OBSERVATION OF THE $\tilde{A} \leftarrow \tilde{X}$ ELECTRONIC TRANSITIONS OF TETRAHYDROPYRANYL AND TETRAHYDROFURANYL PEROXY RADICALS BY ROOM-TEMPERATURE CAVITY RING-DOWN SPECTROSCOPY

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Peroxy radicals are important chemical reaction intermediates in low-temperature combustion systems as well as in the Earth's troposphere; hence spectroscopic detection of peroxies and studies of their kinetics are essential to improving the efficiency of internal combustion engines and reducing air pollution. In this talk, we report the room-temperature cavity ring-down (CRD) spectra of the $\tilde{A} \leftarrow \tilde{X}$ electronic transition of the tetrahydropyranyl peroxy (THPOO) and tetrahydrofuranyl peroxy (THFOO) radicals. Both THP and THF are building blocks of lignocellulose-derived biofuels. THPOO and THFOO therefore play critical roles in the oxidation of biofuels.[a, b, c] In the present experiment, they are produced via hydrogen abstraction of THP and THF by chlorine atoms followed by oxygen addition. Chlorine atoms are produced in 193 nm photolysis of oxalyl chloride $(COCl)_2$. The presence of oxygen in the ring defines 3 distinct positions on THP (α,β and γ) and 2 for THF (α and β), which leads to different regioisomers. Moreover, compared to chain alkyl peroxy radicals, cyclic ones possess significantly different conformational landscapes. Quantum chemical calculations have been performed and provide electronic transition frequencies, vibrational frequencies, Franck-Condon factors, as well as relative energies of isomers and conformers. Spectral simulation using these calculated result suggests that all isomers and most of the possible conformers contribute to the experimentally observed spectra. Also determined in the spectral simulation is the branching ratios of reactions that produce different regioisomers. The CRD technique has been used for lifetime measurements and investigation of the ring-opening mechanism. Comparison between the target molecules and the controls, namely, homocyclic peroxy radicals, will be briefly discussed.

[a]Chen, M. W. et al., Phys. Chem. Chem. Phys., 2018, DOI: 10.1039/c7cp08164b.

[b]Rotavera, B. et al., Proc. Combust. Inst., 2017, 36 (1), 597–606.

[c]Antonov, I. O. et al., J. Phys. Chem. A, 2016, 120 (33), 9823-9840.