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Towards cleaner combustion engines through groundbreaking detailed chemical kinetic models

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Abstract

In the context of limiting the environmental impact of transportation, this critical review discusses new directions which are being followed in the development of more predictive and more accurate detailed chemical kinetic models for the combustion of fuels. In the first part, the performance of current models, especially in terms of the prediction of pollutant formation, is evaluated. In the next parts, recent methods and ways to improve these models are described. An emphasis is given on the development of detailed models based on elementary reactions, on the production of the related thermochemical and kinetic parameters, and on the experimental techniques available to produce the data necessary to evaluate model predictions under well defined conditions (212 references).

A. Introduction

Even with the expected development of new and cleaner sources of energy, it is still believed that the combustion of liquid fuels will remain the main source of energy for transportation for the next 50 years.\textsuperscript{1} It is therefore of the highest importance to limit the environmental impact of using these fuels during this transition period. As traditional fossil fuels are considered to be largely responsible for causing important atmospheric degradations\textsuperscript{2} such as global warming,\textsuperscript{3} acid rain, and tropospheric ozone increase, an important effort has been made by industry to develop both more efficient types of engines and cleaner types of fuels. A good example is the development of Homogeneous Charge Compression Ignition (HCCI) engines. The HCCI engine is characterised by the fact that the fuel and air are mixed before combustion starts and the mixture auto-ignites as a result of the temperature increase in the compression stroke.\textsuperscript{4} This new type of engine has been proposed not only because of its high efficiency compared to that of diesel engines, but also because of its very low emissions compared to gasoline engines with a catalytic converter. With regard to fuels, there is an increasing interest to shift from hydrocarbon fossil fuels to bio-fuels (particularly bioethanol and biodiesel).\textsuperscript{5–9}
While it is especially important to lower the emissions of CO\textsubscript{2} through the use of more efficient powertrains and through an increased biomass derivative content in traditional fuels, the emission reduction of other pollutants should certainly not be neglected. A paper of Wallington et al.\textsuperscript{10} describes the parts of automotive engines which could be sources of organic emissions, as well as the effect of fuel structure and of catalytic converters on these emissions.

Recent measurements in the exhaust gas of diesel engines have been made by Nelson et al.\textsuperscript{11} They have shown the presence of many volatile organic compounds (VOCs), namely 1,3-butadiene, benzene, toluene, xylenes, formaldehyde and acetaldehyde, and of 16 polycyclic aromatic hydrocarbons (PAHs) from naphthalene (C\textsubscript{10}) up to benzoperylene (C\textsubscript{22}). Previous detailed analyses of gas-phase pollutants emitted from the exhaust had been published for diesel\textsuperscript{12} and gasoline.\textsuperscript{13,14} These papers also describe the presence of many VOCs, including noticeable amounts of carbonyl compounds and carboxylic acids. Carbonyl compounds such as aldehydes are known to be toxic for human health (carcinogen risks (e.g. formaldehyde), allergies, liver diseases...).\textsuperscript{15} It has been shown that in addition to sulfuric and nitric acids, carboxylic acids (formic and acetic acids, especially) can contribute to the acidity of gas and aqueous phases of the atmosphere in urban, as well as in remote regions.\textsuperscript{16}

The needed developments of new types of engines and fuels have prompted a recent growth of industrial projects targeting the development of detailed chemical kinetic models for the combustion of a wide range of hydrocarbons.\textsuperscript{17,18} Progress in the development of chemical models has to be made together with advances in physical modelling of combustion in engines (turbulence, spray evaporation...). What cannot be neglected is the coupling between these physical and chemical models.\textsuperscript{19} Integration of the chemical models for combustion and pollutant emissions in computational fluid dynamics (CFD) engine models should be particularly useful in allowing the study of actual engine emissions over a wide range of operating conditions.\textsuperscript{20}

In addition to the propensity of mixtures of oxygen with organic compounds towards ignition, which has promoted their use in engines, these mixtures possess other important specific reactive features. Single or multiple small temperature pulsations (a few tenths of K) accompanied by weak blue light emission due to excited formaldehyde, the so called “cool flames”\textsuperscript{21} are often observed under conditions preceding auto-ignition (usually from 550 K). Closely linked with “cool flames”, a second well known characteristic of these systems is a temperature zone (usually around 650 K) where the reactivity decreases as temperature increases. This is commonly called “negative temperature coefficient” (NTC) zone.\textsuperscript{21}

These features have made the gas phase low temperature oxidation of organic compounds a fascinating field of investigation for kinetic modellers since the end of the 70s, when the first generalized models describing these phenomena appeared.\textsuperscript{22,23} These models were based on formal reactions with kinetic parameters empirically fitted. Satisfactory detailed models based on
elementary reactions (with all the relevant thermochemical and kinetic data) for the oxidation of alkanes at high temperature (above 900 K) appeared in the 80s. But it is only since the middle of the 90s that validated detailed models for the low-temperature phenomena of these species have been fully developed.

The primary focus of the currently developed chemical models is to simulate the main combustion parameters (auto-ignition delay times, laminar flame speed, heat release), which are needed for the design of engines and burners, and to estimate the fuel consumption, and to model the formation of some of the main regulated pollutants (carbon monoxide, nitrogen oxides, unburned hydrocarbons and particulate matter).

The first section of this paper shows how models have now been developed for simplified compositions of reactant mixtures which represent fairly well real fuels. This section also described how the prediction of numerous hazardous minor combustion products still needs to be strongly improved.

The three other sections discuss how more accurate models could be developed in order to better predict the formation of minor products. The second section describes possible improvements in the ways of generating models. The third section focuses on the methods for including in these models more accurate thermochemical and kinetic parameters. Finally, the last section reviews possible methods to obtain the most detailed and accurate experimental data to validate the modelling of the formation of minor combustion products.

While it is not shown in detail in the present paper, the described methodology can easily be used for improving the prediction of NOx formation. As the modelling of the formation of soot requires a very different methodology compared to the case of gas phase pollutants, this paper will not discuss this topic. Details about modelling the formation and oxidation of soot can be found in the papers of Richter and Howard, Stanmore et al., and Wang. Note however that the described methodology could be used also to improve the prediction of the formation of PAHs which are well known soot precursors.

B. Performances of current detailed kinetic models for combustion

Gasoline, diesel fuel and jet fuel have a “near-continuous spectrum” of hydrocarbon constituents. However these constituents can be classed in five main hydrocarbon families: linear alkanes (n-paraffins), branched alkanes (iso-paraffins), cyclic alkanes (napthenes), alkenes (olefins) and aromatic compounds. The cyclic compounds include polycyclic and substituted rings with one or several alkyl chains. Noticeable amounts of alcohols (mainly ethanol) and methyl esters are added in gasoline and diesel fuel, respectively, to produce what is now called “biofuels” for transportation.
Ethanol is produced by alcoholic fermentation of sucrose or simple sugars, which in turn are derived from biomass by hydrolysis process. Methyl esters are obtained by transesterification from vegetal oils (e.g. soybean oil, rapeseed oil).

In order to handle the full complexity of fuels for combustion modelling, it is necessary to represent model fuels by more than one primary component. However in order to avoid an explosion of the size of the models, surrogates have to be composed of only a limited number of components. Surrogates are chosen to best match the properties of a given fuel in terms of physical properties (density, viscosity, boiling point, etc.), combustion parameters and formation of pollutants. To obtain the best match, components representative of as many as possible of different families of species present in fuel have to be included.

Models have been developed for the gas-phase oxidation and combustion of many compounds belonging to the previously mentioned hydrocarbon families, for several methyl esters and for a few alcohols, as well as for mixtures proposed as surrogates. Due to recent reviews, the focus of this part is not to comprehensively describe all the existing detailed kinetic models.

In 2003, Simmie reviewed detailed chemical kinetic models for the intermediate to high-temperature oxidation, ignition, and combustion of hydrocarbons.

In 2008, Battin-Leclerc was interested in the detailed kinetic models used to simulate the low temperature oxidation and autoignition of gasoline and diesel fuels. The paper reviews the reactions of primary components of the surrogate fuels (alkanes, ethers, esters, alkenes, cycloalkanes, aromatics, including more than 4 atoms of carbon), as well as their mixtures.

The more recent paper of Pitz and Mueller describes progress in the development of models for diesel surrogate fuels.

Two papers interested in detailed kinetic models for reactants derived from biomass were published in 2010. The review of Lai et al. is concerned only with methyl esters. Models for both alcohols and methyl esters were considered by Kohse-Höinghaus et al.

While a few years ago, gasoline was often represented only by a n-heptane/iso-octane blend (a mixture of both primary reference fuels (PRF) for octane rating), new models now consider the presence of aromatics, naphthenes and olefins. As an example, Mehl et al. (in Livermore) and Bounaceur et al. (in Nancy) have both proposed detailed models for mixtures containing alkanes,
toluene and 1-hexene. Fig. 1 shows how the latter model can reproduce data obtained in a rapid compression machine\textsuperscript{44} for the auto-ignition of a \textit{iso}-octane/toluene/1-hexene ternary mixture as a gasoline surrogate. A similar agreement was obtained by Mehl et al.\textsuperscript{42} It is worth noting that these recent models can well simulate delay times for both cool flames and ignitions. This shows that the main kinetic features triggering the global reactivity of a complex mixture, such as an \textit{iso}-octane/toluene/1-hexene ternary blend, are now well understood.

![Cool flame and ignition delay times for a 47/35/18\% mol \textit{iso}-octane/toluene/1-hexene ternary mixture. Measurements (points) made in a rapid compression machine by Vanhove et al.\textsuperscript{44} (pressure after compression between 15 and 20 bar, stoichiometric mixtures in air). Modelling (lines) taken from Bounaceur et al.\textsuperscript{43} More detail about rapid compression machines are given in Section E.1.1.](image)

In Milano, Mehl et al.\textsuperscript{45} performed 1D HCCI simulations for mixtures containing \textit{n}-heptane, \textit{iso}-octane, toluene, and 1-pentene. Comparisons with experiments were satisfactory for fuel consumption and for the formation of a few reaction products.

Concerning naphthenes, which have an increasing importance for fuels derived from non-conventional oil, such as Canadian oil sands,\textsuperscript{46} the Milano team has proposed a semi-detailed model for a \textit{n}-heptane, \textit{iso}-octane, methylcyclohexane and toluene mixture with satisfactory validation using data obtained in a counterflow burner\textsuperscript{47} (mass fraction of the fuel as a function of the strain rate at extinction, and temperature of the oxidizer stream at autoignition).

Dooley et al.\textsuperscript{48} have shown that a ternary \textit{n}-decane/\textit{iso}-octane/toluene mixture could be a good surrogate for reproducing a wide range of results for the oxidation of a jet-fuel (POSF 4658). These authors\textsuperscript{48} have also proposed a detailed kinetic model with satisfactory predictions of the experimental results. Experimental data were obtained in a diffusion flame for measuring strained extinction limits, a rapid compression machine and a shock tube for measuring ignition delay times,
as well as in a variable pressure flow reactor. Note that in the flow reactor, carbon oxides and water were the only analysed products.

A binary mixture containing \(n\)-decane and \(\alpha\)-methylnaphthalene is often considered as a suitable surrogate for diesel fuel. \(\alpha\)-methylnaphthalene is one of the reference compounds for cetane rating, with a cetane number of 0 indicating a very low reactivity. Both fuels show good agreement in their physical (density, viscosity, etc.) and chemical (cetane number, aliphatic and aromatic compounds) properties.\(^{49}\)

Fig. 2 shows how a current model can satisfactorily reproduce auto-ignition delay times measured in a shock tube for a binary mixture containing \(n\)-decane and \(\alpha\)-methylnaphthalene (70\% (mol.) of alkane).\(^{50}\)

![Fig. 2 Ignition delay times for a 70/30\% mol \(n\)-decane/\(\alpha\)-methylnaphthalene mixture in a shock tube: stoichiometric mixtures in air, experiments (points) and modelling (lines) from Wang et al.\(^{50}\) More detail about shock tubes are given in Section D.2.](image)

In the case of biofuels derived from vegetal oils, several studies have shown that for modelling global reactivity and the formation of the major products, middle size methyl esters such as methyl octanoate\(^{51}\) or methyl decanoate\(^{52,53}\) are suitable surrogates. However, detailed models have just begun to appear for the oxidation of molecules really representative of those present in biofuels.

As the models for very large compounds are not described in the review papers about methyl esters,\(^{6,39}\) they will be described in little more detail here. Herbinet et al.\(^{52}\) have proposed a model for methyl palmitate (a saturated \(C_{16}\) ester) and Westbrook et al.\(^{54}\) one for methyl stearate, methyl oleate and methyl linoleate (a saturated, a mono-unsaturated and a di-unsaturated \(C_{18}\) methyl ester, respectively). Methyl oleate is the main component of biofuel obtained from rapeseed oil and methyl linoleate is that of soybean oil.\(^{36}\) Note that due to a lack of experimental data, it was not possible to check the validity of the prediction of the models for methyl stearate and methyl linoleate.\(^{54}\) The
models for methyl palmitate\textsuperscript{52} and methyl oleate\textsuperscript{54} were validated using data obtained in a jet-stirred reactor for the oxidation each of these esters in a mixture with \textit{n}-decane.\textsuperscript{55,56}

In the latter experimental studies,\textsuperscript{55,56} a wide range of reaction products were analysed making it possible to evaluate the performance of models. While the models of Herbinet et al.\textsuperscript{52} and Westbrook et al.\textsuperscript{54} are able to reproduce the fuel consumption, as well as the formation of the major and some of the minor products, important deviations are encountered for the prediction of many minor intermediates.

The general performance of hydrocarbon models for predicting minor species is illustrated by a recent study of the oxidation of a simple alkane, \textit{n}-butane.\textsuperscript{57} Using two analytical methods, gas chromatography of the outlet gas and reflectron time-of-flight mass spectrometry after sampling by a molecular beam directly from the reactor, the authors have quantified 36 reaction products, the mole fraction of which is above 1 ppm, for the oxidation of \textit{n}-butane between 550 and 800 K, at atmospheric pressure, in an isothermal jet-stirred reactor. They have simulated the formation of these species using a detailed kinetic model. Fig. 3 summarizes the deviations between experiments and simulations for a temperature of 630 K, corresponding to the maximum of reactivity. About a third of the products have a deviation lower than a factor of 2 (a deviation lower than 1) and those are mainly the major products: carbon oxides, water, formaldehyde, acetaldehyde and butenes. About another third of these products are simulated with a deviation larger than 10 or are not taken into account by the model. However, significant uncertainties also exist on the experimental mole fraction of some species, such as hydroperoxides.
Fig. 3 Deviation between simulations and experimental results for the oxidation of n-butane in a jet-stirred reactor at 630 K (stoichiometric mixtures containing 4% n-butane).57 The deviation is the absolute value of the normalised difference between simulated and experimental mole fractions. When the experimental value was overestimated, the difference was normalised by the experimental mole fraction for species. When the experimental value was underestimated, the difference was normalised by the simulated value. More detail about jet-stirred reactors are given in Section E.1.3.

In another study by Lenhert et al.,58 the deviation in the prediction of minor products has also been observed. These authors have experimentally studied the oxidation of a gasoline surrogate in a pressurized flow reactor between 600 and 800 K at elevated pressure (8 atm). The surrogate was composed of n-heptane, iso-octane, 1-pentene and toluene. The mixture, as well as each individual non-aromatic component, was studied. For each studied system, a detailed speciation was performed. A modelling study has been done using models taken from Curran et al.26,59 for the alkanes and for the mixture. The model of Touchard et al.60 was used for 1-pentene. Simulations can predict well the temperature rise, the fuel consumption and the formation of the major products observed during the oxidation of n-heptane and 1-pentene. The agreement deteriorates for iso-octane and for the formation of minor products in every case.
Note also that the increasing sensitivity of analytical methods has allowed in recent studies the detection of species not usually taken into account in current models: e.g. acetic acid,\textsuperscript{57} hydrocarbons including two carbonyl groups or a carbonyl and an alcohol group,\textsuperscript{57} furanones (cyclic ethers including a ketone).\textsuperscript{61} The modelling of the formation of these new types of species will make it necessary to consider new types of reactions which are not yet taken into account in current models.

The conclusion which can be drawn from this analysis of the performances of the current models for the oxidation of fuels coincides with that recently well stated by Westbrook et al.:\textsuperscript{54} there are many opportunities in kinetic mechanisms for multiple reaction pathways to occur, and it is quite possible to produce an accurate prediction of some integrated property such as an ignition delay time, burning velocity, or overall rate of reaction, and still not describe the complete detail of the reaction.

Note also that while prediction is the final goal of any modelling, uncertainties in the current models hinder often their use in an actual predictive way; the authors agree with Green\textsuperscript{62} that models are “postdictive” instead of predictive.

The purpose of the next three parts of this paper is to review methods which could be used to increase the accuracy of next generation models for better capturing the full detail of the reaction.

C. Methods for improving the development of models

While the manual development of models has up to now produced excellent results, such as the models produced by the team of Livermore, e.g. ref. 26,53,54 and 59 and by the Jet-Surf project,\textsuperscript{63} the use of automatic methods may help gain a better handling of models including complex reactions involving numerous reaction pathways.

This section first gives a brief state of the art of automatic generation of kinetic models and then describes directions on which to improve these methods and models. This is followed by a description of the ways to obtain the associated thermochemical and kinetic data.

C.1 State of the art in automatic generation of kinetic models

In this part, we detail three features, which are common to most automatic generation systems: reaction classes, their application in the generation process and lumping. After this general introduction, we present the major existing systems.
C.1.1 Reaction classes. First attempts in the generation of kinetic models were derived from computer-aided synthesis strategies developed in organic chemistry. Some systems,\textsuperscript{64,65} based on matrix combinations and defining reactions as the creation or the breaking of a bond, were proposed. The main limitations of this approach are the generation of reactions without chemical significance, the duplication of some pathways and the difficulty to find the stage where the generation can be stopped. The definition of a set of possible products, as proposed by Nemés et al.,\textsuperscript{66} can avoid the combinatorial explosion of reactions. A solution considered in latter systems has been the use of realistic reaction rules based on chemical knowledge.

One of the major differences between the development of models for small species, such as those with less than three carbon atoms, and larger species, such as those containing long hydrocarbon chains, is the availability of specific kinetic information for each reaction. For smaller species kinetic parameters can be deduced fairly directly from experiments. However, as the species grow larger, direct experimental measurements are not available and reaction classes based on local properties around the reactive centre have to be employed. In addition, since small species have less possibility of unimolecular reactions (e.g. decompositions or intramolecular isomerizations), a larger number of specific bimolecular reactions can be important.

A fundamental assumption in defining reactivity is that the effect of functional groups around the reactive centre, where the bond making and breaking actually occurs, diminishes rapidly with distance. For small species, this is the entire molecule, but for large species, functional groups at one end of a long hydrocarbon chain have a negligible effect on the reactivity at the other end of the chain. With unsaturated systems, especially if resonance comes into play, the influence of the functional group can be further.

Curran et al.,\textsuperscript{26,59} for example, derived a set of reaction classes for both $n$-heptane and $iso$-octane low-temperature oxidation. These and other reaction classes were developed from a combination of organic chemistry bases, analogies and, more recently, theoretical calculations. A reaction class describes which bonds are made and broken given the types of atoms, bonds and local functional groups involved. A generic rule is used to generate a reaction from a reaction class.

A generic rule is applied to a molecule or a radical by identifying where reactant substructures in the reaction class can be found in the considered species.

The reactant substructures in a reaction class consist not only of the part of the molecule which is transformed to products, but also the surrounding functional groups which can influence the kinetic parameters. The molecule is then modified according to the reaction class to produce the product species. For bimolecular reactions, the substructures have to be found in both reactants.
These types of reaction classes, which are well known for alkanes\textsuperscript{67} (for example Fig. 4), can be found in the literature\textsuperscript{26,68,69} and are updated as far as knowledge is progressing for the different families of reactants.

Fig. 4 Simplified scheme for the primary mechanism of oxidation of alkanes. Degenerate branched chain reactions (production of free radicals from products formed in a chain reaction) have been proposed to explain explosive reactions, such as the autoignition of hydrocarbons.\textsuperscript{67} At low temperature, i.e. below 900 K, the alkyl radicals R’ are produced by H-abstractions mostly by 'OH radicals. They add thereafter to O\textsubscript{2} and yield peroxy radicals ROO’. The existence of the NTC zone is mainly due to the enhanced reversibility of this reaction as the temperature increases. Some consecutive steps will then lead to the formation of hydroperoxides, which are degenerate branching agents explaining the high reactivity of alkanes at low temperature.

C.1.2 Algorithms of automatic generation of kinetic models and lumping procedure. Another difference between the development of mechanisms for small and large species is the complexity of the mechanisms themselves. For small species, it is a manageable task to devise the combinations of possible reactions between all the intermediate species. However, as the size of the species increases, the combinatorial explosion of possible reactions and species also increases. To systematically complete the model, especially with the assurance of being error-free, becomes a daunting and unrealistic task.
Given that models for larger hydrocarbons are already produced with reaction classes, a natural solution is automatic generation. Automatic generation systems apply a set of generic rules systematically to produce a given model. Fig. 5 presents an example of the types of reactions which can be considered in the case of the oxidation of alkenes, as well as a possible structure for an algorithm of generation of mechanism.

![Diagram of reaction mechanism]

**Primary products of termination**

Fig. 5 Algorithm of generation for the primary mechanism of the oxidation of alkenes by the EXGAS software. (*reactions with oxygen leading to HO₂ radicals and an unsaturated molecules for alkylic and allylic radicals and to an oxygenated radicals and molecule for vinylic radicals; **mainly of importance for allylic radicals).

A distinguishing feature of the various generation systems is which reaction classes are represented, i.e. which chemistry is included, and how molecules and reactions are represented (sometimes the representation produces limitations on which types of chemistry and species can be included).

In a single iterative step of generation, a pool of molecules (initially it is just the fuel molecule), is examined with respect to a set of valid reaction classes. As illustrated in Fig. 5, all combinations of possible reaction class applications are performed to produce a set of specific reactions and a new pool of product molecules is formed. Which set of reaction classes, the filtering of produced reactions and which set of molecules is used in the next iteration are features which distinguish the various automatic generation systems. For instance, combinations and H-abstractions could theoretically involve all possible radicals. However in most systems, only radicals which cannot easily decompose by β-scission are actually taken into account.
A full set of reaction classes representing the full chemistry of oxidation applied to a large molecule can produce a combinatorial explosion of reactions and species. A common means to reduce a mechanism is to recognize that many reactive pathways of similar species can be simplified by representing a set of isomers by a single lumped species. The mathematical representation of a lumped species is a linear combination of the specific isomers, where the coefficients represent the species weight in the reactive process. These coefficients can be derived, for example, by taking into account the flow of reactions, which is the most accurate way. However, the values can also be assumed, for example, saying all the values are the same and of equal weight, or even by assuming that one species is dominant (e.g. all the alkenes obtained from the oxidation of alkanes could be 1-alkenes), meaning that all the coefficients are zero except for one. The lumping procedure itself can either be a post-processing method, or even built into the generation process. This is another feature which distinguishes the different generation systems.

**C.1.3 Existing automatic generation systems.** The team at Leeds was among the first to develop a software for generating mechanisms. This expert system for the pyrolysis of alkanes involved a unique representation of acyclic hydrocarbons and was based on ten types of generic elementary processes. Rate parameters were also provided and a comparison of reaction rates for parallel channels was used to eliminate some reactions generated during the derivation of the mechanism. This system was tested successfully on the generation of mechanisms for the pyrolysis of C₁–C₄ hydrocarbons.

As reviewed by Tomlin et al., others have extended, with some success, this approach to the generation of mechanisms for the oxidation of alkanes. We will describe here only the most advanced systems.

In line with their previous work on pyrolysis, a team in Milano has used automatic generation to produce validated semi-detailed mechanisms for the oxidation of a wide range of alkanes from C₅ to C₁₂ in a temperature range from 550 to 1800 K. To have an idea of the size of the mechanisms generated by this system, just consider that the mechanism for the low-temperature oxidation of n-heptane includes more than 2000 reactions. An automatic generator of reactions (MAMOX) is used to provide primary detailed mechanisms (involving only the reactions of initial molecular reactants and their derived radicals). The species representations, the method to distinguish unique species representations and the types of reactions considered were described in detail by Pierucci and Ranzi. Structure-reactivity correlations are proposed to estimate kinetic data (high-pressure limit) for each type of reaction. This primary mechanism is then lumped using the following procedure:

- radicals of the same type and having the same chemical formula are grouped together,
• decomposition reactions are globalized into single equivalent reactions whose stoichiometries (involving fractional coefficients) are only weak functions of process temperature.
• stoichiometric coefficients and rate constants of the lumped mechanism are obtained by optimization using reference simulations with the full mechanism.

Secondary mechanisms (involving the reactions of molecular products formed in the primary mechanism) are also based on lumped reactions involving fractional stoichiometric coefficients. An extensively validated database\(^\text{78}\) including reactions of C\(_0\)–C\(_4\) species, but also reactions of simple aromatic compounds such as benzene, toluene or methylnaphthalene, is added to the generated mechanisms. Mechanisms are developed iteratively, that is to say that a mechanism for n-heptane is based on previous mechanisms for n-pentane and n-hexane.\(^\text{69}\)

A team in Nancy has developed a software (EXGAS) for the automatic generation of mechanisms for the oxidation of alkanes (from C\(_4\) to C\(_{16}\)),\(^\text{28,68,79}\) alkenes,\(^\text{60,80}\) cycloalkanes,\(^\text{81,82}\) ethers,\(^\text{83}\) alcohols\(^\text{84}\) and esters\(^\text{85}\) which have been validated under a wide range of conditions (temperatures from 550 to 2000 K). The mechanism for the low-temperature oxidation of n-heptane includes 1817 reactions,\(^\text{68}\) compared to the 2000 reactions in the mechanism of Milano. That for n-decane includes 3872 reactions.\(^\text{68}\) This software has several similarities with the system of Milano:
• three parts are considered: a primary mechanism, a secondary mechanism and a reaction base,
• a unique representation is considered for each species in the primary mechanism,
• the primary mechanism is generated according to defined reaction classes,
• the secondary mechanism is based on lumped reactions,
• the estimation of kinetic data (high-pressure limit) is mostly performed using structure–reactivity correlations.

Contrary to Milano, the comprehensive generated primary mechanism is not lumped despite its significant size. The lumping of the secondary mechanism is also different: no fractional stoichiometric coefficients are used. The general idea is to promote the formation of radicals, the reactions of which are already included in the primary mechanism.\(^\text{79}\) The reaction base used by the software contains only reactions of C\(_0\)–C\(_2\) species, but it can be supplemented by models for the oxidation of C\(_3\)–C\(_4\) unsaturated species\(^\text{86}\) and of aromatic compounds such as toluene,\(^\text{87}\) indane\(^\text{88}\) or \(\alpha\)-methylnaphthalene.\(^\text{50}\) Reactions of species containing nitrogen can also be included in the reaction basis.\(^\text{89}\) The EXGAS mechanisms are not developed iteratively. Therefore the development of a mechanism for \(n\)-hexadecane does not require the generation of the \(n\)-pentadecane mechanism as a prerequisite. Moreover the system of generation gives a large degree of choice for tailoring the sought mechanisms according to the conditions of study. All the generic rules in the primary and the secondary mechanisms are not by default activated; they can be chosen from a menu.\(^\text{90}\)
The generation of detailed kinetic models (including thermodynamic and kinetic data) is fully automatic for the oxidation of alkanes and methyl esters. The EXGAS software has been publically distributed since 2004 (Software EXGAS-ALKANES-ESTERS is freely available for academic researchers on request (valerie.warth@univ-lorraine.fr)).

The lumped primary mechanisms used in Milano certainly keep the same accuracy as the comprehensive ones used in Nancy. However in both systems, the large size of the comprehensive primary mechanism can become a bottle-neck for the development of models, especially as the fuel molecules become larger. In Milano, the full generated mechanism has to be used to optimize the parameters of the lumped one. In general there is a limitation in the number of reactions which can be handled by simulation or optimization softwares. The use in Milano of fractional stoichiometric coefficients in secondary reactions allows a detailed description of the reactions of primary products. However as no detailed mechanism is available for the optimisation of the used parameters, those are obtained from fitting experimental data and that limits the validity of these models under other conditions.

The REACTION software developed by Blurock was used to generate a low temperature oxidation detailed model for n-decane (with a complete n-heptane submechanism) including 3684 reactions based on the classes of reactions defined by Curran et al. supplemented with reaction classes for other oxygenated species that appear in hydrocarbon combustion. The governing principle of REACTION is to mimic the generation as it is done by hand. For example, the generated n-heptane mechanism is similar to that of Curran et al. The smaller size of the mechanisms is due to a generation method using pathways instead of the exhaustive procedure used by other systems. A pathway is a sequence of sets of reaction classes leading to smaller products (usually, radicals, aldehydes and alkenes). Only the products of the last step are used as seeds for the next step. For example, the main low temperature pathway starts with a seed hydrocarbon and applies low temperature reaction classes (see in Fig. 1 the reactions starting from the addition to oxygen of alkyl radicals) through to the branching agents. Other pathways include low temperature branches of this pathway going through alkene, cyclic ether or QOOH intermediates. The generation of the n-decane mechanism used 8 pathways for the primary mechanism: 4 ‘high’ (based on reaction classes 1–10 of Curran et al.) and 4 ‘low’ (based on reaction classes 11–25 of Curran et al.) temperature pathways for both n-decane and n-heptane. In addition, a full set of ‘high’ temperature pathways of n-nonane through n-pentane oxidation was included. The base mechanism was a validated C₃ mechanism. In a post-processing step, this mechanism was lumped using the principle that if several intermediate isomers were produced and consumed by the same reaction classes (note that primary, secondary and tertiary reaction classes are considered distinct), then they could be lumped. All lumped species have the same weight. This resulted in a reduction of the full mechanism by about two thirds of the original generated mechanism.

In all the previous systems, the basis for the algorithm of generation is implicitly the theory of chain reactions. A team in MIT has developed since 1994 a software for automatic generation of kinetic
models called RMG which is not based anymore on this theory. This system has only recently been used to produce validated models: e.g. one for the oxidation of n-butanol (3381 reactions)\textsuperscript{96} in a temperature range from 900 to 1900 K and one for the combustion of hexadienes in flames.\textsuperscript{97} This software is based on two previous generators, NetGen\textsuperscript{98,99} (only for modelling pyrolysis) and XGM.\textsuperscript{100} The generation is still based on an algorithm taking into account reaction classes. But contrary to the systems of Milano and Nancy, there is no distinction between primary and secondary mechanisms: the generic rules are systematically applied to the reactants and all derived molecules and radicals. An upper limit of the number of atoms of carbon is set. To avoid the creation of an infinite network, a rate constant is estimated “on-the-fly” for each generated reaction. For each iterative step, simulations are run under initial conditions provided by the user. In the next step, only species with a minimum calculated rate of formation are submitted again to generic rules.\textsuperscript{99} As in the systems of Milano and Nancy, the generated mechanisms can be combined with reaction bases (seed mechanisms): i.e. the GRI-Mech 3.0 methane oxidation mechanism\textsuperscript{101} (omitting nitrogen chemistry) and Marinov ethanol oxidation mechanism\textsuperscript{102} are taken into account in the n-butanol mechanism.\textsuperscript{96} A real advantage of this system, compared to those of Milano and Nancy, is that the pressure dependence of the kinetic data related to the generated reactions is automatically considered (details in papers of Matheu et al.)\textsuperscript{103,104} and reported using Chebyshev polynomial format.

Contrary to the systems of Milano and Nancy, the method of generation used in MIT would probably have problems to handle branched chain reactions (see for instance Fig. 4), where species with low formation rates can have an important kinetic effect. That explains certainly why this system has mostly been used to model oxidation at high temperatures (above 900 K and in flames). Another problem with the system of MIT is that an error in a reaction parameter can propagate errors through the full structure of the mechanism by influencing the reactions taken into account.

**C.2. Ways of improving automatic generation of kinetic models**

Generated kinetic models can be significantly improved by continuously defining more and more accurate types of reaction classes for the oxidation of fuel components. Reactions are pretty well defined for alkanes, however it is not yet the case for alkenes, cycloalkanes, substituted aromatic compounds and oxygenated compounds.

The accuracy in the definition of the reaction classes also needs to be strongly improved for several compounds produced by the primary mechanisms. This is mainly the case of aldehydes, ketones and cyclic ethers, for which dedicated experiments have to be performed in order to validate detailed oxidation kinetic models.

The problem with increasing the accuracy of the definition of the reaction classes is that it will certainly lead to an increase in the number of generated reactions. The production of large
mechanisms, which hinders the possibility of performing simulations, has to be coupled with reduction methods.

A priori reduction methods should be explored. Reduction can be achieved based on the comparison of rate constants for concurrent reactions of the same type, as proposed by Chinnick et al.\textsuperscript{72} This method of reduction involves performing “on-the-fly” estimation of rate constants during the generation as it is done in the RGM system. However, when it is not carefully done, this method can lead to erroneous results: e.g. comparisons between reactions which were not of the same type led to errors in the work of Chinnick et al.\textsuperscript{72}

A weak point of both Milano and Nancy systems, as well as of manually developed models, is inaccurate secondary mechanisms. If more sophisticated reaction classes are available for primary products of fuel oxidation, it will be possible to generate full detailed secondary mechanisms. Of course an iterative generation of full detailed n-ary mechanisms cannot be envisaged. However, coupling the generation of full detailed secondary mechanisms with the lumping method used for the primary mechanisms in Milano could be very valuable. A library of lumped secondary mechanisms could then be built up for a list of important primary products to be defined. These lumped secondary mechanisms would retain most of the information of the detailed ones through the use of fractional coefficients. They could then be considered by the generator if needed. For that purpose, it could be of interest to establish bridges between the Nancy system, which has a generator of primary mechanisms able to handle many types of reactants, and that of Milano which has a powerful lumping tool.

At the same time, the accuracy of reaction bases needs to be improved. Here also the creation of a library of reaction bases which could be selected by the generator according the wished application could be envisaged. It would certainly be of great help to define a common format of these reaction bases so that they can be easily shared between modellers.

Fig. 6 shows a possible new structure for the EXGAS software using both a library of lumped secondary mechanisms and a library of reaction bases. According to the applications planned by the user, the software would select the needed stored mechanisms to be connected to the generated one. Using this method, the size of the generated mechanisms would not be unnecessarily increased due to the addition of redundant parts. A critical point is that the obtained mechanism should not be used for applications which were not planned during the generation. For instance, a mechanism for low-temperature oxidation containing many secondary mechanisms for aldehydes or cyclic ethers, and only a few for alkynes or dienes, should not be used for modelling PAH formation in a flame.
Fig. 6 Proposed structure for a new EXGAS software based on an extensive use of library of mechanisms.

In order to facilitate the validation of the generated models, it would be of interest to give error bars on simulated profiles.\textsuperscript{62} This involves not only estimating all the needed thermochemical and kinetic data for running simulations, but also defining the uncertainties on these values. When uncertainties of kinetic parameters are known, it can be envisaged to go further and to use an optimisation procedure in order to produce a model whose predictions deviate the least from given experimental targets.\textsuperscript{105} Note that the choice of the used targets can have a significant influence on the optimized mechanism. This method has been applied to produce the GRI-Mech mechanism.\textsuperscript{101} Such a procedure can help identify model parameter values that are likely to be questionable. However, if some parameters are changed compared to their average recommended value, large discrepancies could be observed under conditions outside of the range used for the optimization. That certainly hinders the use of optimized models in a predictive way.

\textbf{D. Methods for improving the accuracy of the thermochemical and kinetic data used in models}

Several authors\textsuperscript{106,107} have compiled and evaluated the already existing kinetic parameters for combustion modelling. But that concerns almost only species containing up to 4 atoms of carbon.

In this part, we will first focus on the methods which are currently proposed to estimate the thermochemical and kinetic data which are actually used in detailed models. Next we will describe the recent experimental techniques available to measure new kinetic data and on the theoretical methods allowing calculations of these data based on quantum mechanics. Note that an excellent
recent paper by Zador et al.\textsuperscript{108} reviews the experimental and theoretical studies of the elementary reactions important in low-temperature autoignition chemistry.

Estimations are the rougher methods to obtain thermochemical and kinetic parameters, but they can rapidly be applied to the large number of reactions produced by the automatic generators. Simulations followed by uncertainty and sensitivity analyses can identify the parameters which have the greatest influence on the prediction.\textsuperscript{109} More accurate techniques, such as experimental and theoretical methods, can then be used to refine these parameters. Note that a comparison between the kinetic parameters used in the existing large mechanisms for the low-temperature oxidation of alkanes has shown important deviations between models.\textsuperscript{18} Better parameters based on careful experimental and theoretical studies could help to resolve these discrepancies.

D.1. Methods of estimation of thermochemical and kinetic parameters

Thermochemical properties, such as enthalpies of formation, entropies and heat capacities are of great importance to ensure the consistency between the rate parameters of the forward and reverse elementary reactions. They are also useful to estimate the heat release rate. When these parameters are not available in the literature,\textsuperscript{110,111} which is the most frequent case for species derived from automotive fuel, they have to be estimated. The method of estimation which is the most used in detailed kinetic models is the group additivity method proposed by Benson.\textsuperscript{112}

Two software systems\textsuperscript{113,114} have been developed implementing Benson’s method. Both use the same method to calculate molecule’s thermochemical properties from the contribution of the groups involved in the compound of interest. Ring, cis, ortho, gauche, symmetry and optical isomer corrections are added to take into account structural specificities. While THERM\textsuperscript{113} uses free radical group contribution to estimate free radical properties, THERGAS\textsuperscript{114} uses a bond dissociation increment to calculate the enthalpy of formation from the parent molecule. For entropy and heat capacity, a differential analysis between the radical and the parent molecule evaluates differences in vibrations, symmetry, optical isomers, spin and external rotations.

Using group values optimized by Domalski and Hearing,\textsuperscript{115} the deviations between literature and calculated parameters are less than 4 kJ mol\textsuperscript{−1} for 70% of the hydrocarbons and 60% of the oxygenated molecules tested, while only 20% have a deviation larger than 8 kJ mol\textsuperscript{−1}. The method is less efficient when non-neighbour interactions become important, especially in the cases of structures involving mesomeric effect. This approach can easily be extended by using new groups. A new group value can be obtained from experimental or theoretical determination of the thermochemical properties of a set of molecules having that group.\textsuperscript{116}
The major portion of the kinetic parameters, pre-exponential factors and activation energies, used in detailed kinetic models is estimated using correlations. A very frequent type of correlation is based on links between the structural properties of the molecule and its reactivity. The philosophy of studies in the literature that aim at determining correlations between structure and reactivity is based on one of the theoretical foundations of mechanism generation: the definition of reaction classes that can be applied to a large range of analogous reactions (see Section C.1.1).

Table 1 shows an example of the simplest type of such correlations for the abstraction of a hydrogen atom from an alkane molecule. As proposed by Ranzi et al., the rate constants depend only of the type of radical involved and of the type of H-atom which can be abstracted. Of course more types of H-atoms have to be taken into account for unsaturated and oxygenated compounds. This type of correlation is very easy to use for estimating the rate constants for a large number of reactions, but its accuracy is quite low.

Table 1: Rate constants, given per abstractable H-atom for the abstraction of an atom of hydrogen from an alkane molecule, expressed following the modified Arrhenius law, \( k = A \exp(-E/RT) \), with the units cm\(^3\), mol, s, kJ

<table>
<thead>
<tr>
<th>Involved radical</th>
<th>Type of abstracted H-atom</th>
<th>( \lg A )</th>
<th>( b )</th>
<th>( E )</th>
<th>( \lg A )</th>
<th>( b )</th>
<th>( E )</th>
<th>( \lg A )</th>
<th>( b )</th>
<th>( E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>'O'</td>
<td>Primary H-atom—CH(_3)</td>
<td>13.2</td>
<td>0</td>
<td>32.8</td>
<td>13.1</td>
<td>0</td>
<td>21.7</td>
<td>13.0</td>
<td>0</td>
<td>13.7</td>
</tr>
<tr>
<td></td>
<td>Secondary H-atom—CH(_2)</td>
<td>6.98</td>
<td>2</td>
<td>32.2</td>
<td>6.65</td>
<td>2</td>
<td>20.9</td>
<td>6.62</td>
<td>2</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>Tertiary H-atom—CH</td>
<td>5.95</td>
<td>2</td>
<td>1.88</td>
<td>6.11</td>
<td>2</td>
<td>−3.20</td>
<td>6.06</td>
<td>2</td>
<td>−7.80</td>
</tr>
<tr>
<td>'CH(_3)'</td>
<td></td>
<td>−1</td>
<td>4</td>
<td>34.3</td>
<td>11.0</td>
<td>0</td>
<td>39.8</td>
<td>11.0</td>
<td>0</td>
<td>33.1</td>
</tr>
<tr>
<td>HO(_2)'</td>
<td></td>
<td>11.3</td>
<td>0</td>
<td>71.1</td>
<td>11.3</td>
<td>0</td>
<td>64.8</td>
<td>12.0</td>
<td>0</td>
<td>58.5</td>
</tr>
</tbody>
</table>

A large number of correlations between barrier height and reaction energy for the estimation of the rate constants for a given family of analogous reactions have been proposed in the literature. These correlations allow fast and computationally cheap rate estimations. Discussion of all the published correlations of that type in the literature is outside the scope of this review. We will focus our discussion on the most widely used rate rules in the combustion kinetics community.

Evans and Polanyi proposed a relationship between the barrier height and the enthalpy of reaction (\( \Delta rH \)):

\[
\Delta H^\ddagger = E_{oa} + m\Delta rH \tag{1}
\]
where $\Delta H^\#$ is the enthalpy of activation, $E_{0a}$ is the reference activation energy that defines the reaction class and $m$ is the proportionality constant that needs to be defined. Note that this approach assumes the entropy of activation ($[\Delta S]^T$) to be constant for the whole reaction class.

For instance, Dean and Bozzelli\textsuperscript{120} have developed the following correlation for the abstraction of H-atoms from alkanes:

$$k = n_A T^n \exp \left(-\left(E_0 - f(\Delta_0 H - \Delta H)\right)/RT\right) \quad (2)$$

where $n_A$ is the number of abstractable H-atoms; $A$, $n$, and $E_0$ are the rate parameters for the case of the metathesis by the particular radical from ethane; $\Delta_0 H$ is the enthalpy of the H-abstraction by the radical from ethane; $f$ is a correlation factor, the values of which are given by Dean and Bozzelli\textsuperscript{120} for each considered radical; and $R$ is the gas constant. In this case, $\Delta H$ is the enthalpy of the metathesis by the radical from the reacting molecule. The problem of such correlations is that important deviations can appear if it is applied outside of its range of validation.

D.2. Experimental techniques available to measure kinetic data

For a long time, rate constants have been derived from experiments made in carefully designed static or flow reactors.\textsuperscript{121,122} However, now most of the recent measurement methods of kinetic parameters can be divided in two groups: those based on photochemical or electron impact techniques to produce radicals (by laser or by plasma) and those using a shock tube:

- Methods based on photochemical or electron impact techniques

These methods are restricted to low temperatures (usually below 1000 K) and have been mainly developed to determine kinetic parameters for reactions of interest in atmospheric chemistry. That is why the large majority of these data has been determined at around room temperature and at sub-atmospheric pressures.

Below we very briefly describe the two types of apparatuses which are currently used: discharge flow tubes, and laser flash-photolysis cells; the latter being the most used nowadays.

Many discharge flow tubes \textsuperscript{123,124} are made of a quartz (or glass) tube in which a carrier gas with atoms or radicals are flowing and a reactant can be injected through a movable injector (see Fig. 7a). Atomic reactants are usually generated in microwave discharges. These are used either directly or
are converted to radicals by titration reactions (e.g. the reaction of propene with fluorine atoms to produce allyl radicals,\textsuperscript{125} the reaction of acetylene with O-atoms to yield HCCO radicals).\textsuperscript{126}

Flow tube kinetic measurements are usually made by varying the reaction zone length, i.e. the distance between the injector and the detector. Detection can be made by optical techniques,\textsuperscript{123,124} but also by (time-of-flight ) mass spectrometry after molecular beam sampling which gives access to the product distribution (e.g. ref. 125 and 126). Measurements by this technique are limited to low pressures (a few kPa) and can be affected by heterogeneous reactions.

In a flash-photolysis cell\textsuperscript{124,127} (see Fig. 7b), carrier gas, radical precursors and reactants are flowing together. At a given time, a pulse of light is emitted, usually by a laser (pulsed laser photolysis), in order to start the generation of radicals. For instance the 248 nm photolysis of O\textsubscript{3} in excess of H\textsubscript{2}O\textsubscript{2} or that of H\textsubscript{2}O\textsubscript{2}, are commonly used sources of OH radicals.\textsuperscript{128} The decay of the concentration of radicals

Fig. 7 Principle schemes of (a) a discharge flow tube, (b) a flash photolysis cell and (c) the end of a shock tube for studying elementary reactions.
is then followed. Popular methods of detection are laser induced fluorescence (LIF,\textsuperscript{129} often used to probe OH radicals\textsuperscript{128,130} or NO,\textsuperscript{131} cavity ring down spectroscopy (CRDS,\textsuperscript{129} which can be used to detect oxygenated\textsuperscript{132,133} or HO\textsubscript{2}\textsuperscript{134} radicals) or Fourier transform infrared spectroscopy (FTIR).\textsuperscript{125} Measurements using flash-photolysis cells have proved to be possible for temperatures up to 1275 K (with a heated tube in alumina)\textsuperscript{135} and for pressures up to 90 bar.\textsuperscript{136}

Many studies using the previously described photochemical or electron impact techniques lead to a global rate constant for a multichannel elementary reaction which can give a range of products. Future studies need to better take into account the evolution of the product distribution with temperature and pressure. The coupling of laser photolysis with mass spectrometry with tuneable synchrotron photoionization has recently been proven to be a powerful method to study products distribution.\textsuperscript{137,138}

To take better into account the evolution of the product distribution, a new technique should be mentioned: crossed molecular beam scattering with soft ionization detection by tuneable low-energy electrons, such as that developed in Perugia.\textsuperscript{139} Briefly, as shown in Fig. 8, two well-collimated, in angle and velocity, continuous supersonic beams of the reactants (molecules or radicals) are crossed at 90° in a large scattering chamber with background pressure in the 10^{-5} Pa range (this assures the single collision conditions). The mass spectrometer can be rotated around an axis passing through the collision centre so that the velocities of the particles can be measured. This method allows the determination, for a given reaction, of the nature of the primary products, the mechanism of each reaction channel and the relative yield of the competing channels as a function of temperature (or collision energy).\textsuperscript{139} This method has already been used to study the reaction of O-atoms with C\textsubscript{2} unsaturated hydrocarbons or with allyl radicals.\textsuperscript{139}

![Fig. 8 Schematic view of the Perugia crossed molecular beam apparatus.\textsuperscript{139}](image-url)
D.2.1 Shock tube methods. A review of the use of shock tubes as a reactor for kinetic studies was made in 2002 by Bhaskaran and Roth. In this technique, a plane shock wave is created by suddenly expanding a gas at high pressure into a gas at low pressure. The pressure wave then propagates through a long closed tube. The shock wave is used to produce a rapid increase of the pressure and the temperature of a reactive mixture. In most shock tubes, the shock wave is reflected at the end of the tube and produces during its way back a second rise in temperature. The temperature is derived from the measurement of the shock velocity (using regularly spaced pressure transducers) and can vary from about 700 to 3000 K. The time frame available for making measurements is usually shorter than 1 ms. Single pulse shock tubes (chemical shock tubes), in which instantaneous heating followed by a rapid quenching (which allows the analysis of the reacted mixture) have been often used to study the thermal decomposition of organic compounds and the reactions involving heavy radicals. As shown in Fig. 7c, in classical shock tubes, due to the reflected shock wave radicals are obtained by thermal decomposition from a well designed precursor (e.g. the decomposition of C₂H₅I to give I atoms and C₂H₅ radicals and then ethylene and H-atoms). Their evolution is usually followed by optical techniques, such as atomic resonance absorption spectroscopy (ARAS, much used to study H- and O-atoms reactions) or absorption spectroscopy (e.g. for OH radicals or for H₂O), and much more rarely by mass spectrometry. The high temperature used in a shock tube requires that the influence of possible secondary reactions has to be carefully addressed.

Note that the techniques based on photochemical or electron impact production of radicals are mainly used at temperatures up to 500 K and shock tubes are mostly used at temperatures above 1000 K. Therefore, the temperature zone between 550 and 900 K, in which the chemistry of auto-ignition phenomena is the most complex, is also the temperature region for which the rate constants are the least studied. Note also that only very few measurements using the above described techniques have been made at pressures close to those observed in engines (up to about 8 MPa in diesel engines).

All the techniques described above have been abundantly used to study the rate constants of H-abstractions and additions involving small radicals. This is particularly the case of the reactions involving OH radicals which are the rate determining steps for the atmospheric degradation of organic compounds. Less data are available for H- and O-atoms and HO₂ and CH₃ radicals. These reactions can also be of importance under some conditions observed during combustion. A fair number of studies are also related to small species containing nitrogen.

There are significantly fewer studies of the other types of reactions which are important for modelling the oxidation and autoignition of organic compounds included in fuel and biofuel. Some interest has been recently devoted to the study of the reactions of alkyl radicals and oxygen molecules by laser flash photolysis with detection of OH, HO₂, and RO₂ radicals. In the
case of ethyl and propyl radicals, these measurements combined with theoretical calculations using the master equation have allowed the derivation of temperature-dependent parameterizations. This can be used to predict the rate constants for several given pressures for all the different channels of the low-temperature reaction \( R + O_2 \), \( RO_2 \) giving as products QOOH, \( OH + \) aldehydes , \( OH + O \)-heterocycles or \( HO_2 + \) alkene .\textsuperscript{150} As these reactions are really the heart of the chemistry triggering the autoignition phenomena, it will be worth extending this approach to alkyl radicals obtained from reactants present in automotive fuels . It would also be useful to find a way to better study the reactions of QOOH radicals.

D.3. Calculations based on theoretical methods

Recent years have seen an increasing role of electronic structure calculations in the development of detailed chemical kinetic models. Quantum mechanical calculations are nowadays involved in a broad spectrum of methods used for the determination of a priori thermochemical and kinetic parameters, from semi-empirical methods, for example, the calculation of new groups in the framework of Benson’s method,\textsuperscript{112} to computationally expansive quantum dynamics. Ab initio calculations are based on the resolution of the Schrödinger’s equation using different levels of assumptions.\textsuperscript{154} Ab initio calculations are also increasingly interacting with experiments on elementary reactions of importance in combustion , as those described in the previous part. As pointed out previously in this text and by Pilling in a recent review,\textsuperscript{155} experimental studies of elementary reactions are difficult to perform at temperature and pressure conditions of interest for combustion . Therefore the interplay between theory and experiments becomes very important for the extrapolation of experimental results to a wide range of temperature and pressure conditions.

In a first part, we will focus on the use of theoretical calculations to determine reaction products and rate coefficients that can be incorporated directly in chemical kinetic models. The use of these theoretical calculations to derive correlations between structure and reactivity, which are critical for mechanism automatic generation, will be discussed in a second part. Theoretical calculations and derived correlations are the most effective way to increase the accuracy of kinetic parameters in detailed chemical kinetic models involving hundreds to thousands of reactions.

- Theoretical calculations to determine reaction products and rate coefficients

The improvement of electronic structure calculations for potential energy surfaces combined with progress in reaction rate theory has led to the calculation of rate coefficients with an accuracy comparable with experimental uncertainties. The precision of the kinetic data calculated through these methods depends simultaneously on the accuracy of the potential energy surface (PES , up to fractions of a kcal mol\(^{-1}\) using high level methods), of the partition function, and of the rate theory used to describe the reaction.
Determining the accuracy of a calculated PES is a complex task. In the literature, a benchmark strategy is generally used to assess the performance of theoretical methods. Benchmarks consist of comparisons between ab initio calculations and data sets composed of experimental and high-level electronic structure results. Early benchmarks, such as the G2 test set of Pople and co-workers,\textsuperscript{156} focused on thermochemical data, i.e., performance of theoretical methods for the description of stationary points of the PES. In recent years, benchmarks for barrier heights have also been proposed.\textsuperscript{157} Different combinations of methods (wave function theory or density functional theory) and basis sets have been assessed. Composite (multi-level) methods are combinations of several single levels of theory and have also been widely tested. High level wave function theory methods were shown to be able to give very accurate results, but can be time consuming. Multi-level methods, e.g., the Gn\textsuperscript{158,159} (Gaussian-n) and CBS-X (Complete Basis Set)\textsuperscript{160–162} families, were shown to generally provide sufficiently accurate results for kinetic calculations with lower computational costs. Harding et al.\textsuperscript{154} have recently reviewed ab initio methods for reactive potential energy surfaces. They studied ten reactions, which are relevant for combustion, using standard single level quantum chemistry methods and discussed the usefulness and shortcomings of these methods.

If the accuracy of the potential energy surface of a combustion reaction is critical for the precision of the rate coefficients, the effect of the deviation from rigid rotor harmonic oscillator (RRHO) on the calculation of partition functions can also be crucial. Vibrational anharmonicities can affect the accuracy of the rate coefficients through the calculation of the partition functions but also through the tunnelling transmission coefficient. In a review of RRKM theory and its implementation, Klippenstein\textsuperscript{163} discussed the role of vibrational anharmonicities and non-rigidities in detail: in many instances, while deviations from RRHO approximation can be quite substantial, their effects can be reduced by cancellations of errors. In addition, a proper description of low frequency motions such as internal rotations is often necessary to achieve a good accuracy in rate coefficient calculations. As both RRHO and free rotor assumptions fail to well represent these low frequency rotational motions, several methods have been developed to accurately calculate the hindered rotor contributions. Two aspects have been emphasized in the literature: determination of the reduced moment of inertia of the rotor and solving the quantum partition function for the hindering potential. A full description of these methods is beyond the scope of this review but we can mention that several methods exist to treat hindered rotors like the Pitzer and Gwinn’s tabulation\textsuperscript{164} or uncoupled one dimensional hindered rotor models. This approach constitutes the state of the art for accurate hindered rotor corrections for combustion reactions of large molecules.\textsuperscript{165}

In the case of a temperature dependent rate constant based on a potential energy surface with a well-defined saddle point, transition state theory (TST) is often sufficient to calculate the high-pressure limit rate constant. Variational transition state theory (VTST) can improve the accuracy of the kinetic parameters for reactions with a defined barrier by taking into account entropic effect. A variational approach is necessary for reactions with no defined saddle point on the potential energy surface, i.e. no reaction barrier. More details on transition state theory can be found in the in-depth review of Truhlar et al.\textsuperscript{166} The rate constants of a large number of combustion reactions, such as unimolecular reactions, are pressure dependent. For these types of reactions, different theoretical
refinements are necessary to properly account for the pressure effects on the rate coefficients. Elementary reactions involving one isomer (well) and one reaction pathway (channel) were first described using RRKM theory. For multiple-channel and multiple-well systems, more accurate Master Equation (ME) methods have to be envisaged to accurately describe the competition between reaction and collisional stabilisation. Descriptions of these theories can be found in several reviews dealing with RRKM and ME calculations in the field of combustion.\textsuperscript{167,168} These approaches constitute the state of the art for the description of pressure dependent multi-well and multi-channel systems. It is useful to note that accurate predictions of pressure dependent rate coefficient obtained from ME/RRKM calculations still depend on semi-empirical factors such as collisional energy transfer.

The accuracy of rate coefficients based on ab initio potential energy surfaces and reaction rate theory can be affected by several other problems. The prediction of low temperature rate coefficients can be a difficult task. The exponential dependence of the rate coefficient on the height of the energy barrier can lead to inaccurate predictions because of the uncertainties due to ab initio calculations. The barrier height uncertainty can be particularly large for reactions involving spin-contaminated transition states described within the framework of a single-reference theory.\textsuperscript{163} In addition, the accuracy of kinetic parameters in low-temperature reactions involving H-atom transfer can also be affected by quantum tunnelling effects.

Several methods are available in the literature to account for tunnelling, such as one dimensional simple Wigner formula or the more refined calculation of transmission coefficients based on an Eckart potential. Tunnelling contributions to rate coefficients can also be determined from computationally expensive multidimensional tunnelling methods.\textsuperscript{163} However, for temperatures within most combustion processes, the effect of tunnelling on the rate coefficients is well described using the Eckart potential.

Despite substantial improvements in recent years in quantum chemistry calculations, some systems remain challenging for the determination of accurate rate coefficients. Reactions involving diradicals such as cyclic alkane ring opening\textsuperscript{169,170} or the addition of O(3P) atoms on unsaturated hydrocarbons\textsuperscript{198} can be difficult because of the multi-reference characteristics of these species and also because of the crossing of different spin state surfaces.

The crossing of surfaces may also occur in reactions of radicals without barrier, such as combinations or disproportionations.\textsuperscript{171}

In spite of all the limitations detailed above, for standard combustion reactions, the combination of ab initio PES based on high level calculations within the framework of TST-RRHO approximations, taking into account a correction for internal rotations and a transmission coefficient for tunnelling
(via an Eckart potential), generally leads to reaction rate coefficients with uncertainties better than a factor of 2. As an example let us consider the reaction between benzene and O(3P). This system was studied by Taatjes et al.\textsuperscript{138} and constitutes a good illustration of the problems that can be encountered in ab initio rate coefficient calculations. This is a multiple-well multiple-channel system that features an initial chemically activated diradical adduct (see Fig. 9) that can undergo inter-system crossing on the singlet surface. It is also a very good example of the interaction between experiment and theory. Taatjes et al.\textsuperscript{138} have examined the product branching ratios of this reaction by using a mass spectrometer with VUV synchrotron radiation (see Section D.2) for pressures ranging from 0.13 to 1.3 kPa and temperatures between 300 and 1000 K. Ab initio calculations and master equation/RRKM modelling have been used to reproduce the experimental branching ratios and yield pressure-dependent rate expressions for the reaction channels for a wider range of conditions. It is noteworthy to mention that, in the ME /RRKM calculation, the rate coefficient for the inter-system crossing in Fig. 9 (ISC channel) was derived from experiments.

![Potential energy surface of the benzene + O(3P) reaction](image)

**Fig. 9** Potential energy surface of the benzene + O(3P) reaction determined by Taatjes et al.\textsuperscript{138}

Experiments have to be used because in fact, the ISC parameter is still impossible to predict, even with complex dynamic calculations, for large systems. This illustrates the fruitful results that can be obtained from the combination of experiments and theory.

- Correlations between structure and reactivity derived from theoretical calculations

Following what has been described in Section D.1, we present here the methods which are used in the literature to propose correlations between structure and reactivity based on theoretical calculations. An extensive review of methods for a priori estimation of rate constants for kinetic modelling based on theoretical methods has been written by Sumathi and Green.\textsuperscript{172} For a given reaction class two approaches can be distinguished for the estimation of kinetic parameters based on quantum chemistry calculations.
The first one is based on correlations between barrier heights and reaction energies in the same way as the Evans–Polanyi relationship (see eqn (1)). The other approach is an extension of group additivity theory, which was first described for thermochemical parameters of molecules and radicals (see Section D.1), to transition states.

For obtaining correlations, ab initio calculations are systematically applied to a series of reactions of the same class to determine variation of the barrier height with reaction enthalpies. The determination of rate constants by theoretical methods using a few selected reactions of a given class allows the determination of correlations, which can then be used to estimate rate constants for a larger number of reactions. Fig. 10 shows the Evans–Polanyi correlation derived from theoretical calculations for 13 decompositions (by breaking a C–C or a C–H bond) of saturated and unsaturated acyclic hydrocarbon radicals from C$_3$ to C$_7$. However, Sirjean et al. have also shown that applying this correlation to some cyclic compounds can lead to significant errors.

![Evans–Polanyi correlation](image)

Fig. 10 Evans–Polanyi correlation for acyclic hydrocarbon radical decompositions obtained from theoretical calculations (CBS-QB3).\textsuperscript{173}

Recently, Carstensen and Dean\textsuperscript{174} developed a rate constant estimation rule for H-abstractions by H atoms. Assuming a fixed temperature dependence (fixed $b$ in the modified Arrhenius format, see Table 1) of the rate expressions of a reaction, the barrier is calculated with an Evans–Polanyi correlation. The pre-exponential factor is determined from a reference reaction or by averaging rate constants for a given set of reactions. In this method,\textsuperscript{174} all the parameters of the correlations have been calculated from high-level quantum chemistry methods with RRHO-TST corrected for internal rotations and tunnelling. Rate rules were proposed for H-abstraction by H-atoms for alkanes, cycloalkanes, and allylic systems.

Linear Free Energy Relationships (LFER), as proposed by Hammet\textsuperscript{175} (for aromatic compounds) and by Taft\textsuperscript{176} (for aliphatic compounds), belong to the same family of correlations as the Evans–Polanyi
ones, but are based on free energies. If tunnelling is neglected, then according to the transition state theory:

\[
\ln k(T) = \ln k_0(T) + \frac{(\Delta G^\ddagger_0 - \Delta G^\ddagger)}{RT}
\]  

(3)

where \( k(T) \) is the high-pressure limit rate constant of a given reaction belonging to a family of analogous reactions, \( k_0(T) \) is the reference rate coefficient of the reaction class and \( \Delta G^\ddagger_0 \) and \( \Delta G^\ddagger \) are the free energies of activation of the reference reaction and of the given reaction, respectively. A linear relationship can be established between the difference in the free energies of activation and the logarithm of the ratio of the rate constants. For example the Hammett equation can be derived from eqn (3):

\[
\ln k(T) = \ln k_0(T) + \sigma \rho
\]  

(4)

where \( \sigma \) is a parameter that represents the effect of the substituent on the rate constant and \( \rho \) is a constant specific to the reaction class. One can also mention that nonlinear formulae for estimating activation energies have been proposed in the literature, for example Marcus's equation for electron transfer reactions.\(^{177}\)

Correlations between rate coefficients and molecular properties (such as ionization energies, electron affinities, polarizabilities) have also been proposed in the literature. We will not detail these methods here because they are not widely used for the estimation of rate constants based on electronic structure calculations. Details can be found in Sumathi and Green's review.\(^{172}\)

Reaction-Class Transition State Theory\(^{178}\) (RC-TST) is a correlation based method following a similar philosophy. The rate constant of a reaction belonging to the target class is assumed to be proportional to a reference reaction of the class (k<sub>ref</sub>):

\[
k(T) = f(T)k_{\text{ref}}
\]  

(5)

where \( f(T) \) is a temperature dependent function defined by the ratio \( k/k_{\text{ref}} \) factorized into different components (symmetry number, tunnelling, partition function and potential energy factor).
Green and co-workers proposed an extension of Benson’s group additivity theory to transition states. This approach takes advantage of the advances in electronic structure calculations and allows the determination of thermochemical properties of transition states. They were able to propose thermochemical groups (defined by their own values of enthalpy, entropy and heat capacities) corresponding to the reactive moiety in the transition state molecular structure of a given reaction class. Following Benson’s philosophy, this method of so-called supergroups can include steric effects from the substituents on the reactive moiety.

**E. Methods for obtaining experimental data to validate the modelling of the formation of minor combustion products**

In this section, we will describe first the apparatuses which have been designed to study global gas phase reactions under well defined conditions. In the second part, we will present the progress achieved in the techniques allowing the detection of minor products and which can be coupled with the apparatuses described in the first part. A more detailed description of the experimental techniques used to study hydrocarbon oxidation below 1000 K was given in 1997 by Griffiths and Mohamed. Our purpose is then not to give a comprehensive description of these apparatuses and detection techniques, but to focus on those which have been recently developed and allow an improved analysis of minor products.

**E.1. Apparatuses for studying global gas phase reactions**

Three types of apparatuses can be distinguished according to the way the reaction process is induced: compression, flame propagation or external heating. The use of the first and last types of these apparatuses to study the low-temperature oxidation of components of automotive fuel was reviewed in 2008. As the size of the chemical models is often large, and to minimize uncertainties, it is important to use those apparatuses which can be represented by simple physical models (0D or 1D). For these systems, the underlying energy, transport, and mass interaction equations can be solved using available software designed for this purpose: e.g. CHEMKIN, COSILAB or CANtera.

**E.1.1 Apparatuses in which the reaction process is induced by compression.** The two main types of apparatuses in which the reaction process is induced by compression are shock tubes (see description in Section D.2) and rapid compression machines. A rapid compression machine is an instrument designed to simulate a single engine cycle of an internal combustion engine. It allows the study of a reaction process after compression for pressures from 0.2 to about 8 MPa and for temperatures from 550 to about 1300 K. The temperature after compression is derived from the initial pressure and temperature, the initial composition of the reactive mixture and the measured pressure after compression, assuming the adiabatic compression of a core gas. The temperature after compression can be varied by changing the composition of the inert gas. The reaction times which can be studied in a rapid compression machine are usually in the range between around 1 and 200 ms, which is complementary to the range which can be reached in a shock tube.
Rapid compression machines and shock tubes have been used extensively to study autoignition delay times such as those presented in Fig. 1 and 2, respectively. While these apparatuses are well adapted to study low-temperature oxidation phenomena, their use to follow combustion product formation is much more limited.

In Lille, Minetti et al.\textsuperscript{183,186} have developed a system allowing a rapid quenching of the whole reacting mixture inside a sampling vessel. Corresponding samples are analysed by gas chromatography with mass spectrometry, thermal conductivity and flame ionisation detectors. This allows identification and quantification of some heavy products formed during the cool flame. This method has been applied to the study of the low-temperature oxidation of several hydrocarbons.\textsuperscript{183,186} Unfortunately, due to the significant temperature gradients existing in the combustion chamber of such an apparatus,\textsuperscript{187,188} the models in the literature have problems reproducing the observed product formation, even when simulations lead to a satisfactory agreement for delay times (e.g. ref. 60).

For a long time, gas chromatography analyses of the reacted mixtures sampled from single pulse shock tube have been used to study product yields obtained from pyrolysis\textsuperscript{189,190} and oxidation reactions.\textsuperscript{190} The team of Stanford has more recently developed laser absorption methods to quantitatively follow time profiles of species (e.g. $n$-heptane, ethylene, CO$_2$, H$_2$O or OH radicals) during the high-temperature oxidation of organic compounds behind reflected shock wave in classical shock tubes.\textsuperscript{191} In general, the formation of species measured in a shock tube are well reproduced by simulations using published models.\textsuperscript{190,191}

Another limitation of these two apparatuses is related to the difficulties of the introduction of liquid fuel at ambient temperature in a static system. To overcome this problem, heated shock tubes are often used.\textsuperscript{50} An aerosol shock tube, which combines conventional shock tube methodology with aerosol loading of fuel-oxidizer mixtures, has recently been proposed to study diesel fuel ignition delay times.\textsuperscript{192}

In the last decade, models have also been validated using data obtained in HCCI engines. These data consist mainly of the evolution of the pressure and of the heat release with the crank angle, which can easily be simulated using a single zone engine model.\textsuperscript{193}

\textbf{E.1.2 Apparatuses in which the reaction process is induced by flame propagation.} Apparatuses for kinetic studies in which the reaction is induced by flame propagation are of two main types, constant volume bombs and burners with flame stabilization. Constant volume bombs, in which the flame propagation in a premixed reactive mixture is initiated by a pulse of high energy, such as a spark, are mainly used to measure laminar flame speeds,\textsuperscript{194} without any consideration for product formation.
Flames stabilized on a burner can be of several types. They can be classified as either laminar or turbulent depending on their fluid mechanics, but kinetic studies are almost only performed using laminar flames. They can be also classified as premixed or non-premixed. In a premixed flame, the fuel and the oxidizer are mixed prior entering the burner. In a non-premixed flame (diffusion flame), the fuel and the oxidizer do not mix before the flame. A few kinetic studies with product measurements have been carried out in diffusion flames (see the review by McEnally et al.) but the type of flame which is the most investigated for kinetic purposes is the laminar premixed flame.

Fig. 11 shows an example of a laminar premixed flame, as well as the profiles of some species for a methane flame doped with indane.87

Fig. 11 Photograph of the low-pressure laminar premixed flame used in Nancy showing the sampling probe —Examples of profiles of mole fractions of reactant, intermediates and products measured by gas chromatography in a stoichiometric methane flame doped with indane measured using this apparatus (points are experiments and lines simulations, P = 6.7 kPa).87

To enlarge the reaction zone where intermediate species (such as benzene in Fig. 11) can be observed, laminar premixed flames are usually studied under low-pressure conditions (less than 15 kPa). However, a perforated plate located above the burner can move the flame down-stream and allows the measurement of species profiles at atmospheric pressure. Temperatures in the flame, which can reach values above 2000 K, can be measured by optical methods or by using a thin thermocouple coated with an oxide deposit. Species in a laminar premixed flame can easily be probed by an optical method, such as LIF or CRDS. The laser methods which can be used to study flames have been well reviewed by Daily and more recently by Chesiks and Goldman. These optical methods have the advantage of being non-intrusive, but unfortunately they are mainly limited to the detection of small species, such as OH radicals or NO.

Gaseous samples can also be taken from the flame using a quartz probe located inside the flame (see Fig. 11). To freeze the reaction process, the pressure in the probe has to be much lower than in the flame. Samples collected by this method are analysed mostly by mass spectrometry, FTIR or gas chromatography.
Molecular beam mass spectrometry has long been used to analyse species in flame, as reviewed by Biordi.\textsuperscript{198} The advantage of this method is that it allows the measurement of both stable species and radicals. However, it does not allow an easy separation of isomers and straightforward quantifications. Gas chromatographic analysis of samples taken from flame cannot be used to detect radicals, but they can make the separation of stable isomers and the quantification much easier.\textsuperscript{87} The significant disadvantage of using a probe is that its inclusion disturbs the flame structure.\textsuperscript{195} That explains why an empirically shifted temperature profile is always used in a simulation in order to reproduce experimental results.\textsuperscript{87,195}

E.1.3 Apparatuses in which the reaction process is induced by external heating. Heated static reactors have historically been a valuable tool to study autoignition phenomena.\textsuperscript{21} However while their use has allowed progress in the qualitative understanding of the chemistry of several families of hydrocarbons, e.g. alkenes,\textsuperscript{199} this type of reactors is usually not very helpful to obtain reliable data for model validation. Exothermic reactions lead to temperature gradients inside the vessel and then to buoyancy effects which are not easy to model.\textsuperscript{200} Wall reactions can significantly complicate modelling attempts.\textsuperscript{201}

Another source of validation data more commonly used comes from heated reactors inside which a gaseous mixture is continuously flowing. Two common types of such reactors are: flow reactors and jet stirred reactors. Samples can easily be taken from these reactors and analysed by FTIR or by gas chromatography with mass spectrometry, thermal conductivity and flame ionisation detection. The temperature inside these vessels can be measured using thermocouples. These reactors are commonly made of quartz to limit possible wall reactions.

Similar to a discharge flow tube, a flow reactor is just a heated tube in which gaseous fuel is injected in a preheated highly diluted mixture of inert gas with oxygen. Flow reactors using laminar\textsuperscript{202} or turbulent\textsuperscript{203} flows have been proposed. The residence time in the tube can vary from about 10 to 250 ms.\textsuperscript{58,202,203} In most cases, flow reactors are used under atmospheric pressure, but the team of Lyngby has developed a system which can be pressurized up to 100 bar to study the high-temperature oxidation of light hydrocarbons.\textsuperscript{204} A team in Drexel has developed a flow reactor which is pressurisable up to 8 bar to investigate the low-temperature oxidation of fuel components.\textsuperscript{58,61} Flow reactors can be modelled as a plug flow reactor; in some cases it is necessary to consider the experimental temperature profile. One complication with modelling flow reactor data is that there is a finite physical mixing distance of the fuel and oxidizer streams. There is also a thermal mixing distance due to the fuel and oxidizer streams entering at two different temperatures. Both of these result in a poorly defined initial reaction time.\textsuperscript{58} That explains why a shift in time is often needed to well reproduce flow reactor data.
The main type of jet-stirred reactor which has been used in the recent years is that presented in Fig. 12. This type of reactor is well adapted for kinetic studies because the gas phase inside the reactor is well stirred and the concentration is homogenous with a limited effect of possible wall reactions. The jet-stirred reactor consists of a heated sphere in which the stirring is achieved by four turbulent jets located at its centre (injection cross). The sphere is attached to a quartz annular preheating zone in which the temperature of the gases is brought to the desired reactor temperature. The gas mixture residence time inside the annular preheater is very short compared to the residence time inside the reactor (about a few percent). The dilution by inert gas is kept high enough to avoid large temperature gradients inside the reactor due to the reaction exothermicity. The range of residence times accessible with this type of reactor is from 0.1206 up to 10 s. It has been used under atmospheric pressure, but also under pressures up to 4 MPa. The jet-stirred reactor is the device in which the two zones of temperatures characteristic of the oxidation of large acyclic hydrocarbons or esters can be seen the most clearly (see Fig. 12): a zone of low-temperature reactivity below 800 K and a zone of high-temperature reactivity above 800 K, with the NTC zone between 650 and 800 K.

![Fig. 12 Photograph of the jet-stirred reactor used in Nancy showing the injection cross—Examples of evolution with temperature of the mole fractions of reactant and intermediates measured by on-line gas chromatography during the oxidation of a stoichiometric mixture of methyl decanoate/O2 diluted in helium at atmospheric pressure (points are experiments and lines simulations, atmospheric pressure).](image)

**E.2. Progress in the techniques of detection of minor products**

The progress in laser diagnostics of trace species has been reviewed in 2009 by Cheskis and Goldman. These methods have been mainly applied for probing flames, and to a very minor extent the reactive mixture in a shock tube. In the case of shock tubes, it would be worth extending the possibilities of laser diagnostics in order to analyse a wider range of combustion products.

To our knowledge, there is no measurement using laser techniques which have been reported for species formed in a heated flow or a jet-stirred reactor. In general, the quantitative measurement of some light species, such as OH or HO2 radicals, or H2O2, which can easily be performed using laser methods (e.g. LIF or CRDS), would certainly be very valuable, to better understand the low-
temperature oxidation of hydrocarbons both in shock tubes and in reactors. The difficulty of probing radicals from reactors is increased by the fact that the radical concentration is very low at low and intermediate temperatures, usually below 1 ppm.

Concerning gas chromatography, progress can certainly be made by generalising the use of on-line analyses, i.e. connecting the sampling probe to the chromatograph by using heated inert transfer line. That avoids problems due to sample storage (e.g. aging, wall absorption or reaction). The use of on-line gas chromatographic analyses has recently allowed the measurement of important amounts of carboxylic acids during the low-temperature oxidation of alkanes.\textsuperscript{57} Acids were never seen by the analyses of stored liquid\textsuperscript{79} or gaseous\textsuperscript{206} samples probed under similar conditions.

2D-gas chromatography\textsuperscript{207} could be a valuable tool of quantification in the case of reactive mixtures leading to a large number of isomers which are difficult to separate with traditional chromatography (see, for instance, the oxidation of methyl palmitate).\textsuperscript{55} However, a detailed identification of every possible isomer can still remain difficult.

The analytical technique related to combustion studies for which the most important progress has been made in the recent years is mass spectrometry. As reviewed by Li and Qi,\textsuperscript{208} the analysis of combustion products has made tremendous progress due to the increasing use of soft ionisations, especially that obtained using the UV radiation from a synchrotron. Such an ionisation can minimize fragmentation of most hydrocarbons because the total absorbed photon energy barely exceeds the ionization energy.\textsuperscript{208} The high resolution in the energy available for ionization can allow the separation of isomers according to their ionization energy threshold.\textsuperscript{208} This technique was first applied to flames (see the review by Hansen et al.)\textsuperscript{209} where it led to many interesting results: e.g. demonstrating the presence of enols\textsuperscript{210} in laminar premixed flames. This technique has also been applied to flow reactors, but only in the case of pyrolysis.\textsuperscript{208} Very recently, an apparatus (see Fig. 13) coupling a jet-stirred reactor to a time-of-flight mass spectrometer combined with synchrotron photoionization via a molecular beam sampling system has been developed.\textsuperscript{57} For the first time, it has allowed the observation of the formation of ketohydroperoxides (carbonyl compounds including a hydroperoxide function, see Fig. 4) under conditions close to those actually observed before the auto-ignition.\textsuperscript{211} Ketohydroperoxides have a particularly significant role to explain the high reactivity of hydrocarbons/oxygen mixtures at low temperature. The use of this powerful analytical technique to probe autoignition in a shock tube could certainly lead to valuable new data.
Fig. 13 Schematic diagram of an instrument including a heated quartz jet-stirred reactor, a differential pumped chamber (I) with molecular-beam sampling system, and a photoionization chamber (II) with the reflectron time-of-flight mass spectrometer.57

F. Conclusions

The purpose of this review paper was to describe new directions which are being followed in the development of more predictive and more accurate detailed chemical kinetic models for the combustion of fuels. After an analysis of the performance of current models showing the remaining limitations in the prediction of pollutant formation, the recent methods and ways to improve these models have been described. This paper tried to make a critical analysis of the methods used to develop detailed models based on elementary reactions, the methods used to produce the related thermochemical and kinetic parameters, and the techniques used to measure the data necessary to evaluate model predictions under well defined conditions. In each of these three fields, the expected directions of research have been detailed.

Concerning model validations, note that there are still too many models which are validated and even fitted in order to reproduce a single source of experimental data. This type of model validates that there is no obvious error in the experimental data, but it does not add too much valuable information to the global understanding of combustion chemistry. For a model to have a chance to be successfully used in a predictive way, it has to be validated on the widest possible range of experimental conditions, including high pressures which still need to be investigated further. Note also that detailed kinetic models including thousands of reactions should not just be used for simulating global data, such as ignition delay times. Such complex models, with many species, should when possible be used to also model product and intermediate formation. For that purpose, there is
a clear need for more experiments yielding detailed species quantification during the oxidation of fuel components.

The limit in the sought accuracy of the developed detailed models is also a topic which deserves more discussion. Since the 80s, more and more sophisticated models have been developed, with increasing capabilities in term of handling more representative fuel composition and predicting more detailed product formation. However, the impossibility of using an infinite list of reactions will always prevent a comprehensive modelling with both the full description of the fuel composition and including the complete reaction set of all possible products. A choice will have always to be made in tailoring the most representative surrogate to a given fuel and to select the reaction products which have to be the more investigated (e.g. for toxicity reasons). Note also that, even if progress is expected in this field, a drastic reduction of detailed models is needed for the coupling with 3D CFD engine simulations. These reductions are mostly based on mathematical parameterisation methods and thus lower the chemical accuracy of the model.

A last remark concerns the availability of a didactical description of new concepts and methods that are used to develop detailed kinetic models for the combustion of fuel components. The last such book, edited in 1997 by Pilling, includes several chapters which are still considered as a reference for this purpose, e.g. ref. 67, 71, 127 and 179. However, a large amount of work has been made in this field in the last decade. It would be of great interest to have a new didactical book summarizing this progress. That especially concerns topics such as the reactions of large hydrocarbons as those present in diesel fuel, the chemistry of oxygenated reactants as those present in the newly developed biofuels, and the use of more representative fuel compositions. There is also significant progress being made in the reduction methods of detailed kinetic models. The advance in experimental studies of both elementary steps and global reactions also surely deserves a more detailed description than what is given here. Finally, the past 10–15 years have seen a dramatic improvement in the accuracy of quantum mechanical methods as applied to the construction of accurate reactive potential energy surfaces essential for the determination of elementary reaction rates. A more detailed didactical description of the most currently used methods would then certainly also be of great interest for the combustion community.

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