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**Hydroperoxides**

# Experimental Confirmation of the Low-Temperature Oxidation Scheme of Alkanes**

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The control of auto-ignition can be used to increase the efficiency of internal combustion engines which has clear potential positive implications for the problem of global warming.[1] The design of internal combustion engines,[2] as well as improved safety in oxidation processes,[3] rely on a good understanding of the kinetic mechanism of the auto-ignition of organic compounds. Here we experimentally demonstrate a key assumption of this mechanism that has been accepted for more than 20 years but never proven.[4–6] A detailed speciation of the hydroperoxides responsible for the gas-phase auto-ignition of organic compounds has been achieved for the first time, thanks to the development of a new system coupling a jet-stirred reactor to a molecular-beam mass spectrometer combined with tunable synchrotron vacuum ultraviolet (SVUV) photoionization. The formation of alkylhydroperoxides (ROOH) and carbonyl compounds having a hydroperoxide function (ketohydroperoxide) has been observed under conditions close to those actually observed before the auto-ignition. This result gives the experimental confirmation of an assumption made in all the detailed kinetic mechanisms developed to model auto-ignition phenomena.

A good understanding of the kinetic mechanism governing the oxidation and the auto-ignition of organic compounds is important in two significant applications: the design of combustion engines and the safety of oxidation processes in the chemical industry (e.g. petrochemistry). Auto-ignition governs many features of the combustion in internal combustion engines (e.g. knock and related phenomena, octane and cetane rating).[2] The potential explosive properties of mixtures of organic compounds with oxygen seldom has catastrophic consequences, but it very often imposes stringent constraints on the operating conditions of partial-oxidation processes.[3]

In addition to their propensity to auto-ignite, mixtures of organic compounds with oxygen possess the following specific reactive features. Single or multiple small temperature pulsations (a few tenths of K) accompanied by weak emission of blue light due to excited formaldehyde, so-called "cool flames",[7] are often observed under conditions preceding those of auto-ignition (usually from 550 K). Closely linked with "cool flames", a zone of temperature (usually around 650 K) where the reactivity decreases with temperature, commonly called "negative temperature coefficient" (NTC) zone, is a second well-known characteristic of these systems.[2,7] These intriguing features have made the gas-phase low-temperature oxidation of organic compounds a fascinating field of investigation for kineticists since the end of the 19th century. It was proven early on that the auto-ignition of hydrocarbons cannot be explained by solely thermal theory,[8] but is mainly a result of free-radical chain reactions.[9] Following Semenov,[9] who proposed the concept of degenerate branched-chain reactions (production of free radicals from products formed in a chain reaction) to explain explosive reactions, much work has been devoted to elucidate the species responsible for degenerate branched-chain reactions during the oxidation of organic compounds.[7]

Scheme 1 presents the current commonly accepted mechanism for the oxidation of hydrocarbons at low temperatures (below 1000 K).[4] After a short initiation period, a hydrocarbon (RH) mainly reacts with a hydroxyl radical ($^{\bullet}$OH) to give an alkyl radical (R$^{\bullet}$) through reaction (1), followed by the formation of alkylperoxy radicals (ROO$^{\bullet}$) after a barrierless reaction with an oxygen molecule (reaction (2)). The existence of the NTC zone is mainly due to the enhanced reversibility of this reaction as the temperature increases. From ambient temperature up to about 550 K, the only prevalent reaction of alkylperoxy radicals is with $^{\bullet}HO_2$ radicals (reaction (3)) or H abstraction from an organic molecule to yield alkylhydroperoxides (ROOH). The fragility of the RO−OH bond of hydroperoxides (the bond dissociation energy is around 43 kcal mol$^{-1}$), which can easily break when the temperature increases, has made them very good candidates as species responsible for the degenerate branched-chain reactions explaining auto-ignition and the occurrence of cool flames.[4,7]

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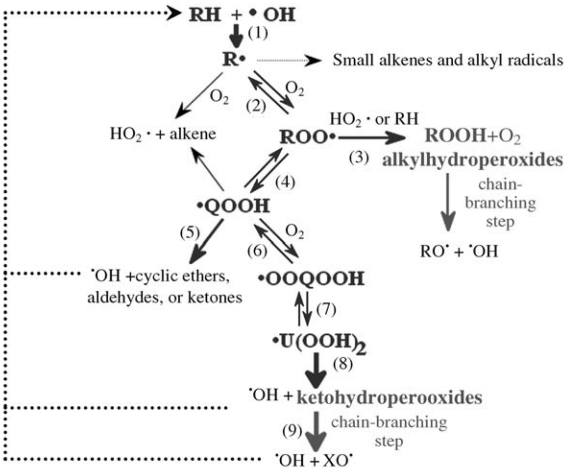


***Scheme 1.*** Simplified scheme of the primary mechanism of oxidation of alkanes at low temperature.

Above 550 K (in the zone of cool flames), a second consumption pathway becomes faster for alkylperoxy radicals: their isomerization (reaction (4)) by internal transfer of a hydrogen atom to give hydroperoxyalkyl radicals (•QOOH). These radicals can easily decompose to yield oxygenated products, amongst which cyclic ethers are the most abundant species (reaction (5)). As cyclic ethers are stable compounds easily analyzed by gas chromatography, the first steps of the oxidation of organic compounds through reactions (1)–(4) (in Scheme 1) are relatively well known.[7]

A second important fate of •QOOH radicals is the second addition to oxygen (reaction (6)). The formation and the reactions of the resulting •OOQOOH radicals have not yet been directly experimentally investigated. However, following Fish,[10] all the detailed kinetic mechanisms developed nowadays to model the low-temperature ignition of organic compounds consider decompositions of •OOQOOH radicals yielding three radicals, amongst them two •OH radicals. Cox and Cole[5] have proposed this global step to occur through the formation of alkylhydroperoxides including a carbonyl group (reaction (8)), mainly ketohydroperoxides, which in turn can easily decompose to give two radicals (reaction (9)) and lead to another possible chain-branching reaction. Many modeling studies have suggested that the direct formation of hydroperoxides by reactions of peroxy radicals was not fast enough and that the inclusion of a chain-branching step deriving from the second addition to oxygen was necessary to satisfactorily simulate the experimental observations.

While several detailed models can now reproduce most features of the oxidation and auto-ignition of alkanes representative of those present in automotive fuels,[6] experimental evidence supporting this commonly used reaction scheme is extremely scarce.[11]

The purpose of this study is to give experimental evidence for the formation of hydroperoxides under conditions similar to those observed prior to the auto-ignition of alkanes and using a method that makes it possible to distinguish between alkylhydroperoxides and ketohydroperoxides. *n*-Butane was studied as it is the smallest alkane with oxidation behavior close to that of the species present in gasoline and diesel fuel.

Minimizing the potential reactions of hydroperoxides between their formation and their detection is possible by creating a molecular beam from a high-pressure reactive zone toward a detection device maintained under vacuum; this results in the "freezing" of the chemical composition of the sampled gas. Since hydroperoxides are expected to be formed in very low amounts along with a large number of other oxidation products, a highly sensitive mass spectrometer with low photon energy to avoid product fragmentation has been used, that is, a time-of-flight mass spectrometer combined with tunable SVUV photoionization. This analytical method has already been used successfully to investigate many reactive systems[12] such as laminar premixed flames.[13,14] Since we must accumulate several scans to obtain good sensitivity, this analysis device must be coupled with a reactive system working under steady conditions. Our purpose was then not to really observe unsteady phenomena, such as cool flames or auto-ignition, but to mimic the chemistry leading to these phenomena. We used a heated jet-stirred reactor. This type of reactor coupled with gas chromatography analyses has already been used many times for studying the low-temperature oxidation of organic compounds.[15,16] In these experiments the presence of a NTC zone was shown and the formation of the same type of products was proved as those actually analyzed prior auto-ignition or during cool flames.[17] Figure 1 presents a simplified scheme of the jet-stirred reactor associating a molecular-beam sampling system to a reflectron time-of-flight mass spectrometer combined with SVUV photoionization.

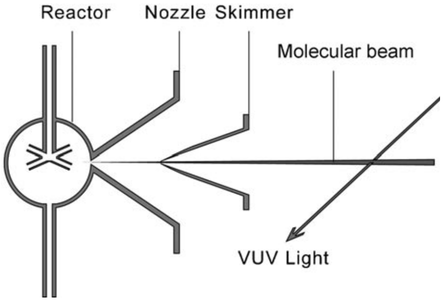


***Figure 1.*** Simplified illustration of the experimental device.

The study of the oxidation of *n*-butane was performed at temperatures between 560 and 720 K, with a mean residence time of 6 s and for an *n*-butane/oxygen/argon mixture composition of 4:26:70 (in mol %), which corresponds to a stoichiometric mixture for the complete combustion reaction.

Figure 2a presents the evolution of the mole fraction of *n*-butane with temperature. The mole fraction of *n*-butane (*m*/*z* 58) was derived directly from the normalized ion signal at *m*/*z* 58 (obtained with a photon energy of 11.0 eV (1 eV = 96.5 kJ mol$^{-1}$)) assuming that no reaction occurred below 590 K. Raw signals of every compound were normalized by the ion signal obtained for argon (*m*/*z* 40) with a photon

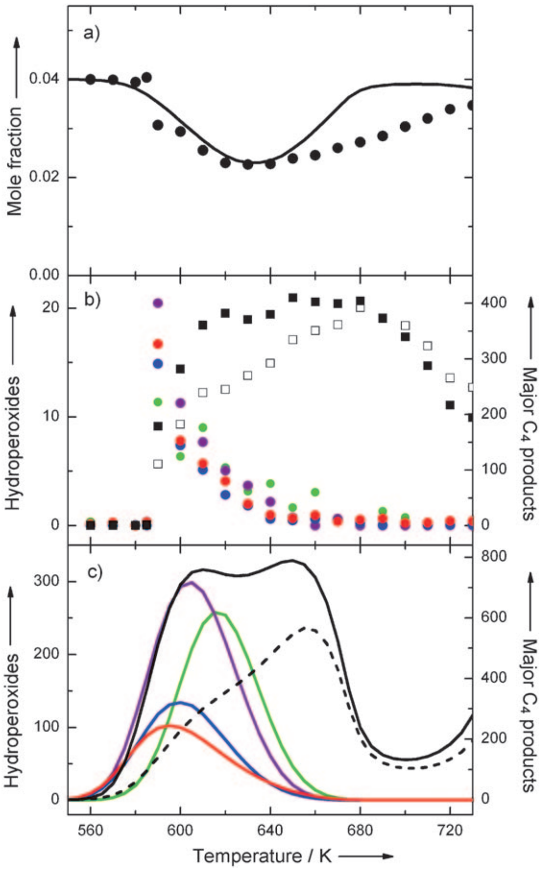


*Figure 2.* Plots of the experimental and simulated mole fractions or signals of the oxidation of *n*-butane, the main products and hydroperoxides with temperature: a) the experimental (black circles) and simulated (line) mole fractions of *n*-butane; b) the experimental ion signals (in arbitrary units) at *m*/*z* 48 (green circles), 56 (white squares, the signal is divided by 7.5), 62 (purple circles), 72 (black squares), 90 (blue circles, the signal is divided by 4) and 104 (red circles); and c) the computed mole fractions (in ppm) of $CH_3OOH$ (green line, mole fraction divided by 5), $C_2H_5OOH$ (purple line), $C_4H_9OOH$ (blue line), the $C_4$ ketohydroperoxides (red line), butenes (dash line, mole fraction divided by 5), and $C_4H_8O$ products (black line).

energy of 16.2 eV which acted as an internal standard. Many products were obtained; the major $C_4$ products were butenes at *m*/*z* 56 and $C_4H_8O$ products at *m*/*z* 72. Figure 2b also displays the normalized ion signal at *m*/*z* 56 and 72 obtained with a photon energy of 10.0 eV to avoid ion fragmentation. The ionization energy (IE) of butenes is between 9.11 and 9.55 eV.[18] The signal at *m*/*z* 72 corresponds to the $C_4H_8O$ oxygenated products which have an IE below 10 eV, for example, butanal, butanone, and all cyclic ethers (except 2-ethyloxirane which has an IE greater than 10 eV).

Note the NTC zone obtained above 630 K (see Figure 2a), which makes the evolution with temperature of the normalized signal of all the products have the same shape as those at *m*/*z* 72 with a kind of "plateau" between 620 and 680 K. This plateau is not observed in the case of species corresponding to four specific masses: 48, 62, 90, and 104 (Figure 2b). For these species, a sharp peak is obtained around 590 K meaning that they are very reactive molecules that decompose very quickly when the temperature increases.

In a system containing only carbon, hydrogen, and oxygen atoms, *m*/*z* 48 can only be related to methylhydroperoxide ($CH_3OOH$). For *m*/*z* 62, 90, and 104, several possibilities exist. However the mass of ethylhydroperoxide ($C_2H_5OOH$) is 62, that of butylhydroperoxides ($C_4H_9OOH$) is 90, and that of $C_4$ ketohydroperoxides ($C_4H_8O_3$) is 104. Figure 3 shows a mass spectrum with signals at *m*/*z* 48, 62, 90, and 104. A substantiation of this identification is given because these four compounds are the only ones having the same particular evolution with temperature, with a sharp peak, characteristic of compounds rapidly decomposing when temperature increases.

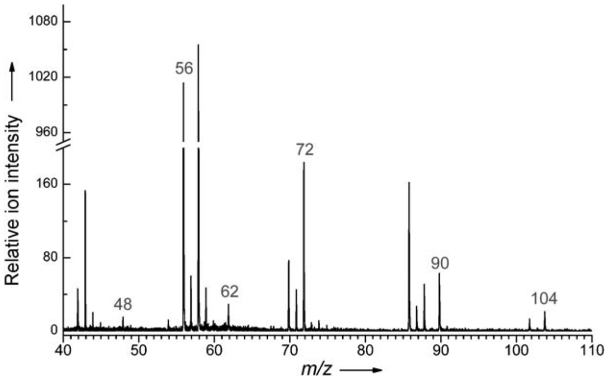
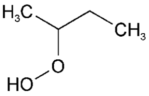
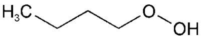
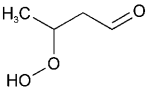
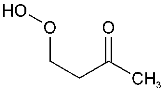


*Figure 3.* Typical mass spectrum obtained for the oxidation of *n*-butane. The temperature in the reactor was 590 K and the photon energy was 10.0 eV.

Additional supporting evidence for this identification relies on IEs from measurements of photoionization efficiency spectra. When such values were not available in the literature,[18] zero-point energy corrected adiabatic IEs have been calculated from the CBS-QB3 method[19] using Gaussian03.[20] An experimental sweeping of photon energies from 8.5 to 11.5 eV has been made. The obtained experimental IEs were 9.91, 9.69, 9.37, and 9.29 ± 0.05 eV for *m*/*z* 48, 62, 90, and 104, respectively (see the Supporting Information). The calculated values for methylhydroperoxide, ethylhydroperoxide, butylhydroperoxides, and $C_4$ ketohydroperoxides were 9.83, 9.61, 9.33–9.36, and 9.34–9.39 eV, respectively. For the last two compounds, a range of energy is given because the calculations were made for all the expected isomers (see Table 1). Note that 1,2-dihydroxyethane, another possibility for *m*/*z* 62, has an ionization energy of 10.16 eV.[18]

Finally, even further substantiation of the proposed assignments is given by simulations performed with a detailed kinetic mechanism of the oxidation of *n*-butane previously proposed[21] (see the Supporting Information). Figure 2a and c show that, while small differences are encountered for the start of the reactivity and the extent of the NTC zone, the model reproduces well the variations of the mole fraction of *n*-butane with temperature, as well as the "plateau" obtained below 680 K for the major products, such as butenes and $C_4H_8O$ compounds. As shown in Figure 2c, simulations reproduce well the particular mole fraction profiles (with a

***Table 1:*** Ionization energies of most expected isomers of $C_4$ hydroperoxides deriving from the oxidation of *n*-butane.

| Mass | Formula | Structure | IE [eV][a] |
|---|---|---|---|
| 90 | $C_4H_9OOH$ |  | 9.33 |
| | |  | 9.36[c] |
| 104[b] | $C_3H_7COOOH$ |  | 9.39 |
| | |  | 9.34 |

[a] When no reference is given the value has been calculated. The mean absolute error of CBS-QB3 for the G2 test is less than 0.05 eV. For hydroperoxides, which can involve hydrogen bonds, lowest energy conformers were searched for a systematic manner. [b] For kinetic reasons, the probability of having two neighboring C atoms each bonded to an oxygen atom is lower. [c] Ref. [18].

sharp peak) obtained for the four hydroperoxides detected in the experiments compared to those of the major products.

This work gives the first speciation of the hydroperoxides formed during the low-temperature oxidation of an organic compound. Further investigations are necessary to connect the structure of the reactant to the type of hydroperoxides obtained. This should help to increase the accuracy of detailed kinetic models of combustion in order to make them really predictive[22] and able to reproduce the formation of minor pollutants, which have a deleterious impact on environment and human health.[23]

## Experimental Section

The utilized spherical quartz jet-stirred reactor (diameter around 5 cm), in which a gas mixture is continuously flowing, was operated at a constant temperature and pressure.[16,24] This type of reactor, which can be heated up to 1200 K, is well suited for kinetic studies: the gas phase inside the reactor is well stirred, meaning the concentrations and temperature are homogenous.[25] Quartz wall effects can usually be considered as negligible. This study has been performed under quasi-atmospheric pressure (1.05 atm). As the type of diluent gas has negligible chemical significance, argon was used instead of nitrogen, for the ease of the mass spectrometric analysis. The coupling between the quartz reactor and the mass spectrometer was made through a quartz conelike nozzle with a 75 μm orifice (the tip of which has been inserted inside the reactor) generating a molecular beam, which was skimmed before the entrance in the spectrometer chamber. In situ detection of intermediates was made possible by combining tunable VUV photoionization and the molecular-beam-sampling mass spectrometer. The produced ions were detected by a reflectron time-of-flight mass spectrometer which can distinguish between different masses.[26]

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