

What do we Really Know about the Low-Temperature Oxidation of Alkanes ?

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Abstract

Due to its importance for engine development, the chemistry related to the low-temperature oxidation of components of fuels has been studied for many years. Several detailed kinetic models giving good predictions of global properties such auto-ignition delay times, as well as satisfactory simulations of detailed product formation, are now available. However the elementary reactions involved in these models and the values of the related kinetic parameters are still based on many assumptions. This paper reviews these assumptions and recent progress made on the elementary reactions important to model alkane low-temperature oxidation, i.e. hydrogen atom abstractions from fuel, the competitive steps involving alkylperoxy radicals (reversible addition of alkyl radicals to oxygen, decompositions yielding a conjugated alkene and a hydroperoxyl radical, internal isomerizations), the formation of cyclic ethers including rings of different sizes, and the sequences of reactions producing and consuming ketohydroperoxides.

Introduction

The chemistry of the low-temperature gas-phase oxidation of fuel components is particularly important in internal combustion engines. This chemistry, which occurs from 500 to about 900 K, is related to anti-knock characteristics which are crucial in spark ignited engines, to auto-ignition properties of importance for the development of newly proposed homogeneous charge compression ignition (HCCI) or low-temperature combustion (LTC) diesel engines [1], and to post-oxidation reactions of the exhaust gases [2].

For long time, several groups around the world have been developing detailed kinetic models for the low-temperature oxidation of fuel components, amongst which alkanes are the most studied molecules [3]. Following the same method as that used to produce their well-known *n*-heptane model [4], the group led by C.K. Westbrook has recently proposed a model including 31400 reactions to model the oxidation of 2-methylalkanes from C₇ to C₂₀ [5]. This model leads to satisfactory predictions, when C₆-C₇ reactants are considered (experimental data are missing to validate models for heavier fuels), of experimental data measured in a rapid compression machine, a shock tube and a jet-stirred reactor.

Considering the large size of the models needed to reproduce low-temperature oxidation of alkanes representative of those present in actual fuels, softwares dedicated to their automatic generation have also been developed [6]. Although it is possible to produce large mechanisms of thousands of reactions by hand (see the examples mentioned above), having a generation system can be more efficient, more systematic and less error-prone. Amongst these softwares, the EXGAS system [7] can generate models for C₃₊ linear and branched alkanes which can lead to satisfactory predictions for both, global parameters such as auto-ignition delay times [8], and the formation of numerous products in jet-stirred reactors [9].

The satisfactory predictions given by literature models under classical experimental conditions deteriorate when studying very rich or weakly diluted mixtures. Also, as noted in [3], it is striking to see the important differences existing between major alkane models of the literature in term of the considered types of elementary steps and the used rate coefficients.

It is then important to examine more deeply the origin of the chemical knowledge used to model the chemistry of alkane low-temperature oxidation. Fig. 1 presents the nowadays commonly accepted mechanism for representing the oxidation of alkanes [3][10].

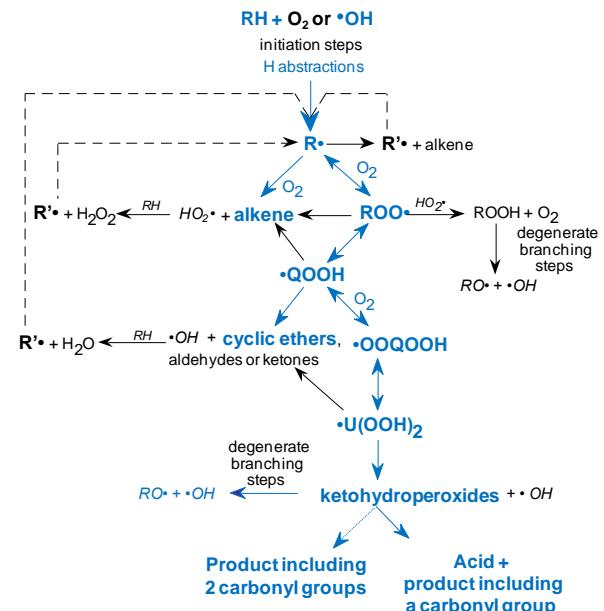


Fig. 1: scheme of the low-temperature oxidation of alkanes (adapted from [3]). The reactions in blue are discussed in this paper.

Fig. 1 shows how, in a few steps, the alkyl radicals ($\text{R}\cdot$) produced from the reactant by hydrogen atom abstractions can yield ketohydroperoxides. The fragility of the RO-OH bond of hydroperoxides, which can

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Proceedings of the European Combustion Meeting 2015

easily break to produce two new radicals, explains the high reactivity of alkanes in air even, at temperature as low as 600 K. The formation of ketohydroperoxydes occurs via the reversible addition of $\text{R}\cdot$ radicals to oxygen molecules followed by isomerizations of the produced peroxy ($\text{ROO}\cdot$) radicals and then a second addition to oxygen molecules followed by a second stage of isomerizations.

This paper reviews some of the involved pathways and kinetic parameters related to hydrogen atom abstractions from reactants, reactions involving peroxy radicals, cyclic ether formation, and reactions producing and consuming ketohydroperoxides, in order to show where additional studies are most needed. Note that while this paper only describes kinetics, accurate thermochemical data determinations are also needed for all the species involved in models.

Hydrogen atom abstractions from reactants

Hydroxyl ($\cdot\text{OH}$) radicals are the main species acting as chain carrier during the low-temperature oxidation of alkanes. Due to the determinant role of these radicals in atmospheric chemistry, there is a huge number of studies in literature concerning the determination of the rate constant of the reactions of $\cdot\text{OH}$ radicals with hydrocarbons close to room temperature [11]. At higher temperatures, the only comprehensive experimental kinetic investigation of this reaction has been performed by Sivaramakrishnan et al. [12-13] in 2009. They have studied nine linear and branched alkanes (from C_3 to C_7) behind reflected shock wave for temperatures up to 1300 K. $\cdot\text{OH}$ radicals were thermally produced from *tert*-butyl hydroperoxide decomposition and detected using multipass absorption at 308 nm. The obtained rate constants (uncertainties > 10%) have been used to derive simple correlations to estimates the kinetic parameters for the various abstraction channels in any large *n*-alkane [13]. However more studies on this important topic can certainly be still valuable.

Hydrogen atom abstractions with radicals, such as hydroperoxy ($\cdot\text{HO}_2$) or $\text{RO}_2\cdot$ radicals, which are present in important concentrations under low-temperature conditions, could also play a role. However, up to now, their rate constants were only obtained from theoretical calculations [14-15] or complex mechanism fitting (e.g. [16]). Direct measurements at moderate temperatures could hopefully be available in a near future for $\cdot\text{HO}_2$ radicals using a technique close to that proposed by Morajkar et al. [17] to study the reaction of $\cdot\text{HO}_2$ radicals with aldehydes.

Reactions Involving Alkylperoxy Radicals

The addition of alkyl radicals to oxygen proceeds through a barrierless addition pathway to form a $\text{RO}_2\cdot$ adduct, which will either be stabilized or further react by “formally direct” (i.e., well-skipping) reaction pathways [10]. The most important of these concurrent pathways is a concerted elimination of $\cdot\text{HO}_2$ radicals to give the conjugated alkene [18]. An accurate representation of the reaction of alkyl radicals with

oxygen requires then parameterizing the rate constants as a function of temperature and pressure. DeSain et al. [19] have combined theoretical calculations with an experimental investigation of the time-resolved formation of $\cdot\text{OH}$ radicals measured by laser-induced fluorescence after pulsed-photolytic initiated oxidation of $\text{C}_2\text{-C}_3$ alkanes. They have then reported kinetic parameters for the different possible channels at different pressures in the case of ethyl and propyl radicals. The quantum mechanically calculated potential energy surfaces published by DeSain et al. [19] for the reactions of *n*-propyl radicals with oxygen molecules is shown in fig. 2. The most important weakness of the nowadays detailed kinetic models for the low-temperature oxidation of alkanes is certainly that similar pressure dependent data are not available for alkyl radicals containing a larger number of carbon atoms. Considering the important influence of the involved pathways [8], this is a key point which has to be solved before more accurate models can be produced.

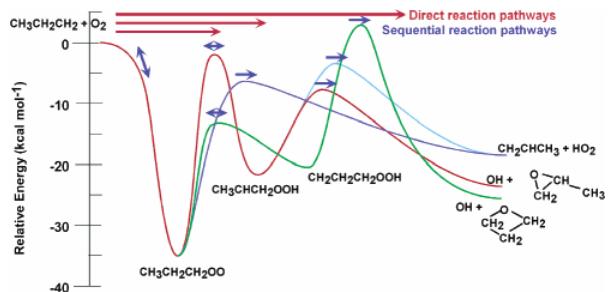


Fig. 2: Schematic potential energy surfaces for the reactions of *n*-propyl radicals with oxygen molecules as calculated by [19] (figure reproduced from [20]).

As mentioned previously, the formation of the conjugated alkene and $\cdot\text{HO}_2$ radicals is an important pathway induced by the $\text{RO}_2\cdot$ adduct. $\cdot\text{HO}_2$ radicals are very unreactive since they mainly cross-react to give H_2O_2 . Their formation pathways, which can almost be considered as termination steps, have a significant influence on global reactivity. First attempts of quantification of these two species under jet-stirred oxidation conditions have been recently made in the case of *n*-butane using spectroscopic techniques, such as continuous cavity ring down spectroscopy (cw-CRDS) which was used to produce the spectra plotted in Fig. 3 [21][22], or Fluorescence Assay by Gas Expansion (FAGE) [23]. The main advantage of using cw-CRDS is that no calibration is needed when the absorption cross section is known. The absorption cross section of H_2O_2 , a stable species difficult to directly calibrate, has been measured in separate experiments, with its concentrations being derived from kinetics measurements on a well-known reaction [21]. FAGE was also used for $\cdot\text{OH}$ radicals quantification attempts [23]. Since spectroscopic methods lead to better selectivity and sensitivity at low temperatures and pressures, species detection are performed after extraction into cells external to the heated reactor.

Losses in the transfer zones (e.g. a probe) between the reactor and the cell have certainly to be accounted, especially in the case of radical quantification.

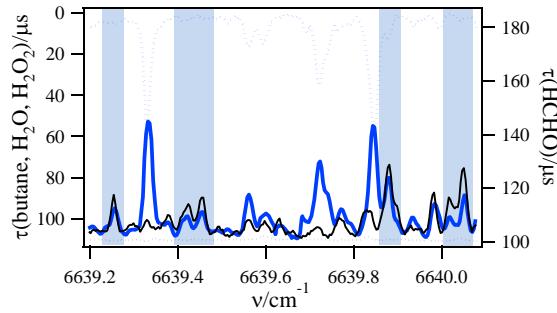


Fig. 3. Typical CRDS spectrum obtained for the oxidation of *n*-butane at 650 K, for stoichiometric mixtures (thick full blue line) compared to the spectrum of $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ mixture (thin full black line), H_2O (thin dotted black line) and HCHO (thin broken blue line, right axis). Shaded area show lines only due to H_2O_2 absorption (figure reproduced from [21]).

Stabilized RO_2^\bullet radicals can easily be produced by laser photolysis of selected precursors and detected by ultraviolet (UV) absorption [24]. This is the reason why several reactions of RO_2^\bullet radicals with other alkylperoxy or with HO_2^\bullet radicals have been for long experimentally investigated, these studies being mostly performed at temperatures close to room temperature [24]. Note that the reaction of RO_2^\bullet and HO_2^\bullet radicals can be a source of hydroperoxydes with a noticeable influence on reactivity when the internal isomerizations of RO_2^\bullet radicals is disfavoured such as in the case of propane oxidation [25]. However the cross-reactions of RO_2^\bullet radicals or their reactions with $\cdot\text{HO}_2$ radicals, for only C₁-C₂ radicals in the last case, have not been investigated above 573 K [24], because at higher temperatures isomerizations are the predominant fate of alkylperoxy radicals.

Internal isomerizations of RO_2^\bullet radicals yielding alkylhydroperoxy ($\cdot\text{QOOH}$) radicals involve the formation of cyclic transition states with different possible ring sizes (see in fig. 4 an isomerization via a 5 membered ring cyclic transition state). Only isomerizations through 5, 6, 7 and 8 membered ring cyclic transition states are considered in detailed kinetic models [3]. In 1982, the first values for the rate parameters of a whole series of isomerizations of peroxy radicals were obtained by Baldwin et al. [26] by studying the chemistry associated with neopentylperoxy radicals when *neo*-pentane is added to slowly reacting mixtures of $\text{H}_2 + \text{O}_2$. Hughes et al. [27] have later studied the isomerization of neopentylperoxy radicals between 660 and 750 K using the laser flash photolysis/laser induced fluorescence technique and rescaled the values of Baldwin et al. by using a more accurate value for the equilibrium constant of the addition of alkyl radicals with oxygen [27].

In the few last years, a large effort to calculate the related high-pressure limiting rate parameters has been undertaken by several teams [28-31]. First methods of

quantum mechanics (e.g. CBS-QB3 [32]) are used to estimate thermochemical properties by the Gaussian suite of programs [33]. Then transition state theory allows rate constants to be derived. This approach is of great value to replace the previous estimates of rate constant by approximations and correlations, which are still mostly used in recent literature models [5][9]. However the largest deviation between these calculated values [28-31] can be up to a factor of 4 at 700 K, as is shown in fig. 4. This uncertainty in theoretical values can have significant impact on low-temperature oxidation modeling. However an increase of this accuracy can be expected from continuous progress made in theoretical methods. Note that more accurate experimental determinations of the related rate constants are complicated by formally direct reactions and by the current lack of detection of the ephemeral $\cdot\text{QOOH}$ radicals which readily further react [20].

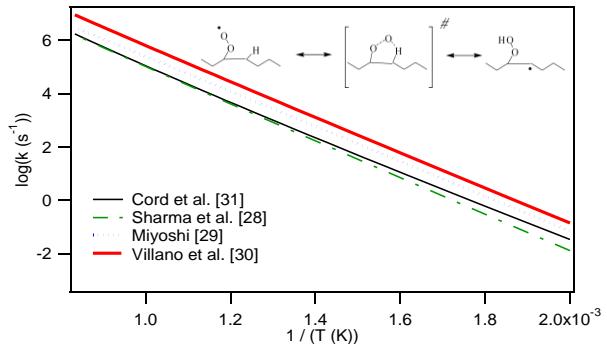


Fig. 4. Comparison between the rate constants theoretically calculated by different groups for the isomerizations involving the transfer of a secondary H-atom with a cyclic transition state with a ring including 5 atoms.

Formation of cyclic ethers with different ring sizes

One of the well-known important fate of $\cdot\text{QOOH}$ radicals is their decomposition to yield cyclic ethers and $\cdot\text{OH}$ radicals [26]. In order to facilitate the identification of these important oxidation products of which the mass spectra are not easily available, Herbinet et al. [34] have studied the formation of three to six membered ring cyclic ethers produced during the oxidation of seven linear alkanes from C₅ to C₁₆ in a jet-stirred reactor. These authors have provided the electron impact mass spectrum of all the detected species and proposed rules about their ion fragmentation.

The only direct measurement of the related rate constant can be found for the formation of a 4 membered ring (oxetane) from the *neo*-pentane study by Baldwin et al. [26]. Recent calculations of the related rate parameters using quantum mechanic methods can also be found [29-31] with slightly more important deviations between the calculations made by different groups than in the case of isomerizations. While cyclic ether formation can also be due to a formally direct pathway from the RO_2^\bullet adduct, the fraction of ethers obtained through this channel seems to be significantly more limited than that of conjugated alkenes [35].

Experimental results such as those recently published by Rotavera et al. [18] for the cyclic ether formation arising from $\text{RO}_2\cdot$ radicals produced by the photolytically initiated oxidation of 2,5-dimethylhexane and detected by multiplexed photoionization mass spectrometry are certainly useful for confirming the trends in the rate constants theoretically calculated for $\text{RO}_2\cdot$ radicals isomerizations and cyclic ether formations.

Recently, rate constants theoretically calculated for $\text{RO}_2\cdot$ radicals isomerizations and cyclic ether formations [31] have been used in a model generated by software EXGAS [8], instead of the automatically generated values. Using also theoretically up-dated thermochemical values for the related species [31], this rate constant change has allowed a noticeable improvement in the prediction of the detailed formation of these cyclic species, three oxiranes (3 membered ring), two oxetanes, two furanes (5 membered ring), and an oxirane (6 membered ring), during the oxidation of *n*-hexane. This improved cyclic ether prediction is presented in fig. 4 [36].

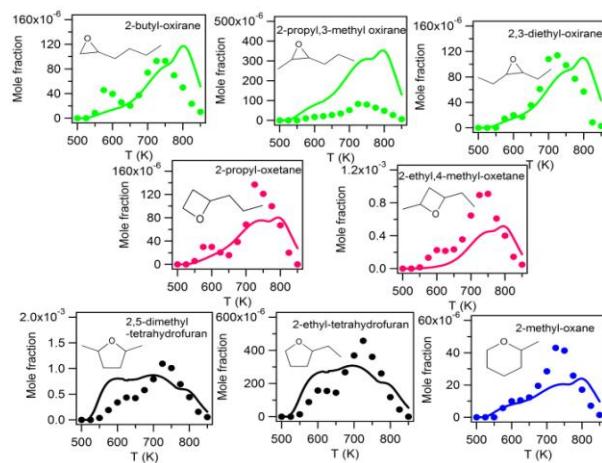


Fig. 5. Comparison between modeling and experiments for the formation of cyclic ethers with six carbon atoms during *n*-hexane oxidation in a jet-stirred reactor (800 Torr, stoichiometric mixtures, residence time = 6 s, initial *n*-hexane mole fraction = 0.02, gas chromatographic analysis; adapted from [36]).

Reactions Producing and Consuming Ketohydroperoxides

As is shown in fig.1, $\bullet\text{QOOH}$ radicals can also add to another oxygen molecule and lead to ketohydroperoxides by the most obscure part of the alkane oxidation mechanism. This involves isomerization of the obtained peroxyalkylhydroperoxy ($\bullet\text{OOQOOH}$) radicals, followed by decomposition. The rate constants of all the involved reactions are still less known than for $\text{RO}_2\cdot$ and $\bullet\text{QOOH}$ radicals.

The detection of ketohydroperoxides has only very recently been investigated under well-defined gas-phase conditions. In 2010, thanks to the coupling of a quartz jet-stirred reactor to a synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS)

through a molecular beam sampling, ketohydroperoxides have been detected under conditions close to those observed before auto-ignition during *n*-butane oxidation [37]. In 2015, the time-resolved formation of ketohydroperoxides has been investigated from $\text{RO}_2\cdot$ radicals produced by photolytically initiated oxidation of *n*-butane using a time-of-flight mass spectrometer with tunable synchrotron radiation [38]. The photoionization spectra at $m/z = 104$ (corresponding to C_4 ketohydroperoxide m/z) obtained by sweeping photon energy are given in fig. 6 for both types of experiments. Both spectra are similar, showing that the same isomer is formed in thermal or photolysis experiments whatever pressure.

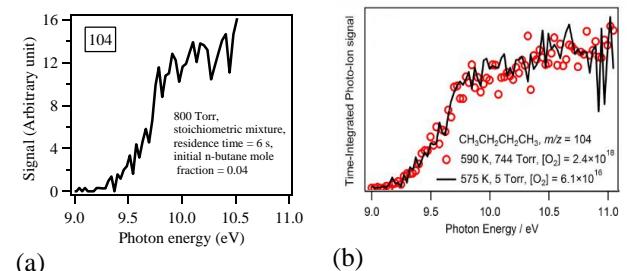


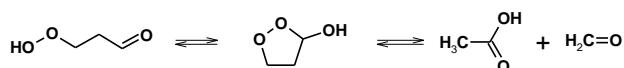
Fig. 6. Experimental photoionization spectrum of the $m/z = 104$ product obtained during *n*-butane oxidation in (a) thermal [37] or (b) photolysis [38] reactors.

The experimental ionization energy of the species at $m/z = 104$ was 9.29 ± 0.05 eV in good agreement with theoretically calculated (CBS-QB3 method) values for two most expected C_4 ketohydroperoxides (9.34-9.39 eV) [37]. By a clever use of deuterated species, Eskola et al. [38] concluded that 3-hydroperoxybutanal was the sole ketohydroperoxide that was observed under their studied conditions.

Ketohydroperoxides have also been detected from jet-stirred reactor oxidation of *n*-heptane [9], as well as from that of linear and branched isomers of hexane [39]. While ketohydroperoxide formation could not be seen during propane oxidation [25], propylhydroperoxides were detected. This was also the case during *n*-butane oxidation [37], but not when $\text{C}_6\text{-C}_7$ reactants were used [39][9]. This is explained by the fact that the possible isomerizations of $\text{C}_3\text{-C}_4$ $\text{RO}_2\cdot$ radicals involve tight cyclic transition states and are more difficult for larger reactants. This involves a noticeable contribution of the reaction between $\text{RO}_2\cdot$ and $\text{HO}_2\cdot$ radicals yielding alkyhydroperoxides. Ketohydroperoxide quantification remains a problem, since their photoionization cross-sections are unknown and certainly not easy to measure.

Until very recently, the only fate considered for ketohydroperoxides was their decomposition to give $\bullet\text{OH}$ and alkoxy ($\text{RO}\cdot$) radicals. The rate constant usually used is that proposed by Sahetchian et al. [40] from hydroperoxide pyrolysis experiments indicating significant pressure dependence. The coupling of SVUV-PIMS with jet-stirred reactor [37] has allowed contemplating two new types of species to be attributed to further reactions of ketohydroperoxides:

(a) Important monocarboxylic acid formation has then been observed, especially acetic acid [9][39]. Through theoretical calculations, Jalan et al. [41] have identified the possible formation from ketohydroperoxides of a cyclic peroxide isomer that decomposes via novel concerted reactions into carbonyl and carboxylic acid products:



These authors also proposed a high-pressure limit rate constant for this new channel. Using detailed kinetic mechanisms, the team of E. Ranzi [42-43] has shown that adding this new channel improved notably the prediction of acid formation measured during jet-stirred reactor oxidation of propane [25], *n*-butane [44] and *n*-heptane [9]. According to their flow rate analysis for *n*-heptane [42], this channel accounts for 30% and 5% of ketohydroperoxides consumption at 550 and 650 K respectively.

(b) The other type of unusual oxidation products identified from the combination of SVUV-PIMS with jet-stirred reactor [9][39][44] concerns species of the same size as the alkane reactant and including two carbonyl groups, which are named hereafter diones. These products were only spotted during the oxidation of alkanes yielding also ketohydroperoxides. As is shown in figure 7, the signals related to diones are significant signals when compared to those of other important oxidation products, for example cyclic ethers.

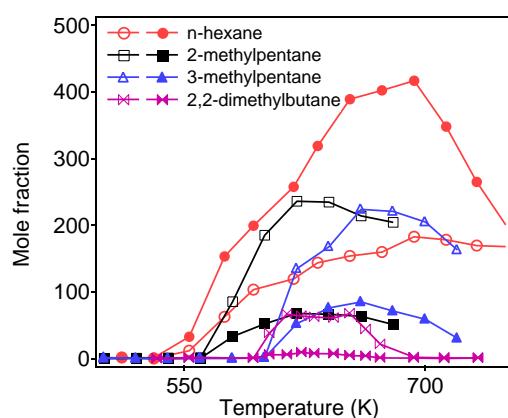


Fig. 7. Signal evolution with temperature at m/z 100 (open symbols) and m/z 114 (full symbols) corresponding to cyclic ethers and diones, respectively. These were obtained by SVUV-PIMS during *n*-hexane oxidation in a jet-stirred reactor (800 Torr, stoichiometric mixtures, residence time = 6 s, initial *n*-hexane mole fraction = 0.02; adapted from [39]).

The structure of diones, which was postulated from comparisons between their experimental ionization energies and theoretical calculations [9][39][44], let to think that they derive from ketohydroperoxides. However the channels proposed in models for their formation have not yet given satisfactory predictions:

- During their work on *n*-heptane oxidation, Herbinet et al. [9] have proposed reactions of alkoxy radicals with O_2 , as well as a direct water elimination from ketohydroperoxides with a theoretically (CBS-QB3 method) calculated rate constant. While the good shape of the evolution with temperature was obtained, the estimated dione mole fraction was underestimated by a factor of 40. Note that, during *n*-heptane JSR oxidation, diones could also be analyzed by gas chromatography, but with certainly an important uncertainty [9].

- Pelucchi et al. [42] have considered hydrogen atom abstractions from ketohydroperoxides to produce radicals, which, as it was demonstrated by theoretical calculations, decompose readily to form diones and $\cdot\text{OH}$ radicals [43]. Models including this sequence of reactions can predict the estimated maximum dione mole fraction [42-43]. However the shape of the evolution with temperature of the related signal was not satisfactorily modeled. Profiles with a sharp peak were predicted, as was experimentally observed for the ketohydroperoxide signal evolution [37]. Experimental dione signal evolutions display wide peaks, with even a kind of plateau, as is shown in fig. 7. More investigations are certainly needed to better understand the chemistry deriving from ketohydroperoxide and especially to unravel the dione formation pathways.

Conclusion

This paper has summarized the actual knowledge on the chemical kinetics considered in alkane low-temperature oxidation. It has shown that related reactions and rate parameters are surprisingly far from being as well-known as it could be expected from literature model performances in predicting laboratory results. If models based on this chemistry are to be used for the development of compression engines in a priori predictive way under extended operation condition ranges, substantial work is certainly still needed in this field. This should aim at improving the accuracy in the rate parameters involved in RO_2^\bullet and $\cdot\text{OOH}$ radical reactions, and at better understanding the chemistry explaining ketohydroperoxide formation and consumption.

Still more is unknown concerning the chemistry of fuel component molecules including a double bond, an oxygen atom or a cycle. The worst case is certainly alkenes, for which there are additional shadow zones on the chemistry involved by radical addition to the double bond or by the formation and consumption of resonance stabilized allylic radicals.

Acknowledgements

The author wishes to thank her many collaborators who are all named in the original publications addressed in this paper, as well as Christa Fittschen, Elizeo Ranzi, Katharina Kohse-Höinghaus, Charlie Westbrook, and all the colleagues of the KinCom team of LRGP for helpful discussions.

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