

## Quantification of hydrogen peroxide during the low-temperature oxidation of n-butane

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A significant reduction of the emissions of greenhouse gases could be achieved through an increase of the efficiency of internal combustion engines. Advanced combustion concepts that rely on compression self-ignition, as well as the improvement of safety in oxidation processes, demand an improved understanding of the detailed mechanisms of organic compounds chemical kinetics, particularly in the low-temperature oxidation regime. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), a key compound for the development of auto-ignition, has been quantified thanks to the development of a new system coupling a jet stirred reactor to a cell with an analysis by continuous wave cavity ring-down spectroscopy (cw-CRDS) in the near infrared, a quantification of H<sub>2</sub>O<sub>2</sub> has been achieved for the first time under conditions close to those actually observed before the auto-ignition. If the UV or IR absorption of H<sub>2</sub>O<sub>2</sub> has been used to follow its decomposition in shock tubes, H<sub>2</sub>O<sub>2</sub> has never been quantified during the gas-phase oxidation of an organic reactant. Cavity ring-down spectroscopy (CRDS) has recently been proven to be a suitable method to analyse hydrogen peroxide which presents a well-structured absorption spectrum near 6639 cm<sup>-1</sup>. CRDS has already been successfully used to investigate many reactive systems, related both to combustion or atmospheric chemistry.

A spherical quartz jet stirred reactor has been associated to a tubular glass cw-CRDS cell. The coupling between the cell and the reactor was performed by using a tubular quartz sonic probe with a hole of about 150 μm diameter at the tip. The size of the hole was adjusted in order to obtain the required pressure drop between the reactor slightly above atmospheric pressure and the cell. The pressure in the CRDS had to be kept around a few kPa for the absorption signal to be high enough. The pressure should nevertheless be low enough to minimize pressure broadening of absorption lines. The residence time of the gas mixture within the CRDS cell was estimated to about 0.3 s.

The study of the oxidation of n-butane was performed at temperatures between 600 and 925 K, with a mean residence time of 6s and for an n-butane/oxygen/argon mixture composition of 2.3/14.9/82.7 (in mol %) corresponding to a stoichiometric mixture for complete combustion reaction. CRDS analyses were carried out in the near infrared at wavelengths from 6620 – 6643 cm<sup>-1</sup>. Note that n-butane has a continuum absorption under these conditions limiting its maximum usable initial mole fraction.

This work gives the first reliable quantification of hydrogen peroxides formed during the low temperature oxidation of an organic compound. This method can be used to build a database for the formation of this key compound for the development of auto-ignition for a wide range of fuels, allowing improving detailed kinetic models for the oxidation of organic compounds, especially the kinetics of the reactions involving HO<sub>2</sub> radicals.

*This work was supported by the European Commission through the "Clean ICE" Advanced Research Grant of the European Research Council.*