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Quantification of Hydrogen Peroxide during the Low-Temperature Oxidation of Alkanes

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Ⓢ *Supporting Information*

ABSTRACT: The first reliable quantification of hydrogen peroxide (H_2O_2) formed during the low-temperature oxidation of an organic compound has been achieved thanks to a new system that couples a jet stirred reactor to a detection by continuous wave cavity ring-down spectroscopy (cw-CRDS) in the near-infrared. The quantification of this key compound for hydrocarbon low-temperature oxidation regime has been obtained under conditions close to those actually observed before the autoignition. The studied hydrocarbon was *n*-butane, the smallest alkane which has an oxidation behavior close to that of the species present in gasoline and diesel fuels.

A significant reduction of the emissions of greenhouse gases could be achieved through an increase of the efficiency of internal combustion engines.[1] Advanced combustion concepts that rely on compression self-ignition[1,2] as well as the improvement of safety in oxidation processes[3] demand an improved understanding of the reaction kinetics governing the detailed mechanisms of hydrocarbons and biofuels, particularly in the low-temperature oxidation regime. The chemistry of the oxidation of hydrocarbons below 1000 K is fundamental to explain the development of autoignition in engines[2] and related knock phenomena.[4] Among the species involved in this chemistry, hydrogen peroxide (H_2O_2) is a very critical one, since its decomposition leads to large amounts of very reactive hydroxyl (·OH) radicals. This reaction really drives the system to ignition under some conditions. If this extreme importance of hydrogen peroxide in the development of autoignition is well-known for many years,[5−7] its quantification under realistic conditions remains a challenge. The quantification presented in this work will be valuable for improving chemistry knowledge and detailed kinetic models in the temperature zone (650−900 K) in which reaction mechanism are the most complex and the kinetic data are the least accurate.[8]

Several reviews of the detailed chemical kinetic models for low-temperature oxidation of fuel components have been recently published.[9,10] Before describing the involved chemical mechanism, let us recall two specific reactive features of mixtures of organic compounds with oxygen:[11]

- Cool flames, which are single or multiple small temperature pulsations (a few tenths of K) accompanied by weak blue light emission due to excited formaldehyde, and which are often observed under conditions starting at about 550 K, preceding those of autoignition.
- The commonly called "negative temperature coefficient" (NTC) zone, which is a zone of temperature (usually around 650 K) where the reactivity decreases with temperature.

Figure 1 presents the nowadays commonly accepted mechanism for representing the oxidation of hydrocarbons.[5]

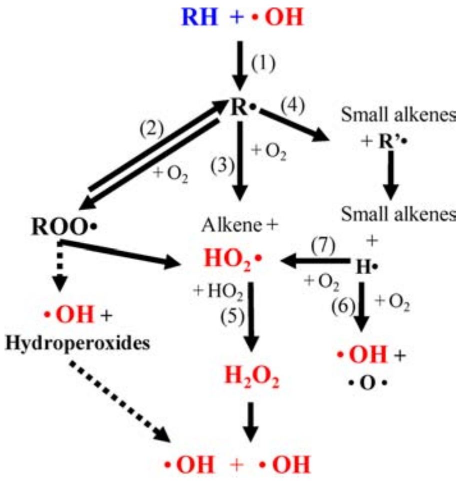

Figure 1. Simplified scheme of the mechanism of oxidation of alkanes (dotted arrows represent a succession of several elementary steps).

After a short induction period, a hydrocarbon (RH) reacts with a hydroxyl radical leading to formation of an alkyl radical (R·) via reaction 1. At low temperatures (below 800 K), alkyl radicals yield alkylperoxy radicals (ROO·) after a barrierless reaction with an oxygen molecule (reaction 2). Alkylperoxy radicals easily lead to the formation of hydroperoxides, either by reaction with $\cdot HO_2$ radicals, or by a complex mechanism involving two isomerizations and a second addition to oxygen molecules, not described here. The fragility of the RO−OH bond of hydroperoxides (the bond dissociation energy is around 180 kJ/mol), which can easily break, leads to degenerate branched chain reactions explaining the high

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reactivity of these mixtures at low-temperature and cool flame occurrence.[5,9−11]

As temperature increases, the enhanced reversibility of reaction 1 makes the formation of alkylperoxy radicals, and consequently of hydroperoxides, to be less favored. Alkyl radicals react then with oxygen yielding conjugated alkenes and $\cdot HO_2$ radicals via reaction 3, or, if temperature is high enough, decompose to give small alkenes and alkyl radicals via reaction 4. Compared to ·OH radicals obtained by the reactions involving alkylperoxy radicals, $\cdot HO_2$ radicals are not very reactive by H-abstractions and mainly react in termination steps, especially with themselves to give hydrogen peroxide (H_2O_2) and O_2 via reaction 5. This reduction of the importance of branched chain reactions in favor of chain terminating reactions leads to a slow down of the reactivity and explains the occurrence of the NTC zone. In this temperature zone, reaction 5 is the main source of H_2O_2 formation and its rate parameters are well-known. An accurate knowledge of the H_2O_2 concentration could then lead to a good estimation of the $\cdot HO_2$ radical concentration.

As the temperature increases still more, the decomposition of H_2O_2 (the bond dissociation energy is about 214 kJ/mol) starts to be the new degenerate branched chain reaction promoting again high reactivity. Above about 1000 K, the small alkyl radicals obtained by reaction 4 can in turn decompose to give alkenes and ·H atoms. The reaction of ·H atoms with oxygen leads to ·OH radicals and ·O· atoms (reaction 6), which is a true branching step ensuring then the full development of the ignition and the complete combustion. Note that this branching step competes directly with reaction 7 which is also a channel of formation of $\cdot HO_2$ radicals.

This scheme shows clearly the critical importance of hydrogen peroxide in the development of ignition. Depending on the concentration of this species which is produced during the cool flame period, the ignition will continue to develop beyond the NTC zone or will abort. The purpose of this study is then to accurately quantify hydrogen peroxide under conditions which mimic those observed during the reaction period prior to the autoignition of alkanes. *n*-Butane has been studied as it is the smallest alkane which has an oxidation behavior close to that of the species present in gasoline and diesel fuels.

The easy titration of hydrogen peroxide in liquid phase (e.g., permanganometric titration) has favored early studies of its gas-phase decomposition and of its formation in H_2/O_2 mixtures after trapping from heated static[12] or flow reactors.[13,14] More recently, the UV[15] or IR[16] absorption of H_2O_2 has been used to follow its decomposition in shock tubes. But to date, H_2O_2 has never been quantified during the gas-phase oxidation of an organic reactant. Note, however, that H_2O_2 has been already detected during the gas-phase oxidation of *n*-butane performed in a jet-stirred reactor, but coupled to a reflectron time-of-flight mass spectrometer via a molecular-beam sampling system.[17] The mole fraction then obtained, using an estimated photoionization cross section, was lower by a factor of 50 compared to theoretically predicted mole fractions, indicating a possibly important fragmentation of this species after ionization.

Hydrogen peroxide presents a well-structured absorption spectrum around 6639 cm^{-1} and cw-cavity ring-down spectroscopy (cw-CRDS) has recently been proven to be a suitable method to analyze H_2O_2.[18] cw-CRDS has already been successfully used in many fields such as spectroscopy[19] or atmospheric chemistry.[20] Even though this technique has been coupled to time-resolved reactors for the investigation of reactive systems,[21] a better sensitivity can be obtained by using a reactor working under steady-state conditions: this way, data can be easily averaged. Our goal was not to directly observe unsteady phenomena, such as autoignition, but to mimic the chemistry leading to this phenomenon. For this purpose, we have used a heated jet-stirred reactor operated at a constant temperature and pressure, in which a gas mixture is continuously flowing.

This jet stirred reactor, which can be heated up to 1200 K, is well adapted for kinetic studies:[8,17,22−24] the gas phase inside the reactor is well stirred leading to homogeneous concentrations and temperature. This type of reactor coupled with gas chromatography analyses has already been used many times for studying the low-temperature oxidation of organic compounds.[8] The use of this reactor coupled to a reflectron time-of-flight mass spectrometer via a molecular-beam sampling system has recently given the proof of the formation of hydroperoxides under conditions close to those actually observed before the ignition of organic compounds.[22] The coupling of the jet-stirred reactor to a detection by cw-CRDS in the near-infrared has already been used to study the oxidation of methane at atmospheric pressure.[24] Some stable species (CH_4, H_2O, and HCHO) have been quantified through their well structured spectra and the obtained mole fractions were in very good agreement with gas chromatography analysis (for CH_4) and with simulation (for the 3 species).

Figure 2 presents a simplified scheme of the spherical quartz jet-stirred reactor associated to a tubular glass cw-CRDS cell (see Supporting Information). This study has been performed under quasi-atmospheric pressure (1.07 atm). The coupling between the cell and the reactor was performed using a tubular quartz probe with an orifice of about 150 μm diameter at the tip. The size of the orifice was adjusted in order to obtain the required pressure drop between the reactor (slightly above atmospheric pressure) and the detection cell (few kPa). The pressure in the CRDS cell has to be kept low in order to avoid pressure broadening of the absorption lines, which decreases the selectivity. On the other hand, a pressure drop results also in a decrease in absolute species concentration and thus in sensitivity. Therefore, a compromise has to be made to satisfy both conditions. The residence time of the gas mixture within the CRDS cell was estimated to about 0.3 s.

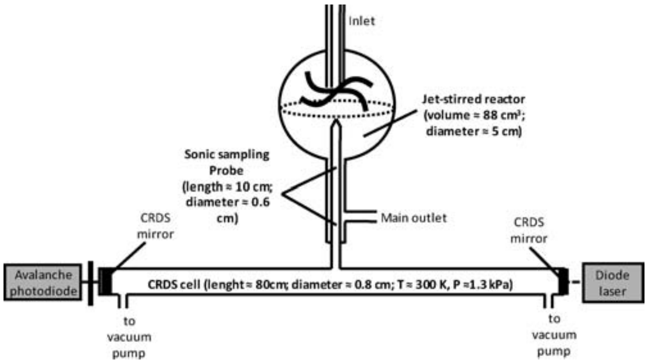

Figure 2. Simplified scheme of the experimental device.

The study of the oxidation of *n*-butane was performed at temperatures between 550 and 925 K, at a mean residence time within the jet-stirred reactor of 6 s and for an *n*-butane/oxygen/helium 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 wavenumbers from 6620 to 6643 cm^{-1}. Note that *n*-butane has a continuum absorption under these conditions limiting its maximum usable initial mole fraction (under the studied conditions, 66% of near-infrared radiation is lost due to *n*-butane absorption). Figure 3 presents a typical CRDS spectrum showing the ring-down time of the cavity (τ) as a function of wavenumber when probing during the oxidation of *n*-butane at 650 K in the 6639.2–6640.1 cm^{-1} range.

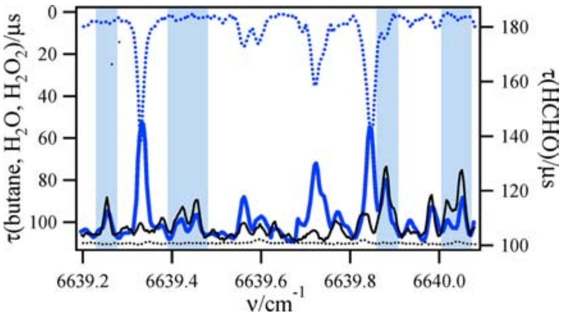

Figure 3. Typical CRDS spectrum obtained for the oxidation of *n*-butane at 650 K (thick full blue line) compared to the spectrum of H_2O_2/H_2O mixture (thin full black line), H_2O (thin dotted black line), and HCHO (thin broken blue line, right axis). Shaded areas show H_2O_2 absorption lines which are not disturbed by other absorbing species.

In addition to H_2O_2, the oxidation of *n*-butane yields other small products which can also have well-structured absorption lines near 6639 cm^{-1}. For a reactor temperature of 650 K, the main reaction products exhibiting this type of absorption are water (H_2O) and formaldehyde (HCHO). Heavier oxygenated species would rather have a continuum absorption, while small hydrocarbons (e.g., methane, ethylene) having also a well-structured absorption spectrum in this wavelength range, are only formed in large amounts above 800 K. Figure 3, therefore, presents also the absorption spectrum in the form of ring-down time (τ) for three different gas mixtures obtained in separate experiments: (a) the thin black line represents the spectrum obtained when bubbling through a commercial H_2O_2/H_2O solution (50% H_2O_2 (Sigma-Aldrich)), that is, containing the absorption features of both, H_2O_2 and H_2O; (b) the dotted black line represents the spectrum of pure H_2O, obtained by bubbling through H_2O only; and (c) the dashed blue line has been obtained by flowing a commercial mixture of 199.6 ppm of HCHO (Air Liquide) in N_2 through the cell. H_2O has only very small absorption lines in this specific wavelength range[19] as can be seen in Figure 3, too small to be visible under our conditions; therefore, the entire absorption spectrum obtained under conditions (a) can be attributed to H_2O_2 only. HCHO also presents absorption lines that are clearly visible and can be identified unequivocally in the absorption spectrum of the reactive mixture. One can observe four wavelength areas where no formaldehyde absorption occurs, but where well-structured H_2O_2 lines are shown both in the spectrum obtained by flowing the H_2O_2/H_2O solution and in that obtained by probing the gas mixtures from the heated reactor. These lines demonstrate very well the presence of hydrogen peroxide among the reaction products of the oxidation of *n*-butane at 650 K.

Figure 4 presents the evolution of the mole fraction of *n*-butane (measured by gas chromatography in the outlet gas) with temperature, as well as the evolution of the mole fraction of the hydrogen peroxide derived from the CRDS measurements using two different absorption lines, both undisturbed by HCHO absorption lines. Below 750 K, the well separated line at 6639.25 cm^{-1} could be used leading to an uncertainty on the mole fraction of about 10%. Above 750 K, absorption lines due to an increasing formation of ethylene disturbed this line, and the doublet line at 6640.02 cm^{-1} had to be used leading to a somewhat higher uncertainty on the mole fraction of about 25%. The absorption cross section used for the quantification (7.50×10^{-23} and 7.90×10^{-23} cm^2, for 6639.25 and 6640.02 cm^{-1}, respectively, at 1.33 kPa) have been obtained in separate experiments using the same apparatus and the same method as in the study of Parker et al.:[18] before measuring the absorption spectrum, the H_2O_2 concentration has been derived from the OH decays measured by time-resolved laser induced fluorescence following the 248 nm photolysis of H_2O_2.

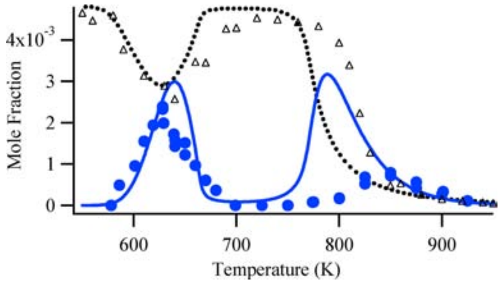

Figure 4. Evolution with temperature of the experimental (points) and computed (lines) mole fractions of *n*-butane (white triangles and dotted line, mole fraction/5) and hydrogen peroxide (blue dots and full line).

Note that the NTC behavior obtained for the reactant explains the shape of the evolution of H_2O_2 with 2 maxima, one around 630 K and one around 850 K. This behavior is well simulated with a detailed kinetic mechanism of the oxidation of *n*-butane previously proposed[22] (see the Supporting Information). Contrary to Herbinet et al.,[17] a correct quantitative agreement is now obtained between measured and simulated mole fractions of H_2O_2 below 750 K, in a temperature range in which the consumption of *n*-butane is also well modeled. This good agreement gives confidence on the accuracy of the quantification of hydrogen peroxide using the method described here. Above 750 K, however, the model considerably overpredicts the reactivity as well as the formation of H_2O_2. Note that, although wall reactions of H_2O_2 and HO_2 radicals cannot be excluded, no change in the H_2O_2 profile has been encountered when using a reactor of which the walls have been fully covered by an inert coating (SilcoNert, see Supporting Information).

Reactions of HO_2 radicals are the main source of H_2O_2 in this temperature range, and it can be noted that the kinetic parameters of the reactions of $\cdot HO_2$ radicals in this temperature range are very uncertain and that the global reactivity is very sensitive to the H_2O_2 decomposition rate. Improving the modeling of H_2O_2 by revisiting the reactions of $\cdot HO_2$ radicals will inevitably lead to a better prediction of the reactivity.

This work gives the first reliable quantification of hydrogen peroxide formed during the low temperature oxidation of an organic compound. This ability of quantifying H_2O_2 adds a key missing piece to the experimental discovery and validation of the low-temperature oxidation mechanism of organic compounds. This method can be used to gather a database for the formation of this key compound for the development of autoignition for a wide range of hydrocarbons and biofuels, allowing improving detailed kinetic models for the oxidation of organic compound, especially the kinetics of the reactions involving $\cdot HO_2$ radicals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional details about the experimental facility, description of the model used for simulations and supplementary references. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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