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DETAILED CHEMICAL KINETIC MODELS FOR THE LOW TEMPERATURE COMBUSTION OF HYDROCARBONS WITH APPLICATION TO GASOLINE AND DIESEL FUEL SURROGATES

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ABSTRACT

This paper presents a review of gas-phase detailed kinetic models developed to simulate the low temperature oxidation and autoignition of gasoline and diesel fuel components (alkanes, ethers, esters, alkenes, cycloalkanes, aromatics, including from 4 atoms of carbon) and of mixtures of several of them, which have been proposed as surrogates. The recently proposed models are summarized, as well as the experimental results available for their validation. A comparison between the major models in terms of considered elementary steps and associated rate constants is also proposed.

Keywords: [Detailed kinetic model], [combustion], [autoignition], [low temperature oxidation], [gasoline], [diesel fuel], [bio-fuel], [surrogate].

NOMENCLATURE

CV: closed vessel

DIPE: di-isopropyl-ether

ETBE: ethyl-tert-butyl-ether

FR: flow reactor

HCCI: homogeneous charge compression ignition

JSR: jet stirred reactor

k: rate constant, $k = A\ T^n \exp(-Ea/RT)$

MON: motor octane number

MTBE: methyl-tert-butyl-ether

NTC: negative temperature coefficient

P: pressure

P_c: pressure after compression in a RCM

PRF: primary reference fuels, i.e. n-heptane and iso-octane (1,2,4-trimethylpentane)

R: gas constant

RCM: rapid compression machine

RON: research octane number

ST: shock tube

T: temperature

T_c: temperature after compression in a rapid compression machine

TAME: tert-amyl-methyl-ether

ϕ: equivalence ratio, i.e. for the reaction

$C_nH_m + (n+m/4)\ O_2 \rightarrow n\ CO_2 + m/2\ H_2O$,

$$\phi = \frac{\left(\frac{\%C_nH_m}{\%O_2}\right)}{\left(\frac{\%C_nH_m}{\%O_2}\right)_{\text{stoichiométric}}} = \frac{\left(\frac{\%C_nH_m}{\%O_2}\right)}{\frac{1}{n+m/4}}$$

τ: residence time (space time) in a JSR

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1/ INTRODUCTION

As reviewed by Westbrook et al. [1] computer simulation of a wide range of phenomena in internal combustion engines has been a particularly fertile research area over the past 30 years. From the chemical point of view, the understanding of knock phenomena and the search for anti-knock additives for fuels used in spark ignition engines [2-4], the modelling of the formation of soot in diesel engines [5-6], the recent development of HCCI (Homogeneous Charge Compression Ignition) engines [7] and the reduction of the emission of toxic gas or pollutants (CO, NOx, aldehydes, dienes…) in every type of engine have led to an increasing need for the development of kinetic models. More and more sophisticated detailed chemical kinetic models, based on a large number of elementary reactions, have thus been proposed and for a large and widening variety of model fuels.

The need to develop more efficient, but cleaner, engines and fuels is of increasing importance for the automotive and oil industries. Car usage has a significant impact on climate change, with about 12% of the overall EU emissions of carbon dioxide (CO2), the main greenhouse gas, coming from the fuel consumed by passenger cars [8]. Regulations have been proposed to reduce the emission of this gas from the fuel consumed by combustion engine vehicles. In Europe, the target to be achieved by 2012 is 120 g CO_2/km for the average new car fleet [8]. The expected dramatic world-wide increase in the number of combustion engine vehicles (compared to 2000, the number of vehicles could more than double by 2050 [9]) is another reason to promote energy conservation efforts. However a shortage of oil is not foreseen within the next two or three decades, because new oil sources continue to be found and the emergence of better oil field technology enables more oil to be recovered from existing oil wells [9].

Figure 1 illustrates well the importance of tailored detailed kinetics to model the

combustion in HCCI engines. Pressure curves have been computed by 3D simulations coupled with detailed kinetic models by means of look-up tables for diesel and HCCI engines using two model fuels of n-heptane and a n-decane/α-methylnaphthalene mixture [10]. In the case of diesel engine, only small differences were observed in the autoignition and remaining combustion processes between both model fuels, while in the case of HCCI engine, the same autoignition delay is predicted with both model fuels, but the pressure rise after ignition is slower for the mixture indicating a lower heat release rate.

FIGURE 1

While gasoline and diesel fuel have a "near-continuous spectrum" of hydrocarbon constituents, surrogates composed of a limited number of components have to be defined in order to develop detailed kinetic models. The limitation in the number of components in surrogates is mainly due to the present availability of detailed kinetic models, but should further persist in order to avoid an explosion of the size of the models. This limitation prevents surrogates reproducing the "near-continuous spectrum" of components in fuels and could induce misleading or inaccurate predicted results. Table 1 presents the composition of a typical European gasoline and shows that its constituents can be divided in six families, each having a carbon number ranging mainly from 4 to 10; they are linear alkanes (n-paraffins), branched alkanes (iso-paraffins), ethers, cyclic alkanes (naphtenes), alkenes (olefins) and aromatic compounds. In the USA, gasolines contain more branched alkanes (~ 45 %) and ethers (~ 11 %), but less alkenes (~ 5 %) and aromatic compounds (~ 30 %) [11]. An example of typical diesel fuel is composed of 30.9 % paraffins, 23.7 % alkylcyclohexanes, 15.1 % alkyldecalines, 9.2 % alkylbenzenes and 19.25 % polycyclic naphtenoaromatic compounds, with constituents containing from 10 to 20 atoms of carbon [11].

TABLE 1

Environmental concerns have led to the increased interest in the future use of fuels, containing a larger fraction of components which have been derived from biomass, such as alcohols (mainly ethanol) in gasoline and methyl or ethyl esters in biodiesel [12-13]. It should be mentioned that the presence of additional oxygenated compounds could reduce the formation of soot in diesel engines [14], but may also promote the formation of some toxic pollutants, such as aldehydes [15-16]. While full life-cycle analyses in order to quantify the extent to which liquid biofuels reduce the impact on global climate are yet to be made [17], methyl and ethyl esters is the seventh family of fuel components, which needs to be taken into account in detailed kinetic models.

The purpose of this review is to analyse the gas-phase detailed kinetic models which have been recently developed to model the oxidation and autoignition of the components of the seven families and of mixtures of several of them, which have been proposed as surrogates. In order to address compounds which are actually representative of those included in gasoline and diesel fuel, only those containing more than four atoms of carbon will be considered. Furthermore, in order to study conditions which are close to those observed in engines, only models which have been tailored to reproduce phenomena occurring at relatively low temperature, i.e. below 900-1000 K, will be reviewed. A more comprehensive and well documented review of detailed chemical kinetic models for the intermediate to high-temperature oxidation, ignition and combustion of alkanes, cycloalkanes, alkenes and aromatic compounds has been recently published by Simmie [18].

The chemistry of nitrogen containing compounds is out of the scope of this review and the kinetic models considering the effect of NOx on combustion [19-22] will not be considered here, despite their interest for the development of HCCI engines by using exhaust gas recirculation (EGR).

As the chemistry of the oxidation of ethers and esters is usually treated using rules very close to those considered for alkanes, this review contains only five sections, (linear and branched) alkanes, ethers and (methyl and ethyl) esters, alkenes, cycloalkanes, aromatic compounds and application to surrogate mixtures. Each section is structured with the following, when relevant:

- A summary of the main chemical features concerning the oxidation of these compounds.
- A short description of the low temperature models recently proposed, as well as the experimental results available for their validation; only experimental data obtained in a system which can be modelled with a simple physical model and post 1993 studies will be taken into account. Previous models and experimental data have been comprehensively reviewed by Griffiths in 1995 [23].
- A comparison between the major models in terms of considered elementary steps and associated rate constants; only the steps important at low temperature will be reviewed.

The operating conditions for validating a model depend on the sought objectives of the application and the quality of this validation is a function of the amount of experimental data available for comparison with simulations. The comparison between low temperature mechanisms is made possible by the fact that they are based on a limited number of classes of elementary steps. The number of available low temperature mechanisms is also much smaller than that of high temperature mechanisms due to the need to consider many more species and reactions at low temperature. Table 2 presents a comparison between the sizes of low and high temperature mechanisms of several alkanes [24][1]. It shows that this difference increases strongly with the number of atoms of carbon included in the reactant.

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[1] Only addresses of web sites from which models, thermochemical data or software can be obtained are given in references.

TABLE 2

Despite being of great importance to ensure the consistency between the rate parameters of a direct and reverse elementary reaction and to estimate the heat release rate, the thermodynamic properties, enthalpies of formation, entropies and heat capacities, used by the different models will not be reviewed here. In most models, the thermodynamic properties for all the species, for which there were no available data in the literature (e.g. [25-26]), were calculated by softwares such as THERM [27] or THERGAS [28] using group additivity rules developed by Benson [29].

The models able to simulate the low temperature oxidation phenomena consider also the typical classes of reactions of high temperature mechanisms [30]. As it is difficult to define classes of elementary steps for reactions involving very small or multi-unsaturated compounds, most detailed mechanisms for the oxidation of hydrocarbons containing more than four atoms of carbon also include a sub-mechanism containing the reactions of smaller species. The development of detailed kinetic models for species representative of components of gasoline and diesel fuel has thus been made possible by the knowledge base which has been previously gained concerning the reactions of light hydrocarbons. Particularly valuable work has been undertaken for two decades by Tsang [31-35] and by Baulch et al. [36-38], who have compiled and evaluated the rate constants of elementary steps important to the oxidation of species containing up to 4 atoms of carbon. The rate constants of the reactions of small species often depend more greatly on pressure and the formalism proposed by Troe [39] has allowed this pressure dependence to be easily taken into account in models. Nevertheless, as reviewed by Simmie [18], the major models [40-43] developed to reproduce the oxidation of methane have been validated against a large spectrum of experiments (species profiles and ignition delay times in shock waves, laminar flame species profiles, laminar flame speeds, temperature and stable species

concentration profiles in flow reactors), but only at temperatures above 900 K and large uncertainties still remain on the reactions and rate constants which are used at lower temperature.

The development of the software library of CHEMKIN [44], which can be used to model a wide range of reactors, has also contributed to the increased development of kinetic models. The CHEMKIN input data format has become a standard for describing the reactions, rate parameters, thermodynamic data and transport properties of species, and so this has favoured the exchange of models between kineticists.

2/ ALKANES, ETHERS AND (METHYL AND ETHYL) ESTERS

As noticed by Simmie [18], alkanes are by far the best studied class of compounds for which reliable and detailed chemical kinetic models for combustion exist. That explains why the search for correlations between fuel chemical structure and octane number rating in spark-ignition engines has mostly been done for alkanes and why n-heptane was often considered as a serviceable surrogate of diesel fuel [1].

2.1/ Main chemical features of their oxidation

The first low temperature reaction channels for the oxidation of alkanes were proposed by Knox in 1967 [45] and by Fish in 1968 [46]. The understanding of this mechanism was then improved successively by Pollard [47], Cox and Cole [48] and Walker and Morley [49]. Figure 2 shows a simplified scheme of the main reactions, which are now usually admitted to model the oxidation of an alkane (RH). Except at very high temperature (above 1200 K), the reaction is initiated by the H-abstraction from the alkane by oxygen molecules to give alkyl (•R) and hydroperoxy (•OOH) radicals. At low temperature (around 500-600 K), alkyl radicals react rapidly with oxygen molecules to give peroxyalkyl radicals (ROO•) which can by several reactions as shown in figure 2, lead to the formation of peroxide species and small radicals which

react with alkane molecules by metatheses to regenerate alkyl radicals. The propagation of the reaction is a chain reaction, in which hydroxyl radicals (•OH) are the main chain carriers.

FIGURE 2

The formation of peroxides is extremely important, because they include an O-OH bond, which can easily be broken and lead to the formation of two radicals, which can in their turn react with alkane molecules to give alkyl radicals. These degenerate branching steps involve a multiplication of the numbers of radicals, which in a chain reaction induces an exponential acceleration of reaction rates leading in some conditions to spontaneous autoignition. The reversibility of the addition of alkyl radicals to oxygen molecules (reaction (1) in figure 2), when the temperature increases to the benefit of the formation of alkenes (reaction (2)), leads to a reduction of the overall reaction rate and is the main cause of the appearance of the negative temperature coefficient (NTC) regime. This distinctive feature of the oxidation of hydrocarbons signifies a zone of temperature in which the global rate of the reaction decreases with temperature.

The existence of the NTC zone explains another specificity of the oxidation of alkanes - the possible occurrence of cool flame phenomenon at temperatures several hundred degrees below the minimum autoignition temperature. During a cool flame, or multiple cool flames, the temperature and the pressure increase strongly over a limited temperature range (typically up to 500 K), but the reaction stops before combustion is complete due to the decrease in reactivity in the NTC zone. Cool flames play an important part in spontaneous phenomena as they are the first stage of two stage ignition [50].

The competition between the channels leading to peroxide species and those producing less reactive products, such as alkenes or cyclic ethers, accounts for (at least in part) why the reactivity of alkanes decreases when the level of branching of the molecule increases and

increases when the length of the included linear chain increases, as shown by the octane numbers (RON and MON)[1] given in Table 2 for some alkanes.

With further increase in temperature, other reactions (such as $H_2O_2 \rightarrow 2OH\bullet$ and $H\bullet + O_2 \rightarrow \bullet OH + \bullet O\bullet$) ensure the multiplication of the number of radicals and are responsible for the propagation of combustion in spark ignited engines and for autoignition in diesel engines. Above 900-1000 K, reaction (3), the decomposition to give a smaller alkyl radical and a 1-alkene molecule is the preponderant fate of most alkyl radicals containing more than three atoms of carbon. H-abstractions followed by isomerizations and successive decompositions of alkyl radicals until the relatively well-known chemistry of C_1-C_2 species [18] is reached, constitute the high temperature mechanism as first proposed by Westbrook and Dryer [51] and by Warnatz [52].

Due to their low reactivity (RON usually above 100 [11]), C_5-C_6 ethers (e.g. methyl tert-butyl ether (MTBE), tert-amyl-methyl ether (1,1-Dimethylpropyl methyl ether, TAME), ethyl tert-butyl ether (ETBE) or di-isopropyl-ether (DIPE)) have been proposed as octane improvers in gasolines. The chemistry of the oxidation of saturated branched ethers seems to be very close to that of alkanes, as shown by the mechanistic studies of the oxidation of MTBE, ETBE and TAME made by the team of Baronnet [53-54] and the modelling study of the oxidation of dimethyl ether (DME) made by the team of Dryer [55-56]. The only specificity of ethers is a molecular reaction involving the transfer of a H-atom bound to an atom of carbon in β position of the atom of oxygen to give an alcohol molecule and an alkyl radical as proposed by Choo et al. [57]. This molecular reaction was proven to be very sensitive to wall effects [58]. The presence of an atom of oxygen also favors the decomposition of radicals derived from ethers,

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[1] Research Octane Number (RON) or Motor Octane Number (MON) are octane ratings depending on the used experimental method and measure of how resistant gasoline is to auto-ignition (knocking).

which occurs at a lower temperature than in the case of alkanes. This easier decomposition, as well as the molecular reaction, produces alkenes, such as iso-butene, that have a strong inhibiting effect, lowering the possibility of formation of hydroperoxide species and which explains the lower reactivity of these compounds [53].

Fuels derived from renewable agricultural fats and oils have the potential to supplant a fraction of petroleum products in diesel engines combustion [13]. Vegetal oils mainly include triglycerides (98%), with small amounts of mono and diglycerides. The fatty acid composition of rapeseed oil, which is of importance in Europe, is 64.4% of oleic (C18:1 monounsaturated), 22.3% linoleic (C18:2 omega-6 polyunsaturated), 8.2% alpha-linolenic (C18:3 omega-3 polyunsaturated), 3.5% palmitic (C16:0 saturated) and 0.9% stearic (C18:0 saturated) acids [59]. Methyl or ethyl esters can be obtained from vegetal oils through a catalytic transesterification reaction with methanol or ethanol, respectively [13]. Comparing results obtained in static reactors at subatmospheric pressures by previous authors, Baronnet and Brocard [60] have noticed that the cool flame behaviour of C_2-C_5 esters strongly depends on their structure. While they are observed for all ethyl esters, cool flames can only be obtained for methyl esters containing at least five atoms of carbon. More recently, Dagaut et al. [61] have shown that n-hexadecane could be a good surrogate model fuel for the oxidation of rapeseed oil methyl ester in a jet-stirred reactor at temperatures between 900 and 1200 K, atmospheric pressure and equivalence ratios from 0.25 to 1.5.

2.2/ Detailed chemical models of low temperature oxidation

It is possible to distinguish two types of mechanism, those of computer aided generation and those which have been manually developed.

2.2.a/ Mechanisms written without computer help

A significant milestone in the modelling of low temperature oxidation of large alkanes

was the appearance in 1975 of the Shell model developed by Halstead et al. [62]. This generalized model was based on formal reactions including initiation, chain propagation, degenerate branching and termination steps, with kinetic parameters fitted empirically. Following this, progress was made in the development of a priori reduced mechanisms (to be distinguished from a posteriori reduced mechanisms obtained by reduction techniques from detailed mechanisms), including elementary steps, but involving globalized species (alkanes were represented by RH, all alkyl radicals by "R•", all peroxy radicals by "ROO•"…) such as the models of Cox and Cole [48], Hu and Keck [63] and the unified one of Griffiths et al. [23]. This last model was particularly well detailed for a reduced model, as it distinguished the different types of alkyl radicals and of isomerizations of peroxy radicals. The model of Hu and Keck [63] has been recently extended by Tanaka et al. [64] to produce a model that included 32 species and 55 reactions with a good prediction of the major autoignition features of n-heptane, iso-octane and mixtures. The development of the older reduced models has greatly helped the writing of the below-described detailed kinetic models.

Since their pioneering detailed modelling of the oxidation of n-butane at low and intermediate temperatures in 1988 [65], the team of Westbrook and Pitz in Livermore has performed an impressive work concerning the modelling of the oxidation and the autoignition of alkanes at low temperature. They have studied isomers of pentane [66-68] and hexane [69], but the largest progress was made for n-heptane [70], iso-octane [70] and the isomers of heptane [72], the mechanisms of which were developed in a systematical way using well-defined classes of reactions. This approach is very close to that of computer aided generation. These mechanisms were built in a stepwise fashion starting with small hydrocarbons and progressing to larger ones. That explains the very large size of these mechanisms: that for n-heptane includes 2450 reactions among 550 chemical and that of iso-octane involves 3600 reactions among 860

species. The Livermore group has also been the first to propose a detailed modelling of the low temperature oxidation of two methyl esters, methyl formate and methyl butanoate [73]. Some qualitative agreement was observed when simulating experimental data obtained in closed vessels at subatmospheric pressure [74-75], but computations consistently indicated an overall reactivity higher by a factor of 10 to 50 compared to experiments.

Several mechanisms that cannot be analyzed in terms of classes of reactions have also be proposed. A mechanism for n-butane has been written by Kojima [76] and one for n-pentane by Ribaucour et al. [77]. Concerning ethers, modelling of the oxidation of TAME, ETBE and MTBE has been published by Böhm et al. [78-79]. In the case of esters, a mechanism of the oxidation of methyl butanoate has been proposed by Gaïl et al. [80] with validation over a wide range of operating conditions, from temperatures of 500 K. In light of the scarcity of models concerning this class of compounds, let us also quote the mechanisms developed by Metcalfe et al. [81] for the high temperature oxidation of methyl butanoate and ethyl propanoate with validation using their shock tube data obtained at temperatures between 1100 and 1670 K.

2.2.b/ Computer aided mechanism generation

The large number of reactions involved in low temperature oxidation mechanisms, with primary reactants of increased size, has led several teams to develop an approach based on an automatic generation of reactions. More details on automatic generation of mechanisms can be found in the well documented review of Tomlin et al. [82]. All the systems developed for low temperature oxidation mechanisms use a logical programming based on the definition of classes of elementary steps, as first proposed by Chinnick (1987) for pyrolysis [83].

In the early 90s, Chevalier et al. [84-86] have created a program for the automatic generation of mechanisms for the description of the low temperature oxidation of higher

hydrocarbons. Their program was written in LISP and used a C_0-C_4 reaction base; but unfortunately their publications do not reveal many technical details. Mechanisms for the oxidation of n-heptane, n-decane and n-hexadecane were generated in order to model ignition delay times.

In order to find a trend between the production rate of branching agents and the blending octane number, two software for the generation of mechanisms for the low temperature oxidation of linear and branched alkanes were developed by Morley [87] and Blurock [88], respectively. The REACTION software developed by Blurock has recently been improved by Moréac et al. [89] and used to generate a low temperature oxidation detailed model for n-heptane and n-decane. The mechanism generation is based on the classes of reactions defined by Curran et al. [70]. This mechanism involves 506 species and 3684 reactions.

The first well validated oxidation mechanisms obtained with a computer aided method have been published by the team of Ranzi and Faravelli in Milano since 1995. In line with their previous work on pyrolysis [90-91], this team has produced semi-detailed mechanisms of the oxidation of alkanes [92-93]. An automatic generator of reactions (MAMOX) provides primary mechanisms (involving only the reactions of initial molecular reactants and their derived radicals) which are then lumped by grouping together the alkyl, peroxy, hydroperoxyalkyl and peroxy hydroperoxyalkyl radicals having the same carbon number and by considering that decomposition reactions can be globalized into single equivalent reactions whose stoichiometries are only weak functions of process temperature [94]. Secondary mechanisms (involving the reactions of molecular products formed in the primary mechanism) are also based on lumped reactions involving fractional stoichiometric coefficients and an extensively validated C_0-C_4 data base which also contains reactions of simple aromatic compounds such as benzene, toluene or methylnaphthalene [95]. Mechanisms are developed iteratively, i.e. a mechanism for n-heptane is

based on previous mechanisms for n-pentane and n-hexane. Four well documented studies were presented, each including a detailed primary mechanism for n-pentane [94], n-heptane [96], iso-octane [97] and n-dodecane [92], respectively. Due to the large size of the C_0-C_4 data base, the mechanism for n-heptane involves more than 100 species and 2000 reactions and that of iso-octane 145 species and about 2500 reactions. An extension of this system has been made to model the oxidation of ethers (MTBE, ETBE, DIPE, TAME) [92, 98]; but while they have been used successfully to model data obtained from 750 K, these mechanisms include only high-temperature reactions.

Following an idea of Côme applied to thermal decompositions in the 80s [99-100], a team in Nancy has also been developing a system of automatic generation of reactions for the gas-phase oxidation of hydrocarbons for several years [101]. This work has benefited from the development of THERGAS software initiated by Scacchi also in the mid 80s for the calculation of thermochemical data [28]. The software for the automatic generation of kinetic models (EXGAS), which has been based on the initial algorithm of Haux et al. [100], is now completely automatic for linear and branched alkanes (EXGAS-ALKANES) [24]. It provides reaction mechanisms made of three parts, as shown in figure 3:

- A comprehensive primary mechanism based only on elementary steps.
- A C_0-C_2 reaction base, including all the reactions involving radicals or molecules containing less than three carbon atoms [102].
- A lumped secondary mechanism [103], which in order have a manageable size, involves lumped reactants (the molecules formed in the primary mechanism, with the same molecular formula and the same functional groups, are lumped into one unique species without distinguishing between the different isomers) and includes global reactions which produce, in the smallest number of steps, molecules or radicals whose reactions are included in the reaction

bases.

During the generation of the mechanism, the thermochemical data of each species and the rate constant for each reaction are produced automatically by using THERGAS [28] and KINGAS [103] software, respectively. The kinetic data are either calculated for the elementary steps by means of thermochemical kinetics or estimated by means of correlations.

FIGURE 3

It is worth noting that contrary to the work performed in Livermore and in Milano, these mechanisms were not developed iteratively. Therefore the development of a mechanism for n-decane does not require the generation of the n-nonane mechanism as a prerequisite and so the size of these mechanisms is relatively restricted as shown in Table 2. Another important point about EXGAS is that the system of generation gives a large degree of choice for tailoring the sought mechanisms according to the conditions of study. All the generic reactions in the primary and the secondary mechanisms are not systematically activated; they can be chosen in a menu [104]. This system has been used to generate mechanisms for the low temperature oxidation of n-butane [24, 103], the isomers of pentane [24], 2-methyl-pentane [24], the isomers of heptane[24, 104], iso-octane [24, 104] and n-decane [24, 106]. An extension of this system has also been made to model the oxidation of ethers (MTBE, ETBE) using comprehensive low temperature mechanisms [107].

2.3/ Experimental results available for validation

The experimental results concerning the autoignition and the oxidation below 900 K of alkanes from C_4, which have been published since 1993, are shown in Tables 3, 4 and 5.

TABLES 3 - 5

For autoignition, two types of experimental facilities have been mainly used: high pressure shock tubes and rapid compression machines. In a shock tube, ignition delay time is

usually measured behind a reflected shock wave, while the corresponding temperature is calculated from the incident shock wave velocity with an estimated error of around 20 K. Four high pressure shock tubes have been used to work with air-hydrocarbon mixtures for pressures behind a reflected shock wave of up to 60 bar and then to observe autoignition at temperatures from 660 K. The first results were obtained by the team of Adomeit [118-119,127] in Aachen for n-heptane, iso-octane and n-decane. The more recent studies of Davidson et al. [121,126] in Standford, Herzler et al. [120] in Duisburg and Zhukov et al. [128] in Moscow were mostly in good agreement with these older results [118,127] and supported the observation of a pronounced low temperature NTC region. The study of Herzler et al. [120] has extended the range of studied equivalence ratios towards small values (up to 0.1), which are of interest for the development of HCCI engines. Zhukov et al. have also studied n-pentane [113] and n-hexane [114] for pressures up to 530 bar; for n-hexane, the experimental results were in good agreement with simulations using the model of Curran et al. [70].

Between 1993 and 2007 (the time period of interest in this review), six rapid compression machine facilities have been used to measure autoignition delay times for alkanes and, in some cases, to analyze pre-ignition products; they are:

1. at the University of Leeds with a compression time of 22 ms [111-112],
2. at the University of Lille with a compression time of 60 ms [108,110,116,122],
3. at the University of Galway with a compression time of 17 ms [115],
4. at M.I.T in Cambridge (USA) with a compression time of 19-30 ms [117],
5. at the University of Michigan with a compression time of about 100 ms [123-125,142]
6. at Case Western Reserve University in Cleveland with a compression time of 20-40 ms [129, 143].

The apparatuses of M.I.T and Case Western Reserve University have been designed to be used at

pressures above 40 bar. In the six rapid compression machines, ignition delay time is measured starting from the end of the compression. The major problem in such an apparatus is the knowledge of the temperature (T_c) of the compressed gas. It is usually calculated for an adiabatic core gas from the initial pressure (P_0) and temperature (T_0), the compressed pressure (P_c) which can be experimentally measured and the ratio of specific heats ($\gamma = C_p/C_v$) by the following equation [116],

$$\int_{T_0}^{T_c} \frac{\gamma}{\gamma-1}\frac{dT}{T} = \ln\frac{P_c}{P_0}.$$

While a simplified method has been proposed by Tanaka et al. [64] to consider wall heat transfer as the result of a volume expansion, several experimental studies have demonstrated that the details of the heat transfer in a rapid compression machine are quite complex, both with respect to the geometry and over the time history of the experiments [72,144-145]. This is of particular importance for the compounds with the longest ignition delay times and it has been shown that simulations with a simple physical model encounter problems in reproducing the experimental results obtained in Leeds for highly branched alkanes, which show a region of temperature around 750 K, in which no autoignition was experimentally observed [112,146]. The experimental results obtained in Galway for highly branched alkanes show also a region of temperature in which no autoignition may be observed, or with a strongly pronounced NTC [115]. In addition, temperatures gradients have been measured in the combustion chamber of such an apparatus [146], which can greatly influence the potential measurement of products. With its longest compression time involving less turbulence formation, the machine of Lille has by far produced the largest number of results which have been successfully used to validate kinetic models for many components of gasoline, as well as for mixtures. Simulations display a satisfactory agreement when using results from this apparatus, albeit assuming adiabaticity even after long ignition delay times.

Most studies in a shock tube or a rapid compression machine have been focused on species included in gasoline, isomers of pentane and heptane and iso-octane; however three independent studies have been devoted to n-decane [127-129] with good agreement in the measured delay times. It is worth noting for n-decane, the satisfactory agreement obtained between results measured in a rapid compression machine [129] and in a shock tube [127]. A similar agreement between data obtained in these two different types of experimental facilities was also observed for iso-octane [119,123,126].

A last type of gas-phase apparatus, a spherical, stainless-steel vessel, has been used by Chandraratna and Griffiths (1994) [109] to investigate the conditions at which autoignition occurs in lean premixed n-butane + air mixtures. As reviewed by Pollard [47] and Griffiths [23], closed vessels have been much used before 1993 to study the low temperature oxidation of hydrocarbons and other gaseous organic compounds. Measurements of autoignition delay times in such an apparatus can be strongly sensitive to wall reactions, as shown for n-butane by Cherneskey and Bardwell in coated reactors [147].

Let us quote also experiments concerning the autoignition and the burning rate of fuel droplets in a heated gas, in some cases under microgravity. The obtained results can be a further test of kinetic mechanisms, even if the complexity of the physical model is strongly increased. A review on this topic has been published by Aggarwal in 1998 [148] and more recent results have been obtained for n-decane at a gas temperature below 900 K [149-150].

Autoignition data are of interest for the validation of kinetic models, because they are closely related to the phenomena occurring in engines. Nevertheless, as noted by Mittal et al. [151], any evaluation of a kinetic scheme by reference to ignition delay times must be treated with some caution when the kinetic uncertainties are not taken into account, since equivalent results may be predicted using very different sets of important parameters. It is then important to

consider for validation different sources of data, including results obtained in reactors for slow oxidation.

A more limited number of experiments concerning the slow oxidation at temperature below 900 K have been published; the teams of D'Anna in Napoli [133], Cernansky in Drexel University [68,138-141] and Dryer in Princeton [136] have used adiabatic pressurized flow reactors and the teams of Dagaut in Orléans [131-132,137] (based on a reactor design first proposed by Matras and Villermaux [152]) and of D'Anna in Napoli [133-135] have developed pressurized isotherm jet-stirred reactors. The main advantage of the data obtained in reactors is to give information about not only the global reactivity of the system, as conversions of reactant and ignition delay times do, but also on the selectivities of the obtained products by using adapted analytical techniques, such as gas chromatography with mass spectrometry, flame ionization or thermal conductivity detection. For n-heptane, with a large dilution in inert gas, Dagaut et al. [131] have detected about fifty species, including large alkenes (heptenes) and cyclic ethers (substituted tetrahydrofurans) in a system which can be reproduced by the simplest physical model. It is worth noting that the study of Lenhert et al. [140-141] and by D'Anna [133] in flow reactors were concerned by the oxidation of n-dodecane and the autoignition of n-tetradecane, respectively, with these large compounds being representative of those included in diesel fuel.

The mechanisms described above have been validated using a large part of these experimental results. As it is of little interest to compare model performance in terms of the best reproduction of experimental data, only one example of the agreement obtained is presented in figures 4-6 in the case of n-heptane. These figures show that the models of Livermore [70], Milano [96] and Nancy [24] for the oxidation of n-heptane perform very similarly when reproducing data obtained in a shock tube [118], a jet-stirred reactor [132] and a rapid

compression machine [116] (validation not found for the model of Milano). The three models reproduce very well the position of the NTC area and its variation with pressure which shifts towards higher temperature when pressure increases. This shift is due to the influence of pressure on the equilibrium of the addition reactions of molecular oxygen to the alkyl and hydroperoxyalkyl radicals [70]. It is interesting to note that ignition delay times obtained in a shock tube and in a rapid compression machine at the same pressure (average 3.2 bar) correspond to the same simulated curve as shown in figure 4 with the model of Nancy. However, the simulations made for the lowest pressure range (from 3 to 4 bar) correspond to the least satisfactory agreement obtained by the model of Nancy and are not presented by other authors. In a rapid compression machine, cool flame delay times (first ignition time) have also been experimentally measured and are well simulated by the models of Livermore and Nancy (see figure 6).

FIGURES 4-6

Validation is slightly less satisfactory for iso-octane [24,71,97], showing that some problems still remain for modelling highly branched alkanes. Well validated detailed modelling studies of the oxidation of n-decane and n-dodecane are still scarce [24,93]. The paper of Herzler et al. [120] concerning the autoignition of n-heptane in lean mixtures (ϕ from 0.1 to 0.4) in a shock tube, shows that the mechanism of Curran et al. [70] reproduces the general trends in the temperature and equivalence ratio dependence of the ignition delay times well, but that the absolute values disagree by a factor of 2. The same modelling results were obtained in Nancy [153], which can lead one to think that an important reaction in lean mixtures is not well understood. More experimental results in lean mixtures would therefore be valuable.

Simulations of the conditions under which autoignition occurs in lean premixed n-butane/air mixtures in a closed vessel were performed by the team of Griffiths using the

models of Nancy and Livermore and compared to experimental data [109]. While the qualitative features are well accounted for, both models overpredict the autoignition temperatures at low concentrations of fuel [154].

The model of Milano has been successfully used to reproduce results of autoignition [149] and burning rates [150] of fuels droplets of n-decane in a heated gas at constant pressure [155]. The variation of the cool flame and the total ignition delay times with the ambient temperature was properly predicted.

Tables 6 presents the experimental results concerning the autoignition and the oxidation below 900 K of ethers and esters from C_4, which have been published since 1993 and shows that these results are much less numerous than those for alkanes. The most investigated ether is MTBE, which is the only one for which autoignition delay times in a shock tube have been measured [119], but not yet modelled. No data have been obtained in a rapid compression machine. Several studies in pressurized isotherm jet-stirred reactors have been published [98,107,156]; the models of Milano and Nancy can correctly reproduce the measurements made by the team of Dagaut above 850 K, but at lower temperature a catalytic reaction needs to be taken into account to explain the early formation of alcohol. Data have also been obtained in a pyrex closed vessel [54]. In this type of reactor, the model of Nancy fails to simulate the results for ETBE, which were found to be sensitive to wall effects, although it can satisfactorily predict the older data obtained by Brocard et al. for MTBE [53].

TABLE 6

To our knowledge, no experimental measurements concerning the oxidation of ethyl esters or the ignition of esters in a shock tube or a rapid compression machine have been published since 1993. Despite the environmental interest of this topic, the amount of experimental data concerning methyl esters is still very limited. Methyl butanoate is the most

studied compound of this family, with measurements using flow and jet-stirred reactors performed by the teams of Dryer [80] and Dagaut [80, 157], respectively, and leading to a reasonable agreement with the modelling of Gaïl et al. [80]. Flow reactor experiments were performed between 500 and 900 K, but no NTC behaviour was observed. Jet-stirred experiments were also carried out in order to study the influence of an unsaturation in C_4 methyl esters [157]: both fuels have similar reactivity, but methyl crotonate combustion produces much higher levels of soot precursors (acetylene, propyne, 1,3-butadiene). Although slightly outside the scope of this paper, recent measurements in coflowing laminar non-premixed flames for methyl butanoate, methyl isobutyrate and ethyl propionate [158] and in opposed-flow diffusion flames for saturated and unsaturated C_4 methyl esters [80,157] can also be quoted.

2.4/ Comparison between the major models in terms of elementary steps and associated rate constants

Whether they were generated by a computer aided system or by careful human analysis, the mechanisms of Livermore, Milano (the detailed primary mechanisms were analysed) and Nancy have all been developed in a systematic way by applying well defined classes of reactions. Table 7 presents a comparison of the different classes of reactions considered by the three teams.

TABLE 7

While the classes of reactions involved in the high temperature primary mechanisms (initiations, H-abstractions from alkane molecules, isomerizations and decompositions by β-scission of alkyl radicals) are the same whatever the team and will not be reviewed here, there are more differences concerning the low temperature primary and the secondary mechanisms. As the secondary reactions of alkenes are mainly important at high temperature, this paper will only focus on the reactions involved in the low temperature primary mechanism, on the secondary

reactions of hydroperoxides and cyclic ethers and on the specificities of the reactions of ethers and esters.

In the models of Livermore, the rate coefficients of the reverse of each reaction were obtained by fitting of the rate constants computed from the thermochemistry. In Milano and Nancy, reverse reactions were considered only for additions to oxygen molecules and isomerizations, with specified rate constants in the team of Ranzi and Faravelli and with rate parameters automatically deduced by the solver from those of the direct reaction using thermodynamic data in EXGAS models. This latter method ensured the best consistency between kinetics and thermochemistry.

2.4.a/ Reactions of alkyl radicals (R•)

At low temperature, the main reactions of alkyl radicals take place with oxygen molecules. The current understanding of these reactions for small alkyl radicals, such as ethyl or propyl radicals, is in agreement with the fact that the R• + O_2 reaction proceeds through a barrierless addition pathway to form the RO_2• adduct, which will either be stabilized or react via a concerted elimination of •HO_2 to give the conjugated alkene [159]. The potential energy surfaces, calculated quantum mechanically by DeSain et al. [159], for the reactions of n-propyl radicals with oxygen molecules are displayed in figure 7. An accurate representation of this type of reaction would require parameterizing the rate constants as a function of temperature and pressure, which has not yet been done for alkyl radicals containing a large number of carbon atoms. This explain why deviations were observed when modelling experimental data obtained at low pressures, as already mentioned for n-heptane.

FIGURE 7

Benson [29] proposed an average value of the rate constant of the addition of alkyl radicals to oxygen molecules of $2x10^{12}$ $cm^3mol^{-1}s^{-1}$ at 650 K and several studies have shown that

this reaction displays a negative temperature dependence which is not is not the result of an energy barrier [160-161]. Lower values of the rate constant were measured for branched radicals (iso-butyl, neo-pentyl) than for straight-chain ones [160]. The rate constant of the reverse reaction is also of importance and can be deduced from microscopic reversibility.

At Livermore, the rate constant of the addition of alkyl radicals to oxygen molecules was assumed to be dependent on the type of alkyl radicals: $k = 4.52 \times 10^{12}$ $cm^3mol^{-1}s^{-1}$ for primary radicals, $k = 7.54 \times 10^{12}$ $cm^3mol^{-1}s^{-1}$ for secondary radicals and $k = 1.42 \times 10^{13}$ $cm^3mol^{-1}s^{-1}$ for tertiary radicals [70]. In the detailed primary mechanisms of Milano, the values were taken to be equal to 9×10^{11} $cm^3mol^{-1}s^{-1}$ for all heptyl radicals [96] and 1×10^{12} $cm^3mol^{-1}s^{-1}$ for other alkyl radicals [92,94,97]. At Nancy, a unified approach has been proposed whatever the size of alkyl radicals [24], but taking into account the branching level through an additivity method :

$$k_{add} = n_p.k_p + n_s.k_s + n_t.k_t + n_q.k_q,$$

with :

n_p: number of primary groups (CH_3) linked to the radicalar atom of carbon,

n_s: number of secondary groups (CH_2) linked to the radicalar atom of carbon,

n_t: number of tertiary groups (CH) linked to the radicalar atom of carbon,

n_q: number of quaternary groups (C) linked to the radicalar atom of carbon,

$k_p = 8.0 \times 10^{18}\ T^{-2.5}\ cm^3.mol^{-1}.s^{-1}$, $k_s = 9.0 \times 10^{18}\ T^{-2.5}\ cm^3.mol^{-1}.s^{-1}$,

$k_t = 1.5 \times 10^{18}\ T^{-2.5}\ cm^3.mol^{-1}.s^{-1}$, $k_q = 1.0 \times 10^{18}\ T^{-2.5}\ cm^3.mol^{-1}.s^{-1}$.

This leads to values of about 2×10^{12} $cm^3mol^{-1}s^{-1}$ for heptyl radicals (in agreement with the values proposed by Benson [29]) and between 1.1×10^{11} $cm^3mol^{-1}s^{-1}$ and 2.8×10^{12} $cm^3mol^{-1}s^{-1}$ for octyl radicals at 600 K. For these parameters, which have by far the highest sensitivity coefficient in the analyses of Buda et al. [24], there is clearly an important discrepancy between the low values used in Milano and Nancy and the higher ones used in Livermore, and no new experimental

study of this reaction has been published since the end of the 80s.

As they consider that the contribution of the reaction leading to •HO_2 radicals and alkenes decreases significantly with increasing number of atoms of carbon in the alkyl radical, due to an increased possibility of stabilisation of the adduct by vibrations, Curran et al. [70] neglect this class of reaction for alkyl radicals containing more than 4 atoms of carbon. As discussed by Walker and Morley [49], the mechanism of this reaction has been the subject of considerable controversy and the values of these rate parameters are not well known for alkyl radicals heavier than ethyl radicals. Nevertheless, the values used in Milano and Nancy are not so different. Ranzi et al. [92,94,96- 97] considered A-factors ranging from $1.5x10^{11}$ $cm^3mol^{-1}s^{-1}$ to $2.5x10^{11}$ $cm^3mol^{-1}s^{-1}$ (per abstractable H-atom) and an activation energy between 1.5 and 6.2 kcal/mol. Buda et al. [24] proposed A-factors depending on the type of abstracted H-atoms and ranging from $2.7x10^{11}$ $cm^3mol^{-1}s^{-1}$ to $1x10^{12}$ $cm^3mol^{-1}s^{-1}$ (per abstractable H-atom, for alkyl radicals containing more than four atoms of carbon) and an activation energy equal to 5 kcal/mol [162].

2.4.b/ Reactions of peroxyalkyl radicals (ROO•)

There are two types of reactions of peroxyalkyl radicals, isomerizations by internal transfer of H-atom and disproportionations with other radicals.

2.4.b.α/ Isomerizations

An example of isomerization by internal transfer of an H-atom is presented in figure 8. Isomerizations with a transition state ring including from 5 to 8 members were taken into account in Livermore, from 5 to 7 members in Milano and from 4 to 8 members in Nancy.

FIGURE 8

The first values for the rate parameters of a whole series of isomerizations of peroxy radicals were obtained by Baldwin et al. [163] in the team of Hull by studying the chemistry

associated with neopentylperoxy radicals when neopentane is added to slowly reacting mixtures of $H_2 + O_2$ between 673 and 773 K. This indirect measurement was dependent on the equilibrium constant of the addition of alkyl radicals with oxygen, the thermochemistry of which was a subject of controversy [161] in the late 80s. Hughes et al. [164] in the team of Pilling 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 [161]. Quantum mechanical calculations by Chan et al. [165] give activation energies between 5 and 7 kcal/mol higher than those proposed by the team of Pilling [161] and have not been considered in any models.

In Livermore [70], A-factors were calculated using RADICALC [166], a computer code that implements transition state theory and calculates the change in entropy when the radical moves to the transition state. In Milano, A-factors only depended on the size of the transition state ring. In Nancy, A-factors were mainly based on the changes in the number of internal rotations as the reactant moves to the cyclic transition state and were estimated using [53]:

$$A = e^{1} \frac{k_B T}{h} \times rpd \times \exp\left[\frac{\left(\Delta n_{i.rot.}^{\neq}\right) \times 3{,}5}{R}\right] s^{-1}$$

with :

h Planck constant,

rpd reaction path degeneracy = number of identical abstractable H atoms,

k_B Boltzmann constant,

$\Delta n_{i.rot.}^{\neq}$ change in the number of internal rotations as reactant moves to the transition state.

As proposed by Benson [29], activation energies for isomerization were set equal to the sum of the activation energy for H-abstraction from the substrate by analogous radicals and the

strain energy of the cyclic transition state.

Table 8 compares the values of A-factors and activation energies used by the groups of Livermore [70] Milano [92,94] and Nancy [24], with the ones recommended by the team of Pilling [161]. The parameters used by the group of Nancy were directly derived from the values proposed by the team of Pilling, while those of Livermore and Milano have been adjusted in order to reproduce experimental results.

TABLE 8

2.4.b.β/ Disproportionations

Above 600 K, the rate constants of isomerizations are high enough for reactions of peroxy radicals with other radicals to be of negligible importance, as shown by the sensitivity analyses of Curran et al. [70] and Buda et al. [24]. This class of reaction was therefore not considered by Ranzi et al. [94] and only the reactions with $\bullet HO_2$ radicals to give ROOH and O_2, were taken into account by Buda et al. [24]. Deriving from parameters proposed for $CH_3OO\bullet$ radicals [167], the rate constants of the disproportionation of peroxyalkyl radicals with $\bullet HO_2$ radicals were very close in Livermore and Nancy: $1x10^{11}$ $cm^3mol^{-1}s^{-1}$ in Livermore [70] and to $2x10^{11}$ exp(2600/T) $cm^3mol^{-1}s^{-1}$ in Nancy [24].

2.4.c/ Reactions of hydroperoxyalkyl radicals (•QOOH)

There are three types of reactions of hydroperoxyalkyl radicals, addition to oxygen molecules, decomposition to give cyclic ethers and decompositions to give acyclic species.

2.4.c.α/ Addition to oxygen molecules

The three research groups have taken the rate expressions of this class of reaction as identical to those for the addition of alkyl radicals to oxygen molecules.

2.4.c.β/ Decomposition to give cyclic ethers

An example of formation of cyclic ether is given in figure 9, in the case of the formation

of a tetrahydrofuran, i.e. a cyclic ether including 5 atoms. The formation of oxirans, oxetans and tetrahydropyrans, containing 3, 4 or 6 atoms, respectively, is also possible. This process competes directly with the addition of hydroperoxyalkyl radicals to oxygen, which leads ultimately to the formation of hydroperoxides, and has an inhibiting effect on the global reactivity. The rate constants of these reactions are thus very sensitive parameters, but a direct measurement is only available for the formation of *a* four membered ring during the oxidation of neo-pentane [163] ($k = 2.0x10^{11}exp(-7830/T)\ s^{-1}$) and the parameters used for other cycles rely only on estimations. The models of Livermore and Nancy include the formation of cyclic ethers rings containing from three to six atoms. *I*n the model of Milano the formation of six membered rings is neglected. Table 9 compares the values of A-factors and activation energies used by the three groups [24,71,92].

FIGURE 9

TABLE 9

In the models of Milano [96,97], apart from the recent study of n-dodecane [92], A-factors were kept constant at $2.0x10^{11}\ s^{-1}$, whatever the size of the ring. In the Livermore models [70], the n-dodecane model of Milano and the Nancy mechanisms [24], the loss in entropy due to the loss in free rotors when forming the cycle was taken into account leading to a decrease in the A-factor when increasing the size of the formed ring. Nevertheless, in the models of Livermore and Milano, there was a consistent decrease of the A-factor by 8 and 6.3, respectively, for each increase of one atom in the ring, while the decrease in the models in Nancy varied from 6 to 25. In the three research groups, activation energies have mainly been fitted to reproduce the distribution of ethers experimentally measured. Nevertheless, these values were consistent with a decrease of the ring strain energy when increasing the size of the cycle. This is not the case for the values calculated by quantum mechanical methods by Chan et al. [168],

which lead to an activation energy of 15 kcal/mol for the formation of oxiranes, 24 kcal/mol for that of oxetanes, 16 kcal/mol for that of furans and 18 kcal/mol for that of pyrans.

2.4.c.γ/ Decomposition to give acyclic species

Figure 10 illustrates the different possibilities of decomposition. A hydroperoxyalkyl radical can decompose to give an alkene and a •HO_2 radical by breaking of a C-O bond; this reaction was considered by the three groups. The breaking of a C-C bond can lead either to an alkene and a smaller hydroperoxyalkyl radical, as also considered by the three groups, or to an unsaturated hydroperoxide molecule and a smaller alkyl radical, as taken into account only in Nancy. In the models of Livermore and Milano, the smaller hydoperoxyalkyl radical obtained is immediately decomposed to give an aldehyde and an •OH radical. The breaking of *an* O-O bond is only possible when the atom of carbon bound to an atom of oxygen bears also the radical center, which is only the case in the models of Nancy, due to the possibility of an isomerization involving a transition state including a four-membered ring. This channel leads to the formation of an aldehyde or a ketone and an •OH radical. Table 10 compares the values of A-factors and activation energies used by the three groups [24,71,92].

FIGURE 10

TABLE 10

The formation of an alkene and an •HO_2 radical is an important channel in the models of Livermore, because it is the only way for the formation of alkenes including the same number of carbon atoms as the reactant. The rate parameters of this reaction in Livermore were deduced using thermochemistry from those of the reverse reaction of the addition of •HO_2 radicals to alkenes, as proposed by Chen and Bozzelli [169] for ethylene, propene and isobutene. The rate constant used in Nancy was taken from Baldwin et al. [170] and has been deduced also from that of the reverse reaction of the addition of •HO_2 radicals to small alkenes.

Because of their importance in the high-temperature oxidation mechanism, the rate constant of the decomposition involving the breaking of a C-C bond are relatively well known [33,34,84,171] and a good agreement is observed between the values used in Livermore and Nancy. The value for the decomposition by breaking of an O-O bond used in Nancy was taken from Chevalier et al. [84].

2.4.d/ Reactions of peroxyhydroperoxyalkyl radicals (•OOQOOH)

In the same way as peroxy radicals, peroxyhydroperoxyalkyl radicals can isomerizes by an internal transfer of an H-atom. In the system of Nancy, the dihydroperoxyalkyl radicals (•$U(OOH)_2$) obtained can react by decomposition to give cyclic ethers, alkenes, ketones and aldehydes including a hydroperoxide function. But, during their study of the oxidation of n-heptane, Glaude et al. [104] have noticed that 51 hydroperoxyalkyl radical isomers (•QOOH) were produced leading to the formation of 51 peroxyhydroperoxyalkyl radical isomers (•OOQOOH) by addition of oxygen, 162 dihydroperoxyalkyl radical isomers (•$U(OOH)_2$) by isomerizations of these •OOQOOH radicals and numerous hydroperoxide species which decomposed rapidly by degenerate branching steps and led to smaller species. The nature of these hydroperoxide species had no kinetic importance, as their decomposition was governed by the breaking of the O-OH bond. Therefore, in line with the work of Livermore and Milano, the models of Nancy can be simplified on request by the izomerisation and the decomposition being globalized into a single step. This step leads to the formation of a ketohydroperoxide ($C_{n-1}H_{2n-1}OOHCO$) with a rate constant equal to that for isomerization. But, while in Livermore and Milano, only the isomerization abstracting an H-atom bound to the atom of carbon bound to an oxygen atom (see figure 11) was considered, all the possible isomerizations were taken into account in Nancy. In Livermore, isomerizations of •OOQOOH radicals deriving from the initial H-abstraction of a tertiary H-atom from the parent fuel and involving the transfer of alternative

H-atoms (i.e. not bound to the atom of carbon bound to an oxygen atom, as this reaction is not possible) have been considered. A promoting effect of this reaction on the computed ignition rates has been shown [72].

In the three research groups, the rate constants of these isomerizations were taken equal to those of peroxy radicals. In the case of an isomerization involving the transfer of an H-atom bound to a carbon atom bound to an oxygen atom, as shown in figure 11, the activation energy has been reduced by 3 kcal/mol in Livermore [70] and by 2 kcal/mol in Nancy [24], in order to take into account the fact that this H-atom can be more easily removed.

FIGURE 11

2.4.e/ Secondary reactions of hydroperoxides

Hydroperoxide species are degenerate branching agents, which can easily decompose by breaking an O-OH bond and induce an increase of the amounts of •OH radicals which ensure the propagation of the reaction. The reactivity of alkanes is directly related to the amount of hydroperoxides formed and the rate constant of the decomposition of these compounds is then an important parameter.

The values used by the three research groups have been derived from a measurement of Sahetchian et al. [172] for the decomposition of hydroperoxides and were the following:

- $k = 1.5x10^{16}exp(-21000/T)\ s^{-1}$ for every hydroperoxides in Livermore [70],
- $k = 2x10^{14}exp(-20500/T)\ s^{-1}$ for hydroperoxides deriving from n-pentane [94], $k = 1x10^{15}exp(-20500/T)\ s^{-1}$ for hydroperoxides deriving from n-heptane [96] and n-dodecane [92] and $k = 1x10^{16}exp(-20500/T)\ s^{-1}$ for hydroperoxides deriving from iso-octane [97], in Milano,
- $k = 1.5x10^{16}exp(-21200/T)\ s^{-1}$ for hydroperoxides deriving from initial linear reactant and $k = 0.3x10^{16}exp(-21200/T)\ s^{-1}$ for hydroperoxides deriving from initial branched

reactant, in Nancy [24].

As explained previously, in order to limit the size of the mechanism, the secondary mechanisms developed in Milano and Nancy did not contain elementary steps, but globalized reactions. The lower value of the rate constant of branched compounds proposed in Nancy reflects the fact that the decomposition of hydroperoxides deriving from branched alkanes leads to less reactive molecules and radicals than in the case of straight-chain alkanes.

2.4.f/ Secondary reactions of cyclic ethers

In the mechanisms of the three groups, the reactions of cyclic ethers proceed first by an H-abstraction. In Livermore [70], H-abstractions by $\bullet HO_2$ and $\bullet OH$ radicals have been considered; while in Nancy, •H atoms, $\bullet HO_2$, $\bullet OH$, $\bullet CH_3$, $\bullet CH_3O_2$ and $\bullet C_2H_5$ radicals did react. In Milano, the abstracting radicals were all the radicals for which the abstraction reaction competes with their β-scission decomposition.

The radicals obtained can decompose to give either smaller acyclic oxygenated molecules or radicals and alkenes or alkyl radicals. In Milano and Livermore, the H-abstractions and the decompositions were globalized into a single step. There was a specificity in Nancy for this secondary mechanism: the radicals obtained from cyclic ethers including more than 3 atoms can also react with oxygen as shown in figure 12. The reactions with oxygen involved the classical sequence of oxygen addition, isomerization, second oxygen addition, second isomerization and beta-scission to led to the formation of hydroperoxydes, degenerate branching agents, which decomposed to give •OH free radicals and several molecules or radicals whose reactions were included in the C_0-C_2 reactions base [162]. This additional degenerate branching step increased the reactivity of the system and is a source of CO_2 at low temperature.

FIGURE 12

In Livermore, the rate constants for the H-abstractions depended on the type of abstracted

H-atom (primary, secondary, tertiary) and on whether the atom of carbon bound to it is bound or not to an atom of oxygen. In Milano and Nancy, due to the lumping of the primary products, such a detailed treatment was not possible.

2.4.g/ Classes of reactions and kinetic data specific to the oxidation of acyclic ethers

The only class of reactions specific to ethers is a molecular reaction involving a four-membered transition state and leading to the formation of an alcohol and an alkene molecule as shown in figure 13a. The rate constants used in the models were in line with previous work of the literature [57,173] and were the following :

- $k = 2.0x10^{14}exp(-29440/T)\ s^{-1}$ for MTBE and TAME and $k = 2.0x10^{14}exp(-28940/T)\ s^{-1}$ for ETBE and DIPE, in Milano [92],
- $k = 1.6x10^{14}exp(-29690/T)\ s^{-1}$ for MTBE and $k = 1.6x10^{14}exp(-30170/T)\ s^{-1}$ for ETBE, in Nancy [107].

FIGURE 13

While they are a class of reactions included in high temperature models, the decompositions of alkyl radicals by β-scission involving the breaking of the relatively weak C-O bond are of importance even at low temperature. These reactions have an activation energy from 1 to 3 kcal/mol lower than that involving the breaking of a C-C bond [98,107]. In Milano, these decompositions were globalized into a single step to give C_1-C_4 species [98]; in Nancy, they can lead to the formation of alkoxy radicals (RO•) which can also easily decompose to give an alkyl radical and a ketone or an aldehyde, with a low activation energy, i.e. 15 kcal/mol [107].

2.4.h/ Classes of reactions and kinetic data specific to the oxidation of methyl and ethyl esters

The few models [74,80-81] available for the oxidation of esters have been based on the same classes of reactions as for alkanes. The only class of reactions specific to esters is

molecular reactions. While this class of reaction has been found negligible for methyl esters [81], the unimolecular elimination involving a six-membered transition state and leading to the formation of ethylene and an acid molecule has been proven to be of importance for ethyl esters by Metcalfe et al. [81] and Schwartz et al. [158]. An example of this reaction is shown for methyl propanoate in figure 13b; the rate constant proposed by Metcalfe et al. [81] was: $k = 4.0x10^{12}exp(-25163/T)\ s^{-1}$.

As in the case of ethers, the presence of oxygen atoms involves differences in the activation energies of some β-scission decompositions. This has been discussed by El-Nahas et al. [174]. Changes can also be expected for the rate constants of isomerisations of peroxy radicals and the formation of cyclic ethers.

2.5/ Conclusion on the modelling of the oxidation of alkanes, ethers and methyl and ethyl esters

Several models exist for the oxidation of alkanes representative of those contained in gasoline, notably n-heptane and iso-octane. However, the modelling of the oxidation of compounds representative of those present in diesel fuel has not been much developed. The models proposed for alkanes containing from 4 to 8 carbon atoms can correctly reproduce most of the results published in the literature, apart from those obtained in very lean mixtures or with highly branched compounds. There is a lack of experimental data for very rich mixtures (equivalence ratio above 3) in well validated experimental systems.

Considering the discrepancies of the models in terms of classes of reactions and rate constants, and the weakness of the basis on which these rate parameters have been estimated, the good results obtained by the existing models are almost surprising. Differences in the used thermochemical properties, which were not reviewed here, probably partly compensate for the difference in kinetic data. The only reliable estimations of rate parameters were deduced from a few excellent studies by the teams of Walker and Pilling performed before 1995.

If an increased accuracy of the prediction of the models is needed, additional experimental and theoretical work on the elementary steps described above would be of great interest. This will be particularly true when not only a calculation of global reactivity, such as what is given by autoignition delay times, will be required, but also the prediction of minor pollutants which can have some impact on the chemistry of the earth's atmosphere: alkenes, dienes, aldelydes, acids. More studies are especially needed to define better the rate constants of the reactions of different types of alkyl radicals with oxygen molecules by addition or through the formation of alkenes, the isomerisation of peroxy radicals, the formation and the consumption of cyclic ethers and the decomposition of hydroperoxides. This should be achieved by calculations based on quantum mechanics [175-178] or master equation [179] methods and confirmed by some well designed experimental results.

The models and experimental results are far less abundant in the case of ethers and esters than in the case of alkanes. No model can reproduce autoignition delay times for these compounds and experimental data are available only for MTBE. More studies about ETBE, which can be considered as a semi-renewable compound, since the raw material used for its production – ethanol – derives from biomass [180], and about esters more representative of those actually present in biodiesel could certainly be of great interest. Since the experimental investigation and the development of detailed mechanisms for the low temperature oxidation of saturated and unsaturated esters containing up to 19 atoms of carbon will certainly be difficult, useful information should certainly be gained by using lighter compounds, e.g. C_6-C_{10} methyl esters, as model molecules.

3/ ALKENES

The presence of a double bond in alkene molecules has led kineticists to make an

additional step in the complexity of the chemistry of low temperature oxidation. The radicals directly deriving from the reactant are no longer of a single type, as alkyl radicals from alkanes, but of at least three types, as shown in Figure 14, alkylic and allylic alkenyl radicals being obtained by H-abstraction and hydroxyalkyl radicals being obtained by addition of •OH radicals to the double bond. This explains the scarcity of models related to alkenes, representative of the compounds present in gasoline, even if these unsaturated compounds are the major products of the oxidation of alkanes, with yields of 65% for butyl radicals and about 50% for larger alkyl radicals [49], and some of them have an important kinetic effect as they can lead to resonance stabilized radicals. Experiments are also made more difficult when using these unsaturated reactants as the possibilities of polymerisation are favoured.

FIGURE 14

3.1/ Main chemical features of their oxidation

The largest contribution to the understanding of the reactions of alkenes at low temperature has been made by the team of Hull. A study of the addition of alkenes from C_2 to C_5 to slowly reacting mixtures of $H_2 + O_2$ at 750 K allowed Baldwin and Walker [181] to review the elementary reactions specific to the oxidation of alkenes in 1981. Further improvements of the proposed rate constants were progressively proposed [182-185] and reviewed in 1997 by Morley and Walker [49]. A large number of rate constants for the reactions of alkenes have also been proposed by Tsang for propene [35].

The typical reactions which are important in the low temperature of alkenes from C_4 are illustrated in figure 15 by a rate of reaction analysis performed for the oxidation of 1-pentene at 800 K, with a detailed kinetic model [186] which will be further described next.

FIGURE 15

The reactions occuring from the initial alkene molecules are of two types, H-abstractions

by oxygen molecules or by •OH radicals and additions of atoms or radicals across the double bond.

When H-abstraction occurs at the atom of carbon in a β position to the double bond, electron delocalisation occurs in the emerging alkenyl radical (allylic 1-penten-3-yl radical in figure 15) with several significant consequences. The enthalpy of reaction of the initiations with oxygen molecules leading to allylic radicals is about 15 kcal/mol lower than those leading to alkyl radicals, but the A-factors are lower by about a factor of 10 due to the reduction of the entropy of activation, caused by the loss of one rotation in the delocalized radical [185]. The stability of allylic radicals favours recombination reactions, with HO_2 radicals especially, which is a source of hydroperoxides. As mentioned by Knyazev and Slagle [187], due to the electron delocalization, an allylic radical can lead to the formation of two peroxyalkenyl radicals. Lodhi and Walker [183] have proposed a mechanism by which peroxyallyl radicals react by an internal addition to the double bond and lead to the formation of formaldehyde and •CH2CHO radicals. The stability of allylic radicals explains why alkenes always have a larger octane number than the alkane of same structure; e.g. RON is 24.8 for n-hexane (MON = 26) and 76.4 (MON = 63.4) for 1-hexene, 92.7 (MON = 80.8) for 2-hexene and 94 (MON = 80.3) for 3-hexene (the octane number is the highest for the isomers which can lead to two different allylic radicals) [11]. While the difference between RON and MON (sensitivity) is weak for alkanes as shown in Table 2, it is far larger for alkenes. The sensitivity is related to the temperature dependence of the rate of the reactions leading to autoignition [188].

Below 1000 K, H-abstractions from atoms of carbon engaged in the double bond can be neglected. The H-abstractions, occurring at the atom of carbon in a γ or further position to the double bond, involve the formation of alkylic alkenyl radicals (1-penten-4-yl and 1-penten-5-yl radicals in figure 15), which have a reactivity very close to that of alkyl radicals, with

nevertheless, a possibility of the formation of dienes and of cyclization. It is worth noting that unsaturated ethers could be obtained if the mechanism proposed for alkyl radicals is taken into account, as shown in figure 15.

Additions across the double bond occur mainly with •H atoms and •OH and •HO_2 radicals. For asymmetric alkenes, two adducts are formed for each radical undergoing addition. Additions of •H atoms lead to alkyl radicals (2-pentyl radicals in figure 15; 3-pentyl was not shown, because its rate of production was too small). Walker et al. [182] have shown that the addition of •HO_2 radicals does not lead to the formation of hydroperoxyalkyl radicals, but directly to the formation of oxiranes and •OH radicals. Kinetic evidence for the formation of oxiranes and alkoxy radicals (RO•) from the reactions of alkenes and RO_2• radicals has been found by Stark [189]. The addition of •OH radicals lead to hydroxyalkyl radicals (1-hydroxy-penten-2-yl and 2-hydroxy-penten-1-yl radicals in figure 15), the reactivity of which is close to that of alkyl radicals and lead to a potential formation of hydroxy cyclic ethers. The isomerization of hydroxyalkylperoxy radicals can occur through the mechanism proposed by the team of Waddington [190] and leads to the formation of aldehydes and •OH radicals, as shown in figure 16.

FIGURE 16

These different channels lead to the formation of hydroperoxide species, the decomposition of which promotes the reactivity in the same way as during the oxidation of alkanes. The reversibility of the addition of oxygen to alkylic alkenyl and hydroxyalkyl radicals, which react very much as alkyl radicals, is responsible for the existence of a negative temperature coefficient (NTC) regime.

3.2/ Low temperature oxidation models and experimental results available for their validation

The first detailed kinetic models for an alkene heavier than ethylene were proposed for

propene. The team of Livermore was again leading the way in 1989, with a mechanism considering only one addition to oxygen [191], followed ten years later by the team of Nancy using a version of EXGAS extended to alkenes [192]. The purpose of these two mechanisms was to reproduce results obtained in a static reactor from 580 to 740 K by Wilk et al. [193]. The mechanism of Nancy showed that the observed NTC was mainly due to the reversibility of the addition to oxygen of the adduct, $\bullet C_3H_6OH$ which, via a mechanism similar to that of alkyl radicals and involving two additions to oxygen, yielded degenerate branching agents. Table 11 summarizes the experimental data available for the model validation in the case of alkenes containing more than three carbon atoms.

TABLE 11

Concerning C_4 alkenes, a low temperature mechanism for the oxidation of 1-butene, 2-butene and iso-butene has been proposed by Pitz et al. [194] to model combustion products in an engine. Two mechanisms have been proposed by Dagaut and Cathonnet [195] and by Baugé et al. [196] to model the oxidation of iso-butene in jet stirred reactors. But, while they aimed at modelling results below 900 K, these two mechanisms considered only high temperature reactions.

The first modelling study concerning alkenes of C_5 has been published by Ribaucour et al. [77]. A mechanism including 888 reactions and 179 species has been proposed to reproduce autoignition delay times measured in a rapid compression machine [197]. The model allowed the experimental values of autoignition delay times to be satisfactorily enough modelled, but the NTC zone was not really captured. The abstractions of alkylic H-atoms, the isomerizations of the peroxy radicals deriving from the successive additions of hydroxyl radicals and oxygen molecules or the formations of unsaturated cyclic-ethers have not been considered in this model.

A modelling of the oxidation of 1-pentene has very recently been published by the team

of Ranzi and Faravelli [201-202] with validation using data in a rapid compression machine [197], but the building of the mechanism was not much detailed.

In recent years, the team of Nancy has improved the new version of EXGAS extended to alkenes in order to model the oxidation of alkenes, representative of those present in gasoline. Touchard et al. [186] have proposed mechanisms for 1-pentene and 1-hexene, which include 3385 reactions involving 837 species and 4526 reactions involving 1250 species, respectively. These mechanisms were validated using data measured for the autoignition of 1-pentene [197] and 1-hexene [199] in a rapid compression machine, showing well the difference of reactivity between the two compounds (RON is 90.9 for 1-pentene and 76.4 for 1-hexene [11]) as displayed in figure 17, and for the oxidation of 1-pentene in a flow tube [198].

FIGURE 17

Vanhove et al. [199] have measured cool flame and autoignition delay times, as well as the formation of 25 pre-ignition products for the 3 linear isomers of hexene in a rapid compression machine. Data in a jet-stirred reactor have also been measured for the oxidation of 1-hexene by Yahyaoui et al. [200] at temperatures from 750 K; simulations performed using the high temperature mechanism proposed by the authors strongly underestimate the formation of products below 850 K. The data measured by Vanhove et al. [199] for 2-hexene and 3-hexene and by Tanaka et al. [117] for linear isomers of heptene have not yet been modelled. To our knowledge, no data for heavier alkenes are available.

As shown in figure 18 for 1-hexene, the models of Nancy reproduce within a factor 2.5 the formation of dienes, saturated cyclic ethers and C_6 aldehydes, but deviate more for the formation of unsaturated cyclic ethers and smaller aldehydes, and predict the formation of hydroxy cyclic ethers, which has not yet been experimentally demonstrated. Concerning unsaturated cyclic ethers, Vanhove et al. [199] have analysed 2-methyl-4-vinyl-oxetane, 2-vinyl-

tetrahydrofuran and 2-ethyl-2,5-dihydrofuran (the structures of which are given in figure 19) during the oxidation of 1-hexene. The formation of 2-methyl-2,5-dihydrofuran was observed by Prabhu et al. during the oxidation of 1-pentene [198]. These unsaturated cyclic ethers were amongt those proposed by the models of 1-pentene and 1-hexene of Nancy [203], but the predicted quantities were much overestimated.

FIGURES 18-19

3.4/ Elementary steps and associated rate constants specific to the reactions of alkenes

The purpose of the following section is to review the differences in elementary steps and rate constants existing in the mechanisms for the low temperature oxidation of alkenes and to make a comparison to what has been previously described for alkanes. The data will be taken from the work of Nancy [186,192,203-204], as it is the best documented source of comprehensive models for alkenes representative of those included in gasoline. The rate constants for the reactions important at high temperature, molecular reactions (ene and retro-ene reactions), unimolecular and bimolecular initiations, H-abstractions from alkenes by small radicals, isomerization of alkylic radicals, decompositions by β-scissions, can be found elsewhere [205-208].

An up-date of THERGAS software for the estimation of thermochemical data [28] was also necessary, as many groups related to unsaturated compounds were missing in the tables of Benson [29] and some bond dissociation energies had to be re-evaluated; this was made using mainly the work of Ritter and Bozzelli [25], Knyazev and Slagle [187], Tsang [209], Luo [210] and Denisov and Denisova [211].

3.4.a/ Additions to the double bond

Table 12 presents the rate constants used for the additions of small radicals to the double bond. These values were derived from data proposed for propene [35,91]. In the case of the

additions of •HO_2 radicals, the direct formation of oxiranes and •OH radicals has been considered, while in the case of the addition of •H atoms and •OH and •CH_3 radicals the formation of the two adducts has been taken into account. Several studies [192,195-196,212] have indicated that when temperature increases the adduct cannot be stabilized, but breaks down into decomposition products. A direct addition/decomposition leading to aldehydes (e.g. formaldehyde and butanal in the case of 1-pentene) and alkyl radicals (e.g. methyl and butyl radicals in the case of 1-pentene) has then been written (for temperatures above 800 K), but the transition between the two channels was not well defined and should be better investigated.

TABLE 12

3.4.b/ Reactions of alkenyl and hydroxyalkyl radicals

As for alkyl radicals, the main low temperature reactions of alkenyl and hydroxyalkyl radicals take place with oxygen molecules. The rate parameters of these reactions are summarized in Table 13. These radicals can all react by addition with oxygen molecules to form peroxy radicals, or by oxidation to gives dienes, hydroxyalkenes, aldehydes or ketones and •HO_2 radicals. These elementary reactions have not been much studied, and the proposed rate parameters had to be mostly estimated. As shown in figure 15 for 1-penten-3-yl radicals, the addition to oxygen of the allylic alkenyl radicals can lead to two different peroxy radicals; a branching ratio of 0.5 being considered for both channels.

TABLE 13

Allylic radicals can also react by termination steps, mainly by combination with •HO_2 radicals to give an hydroperoxide ($k = 1.0x10^{15}\ T^{-0.8}\ mol^{-1}\ cm^3\ s^{-1}$ [192]), the decomposition of which is a source of unsaturated aldehydes, such as acrolein. In the case of long chain alkenes, the possible cyclization of alkylic alkenyl radicals was taken into account, with an A-factor of $1.4x10^{11}\ s^{-1}$ and an activation energy of E = 16.2 kcal/mol as proposed by Gierczak et al. [216].

3.4.c/ Reactions of peroxyradicals

The same two types of reactions as for peroxyalkyl radicals, isomerizations by internal transfer of H-atom and disproportionations with other radicals, have been considered. The rate constants of disproportionations have been taken to be equal to those of peroxyalkyl radicals previously presented (paragraph 2.4.b.β).

In the case of isomerizations, the rate parameters were obtained by the same method as presented previously (paragraph 2.4.b.α) with slight adjustments:

- The activation energy of the abstraction of a hydrogen atom from an atom of carbon linked to an atom of oxygen in hydroxyperoxyalkyl radicals was considered to be 2 kcal/mol lower than from an atom of carbon linked to only atoms of carbon or of hydrogen, as in the case of hydroperoxyperoxyalkyl radicals.
- For the isomerization of hydroxyperoxyalkyl radicals involving the transfer of an H-atom from the OH group, the cyclic transition state decomposed and gave two aldehydes and •OH as proposed by Stark and Waddington [190] with an energy for the abstraction of the H-atom of 18.6 kcal/mol, as proposed by Ranzi et al. [95] for the reaction of CH_3O_2• radicals with methanol.
- The activation energy of the abstraction of a hydrogen atom leading to an allylic radical was lowered by 2-3 kcal/mol compared to that forming an alkyl radical.
- The strain energy of the cyclic transition states containing two oxygen atoms and a double bond was taken as equal to 15 kcal/mol (for a five membered ring), 10 kcal/mol (for a six membered ring), 1 kcal/mol (for a seven membered ring) and 0 kcal/mol (for an eight membered ring) according to the differences of ring correction between saturated and unsaturated cycles proposed by Benson [29].

A third kind of reaction has been considered for allylic radicals, the internal

addition/decomposition proposed by Lodhi and Walker [183] with, $k = 1.7 \times 10^{9} T \exp(13200/T)$ $mol^{-1}\ cm^{3}\ s^{-1}$). Figure 20 illustrates this reaction for 1-penten-3yl-peroxy radicals. As for isomerizations, the A-factor was estimated from the changes in the number of internal rotations (2 rotations are lost) when the reactant moves to give the transition state and the activation energy from the sum of the energy for the addition and the strain energy of the four membered cyclic transition state.

FIGURE 20

A more accurate estimation of the parameters related to the reaction of peroxy radicals deriving from alkenes using theoretical calculations and a better consideration of steric effects, would certainly be useful to improve the modelling of the formation of products during the oxidation of large alkenes.

3.4.d/ Reactions of hydroperoxyradicals

The same three types of reactions have been considered as for hydroperoxyalkyl radicals deriving from alkanes, addition to oxygen molecules, decomposition to give cyclic ethers and decompositions to give acyclic species, using the same rate constants with slight changes:

- Cyclic ethers including rings, which contain from 3 to 6 members, a double bond or an alcohol function can also be obtained. Molecules containing a three-membered ring and a double bond inside the ring or just close to it cannot be formed. The rate constants for the formation of saturated cycles were close to those presented previously, with an activation energy 1 kcal/mol higher for the cycles bearing an alcohol function. The rate constants for the formation of an unsaturated cycle (e.g. 2-ethyl-2,5-dihydrofuran) and of a cycle conjugated to a double bond (e.g. 2-vinyl-tetrahydrofuran) are given in table 14. A-factors for the formation of unsaturated cycles ($A_{unsat.}$) were estimated from those of saturated cycles ($A_{sat.}$), by considering that an unsaturated free radical contains one less internal rotation than

the corresponding saturated radical and can then lose one less rotation to give the transition state, i.e. log ($A_{unsat.}$) = 0.76 + log ($A_{sat.}$). Activation energies were estimated from the differences of enthalpies of formation between cycloalkanes and cycloalkenes [29]. As the work of Pedley et al. [217] showed that the strain energy of methylenecyclopentane (5.7 kcal/mol) was very close to that of cyclopentene (5.9 kcal/mol [29]), the same values have been used for cycles conjugated to a double bond.

TABLE 14

- For decompositions giving acyclic species, when an enol group (-C=C(OH)-) was formed, it was supposed to isomerize instantaneously to give an aldehyde/ketone group (-CH-C(=O)-). Table 15 summarizes the rate coefficients specific to the decompositions of hydroperoxyalkenyl radicals; for the other types of reactions, the same values have been used as for hydroperoxyalkyl radicals.

TABLE 15

3.4.e/ Secondary reactions

At low and high temperatures, a weak point of the model of Nancy is that no reaction of consumption of dienes has been written. Cyclic ethers with a double bond or with an alcohol function were treated according to the same rules as unsubstituted and saturated cyclic ethers; the formation of acid from cyclic ethers bearing an alcohol function has not been considered. Unsaturated aldehydes were treated according to the same rules as saturated aldehydes, including the abstraction of the aldehydic H-atom followed by a decomposition of the obtained alkoxy radicals.

3.5/ Conclusion on the modelling of the oxidation of alkenes

Contrary to alkanes, there are only very few modelling studies of the low temperature oxidation of alkenes representative of those included in gasoline. Only one group has proposed a

mechanism for 1-hexene and no model has been proposed for the other straight-chain isomers of hexene and for heptenes, despite experimental data having been produced for these compounds. Low temperature models for branched species, even for the smallest one, iso-butene, are missing. Experimental data concerning branched alkenes are also much too scarce, as well as measurements obtained for equivalence ratios outside the 0.4-1 range.

Concerning the existing models of the low temperature oxidation of 1-alkene, while they can satisfactorily enough predict the global reactivity, especially the ignition delay times, they encounter important problems to give an actual repartition of the products: the formation of unsaturated and hydroxy cyclic ethers is overestimated while an important amount of aldehydes is missing. This discrepancy is probably due to the fact that the types of elementary steps and the evaluation of rate constants have been too closely extrapolated from those used for alkanes. Theoretical calculations should allow a better understanding of the reactions channels and to more accurately estimate the related rate parameters. That could be of importance for the addition of OH• radicals to the double bond, for the reactions of the peroxy radicals deriving from allylic alkenyl radicals, for the isomerization of hydroxyperoxyalkyl radicals (mechanism of Waddington) and for the formation of the new types of cyclic ethers. New experimental measurements on these elementary steps would also be valuable.

4/ CYCLOALKANES

With the possible increasing importance of fuels derived from non-conventional oil, such as Canadian oil sands [218], the content of cycloalkanes in diesel fuel is expected to increase [219]. That explains why the oxidation of this class of hydrocarbons has been the subject of several studies in the recent years.

4.1/ Main chemical features of their oxidation

As for alkanes and alkenes, the first picture of the oxidation of cycloalkanes has been

drawn by the team of Walker. From 1989, they have studied separate additions of cyclohexane (753 K) [220] and cyclopentane (673-783 K) [221] to slowly reacting mixtures of H_2 and O_2. At about the same time, motivated by industrial safety problems, an experimental study of the oxidation of cyclohexane at 635 K in a static reactor was performed by the team of Baronnet [222], who proposed the first modelling study of this reaction [223].

These studies have shown that the low temperature chemistry of the oxidation of cycloalkanes is very close to that of alkanes. Figure 21 shows an example of the scheme which is nowadays proposed for cyclohexane. While cycloalkyl radicals also react with oxygen molecules to give cycloalkylperoxyradicals, the yield of formation of the conjugated cycloalkene is larger than for the alkyl radical of the same size under the experimental conditions used by the team of Walker [49]. That is one reason why a cycloalkane always has a larger octane number than the linear alkane of same size; e.g. RON is 24.8 for n-hexane and 83 for cyclohexane (MON = 77.2) [11]. By successive losses of H-atoms, cyclohexene leads rapidly to the formation of benzene. Isomerizations of cycloalkylperoxyradicals by internal transfer of H-atom are possible, but are hindered by the fact that the involved transition state is bicyclic. Disproportionation between cyclohexylalkoxy radicals was proposed to explain the observed formation of cyclohexanol and cyclohexanone [222]. The reactions of hydroperoxycycloalkyl radicals can produce aldehydes, such as hexenal during the oxidation of cyclohexane, and bicyclic ethers, such as 1,2-epoxycyclopentane, 1,2-epoxycyclohexane or 1,4-epoxycyclohexane [49]. The addition to oxygen of hydroperoxy cycloalkyl radicals can lead to hydroperoxide molecules. This low temperature chemistry of cycloalkanes is in agreement with the existence of the NTC zone during the oxidation of these compounds.

FIGURE 21

4.2/ Low temperature oxidation models and experimental results available for their validation

Due to great similarities in their oxidation chemistry between alkanes and cycloalkanes, the three main teams having performed a modelling of the oxidation of cycloalkanes were also those of Livermore, Milano and Nancy.

Up-dating the classes of reactions and the kinetic data proposed for alkanes [70], the team of Westbrook and Pitz has proposed models for the oxidation of cyclohexane (5859 reactions) [224] and methylcyclohexane (7026 reactions) [225]. The team of Ranzi and Faravelli has first proposed a globalized mechanism to model the oxidation of cyclohexane [226], with 2 globalized steps to reproduce the high temperature decomposition and 6 reactions to take into account the low temperature behaviour, but a second more detailed mechanism, with 12 sensitive rate constants estimated through quantum mechanics, has been more recently proposed [227]. The team of Nancy has improved EXGAS software to take into account cyclic reactants [101] and has generated a model for cyclohexane [228] (2446 reactions). Due to the progress made in EXGAS to model the oxidation of alkenes, the low temperature reactions of alkenyl radicals obtained by β-scission decompositions have been comprehensively considered, but were shown to be mostly of negligible importance.

Table 16 summarizes the little experimental data available for model validation in the case of cycloalkanes. The most studied compound of this family is cyclohexane, which has been studied in rapid compression machines in Lille [229] and in Cambridge (USA) [117], in a jet-stirred reactor by the team of Dagaut (only above 750 K) [230-231] and in a pyrex static reactor at low pressure by the team of Baronnet [222]. An important overprediction of the reactivity has been obtained when attempting to model these last results with the model of Nancy. The low temperature oxidation of methylcyclohexane has been studied in two rapid compression machines [117,225] and in a shock tube [232]. The autoignition delay times

obtained in the rapid compression machine of Galway were well captured by the model of Livermore [225], while those obtained in a shock tube were considerably overestimated. Some measurements have been made in a jet-stirred reactor in Orléans for n-propylcyclohexane [231], but only at temperatures above 950 K. At Drexel University [138], the formation of carbon monoxide has been followed during the oxidation of n-butylcyclohexane in a pressurized flow reactor between 600 and 800 K; these data are still to be modelled. Let us also quote the high temperature (1160 K) data obtained by Zeppieri et al. [233] for methylcyclohexane in an atmospheric flow tube, as a wide range of products have been analysed. While data have been obtained at high temperature for the autoignition of tricyclodecane (tetrahydrodicyclopentadiene), a component of JP-10 jet fuel [234], there is no published study of the low temperature oxidation of polycyclic alkanes.

TABLE 16

Figures 22 and 23 show a comparison between the models of Livermore, Milano and Nancy concerning their abilty to reproduce the data of Lille for the autoignition of cyclohexane in a rapid compression machine and for the formation of oxygenated products during the pre-ignition phase, respectively. The three models reproduce well the occurrence of cool flames and of the negative temperature coefficient zone between 725 and 800 K, but the models of Livermore and Milano do not reproduce the formation of a cool flame at 790 K, while the model of Nancy overestimates the ignition delay times between 750 and 850 K. The three models simulate rather correctly the formation of hexenal (not shown in the figure for the model of Milano, but overestimated by a factor 2), which is the main C_6 oxygenared products, and of bicyclic ethers. The model of Nancy does not take into account the formation of 1,3-epoxycyclohexane, which was considered as unstable by the team of Walker [220], that of Livermore underestimates the production of 1,2-epoxycyclohexane and that of Milano

overestimates the formation of 1,4-epoxycyclohexane.

FIGURES 22-23

4.3/ Comparison between the major models in terms of elementary steps and associated rate constants

The chemistry involved in the oxidation of cycloalkanes being close to that proposed for alkanes, the groups of Livermore [224-225], Milano [227] and Nancy [228] have mainly considered the same types of reactions with close kinetic parameters to what is described in paragraph 2.4. We shall then only review here the differences which had to be taken into account due to the presence of the cycle, mainly in the case of isomerizations and the formations of bicyclic ethers.

4.3.a/ Reactions of cyclo-alkylperoxy radicals

The presence of the cycle has an important impact on the rate parameters of isomerizations which are presented for the three teams in table 17. The presence of the cycle increases the strain energy of the transition state and the conformational aspects of the cyclic structure disfavours some channels, as the isomerization of cyclohexanylperoxy radicals involving a 7 membered transition state ring, as shown in figure 24 [235].

FIGURE 24

While in Milano, quantum mechanical calculations were used to determine these rate constants, in Livermore and Nancy, estimations were based on the work of the team of Walker. In Livermore, these parameters have been mainly deduced from the values proposed in their model of iso-octane (see table 8) using corrections obtained by comparison between the values proposed by Handford-Stryring and Walker for cyclohexane [235] and those proposed by Morley and Walker for acyclic alkanes [49] (i.e. A x 0.62, Ea + 0.645 kcal/mol, for a 5 membered transition ring, A x 3.72, Ea + 3.226 kcal/mol, for a 6 membered transition ring, A x

3.47, Ea + 5.305 kcal/mol, for a 7 membered transition ring). This method of correction should be easily applicable to other substituted cyclohexanes. In Nancy, rate parameters were obtained using the method described in paragraph 2.4.b.α. For A-factors, the loss of one rotation was considered in every case; the A-factor of the isomerizations involving a transition state with a 7 members ring was divided by 200 to take into account the ratio of molecules which are in the "boat" form, instead of in the "chair" one (i.e. 0.5 % [49]). While the activation energy for H-abstraction from the substrate by analogous radicals was not changed compared to what is presented in Table 8, the strain energy had to be estimated for bicyclic transition states apart from that of the 4 membered transition ring which was assumed unchanged. The strain energy of the 6 membered transition ring was deduced from the experimental enthalpy of bicyclo[3,3,1]nonane [217]. Those of 5 and 7 membered transition rings were calculated using A-factors, the rate constant of the isomerization involving a 6 membered transition ring and the ratio between the rates of these 3 channels measured by Gulati and Walker at 753 K [220]. Table 17 shows that the activation energies used by the three research groups for cycloalkanes are much larger than for acyclic compounds (up to 9.5 kcal/mol difference) leading to lower rate constants. While the 3 models agree with Handford-Styring and Walker [235] that the isomerization involving a 6 membered transition ring is the most favoured, discrepancies are found for the value of this rate constant at 753 K. The values of Livermore and Milano are about two and twenty times larger, respectively, than the values of Nancy and Hull which are similar. This induces important differences between Livermore, Milano and Nancy in the ratio between the constants of the 3 main possible channels. Differences in thermochemical properties which are not reviewed here can partly compensate for these differences in rate constants and explain why the predictions of products are not so far off, as shown in figure 23.

TABLE 17

The lower reactivity of cyclic alkylperoxy radicals towards isomerizations can lead to an increasing influence of disproportionations. While this class of reaction was not considered in Milano, the disproportionations of alkylperoxy radicals and •HO_2 radicals has been taken into account in Livermore and Nancy with the same rate constant as for acyclic alkanes, as well as the disproportionations between two peroxyalkyl radicals, which can be of two kinds as proposed by Lightfoot et al. [167]:

- Disproportionation of two alkylperoxy radicals to give two alkoxy (RO•) radicals, which then react by decomposition, and an oxygen molecule, with $k = 1.4x10^{16}T^{-1.62}exp(-936/T)$ $cm^3.mol^{-1}.s^{-1}$ in Livermore and with $k = 6.3x10^{10}exp(364/T)$ $cm^3.mol^{-1}.s^{-1}$ in Nancy (only for cyclic radicals),
- Disproportionation of two alkylperoxy radicals to give an alcohol (e.g. cyclohexanol), a ketone (e.g. cyclohexanone) or an aldehyde and an oxygen molecule; this channel has only been considered in Nancy with $k = 1.4x10^{10}exp\ (364/T)$ $cm^3.mol^{-1}.s^{-1}$.

In the case of cyclohexane, based on the recent work of Carstensen et al. [236] on the reaction of ethyl radicals with oxygen, the teams of Livermore and Milano have also considered the direct elimination of cyclohexene and •HO_2 radicals with an A-factor equal to $3.85x10^{12}$ $cm^3mol^{-1}s^{-1}$ in Livermore and to $7.7x10^{11}$ $cm^3mol^{-1}s^{-1}$ in Milano and an activation energy of 29 kcal/mol. This reaction has not been considered in Nancy, while Silke et al. [224] found ignition delay times to be highly sensitive to the rate expression in use for this reaction. This reaction would not be so important in the case of acyclic peroxy radicals for which the activation energies of isomerizations are lower.

4.3.b/ Reactions of cyclo-hydroperoxyalkyl radicals

The presence of the cycle can also modify the kinetics of the decompositions of hydroperoxyalkyl radicals to give bicyclic ethers, the rate parameters of which are given in Table

18 for the models of cyclohexane of the three teams. In Milano, the rate constants of these decompositions have been calculated by quantum mechanical calculations and the rate parameters used in Livermore have been based on the values proposed in Milano. In Nancy, the activation energies have also been evaluated from quantum mechanical calculations, while A-factor have been mainly based on the changes in the number of losses of internal rotations induced by the formation of the cyclic ether (here one rotation is lost in every case). Important discrepancies between the three teams are also observed here, especially for the formation of 1,2-epoxycyclohexane.

TABLE 18

For the decompositions of cyclo-hydroperoxyalkyl radicals to give others products, the teams of Livermore and Nancy have mainly used the same classes of reactions and rate parameters as for acyclic compounds. In Milano, quantum mechanical calculations have been used to determine the products obtained and to derive the rate parameters for complex decompositions involving the breaking of several bonds.

4.3.c/ Reactions of cyclo-hydroperoxyalkylperoxy radicals

As for acyclic compounds the isomerization/decompositions of hydroperoxyalkylperoxy radicals have been considered. In the model of cyclohexane of Livermore, all the isomerizations have been considered and not only those abstracting an H-atom bound to the atom of carbon bound to an oxygen atom, as was done for acyclic alkanes (see paragraph 2.4.d). The decompositions of the obtained •U(OOH) radicals have been considered in detail. All the rate parameters for isomerizations have been deduced from the values proposed in their model of iso-octane (see table 8) using the corrections obtained by comparison between the values proposed by Handford-Stryring and Walker for cyclohexane [235] and those proposed by Morley and Walker for acyclic alkanes [49] and applying a reduction of 3 kcal/mol to the

activation energy, e.g. for a 5 membered transition state, A = 0.62 x $1x10^{11}$ = $6.2x10^{10}$ s^{-1} per H-atom and Ea = 26.850 + 0.645 - 3 = 24.495 kcal/mol. The reduction of 3 kcal/mol has been proven to have a very large influence on the ignition delay times. In Milano and Nancy, the same rules have been applied as for acyclic compounds, with the rate parameters being derived from those proposed for cyclohexanyl peroxy radicals.

4.4/ Conclusion on the modelling of the oxidation of cycloalkanes

Three models of the oxidation of cyclohexane have emerged in the last two years with satisfactory predictions of the experimental data obtained in a rapid compression machine and in a jet-stirred reactor. Unfortunately, there are no data available below 750 K and in the negative temperature coefficient zone for this last type of apparatus. It is also worth noting that in this recent modelling work, quantum mechanical calculations have been used by several teams to calculate the rate parameters of important channels of the oxidation of cyclohexane

Although there is an understanding of the low temperature oxidation of cyclohexane, at least in a range of equivalence ratios limited to 0.5-1.5, there is no model for the low temperature oxidation of cyclopentane and only one for a substituted cyclo-alkane (methyl cyclohexane). The study of alkyl-cyclohexanes bearing an alkyl chain containing more than one atom of carbon would be interesting, as the lengthening of the substituted alkyl chain would increase the possibilities of isomerization and the complexity of the mechanism. The study of the effect of a second cycle, such as in decalin or tetalin should also be undertaken, as these compounds are found in diesel fuels. In parallel to the development of new models, it will also be fundamental to obtain new experimental data for the oxidation at low temperature for cyclopentane, decalin, tetralin and substituted cycloalkanes (ethyl, propyl, butyl-cyclohexane).

5/ AROMATIC COMPOUNDS

The phasing out of tetraethyl lead as an anti-knock additive in gasoline has led to an

increasing content of aromatic compounds, which are now the most important family included in this fuel, as shown in Table 1. This is due to their high octane number, e.g. RON is 120 (MON is 103.5) for toluene and between 116 and 118 for xylenes (MON from 100.0 to 115) [11]. Nevertheless, it is worth mentioning the problems of toxicity involved by the presence of benzene at a concentration above 1%.

5.1/ Main chemical features of their oxidation

Due to the presence of the aromatic cycle, the chemistry involved in the oxidation of aromatic compounds strongly differs from that previously described for alkanes, ethers, alkenes and cycloalkanes. Using their experimental results obtained in the Princeton flow tube, the team of Brezinsky has made a pioneering work for the understanding of the mechanism of the oxidation of aromatic hydrocarbons. A review paper has been published in 1986 [237] and has described most of the reaction channels that are still used in the models developed today. These reactions are proposed as a high-temperature mechanism for a temperature range *of* 875-1500 K, but apart from some alkyl benzenes, there are very few studies concerning aromatic compounds at lower temperatures.

Figure 25 presents the main channels of the oxidation of benzene and toluene as proposed by Brezinsky [237]. Benzene can mainly react by H-abstractions with OH• radicals to give phenyl radicals or with O-atoms to give phenol or resonance stabilised phenoxy radicals and H-atoms [238]. The main reactions of phenyl radicals considered by Brezinsky were those giving phenoxy radicals, by reaction with O-atoms, HO_2 radicals or oxygen molecules. The reaction of phenyl radicals with oxygen molecules giving phenoxy radicals and O-atoms, which is a key step as it is a branching reaction, is not the only possible channel. Other channels can also be considered at low temperature as will be discussed in paragraph 5.4.b. Phenol can react by H-abstraction to give phenoxy radicals, which can decompose to give carbon monoxide and

cyclopentadienyl radicals, through a two or three-step process [239]. The resonance stabilised cyclopentadienyl radicals react mainly by termination steps to give cyclopentadiene by combination with H-atoms or cyclopentadionyl radicals by reaction with •HO_2 radicals or O-atoms. The opening of the cycle occurs by the decomposition of cyclopentadionyl radicals to give butadienyl radicals and carbon monoxide. Only two cyclic compounds were found by the team of Brezinsky in their study of the oxidation of benzene in a flow reactor at 1115 K, namely: phenol and cyclopentadiene [240].

FIGURE 25

Toluene can mainly react by H-abstractions to give benzyl radicals, with O-atoms to produce cresols or cresoxy radicals [238] or by ipso-addition of H-atoms to form benzene and methyl radicals [241]. Resonance stabilised cresoxy radicals do not have many possibilities of reaction, apart from the combination with H-atoms to give cresols. The fact that benzyl radicals are resonance stabilised has two consequences, first a large number of radicals can be involved in the H-abstractions from toluene and second they mainly react by termination steps. Benzyl alcohol, bibenzyl and ethyl benzyl are produced by combinations between benzyl radicals and •OH radicals, themselves and methyl radicals, respectively. Benzaldehyde is obtained by reaction of benzyl radicals with •HO_2 radicals or with O-atoms and mainly reacts by H-abstraction to give benzoyl radicals, which decomposes easily to yield CO and phenyl radicals. The additional cyclic compounds found by the team of Brezinsky in their study of the oxidation of toluene in a flow reactor at 1180 K [242] were benzaldehyde, benzyl alcohol, ethyl benzene, styrene, (ortho, meta, para) cresols and bibenzyl. A study of the team of Walker on the addition of toluene to slowly reacting mixtures of H_2 and O_2 at 773 K has allowed them to support the formation of benzylperoxy radicals, its isomerization by internal H-atom transfer and the decomposition to give benzaldehyde and OH radicals [243].

Alkyl benzenes including a side-chain containing more than one carbon atom can react by H-abstractions to give resonance stabilized 1-phenylalkyl radicals, but also other phenylalkyl radicals, with O-atoms to produce alkyl phenols or alkyl phenoxy radicals [238] or by ipso-addition of H-atoms to form benzene and an alkyl radical including the same number of carbon atoms as the side-chain. At high temperature, phenylalkyl radicals readily decompose by β-scission to give styrene or substituted styrenes, especially. At low temperature, phenylalkyl radicals can react with oxygen molecules like alkyl radicals, including the formation and the isomerization of peroxy radicals and inducing the formation of phenyl cyclic ethers, alkenylbenzenes and aromatic aldehydes and ketones. For instance, during their study of the oxidation of n-butylbenzene in a rapid compression machine, Roubaud et al. [244] have detected the cyclic ethers shown in figure 26.

FIGURE 26

Using the same methodology and an extension of the similar types of reactions, the team of Brezinsky has also proposed a mechanism for 1-methylnaphthalene [245].

5.2/ Detailed chemical models of oxidation

The two aromatic compounds for which the largest number of models has been developed are the simplest ones, benzene and toluene. Due to the low reactivity of these compounds, there is no real low temperature model for their oxidation. To our knowledge no model of the oxidation of neat benzene or toluene has been satisfactorily validated at temperature below 850 K. Consequently, we will review here models validated in a higher range of temperature than for other hydrocarbons.

The two first detailed models of the oxidation of benzene were those developed in the early 90s by Bittker [246] and Emdee et al. [247] which were both based on the qualitative scheme proposed by Brezinsky [237]. The lowest temperature for which these models were

validated was 1100 K using the flow tube data of Lovell et al. [240]. The next models were proposed by Lindstedt and Skevis [248], Zhang and McKinnon [249], Tan and Frank [250], Shandross et al. [251] and Richter et al. [252], but were mainly interested in modelling the results of Bittner and Howard obtained in a low-pressure laminar near-sooting benzene flame [253]. Since 2000, four models have appeared with the aim of modelling the oxidation of benzene in a lower temperature range and were each developed by Alzueta et al. in Lyngby [254], by Ristori et al. in Orléans [255], by Da Costa et al. in Nancy [256] and by Schöbel-Ostertag et al. in Stuttgart [257]. The lowest temperature for which these models were validated was 850 K. Each of the four teams has modelled its own experimental data obtained in a continuous reactor, which will be described further in this paper. Alzueta et al. [254] and Da Costa et al. [256] have also modelled the results of Lovell et al. [240] in a flow tube.

The two first detailed models of the oxidation of toluene were developed by Emdee et al. [247] and Linsdstedt and Maurice [258]. The lowest temperature for which these models were validated was 1200 K using the flow tube data of Brezinsky et al. [242]. The model of Emdee et al. was continuously improved by the team of Brezinsky [259-260]. Two recent up-dates of this mechanism have also been made by other teams. The first one was proposed by Andrae et al. [261] in Stockholm (49 species and 229 reactions in a submechanism planned to be used with the model of iso-octane of Livermore [70]) and validated using new shock tube data obtained at high pressure between 1050 and 1250 K [126]. The second one was mentioned by Chaos et al. [262] in Princeton to model their results obtained in a flow reactor between 850 and 950 K, but was not described in detail. While models for the oxidation of toluene have been recently developed by Djurisic et al. [263] and by Pitz et al. [264] using the data of the team of Brezinsky for their validation in the lowest range of temperatures, two models aiming at being used in a lower temperature range have also been recently proposed by Dagaut et al. (120 species and 920

reactions) [265] and Bounaceur et al. (128 species and 1036 reactions) [266]. The teams of Orléans and Nancy have validated them at temperatures from 873 K, each using their own jet-stirred reactor data. Bounaceur et al. [266] have also modelled the results of Brezinsky et al. [242] in a flow tube.

Very few models have been developed for monoaromatic compounds heavier than toluene. The team of Orléans has published mechanisms for the oxidation of para-xylene [267], meta-xylene [268] and n-propylbenzene [269] validated at temperatures from 900 K using their data obtained in a jet-stirred reactor. Mechanisms for the three isomers of xylenes were also proposed by the team of Nancy [270] and were able to well reproduce the difference of reactivity between these three compounds measured by the team of Brezinsky in a flow tube below 1200 K [271-272], as shown in figure 27. These models did not contain low temperature reactions involving isomerizations of peroxy radicals.

FIGURE 27

The only real low temperature oxidation model for the oxidation of alkylaromatics heavier than xylene was proposed by Ribaucour et al. [273] to reproduce results obtained for butylbenzene in a rapid compression machine. This model was derived from the mechanism of n-butane extracted from the n-heptane mechanism of Livermore [70] by considering that one H-atom of the n-butane molecule is substituted by an unreactive aromatic nucleus. The particular kinetics associated with benzylic-type radicals, which can be obtained by H-abstractions from the atom of carbon next to the phenyl group, has been added. The full mechanism included 1149 reactions of 197 species, among them 105 aromatic species. This model satisfactorily reproduced experimental cool flame and ignition delay times, as well the selectivity of the main observed products, including the formation of the cyclic ethers shown in figure 26.

As 1-methylnaphthalene can be considered as a model molecule of polyaromatic

compounds present in diesel fuel, two detailed kinetic mechanisms have been proposed by Pitsch [274] and by Bounaceur et al. [10], respectively. Figure 28 presents the primary reactions taken into account by the team of Nancy based on the experience gained by modelling the oxidation of benzene and toluene and shows that the formation of a wide range of bicyclic aromatic compounds had to be considered.

FIGURE 28

5.3/ Experimental results available for validation

The experimental results concerning the autoignition and the oxidation below 1200 K of benzene and toluene are presented in Table 19 and those of heavier aromatic compounds in Table 20. Due to the low reactivity of aromatic compounds, the range of investigated temperatures has been extended up to 1200 K and, as they represent an important part of the available experimental data, papers by the team of Brezinsky published a few years before 1993 have also been quoted.

TABLES 19 - 20

The only experiental study concerning the ignition of benzene was performed in the rapid compression machine of Cleveland [275]. Apart some results on the ignition of toluene obtained in rapid compression machines in Cambridge (USA) [117], Leeds [111] and Cleveland [275] and in a shock tube in Standford [126] and on that of 1-methylnaphthalene measured in a shock tube in Aachen [127], the main experimental results on the low temperature oxidation of aromatic compounds have been obtained by the team of Minetti in Lille [244-277] in a rapid compression machine between 600 and 900 K. These authors have defined two groups of species. The first group includes toluene, m-xylene, p-xylene and 1,3,5-trimethylbenzene which ignite only above 900 K and 16 bar. The second group is composed of o-xylene, ethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, n-propylbenzene, 2-ethyltoluene and

n-butylbenzene, which ignite at much lower temperature and pressure. Results under lean conditions (ϕ from 0.3 to 0.5) have been very recently obtained by the same team in the case of n-butylbenzene [282]. Apart from the results on n-butylbenzene from Lille, which were well simulated by Ribaucour et al. [273], and the results on 1-methylnaphthalene from Aachen, which were successfully modelled by Pitsch [274] and by Bounaceur et al. [10], no mechanism able to reproduce satisfactorily low temperature ignition data for aromatic compounds has yet been published. In the case of toluene, the mechanism of Nancy overestimated the delay times obtained in Lille [277] by a factor of about 2, but did predict ignition at pressures below 16 bar [286]. Davidson et al. [126] have shown that the models of Pitz et al. [264] and Dagaut et al. [269] significantly overpredict the data measured for toluene at Standford. Mittal and Sung [275] have tested several models for the oxidation of toluene (Klotz et al. [259], Sivaramakrishnan et al. [260], Djurisic et al. [263], Pitz et al. [264], Bounaceur et al. [266], Dagaut et al. [269]) and have shown that they all fail to reproduce the experimental results obtained in Cleveland.

Even if only temperatures above 900-1000 K have been studied, the team of Dagaut and that of Brezinsky have made impressive progress by measuring gas chromatographically the profiles of species during the oxidation of a wide range of aromatic compounds in an isothermal jet-stirred reactor and an adiabatic flow-tube, respectively. A recurrent problem in the measurements made in the flow tube used by the team of Brezinsky is the definition of the origin of reaction times. Nevertheless, these results have been used with success by many teams to validate most of the models proposed for benzene, toluene, xylenes and 1-methylnaphthalene. The flow-tube results concerning ethylbenzene, styrene, n-propylbenzene and n-butylbenzene are still to be modelled. The results of Orleans were mainly modelled by the team of Dagaut, but the results of Marchal concerning toluene and 1-methylnaphthalene [278] were successfully modelled by Bounaceur et al. [10,286]. It is worth noting that experimental results concerning

indane, the simplest naphthenoaromatic hydrocarbon, have been reported in Orléans [285], but not yet modelled.

Five other teams have been recently involved in the study of the slow oxidation of benzene or toluene in continuous reactors at moderate temperature. Chaï and Pfefferle [276] used a micro-jet reactor coupled to a time-of-flight mass spectrometer allowing them to detect a wide range of molecules and radicals during the oxidation of benzene. They have thus analysed the formation of oxygenated species, such as cyclopentadienone (see figure 29a), cyclopentenone, phenoxy radicals, phenol, cyclopentenone and cyclohexenone radicals, benzaldehyde, benzoquinone (see figure 29b) and phenyl peroxide. These results were modelled by Alzueta et al. [254], with important discrepancies concerning phenol, benzoquinone and cyclopentadienone. Alzueta et al. [254] have used a plug flow reactor and followed the consumption of benzene and the formation of carbon oxides, the same apparatus being also used to investigate the pyrolysis and the oxidation of phenol and para-benzoquinone [287]. The team of Nancy [256] has used a jet-stirred reactor with chromatographic analyses to study the oxidation of benzene and toluene, the detected cyclic species being the same as in the work of Brezinsky's team. As relatively high concentrations of reactant were used, significant conversions of benzene or toluene (above 50 %) were reached around 900 K. In order to reproduce conditions encountered in the cold zones of a waste incinerator, Schöbel-Ostertag et al. [257] have used chromatographic analyses to follow the species profiles in a heated laminar flow reactor in which benzene was injected downstream of the burned gas from a near stoichiometric flame of methane + air. Due to the presence of radicals from the flame entering the reactor, an important conversion of benzene was observed at temperatures as low as 850 K. While the other studies of the oxidation of toluene have been carried out at atmospheric pressure, the team of Dryer in Princeton has worked with a variable pressure flow reactor operated at 12.5 bar, allowing them to also observe a noticeable conversion

of reactants at temperatures as low as 850 K [262]. Under these conditions, the consumption of oxygen was underestimated by the models of Dagaut et al. [269], Bounaceur et al. [266] and Sivaramakrishnan et al. [260], confirming the fact that the reaction scheme of this aromatic species is still not well understood at high pressure and low temperature.

FIGURE 29

5.4/ Comparison between the major models in terms of elementary steps and associated rate constants

As for straight-chain hydrocarbons containing less than three atoms of carbon, it is difficult to describe well-defined types of reactions in the case of the oxidation of monocyclic aromatic compounds. Nevertheless the following part aims at comparing the channels and rate constants used for the additions to the aromatic cycles and the reactions of phenyl, benzyl and cyclopentadienyl radicals by the models proposed to simulate the oxidation of benzene and toluene at the lowest temperatures, i.e. the models of Alzueta et al. [254], Ristori et al. [255], Da Costa et al. [256] and Schöbel-Ostertag et al. [257] for benzene and those of Andrae et al. [261], Dagaut et al. [265] and Bounaceur et al. [266] for toluene. As they have been the basis of many mechanisms in the literature, the reactions proposed by Emdee et al. [247] for the oxidation of benzene, which are included in the mechanism of Andrae et al. [261], will also be taken into account.

5.4.a/ Additions to the aromatic cycles and derived reactions

The addition of O-atoms to benzene has been considered by the five models of benzene with a rate constant close to that measured by Nicovich et al. [238] over the temperature range 298-950 K, $k = 2.78 \times 10^{13} \exp(-2470/T)$ $cm^3 mol^{-1} s^{-1}$. While Schöbel-Ostertag et al. [257] have considered the formation of phenol; the other models included the formation of phenoxy radicals and H-atoms. The addition of O-atoms to toluene to give cresoxy radicals has been considered

by Andrae et al. [261] and by Bounaceur et al. [266] with a rate constant close to that proposed by Nicovich et al. [238], $k = 2.56x10^{13} \exp(-1910/T)$ $cm^3mol^{-1}s^{-1}$; this reaction was neglected by Dagaut et al. [265].

The decomposition of phenoxy radicals with the ejection of a carbon monoxide molecule was considered by all models with a rate constant close to that recommended by Baulch et al. [38] of $k = 7.4x10^{11} \exp(-22070/T)$ s^{-1}; a similar type of reaction has been assumed for cresoxy radicals by Andrae et al. [261] and by Bounaceur et al. [266]. Terminations have also been proposed for these two resonance stabilized radicals. Combinations with H-atoms to give phenol or cresol have been written in all models. Reactions of phenoxy radicals with O-atoms to give benzoquinone and H-atoms have been considered by Alzueta et al. [254], Da Costa et al. [256] and Schöbel-Ostertag et al. [257]. Alzueta et al. [254] have written the formation of the ortho and para isomers, the other authors considered only one isomer. As proposed by Buth et al. [288], Alzueta et al. [254] and Da Costa et al. [256] have also written the minor channel leading to cyclopentadienyl radicals and carbon dioxide. The disproportionations of phenoxy and cresoxy radicals with HO_2• radicals to give an alcohol and an oxygen molecule, which were only considered in Nancy and in Lyngby, have been shown to have an important retarding effect near 900 K under jet-stirred reactor conditions [256,266]. A recent theoretical treatment [289] of the reaction of phenoxy and HO_2• radicals has shown the formation of phenoxy-OOH adducts with the OOH group in ortho or para positions. These adducts decompose to give mainly phenol and oxygen molecules or benzoquinones and water. While there is some consensus between the different teams on the main reactions of formation and consumption of phenoxy radicals, the reactions of cresoxy radicals are still uncertain and would need additional studies.

While the addition of H-atoms to benzene to give cyclohexadienyl radicals has only been considered by Da Costa et al. [256], the addition of H-atoms to toluene to give benzene and

methyl radicals have been written in the three models with a rate constant close to that recommended by Baulch et al. [38] of $k = 5.8x10^{13} \exp(-4070/T)$ $cm^3mol^{-1}s^{-1}$.

The additions of •OH radicals to benzene and toluene to give phenol and cresol, respectively, have only been considered by the team of Nancy. It is worth noting that this addition followed by the addition to oxygen of the adduct mainly controls the chemistry of the decomposition of aromatic compounds under atmospheric conditions [290]. One could wonder if such reactions, which are similar to those considered for alkenes, could be of importance during the oxidation of benzene and toluene at much lower temperatures than what has been investigated during the validation of the present models. Such conditions could be met when studying the oxidation of mixtures of an aromatic compound and a more reactive hydrocarbon.

5.4.b/ Reactions of phenyl radicals

While phenyl radicals can react by additions to unsaturated molecules (e.g. Dagaut et al. [265] have considered additions to C_2H_2, C_2H_4, C_4H_2, C_4H_4) or by combinations with some radicals (e.g. Da Costa et al. [256] have considered combinations with O-atoms, •OH, methyl, HCO•, vinyl, ethyl, HO_2•, propargyl and phenyl radicals), a rate of reaction analysis at 923 K under the jet-stirred reactor conditions [256] has shown that the dominant consumption channels of phenyl radicals were with oxygen molecules. The five models have considered the branching reaction involving the formation of phenoxy radicals and O-atoms with a rate constant close to that proposed by Frank et al. [291], $k = 2.6x10^{13} \exp(-3080/T)$ $cm^3mol^{-1}s^{-1}$. The models of Alzueta et al. [254], Da Costa et al. [256] and Schöbel-Ostertag et al. [257] also included the formation of benzoquinone and H-atoms with a rate constant proposed by Frank et al. [291], $k = 3.0x10^{13} \exp(-4520/T)$ $cm^3mol^{-1}s^{-1}$. A doubt remains about the structure of the molecule of benzoquinone obtained. Frank et al. [291] and Schöbel-Ostertag et al. [257] considered para-benzoquinone and Alzueta et al. [254] and Da Costa et al. [256] the ortho-isomer. A mechanism

for the oxidation of para-benzoquinone was developed by Alzueta et al. [287]. To reproduce their experimental results at 923 K, Da Costa et al. [256] have also considered the formation of phenylperoxy radicals with a rate constant estimated to $k = 3.2x10^{19}\ T^{-2.5}\ cm^3mol^{-1}s^{-1}$, in agreement with the value measured by Yu and Lin [292] at 473 K and the decomposition of these peroxy radicals to give o-benzoquinone and H-atoms or cyclopentadienone and HCO• radicals.

A more theoretical treatment of the reaction of phenyl with oxygen molecules has been undertaken by several teams. Recent quantum mechanical calculations have been performed by Bozzelli et al. [293-294], Sirjean et al. [295] and Tokmakov et al. [296] by using GAUSSIAN [297]. To illustrate the obtained results, figure 30 presents the reaction mechanisms leading to o-benzoquinone and cyclopentadienone as calculated by Sirjean et al. [295]. The rate constants proposed by Bozzelli et al. [293] were incorporated in the mechanism for toluene proposed by Pitz et al. [264]. The most complete scheme was computed by Tokmakov et al. [296], who proposed as major products cyclopentadienyl radical + carbon dioxide, pyranyl + carbon monoxide, o-benzoquinone + H, and 2-oxo-2,3-dihydrofuran-4-yl (C_4OH_3O) + acetylene. While the presence of benzoquinone and cyclopentadienone has been detected by Chaï and Pfefferle [275], no evidence of the formation of products deriving from pyranyl and oxodihydrofuranyl radicals has been found in the different experimental studies of the oxidation of benzene published in the literature.

FIGURE 30

5.4.c/ Reactions of benzyl radicals

At low temperature, the main reactions of resonance stabilized benzyl radicals are termination steps and addition to oxygen molecules. The termination with HO_2• radicals has been shown to have an important promoting effect at 893 K under jet-stirred reactor conditions

[266]. The teams of Stockholm [261] and Orléans [265] have considered the direct formation of benzyl alkoxy and •OH radicals, while the team of Nancy [266] has written the formation of benzyl hydroperoxide molecules, which further decompose to give the same products; theoretical calculations by Davis et al. [298] have shown that the distinction between the two channels becomes academic above 800-900 K. The three teams have used a rate constant close to that proposed by Hippler et al. [299] over the temperature range of 1200-1500 K, $k = 5x10^{12}$ $cm^3mol^{-1}s^{-1}$, and have written (i) the decomposition of benzoxy radicals to give benzaldehyde and H-atoms (enthalpy of reaction of 15.9 kcal/mol). The teams of Nancy and Stockholm have also considered (ii) the formation of formaldehyde and phenyl radicals (enthalpy of reaction of 23.6 kcal/mol). In Nancy, the same rate was taken into account for both channels, $k_i = k_{ii} = 2x10^{13} \exp(13900/T)\ s^{-1}$. In Stockholm, the following values were used: $k_i = 1.3x10^{14} \exp(550/T)\ s^{-1}$ as proposed by Brezinsky et al. [242] (the same value as in Orléans) and $k_{ii} = 4x10^{13} \exp(1010/T)\ s^{-1}$. This important discrepancy between the rate constants used in the different models and the lack of consistency with the enthalpies of reaction make new experiments or calculations giving more information about the decomposition of benzoxy radicals particularly needed.

At low temperature, the other important combination takes place between benzyl radicals themselves to produce bibenzyl, but was not taken into account by Dagaut et al. [265]. Andrae et al. [261] and Bounaceur et al. [266] have used the rate constant proposed by Müller-Markgraf and Troe [300] over the temperature range 300-1500 K, $k = 2.51x10^{11}\ T^{0.4}\ cm^3mol^{-1}s^{-1}$. The terminations with methyl and •OH radicals to give ethyl benzene and benzylalcohol, respectively, are of minor importance.

The reactions of benzyl radicals with oxygen molecules were not of great influence under jet-stirred reactor conditions [266], but they were much more important during the preignition

phase in a shock tube [261], as they can be a source of reactive radicals. Andrae et al. [261] have written two branching steps (i) the formation of O-atoms, phenyl radicals and formaldehyde and, a minor channel, (ii) the production of O-atoms and benzoxy radicals, with the following rate constants, $k_i = 6.32x10^{11}$ exp(7300/T) $cm^3mol^{-1}s^{-1}$ and $k_{ii} = 6.32x10^{12}$ exp(21600/T) $cm^3mol^{-1}s^{-1}$ as proposed by Brezinsky et al. [242]. As stated by the authors [261], k_i has been tuned to match shock tube data for neat toluene [126] and for n-heptane/toluene mixtures [301]. Dagaut et al. [265] have also written (iii) the formation of benzaldehyde and •OH radicals, with $k_{iii} = k_{ii}$. Bounaceur et al. [266] have considered reaction (ii) with the rate constant proposed by Brezinsky et al. [242]. The idea of a fourth channel, (iv) the formation of benzyl hydroperoxy radicals, which can isomerise and decompose to give benzaldehyde and •OH radicals, is supported by experimental results of Ellis et al. [243] and theoretical calculations of Clothier et al. [302]. This sequence of reactions, which was taken into account by Lindstedt and Maurice [258], was included in the model of Nancy with the rate constant for the addition to oxygen molecule proposed by Fenter et al. [303] over the temperature range 298-398 K, $k_{iv} = 4.6x10^{11}$ exp(190/T) $cm^3mol^{-1}s^{-1}$. The rate parameters for the isomerization were calculated using the method described in paragraphs 2.4.B.α and 3.4.c, $k_{Nancy} = 3.4x10^9$ T exp(-18900/T) s^{-1}. This rate constant, which was not a sensitive parameter under the conditions of Bounaceur et al. [266], was much lower than that proposed by Ellis et al. [243] at 773 K ($k_{Nancy} = 6.3x10^1$ s^{-1} instead of $k_{Hull} = 2.8x10^3$ s^{-1}), with a much higher activation energy than that calculated by Clothier et al. [302] (Ea/R = 14570 K).

More investigations about the rate constant of the reactions of benzyl radicals with HO_2• radicals and oxygen molecules are greatly needed to better model the oxidation of toluene at low temperature and high pressure.

5.4.d/ Reactions of cyclopentadienyl radicals

Zhong and Bozzelli [304] have theoretically investigated the reactions of resonance stabilized cyclopentadienyl radicals with oxygen radicals, hydrogen and oxygen atoms and •OH and •HO_2 radicals. The combinations with H-atoms to produce cyclopentadiene have been considered in all models with a rate constant close to that proposed by Allara et al. [171] for that type of reaction, k = $1x10^{14}$ $cm^3mol^{-1}s^{-1}$. Dagaut et al. [265] have considered its pressure dependence. But the main reactions at low temperature are with •HO_2 radicals and oxygen molecules. This last reaction was not taken into account in Orléans and Princeton. In Nancy and Lyngby, it was considered to produce (i) vinyl ketene (CH_2=CHCH=C=O) and •HCO radicals, with the rate constant calculated by Zhong and Bozzelli [304] at 1 bar over the temperature range 900-1300 K, k_i = $1.2x10^{19}$ $T^{-2.48}$ exp(-5520/T) $cm^3mol^{-1}s^{-1}$. In Stuttgart the formation of (ii) cyclopentadienone and •OH radicals was written with a rate constant, k_{ii} = $2.3x10^{12}$ exp(-18228/T) $cm^3mol^{-1}s^{-1}$ [257]. The calculations of Zhong and Bozzelli [304] have shown the ratio k_{ii}/k_i to be equal to 1/5000 at 900 K. Apart from that of Schöbel-Ostertag et al. [257], all the models have considered the combinations of cyclopentadienyl and •HO_2 radicals leading to cyclopentadionyl and OH radicals. Alzueta et al. [254] have used the rate constant calculated by Zhong and Bozzelli [304], k = $6.3x10^{29}$ $T^{-4.69}$ exp(-5863/T) $cm^3mol^{-1}s^{-1}$ (k = $1.3x10^{13}$ $cm^3mol^{-1}s^{-1}$ at 900 K), the other teams have used estimated values, k = $3x10^{12}$ $cm^3mol^{-1}s^{-1}$ in Nancy [256] and k = $3x10^{13}$ $cm^3mol^{-1}s^{-1}$ in Princeton and in Orléans [247, 255]. It is worth noting that the reactions of consumption of vinyl ketene, cyclopentadione and cyclopentadionyl radicals are still very uncertain.

Two other combinations should be quoted as they lead to the formation of aromatic compounds: the combinations with methyl radicals, which is a source of benzene, and that with cyclopentadienyl radicals, which can produce naphthalene. Lifshitz et al. [305] have studied the

thermal reaction of methylcyclopentadiene, including the formation of benzene, which takes place only from radical intermediates that have a methylene group connected to the five-membered ring. Melius et al. [306] have calculated the potential energy surface for the formation of naphthalene from two cyclopentadienyl radicals and have proposed that it occurs in two steps: the formation of H-atoms and dihydrofulvalenyl ($\bullet C_{10}H_9$) radicals followed by the decomposition of these radicals to give naphthalene and H-atoms. While this channel has been proven to be important under flame conditions [307], the formation of dihydrofulvalene ($C_{10}H_{10}$, see figure 29c) should be also envisaged at low temperature [256,308].

5.5/ Conclusion on the modelling of the oxidation of aromatic compounds

While numerous validated models have been proposed for the oxidation of pure benzene and toluene above 850 K, there is a complete lack of such mechanisms for lower temperatures. That is related to a deficit in experimental data under these conditions because of the low reactivity of these aromatic species. Autoignition data for toluene are not well simulated below 900 K, mainly due to problems in the understanding of the reactions of benzyl radicals. Experimental data obtained for mixtures of benzene and toluene with more reactive hydrocarbons should be used to test these models below 900 K. Low temperature (600-900 K) ignition data have been published for xylenes, ethyl benzene, trimethylbenzenes, ethyltoluenes and butyl-benzene, but this last compound is the only alkylbenzene, the low temperature oxidation of which has been modelled. Even high temperature validated models are relatively scarce for alkylaromatics, detailed mechanisms being only available for xylenes, n-propylbenzene and 1-methylnaphthalene. Intermediate temperature (950-1350 K) oxidation data have been obtained for a naphthenoaromatic compound, indane, but have not yet been modelled. Low temperature data for the ignition of this last compound would also be very valuable. As for the other families of compounds reviewed in the previous parts of this paper,

there is a need for experimental data to validate the models in an extended range of equivalence ratios, i.e. below 0.5 and above 3.

The extension of the validity of the models for the oxidation of aromatic compounds towards lower temperatures will require more experimental and theoretical information about some potentially important elementary steps under these conditions: the addition of •OH radicals to aromatic rings, the reactions between phenylic-type (such as phenyl, naphthyl, etc) and benzylic-type (such as benzyl, 1-phenyl-1-alkyl, phenylbenzyl, etc) radicals with •HO_2 radicals or oxygen molecules, the reactions of oxy-aromatic (such as phenoxy, cresoxy, naphthoxy) or alkoxy-aromatic (such as benzoxy) radicals. For polyalkylbenzenes such as xylenes, the kinetics of the isomerization involving the transfer of a H-atom from one branch to another one in peroxy radicals [244] should be investigated. A better understanding of the chemistry of C_5 oxygenated compounds, such as cyclopentadienone, would also be of interest.

6/ APPLICATIONS TO SURROGATE MIXTURES

The procedure for the development of chemical surrogates for gasoline and diesel fuel can certainly be inspired from the strategy well stated by Ranzi et al. [309-310] in two papers describing the formulation of a JP-8 surrogate fuel. This strategy was the following:

"1. Feasibility. Candidates in the formula must have known detailed kinetic mechanisms.

2. Simplicity. Mainly limited for computational capabilities to normal paraffins with less than 12 carbons, monocyclic paraffins with less than 8 carbons, and simple aromatics such as benzene, alkyl-benzenes and naphthalene.

3. Similarity. The surrogate is required to match practical fuels on both physical and chemical properties: (i) volatility (boiling range and flash point), (ii) sooting tendency (smoking point and luminous number), (iii) combustion property (heat of combustion, flammability limits and laminar premixed mass burning rate).

4. Cost and availability."

Of course, in the case of gasoline surrogates, branched paraffins and alkenes should also be taken into account. In the case of diesel surrogates, the presence of parraffins including more than 12 atoms of carbons and naphtheno-aromatics might be envisaged. For the development of HCCI engines, the autoignition properties of surrogates are also of particular importance. Two recent papers written by authors from various US laboratories have assessed the current state of research concerning surrogates for gasoline [311] and diesel fuel [312] and outline the main development needed for the related experimental database and modelling tools.

6.1/ Main features about reaction coupling

There are two main theories concerning the interactions between fuels during the oxidation of mixtures. The first one, which was taken as a basis by Klotz et al. [259] during their study of the oxidation of toluene/butane blend at 1200 K, postulated that chemical interactions were limited to an effect on the common pool of free radicals. That means that retarding influence of the addition of toluene during alkane oxidation would be mainly due to a decrease of the concentrations of small radicals, such as H- and O-atoms and •OH and •HO_2 radicals, which can be trapped by H-abstractions from toluene to give unreactive benzyl radicals. The second theory considers "cross term" reactions to account for a possible fuel interactivity. A pioneering study of the low temperature oxidation of alkanes mixtures was performed by Westbrook, Warnatz and Pitz in 1988 [313] for iso-octane/n-heptane mixtures It proposed "cross term" reactions between heptyl radicals and iso-octane and between iso-octyl radicals and n-heptane, but found them of little influence because the concentrations of alkyl radicals were small. A wide range of "cross term" reactions have been used in more recent models, e.g. H-abstractions from a parent fuel (RH) by phenyl, benzyl and R'O_2• radicals which are derived from another R'H parent fuel, and will be detailed further in this paper. An experimental

demonstration of the occurrence of “cross term” reactions has been given by Vanhove et al. [314]. They have detected, during the preignition phase of a 1-hexene/toluene mixture, the formation of 1-buten-3yl-benzene and 1-hepten-3yl-benzene which can only be obtained by combinations of radicals deriving from both fuels (benzyl radicals from toluene and allyl and 1-hexene-3-yl radicals from 1-hexene).

6.2/ Detailed chemical models of the low temperature oxidation

As the model of a mixture is based on the combination of models for each of its components, the main groups active in modelling the oxidation of mixtures are those who have already worked on models of neat fuels, i.e. mainly the teams of Livermore, Milano, Nancy and Stockholm.

Normal-heptane and iso-octane are primary reference fuels (PRF) for octane rating in spark-ignited internal combustion engines; their octane numbers are 0 and 100, respectively. Reference fuels, which have intermediate octane numbers, are obtained from mixtures of these two compounds and are used to measure the octane number of actual gasoline in CFR engines. For a given octane number, the modelling of the reference mixture is important to understand the chemical phenomena which govern the autoignition of relevant gasoline. That explains why the n-heptane/iso-octane blend (PRF mixture) has long been the most studied mixture.

In Livermore, based on the classes of reactions and the estimations of rate expressions defined to model the oxidation of n-heptane [70] (see paragraph 2.2.a), a model for the low temperature oxidation of PRF mixtures [315] has been written and validated using experimental data obtained in a flow reactor [136] and in a shock tube [119]. The more recent model for the oxidation of iso-octane [70] included that for n-heptane and can then be used to model the oxidation of PRF mixtures. In this model, the chemical interactions between n-heptane and iso-octane were only induced by an action on the common pool of free radicals. Still more

recently, the team of Westbrook and Pitz has published a model for a surrogate for gasoline containing n-heptane, iso-octane, 1-pentene, toluene and methylcyclohexane [316-317]. This model was based on the mechanism for the low temperature oxidation PRF mixtures [70], which initially included high temperature reactions for 1-pentene. Their recent models for toluene [264] (see paragraph 5.2) and methylcyclohexane [225] (see paragraph 4.2), which are previously described in this paper, as well as "cross term" reactions, were added to produce a global mechanism consisting of 1214 species and 5401 reactions. This model was used to reproduce satisfactorily experimental data obtained in a HCCI engine for mixtures of these five components and in a shock tube for n-heptane/iso-octane/toluene blends [121].

In Stockholm, a model for the low temperature oxidation of PRF mixtures was proposed based on that of Livermore [70], but including additional 131 "cross term" reactions, and validated on experimental data obtained in a shock tube [119], a rapid compression machine [117] and the measurements of the authors in a HCCI engine [318]. At the same time, a model for the oxidation of n-heptane/toluene blends was obtained by merging the model for toluene oxidation of Dagaut et al. [265] (see paragraph 5.2) and the newest version for n-heptane of Livermore [70] and by adding 12 "cross term" reactions. This model was used to reproduce data obtained in the same HCCI engine [318]. In the more recent paper describing their model for the oxidation of toluene, Andrae et al. [261] have also presented a new model for the oxidation of PRF/toluene mixtures, which was obtained by merging the model of Livermore for PRF mixtures [70] with their new model for toluene written for this study (see paragraph 5.2) and by adding 167 "cross term" reactions. This model (1083 species in 4535 reactions) was used with success to reproduce the data obtained in shock tubes at high pressure for n-heptane/toluene blends [301] and for PRF/toluene mixtures [121].

Three other models have been derived from the work of Livermore. Dubreuil et al. [22]

from Orléans have satisfactorily modelled their results obtained in a jet-stirred reactor for the oxidation of the n-heptane/toluene blend with a mechanism made by merging that of Livermore for n-heptane [70] and that of Nancy for toluene [266] (see paragraph 5.2). No “cross term” reaction was described. Vanhove et al. [319] in Lille have simulated their own results obtained in a rapid compression machine for binary and tertiary mixtures containing iso-octane, 1-hexene and toluene [314]. This tertiary mixture can be considered as a good gasoline surrogate candidate. They have used the mechanism of Livermore for iso-octane [70], that of Nancy for 1-hexene [186] and an in-house one for toluene. “Cross term” reactions were mentioned: H-abstractions between peroxyalkyl or hydroxyperoxyalkyl radicals and iso-octane or 1-hexene molecules and H-abstractions from toluene by allylic alkenyl radicals. Chaos et al. [262] in Princeton have coupled a minimized model derived from the PRF mechanism of Livermore [70] with their recent one for toluene written for this study (see paragraph 5.2). They have used it to simulate their own results obtained in a flow reactor, as well as measurements made for PRF [119], n-heptane/toluene [301] and PRF/toluene [121] mixtures in shock tubes. No “cross term” reactions were considered.

In Milano, a semi-detailed model for the low-oxidation of PRF mixtures was obtained by merging their models for n-heptane [96] and iso-octane [97] (see paragraph 2.2.b). This model [136], involving about 150 species and 3000 reactions, was validated using experimental data obtained in a flow reactor in Princeton, in a rapid compression machine in Lille and in a jet-stirred reactor in Orléans [320]. By adding their mechanisms for MTBE and ETBE (see paragraph 2.2.b) to their model of n-heptane, the group of Ranzi and Faravelli has been able to reproduce the retarding effect of the addition of these ethers on the oxidation of n-heptane in a jet-stirred reactor [92], as was experimentally measured in Orléans [321]. Based on their semi-detailed model for the low temperature oxidation of n-dodecane [92], which already contains

reactions for simple aromatic compounds (see paragraph 2.2.b), on a semi-detailed sub-mechanism for the low-oxidation of iso-cetane (2,2,4,4,6,8,8-heptamethylnonane) and on high temperature lumped reactions for methylcyclohexane, models for the oxidation of n-dodecane/iso-cetane, n-dodecane/methylcyclohexane and n-dodecane/1-methylnaphthalene blends have been proposed [140-141]. The validation of the models for these binary mixtures, which can be considered as surrogates for diesel fuel, was performed using experimental data obtained in a flow reactor. A model for a surrogate of kerosene containing n-dodecane, iso-octane, methylcyclohexane, benzene and toluene has been written [309] and validated under flame conditions [322]. Models for still more complex fuels have been obtained by adding high temperature lumped reactions for n-tetradecane and decalin [310]. Only the "cross term" reactions involving the H-abstraction from the parent fuel by isobutyl and isobutenyl radical, which come from the iso-octane decomposition, were systematically considered.

In Nancy, a model for the low temperature oxidation of PRF mixtures was generated using EXGAS software (see paragraph 2.2.b). The first version [323] was validated using data obtained in a jet-stirred reactor [320] and an improved version (529 species and 2477 reactions) [24] was generated to model ignition data obtained in a rapid compression machine [136] and in a shock tube [119]. No "cross term" reaction was taken into account. In order to test a surrogate for gasoline, Pires da Cruz et al. [324] have merged this last model for PRF mixtures with that for the oxidation of toluene previously developed in Nancy [266] (see paragraph 5.2), with the addition of 21 "cross term" reactions. Validation for n-heptane/toluene blends was performed using experimental results obtained in a rapid compression machine [314], a jet-stirred reactor [22] and a HCCI engine [318]. Simulations for iso-octane/toluene mixtures were made in order to reproduce data measured in a rapid compression machine [314] and a HCCI engine [318]. Tests for PRF/toluene blends were made against data obtained in a shock tube [119] and in a

rapid compression machine [117]. The reactivity of n-heptane/toluene was underestimated at low temperature (below 800K) and the rate constant of the decomposition of H_2O_2 molecules needed to by increased by a factor of 4 in order to fit results above 40 bar. For the PRF/toluene blends in a rapid compression machine, figure 31 shows that the sensitivity of the reactivity to small variations of the iso-octane to n-heptane ratio with a fixed amount of toluene is well captured by the mechanism [324], although the simulated ignition delay differences between fuels are smaller than the experimental ones [117]. A surrogate for diesel fuel has also been investigated: a mechanism for the oxidation of n-decane/1-methylnaphtalene mixtures [10] has been obtained by merging the low temperature mechanism for n-decane, as generated by EXGAS software, with that for 1-methylnaphtalene developed in the same study, with the addition of the two types of "cross term" reactions shown in figure 32. Qualitative validation was made against experimental autoignition delay times measured in a pressurized chamber at 3 bar in which a suspended droplet was suddenly brought to a temperature from 600 K to 750 K [149]. Models for n-heptane/MTBE and n-heptane/ETBE blends [107] were also generated by using EXGAS software and successfully tested against the experimental results obtained in a jet-stirred reactor [321]; "cross term" reactions were neglected. The new version of EXGAS designed to generate models for the oxidation of alkenes (see paragraph 3.2) was used to produce a mechanism for an iso-octane/1-hexene blend [325], which was satisfactorily used to model data obtained in a rapid compression machine [314]; for this last mechanism, "cross term" reactions were automatically generated.

FIGURES 31- 32

Böhm et al. [79] have qualitatively reproduced their experimental results obtained in a static reactor [54] for n-pentane/ether mixtures by incorporating their models for ethers in the n-heptane oxidation mechanism of Chevalier et al. [85] (see paragraph 2.2.a). No "cross term"

reactions were mentioned.

6.3/ Experimental results available for validation

The experimental results concerning the autoignition and the oxidation below 900 K of mixtures of compounds containing more than 4 atoms of carbon are shown in Tables 21 to 23. The two types of mixtures the most often investigated are binary mixtures containing either PRF (Table 21) or an alkane and an aromatic compound (Table 22). In the mid 90s, due to the interest in octane improvers, few studies have been focused on binary mixtures of an alkane and an ether molecules (Table 21). In the five last years, binary mixtures (Table 22), as well as ternary and quaternary blends (Table 23), containing an alkene molecule, have also been investigated. Only two studies of Drexel University have dealt with blends containing a cyclo-alkane.

TABLES 21-23

Concerning autoignition, the rapid compression machine of Lille was used to study an impressive range of blends containing PRF [136], 1-hexene, benzene or toluene [314], but not the PRF/toluene mixture, which has often been proposed as a valuable gasoline surrogate candidate. The machine of Cambridge (USA) has been used to investigate PRF, n-heptane/toluene and PRF/toluene blends [117] and that of Cleveland in the case of toluene/diisobutylene (2,4,4-trimethyl-2-pentene) and iso-octane/toluene mixtures [328]. Results in shock tubes are less abundant. The high-pressure shock tube of Aachen was used to study PRF mixtures [121], measurements concerning PRF/toluene mixtures were made in Standford [119] and the apparatus of Duisburg was used to investigate PRF mixtures [326], n-heptane/toluene [301] and n-heptane/toluene/iso-octane/di-iso-butylene blends [330]. The two recent studies concerning di-iso-butylene, which has a similar structure to iso-octane, are of particular interest due to the great lack of results concerning branched alkenes.

Apart from the results obtained in the flow reactor of Princeton by the team of Dryer for

the oxidation of PRF mixtures [136] and PRF/toluene blends [262] and those published by the team of D'Anna of Napoli for the oxidation of n-heptane/toluene mixtures in a jet-stirred reactor [134], most data obtained in a continuous flow reactor for the oxidation of mixtures were obtained by the team of Dagaut in Orléans in an isothermal jet-stirred reactor [22,320-321,327,329] and by the team of Cernansky in a flow reactor [138-141]. Mainly focused on the search of gasoline surrogates, the team of Dagaut has studied PRF mixtures [320], mixtures of n-heptane with ethers [321] and with toluene [22] and blends containing iso-octane, 1-hexene or toluene, including a quaternary iso-octane /1-hexene/ETBE/toluene mixture [327,329]; a high temperature model has been proposed by this team to reproduce these last results. While the other studies have been only performed from 800 K, the oxidation of PRF, n-heptane/MTBE, n-heptane/ETBE and n-heptane/toluene mixtures has been investigated from 550 K, i.e. including the complete NTC zone, and has shown that the addition of iso-octane, ethers and toluene has a strong retarding effect on the reactivity of n-heptane. Mainly interested in the surrogates of diesel and jet fuels, the team of Cernansky [138-141] has studied the oxidation of n-decane/iso-octane, n-dodecane/iso-cetane, n-dodecane/methylcyclohexane and n-dodecane/ 1-methylnaphthalene binary mixtures and of tertiary blends, containing n-decane, n-butylcyclohexane or methylcyclohexane and n-butylbenzene or toluene, using the control cool down method (CDD), in which the reactor was stabilized to a specified maximum temperature and then allowed to cool at a fixed rate and a constant pressure and residence time. The results concerning tertiary blends are still to be modelled

A study of the effect of the addition of TAME, MTBE, ETBE on the induction periods of the cool flames of n-pentane oxidation has been carried out by the team of Baronnet [54] in a static reactor at low pressure for very rich mixtures. The strong non-linear increase of the induction period with the added amount of ether well demonstrates the anti-knock effect of these

compounds.

6.4/ Comparison between the major models in terms of elementary steps and associated rate constants

The types of considered "cross term" reactions depend on the nature of the mixtures. We will distinguish "cross term" reactions for alkane mixtures, for alkane/alkene blends and for mixtures containing an aromatic compound. The rate parameters used by the three teams for the reactions involving peroxy radicals or species deriving from toluene are summarized in Tables 24 and 25, respectively. The "cross term" reactions involving H-abstraction from alkanes, cycloalkanes and alkenes by alkyl and alkenyl radicals are in most cases negligible below 900K and are therefore not detailed here.

TABLES 24-25

6.4.a/ Mixtures of alkanes

"Cross term" reactions for alkane mixtures have been considered in Stockholm [126], Livermore [316-317] and Nancy [103]. In Stockholm, "cross term" reactions involved in the oxidation of PRF mixtures have been comprehensively taken into account [126]. They have written all the H-abstractions from n-heptane by iso-octyl and iso-octylperoxy radicals and from iso-octane by linear or branched heptyl and heptylperoxy radicals; the reactions of branched C_7 radicals are not really "cross term" reactions, as these species are derived from iso-octane. The users of the mechanisms of Stockholm should be aware that the rate coefficients for "cross term" reactions have been reevaluated between the first [318] and the second [126] papers. The more realistic rate coefficients used in the last paper lead to a strong decrease of the influence of these reactions.

In the model of Livermore for a surrogate of gasoline [317], some "cross term" reactions between PRF that were missing in their first mechanism [70] and that were proposed by Andrae

et al. [318] were included using rate coefficients modified to be consistent with their previous rate rules [317]. The H-abstractions from n-heptane, iso-octane and methylcyclohexane by small alkylperoxy radicals were considered, as well as reactions between alkylperoxy radicals for various alkyl groups of different fuel components. “Cross term” reactions between the species of the base PRF mechanism and methylcyclohexane were also incorporated.

In Nancy, the software EXGAS is designed to consider systematically the "cross-term" reactions: each time a radical is created, it is submitted to all the possible generic propagations without considering its reactant of origin. That means that “cross term” reactions involving H-abstractions from parent a fuel (RH) by R’• and R’O_2• radicals could be taken into account on request [104]. But these reactions have been shown to have a negligible influence in the case of alkane blends and their generation was usually not performed. The rate parameters for alkylperoxy radicals, which were close to those used in Livermore and Stockholm, were taken from Chevalier et al. [84].

6.4.b/ Alkane/alkene blends

The oxidation of alkane/alkene mixtures has only been modelled in Livermore [316-317] and Nancy [325]. In Livermore, the H-abstractions from 1-pentene by small alkylperoxy radicals and from n-heptane, iso-octane and methylcyclohexane by 1-penten-3-yl radicals have been written.

In the Nancy model for iso-octane/1-hexene blends, two types of “cross term” reactions have been generated and found to be of negligible importance [325]:

- The H-abstractions from iso-octane or 1-hexene by peroxy radicals.

In the mechanisms concerning a single class of hydrocarbon, only the peroxy radicals deriving directly from the reactant (i.e. those which can be obtained through only 2 elementary steps: an H-abstraction or an addition of OH to the double bond followed by an addition to an oxygen

molecule) can react by H-abstraction. Applying this rule in the present case, only iso-octyl peroxy ($C_8H_{17}OO$•), 1-hexenylperoxy ($C_6H_{11}OO$•) or hydroxyhexylperoxy ($C_6H_{12}OHOO$•) radicals were involved.

- The combinations of the allylic radicals deriving from 1-hexene, 1-hexen-3-yl radicals and 3-hexen-2-yl radicals, with tC_4H_9 and iC_3H_7 radicals, with a rate constant k= $4.2x10^{12}$ $cm^3mol^{-1}s^{-1}$.

Amongst the radicals obtained from the decompositions by beta-scission of iso-octyl or derived radicals, only tC_4H_9 and iC_3H_7 radicals were taken into account for combinations because they cannot decompose by beta-scission involving the breaking of a C-C bond and are consequently less reactive than other radicals.

6.4.c/ Mixtures containing an aromatic compound

"Cross term" reactions for mixtures containing an aromatic compound have been considered, in Stockholm [126], Livermore [316-317] and Nancy [10-324]. The three teams have considered the H-abstractions from toluene by alkyl and alkylperoxy radicals, with notable differences in the used rate constants in the case of alkylperoxy radicals. In Nancy, only the H-abstraction from toluene with methylperoxy radicals has been found of importance [324]. The teams of Stockholm [126] and Livermore [316-317] have also written the H-abstractions from benzaldehyde by peroxyalkyl radicals and the Stockholm team [126] has further written H-abstractions from PFRs by phenyl radicals. The team of Livermore [316-317] has taken into account the H-abstractions from 1-pentene by 1-penten-3-yl radicals and from 1-pentene and methylcyclohexane by benzyl radicals. Finally, the team of Nancy [324] has also considered the H-abstractions from toluene by resonance stabilized iso-butenyl, iso-octenyl and heptenyl radicals and the combinations between benzyl and alkyl radicals. In the case of the n-decane/1-methylnaphthalene blends [10], the H-abstractions from n-decane by phenylbenzyl

radicals have been written, as well as the combinations between phenylbenzyl and decyl radicals (see figure 32), this last reaction having the same rate constant as that with benzyl radicals.

6.5/ Conclusion on the modelling of the oxidation of mixtures

While kinetic mechanisms for the oxidation of gasoline surrogates have been first restricted to PRF, these few last years have seen the emergence of numerous models for a widening range of mixtures, as well as an important production of experimental data to validate them, even if, as for pure fuels, the range of investigated equivalence ratios would need to be extended. This effort has been motivated by the strong interest of the automotive industry in the development of HCCI engines.

The studies concerning gasoline surrogates have been focused towards blends made of an alkane mixed with an alkene or an aromatic compound, mainly toluene, and towards mixtures containing more than two components. Several models are now available for the oxidation of PRF/toluene mixture, but they suffer from the uncertainties in the mechanism of the oxidation of toluene at low temperature and high pressure, e.g. in Stockholm, the rate constant of the reaction of benzyl radicals and oxygen molecules had to be tuned in order to get satisfactory results, while in Nancy, an arbitrary variation of the A-factor of the decomposition of H_2O_2 molecules was made. A five component surrogate (PRF/toluene/methylcyclohexane/1-pentene) has even been proposed, but with high temperature chemistry for the alkene oxidation.

Models for diesel fuel surrogates have also just appeared, e.g. n-dodecane/iso-cetane or n-dodecane/1-methylnaphthalene, even if the experimental data available for their validation are still very scarce.

In mixtures containing alkanes or alkenes, the proposed “cross term” reactions have been found to be of negligible importance when cross effects occur quasi-exclusively via the radicals pool. For mixtures containing toluene, H-abstractions from toluene, as well as combinations

involving benzyl radicals could be of some importance and may at least explain the formation of minor products, as shown by the experimental work of Vanhove et al. [314].

8/ CONCLUSION

This review has assessed the recent gas-phase detailed kinetic models developed to simulate the low temperature (below 900 K) oxidation and autoignition of the components of gasoline and diesel fuel (alkanes, ethers, esters, alkenes, cycloalkanes and aromatics, each including 4 or more atoms of carbon) and of the mixtures of several of them, which have been proposed as surrogates for actual fuels.

Concerning pure compounds, this analysis has shown that numerous models have been proposed for alkanes, with a wide range of experimental data available to validate them. This abundance of models diminishes when other families of components are considered. Branched compounds and those containing more than ten carbon atoms have been far less thoroughly studied. For alkenes containing more than five carbon atoms, only the reactions of straight-chain 1-pentene and 1-hexene have been modelled, and discrepancies with experimental results for the formation of the products were obtained. There is no model for the low temperature oxidation of branched alkenes. Models have been proposed for cyclohexane and methylcyclohexane, but there are no simulations concerning cyclopentane or other substituted cycloalkanes. Important problems remain in the modelling of the oxidation of aromatic compounds, especially at low temperature and high pressure. This is particularly true for toluene, which is frequently considered in gasoline surrogates. Experimental and modelling studies are also missing for naphtheno-aromatic compounds. The range of validity of models in term of equivalence ratio is narrow and close to stoichiometry. Validated modelling for equivalence ratios below 0.5, which can be of importance in HCCI engines, and above 3, which can be observed in some parts of the combustion chamber of diesel engines, are very scarce, combined with a lack of experimental

data. Kinetic models can qualitatively explain the differences in RON between various compounds. However the observed variations of sensitivity (the difference between RON and MON) with the type of fuel are still not well understood, e.g. sensitivity is far larger for alkenes than for alkanes

The literature is relatively rich in detailed kinetic models for the oxidation of mixtures of components of gasolines, but far poorer for species included in diesel fuel. These models can in most cases satisfactorily capture the evolution of autoignition delay times with temperature and pressure, and the formation of the major products (carbon oxides, ethylene). Validated models for multicomponent mixtures representative of gasoline (e.g. n-heptane/iso-octane/toluene or iso-octane/1-hexene//toluene blends) and to a lesser extent diesel fuel, are starting to become available. The question about the optimum number of components which should be considered in a surrogate for it to be well representative of an actual fuel, without increasing unreasonably the size of the model, is still open. It is certainly important that the components of a surrogate are carefully chosen so that they are well representative of the species present in the actual fuel. Models for each component of the surrogate should first be well defined separately and validated on a wide range of experimental conditions. In most types of mixtures, “cross term” reactions have been found to be negligible. Co-oxidation between reactants occurs quasi-exclusively via the radical pool. For mixtures containing aromatic compounds, “cross term” reactions involving resonance stabilized radicals could be of some importance, at least to explain the formation of minor products.

In the case of both pure compounds and multicomponent mixtures, it is important that the experimental database will still be increasing, with results obtained in systems, which are physically well characterised, such as rapid compression machines, shock tubes, jet-stirred or flow reactors. More detailed measurements of reaction products would also be of help for a

better understanding of the reaction channels. The development of new techniques allowing the measurement of the concentration of radical species (e.g. HO_2• radicals) in these apparatus would also be of great interest.

As it is important that no determining reaction is omitted, the development of detailed kinetic models mainly involves the inclusion of a comprehensive reactions base and the systematic writing of relevant elementary steps according to given rules. This necessary method of development means that low temperature models include hundreds of species and thousands of reactions, which hinders their use for practical applications and even prohibits their incorporation into a reactive flow solver, even for 1D computation. However, the fact that detailed models are based on elementary steps should also allow them to be used in a predictive way to give clues in cases where experimental investigations are difficult. Comprehensive models are also of interest for a better identification of the elementary steps which govern combustion reactions.

When analysing major models of the literature in term of the considered types of elementary steps and in the used rate coefficients, it is striking to see the important differences existing even for simple compounds such as alkanes. The differences in kinetic data are certainly also related to differences in thermochemical properties. That explains why similar agreement with experimental data can be observed when comparing simulations using various models. These differences would however probably lead to important deviations between models when trying to model the formation of minor products, such as heavy alkenes, dienes, aromatic compounds, aldehydes, ketones, alcohols and acids, which can be toxic to human health and are of great importance in air pollution, as they are involved in the formation of urban smog and acid rain. If a satisfactory prediction of the formation of these species is desired, the degree of accuracy of the models should be increased and fundamental studies on the involved elementary

steps would be needed, including experimental work and theoretical calculations. The parameterizing of the rate constants as a function of temperature and pressure (P-T parameterization) should also be used for an increasing range of multi-channel reactions, e.g. the reactions of oxygen molecules with phenyl radicals or alkyl radicals containing more than four atoms of carbon. The mechanism of the degradation of the first oxidation products, such as hydroperoxides, alkenes, cyclic ethers and aldehydes, needs also to be better understood.

New determinations of rate constants, based on both recent experimental techniques and calculations using quantum mechanical and master equation methods, should certainly lead to a reduction of the existing uncertainties. That would be of particular interest for the following elementary steps which are important in low temperature oxidation models:

- The reactions with oxygen molecules of alkyl, alkenyl, allylic and benzylic radicals including more than four carbon atoms, with a careful P-T parameterization for the concurrent channels, e.g. the formation of peroxy radicals and that of alkenes and $\bullet HO_2$ radicals.
- The formation of cyclic ethers including bicyclic compounds, with a characterisation of the possible products in the case of alkenes.
- The reactions of large allylic and derived radicals, which are taken at the moment to be those of allyl radicals.
- The reactions with $\bullet HO_2$ radicals, especially with allylic and benzylic radicals.
- The additions of •OH radical to a double bond or to a phenyl ring.
- The low temperature reactions of cyclic compounds, with a determination of the influence of the presence of an alkyl chain or of a strained cycle.
- The reactions of oxy radicals, especially during the oxidation of aromatic species (e.g. phenoxy and cresoxy radicals).

More accurate determinations of rate constants will hopefully allow a better agreement to be obtained between the models which will be developed in the future. Nevertheless, differences will certainly remain due to the manner in which these models are developed. If we consider the groups of Livermore, Milano and Nancy, which have produced the biggest part of the models quoted in this paper, they each have a specific way of doing it. The "hand-made" work of Livermore has led to the thoroughly validated mechanisms for a few key reactants (up to C_8) and mixtures of them which are important in gasoline. At Milano, the coupling of automatic generation with a clever work of lumping has allowed them to study several compounds, as well as mixtures, representative of those included in diesel fuels. The completely automated method used in Nancy was well suited to propose models for alkenes, the complexity of their chemistry making manual and semi-manual methods difficult to be used. This last system could also be of interest to rapidly write mechanisms for alkanes or alkenes never investigated before or to systematically test changes in generic reactions and rate constants. With these three systems being rather complementary, it could be tempting to amalgamate the best pieces from each of them. That could certainly be of interest as shown by Dubreuil et al. [22], who have coupled the mechanism of n-heptane of Livermore [70] with that of toluene of Nancy [266]. Thist should however be carefully done, as the models produced by each system are self-consistent, i.e. in each group, the thermochemical data, the reaction base for small species and the primary and secondary mechanisms have been tailored to work together.

The uncertainties in the rate constants of the key reactions of importance in low temperature oxidation mechanisms can certainly be still reduced by a large factor after additional studies. However, unavoidable errors on these parameters would probably always limit the possible accuracy which can be reached. An optimization procedure, as that used in the GRI-Mech database for the oxidation of methane [40], could certainly be extended to the case of

heavier hydrocarbons, but it is feared that this procedure, which changes some parameters compared to their average recommended value, would lead to large discrepancies when leaving the range of conditions used for the optimization and would then hinder the use of the obtained models in a predictive way. Nevertheless, detailed kinetic models can only gain to be validated on the widest possible range of experimental conditions. That involves a better organisation of the collaborations between model developers and (experimental and theoretical) data providers, preferentially at an international level. The sharing of experimental data and models, such as that proposed in the PrIMe (Process Informatics Models) network described by Frenklach [331], should be strongly encouraged. The development of kinetic mechanisms should also be more and more seen as a part of a multiscale approach, which needs theoretical data obtained at the quantum level, but also aims at providing models to be used in engines simulations by oil and automotive industrial researchers.

Their large size explains why an important effort has been made for several years to reduce detailed schemes. The methods of reduction have been well reviewed in 1997 by Tomlin et al. [81] and summarized in 2007 by Law [332]. The majority of the methods developed for mechanism reduction falls into two categories, that is, skeletal reduction that eliminates unimportant species and reactions, and time-scale reduction that moderates the stiffness. A first method of the skeletal reduction is the elimination of unimportant species and reactions using sensitivity analysis, principal components analysis [333] or rate of reaction analysis. The detailed mechanisms of Livermore for iso-octane (860 species) [70] has been reduced by Lu and Law [334] and Saylam et al. [335] to skeletal mechanisms consisting of 233 and 300 species, respectively. Automated procedures have been applied by Porter et al. [336] to reduce the reaction mechanism of Nancy describing the oxidation of cyclohexane [228] from 499 species to 60 necessary species. The level of reduction is a function of the modelling abilities that are

sought to be kept in the reduced model: the skeletal model of Saylam et al. [335] is still relatively large, but it is able to represent the formation of heavy alkenes and cyclic ethers.

A second method is the lumping of different isomers into a single species, e.g. the four heptylperoxy radicals are represented by $C_7H_{15}OO$• or ROO •. This method has been widely and successfully used in Milano by Ranzi et al. [92] to obtain semi-detailed mechanisms, as well as tested in Nancy [337]. As it cannot be applied to the reactions of small species, this method does not allow very important reduction factors for reactants containing less than 10 atoms of carbon. Nevertheless, it is well suited to reduce primary or secondary mechanisms and can be of great interest when treating species of large size, such as those included in diesel fuel [93], or mixtures of several compounds.

The methods of reduction based on the time-scales involved in the kinetic equations include the quasi-steady-state approximation (QSSA) [338], the computational singular perturbation (CSP) method [339] and the low-dimensional manifold (ILDM) method [340]. Few applications of these techniques to model the low temperature oxidation of large hydrocarbons have been published. By introducing QSSA, Soyhan et al. [341] have reduced a skeletal n-heptane/iso-octane mechanism (63 species and 386 reactions) deriving from the work of Chevalier [84] to 19 species and 16 global reactions. By using the CSP method from the detailed mechanisms of Livermore for n-heptane (561 species) [70], Valorani et al. [342] have obtained a skeletal mechanism consisting of 124 species.

Detailed or reduced models can also be used to run large numbers of simulations in order to derive fitted functions or repro-models (mostly polynomials) [338, 343] or look-up tables in order to store target data under a wide range of conditions (pressure, temperature, mixture compositions) and to use them to run reactive flow simulations. Look-up tables, including chemical progress rate, cool flame ignition delay time and heat release [344] or mole fractions of

major species [345], have been recently built from the mechanisms of Nancy for n-heptane and n-decane/1-methylnaphthalene blends. They have been used satisfactorily to run real engine CFD 3D computations and to obtain the results shown in figure 1 [10].

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Table 1
Composition of a European commercial gasoline (Guibet, 1997 [11]).

	Families of components (%)						
Number of atoms of carbon	Saturated compounds			Unsaturated compounds			
	Linear alkanes	Branched alkanes	Ethers	Cyclic alkanes	Alkenes	Aromatic compounds	Total
4	5.14	0.30			1.49		6.93
5	1.26	7.84	0.50		10.11	0.50	19.71
6	0.64	6.34	3.00	1.19	5.07	1.23	17.47
7	0.65	3.22		1.05	1.56	8.11	14.59
8	0.48	11.47		0.43	0.34	13.61	26.33
9	0.11	1.12		0.16	0.07	9.49	10.95
10	0.01	0.09		0.09	0.02	2.80	3.01
11		0.10				0.25	0.35
12		0.61					0.61
13		0.01					0.01
Total	8.29	31.10	3.50	2 .92	18.66	35.49	99.96

Table 2
Comparison between the size of the low temperature and high temperature mechanisms for alkanes, as generated by EXGAS-ALKANES software [24] and octane numbers (RON and MON) of several alkanes [11].

Type of alkane	Low temperature		High temperature		RON	MON
	Number of species[a]	Number of reactions[a]	Number of species[a]	Number of reactions[a]		
n-butane	128	731	80	585	95	92
n-pentane	196	989	97	674	61.7	61.9
iso-pentane	210	1039	104	716	92.3	90.3
neo-pentane	148	789	98	666	85.5	80.2
2-methyl-pentane	325	1643	127	841	73.4	73.5
n-heptane	360	1817	114	783	0	0
iso-octane	351	1684	156	958	100	100
n-decane	530	3834	145	966	< 0	< 0

[a]: All the mechanisms contain the C0-C2 reaction base which involves 448 reactions among 54 species.

Table 3
Summary of the experimental results concerning the autoignition of alkanes from C_4 to C_6 below 900 K.

Compounds	Type of reactor[a]	Temperature Range (K)	Pressure Range (bar)	Equivalence ratio range	References
n-butane	RCM	700-900	8.9-11.5	1	Carlier et al. (1994) [108]
	CV	550-800	1-6	0.06- 0.66	Chandraratna and Griffiths (1994) [109]
n-pentane	RCM	600-900	6-11	1	Minetti et al. (1996) [110]
		650-900	6-9	1	Griffiths et al. (1993, 97) [111-112]
	ST	867-1534	11-530	0.5	Zhukov et al. (2005) [113]
Iso-butane	RCM	900	7.5-9	1	Griffiths et al. (1997) [112]
Iso-pentane	RCM	680-900	8-11	1	Minetti et al. (1996) [110]
Neo-pentane	RCM	680-950	4-11	1	Minetti et al. (1996) [110]
		750-900	7.5-9	1	Griffiths et al. (1997) [112]
Isomers of hexane	RCM	680-950	6-9	1	Griffiths et al. (1993, 97) [111-112]
n-hexane	ST	822-1380	56-244	0.5	Zhukov et al. (2004) [114]

[a]: see nomenclature.

Table 4
Summary of the experimental results concerning the autoignition of alkanes from C_7 below 900 K.

Compounds	Type of reactor[a]	Temperature Range (K)	Pressure Range (bar)	Equivalence ratio range	References
Isomers of heptane	RCM	700-950	7.5-9	1	Griffiths et al. (1997) [112]
		685-868	7.5-9	1	Westbrook et al. (2002) [72]
		640-960	15	1	Silke et al. (2005) [115]
n-heptane	RCM	600-900	6-11	1	Minetti et al. (1995) [116]
		700-960	6-9	1	Griffiths et al. (1993, 97) [111-112]
		798-878	40-44	0.2-0.5	Tanaka et al. (2003) [117]
	ST	650-1200	3.2-42	0.5-3	Adomeit et al. (1993) [118-119]
		720-1100	50	0.1-0.4	Herzler et al. (2005) [120]
		850-1280	15-60	0.5-2	Gauthier et al. (2004) [121]
Iso-octane	RCM	600-900	6-11	1	Minetti et al. (1996) [122]
		750-900	7.5-9	1	Griffiths et al. (1997) [112]
		798-878	40-44	0.2-0.5	Tanaka et al. (2003) [117]
		900-1020	8.5-16.6	0.25-1.98	He et al. (2005,0,6, 07) [123-125]
	ST	650-1200	13-45	1	Fieweger et al. (1997) [119]
		855-1269	14-59	0.5-1	Davidson et al. (2005) [126]
n-decane	ST	650-1200	12-50	1-2	Pfahl et al. (1996) [127]
		800-1100	12-80	0.5-1	Zhukov et al. (2005) [128]
	RCM	630-706	7-30	0.8	Kumar et al. (2007) [129]

[a]: see nomenclature.

Table 5
Summary of the experimental results concerning the oxidation of alkanes from C_4 in continuous reactors below 900 K.

Compounds	Type of reactor[a]	Temperature range (K)	Pressure range (bar)	Equivalence ratio range	References
Neo-pentane	FR	620-810	8	0.3	Wang et al. (1999) [68]
	JSR	800-1230	1-10	0.25-2	Dagaut and Cathonnet (1999) [130]
n-heptane	JSR	550-1150	1-40	0.3-1.5	Dagaut et al. (1994) [131-132]
		550-750	2-10	1	Ciajolo et al. (1993, 98) [133-135]
	FR	550-850	12.5	1	Callahan et al. (1996) [136]
Iso-octane	JSR	550-1100	10	0.3-1.5	Dagaut et al. (1994, 1995) [132]
		550-750	2-10	1	Ciajolo et al. (1993, 98) [134-135]
	FR	600-850	12.5	1	Callahan et al. (1996) [136]
n-decane	JSR	550-1100	10	0.3-1.5	Dagaut et al. (1994) [137]
	FR	600-800	8	0.3	Cernansky et al. (2007) [138-139]
n-dodecane	FR	600-800	8	0.2-0.3	Cernansky et al. (2004)(2005) [140-141]
n-tetradecane	FR	500-950	3	1	Cavaliere et al. (1993) [133]

[a]: see nomenclature.

Table 6
Summary of the experimental results concerning the autoignition and oxidation of ethers and esters from C_4 below 900 K.

Compounds	Type of reactor[a]	Temperature range (K)	Pressure range (bar)	Equivalence ratio range	References
MTBE	ST	750-1200	13-40	1	Fieweger et al. (1997) [119]
	JSR	800-1150	10	0.5-2	Glaude et al. (2000) [107]
		450-750	7	1	Ciajolo et al. (1997)[156]
ETBE	JSR	800-1150	10	0.5-2	Glaude et al. (2000) [107]
	CV	573-873	0.09-0.52	9	El Kadi and Baronnet (1995) [54]
DIPE	JSR	800-1150	10	0.5-2	Goldaniga et al. 1998)[98]
TAME	CV	573-873	0.09-0.52	9	El Kadi and Baronnet (1995) [54]
	JSR	800-1150	100	0.5-2	Goldaniga et al. 1998)[98]
Methyl butanoate	FR	500-900	12.6	0.35-1.5	Gaïl et al. (2007) [80]
	JSR	800-1300	1	1-1.13	Gaïl et al. (2007) [80] Sarathy et al. (2007) [157]
Methyl crotonate (2-butenoate)	JSR	800-1300	1	1	Sarathy et al. (2007) [157]

[a]: see nomenclature.

Table 7
Comparison between the classes of reactions included in the mechanisms of Livermore [70], Milano [96] and Nancy [24].

Class of reaction	Models of Livermore	Models of Milano	Models of Nancy
Primary mechanism			
High temperature			
Unimolecular initiation	yes	yes	yes
H-abstraction by O_2 and small radicals	yes	yes	yes
Decomposition and isomerization alkyl (R•) radicals	yes	yes	yes
Low temperature			
Oxidation of R• to give alkene + •HO_2	only for alkyl radicals up to C_4	for all alkyl radicals	for all alkyl radicals
Addition of O_2 to R• and •QOOH	yes	yes	yes
Isomerization of RO_2•	yes	yes	yes
Disproportionation of RO_2•	with HO_2•, CH_3O_2•, R'• and R'O_2• (formation of RO•)	no	only with •HO_2
Decomposition of RO•	yes	no	no
RO_2•+ H_2O_2	yes	no	no
Decomposition of •QOOH to give cyclic ethers	yes	yes	yes
Other decomposition of •QOOH to give alkene + •HO_2	to give alkene + •HO_2, alkene + carbony l+•OH	to give alkene + •HO_2, alkene + carbony l+•OH	to give alkene + •HO_2, R'• + ZOOH, carbonyl + •OH
Isomerization of •O_2QOOH	to give ketohydroperoxide	to give ketohydroperoxide	to give ketohydroperoxide or on request •U(OOH)$_2$ and derived reactions
Secondary mechanism			
Decomposition of peroxides	yes	lumped	lumped
H-abstraction from alkenes	yes	lumped	lumped
Decomposition of alkenyl radicals	yes		
Addition of small radicals to alkenes	yes	lumped	lumped
Alkene decomposition	yes	no	no
H-abstraction from cyclic ethers	yes, followed by ring opening	lumped, followed by ring opening	lumped, followed by ring opening or by addition to oxygen
H-abstraction from C_{4+} aldehydes and ketones	no	no	yes

Table 8
Comparison between the rate expressions of the isomerizations of peroxy radicals considered in the models of Livermore [70], Milano [92,94] and Nancy [24] and those proposed by the team of Pilling [161].

		Models of Livermore[a]	Models of Milano	Models of Nancy	Proposition of the team of Pilling
Size of the transition ring		*A-factors at 600 K (in s^{-1}, per abstractable H-atoms)*			
4		-	-	5.8×10^{12}	-
5		1×10^{11}	6.3×10^{11}	1×10^{12}	1.41×10^{12}
6		1.25×10^{10}	1×10^{11}	1.7×10^{11}	1.76×10^{11}
7		1.56×10^{9}	4×10^{10}	3×10^{10}	2.2×10^{10}
8		1.95×10^{8}	-	5×10^{9}	2.75×10^{9}
Size of the transition ring	Type of H-atom	*Activation energy (kcal/mol)*			
4	primary	-	-	43	-
	secondary	-	-	40	-
	tertiary	-	-	37	-
5	primary	29.7 (8.6)	29.1	35.5 (15.5)	37.0 (16.5)
	secondary	27.9	25.9	32.5	32.5
	tertiary	25.4	23.6	29.5	28.2
6	primary	23.9 (2.8)	23.0	28 (8)	28.8 (9.1)
	secondary	22.15	19.8	25	26.0
	tertiary	19.7	17.5	22	-
7	primary	21.1 (0)	23.0	25 (5)	25.1 (4.6)
	secondary	19.35	19.8	22	21.7
	tertiary	16.4	17.5	19	-
8	primary	23.9 5 (2.8)	-	24 (4)	22.1 (1.65)
	secondary	22.15	-	21	-
	tertiary	19.7	-	18	-

[a]: A-factor for iso-octyl radicals has been multiplied by 0.3.
[b]: The value in brackets is the ring strain energy.

Table 9
Comparison between the rate expressions (in s^{-1}, kcal, mol units) of the decompositions of hydroperoxyalkyl radicals to give cyclic ethers considered in the models of Livermore [70], Milano [92] and Nancy [24].

Size of the cyclic ethers	Models of Livermore			Models of Milano			Models of Nancy		
	A	n	Ea	A	n	Ea	A	n	Ea
3	$6x10^{11}$	0	22	$1x10^{12}$	0	18	$6x10^{11}$	0	17.95
4	$7.5x\ 10^{10}$	0	15.25	$1.6x10^{11}$	0	17	$9.1.10^{10}$	0	16.6
5	$9.38x10^{9}$	0	7	$2.5x10^{10}$	0	8.5	$3.6.10^{9}$	0	7
6	$1.17x10^{9}$	0	1.8	-	-	-	$1.7.10^{8}$	0	1.95

Table 10
Comparison between the rate expressions (in s^{-1}, kcal, mol units) of the decompositions of hydroperoxyalkyl radicals to give acyclic species considered in the models of Livermore [70], Milano [94] and Nancy [24].

Broken bond	Models of Livermore			Models of Milano			Models of Nancy		
	A	n	Ea	A	n	Ea	A	n	Ea
C-O	[a]		18-21.3 [a]	$5x10^{13}$	0	23	$8x10^{12}$	0	26
C-C	[a]		26.8-31 [a]	$3.2x10^{13}$	0	22.5	$2x10^{13}$	0	26.7- 31[b]
O-O	-	-	-	-	-	-	$1x10^{9}$	0	7.5

[a] : Values calculated from the data of the reverse reaction using thermochemistry,
[b]: Values depending on the type of radical obtained radical (CH_3•: 31, primary radical: 28.7, secondary radical: 27.7, tertiary radical: 26.7).

Table 11
Summary of the experimental results concerning the autoignition and oxidation of alkenes from C_4 below 900 K.

Compounds	Type of reactor[a]	Temperature range (K)	Pressure range (bar)	Equivalence ratio range	References
Iso-butene	JSR	800-1230	1-10	0.2-2	Dagaut and Cathonnet (1998) [195]
		833-913	1	3-6	Baugé et al. (1998) [196]
1-pentene	RCM	600-900	6.8-9.2	1	Ribaucour et al. (2000) [77,197]
	FR	600-800	6	1	Prabhu et al. (1996) [198]
Straight-chain isomers of hexene	RCM	630-850	6.8-8.5	1	Vanhove et al. (2006) [199]
1-hexene	JSR	750-1150	10	0.5-1	Yahyaoui et al. (2006) [200]
Straight-chain isomers of heptene	RCM	827	41.6	0.4	Tanaka et al. (2003) [117]

[a]: see nomenclature.

Table 12
Rate constants for the additions of small radicals to the double bond of alkenes (high pressure limits, in s^{-1}, kcal, mol units).

Added radicals	References	Addition to =CH2			Addition to =CH-		
		A	n	Ea	A	n	Ea
•H	Tsang (1991) [35]	1.32×10^{13}	0	1.56	1.32×10^{13}	0	3.26
•CH_3	Tsang (1991) [35]	1.69×10^{11}	0	7.40	9.64×10^{10}	0	8.00
•OH	Wilk et al. (1989) [191]	1.37×10^{12}	0	-1.04	1.37×10^{12}	0	-1.04
•HO_2	Tsang (1991) [35]	1.0×10^{12}	0	14.20	-	-	-

Table 13
Rate constants for the reactions of oxygen molecules with the radicals deriving from alkenes (in s^{-1}, kcal, mol units).

Additions				
Initial radical	References	A	n	Ea
alkylic alkenyl	Morgan et al. (1982) [213]	as for alkyl radicals		
allylic alkenyl		1.2×10^{10}	0	-2.30
hydroxyalkyl		as for alkyl radicals		

Oxidations											
			Abstraction of a primary H-atom or formation of an aldehyde			Abstraction of a secondary H-atom or formation of an ketone			Abstraction of a tertiary H-atom		
Initial radical	Abstracted H-atoms	References	$A\times10^{11}$	n	Ea	$A\times10^{11}$	n	Ea	$A\times10^{11}$	n	Ea
alkylic	alkylic	Warth et al. (1998) [103]	2.3	0	5.0	7.9	0	5.0	4.5	0	5.0
	allylic	Touchard et al. (2005) [186][a]	-	-	-	1.3	0	2.5	0.75	0	2.5
allylic	alkylic	Touchard et al. (2005) [186][b]	2.3	0	15.2	7.9	0	15.2	7.9	0	15.2
	vinylic	Stothard and Walker (1992) [184]	-	-	-	-	-	-	10.0	0	22.7
hydroxy alkyl	hydroxy	Touchard et al. (2005) [186][c]	79	0	5.0	7.9	0	5.0	-	-	-
	alkylic	Warth et al. (1998) [103]	2.3	0	5.0	7.9	0	5.0	4.5	0	5.0

[a]: A-factors divided by 6, compared to those of alkyl radicals, to consider the fact that the formation of the conjugated diene from a non resonance stabilized radical involves a loss of an additional free rotation compared to the formation of an alkene from an alkyl radical; a difference of activation energy of 2.5 kcal/mol compared to alkylic H-atoms has been taken into account.
[b]: A-factors taken equal to those of alkyl radicals; activation energy derived from the experimental measurement of the ratio between the concentration of 1,3-pentadiene and that of 1,3-butadiene at 753 K by Baldwin and Walker [181] and from the values proposed by Perrin et al. (1988) [214] for the decomposition of 1-pentene-3-yl radicals to give 1,3-butadiene and methyl radicals.
[c]: Rate parameters deduced from the measurements of Miyoshi et al. at room temperature [215].

Table 14
Rate expressions (in s^{-1}, kcal, mol units) of the formation of cyclic ethers including an unsaturated ring or a ring conjugated to a double bond [186].

Size of the cyclic ethers	A	n	Ea	Difference in strain energy between the cycloalkane and the cycloalkene [29]
4	$1.4x10^{11}$	0	18.9	3.6
5	$1.2x10^{10}$	0	6.5	-0.4
6	$8.6.10^{8}$	0	3.2	1.4

Table 15
Rate expressions (in s^{-1}, kcal, mol units) of the decomposition of hydroperoxyalkenyl radicals to give acyclic species.

Broken bond	Type of initial radical	Obtained products	A	n	Ea
C-O	Allylic	Diene + HO_2•	$8x10^{12}$	0	33.2 [a]
C-C	Allylic	Diene + hydroperoxyalkyl radical	$1.3x10^{13}$	0	33.9-35.9[b]
	Alkylic	Allylic radical + hydroperoxyalkene	$2x10^{13}$	0	22.5 [c]
O-O	Allylic	Unsaturated aldehyde or ketone+ OH•	$1x10^{9}$	0	14.7 [a]

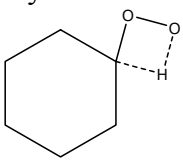
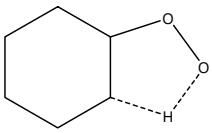
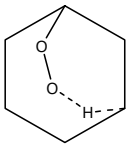
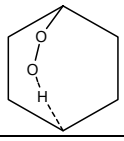
[a]: Values deduced from those proposed for hydroperoxyalkyl radicals with an activation energy 7.2 kcal/mol higher accounting for the equal difference between allylic and alkyl radicals as for the breaking of a C-C bond.
[b]: Values depending on the type of radical hydroperoxyalkyl (primary radical: 35.9, secondary radical: 34.9, tertiary radical: 33.9) and deduced from the values proposed by Perrin et al. (1988) [214] for the decomposition of 1-pentene-3-yl radicals to give 1,3-butadiene and methyl radicals and from the values used for hydroperoxyalkyl radicals.
[c]: Values deduced from those proposed for the decomposition of 1-pentene-5-yl radicals to give ethylene and allyl radicals proposed by Gierczak et al. (1986) [216].

Table 16
Summary of the experimental results concerning the autoignition and oxidation of cycloalkanes from C_4 below 1000 K.

Compounds	Type of reactor[a]	Temperature range (K)	Pressure range (bar)	Equivalence ratio range	References
Cyclohexane	RCM	600-900	7-14	1	Lemaire et al. (2001) [229]
		827	41.6	0.4	Tanaka et al. (2003) [117]
	JSR	750-1200	1-10	0.5-1.5	Voisin et al. (1992)[230] Dagaut (2002)[231]
	CV	635	0.059	9	Klaï et al. (1993)[222]
Methylcyclohexane	RCM	680-980	10-20	1	Pitz et al. (2007) [225]
		827	41.6	0.4	Tanaka et al. (2003) [117]
	ST	795-1560	1-50	0.5-2	Vasu et al. (2007) [232]
n-propylcyclohexane	JSR	950-1200	1	1	Dagaut (2002)[231]
n-butylcyclohexane	FR	600-800	8	0.3	Natelson et al. (2007) [138]

[a]: see nomenclature.

Table 17
Comparison between the rate expressions of the isomerizations of cyclic peroxy radicals considered in the models of Livermore [224,225] , Milano [227] and Nancy [228] and those proposed by Handford-styring and Walker [235].

		Models of Livermore[a]	Model of Milano	Model of Nancy	Estimation of the team of Walker
Size of the transition ring	Structure of the transition state in the case of cyclohexane	*A-factors at 600 K (in s^{-1}, per abstractable H-atoms)*			
4		-	-	$5.8x10^{12}$	-
5		$1.2x10^{11}$/ $6.2x10^{10}$	$5.5x10^{11}$	$5.8x10^{12}$	$8.71x10^{11}$
6		$4.63x10^{10}$	$3.0x10^{11}$	$5.8x10^{12}$	$6.46x10^{11}$
7[b]		$5.5x10^{9}$	$4.1x10^{11}$	$2.9x10^{10}$	$7.59x10^{10}$
Size of the transition ring		*Activation energy (kcal/mol)*			
4		-	-	35.0	-
5		31.0/27.5 *(29.7)*[c]	32.0 *(25.9)*	35.3 *(32.5)*	32.4
6		24.07 *(22.15)*	24.4 *(19.8)*	32.8 *(25)*	29.5
7		24.35 *(19.35)*	29.3 *(19.8)*	25.5 *(22)*	26.8
Size of the transition ring		*Rate constant at 753 K (in s^{-1}) for cyclohexane*			
4		-	-	$5.1x10^{2}$	-
5		$4.8x10^{2}$	$2.8x10^{2}$	$1.7x10^{3}$	$1.4x10^{3}$
6		$1.9x10^{4}$	$1.3x10^{5}$	$8.8x10^{3}$	$7.1x10^{3}$
7		$9.4\ x10^{2}$	$2.5x10^{3}$	$2.9x10^{3}$	$2.3x10^{3}$

[a]: Value for cyclohexane [224]/value for methyl cyclohexane [225], when they are different.
[b]: See figure 24.
[c]: The value in parenthesis is for acyclic alkanes (Table 8).

Table 18
Comparison between the rate expressions (in s^{-1}, kcal, mol units) of the formation of bicyclic ethers deriving from cyclohexane considered in the models of Livermore [224], Milano [227] and Nancy [228].

Size of the cyclic ethers	Model of Livermore			Model of Milano			Model of Nancy		
	A	n	Ea	A	n	Ea	A	n	Ea
3	$5.8x10^{12}$	0	13.4	$2.9x10^{12}$	0	15.4	$2.06x10^{13}$	0	9.68
4	$1.4x10^{12}$	0	20.0	$1.4x10^{12}$	0	23.4	$2.06x10^{13}$	0	19.6[a]
5	$8.6x10^{12}$	0	18.5	$8.6x10^{12}$	0	20.7	$2.06x10^{13}$	0	17.1

[a]: The direct formation of 1-hexenal is assumed.

Table 19: Summary of the experimental results concerning the autoignition and oxidation of benzene and toluene below 1200 K.

Compounds	Type of reactor[a]	Temperature range (K)	Pressure range (bar)	Equivalence ratio range	References
Benzene	RCM	920-1100	25-45	0.5-1	Mittal et al. (2007) [275]
	JSR	900-1300	0.46	0.1961.02	Chai and Pferfferle (1998) [276]
		950-1350	1-10	0.3-1.5	Ristori et al. (2001) [255] Marchal (1997) [277]
		923	1	1.9-3.6	Da Costa et al. (2003) [256]
	FR	1100	1	0.76-1.3	Lovell et al. (1988) [240]
		900-1450	1	0.0016-0.96	Alzueta et al. (2000) [254]
	FR in the flue gas of a methane flame	850–960 K	1	0.1-1.3	Schöbel-Ostertag et al. (2005) [257]
Toluene	ST	975-1269	14-59	0.5-1	Davidson et al. (2005) [126]
	RCM	850-950	6-9	1	Griffiths et al. (1993) [111]
		900	1-24	1	Roubaud et al. (2000) [277]
		827	41.6	0.4	Tanaka et al. (2003) [117]
		920-1100	25-45	0.5-1	Mittal et al. (2007) [275]
	JSR	1000-1375	1	0.5-1.5	Marchal (1997) [278] Dagaut et al. (2002) [231-265]
		873-923	1	0.45-0.91	Bounaceur et al. (2005) [266]
	FR	1190	1	0.69-1.33	Emdee et al. (1992) [247], Klotz et al. (1998) [259]
		850-950	12.5	1	Chaos et al. (2007) [262]

[a]: see nomenclature.

Table 20: Summary of the experimental results concerning the autoignition and oxidation of C_{7+} aromatic compounds below 1200 K.

Compounds	Type of reactor[a]	Temperature range (K)	Pressure range (bar)	Equivalence ratio range	References
Xylenes	RCM	600-900	8-24	1	Roubaud et al. (2000) [244-277]
	FR	1093-1199	1	0.47-1.7	Emdee et al. (1990, 91) [259-260]
	JSR	900-1300	1	0.3-1.5	Gaïl et al. (2005) [247-268,279
Ethylbenzene	RCM	600-900	8-24	1	Roubaud et al. (2000) [277]
	FR	1060	1	0.64-1.3	Litzinger et al. (1986) [280]
Styrene	FR	1060	1	0.56	Litzinger et al. (1986) [280]
Trimethylbenzenes	RCM	600-900	8-24	1	Roubaud et al. (2000) [277]
n-propylbenzene	RCM	600-900	8-24	1	Roubaud et al. (2000) [277]
	FR	1060	1	0.65-1.5	Litzinger et al. (1986) [281]
	JSR	900-1250	1	0.5-1.5	Dagaut et al. (2002) [269]
Ethyltoluenes	RCM	600-900	14-19	1	Roubaud et al. (2000) [244]
n-butylbenzene	RCM	600-960	8-24	0.3-1	Roubaud et al. (2000) [244-277] Ribaucour et al. (2000) [273] Crochet et al. (2007)[282]
	FR	1069	1	0.98	Brezinsky et al. (1986) [283]
1-methylnaphthalene	ST	900-1500	13	1	Pfahl et al. (1996) [127]
	FR	1170	1	0.6-1.5	Shaddix et al. (1992) [284]
	JSR	800-1150	10	1	Marchal (1997) [278]
Indane	JSR	950-1350	1	0.5-1	Dagaut et al. (2001) [285]

[a]: see nomenclature.

Table 21: Summary of the experimental results concerning the autoignition and oxidation of binary mixtures containing only saturated compounds from C_4 below 900 K.

Compounds	Type of reactor[a]	Temperature range (K)	Pressure range (bar)	Equivalence ratio range	References
Mixtures of alkanes					
Mixtures of n-heptane/iso-octane (PRF)	RCM	680-930	6-9	1	Griffiths et al. (1993) [111]
		630-910	12-17	1	Callahan et al. (1996) [136]
		798-878	40-44	0.2-0.5	Tanaka et al. (2003) [117]
	ST	650-1200	12-50	1	Fieweger et al. (1997) [119]
		673-1184	40	1	Hartmann et al. (2007) [326]
	JSR	550-1100	10	0.2-1	Dagaut et al. (1994) [320] Dubreuil at al. (2007) [22]
	FR	550-900	12.5	1	Callahan et al. (1996) [136]
Mixtures of n-decane/iso-octane	FR	600-800	8	0.3	Kurman et al. (2007) [139]
Mixtures of n-dodecane/iso-cetane	FR	600-800	8	0.3	Cernansky et al. (2004)(2005) [140-141]
Alkane/ether mixtures					
Mixtures of n-pentane/MTBE	CV	580	0.059	7.75-8	El Kadi and Baronnet (1995) [54]
Mixtures of n-pentane/ETBE	CV	580	0.059	8-8.5	El Kadi and Baronnet (1995) [54]
Mixtures of n-pentane /TAME	CV	580	0.059	8-8.5	El Kadi and Baronnet (1995) [54]
Mixture n-pentane /MTBE	JSR	570-1150	10	1	Dagaut et al. (1997) [321]
Mixtures of n-heptane/ETBE	JSR	570-1150	10	1	Dagaut et al. (1997) [321]
Alkane/cyclo-alkane mixtures					
Mixtures of n-dodecane/ methylcyclohexane	FR	600-800	8	0.3	Cernansky et al. (2004)(2005) [140-141]

[a]: see nomenclature.

Table 22: Summary of the experimental results concerning the autoignition and oxidation of binary mixtures containing unsaturated compounds from C_4 below 900 K.

Compounds	Type of reactor[a]	Temperature range (K)	Pressure range (bar)	Equivalence ratio range	References
Alkane/alkene mixtures					
Mixtures of iso-octane/1-hexene	MCR	650-900	12.6-13.9	1	Vanhove et al. (2006) [314]
	JSR	750-1150	10	0.5-1.5	Yahyaoui (2005) [327]
Aromatic/alkene mixtures					
Mixtures of toluene/1-hexene	MCR	650-900	11.8-14.8	1	Vanhove et al. (2006) [314]
	JSR	750-1170	10	0.5-1.5	Yahyaoui (2005) [327]
Mixtures of toluene/di-*iso*-butylene	MCR	740-1150	15-45	0.75	Mittal and Sung (2007) [328]
Alkane/aromatic mixtures					
Mixtures of n-heptane/benzene	MCR	600-950	3.3-4.9	1	Vanhove et al. (2006) [314]
Mixtures of n-heptane/toluene	ST	620-1180	10-50	0.3-1	Herzler et al. (2007) [301]
	MCR	600-950	3.9-4.9	1	Vanhove et al. (2006) [314]
		827	41.6	0.4	Tanaka et al. (2003) [117]
	JSR	580-640	7	1	Ciajolo et D'Anna (1993) [134]
		550-1000	10	0.2	Dubreuil at al. (2007) [22]
	FR	550-950	12.5	1	Chaos et al. (2007) [262]
Mixture iso-octane/ toluene	MCR	600-900	12.0-14.6	1	Vanhove et al. (2006) [314]
		740-1150	15-45	0.75	Mittal and Sung (2007) [328]
	JSR	750-1170	10	0.5-1.5	Yahyaoui (2005) [327]
	FR	550-950	12.5	1	Chaos et al. (2007) [262]
Mixtures of n-dodecane/ 1-methylnaphthalene	FR	600-800	8	0.3	Cernansky et al. (2004)(2005) [140-141]

[a]: see nomenclature.

Table 23: Summary of the experimental results concerning the autoignition and oxidation of tertiary or quaternary mixtures containing compounds from C_4 below 900 K.

Compounds	Type of reactor[a]	Temperature range (K)	Pressure range (bar)	Equivalence ratio range	References
Alkanes/aromatic mixtures					
Mixture n-heptane/ iso-octane/toluene	ST	850-1280	15-60	0.5-2	Gauthier et al. (2004) [121]
	MCR	827	41.6	0.4	Tanaka et al. (2003) [117]
	FR	550-950	12.5	1	Chaos et al. (2007) [262]
Mixtures of n-dodecane/ 1-methylnaphthalene	FR	600-800	8	0.3	Cernansky et al. (2004)(2005) [140-141]
Alkanes/alkene/aromatic mixtures					
Mixtures of iso-octane/ 1-hexene/toluene	MCR	650-900	11.4-13.9	1	Vanhove et al. (2006) [314]
	JSR	800-1130	10	1	Yahyaoui et al. (2007) [329]
Mixtures of n-heptane/iso-octane/ toluene/ diisobutylene	ST	690-1200	10-50	1	Fikri et al. [330] (2007)
Alkane/alkene/ether/aromatic mixtures					
Mixtures of iso-octane/ 1-hexene/ETBE/toluene	JSR	800-1130	10	1	Yahyoui et al. (2007) [329]
Alkane/cycloalkane/ether/aromatic mixtures					
Mixtures of n-decane/ n-butylcyclohexane/ n-butylbenzene	FR	600-800	8	0.3	Natelson et al. (2007) [138]
Mixtures of n-decane/ n-butylcyclohexane/ toluene	FR	600-800	8	0.3	Natelson et al. (2007) [138]
Mixtures of n-decane/ methylcyclohexane/ n-butylbenzene	FR	600-800	8	0.3	Natelson et al. (2007) [138]
Mixtures of n-decane/ methylcyclohexane/ toluene	FR	600-800	8	0.3	Natelson et al. (2007) [138]

[a]: see nomenclature.

Table 24
Comparison between the rate expressions (in s^{-1}, kcal, mol units) of the "cross term" reactions involving peroxy radicals considered in the models for mixtures of Livermore [71,316-317], Stockhom [261] and Nancy [24,203,325].

	Models of Livermore			Models of Stockhom			Models of Nancy		
RH + R'OO• = R'OOH + R•[a]									
RH is an alkane, a methylcyclohexane or an alkene molecule, A per abstractable H-atom									
Type of abstracted H-atom	A	n	Ea	A	n	Ea	A	n	Ea
Primary alkylic	$2.0\text{-}2.8\times10^{12}$	0	20.43	2.0×10^{12}	0	20.43	2.0×10^{12}	0	20.0
Secondary alkylic	$2.0\text{-}2.8\times10^{12}$	0	17.7	2.0×10^{12}	0	17.7	1.5×10^{12}	0	17.5
Tertiary alkylic	2.8×10^{12}	0	16.0	2.0×10^{12}	0	16.0	1.5×10^{12}	0	15.0
Primary alkylic[b]	7.9×10^{3}	2.6	17.49	-	-	-	-	-	-
Secondary alkylic[b]	4.8×10^{3}	2.6	14.91	-	-	-	-	-	-
Tertiary alkylic[b]	3.6×10^{3}	2.6	11.53	-	-	-	-	-	-
Secondary allylic	1.6×10^{11}	0	14.9	-	-	-	5×10^{11}	0	14.55
ROO• + ROO'• = RO• + RO'• + O_2[c]									
	1.4×10^{16}	-1.61	1.86	-	-	-	-	-	-

[a]: R' is methyl, ethyl, propyl and butyl in Livermore, heptyl and iso-octyl in Stockholm and in Nancy.
[b]: For methylcyclohexane.
[c]: R is methyl, ethyl, propyl and butyl in Livermore, R' is n-pentyl, n-heptyl, iso-octyl and benzyl.

Table 25
Comparison between the rate expressions (in s^{-1}, kcal, mol units) of the "cross term" reactions considered in the models for mixtures containing toluene of Livermore [316-317], Stockhom [261] and Nancy [324].

	Models of Livermore			Models of Stockhom			Models of Nancy		
RH + R'• = R'H + R•									
Type of abstracted H-atom	A	n	Ea	A	n	Ea	A	n	Ea
RH is an toluene molecule, R'• is an alkyl or allylic radical, A per abstractable H-atom									
Primary alkyl	-	-	-	$3.3x10^{10}$	0	12	-	-	-
Secondary alkyl	-	-	-	$3.3x10^{10}$	0	12	-	-	-
Tertiary alkyl	-	-	-	$3.3x10^{10}$	0	12	-	-	-
Allylic	$1x10^{11}$	0	15.5	-	-	-	$1.6x10^{12}$	0	15
RH is an alkane or a methylcyclohexane molecule, R'• is an benzyl radical, A per abstractable H-atom									
Primary alkyl	$1.0x10^{11}$	0	20.9	-	-	-	1.6	3.3	19.84
Secondary alkyl	$0.5x10^{11}$	0	17.9	-	-	-	1.6	3.3	18.17
Tertiary alkyl	$1.0x10^{11}$	0	15.4	-	-	-	1.6	3.3	17.17
Primary alkyl[a]	$7.55x10^{-1}$	3.46	15.5	-	-	-	-	-	-
Secondary alkyl[a]	$7.55x10^{-1}$	3.46	15.5	-	-	-	-	-	-
Tertiary alkyl[a]	$3.0x10^{-10}$	6.36	10.9	-	-	-	-	-	-
RH is an alkane molecule, R'• is phenyl radical, A per abstractable H-atom									
Primary	-	-	-	1 - $1.5x10^{11}$[b]	0	15.0-15.5[b]	-	-	-
Secondary	-	-	-	0.5 - $6x10^{11}$[b]	0	10.0-15.5[b]	-	-	-
Tertiary	-	-	-	$1x10^{11}$	0	11.0	-	-	-
RH is an alkene molecule, R'• is an benzyl radical, per abstractable H-atom[c]									
	$1x\ 10^{11}$	0	17.0	$1x\ 10^{11}$	0	17.0	-	-	-
RH + R'OO• = R'OOH + R•									
RH is toluene, A per abstractable H-atom[c]									
	$3.3x10^{3}$	2.5	12.3	$1.3x10^{11}$	0	14	$1.3x10^{13}$	0	12
RH is benzaldehyde, A per abstractable H-atom[c]									
	$3x10^{12}$	0	12.0	$3x10^{12}$	0	9	-	-	-
R• + R'• = R-R'									
R• is benzyl radical, R'• is an alkyl radical									
	-	-	-	-	-	-	$1x10^{13}$	0	0

[a]: For methylcyclohexane.
[b]: The values depend on the radicals obtained.
[c]: R' is methyl, ethyl, propyl and butyl in Livermore, heptyl and iso-octyl in Stockholm and methyl in Nancy.

FIGURES CAPTIONS

Figure 1: Simulated influence of the fuel composition (n-heptane or n-decane/α-methylnaphthalene mixture) on the simulated pressure evolutions in (a) a low load direct injection diesel engine and in (b) a split injection HCCI engine [10].

Figure 2: Simplified scheme for the primary mechanism of oxidation of alkanes.

Figure 3: Schematic structure of EXGAS software.

Figure 4: Comparison between the validation of the models of Livermore [70], Milano [96] and Nancy [24] for n-heptane in a shock tube (ϕ = 1 [118], rapid compression machine data at P_c from 3 to 4 bar [116] are also shown on the graph of Nancy). Symbols correspond to experiments and lines to simulations.

Figure 5: Comparison between the validation of the models of Livermore [70], Milano [96] and Nancy [24] for n-heptane in a jet-stirred reactor (0.1% n-heptane, 10 atm, ϕ = 1, τ = 1s [132]). Symbols correspond to experiments and lines to simulations.

Figure 6: Comparison between the validation of the models of Livermore [70], Milano [96] and Nancy [24] for n-heptane in a rapid compression machine (P_c from 3.7 bar to 4.6 bar , ϕ = 1 [116]). Symbols correspond to experiments and lines to simulations.

Figure 7: Schematic potential energy surfaces for the reactions of n-propyl radicals with oxygen molecules according to DeSain et al. [159].

Figure 8: Isomerization by internal transfer of H-atom from 2-heptylperoxy radicals.

Figure 9: Formation of a cyclic ether from 2-hydroperoxy-5-heptyl radicals.

Figure 10: Examples of decompositions of hydroperoxy octyl radicals.

Figure 11: Example of an isomerization involving the transfer of an H-atom bound to a carbon atom bound to an oxygen atom.

Figure 12: Secondary reactions considered in the mechanism of Nancy for a cyclic ether

deriving from n-heptane [162].

Figure 13: Examples of molecular reaction in the case of (a) MTBE and (b) ethyl propanoate.

Figure 14: Examples of alkenyl and hydroxyalkyl radicals illustrated in the case of 1-pentene

Figure 15: Low-temperature mechanism oxidation of alkenes exemplified by a rate of reaction analysis of the oxidation of a stoichiometric 1-pentene/air mixture at 800 K [186].

Figure 16: Isomerization of hydroxypentylperoxy radicals according to the mechanism of Waddington [190].

Figure 17: Validation of the models Nancy [186] for (a) 1-pentene and (b) 1-hexene using results obtained in the rapid compression machine of Lille (P_c from 6.8 bar to 10.9 bar , ϕ = 1 [197,199]). Symbols (white dots for cool flame and black ones for autoignition) correspond to experiments and lines to simulations.

Figure 18: Comparison between the experimental (light grey) [199] and the predicted (dark grey) [203] selectivity of products during the pre-ignition period of 1-hexene under the conditions of figure 17b (T_c= 707 K).

Figure 19: Unsaturated cyclic ethers observed by Vanhove et al. [199] during the pre-ignition period of 1-hexene in a rapid compression machine.

Figure 20: Internal addition/decomposition of 1-penten-3yl-peroxy radicals extrapolated from the mechanism proposed by Lodhi and Walker [183].

Figure 21: Low temperature mechanism oxidation of cycloalkanes as proposed by the team of Milano for cyclohexane [227].

Figure 22: Comparison between the validation of the models of Livermore [224], Milano [227] and Nancy [228] for the oxidation of cyclohexane in a rapid compression machine (P_c from 7 to 9 bar, ϕ = 1 [229]) for autoignition and cool flame delay times vs. temperature. Symbols correspond to experiments and lines to simulations.

Figure 23: Comparison between the validation of the models of Livermore [224], Milano [227] and Nancy [228] for the oxidation of cyclohexane in a rapid compression machine (P_c from 7 to 9 bar, ϕ = 1 [229]) for the formation of oxygenated products at 722 K. Symbols correspond to experiments and lines to simulations.

Figure 24: Internal isomerization of peroxycyclohexanyl radicals involving a 7 membered transition state ring.

Figure 25: Mechanism for the oxidation of benzene and toluene as proposed by Brezinsky [237].

Figure 26: Cyclic ethers detected by Roubaud et al. [244] during the oxidation of n-butylbenzene in a rapid compression machine prior autoignition (T_c =691 K).

Figure 27: Comparison between the experimental [271-272] (symbols) and simulated [270] (lines) conversions of the three isomers of xylene in a flow reactor (T = 1155 K, P = 1 atm and ϕ close to 1).

Figure 28: Primary mechanism of the oxidation of 1-naphthalene as proposed by Bounaceur et al. [10].

Figure 29: Structure of some species involved in the oxidation of benzene: (a) cyclopentadienone, (b) ortho-benzoquinone and (c) dihydrofulvalene.

Figure 30: Possible pathways leading to o-benzoquinone and cyclopentadienone from phenyperoxy radicals according to Sirjean et al. (numbers are relative free energies (298 K, kcal/mol) calculated at the B3LYP/6-311++G** level) [295].

Figure 31: Experimental [117] and simulated [324] pressure change (Δp) curves for fuels A (26 % n-heptane, 74 % toluene), B (5 % iso-octane, 21 % n-heptane, 74 % toluene) and C (10 % iso-octane, 16 % n-heptane, 74 % toluene) in the rapid compression machine of Cambridge (USA) (T_c = 827 K, P_c = 41.6 bar, ϕ = 0.4).

Figure 32: Examples of “cross term” reactions during the oxidation of n-decane/1-methylnaphthalene mixture: (a) H-abstractions by phenylbenzyl radicals from n-decane (the 5 isomers of decyl radicals can be obtained), (b) combinations between phenylbenzyl and decyl radicals [10].

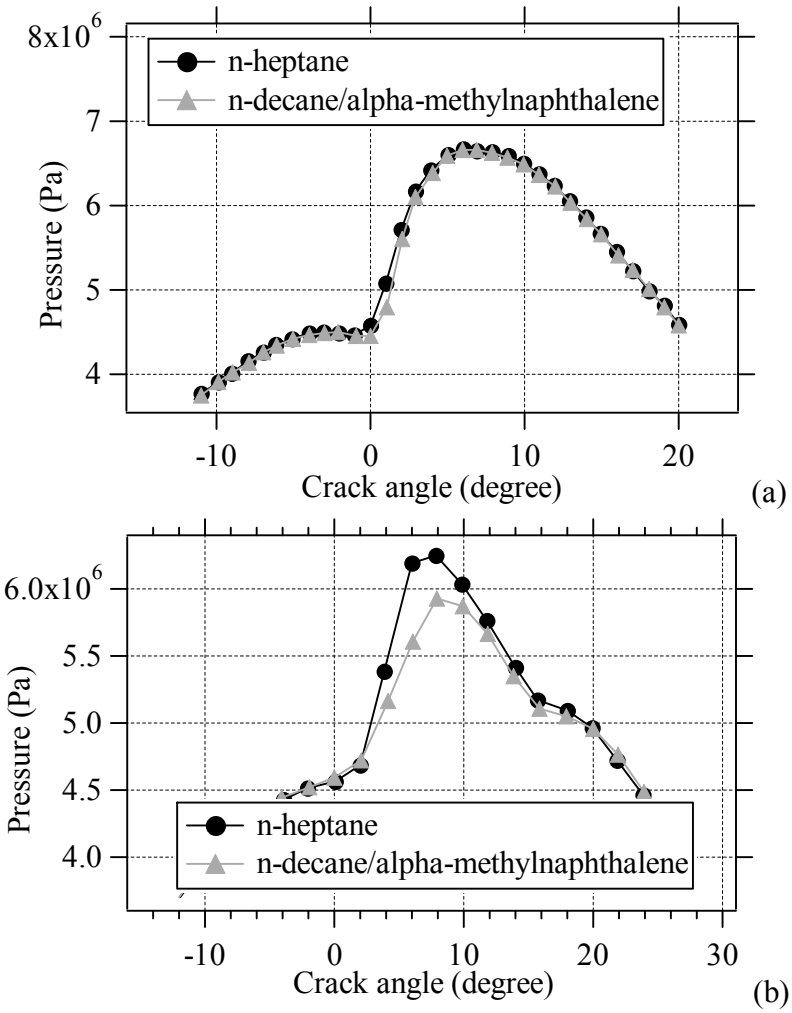


Figure 1: Simulated influence of the fuel composition (n-heptane or n-decane/α-methylnaphthalene mixture) on the simulated pressure evolutions in (a) a low load direct injection diesel engine and in (b) a split injection HCCI engine [10].

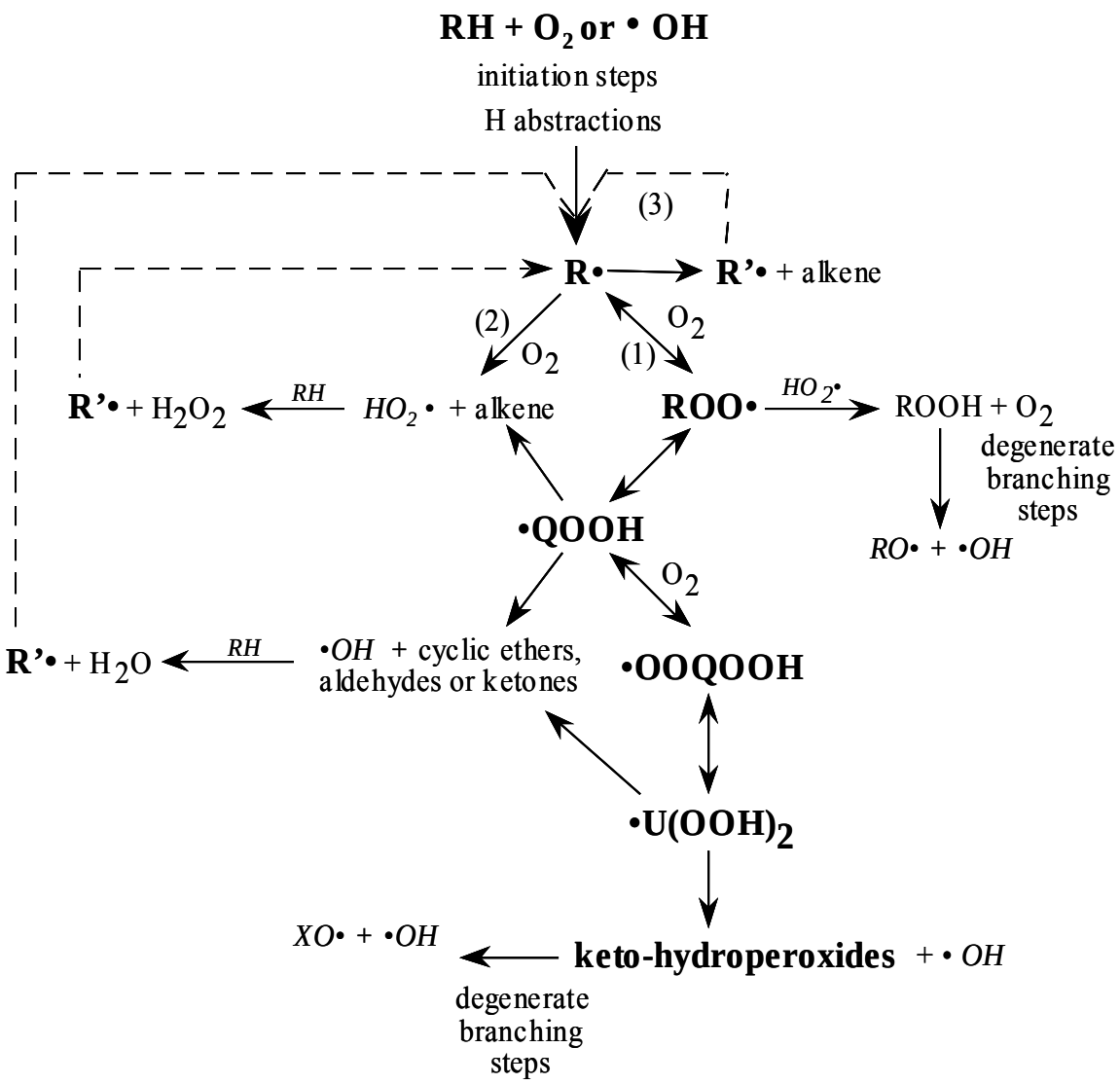


Figure 2: Simplified scheme for the primary mechanism of oxidation of alkanes.

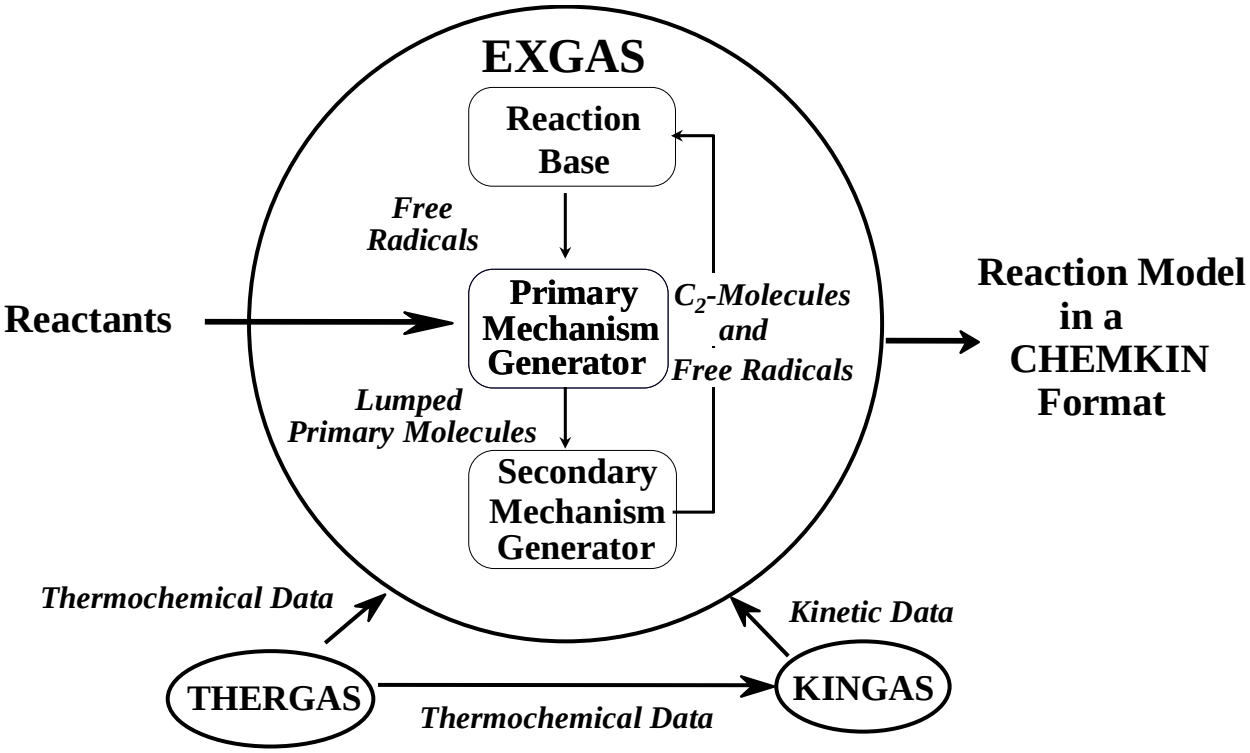


Figure 3: Schematic structure of EXGAS software.

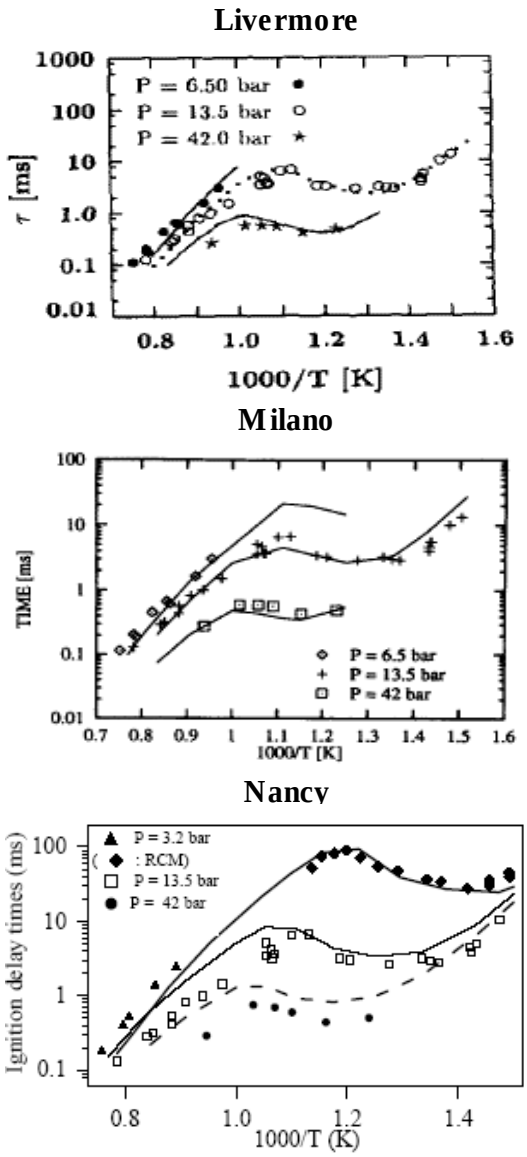


Figure 4: Comparison between the validation of the models of Livermore [70], Milano [96] and Nancy [24] for n-heptane in a shock tube ($\phi = 1$ [118], rapid compression machine data at P_c from 3 to 4 bar [116] are also shown on the graph of Nancy). Symbols correspond to experiments and lines to simulations.

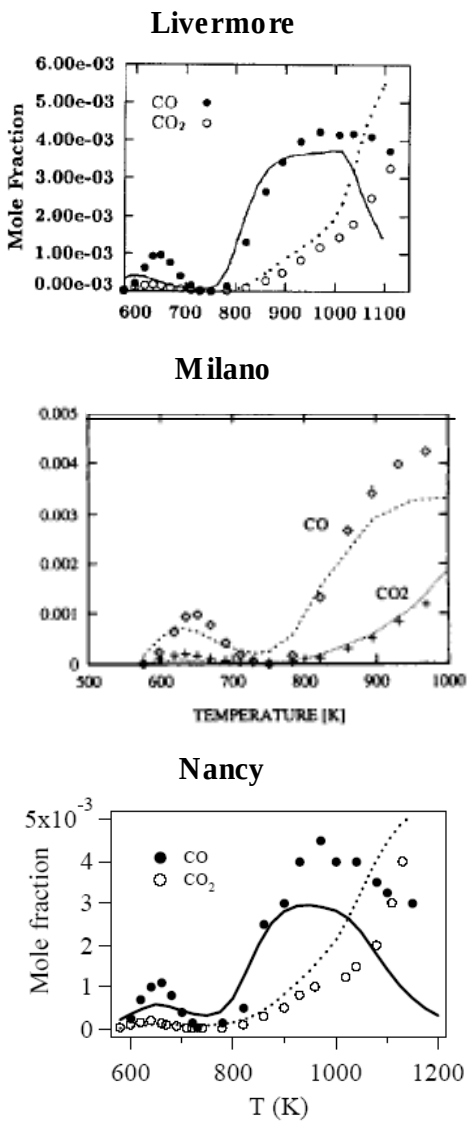


Figure 5: Comparison between the validation of the models of Livermore [70], Milano [96] and Nancy [24] for n-heptane in a jet-stirred reactor (0.1% n-heptane, 10 atm, $\phi = 1$, $\tau = 1$s [132]). Symbols correspond to experiments and lines to simulations.

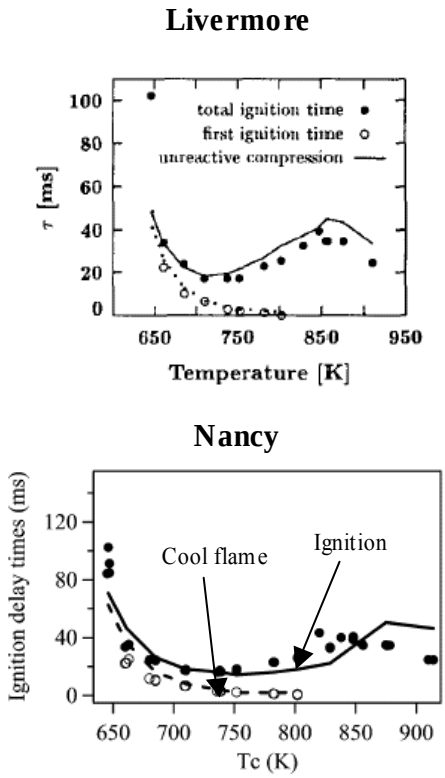


Figure 6: Comparison between the validation of the models of Livermore [70] and Nancy [24] for n-heptane in a rapid compression machine (P_c from 3.7 bar to 4.6 bar , $\phi = 1$ [116]). Symbols correspond to experiments and lines to simulations.

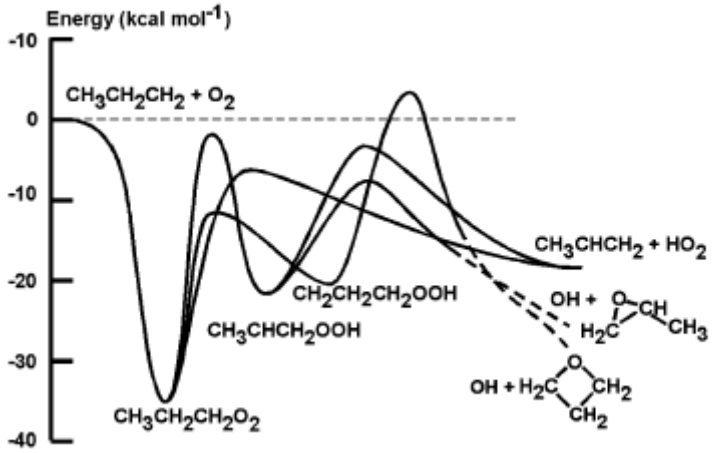


Figure 7: Schematic potential energy surfaces for the reactions of n-propyl radicals with oxygen molecules according to DeSain et al. [159].

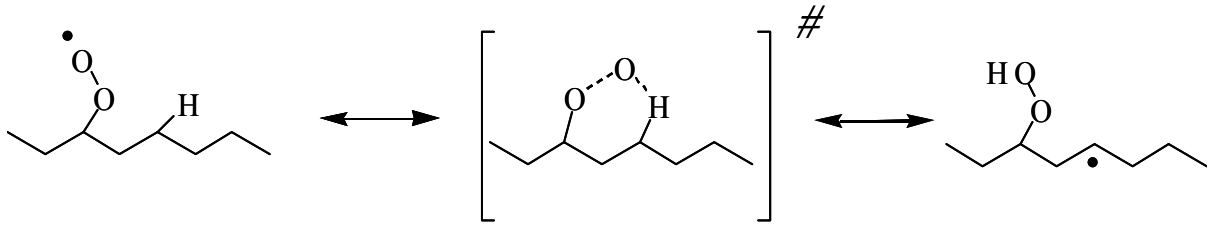


Figure 8: Isomerization by internal transfer of H-atom from 2-heptylperoxy radicals.

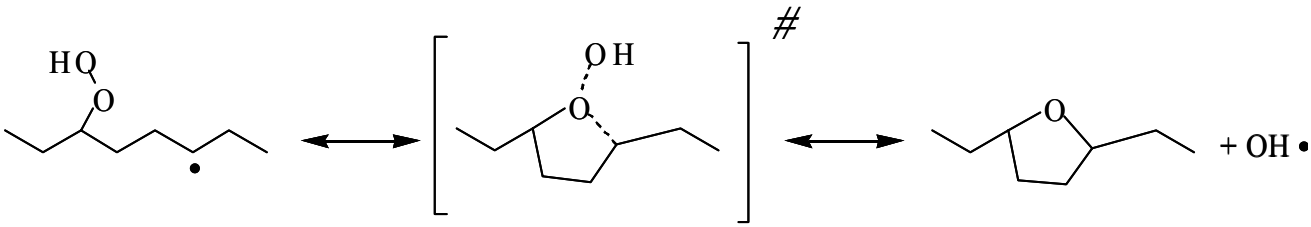


Figure 9: Formation of a cyclic ether from 2-hydroperoxy-5-heptyl radicals.

Figure 10

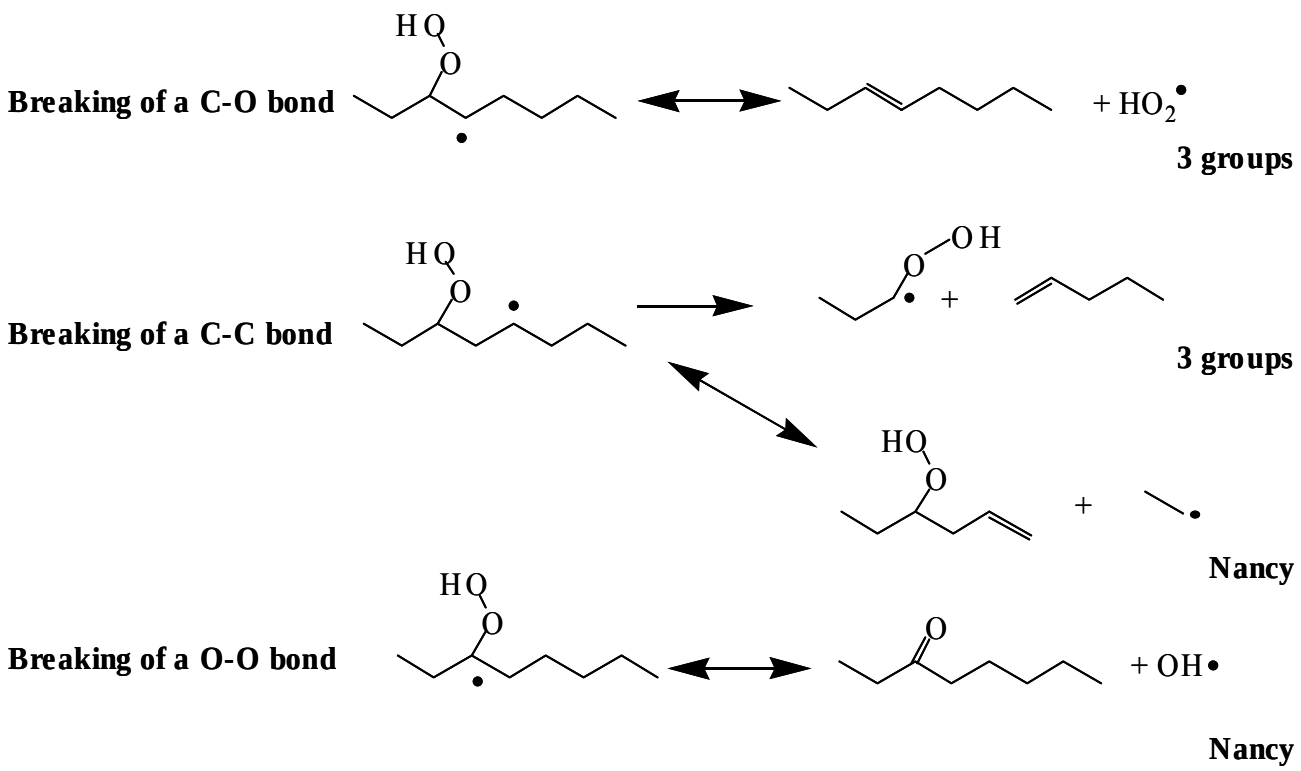


Figure 10: Examples of decompositions of hydroperoxy octyl radicals.

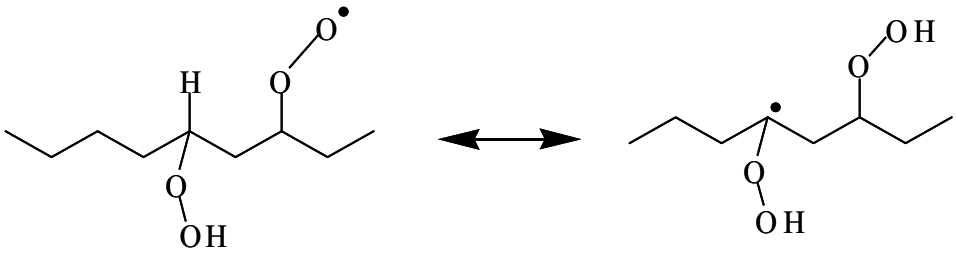


Figure 11: Example of an isomerization involving the transfer of an H-atom bound to a carbon atom bound to an oxygen atom.

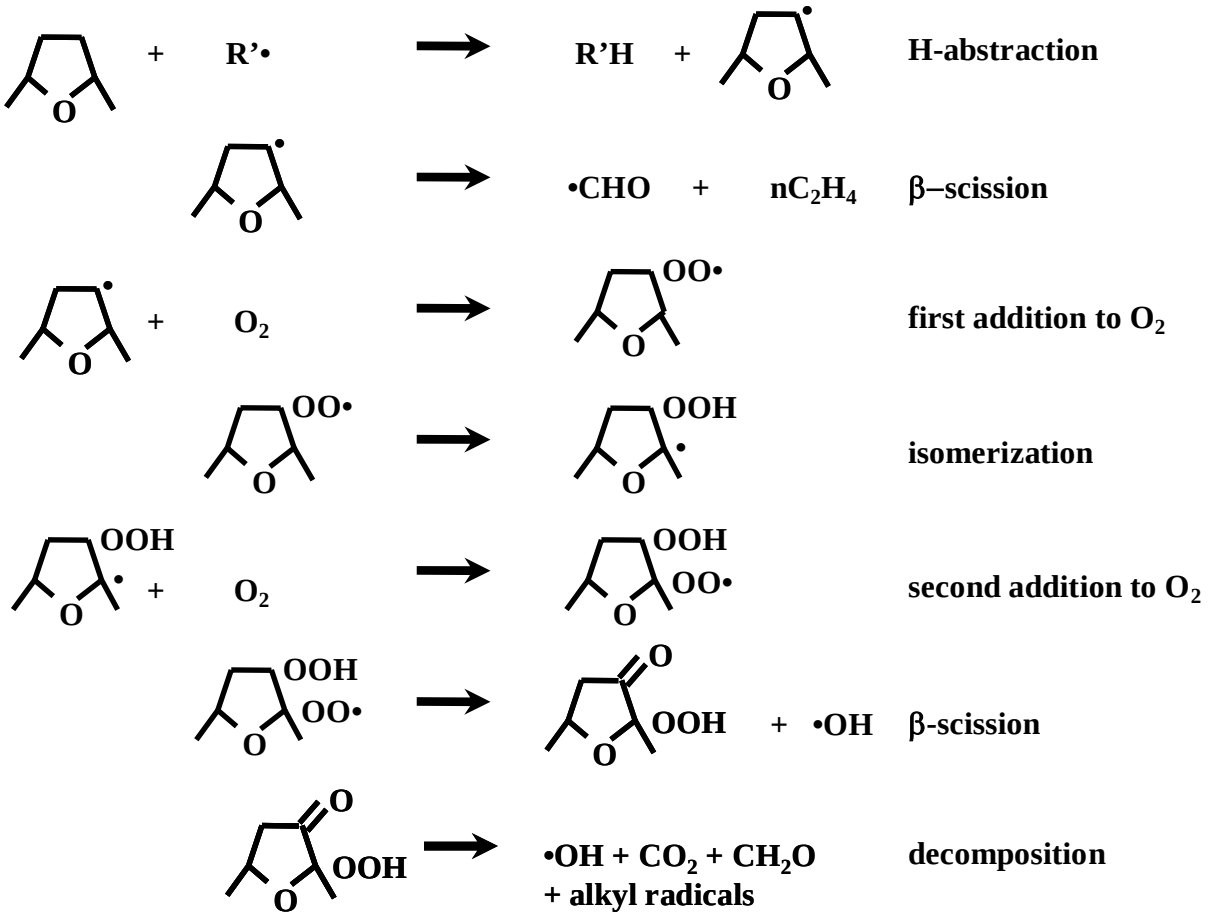


Figure 12: Secondary reactions considered in the mechanism of Nancy for a cyclic ether deriving from n-heptane [162].

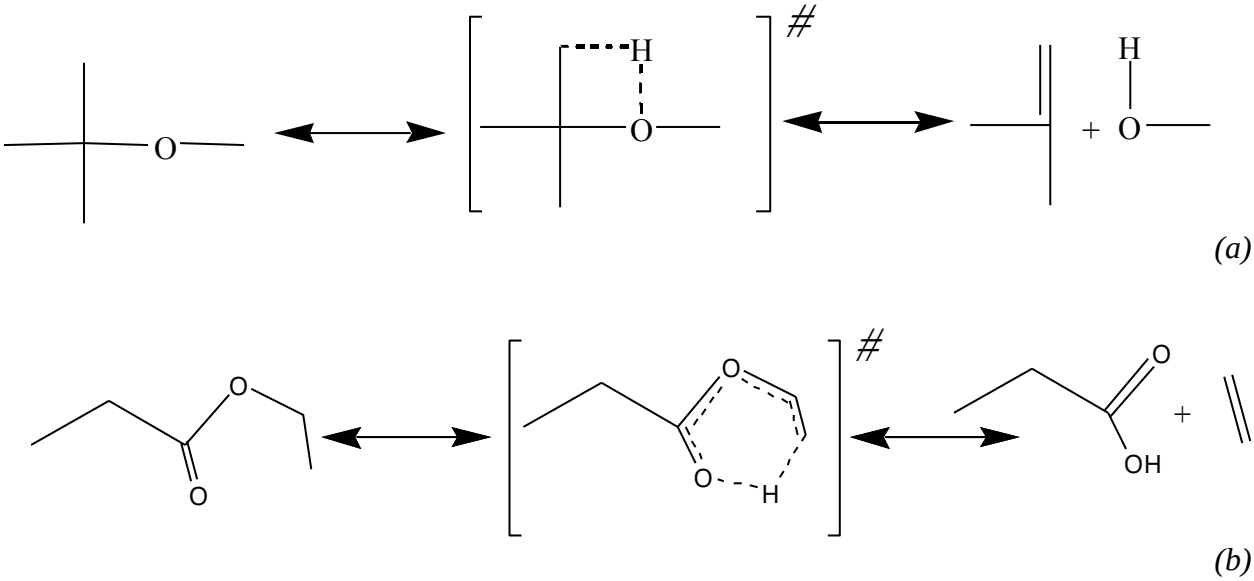


Figure 13: Examples of molecular reaction in the case of (a) MTBE and (b) ethyl propanoate.

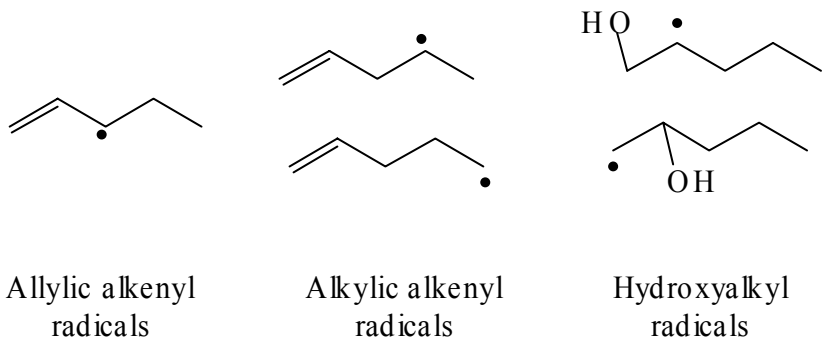


Figure 14: Examples of alkenyl and hydroxyalkyl radicals illustrated in the case of 1-pentene.

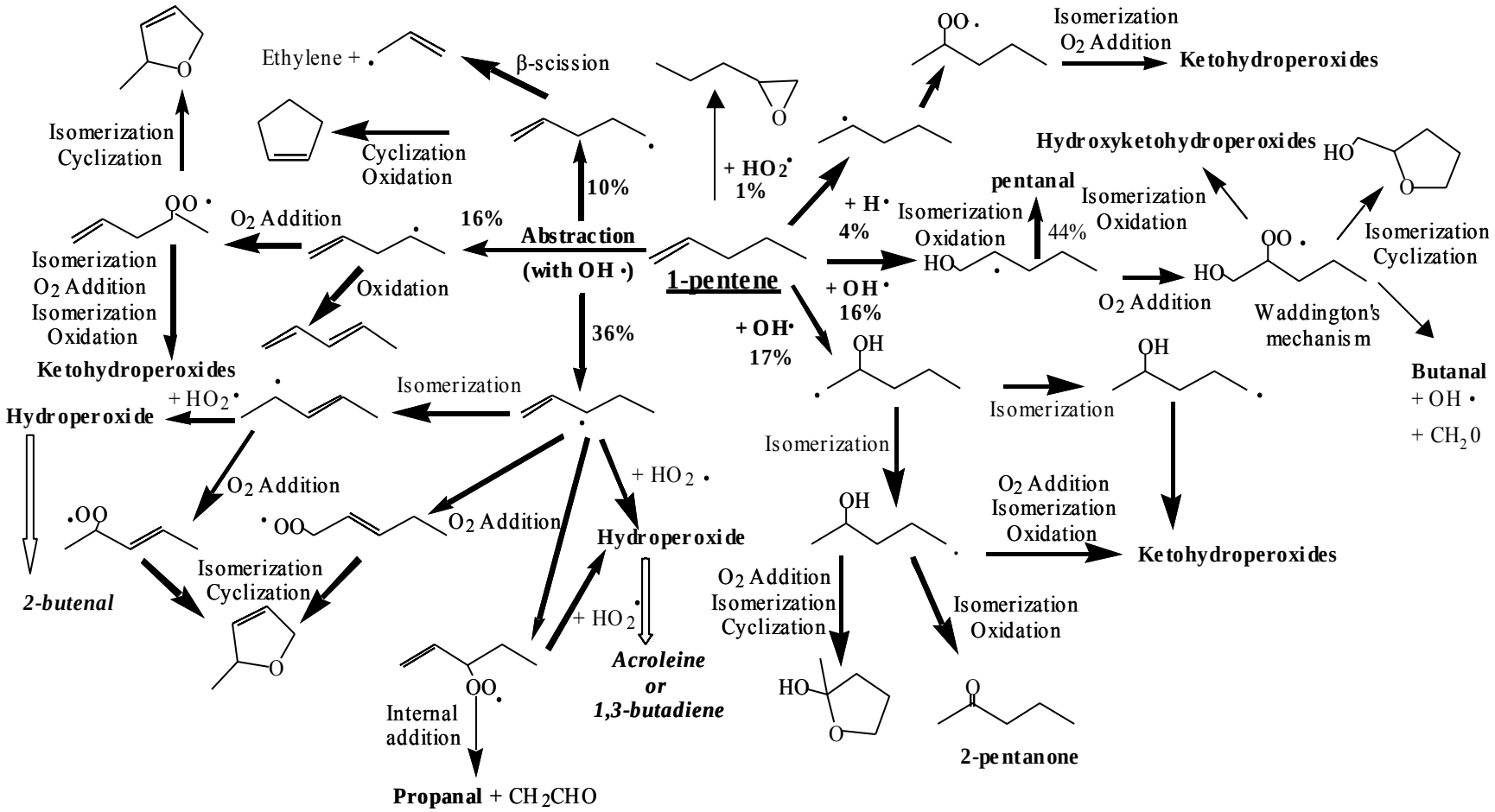


Figure 15: Low temperature mechanism oxidation of alkenes exemplified by a rate of production analysis of the oxidation of a stoichiometric 1-pentene/air mixture at 800 K and 7.5 bar [186].

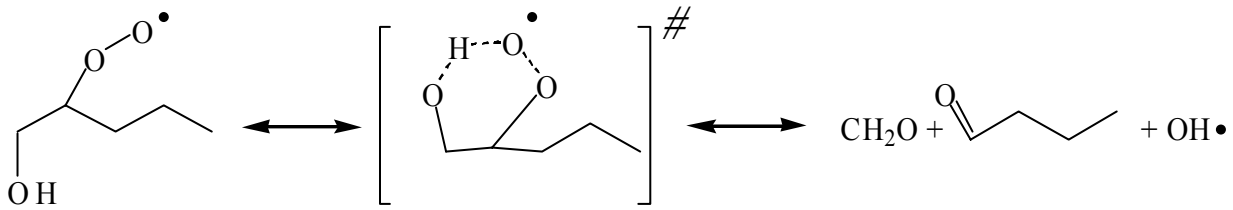


Figure 16: Isomerization of hydroxypentylperoxy radicals according to the mechanism of Waddington [190].

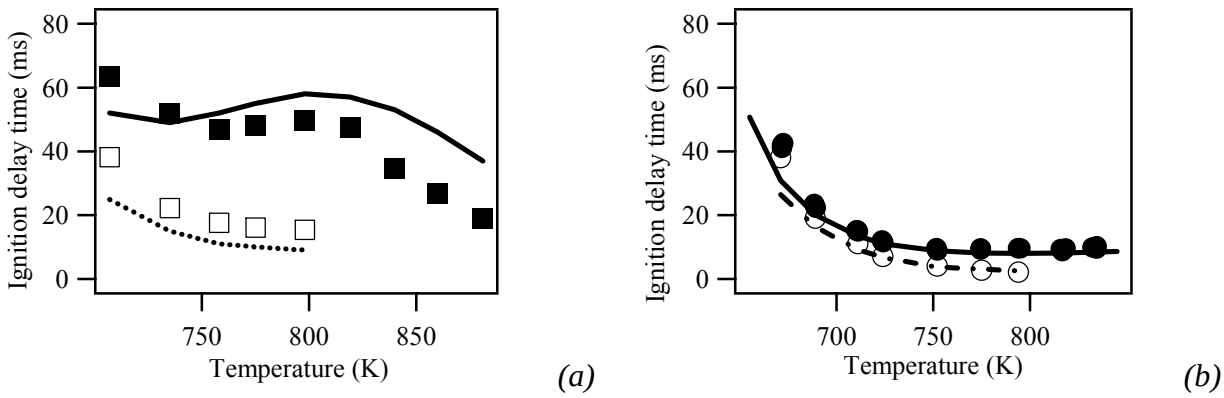


Figure 17: Validation of the models Nancy [186] for (a) 1-pentene and (b) 1-hexene using results obtained in the rapid compression machine of Lille (P_c from 3.7 bar to 4.6 bar , $\phi = 1$ [197,199]). Symbols (white dots for cool flame and black ones for autoignition) correspond to experiments and lines to simulations.

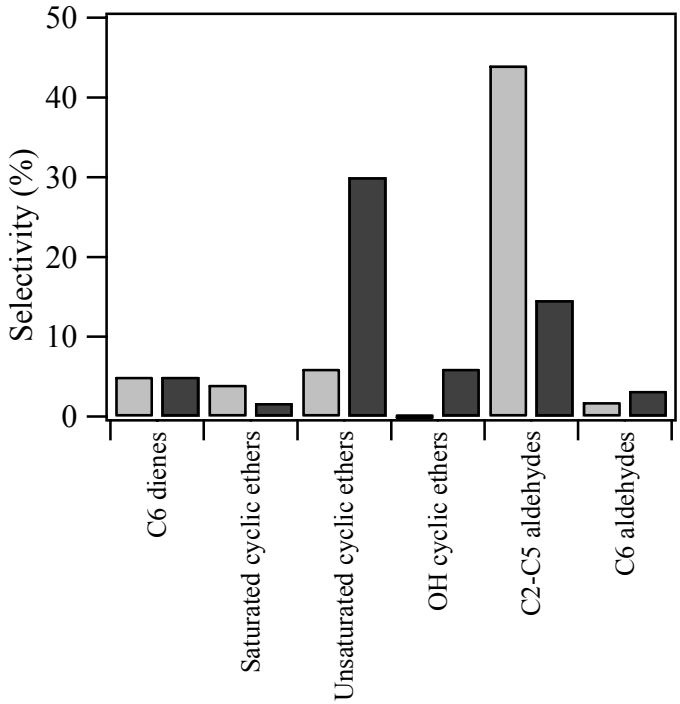
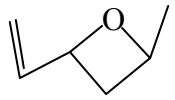
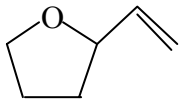


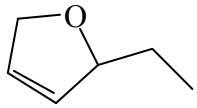
Figure 18: Comparison between the experimental (light grey) [198] and the predicted (dark grey) [203] selectivity of products during the pre-ignition period of 1-hexene under the conditions of figure 17b (T_c= 707 K).



2-methyl-4-vinyl-oxetane



2-vinyl-tetrahydrofuran



2-ethyl-2,5-dihydrofuran

Figure 19: Unsaturated cyclic ethers observed by Vanhove et al. [199] during the pre-ignition period of 1-hexene in a rapid compression machine.

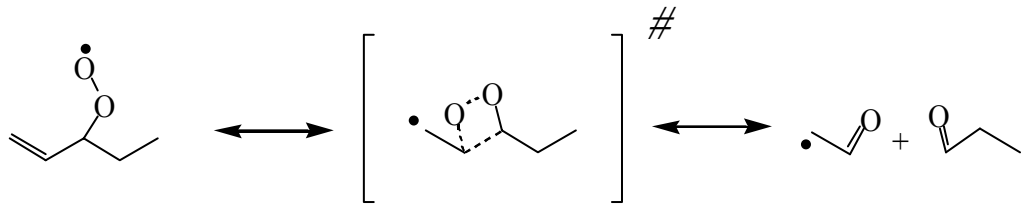


Figure 20: Internal addition/decomposition of 1-penten-3yl-peroxy radicals extrapolated from the mechanism proposed by Lodhi and Walker [183].

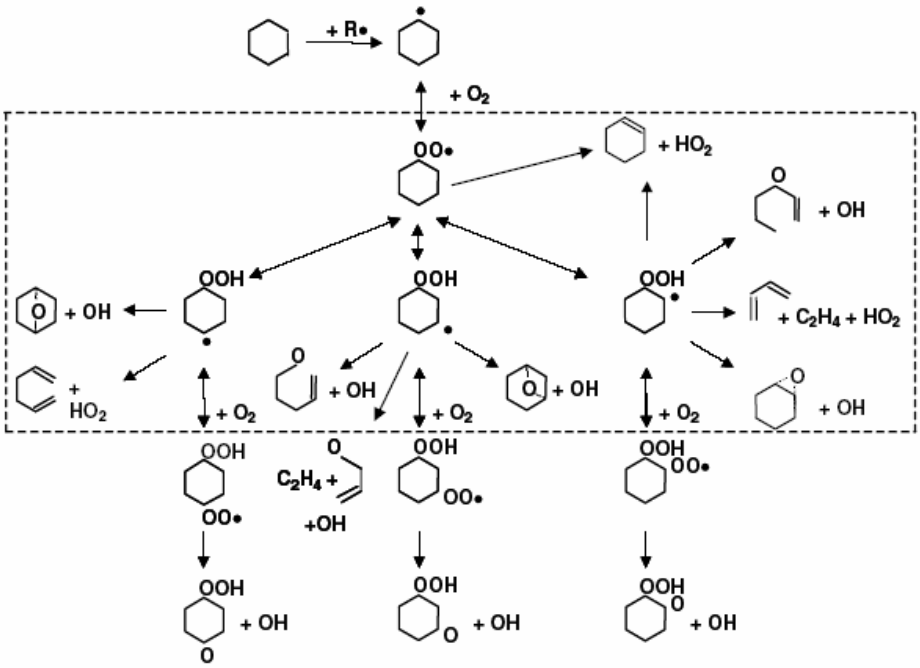


Figure 21: Low temperature mechanism oxidation of cycloalkanes as proposed by the team of Milano for cyclohexane [227].

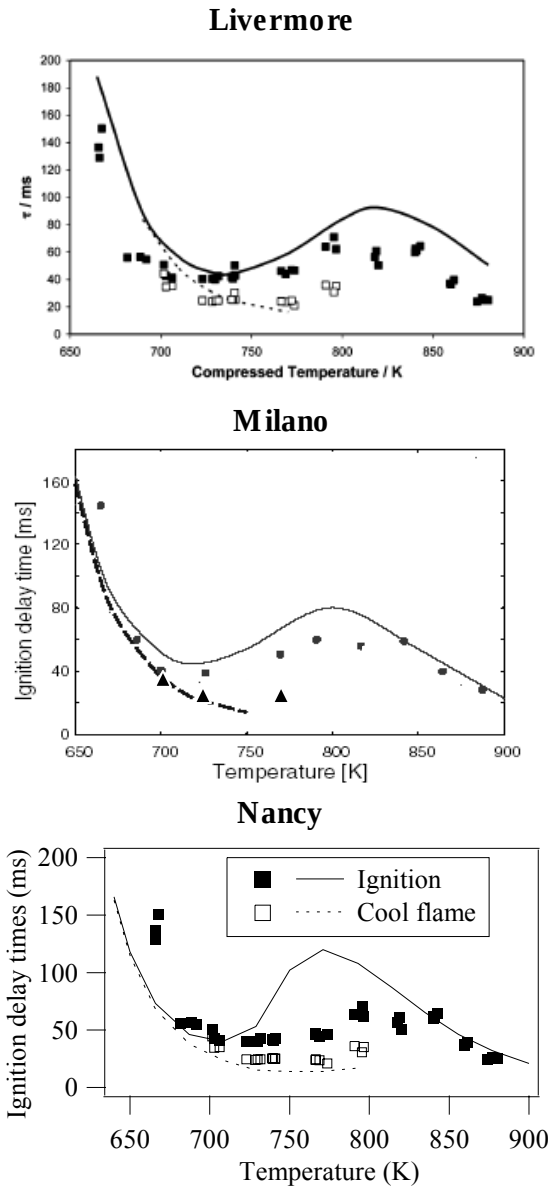


Figure 22: Comparison between the validation of the models of Livermore [224], Milano [227] and Nancy [228] for the oxidation of cyclohexane in a rapid compression machine (P_c from 7 to 9 bar, $\phi = 1$ [229]) for autoignition and cool flame delay times vs. temperature. Symbols correspond to experiments and lines to simulations.

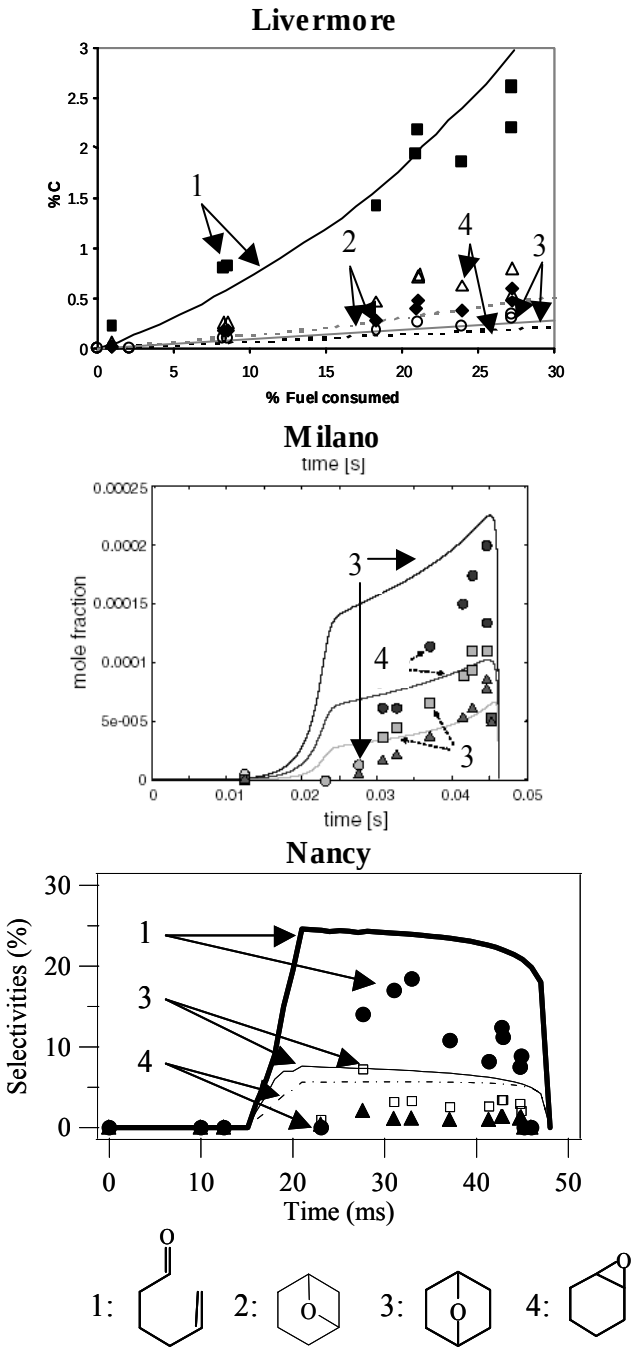


Figure 23: Comparison between the validation of the models of Livermore [224], Milano [227] and Nancy [228] for the oxidation of cyclohexane in a rapid compression machine (P_c from 7 to 9 bar, $\phi = 1$ [229]) for the formation of oxygenated products at 722 K. Symbols correspond to experiments and lines to simulations.

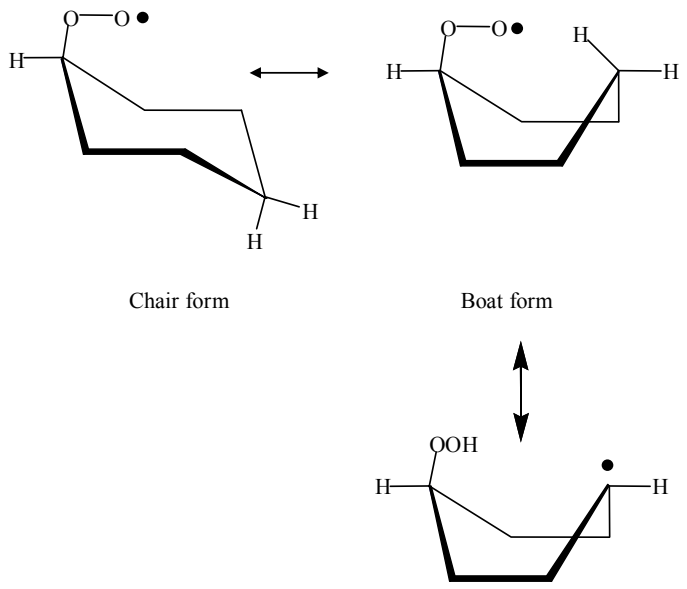


Figure 24: Internal isomerization of peroxycyclohexanyl radicals involving a 7 membered transition state ring.

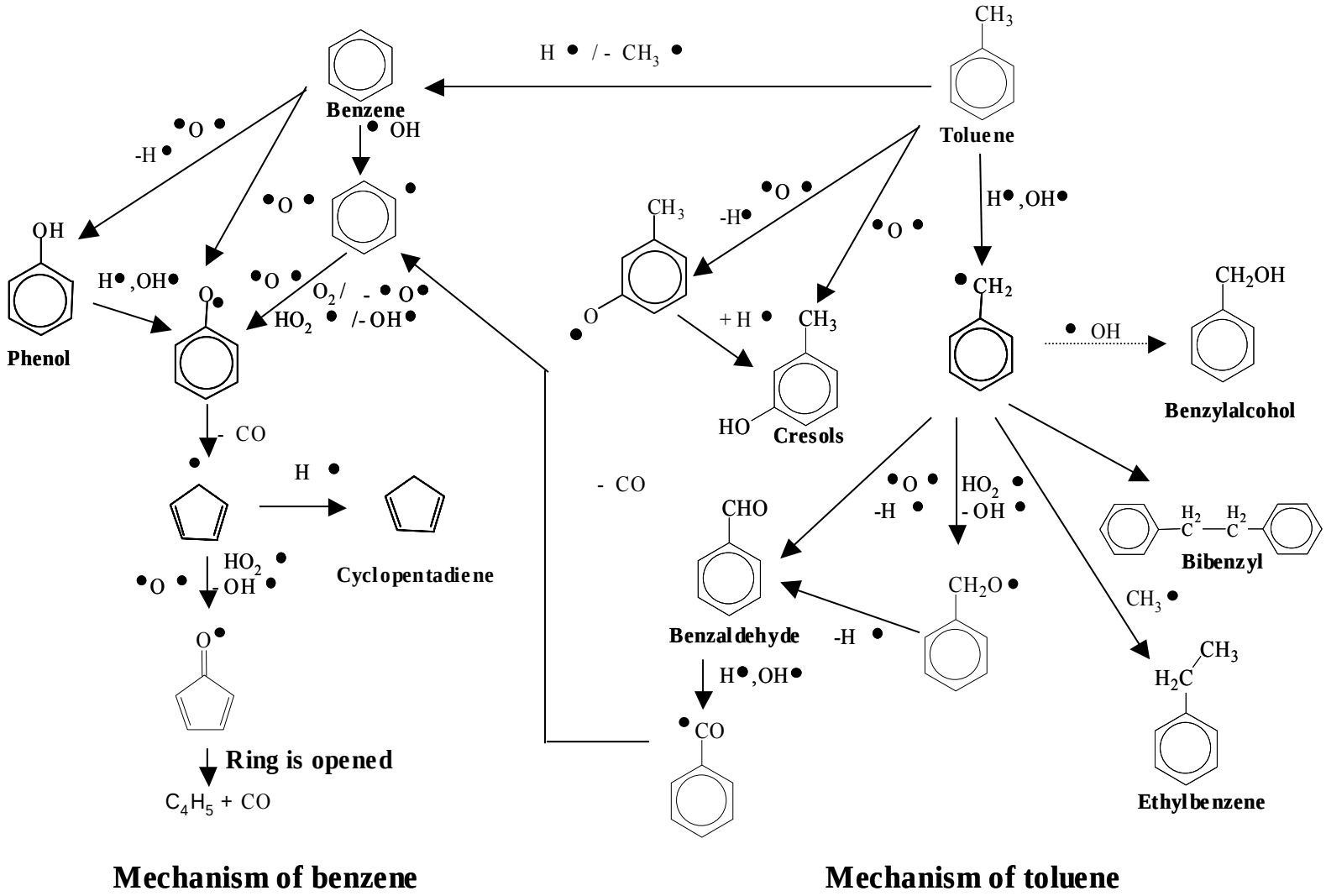
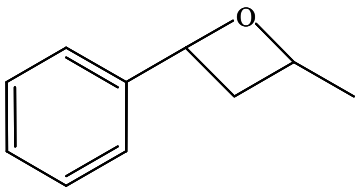
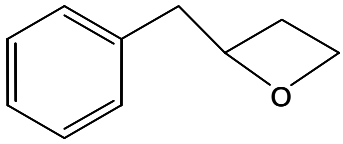


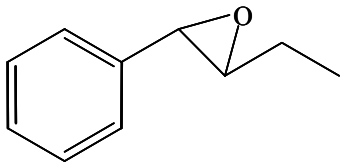
Figure 25: Mechanism for the oxidation of benzene and toluene as proposed by Brezinsky [237].



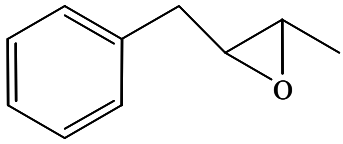
2-methyl-4-phenyloxetane



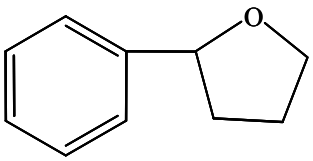
2-benzyloxetane



2-ethyl-3-phenyloxirane



2-benzyl-3-methyloxirane



2-phenyltetrahydrofuran

Figure 26: Cyclic ethers detected by Roubaud et al. [244] during the oxidation of n-butylbenzene in a rapid compression machine prior autoignition (T_c =691 K).

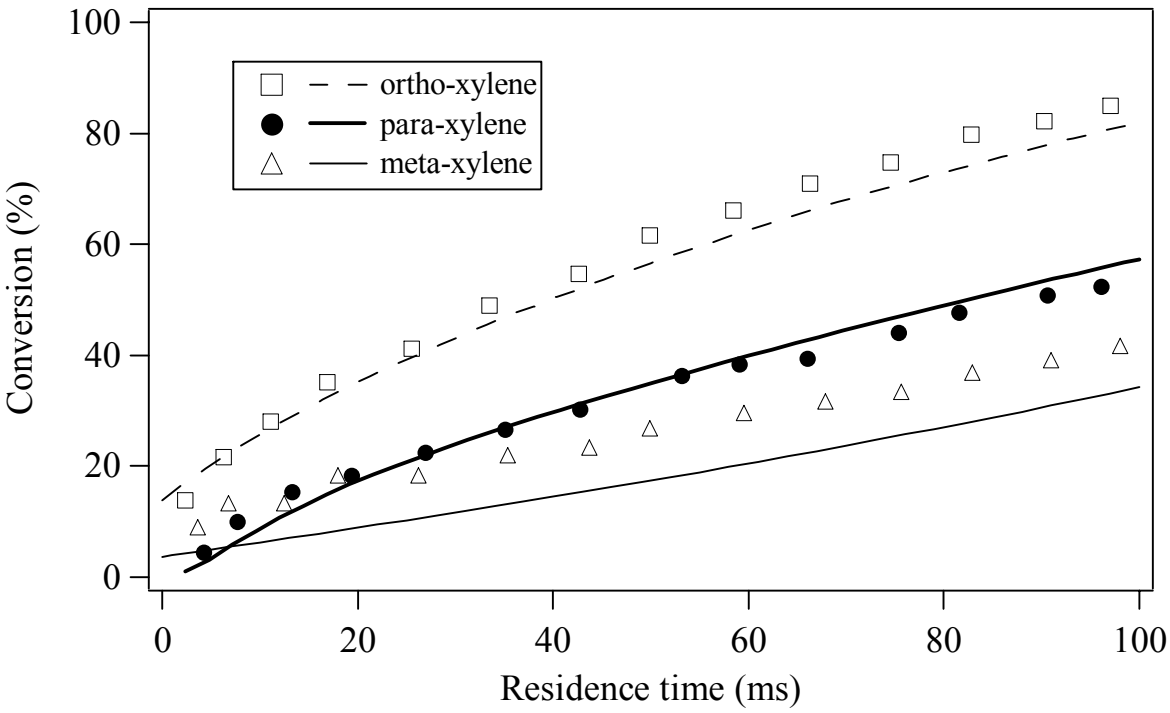


Figure 27: Comparison between the experimental [271-272] (symbols) and simulated [270] (lines) conversions of the three isomers of xylene in a flow reactor (T = 1155 K, P = 1 atm and ϕ close to 1).

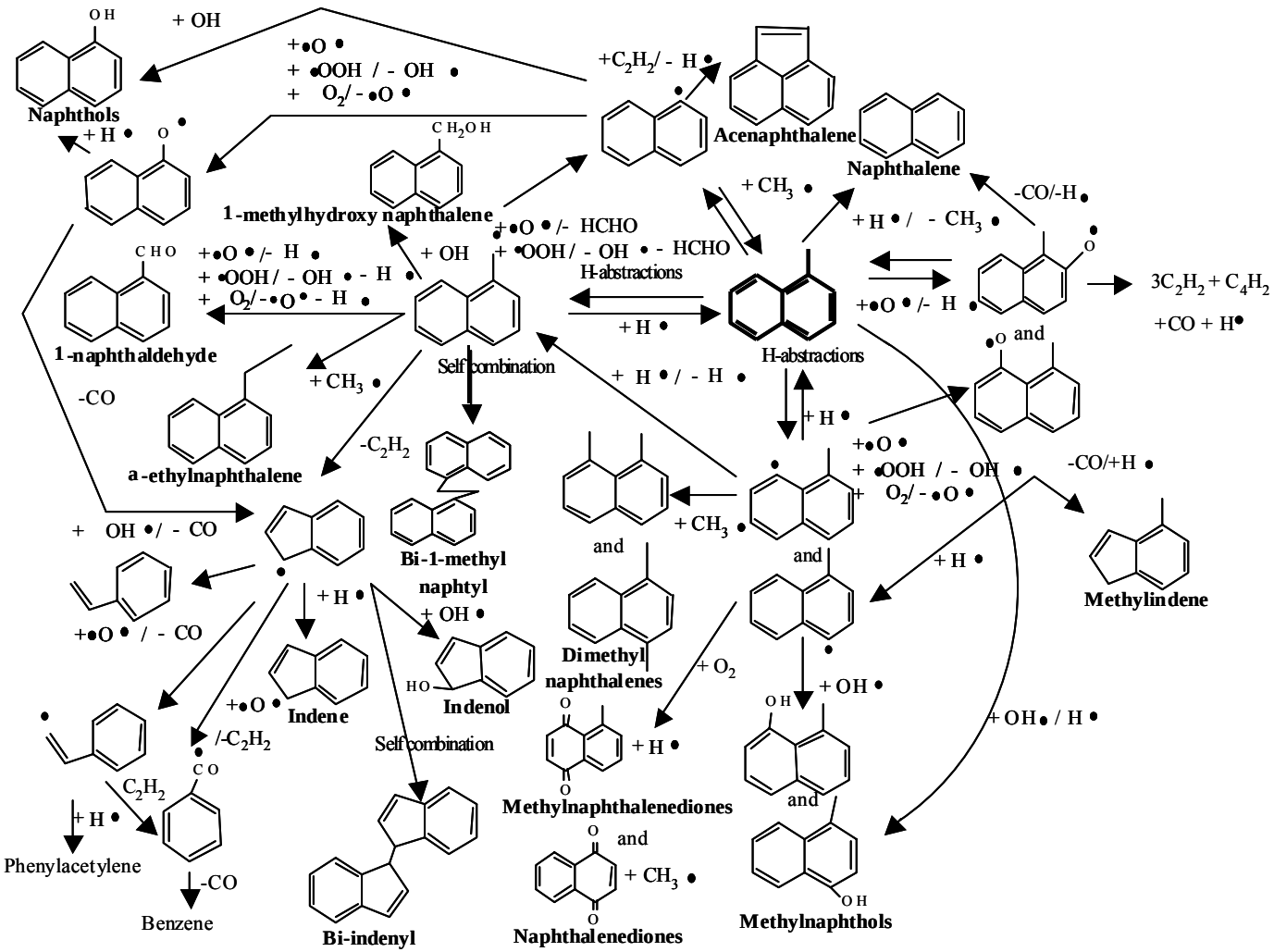


Figure 28: Primary mechanism of the oxidation of 1-naphthalene as proposed by Bounaceur et al. [10].

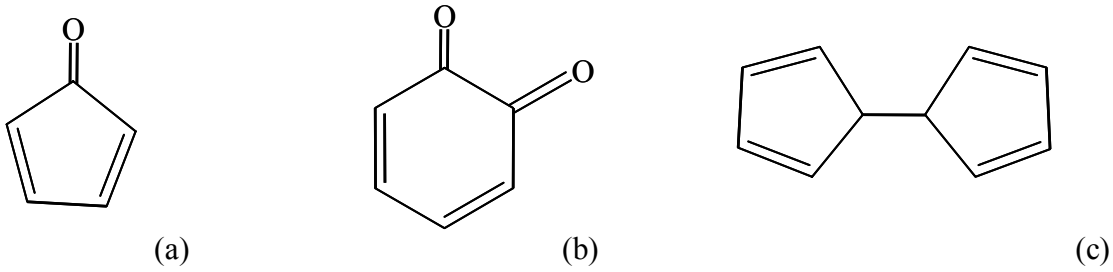


Figure 29: Structure of some species involved in the oxidation of benzene: (a) cyclopentadienone, (b) ortho-benzoquinone and (c) dihydrofulvalene.

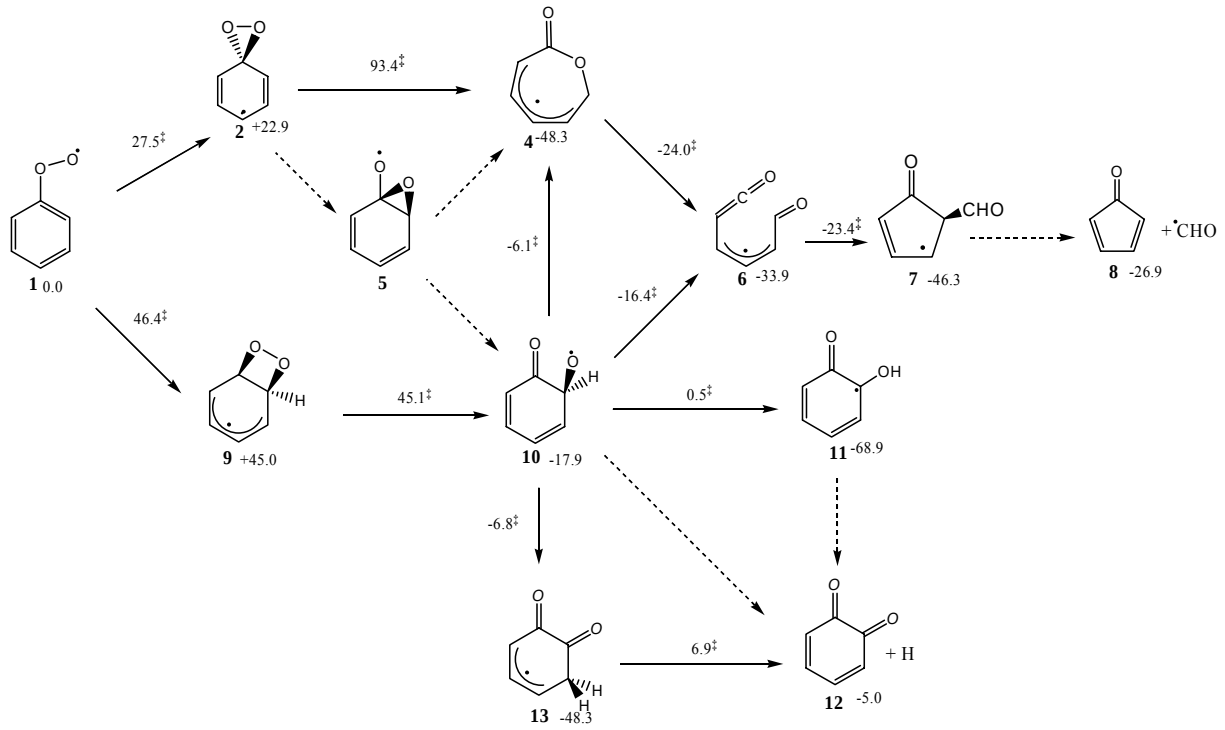


Figure 30: Possible pathways leading to o-benzoquinone and cyclopentadienone from phenyperoxy radicals according to Sirjean et al. (numbers are relative free energies (298 K, kcal/mol) calculated at the B3LYP/6-311++G** level) [295].

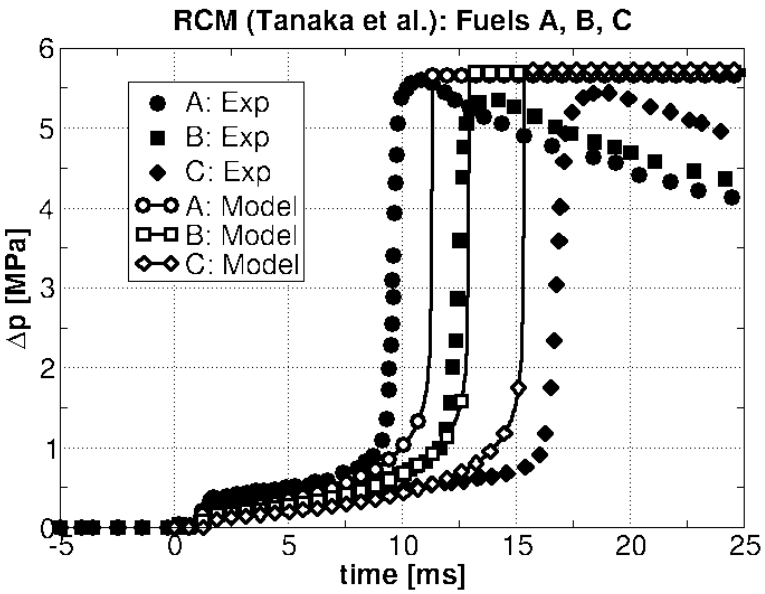


Figure 31: Experimental [117] and simulated [324] pressure change (Δp) curves for fuels A (26 % n-heptane, 74 % toluene), B (5 % iso-octane, 21 % n-heptane, 74 % toluene) and C (10 % iso-octane, 16 % n-heptane, 74 % toluene) in the rapid compression machine of Cambridge (USA) (T_c = 827 K, P_c = 41.6 bar, ϕ = 0.4).

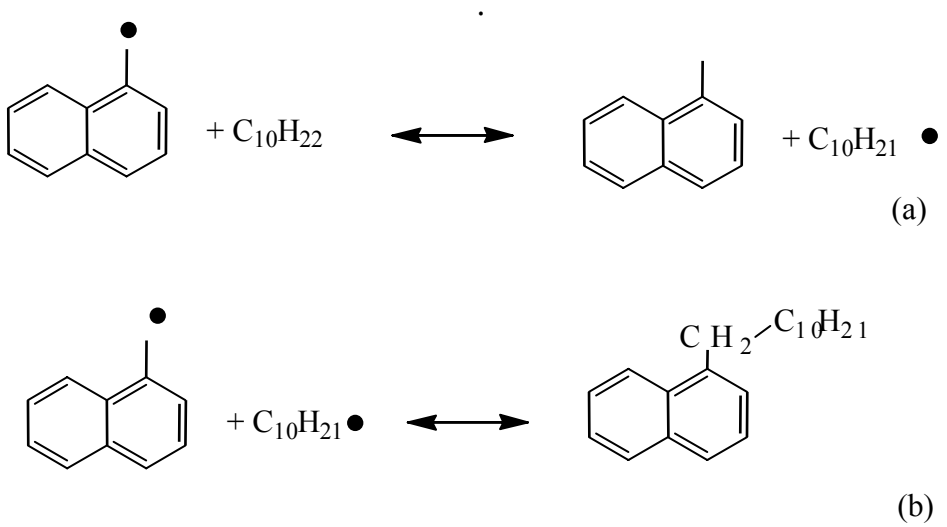


Figure 32: Examples of "cross term" reactions during the oxidation of n-decane/1-methylnaphthalene mixture: (a) H-abstractions by phenylbenzyl radicals from n-decane (the 5 isomers of decyl radicals can be obtained), (b) combinations between phenylbenzyl and decyl radicals [10].