CAVITY RING-DOWN SPECTROSCOPY OF 1-, 2- AND 3-METHYL ALLYL PEROXY RADICALS

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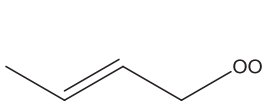
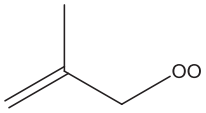
Peroxy radicals are key reaction intermediates formed during the oxidation of hydrocarbons in the atmosphere and in low-temperature combustion. Allyl group-containing peroxy radicals are particularly important because they are generated in large quantities by the OH-initiated oxidation of isoprene, the most abundant non-methane biogenic hydrocarbon. In this talk, room-temperature cavity ring-down (CRD) spectra of the $\tilde{A} \leftarrow \tilde{X}$ electronic transition of 1-, 2- and 3-methyl allyl peroxy radicals will be reported. Peroxy radicals were produced in 193 nm photolysis of selected methyl-substituted allyl chlorides, e.g., 1-chloro-2-butene, 3-chloro-2-methyl-1 propene, and 3-chloro-1-butene, in the presence of O_2. Vibronic structure of the experimentally observed spectra are simulated using calculated electronic transition frequencies, vibrational frequencies, and Franck-Condon factors. Spectroscopic detection and characterization of isoprene peroxy radicals[a] are underway.



1-methyl allyl peroxy



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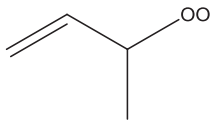

3-methyl allyl peroxy

[a] A. P. Teng, J. D. Crounse, and P. O. Wennberg, J. Am. Chem. Soc. 139, 5367 (2017).