

# Detection of hydroperoxide chain-branching agents in the low-temperature oxidation of alkanes

Olivier Herbinet,<sup>1</sup> Anne Rodriguez,<sup>1</sup> Zhandong Wang<sup>2</sup>, Fei Qi<sup>2</sup>, Christa Fittschen<sup>3</sup>, Philip R. Westmoreland<sup>4</sup> and Frédérique Battin-Leclerc<sup>1,\*</sup>

<sup>1</sup> LRGP, CNRS, Université de Lorraine, Nancy, France

<sup>2</sup> NSRL, University of Science and Technology of China, Hefei, P. R. China

<sup>3</sup> PC2A, CNRS, Université de Lille, Villeneuve d'Ascq, France

<sup>4</sup> CBE, North Carolina State University, Raleigh, USA

\* Corresponding author: frederique-battin-leclerc@univ-lorraine.fr

The reactions of chain-branching agents involved in the oxidation of fuels, such as H<sub>2</sub>O<sub>2</sub> and hydroperoxides, have a decisive role in the occurrence of autoignition in engines. Due to their fragility, these species cannot be detected using classic analytical methods like gas chromatography and their formation is rarely reported in the literature. Thus more specific analytical methods have to be used. As an example, ketohydroperoxides, the formation of which was postulated in detailed kinetic models, were only observed recently in conditions close to those of engines thanks the coupling of a jet-stirred reactor to a mass spectrometer with ionization by vacuum ultra-violet synchrotron radiation (1). In the present study, the formation of these branching agents has been investigated in an atmospheric-pressure jet-stirred reactor during the low-temperature oxidation of *n*-pentane (initial fuel mole fraction of 0.01, residence time of 2-s) using three different diagnostics: time-of-flight mass spectrometry combined with tunable synchrotron photoionization, time-of-flight mass spectrometry combined with laser photoionization, and cw-cavity ring-down spectroscopy. These three diagnostics enabled a combined analysis of a wide range of hydroperoxide species: H<sub>2</sub>O<sub>2</sub>, C<sub>1</sub>-C<sub>2</sub>, C<sub>3</sub>-C<sub>5</sub> alkylhydroperoxides, C<sub>3</sub>-C<sub>5</sub> alkenylhydroperoxides, and C<sub>5</sub> alkylhydroperoxides including a carbonyl function (keto- and aldo-hydroperoxides). Results using both types of mass spectrometry were compared for the stoichiometric mixture. Formation data are presented at equivalence ratios from 0.5 to 2 for these peroxides and for two oxygenated products, ketene and pentanediones, which are not usually analyzed during jet-stirred reactor oxidation. A recently developed model of *n*-pentane oxidation (2) aids discussing the kinetics of these products and of proposed pathways for C<sub>3</sub>-C<sub>5</sub> alkenylhydroperoxides and the pentanediones.

**Acknowledgements:** This work was supported by European Commission ("Clean ICE" ERC Advanced Research Grant) and by COST Actions CM0901 and 1404.

## References

- (1) Herbinet, O.; Battin-Leclerc, F.; Bax, S.; Gall, H. L.; Glaude, P.-A.; Fournet, R.; Zhou, Z.; Deng, L.; Guo, H.; Xie, M.; Qi, F. *Phys. Chem. Chem. Phys.* **2011**, 13 (1), 296–308.
- (2) Bugler, J.; Rodriguez, A.; Herbinet, O.; Battin-Leclerc, F.; Togbé, C.; Dayma, G.; Dagaut, P.; Curran, H. *Proc. Combust. Inst.* **2017**, submitted.