ionization energies (AIEs) and Franck-Condon factors. Moreover, the structures of dimeric products (ROOR) from the self-reaction of peroxy radicals are also clearly identified.

References

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