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Detailed chemical kinetic models for the combustion of hydrocarbon fuels

John M. Simmie*

Department of Chemistry, National University of Ireland, Galway, Ireland

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Abstract

The status of detailed chemical kinetic models for the intermediate to high-temperature oxidation, ignition, combustion of hydrocarbons is reviewed in conjunction with the experiments that validate them.

All classes of hydrocarbons are covered including linear and cyclic alkanes, alkenes, alkynes as well as aromatics.

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Keywords: Combustion; Ignition; Oxidation; Hydrocarbons; Kinetic modeling; Kinetic modelling

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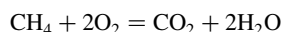
* Tel.: +353-91-750388; fax: +353-91-525700.

E-mail address: john.simmie@nuigalway.ie (J.M. Simmie).

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1. Introduction

Detailed chemical kinetic mechanisms are routinely used to describe at the molecular level the transformation of reactants into products, such as the combustion of methane in air which has a deceptively simple overall summary:



but proceeds, as is well known, through a large number of elementary steps. The sets of differential equations describing the rates of formation and destruction of each species are then numerically integrated and the computed concentrations of reactants, intermediates and products compared to experiment. This procedure, known as modeling or modelling, is widely used in studies of combustion but also for other complex chemical phenomena, such as reactions in the atmosphere and chemical vapour deposition [1], astrochemistry [2] and, even petroleum cracking in geological basins [3].

Previous reviews include a much cited, comprehensive review of chemical kinetic modelling of hydrocarbon combustion by Westbrook and Dryer [4], a selective view of chemical kinetics and combustion modelling by Miller and Kee [5], a discussion on hydrocarbon ignition by Westbrook et al. [6], and a progress report of the last 25 years of combustion modelling allied to a forward projection by Cathonnet [7]. Volume 35 in a series on comprehensive chemical kinetics entitled 'Low Temperature Combustion and Autoignition' [8] contains many interesting chapters.¹

Other reviews have a slightly different focus such as Westbrook [9] on the chemical kinetics of hydrocarbon ignition in practical combustion systems, Ranzi et al. [10] on lumping procedures in detailed chemical kinetic modelling of gasification, pyrolysis, partial oxidation as well as combustion of hydrocarbon mixes, Lindstedt [11] on modelling complexities of hydrocarbon flames, Richter and Howard [12] and Frenklach [13] on the formation of

polycyclic aromatic hydrocarbons and soot, Williams [14] on detonation chemistry, and, Battin-LeClerc [15] on the development of kinetic models for the combustion of unsaturated hydrocarbons.

More specific topics which are of importance in combustion modelling include a plenary lecture on theory and modelling in combustion chemistry by Miller [16], an insightful review of unimolecular falloff by Kiefer [17], Gardiner's book on gas-phase combustion chemistry [18] and a handbook of chemical reactions in shock waves [19].

This review will consider post-1994 work and will focus on the modelling of hydrocarbon oxidation in the gas-phase by detailed chemical kinetics and those experiments which validate them. The word detailed is used for those models which attempt to describe at the molecular level the chemical changes which occur during combustion and which is essential for trace species predictions. Of course the actual number of elementary reactions required to outline a particular reaction mechanism can be the subject of debate with many authors using truncated or skeletal mechanisms which neglect some intermediates completely or which do not differentiate between various quantum states of one compound.

As the number of steps and species required to describe a particular oxidation process increases, the computational burden can become too great and methods of simplification are needed; this is an active area of research, see for example, work on reduced kinetic schemes based on intrinsic low-dimensional manifolds by Maas and co-workers [20], on reaction rate analysis by Sung et al. [21] and on computational singular perturbation by Massis et al. [22] and by Valorani and Goussis [23]. Once this reduction has taken place then simulation of a complex combustion device can proceed [24].

1.1. Reaction mechanism design

The design of a reaction mechanism is still a black art with the majority being constructed on an ad hoc basis relying heavily on intuition, rules of thumb, etc. and building on previous sub-mechanisms. The computer-aided design

¹ Although dated 1997 it appears to have been mainly completed in 1995.

approach (or logical programming as Tomlin et al. [25] refer to it in their overview of the mathematical tools for the construction, investigation and reduction of combustion mechanisms) has been applied by several groups, see for example, work by Ranzi et al. [26], Côme et al. [27,28], Nehse et al. [29] but has not had the impact or the success that might have been expected. An alternative, more optimistic view of progress is given by Green et al. [30].

The approach used to produce the well-known Gas Research Institute methane mechanism was outlined by Frenklach et al. [31] and bears repeating here, lightly paraphrased, because it encapsulates what is probably best practice:

1. Assemble a reaction model consisting of a complete set of elementary reactions.
2. Assign values to their rate constants from the literature or by judicious estimation; treating temperature and pressure dependences in a proper and consistent manner. Evaluate error limits and thermodata required for the calculation of equilibrium reverse rate constants.
3. Carry out and/or find in the literature reliable experiments that depend on some or all of the rate and transport parameters in the model.
4. Use a computer application to solve the reaction mechanism kinetics and any transport equations, computing values of the observables for these ‘target’ experiments. Also apply sensitivity analysis to determine how the model rate constants affect the final result.
5. Choose experimental targets sensitive to a representative cross-section of the rate parameters. Also select those parameters making the largest impacts on a given target; these are then the potential optimisation parameters.

1.2. Modelling applications

There are a number of different computer applications [32–36] available to the chemical kinetic modelling community with Chemkin-III [37] probably the dominant one, perhaps because the Chemkin input data format [38] is, de facto, an evolving standard for describing the reactions, the rate parameters and the thermodynamic and transport properties of species. The transferability of this data is crucial to advancing the field but the current formats are not helpful relying as they do on cumbersome notation such as inline formulas for describing species; for example, although pC_3H_4 and aC_3H_4 are sufficient to distinguish between propyne ($\text{H}_3\text{C}-\text{C}\equiv\text{CH}$) and allene ($\text{H}_2\text{C}=\text{C}=\text{CH}_2$) more complicated species are virtually impossible to specify unambiguously in this fashion. Some hope is held out for XML, a metalanguage for describing markup languages [39], but to date, there are no working models from which one can judge the utility of such a concept. Although there is interesting ongoing work, such as OpenChem Workbench [40] which, if brought to fruition, might knit together kinetic

modelling and computational chemistry in a seamless whole and circumvent many of the problems encountered today.

Whilst the primary focus here is on the mechanism and rates of reactions (Baulch [41] discusses the data needs for combustion modelling, whilst Sumathi and Green [42] review progress in obtaining fast and accurate estimates of rate constants) it must not be forgotten that the thermodynamic [43] and transport data of species are probably equally important and in some cases more important. Thus, an adiabatic flame temperature is mainly sensitive to the enthalpies of formation of key species such as OH [44]. Numerical concerns have been addressed by Schwer et al. [45] who have studied the effect of re-writing legacy Fortran coding, as exemplified by Chemkin-II, and shown a factor of ten reduction in computation time for an *n*-heptane calculation whilst Manca et al. [46] consider new numerical integration methods, used to solve the coupled differential and algebraic equations in order to determine species concentrations as a function of time. While Song et al. [47] explore the interaction between the structure, that is the number of reactions and species, of a chemical kinetic model and the parameter range over which it is applied, that is the concentration ranges, and although they discuss the pyrolysis of methane/ethane mixtures, their findings apply equally to combustion.

1.3. Environments

Since combustion experiments can be carried out in many different environments² (depending on the geometry of the equipment, the pressure and temperature ranges spanned, etc.; see, for example, Ref. [52]) the modelling application must not only model the chemistry but also the environment. Thus, Chemkin-III provides modelling of shock tubes, premixed flames, diffusion flames, partially and perfectly stirred reactors, internal combustion engines, stagnation flow, rotating-disk reactors, cylindrical or planar channel flow, and well mixed plasma reactors. In most cases these environments are treated as ideal, with symmetry and other considerations being used to minimise complexity; Roesler [53], is one of the few to address these issues, when he explored the performance of a laminar, non-plug-flow reactor in methane–O₂ and CO/H₂–O₂ in a 2D-modelling and experimental study. Whilst Gokulakrishnan et al. [54] have considered the kinetic difficulties posed by the mixing of reactants before entry to a variable pressure flow reactor and shown that the ‘time shifting’ technique that this group normally uses in comparing experiment and simulation can be problematic.

More complex environments may also be modelled via so-called reactor networks, that is, combinations of plug and/or perfectly stirred reactors; thus a complex environment

² Note that gas-phase mechanisms may well be of use in describing the oxidation of hydrocarbons [48–50] in supercritical water [51].

can be broken down, via three-dimensional (3D) computational fluid dynamics (CFD) calculations, into simplified flow models and detailed chemical kinetics employed [55, 56]. This approach will be of increasing importance, particularly for industrial applications (for a good example, see the work by Niksa and Liu [57] who employed ~56 continuously-stirred tank reactors to estimate NO_x emissions in a coal-fired furnace), but is only an interim measure, with the addition of detailed chemical kinetic modelling to CFD calculations being the next big challenge for the kineticist, although Williams [14] states that this aim still remains too challenging.

2. Alkanes

Hydrocarbons are by far and away the best studied class of compounds for which reliable and detailed chemical kinetic models for combustion exist. This is not surprising given that the bulk of automotive fuels are comprised almost exclusively of hydrocarbons.

Detailed chemical mechanisms describing hydrocarbon combustion chemistry are structured in a hierarchical manner with hydrogen–oxygen–carbon monoxide chemistry at the base, supplemented as needed by elementary reactions of larger chemical species and reactions of nitrogen species if air is used as the oxidant. So, a validated comprehensive mechanism for H₂/CO/(N₂) is an essential starting point

2.1. Methane

The lower alkanes are probably the most extensively studied and hence the best understood chemical kinetic models with methane in particular being the object of a sustained campaign culminating in the Gas Research Institute study [58]. The mechanism was developed and published in a number of electronic versions [59] but ceased as of February 2000 and was primarily constructed to describe the ignition of methane and natural gas³ including flame propagation as well.

The last version, GRI-Mech 3.0, consisted of 325 elementary chemical reactions and associated rate coefficient expressions and thermochemical parameters for the 53 species optimized (within a set of constraints) to perform over the ranges 1000–2500 K, 1.0–1000 kPa, and equivalence ratios from 0.1 to 5 for premixed systems. Some aspects of natural gas combustion chemistry such as soot formation are not described by GRI-Mech 3.0 and although species such as methanol and acetylene are present in the mechanism, the GRI model cannot be used, for example, to describe the burning of pure methanol. In spite of these shortcomings the methodology employed was of the highest

quality with specific targets in mind and attempts being made to model widely differing experiments. The ready availability of the complete dataset, including that of the validating experiments (too numerous to quote here), in an electronic form over the Internet was another very positive feature and undoubtedly contributed to its widespread use. It is most unfortunate that such a useful collaborative venture, which began accidentally, has been extinguished.

An experimental and modelling study of methane (and ethane) oxidation at atmospheric pressure between 773 and 1573 K was carried out by Barbé et al. [60] in both isothermal perfectly stirred and tubular flow reactors. They determined stable species profiles and matched these against a mechanism of 835 reactions and 42 species.

Although GRI-Mech did include a very comprehensive set of experiments (targets) including shock-tube ignition delay and species profiles measurements, laminar flame speed and species profiles, and, flow and stirred reactor data it did not consider the work of Musick et al. [61] who measured species profiles of H, H₂, C₂H₃, HO, H₂O, C₂H₂, CO, CO₂, C₃H₃, C₃H₄, C₄H₂ and CH₄ by molecular beam mass spectrometry in five methane–oxygen–argon low pressure flames. In this strangely neglected paper they compared their results with eight then-current mechanisms for methane, Table 1, concluding that none of them gave a satisfactory account of experiment. Finally they proposed a new mechanism, MMSK, which performed better but still needed an improved understanding of C3 and C4 chemistry.

Another purely electronic detailed reaction mechanism for methane and natural gas combustion due to Konnov [69] also deals with C₂ and C₃ hydrocarbons and their derivatives, *n*-H–O chemistry and NO_x formation in flames. The mechanism comprises some 1200 reactions and 127 species and is extensively validated against a large dataset of experiments including species profiles and ignition delay times in shock waves, laminar flame species profiles, laminar flame speeds, and, temperature and stable species concentration profiles in flow reactors—although the bulk of the validating experiments are focused on H₂, CO, N₂O,

Table 1
Characteristics of methane mechanisms [61]

Reactions	Reversible	Species	Remarks	Reference
82	All	C1–C2	No third body	[62]
168	All	C1–C2	Third body; fall-off	[59]
67	Some	C1–C2	No third body	[63]
141	All	C1–C4	Third body; fall-off	[64]
78	All	C1–C2	No third body	[65]
89	Some	C1–C2	No third body; fall-off	[66]
92	All	C1–C2	No third body	[67]
138	Some	C1–C4	Third body	[68]

³ Real natural gas is a mixture of highly variable composition and hence quite difficult to model.

NO₂ and NH₃ kinetics rather than on the hydrocarbons CH₄, C₂H₆, and C₃H₈.

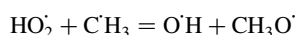
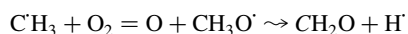
Methane pyrolysis and oxidation was studied by Hidaka et al. [70] behind reflected shock waves in the temperature range 1350–2400 K at pressures of 162–446 kPa. Methane decay in both the pyrolysis and oxidation reactions was measured by using time-resolved infrared laser absorption at 3.39 μm, CO₂ by IR emission at 4.24 μm and the product yields were also studied using the single-pulse technique. The pyrolysis and oxidation of methane were modelled using a kinetic reaction mechanism, with 157 reaction steps and 48 species, including the most recent mechanism for formaldehyde, ketene, acetylene, ethylene, and ethane oxidations.

The ignition of methane–oxygen mixtures of equivalence ratio 0.4–1.0, highly dilute in argon, was determined by Jee et al. [71] at 1520–1940 K and in reflected shock waves with initial pressures of 2.7 kPa; the results were modelled with GRI-Mech 1.2 with which they were in satisfactory agreement.

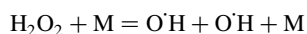
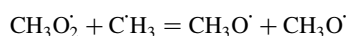
Crunelle et al. [72,73] studied premixed laminar methane/O₂/Ar low pressure flat flames at three equivalence ratios (0.69, 1 and 1.18) measuring a large number of species profiles by molecular beam mass spectrometry as a function of height above the burner. They compared their results with the predictions of a natural gas mechanism by Tan et al. [74] and with GRI-Mech 2.11; the latter gives good agreement with experiment, except for C₃ species for which it is not parameterised. The Tan mechanism covers a wider range of species, up to C₆, and was updated to give a good account of the results although the rates of formation and consumption of formaldehyde are still discrepant.

Petersen et al. [75] conducted an analytical study to supplement extreme shock-tube measurements of CH₄/O₂ ignition [76] at elevated pressures (4–26 MPa), high dilution (fuel plus oxidizer ≤ 30%), intermediate temperatures (1040–1500 K), and equivalence ratios as high as 6. A 38-species, 190-reactions model (RAMEC), based on GRI-Mech 1.2, was developed using additional reactions that are important in methane oxidation at lower temperatures. The detailed-model calculations agree well with the measured ignition delay times and reproduce the accelerated ignition trends seen in the data at higher pressures and lower temperatures. Although the expanded mechanism provides a large improvement relative to the original model over most of the conditions of this study, further improvement is still required at the highest CH₄ concentrations and lowest temperatures. Sensitivity and species flux analyses were used to identify the primary reactions and kinetic pathways for the conditions studied. In general, reactions involving HO₂, CH₃O₂, and H₂O₂ have increased importance at the conditions of this work relative to previous studies at lower pressures and higher temperatures. At a temperature of 1400 K and pressure of 10 MPa, the primary ignition

promoters are:



Methyl recombination to ethane is a primary termination reaction and is the major sink for C'H₃ radicals. At 1100 K and 10 MPa, the dominant chain-branching reactions become:



These two reactions enhance the formation of H' and O'H radicals, explaining the accelerated ignition delay time characteristics at lower temperatures.

Mertens [77] has studied the reaction kinetics of CH* (a useful diagnostic for determining ignition) in shock-heated CH₄/O₂/Ar and C₂H₂/O₂/Ar mixtures, at 2880–3030 K and 100–152 kPa, by comparing emission traces at 431 nm against simulated CH* concentrations based on a GRI-Mech 2.11 model. He concludes that HC≡C + O₂ → CH* + CO₂ proceeds at higher rates than previously thought and recommends a rate constant of 9.0 × 10¹² exp(−1780/T) cm³ mol^{−1} s^{−1}. Walsh and co-workers [78] have extended measurements on a lifted axisymmetric laminar nitrogen–diluted methane diffusion flame to measure C'H, C'H* and O'H* and to model their two-dimensional (2D) results quite successfully (except for peak concentrations of CH*) with both GRI-Mech 2.11 and a 26-species C₂ mechanism due to Smooke et al. [79], after adding in additional reactions to account for the production and destruction of excited state species, CH* and O'H*, which are absent from most mechanistic schemes.

A comprehensive methane oxidation mechanism [80], due to Hughes et al. [81], has appeared which also deals with the oxidation kinetics of hydrogen, carbon monoxide, ethane and ethene in flames and homogeneous ignition systems. This Leeds mechanism (version 1.4) consists of 351 irreversible reactions of 37 species, built with an overall philosophy akin to that of GRI-Mech, and using much the same set of experiments on laminar flame speeds [82–88], ignition delay measurements [89–92] and species profiles in laminar flames [93], except that the authors argue that their approach is less restrictive and can be used unaltered to construct more elaborate kinetic mechanisms. This latter point is almost certainly untrue, since the validating experiments never illuminate equally all of the reactions in a postulated mechanism; subsequent studies on higher fuels may well throw light on aspects of the methane model which then needs to be re-evaluated.

The overall performance of the Leeds model is similar to that of GRI-Mech and other earlier models although many of the most important reactions differ significantly;

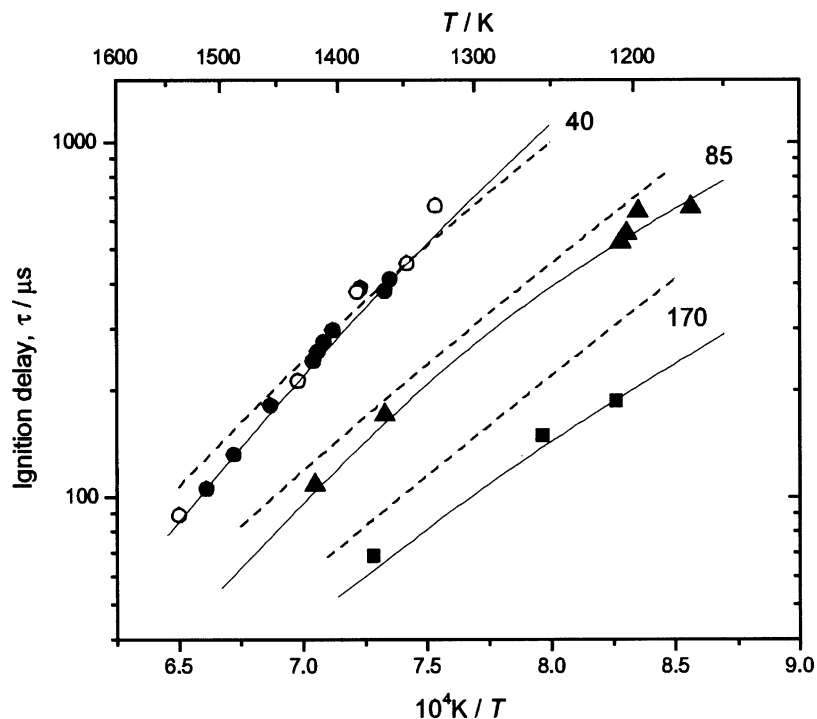
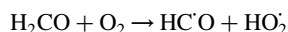
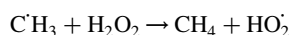
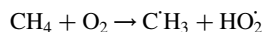


Fig. 1. Leeds (---) vs. RAMEC (—) mechanisms; data from Fig. 5 of Ref. [75].

the conclusion that the authors draw is noteworthy and disturbing—the chemistry of oxidation of simple fuels such as CO, CH₄ and C₂H₆ is still not yet well characterised at the elementary level. Thus, for example, the Leeds and RAMEC [75] mechanisms predict comparable ignition delays, Fig. 1, but use very different rate expressions⁴ for the reactions:

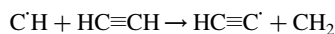
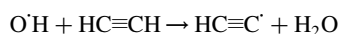
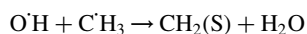
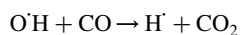
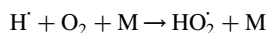
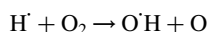


McEnally et al. [95] studied a non-sooting methane/air coflowing non-premixed flame carrying out 2D mapping of gas temperature, major (CH₄, O₂, CO, CO₂, H₂) and minor (C₂H₂, C₆H₆, H₂CCO) species concentrations with both probes (thermocouples and mass spectrometry) and optical diagnostics (Rayleigh and Raman scattering). The detailed chemical kinetic model of 140 reactions and 39 species, adapted from earlier work [79], is quite good at predicting both major and minor species to within experimental error.

Gurentsov et al. [96] have modelled the ignition delay times that they obtained for pure methane and methane/

water/carbon monoxide/hydrogen mixtures using a kinetic scheme for methane–air combustion due to Dautov and Starik [97] with only moderate success.

In an interesting paper Turányi and colleagues [44] analyse the effect of uncertainties in kinetic and thermodynamic data on the simulation of premixed laminar methane–air flames using the Leeds methane oxidation mechanism. They conclude that accurate enthalpies of formation for the species O'H⁵, CH₂(S), C'H₂OH, HC'C=O and C'H₂CHO are required as well as refined values for the rates of the reactions:



and they remind us that simulations should be accompanied by an uncertainty analysis.

⁴ Comparisons can be difficult sometimes because either forward, k_F , or reverse, k_R , rate constants may be quoted; an excellent tool, GasEq, for transforming $k_F \leftrightarrow k_R$ and other calculations, is available [94].

⁵ Ruscic et al. [98] and Herbon et al. [99] have recently revised $\Delta H_F(\text{OH}, 298 \text{ K})$ downwards to $37.3 \pm 0.67 \text{ kJ/mol}$.

Rozenchan et al. [100] have measured stretch-free laminar burning velocities for methane–air flames up to 2 MPa and methane–oxygen–helium flames up to 6 MPa. Simulation with GRI-Mech 3.0 shows good agreement with these and other recent experiments [101–103] for pressures up to 2 MPa but substantial disagreement above this pressure which is unsurprising given that the mechanism was not calibrated over this extended pressure range.

Lamoureux et al. [104] have measured ignition delays for methane, ethane and propane from 1200 to 2700 K, 0.1–1.8 MPa, equivalence ratios of 0.5–2 and in high dilution in argon. As well as presenting a useful summary of all previous work they also model their data with three detailed mechanisms. The first, due to Tan et al. [74] contains 78 species and 450 reactions and is essentially a natural gas mechanism as is the second, GRI-Mech 3.0, whilst the third is a methane oxidation mechanism due to Frenklach and Bornside [105]. Shortcomings in all three are noted.

Davidenko et al. [106] surveyed a number of methane mechanisms, GRI-Mech 1.2 [107], GRI-Mech 3.0 [58], Princeton [108], Leeds 1.5 [81], LCSR [109] and LLNL [110], on their way to producing skeletal models which they could employ in multi-dimensional simulations of complex reacting flows; they were surprised by the lack of agreement between the models and concluded that the LCSR mechanism performed best—but on the basis of a quite limited comparison with shock-tube experiments [111,112].

A comprehensive re-evaluation of all extant methane mechanisms would be welcome if exceedingly time-consuming; Rolland [113] is currently developing Visual Basic software tools for the *automatic* comparison of Chemkin-formatted mechanisms. Tables 2 and 3 show the inter-relationships as regards species and reactions for a number of methane mechanisms including Konnov [69], NUIG [114], BGD [115], GRI-Mech 3.0 [58] and Leeds [81].

The figures in brackets in Table 2 are the total number of species for the considered mechanism. The intersection of row and column shows the number of species in common between two mechanisms. Thus there are, for example, 48 species in common between the GRI-Mech and Konnov mechanisms, which means that around 91% of GRI-Mech's species are present in the Konnov mechanism.

In Table 3, the figures in brackets are the total number of individual reactions in the considered mechanism. Two numbers are present at the intersection; the first corresponds

Table 2
Species in common

Konnov (127)					
41	NUIG (81)				
60	34	BGD (77)			
48	32	48	GRI-Mech		
			3 (53)		
34	29	31	30	Leeds (37)	

Table 3
Reactions in common

Konnov (1207)					
140; 196	BGD (484)				
29; 121	42; 79	NUIG (356)			
56; 160	75; 150	35; 68	GRI-Mech		
			3 (325)		
76; 66	48; 80	15; 67	21; 90	Leeds	
				(175)	

to the number of identical (exactly the same reactants, products and Arrhenius parameters) reactions between the two mechanisms. The second is the number of otherwise identical reactions but which are numerically different, in a non-trivial sense. For instance, the Leeds and Konnov mechanisms share 142 similar reactions, 76 of which are identical but the remaining 66 differ *numerically*.

2.1.1. Mixtures

While studying the combustion chemistry of a pure compound is the best starting point for any investigation, studies of mixtures are often illuminating and are, of course, economically important [116]. There is a large body of work in this area and here we present only a select few. Spadaccini and Colket [117] determined ignition delay times for mixtures of methane with ethane, propane and butane and for typical natural gas at 1300–2000 K, pressures of 0.3–1.5 MPa and equivalence ratios of 0.45–1.25 in a comprehensive paper which also summarises much previous work. They adopted a mechanism due to Frenklach et al. [31], adapting it slightly and finding generally consistent agreement with experiment.

Tan et al. [118] studied the kinetics of oxidation of methane/ethane blends in a jet-stirred reactor at 850–1240 K and 100–1000 kPa, whilst Yang et al. [119] carried out a combined experimental and modelling study of methane and methane mixtures with ethane and propane. Ignition delays in shock-heated $\text{CH}_4 + \text{O}_2$ mixtures, with and without ignition-promoting additives, account for most of the available validation data. Additional reflected shock wave ignition experiments were done to explore possible reasons for the mismatches and to study the promotion of CH_4 ignition by small amounts of C_2H_6 and C_3H_8 additives. Empirical correlations were derived that describe ignition delays in $\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8 + \text{O}_2$.

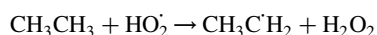
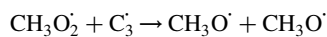
Even more complex mixtures such as natural gas, kerosene and gas oil are discussed by Dagaut [120] who has developed simple mixtures in an attempt to simulate the actual fuel. Thus he shows that an appropriate methane–ethane–propane blend is a good representation of natural gas, whilst Violi et al. [121] attempt to model JP-8 fuel with a blend of *m*-xylene, *iso*-octane, methylcyclohexane, dodecane and tetralin.

Future work will increasingly focus on *multi-dimensional modelling* as exemplified by the recent study of

Agarwal and Assanis [122] who reported on the autoignition of natural gas injected into a combustion bomb at pressures and temperatures typical of top–dead–center conditions in compression ignition engines. This study combined a detailed chemical kinetic mechanism, consisting of 22 species and 104 elementary reactions, with a multi-dimensional reactive flow code. The effect of natural gas composition, ambient density and temperature on the ignition process was studied by performing calculations for three different blends of natural gas on a 3D computational grid. The predictions of ignition delay compared very well with measurements in a combustion bomb. It was established that a particular mass of fuel burned is a much better criterion to define the ignition delay period than a specified pressure rise. The effect of additives like ethane and hydrogen peroxide in increasing the fuel consumption rate as well as the influence of physical parameters like fuel injection rate and intake temperature was studied. It was thus shown that apart from accurate predictions of ignition delay the coupling between multi-dimensional flow and multi-step chemistry is essential to reveal detailed features of the ignition process.

2.2. Ethane

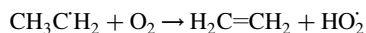
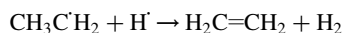
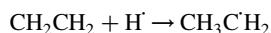
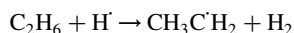
Ethane oxidation has been studied by Hunter et al. [123] in the intermediate temperature regime under lean conditions using a flow reactor. Species profiles have been obtained for H₂, CO, CO₂, H₂CO, CH₄, C₂H₄, C₂H₆, C₂H₄O (ethylene oxide or oxirane), and CH₃CHO at pressures of 300, 600, and 1000 kPa for temperatures ranging from 915 to 966 K using a constant equivalence ratio of 0.2 (in air). To model this data a detailed chemical kinetic model for ethane oxidation was developed and expanded, from a GRI-Mech 1.1 basis, to include reactions pertinent to the lower temperatures and elevated pressures. The expanded mechanism consists of 277 elementary reactions and contains 47 species. By adjusting the rate coefficients of two key reactions



the model was brought into agreement with experiment at 600 kPa; however, the model indicates a larger pressure sensitivity than was measured experimentally. Note too that the model takes measured values obtained at the first sampling point as its starting point and not as is more commonly done the initial input streams of reactants; this was done to obviate the mixing problem. Results indicate that HO₂[·] is of primary importance in the regime studied controlling the formation of many of the observed intermediates including the aldehydes and ethylene oxide. The results also point to the importance of continued investigation of the reactions of HO₂[·] with C₂H₆, CH₃C[·]H₂, and C₂H₄ to further the understanding of ethane oxidation in

the intermediate temperature regime. The expanded mechanism has also been tested against shock-tube ignition delay [91,124] and laminar flame speed data and was found to be in good agreement with both the original GRI-Mech and the experimental data for both methane and ethane.

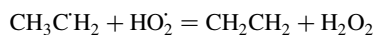
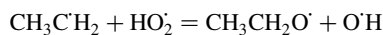
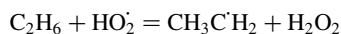
Pyrolysis and oxidation of ethane were studied behind reflected shock waves by Hidaka and co-workers [125] in the temperature range 950–1900 K and at pressures of 120–400 kPa using the same techniques as those they used for methane [70]. The present and previously reported shock-tube data were reproduced using this mechanism and comparisons drawn with GRI-Mech 1.2 and one due to Dagaut et al. [126]. The rate constants of the reactions



are discussed in detail as they are important in predicting the previously reported and the present data.

An experimental and numerical investigation on ethane–air two-stage combustion in a counterflow burner where the fuel stream, which is partially premixed with air for equivalence ratios from 1.6 to 3.0, flows against a pure air stream was reported by Waly et al. [127]. The two-stage ethane combustion exhibits a green, fuel-rich, premixed flame and a blue diffusion flame. Flame structures, including concentration profiles of stable intermediate species such as C₂H₄, C₂H₂ and CH₄, are measured by gas chromatography and are calculated by numerical integrations of the conservation equations employing an updated elementary chemical-kinetic data base. The implications of the results from these experiments and numerical predictions are summarized, the flame chemistry of ethane two-stage combustion at different degrees of premixing (or equivalence ratio) is discussed, and the relationship between NO_x formation and the degree of premixing is established.

Ikeda and Mackie [128] have modelled ignition delays in shock-heated ethane–oxygen mixes with $0.68 \leq \phi \leq 1.7$ between 1155 and 1500 K and at pressures of 1–1.5 MPa with GRI-Mech 3.0; they have shown that some additional reactions are necessary, including:



Extremely high-pressure oxidation measurements have been made by Tranter et al. [129] in a remarkable single

pulse shock tube at 1050–1450 K and at 34 and 61.3 MPa, and latterly at 4 MPa [130]; the dwell times range from 1.12 to 1.68 ms [131]. Such conditions present a severe test of reaction mechanisms as they lie well outside the typical range of most studies. The authors tested three existing mechanisms, GRI-Mech [58], Marinov et al. [132], and, Pope and Miller [133] and found that this last mechanism (developed to explore the formation of benzene in low-pressure, ethyne, ethene and propene laminar flat flames) performs best at simulating the high-pressure oxidation results, although it is not quite as good as the other two at accounting for pyrolytic reactions.

The low temperature, 500–900 K, oxidation of ethane (and propane) has been tackled by Naik et al. [134] who applied their model to rate measurements for $\text{CH}_3\text{C}_2\text{H}_5 + \text{O}_2$ by Slagle et al. [135], to ethylene yields by Kaiser et al. [136] and to ignition data of Knox and Norrish [137] and Dechaux and Delfosse [138]. They suggest that the elimination reaction $\text{CH}_3\text{C}_2\text{H}_5\text{OO} \cdot \rightarrow \text{CH}_2\text{C}_2\text{H}_5 + \text{HO}_2$ proceeds much faster than the isomerisation $\text{CH}_3\text{C}_2\text{H}_5\text{OO} \cdot \rightarrow \text{C}_2\text{H}_5\text{C}_2\text{H}_5\text{OOH}$; therefore that the branching process $\text{C}_2\text{H}_5\text{C}_2\text{H}_5\text{OOH} + \text{O}_2$ will be impeded and consequently ethane will not show negative temperature coefficient (NTC) behaviour.

2.3. Propane

A study of detailed chemical kinetics in coflow and counterflow propane (and methane) diffusion flames was presented by Leung and Lindstedt [139] using systematic reaction path flux and sensitivity analyses to determine the crucial reaction paths in propane and methane diffusion flames. The formation of benzene and intermediate hydrocarbons via C3 and C4 species has been given particular attention and the relative importance of reaction channels has been assessed. The developed mechanism considers singlet and triplet CH_2 , isomers of C_3H_4 , C_3H_5 , C_4H_3 , C_4H_5 and C_4H_6 for a total of 87 species and 451 reactions.

Computational results show that benzene in methane–air diffusion flames is formed mainly via reactions involving propargyl radicals and that reaction paths via C4 species are insignificant. It is also shown that uncertainties in thermodynamic data may significantly influence predictions and that the reaction of acetylene with the hydroxyl radical to produce ketene may be an important consumption path for acetylene in diffusion flames. Quantitative agreement has been achieved between computational results and experimental measurements of major and minor species profiles, including benzene, in methane–air and propane–air flames. It is also shown that the mechanism correctly predicts laminar burning velocities for stoichiometric propane (and methane) flames.

A pressure-dependent kinetic mechanism for propane oxidation was developed by Koert et al. [140] to match high-pressure flow reactor experiments from 1 to 1.5 MPa, 650–800 K and dwell time of 198 ms for a 1:1 propane: O_2 mix in

nitrogen. The data show a dramatic NTC region between 720 and 780 K where the rate of overall reaction decreases with increasing temperature. The model gives a satisfactory fit to the bulk of the data but formaldehyde, acetaldehyde, ethylene and CO_2 concentrations are out by factors of 3 and acrolein is 20 times less abundant than the model predictions.

Qin et al. [141] undertook a computer modelling study to discover whether optimizing the rate parameters of a 258-reaction C_3 combustion chemistry mechanism that was added to a previously optimized 205-reaction $\text{C}_{<3}$ mechanism would provide satisfactory accounting for C_3 flame speed and ignition data. It was found in sensitivity studies that the coupling between the C_3 and the $\text{C}_{<3}$ chemistry was much stronger than anticipated. No set of C_3 rate parameters could account for the C_3 combustion data as long as the previously optimized (against $\text{C}_{<3}$ optimisation targets only) $\text{C}_{<3}$ rate parameters remained fixed. A reasonable match to the C_3 targets could be obtained without degrading the match between experiment and calculation for the $\text{C}_{<3}$ optimisation targets, by reoptimizing six of the previously optimized and three additional $\text{C}_{<3}$ rate parameters. In essence then, this study shows that optimising a reaction sub-mechanism does not guarantee that further optimisation will not be required as the mechanism is expanded—put simply, studying larger fuels can still teach you something new about smaller fuels.

Cadman et al. [142] have determined autoignition times of up to 6 ms duration in quite concentrated mainly lean propane–air mixtures in a monatomic bath gas, from 850 to 1280 K and at pressures between 0.5 and 4 MPa; the rather long dwell times were obtained by tailoring of the driver gas. They compared their delay times with predictions based on mechanisms originally by Jachimowski [143], Dagaut et al. [144] and Voisin [109], none of which could account in a satisfactory manner for the experiments even when these mechanisms were supplemented with additional reactions in an attempt to enhance coverage of the chemistry below 1110 K. Propane autoignition times at 4 MPa and 750–1050 K measured by Gallagher [145] in a rapid compression machine are substantially longer than those observed by Cadman et al. and are in better agreement with the predictions of the Voisin mechanism [109].

Kim and Shin [146] investigated the ignition of propane behind reflected shock waves in the temperature range of 1350–1800 K and the rather narrow pressure range of 75–157 kPa. The ignition delay time, τ , was measured from the increase of pressure and OH emission and they present a relationship between τ and the concentrations of propane and oxygen, but not the third component argon, in the form of the usual mass-action expression with an Arrhenius temperature dependence, $\tau = A[\text{C}_3\text{H}_8]^\alpha[\text{O}_2]^\beta \exp(\theta/T)$. Numerical calculations were also performed to elucidate the important steps in the reaction scheme using various mechanisms due to Qin [147], Sung et al. [148], Glassman [149], Konnov [150] and GRI-Mech 3.0 [58]. The measured

ignition delay times were in best agreement with those calculated from the mechanism of Sung et al. [148], which was developed from temperature and species measurements in propane/nitrogen diffusion flames.

Davidson et al. [151] have obtained OH concentration time histories during the ignition of stoichiometric propane/oxygen mixtures highly dilute in argon ($\geq 99.1\%$) between 1500 and 1690 K at an average reflected shock pressure of 220 kPa. These high-quality measurements (also obtained for butane, *n*-heptane and *n*-decane) show an initial rapid rise in [OH] to a constant value and then a later rise to an essentially constant post-ignition value; the authors ascribe this behaviour to an initial rapid growth of OH, formed in branching reactions, this phase is then succeeded by a period during which propane or its decomposition products keeps the population in check followed by a third phase during which OH removal is no longer so important and therefore [OH] increases unchecked. The performance of three propane models, due to Smith et al. [58], Qin et al. [141] and Laskin et al. [152], was compared with the data and although all three give a reasonable fit to the ignition time none of them give a satisfactory account of the complete concentration–time history. Sensitivity analysis shows, unsurprisingly, very large sensitivity towards $H + O_2 \rightarrow O + OH$ but other reactions do figure, with fuel decomposition featuring strongly initially.

The reduction of nitric oxide by propane in simulated conditions of the reburning zone has been studied in a fused silica jet-stirred reactor operating at 100 kPa from 1150 to 1400 K by Dagaut et al. [153]. Some work on the neat oxidation of propane ($\phi = 1.25$) highly dilute in nitrogen (2930 ppm of propane) at 100 kPa from 1000 to 1350 K is also reported. A detailed chemical kinetic modeling of these experiments was performed using an updated and improved kinetic scheme of 892 reversible reactions and 113 species with overall reasonable agreement.

The oxidation and combustion of propane has been modelled for low temperatures, 500–800 K, and pressures of 200 Pa to 1.5 MPa by Barckholtz et al. [154]; a copy of GRI-Mech version 2.11 was enhanced to 3078 reactions of 216 species by including C_4 chemistry and compared to the HO_2 yield data of DeSain et al. [155] for the reaction $CH_3CH_2CH_2 + O_2$, the flow tube data of Koert et al. [156] and the static reactor experiments of Wilk et al. [157] with quite good agreement.

The low temperature, 500–900 K, oxidation of propane (and ethane) has been tackled by Naik et al. [134] who applied their extended ethane model to yield measurements of HO_2 from $CH_3C_2H_5 + O_2$ by DeSain et al. [155], to ignition times by Wilk et al. [157], and, to propane consumption data of Koert et al. [156] with some success. They conclude that for propane the isomerisation path is faster than concerted elimination and produces NTC behaviour, in contrast to their conclusions for ethane.

2.4. Butanes

The complexity of isomerisation arises now with two different butanes, of molecular formula C_4H_{10} , the straight-chain version *n*-butane and the branched-chain *iso*-butane; for pentadecane, $C_{15}H_{32}$, there will be 4347 isomers.

An experimental investigation by Wilk et al. [158] has examined the transition in the oxidation chemistry of *n*-butane across the region of NTC from low to intermediate temperatures. The experimental results, obtained in a static cylindrical Pyrex reactor at 73 kPa for a fuel-rich mixture in nitrogen, indicated a region of NTC between approximately 640 and 695 K and a shift in the nature of the reaction intermediates and products across this region. On the basis of these experimental results and earlier work by Slagle et al. [135] for the reaction $R' + O_2 \rightleftharpoons RO_2$, a new mechanism is presented for *n*-butane to describe the observed phenomena. At low temperatures the major reaction path of butylperoxy is isomerization, followed by O_2 addition, further isomerization, and decomposition to mainly carbonyls and OH radicals. At intermediate temperatures, the major reaction of butylperoxy is isomerization followed by decomposition to butenes and HO_2 and to epoxides and OH. The mechanism is consistent with these and other experimental results and predicts the NTC and the shift in product distribution with temperature.

An *n*-butane oxidation mechanism from the Nancy group [159], with 778 reactions involving 164 species, was validated by modelling the normal-butane oxidation at low temperature between 554 and 737 K, in the NTC region, and at a higher temperature of 937 K. The system yielded satisfactory agreement between the computed and the experimental values for the macroscopic data, induction periods and conversions, and also for the product distribution.

A mechanism focusing on the formation of aromatics and polycyclic aromatics in a laminar premixed *n*-butane–oxygen–argon flame ($\phi = 2.6$) has been developed by Marinov et al. [132]; the atmospheric-pressure flame was sampled for a number of low molecular weight species, aliphatics, aromatics and 2–5-membered polycyclic aromatics. The model gives a reasonable account of the concentrations of benzene, naphthalene, phenanthrene, anthracene, toluene, ethylbenzene, styrene, *o*-xylene, indene and biphenyl but a poor account of phenyl acetylene, fluoranthene and pyrene. This bald recital of the products found highlights the difficulties associated with giving a proper description of what is in essence a very simple reaction, viz. butane + O_2 .

A perfectly stirred reactor study by Dagaut et al. [160] concentrated mainly on the reduction of NO by *n*-butane, but also presented some results for the stoichiometric oxidation of neat *n*-butane at 1050–1230 K and 100 kPa for residence times of 160 ms. Modelling of the results for a range of reactants, intermediates and products, whose concentrations were measured by GC and FTIR, was

achieved with a kinetic scheme of 892 reversible reactions and 113 species with good agreement.

Iso-butane oxidation has received very little attention; a pyrolytic study in a static reactor [161] at 773 K included some results in the presence of oxygen but the oxygen:*iso*-butane ratio was only 1:50 and no oxidation products, other than CO, were detected. In addition the reactor walls were found to promote heterogeneous reactions.

An atmospheric-pressure perfectly stirred reactor study by Dagaut et al. of NO reduction by *iso*-butane [162] also obtained some results for the oxidation of *iso*-butane itself at 1000–1300 K, for $\phi = 0.5, 1.0$ and 1.5 and with a residence time of 160 ms. The products include CO, CO₂, CH₄, *iso*-butene, H₂CO, ethene, propene, ethane, ethyne and C₄H₈.⁶ The computed mole fractions are in generally good agreement with experimentally determined ones except for methane which is overestimated at temperatures > 1250 K.

Davidson et al. [151] have obtained OH concentration time histories during the ignition of a stoichiometric butane/oxygen mixture highly dilute in argon (99.6%) between 1530 and 1760 K at an average reflected shock pressure of 210 kPa. The results parallel those of propane by the same Stanford group (see above) and in comparing two butane models the authors found that the one due to Marinov et al. [132] performs slightly better than the Warth et al. [159] mechanism.

Dagaut and Hadj Ali [163] have conducted a detailed study of the oxidation of liquefied petroleum gas (LPG) in a jet-stirred reactor from 950 to 1450 K at 1 bar; the LPG used consisted of 24.8% *iso*-butane, 39.0% *n*-butane and 36.2% propane. Kinetic modelling with a 112 species and 827 reactions mechanism gives good agreement with the experimentally determined concentrations of fuels, intermediates and partially oxidised products.

2.5. Pentanes

Autoignition of *n*-pentane (and 1-pentene) were studied by Ribaucour et al. [164] in a rapid compression machine between 600 and 900 K at pressures of 750 kPa with both hydrocarbons showing two-stage ignition and a NTC region and with the alkene being less reactive than the alkane. Analysis of products found by quenching the reaction prior to total autoignition led to a range of cyclic ethers of which 2-methyltetrahydrofuran dominated in *n*-pentane combustion. The generalised mechanism of 975 reactions and 193 species gives a reasonable account of delay times.

Experiments in a rapid compression machine have examined the influences of variations in pressure, temperature, and equivalence ratio on the autoignition of *n*-pentane by Westbrook et al. [165]. Equivalence ratios included values from 0.5 to 2.0, compressed gas initial temperatures were varied between 675 and 980 K, and compressed gas

initial pressures varied from 0.8 to 2 MPa. Numerical simulations of the same experiments were carried out using a detailed chemical kinetic reaction mechanism. The results are interpreted in terms of a low-temperature oxidation mechanism involving addition of molecular oxygen to alkyl and hydroperoxyalkyl radicals. Idealized calculations are also reported that identify the major reaction paths at each temperature. Results indicate that in most cases, the reactive gases experience a two-stage autoignition. The first stage follows a low-temperature alkylperoxy radical isomerization pathway that is effectively quenched when the temperature reaches a level where dissociation reactions of alkylperoxy and hydroperoxyalkylperoxy radicals are more rapid than the reverse addition steps. The second stage is controlled by the onset of dissociation of hydrogen peroxide. Results also show that in some cases, the first-stage ignition takes place during the compression stroke in the rapid compression machine, making the interpretation of the experiments somewhat more complex than commonly assumed. At the highest compression temperatures achieved, little or no first-stage ignition is observed.

Experiments in a rapid compression machine were used by Ribaucour et al. [166] to examine the influences of variations in fuel molecular structure on the autoignition of all *three* possible isomers of pentane; stoichiometric mixtures of the various pentanes (2,2-dimethylpropane or neopentane, 2-methylbutane and *n*-pentane) were studied at compressed gas initial temperatures between 640 and 900 K and at pre compression pressures of 40–53 kPa. Numerical simulations of the same experiments were carried out using a detailed chemical kinetic reaction mechanism.

An intermediate temperature combustion study of neopentane by Curran et al. [167] modelled the concentration profiles obtained during the addition of neopentane to slowly reacting mixtures of H₂ + O₂ + N₂ in a closed reactor at 753 K and 67 kPa. Amongst the primary products identified were *iso*-butene, 3,3-dimethyloxetane, acetone, methane and formaldehyde.

A detailed chemical kinetic reaction mechanism (1875 reactions of 390 species) for neopentane oxidation [168] was applied by Wang et al. to experimental measurements taken in a flow reactor operating at a pressure of 800 kPa. The reactor temperature ranged from 620 to 810 K, mixture composition of 0.2% neopentane, 5.2% oxygen, and 94.6% nitrogen, and, residence times of 200 ms. Initial simulations identified some deficiencies in the existing model [167] and the paper presented modifications which included upgrading the thermodynamic parameters of alkyl radical and alkylperoxy radical species, adding an alternative isomerization reaction of hydroperoxy–neopentyl–peroxy, and a multi-step reaction sequence for 2-methylpropan-2-yl radical with molecular oxygen. These changes improved the calculation for the overall reactivity and the concentration profiles of the following primary products: formaldehyde, acetone, *iso*-butene, 3,3-dimethyloxetane, methacrolein, carbon monoxide, carbon dioxide, and

⁶ It is unclear from the single set of results presented in Fig. 1 of that paper to which mixture they apply.

water. Experiments indicate that neopentane shows NTC behaviour similar to other alkanes, though it is not as pronounced as that shown by *n*-pentane for example. Modelling results indicate that this behaviour is mainly caused by the chain propagation reactions of the hydroperoxyl-neopentyl radical.

The oxidation of neopentane (2,2-dimethylpropane) has been studied by Dagaut and Cathonnet [169] experimentally in a perfectly stirred reactor, operating at steady state, at 100, 500, and 1000 kPa, for equivalence ratios ranging from 0.25 to 2 and temperatures of 800–1230 K. The kinetics of the oxidation of neopentane was measured by probe sampling and off-line gas chromatography analysis of the reacting mixtures. Concentration profiles of the reactants (0.1–0.2 mol% neopentane/O₂/N₂), stable intermediates, and products have been obtained, leading to a detailed chemical kinetic reaction mechanism (746 reversible reactions and 115 species). Good agreement between the data and modelling was found. The major reaction paths for the oxidation of neopentane have been identified through detailed kinetic modelling.

An experimental study of the oxidation of neopentane and *iso*-pentane was performed by Taconnet et al. [170] at 873 K in a perfectly or jet-stirred reactor at 84 kPa, with dwell times of 0.4–1.2 s and for rich mixtures with $\phi = 2$ and the results modelled with a generalised mechanism; this study complements an earlier one on *n*-pentane by the same group [171] also at 873 K, but at 72 kPa and times of 0.2–0.6 s. The comparisons show that the different behaviour of these hydrocarbons can be explained, at least in part, by the presence of resonance-stabilized radicals.

2.6. Hexanes

Curran et al. [172] have studied the chemistry of all *five* isomers of hexane by comparing a detailed kinetic model with measurements of exhaust gases from a motored engine operated at a compression ratio just less than that required for autoignition. The relative ordering of the isomers as regards critical compression ratios for ignition and the major intermediates produced are well reproduced by the model.

Burcat and co-workers [173] measured both ignition delay times and product distributions for methane, ethene and propene, in preignited mixtures of *n*-hexane–O₂–Ar mixtures from 1020 to 1725 K and 100–700 kPa. Computer modelling employed a 386 reaction, 61 species scheme which was in moderate agreement with the results.

The ignition of 2-methyl-pentane, has been modelled and compared to experiments of ignition delay time in a shock tube by Burcat et al. [174], using 2-methyl-pentane in mixtures with oxygen diluted with argon. The product distribution (of methane, ethene, propene, C₄H_x and CO) of the preignited mixtures were also investigated and numerical modelling of the combustion kinetics was performed. The 2-methyl-pentane experiments were run at temperatures of 1175–1770 K and pressures of 200–460 kPa.

The numerical modelling was performed with a large kinetic scheme containing 430 elementary reactions, and then reduced to a scheme containing 110 reactions—resulting in very little difference in the predicted outcomes.

2.7. Heptanes

A 659-reaction, 109 species *n*-heptane combustion mechanism of Lindstedt and Maurice [175] has been systematically validated against data from species profiles in counterflow diffusion flames [176] and stirred reactors [177], and burning velocities in premixed flames [178].

Normal heptane oxidation in a high-pressure, perfectly stirred reactor has been investigated by Dagaut et al. [179] from 550 to 1150 K for a stoichiometric mixture of *n*-heptane and oxygen highly diluted by nitrogen at pressures of 100–4000 kPa and residence times of 0.1–2 s. Some fifty species were quantitatively detected and the results discussed in terms of a generalised mechanism comprising a low temperature region, ≤ 750 K, where the formation of peroxy radicals is the dominant feature, and, a high-temperature region, > 750 K, where intermediate hydrocarbons are rapidly formed and then consumed.

A perfectly stirred reactor study at 923 K by Simon et al. [180] of *n*-heptane oxidation with dwell times of 0.1–0.9 s and sub-atmospheric pressure determined quantitatively the formation of some 16 products, and, the results modelled with a generalised mechanism.

A rapid compression machine study of the autoignition of *n*-heptane (and *iso*-octane) by the Lille group of Minetti et al. [181] sampled the concentration of intermediates during the preignition period and as well determined the ignition delay times from 645 to 890 K.

Temperature and species mole fraction profiles have been measured in laminar premixed *n*-heptane/O₂/N₂ (and *iso*-octane/O₂/N₂) atmospheric pressure flames by El Bakali and co-workers [182]. Species identification and concentration measurements have been performed by GC and GC–MS analysis. For both flames, the equivalence ratio was equal to 1.9 and a faint yellow luminosity due to soot particles was observed. The main objective of this work was to provide detailed experimental data on the nature and concentration of the intermediate species formed by consumption of a linear or highly branched fuel molecule. In addition to reactants and major products (CO, CO₂, H₂, H₂O), the mole fraction profiles of C1 (methane), C2 (ethyne, ethene, ethane), C3 (allene, propyne, propene, propane), C4 (diacetylene, vinylacetylene, 1,2- and 1,3-butadienes, 1-butyne, butenes), C5 (pentadienes, methyl butenes, pentenes), C6 (hexenes, hexadienes, dimethyl butenes, methyl pentenes) and C7 species (heptenes, dimethyl pentenes) have been measured.

A detailed reaction mechanism of *n*-heptane combustion has been elaborated by Douté et al. [183] and validated by comparison of computed mole fraction profiles with those

measured in four premixed flames stabilized on a flat-flame burner at 6 kPa, in a wide range of equivalence ratios (0.7–2.0) [184]. Both stable and reactive species were measured by molecular beam mass spectrometry. The predictions of the model are in good agreement with the experimental results for most stable species. The main active species H, OH and O are fairly well predicted in rich flames while disagreements are observed in the lean and the stoichiometric flames. The intermediate radicals can be grouped in three classes depending on the accuracy of the model predictions: (i) good agreement in the whole range of equivalence ratios, (ii) predicted mole fractions differing from the experimental values by a constant factor in the four flames studied, (iii) difference between computed and measured maximum mole fractions varying from lean to rich flames. In the discussion of the results, the observed disagreements between the model and the experiments have been generally interpreted in terms of experimental inaccuracies. However, the modelling of the combustion chemistry for heavy fuel molecules has been carried out so far on the basis of experimental data referring only to stable species and the problems faced with intermediate radicals can result from experimental uncertainties but also from deficiencies in the mechanism or inaccuracies in the kinetic data.

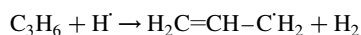
A similar study [185] was carried out by the same Orléans group but species mole fractions were measured by gas chromatography so that isomers that could not be distinguished by the mass spectrometer were identified and analysed separately. Hence, although the main objective of this work was to extend the *n*-heptane combustion mechanism to atmospheric pressure, it was also to take advantage of the new data on the isomers to refine the mechanism. Modifications to the low-pressure mechanism have been strictly limited to (i) calculation of high pressure values for reactions in the fall-off regime and (ii) distinction of the isomeric forms of heptenes. The reliability of the mechanism was evaluated by comparison of computed mole fraction profiles with those measured in a rich premixed *n*-heptane flame (equivalence ratio of 1.9). Good agreement was obtained for most molecular species, especially intermediate olefins, dienes and alkynes while calculated benzene concentrations were also in reasonable agreement with experiment. Analysis of the main reaction pathways show that the main effect of the change of pressure from 6 to 101 kPa is to increase the relative importance of the thermal decomposition reactions, especially for the intermediate olefins.

Davis and Law [186] have measured stretch-corrected, laminar flame speeds of *n*-heptane–air mixtures at atmospheric pressure and compared their results to three *n*-heptane mechanisms [29,175,187]. The Held et al. [187] mechanism performs best over the complete range of stoichiometries particularly for $\phi \leq 0.9$.

Ingemarsson et al. [188] investigated an atmospheric pressure, premixed laminar *n*-heptane/air flame

using GC–MS sampling to determine species profiles for a stoichiometric mixture. Key findings of this study are that alkene concentrations are significantly higher than corresponding alkanes, that 1-alkene concentrations decrease with increasing chain length from C2 through C7, that C4–C7 intermediates peak early whilst C1–C3 peak late, and, that 1,3-butadiene peaks early during the oxidation of *n*-heptane. A reaction mechanism for *n*-heptane oxidation including thermodata due to Held et al. [187] was used to model the results with moderately satisfactory agreement except that several detected species (propane, propyne, methanol, *iso*-butene, 2-butene and 1-heptene) were absent from the model.

The performance of the Lindstedt and Maurice [175], Held et al. [187] and Curran et al. [189] mechanisms was also tested by Davidson et al. [190] against *n*-heptane ignition delay times, based on emission from methylidyne, CH, obtained between 1400 and 1550 K and at reflected shock pressures of 120 and 220 kPa for mixtures containing 0.4% *n*-heptane and 4.9% O₂ in argon. The Held mechanism best fits the data and signals that the formation of allyl is almost as important as $\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$ in influencing the ignition delays:



Seiser and co-workers [191] studied extinction and autoignition of *n*-heptane in a counterflowing non-premixed system, where transport processes are important, and modelled the results with a truncated version (770 reversible reactions of 159 species) of a detailed model of 2540 reactions of 555 species [189]. The truncated model, necessary because of the larger computational demands of a heterogeneous configuration, was able to give a satisfactory account of the data showing, inter alia, that high-temperature chemistry dominates the autoignition process in the counterflow flame.

High-temperature detailed chemical kinetic reaction mechanisms were developed by Westbrook et al. [192] for all *nine* chemical isomers of heptane, following techniques and models developed previously for other smaller alkane hydrocarbon species. These reaction mechanisms were tested by computing shock-tube ignition delay times for stoichiometric heptane/oxygen mixtures diluted by argon [190]. Differences in the overall reaction rates of these heptane isomers are discussed in terms of differences in their molecular structure and the resulting variations in rates of important chain branching and termination reactions. A similar exercise was carried out [193] in conjunction with rapid compression machine autoignition data for 2-methyl hexane, 2,2- and 2,4-dimethyl pentanes [194]. The computations [195] predict that *n*-heptane, 2-methyl hexane and 3-methyl hexane are the most reactive, Fig. 2, 3-ethyl pentane is less reactive, Fig. 3, and the remaining isomers are least reactive, Fig. 4. These observations are only approximately consistent with the octane rating of each isomer.

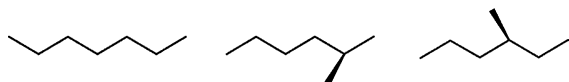


Fig. 2. Most reactive heptanes.

Davidson et al. [151] have obtained O'H concentration time histories during the ignition of stoichiometric *n*-heptane/oxygen mixture highly dilute in argon (99.6%) between 1540 and 1790 K at reflected shock pressures of 200–380 kPa. The results parallel those of propane and butane by the same Stanford group (see above) and in comparing three *n*-heptane models—those due to Lindstedt and Maurice [175], Held et al. [187] and Curran et al. [189]—the authors found that none of the three were at all satisfactory.

Colket and Spadaccini [196] have determined ignition delay times for *n*-heptane (and also for ethene and JP-10) from 1000 to 1500 K, pressures of 300–800 kPa and equivalence ratios of 0.5–1.5; in a model paper as regards the presentation of experimental data (experimentalists please imitate!), they summarise all previous work on *n*-heptane.

The Stanford group have also presented [197,198] ignition time measurements, in reasonably good agreement with previous measurements by Burcat et al. [199] and Colket and Spadaccini [196], for the combustion of *n*-heptane (also propane, *n*-butane, and *n*-decane) behind reflected shock waves over the temperature range of 1300–1700 K and pressure range of 100–600 kPa. The test mixture compositions varied from approximately 0.2–2% *n*-heptane, 2–20% O₂, and the equivalence ratios ranged from 0.5 to 2.0. Improved methods of determining the fuel mole fraction of the test mixture in situ and of measuring the ignition delay times by a C'H emission diagnostic at the shock-tube endwall were employed. A parametric study revealed marked similarity in the ignition delay times of the four *n*-alkanes, and they expressed *stoichiometric* ignition time data for all four *n*-alkanes, with a correlation coefficient of 0.992, as

$$\tau = 9.4 \times 10^{-12} p^{-0.55} x(\text{O}_2)^{-0.63} n^{-0.50} \exp(+23\,245/T)$$

where the ignition time, τ , is in seconds, pressure, p , in atmospheres, $x(\text{O}_2)$ is the mole fraction of oxygen in the test mixture, and n is the number of carbon atoms in the *n*-alkane. The authors present comparisons to past ignition time studies and detailed kinetic mechanisms to further validate this correlation. This is an extraordinary result at first sight since there is no obvious connection between the four compounds, although all hydrocarbons share common

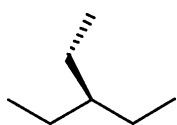


Fig. 3. Intermediate reactivity.

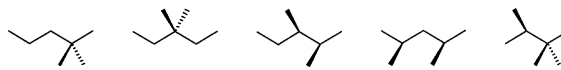


Fig. 4. Least reactive heptanes.

intermediates and pathways as they react, and, normally the most important reactions as regards high-temperature oxidation tend not to be that fuel-specific. Multiple regression analysis to determine the five parameters in the global correlation above, can be problematic since the variables usually span a very limited range, for example in this case the argon concentration ranges from ≈ 80 to 96% but these results are in agreement with work by Toland [200] who finds that at 1% fuel and either 2 or 4% oxygen, $\tau(\text{propane}) < \tau(\text{butane})$, and, at 8% O₂ $\tau(\text{propane}) \approx \tau(\text{butane})$, all for pressures of 350 kPa.

Silke [201] has determined the reactivities of eight out of the nine heptane isomers in a creviced-piston rapid compression machine study, Fig. 5, and finds that, in general, the modelling predictions of Westbrook et al. [192] for the most reactive are borne out, although the correlation of RON and reactivity for the least reactive isomers is less clearcut.

2.8. Octanes

Of the 18 isomers only two, *n*-octane and *iso*-octane, have been extensively studied, the most important being 2,2,4-trimethylpentane or *iso*-octane. A perfectly stirred reactor study at 923 K by Simon et al. [180] of *iso*-octane oxidation with dwell times of 0.1–1.1 s and at sub-atmospheric pressure determined quantitatively the formation of some 16 products, and, the results modelled with a generalised mechanism. The formation of hydrogen presented problems and was not reproducible.

A semi-detailed kinetic scheme from Ranzi and co-workers [202] is available for *iso*-octane which simulates turbulent flow reactor [203], stainless steel and quartz [204] jet-stirred reactors, rapid compression machine and shock-tube studies [205] covering the range from 550 to 1500 K and up 4000 kPa pressure.

Davis and Law [186] determined the stretch-corrected laminar flame speeds of *iso*-octane–air mixture over a range of stoichiometries (their speeds are not in good agreement with those of Bradley et al. [206]) and modelled the results with a mechanism assembled from a compact *n*-heptane mechanism [187] and an early version of high-temperature *iso*-octane chemistry [207]. The model underestimates the experimental flame speeds by a considerable margin except for the very leanest mix, $\phi = 0.7$; however it does better in matching the flow reactor experiments of Dryer and Brezinsky [203] particularly for fuel decay, and major intermediates such as *iso*-butene and propene, although methane and CO are not at all properly represented.

A detailed chemical kinetic mechanism has been developed and used by Curran et al. [207] to study

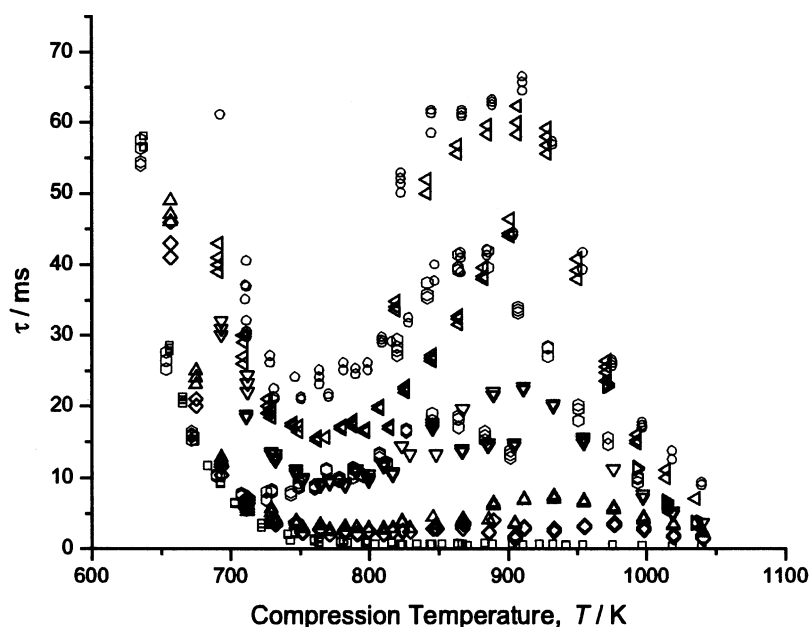


Fig. 5. Ignition delay times at post-compression pressure of 1.5 MPa except heptane at 2 MPa: (\square) heptane (0), (\diamond) 2-methylhexane (42.4), (Δ) 3-methylhexane (52.0), 3,3-dimethylpentane (80.8), (∇) 2,4-dimethylpentane (83.1), (\circ) 2,3-dimethylpentane (91.1), (\triangleleft) 2,2-dimethylpentane (92.8), (\triangleright) 2,2,3-trimethylbutane (112); research octane numbers in brackets.

the oxidation of *iso*-octane in a jet-stirred reactor [204], flow reactors [208,209], shock tubes [210] and in a motored engine [211] but not against the flame speed measurements of Davis and Law [186]. Over the series of experiments investigated, the initial pressure ranged from 100 to 4500 kPa, the temperature from 550 to 1700 K, the equivalence ratio from 0.3 to 1.5, with nitrogen–argon dilution from 70 to 99%. This range of physical conditions, together with the measurements of ignition delay time and concentrations, provide a broad-ranging test of the chemical kinetic mechanism which was based on *n*-heptane oxidation. Experimental results of ignition behind reflected shock waves were used to develop and validate the predictive capability of the reaction mechanism, comprising 3600 elementary reactions of 860 species, at both low and high temperatures. Moreover, the concentrations of compounds found in flow and jet-stirred reactors were used to help complement and refine the low and intermediate temperature portions of the reaction mechanism, leading to good predictions of intermediate products in most cases. In addition, a sensitivity analysis was performed for each of the combustion environments in an attempt to identify the most important reactions under the relevant conditions of study.

Davidson et al. [212] have carried out measurements of ignition delay times and OH concentration profiles for *iso*-octane at 1180–2010 K, 120–820 kPa and for mixtures with $0.25 \leq \phi \leq 2$. The OH time history differs quite markedly from those this group measured for *n*-alkanes [151] featuring a drop-off just prior to ignition.

Detailed modelling of the oxidation of *n*-octane (and *n*-decane) in the gas phase was performed by Glaude and co-workers [213] using computer-designed mechanisms. For *n*-octane, the predictions of the model were compared with experimental results obtained by Dryer and Brezinsky in a turbulent plug flow reactor [203] at 1080 K and 100 kPa. Considering that no fitting of any kinetic parameter was done, the agreement between the computed and the experimental values is satisfactory both for conversions and for the distribution of the products formed. This modelling has required improvement in the generation of the secondary reactions of alkenes, which are the main primary products obtained during the oxidation of these two alkanes in the range of temperature studied and for which reaction paths are detailed.

2.9. Decanes

Dagaut et al. [214] have modelled the oxidation of *n*-decane in a jet-stirred reactor at 1 MPa pressure, from 550 to 1150 K, at residence times of 0.5 and 1 s, and for $0.1 \leq \phi \leq 1.5$; their detailed mechanism gives a good description for species profiles at temperatures over 800 K but does not match the data that well in the intermediate to low temperature regions.

The chemical structure of a premixed *n*-decane/O₂/N₂ flame ($\phi = 1.7$) stabilized at atmospheric pressure on a flat-flame burner has been computed with two reaction mechanisms by Douté et al. [215]. In the first one,

the consumption of the fuel molecule is described in detail. The five different *n*-decyl radicals formed by H atom abstraction from the decane molecule were distinguished and their consumption reactions were considered in a systematic way. This mechanism comprises 78 species involved in 638 elementary reactions, modelling with this detailed mechanism led to species mole fraction profiles in good agreement with the experimental results. The main reaction paths for the formation of final and intermediate species have been identified with special emphasis on benzene formation. The second mechanism was derived from the first one by successively removing an increasing number of *n*-decyl radicals. For most species, it is possible to maintain the reliability of the model with only one *n*-decyl radical in the mechanism—an example of the successful adoption of the ‘principle of shortsightedness’ [216]. In this simplified version of the mechanism, the species number is reduced to 62 and the reaction number to 467. The only species affected are the large intermediate olefins.

Detailed modelling of the oxidation of *n*-decane was carried out by Glaude et al. [213] with an automatically generated mechanism and compared with the jet-stirred reactor species profiles data of Balès-Guéret et al. [217] obtained at temperatures of 922–1033 K, residence times of 0.1–0.25 s and atmospheric pressure.

Battin-Leclerc and co-workers [218] have simulated *n*-decane experiments performed in a jet-stirred reactor [217] and in a premixed laminar flame [219] from 550 to 1600 K. Their mechanism, generated automatically, included a massive 7920 reactions.

Zeppieri et al. [220] have developed a partially reduced mechanism for the oxidation and pyrolysis of *n*-decane validated against flow reactor, jet-stirred reactor [217] and *n*-decane/air shock-tube ignition delay [29] data. The approach includes detailed chemistry of *n*-decane and the five *n*-decyl radicals, and it incorporates both internal hydrogen isomerization reactions and β -scission pathways for the various system radicals. To include this additional detailed reaction information and simultaneously minimize the number of species present in the model, an important assumption was made regarding the distribution of radical isomers. It was assumed that the different isomers of a given alkyl radical are in equilibrium at each carbon number above the C4 level, thereby allowing the inclusion of the reaction channels associated with each isomer, without imposing the computational penalty associated with including each isomer as a separate species in the mechanism. As a result, only a single radical is needed to represent all the isomers associated with it. Thus, the new mechanism contains detailed reaction chemistry information, while maintaining the compactness necessary for use in combined fluid mechanical/chemical kinetic computational simulations.

Davidson et al. [151] have obtained OH concentration time histories during the ignition of a stoichiometric *n*-decane/oxygen mixture highly dilute in argon ($\geq 96.7\%$)

between 1350 and 1700 K at reflected shock pressures of 220 kPa. The results parallel those of propane, butane and *n*-heptane by the same Stanford group (see above); the *n*-decane oxidation mechanism of Lindstedt and Maurice [175] does not give a satisfactory account of the OH profile whilst the Battin-Leclerc et al. mechanism [218] could not be run because of its large size.

A chemical kinetic mechanism for the combustion of *n*-decane has been compiled and validated by Bikas and Peters [221] for a wide range of combustion regimes. Validation has been performed by using measurements on a premixed flame of *n*-decane, O₂ and N₂, stabilized at 100 kPa on a flat-flame burner [215], as well as from experiments in shock waves [222], in a jet-stirred reactor [223] and in freely propagating premixed flame [224]. The reaction mechanism features some 600 reactions and 67 species including thermal decomposition of alkanes, H-atom abstraction, alkyl radical isomerization, and decomposition for the high temperature range, and a few additional reactions at low temperatures. The transition between low and high temperatures with a negative temperature dependence is quite well reproduced.

Ignition delay times from 1260 to 1560 K, 500–1000 kPa and $0.5 \leq \phi \leq 1.5$, and, flame speeds in an atmospheric pressure, laminar, premixed flame $0.9 \leq \phi \leq 1.3$ of *n*-decane have been determined by Skjøh-Rasmussen et al. [225] and compared with the predictions of a number of decane mechanisms [213,220,221,223] with only the classical detailed mechanism of Dagaut et al. [223] in agreement with the measured flame speeds; the ignition delays are not matched at all well by any of the models.

2.10. Higher hydrocarbons

A modelling study by Ristori et al. [226] of the oxidation of a key diesel fuel component, *n*-hexadecane or cetane, was based on experiments performed in a jet-stirred reactor, at temperatures ranging from 1000 to 1250 K, at 100 kPa pressure, a constant mean residence time of 70 ms, and a high degree of nitrogen dilution (0.03 mol% of fuel) for equivalence ratios equal to 0.5, 1, and 1.5. The kinetic model features 242 species and 1801 reactions and gives reasonable agreement with species profiles except, somewhat surprisingly, for the parent fuel, *n*-C₁₆H₃₄ itself whose reactivity is underestimated. In a parallel paper based on the same experiments a detailed kinetic mechanism [227] was automatically generated [228] by using the computer package, EXGAS, developed in Nancy. The long linear chain of this alkane necessitates the use of a detailed secondary mechanism for the consumption of the alkenes formed as a result of primary parent fuel decomposition. This high-temperature mechanism includes 1787 reactions and 265 species, featuring satisfactory agreement for the formation of products but still does not adequately account for the consumption of hexadecane.

2.11. Cyclics, rings

Ring systems may well exhibit dramatically different mechanisms not just from linear analogues but also with each other.

2.11.1. Three and four

Monocyclic small ring hydrocarbons do not appear to have been much studied; Slusky et al. [229] have determined the ignition delays, τ , of cyclopropane and cyclobutane (as well as substituted derivatives and bicyclic species) in stoichiometric air-like argon mixtures between 1200 and 1600 K and at reflected shock pressures of 600 ± 100 kPa. Interestingly they find that cyclopropane is less reactive than cyclobutane, that is, $\tau(\text{C}_3\text{H}_6) > \tau(\text{C}_4\text{H}_8)$, although the latter mixture contains more oxygen and since normally $\tau \propto [\text{O}_2]^{-1}$ it is not possible to get a true comparison. The authors argue from known rates of isomerisation that the transformation of cyclopropane to propene is completed long *before* ignition occurs but then present data which shows that $\tau(\text{propene}) \approx 1.8 \times \tau(\text{cyclopropane})$; this is not consistent. A similar argument is made for cyclobutane and its decomposition product of two ethylene molecules.

2.11.2. Five

An experimental study of the oxidation of cyclopentane (and *n*-pentane) was performed at 873 K in a jet-stirred reactor by Simon et al. [171] with residence times of 0.1–0.5 s at 53 kPa corresponding to between 2 and 24% fuel consumption for a rich mixture with $\phi = 2$; they discuss species profiles in terms of a generalised mechanism.

Laminar premixed flat cyclopentene/oxygen/argon flames with different stoichiometries ($\text{C/O} = 0.6, 0.77, \text{ and } 0.94$) were studied by Lamprecht et al. [230] at 5 kPa under fuel-rich non-sooting conditions motivated by the scarcity of information on C_5 fuel combustion. Concentrations as a function of height above the burner were measured for more than 30 stable and radical species using molecular beam mass spectrometry. Temperature was measured in the unperturbed flame with laser-induced fluorescence of seeded NO. Stable species concentrations in the burned gases were found in good agreement with equilibrium calculations. For information on the flame structure in the reaction zone, species profiles for intermediates of relevance in the formation of aromatics were inspected regarding in particular several C_xH_y compounds with $2 \leq x \leq 10$. The measured data was analysed with respect to the formation of C_6 species, in particular of benzene as a key species in the soot formation mechanism. A reaction flow analysis has been performed which reveals striking differences to other fuels, including acetylene and propene. It does not seem feasible to rely on a single dominant pathway to benzene in cyclopentene flames. Reactions of C_5H_5 and C_5H_6 were found to be important, that of $\text{C}_5\text{H}_6 + \text{CH}_3$ being of similar influence on C_6H_6

formation as the propargyl recombination, a result of interest for detailed flame modeling, which was however not carried out.

Cyclopentadiene ignition was measured by Burcat et al. [231] in a study from 1280 to 2110 K, 240–1250 kPa and with $\phi = 0.5$ –2; as usual there is very little dependence of ignition delay on fuel concentration and the normal reciprocal dependence on $[\text{O}_2]$. In addition some experiments were performed to determine intermediate concentrations prior to ignition; the main products apart from CO are acetylene and benzene (in surprisingly large amounts). The detailed model of 439 reactions could be reduced to a skeletal 125 and still represent the experiments except for the leanest mixtures. Cyclopentadiene combustion is important because of the light that it can throw on benzene oxidation since phenoxy decomposes to cyclopentadienyl.

2.11.3. Six

Cyclohexane oxidation has been studied by Voisin et al. [232] in a jet-stirred reactor in the temperature range of 750–1100 K at 1000 kPa. Major and minor species profiles have been obtained by probe sampling and GC analysis. A chemical kinetic reaction mechanism developed from previous studies on smaller hydrocarbons is used to reproduce the experimental data. It has been updated and validated for C1–C5 sub-mechanisms. Good agreement is obtained between computed and measured mole fractions. The major reaction paths of cyclohexane consumption and the formation and the consumption routes of the main products have been identified for the experimental conditions with the formation of ethylene identified as the key thermal decomposition step: $\text{C}_6\text{H}_{12} \rightarrow 3\text{H}_2\text{C}=\text{CH}_2$.

In an extension of this work to lower pressures (but similar temperatures) and with an improved analytical technique for the detection of intermediates, a detailed reaction mechanism [233] for cyclohexane oxidation has been evaluated by comparison of computed and experimental species mole fraction profiles measured in a jet-stirred reactor for $\phi = 0.5$ –1.5 and 100, 200, and 1000 kPa. Major and minor species mole fractions were obtained for O_2 , CO, CO_2 , H_2 , H_2CO , CH_3CHO , $\text{H}_2\text{C}=\text{CH}-\text{CHO}$ or acrolein, CH_4 , C_2H_6 , C_2H_4 , C_3H_6 , C_2H_2 , allene, propyne, 1- C_4H_8 , 2- C_4H_8 (both *trans* and *cis*), butadiene, cyclopentene, cyclohexadiene, 1-hexene, cyclohexene, and C_6H_6 . Good agreement was obtained for most molecular species, especially intermediate olefins, dienes, and oxygenated species such as H_2CO and acrolein. This mechanism assumes thermal decomposition of the cyclohexane to ethylene and cyclobutane initially, although cyclobutane is not observable.

Computed benzene and cyclopentene concentrations are in reasonable agreement with experimental data but cyclohexene and 1,3-cyclohexadiene are over-predicted. The mechanism, comprising 107 species and 771 reactions, was also validated at higher temperature by modelling

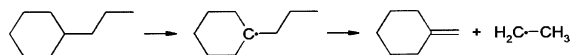
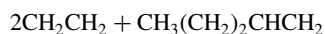
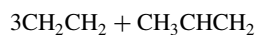


Fig. 6. Abstraction by O_2 from C_9H_{18} and formation of methylenecyclohexane.

the laminar flame speeds of cyclohexane–air flames measured by Davis and Law⁷ [234] over a wide range of equivalence ratios, although there is not much sensitivity exhibited to reactions involving large ring fragments except, oddly, for phenoxy, $C_6H_5O^{\cdot}$

The oxidation of *n*-propylcyclohexane has been studied by Ristori et al. [235] at atmospheric pressure in a jet-stirred reactor from 950 to 1250 K with $0.5 \leq \phi \leq 1.5$; concentration profiles of reactants, intermediates and final products, formed during the 70 ms reaction time, were determined. The detailed model of 176 species and 1369 reactions attempts to trace some of the main pathways which they show proceeds via H-atom abstraction to form seven propylcyclohexyl radicals that react by β -scission to yield ethylene, propene, methylenecyclohexane, cyclohexene and 1-pentene, Fig. 6.

Principal decomposition channels involve the parent propylcyclohexane pyrolysing to:



as well as some additional channels involving bond-breaking reactions.

2.11.4. Multiple rings

Recent interest in exo-tetrahydrodicyclopentadiene has been driven by the potential of this high-energy compound, for use in scramjets and pulse detonation engines, since it is the principal component of the jet fuel JP-10, Fig. 7. Williams and co-workers [236,237] have established a partially detailed mechanism with 174 reactions, not all of which are elementary, dealing with 36 species. In essence this study utilises the ignition times and O'H concentration time histories for JP-10/ O_2 /Ar mixtures measured behind reflected shock waves over the temperature range of 1200–1700 K, pressure range of 100–900 kPa, fuel concentrations of 0.2 and 0.4%, and stoichiometries of 0.5, 1.0, and 2.0 by Davidson et al. [238]. Colket and Spadaccini [196] have also reported autoignition data for JP-10 (as well as ethylene and *n*-heptane) at 1100–1500 K, 300–800 kPa and equivalence ratios of 0.5–1.5 but did not carry out any detailed

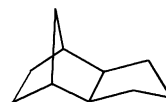


Fig. 7. Exo-tetrahydrodicyclopentadiene or JP-10.

modelling. Neither did Olchansky and Burcat [239] who have determined ignition delay times as well but also sampled species formed between 1050 and 1135 K finding inter alia cyclopentene, pentadiene, ethene, benzene, butadiene, butenes, propene, toluene, CO, etc. nor Mikolaitis et al. [240] who have reported JP-10/air ignition delay times at reflected shock pressures of 1–2.5 MPa and temperatures from 1200 to 2500 K.

An earlier kinetic model for JP-10 oxidation used *global* decomposition reactions proposed by Williams et al. [241] in conjunction with a larger alkane mechanism of Lindstedt and Maurice [175]. This modelling gave good agreement with the ignition times at higher pressures, and sensitivity studies using this model indicated the important role of C_2 chemistry in JP-10 decomposition. However, as the authors acknowledge, the mechanism is incomplete and is not good at describing the early stages of fragmentation and oxidation of tetrahydrodicyclopentadiene.

Some earlier work compared the ignition delay times for stoichiometric air (with the nitrogen replaced by argon) mixtures of spiro-pentane, hexane and heptane [229,242] at 1100–1600 K and reflected shock pressure of 600 ± 100 kPa. The reactivities increase from spiroheptane through spiro-pentane to spirohexane, Fig. 8, with the high reactivity of the C_6 compound being ascribed to the prompt formation of ethylene and butadiene which then react with oxygen.

3. Alkenes and dienes

3.1. Ethene

The simplest alkene, ethene or ethylene, $H_2C=CH_2$, has been the subject of numerous combustion experiments and associated modelling studies, many of them dealing with the formation of soot particles—these will not be dealt with here.

Experiments and detailed modelling has been performed by Castaldi et al. [243] to investigate the mono and polycyclic aromatic formation pathways in premixed, rich ($\phi = 3.06$), sooting, ethylene–oxygen–argon burner



Fig. 8. Spiro compounds.

⁷ This paper also contains reliable flame speed data for propene, butanes, butenes, 1,3-butadiene, *n*- and cyclopentane, *n*-hexane, benzene and toluene.

stabilised atmospheric-pressure flame. Species detected in the flame and post-flame regions included allene and propyne, diacetylene, vinylacetylene, 1,2- and 1,3-butadienes, 1- and 2-butyne, 1- and 2-butenes, cyclopentadiene, toluene, ethylbenzene, styrene, phenylacetylene, *o*-xylene, indene, methylnaphthalene, acenaphthalene, biphenylene, biphenyl, cyclopenta[*cd*]pyrene and benzo[*ghi*]fluoranthene. The detailed model of 664 reactions of 150 species struggles to match the experimental data.

A detailed chemical kinetic mechanism, including 340 elementary steps and 90 species, has been developed by D'Anna and Violi [244] to simulate the formation of aromatic compounds in rich premixed flames of aliphatic hydrocarbons. The mechanism can reproduce the concentration profiles and net rates of benzene and larger aromatic hydrocarbons (two- and three-ring polycyclic aromatic hydrocarbons (PAHs)) in a wide range of temperatures for a slightly sooting, premixed ethylene–oxygen flame. Key sequences of reactions in the formation of aromatics are the combination of resonantly stabilized radicals, whereas the alternative mechanism that involves acetylene addition does not seem to be fast enough to explain the observed formation rates of aromatics in the flames examined. The main routes involved in the formation of the first aromatic ring are the propargyl self-combination and its addition to 1-methylallenyl radicals. Cyclopentadienyl radical combination, propargyl addition to benzyl radicals, and the sequential addition of propargyl radicals to aromatic rings are the controlling steps for the formation of larger aromatic species.

Pyrolysis and oxidation of ethylene was studied behind reflected shock waves by Hidaka et al. [245] in the temperature range 1100–2100 K and at pressures of 150–450 kPa. Ethylene decay in both the pyrolysis and oxidation reactions was measured by absorption at 3.39 μm and emission at 3.48 μm . CO_2 production was also measured by time-resolved IR-emission at 4.24 μm while species yields were also determined by the single pulse sampling. The pyrolysis and oxidation of ethylene were modeled using a kinetic reaction mechanism of 161 reactions and 51 species, including the most recent mechanism for formaldehyde, ketene, methane, ethane and acetylene oxidations.

Wang [246] has explored the importance of carbenes as free-radical chain initiators in the oxidation of ethylene (also propyne and allene) by combined DFT calculations and kinetic modelling of ignition delay measurements [245,247,248] and concludes that the carbene pathway dominates the initial radical pool production.

Ethylene ignition and detonation was modelled by Varatharajan and Williams [249] for a series of shock-tube measurements covering the ranges 1000–2500 K, 50–10,000 kPa and equivalence ratios between 0.5 and 2 and usefully summarised in the paper. Their mechanism of 148 elementary reactions involving 34 species is in good agreement with experimental burning velocities for

laminar ethylene flames (although the measurements were not stretch-free) and with the shock-tube induction times; unsurprisingly, the mechanism performs better than GRI-Mech 3.0.

Ethene combustion has been modelled by Carriere et al. [250] using data from the Princeton flow reactor from 850 to 950 K, 500–1000 kPa and $\phi = 2.5$, and, for a premixed, low-pressure (2.7 kPa), laminar, fuel-rich ($\phi = 1.9$) flame [251]. In the low-pressure flame ethene is consumed mainly by abstraction reactions, to $\text{H}_2\text{C}=\dot{\text{C}}\text{H}$, whilst in the flow reactor abstraction by O'H competes with H-addition to $\text{H}_3\text{CC}\dot{\text{C}}\text{H}_2$. Their reaction mechanism of 737 reactions (of which 641 were reversible) and 86 species was judged to compare favourably with experiment and thereby to perform appreciably better than mechanisms by Dagaut et al. [252], GRI-Mech 3.0 [58] and Wang and Laskin [253].

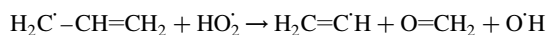
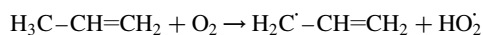
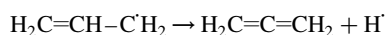
3.2. Propene

Propene oxidation chemistry in laminar premixed flames was studied by Thomas et al. [254] in a lean ($\phi = 0.229$), low pressure laminar premixed $\text{C}_3\text{H}_6\text{-O}_2\text{-Ar}$ flame and comparisons with experiment made in order to assess existing uncertainties in the propene oxidation chemistry. It is shown that propene is mainly consumed by O atom addition reactions. However, reactions involving the O'H radical remain important and a tentative branching ratio between abstraction and addition channels for the O'H attack on propene is also proposed. Furthermore, it has been shown that computed allyl radical levels are sensitive to the choice of rate for the molecular oxygen attack and a tentative product distribution for the latter is also proposed. Generally good agreement is obtained between computations and measurements for major flame features and key combustion intermediates. Moreover, allyl radical and total C_3H_4 levels are successfully reproduced. A tentative reaction mechanism for C-3 oxygenated species has also been formulated and validated against experimental data. Finally, the study identifies specific aspects of the propene oxidation chemistry where further theoretical and experimental work is required.

The pyrolysis and oxidation of propene or propylene was studied experimentally in an atmospheric-pressure plug flow reactor with residence times of 4–180 ms by Davis et al. [255]. Species profiles were obtained in the intermediate to high temperature range (close to 1200 K) for lean, stoichiometric, rich, and pyrolytic conditions; only one oxygenated product, apart from the obvious CO , CO_2 and H_2O , was detected but not identified. Laminar flame speeds of propene/air mixtures were also determined over an extensive range of equivalence ratios (0.7–1.7), at room temperature and atmospheric pressure, using the counter-flow twin flame configuration.

A detailed chemical kinetic model consisting of 469 reactions and 71 species was used to describe the high-temperature kinetics of propene; the authors also discuss

flow reactor species profiles, laminar flame speeds and ignition delays for propyne oxidation, shock-tube ignition for allene, and laminar flame speeds and ignition delays for propane combustion. The kinetic model is in good agreement with the measured stretch-compensated laminar premixed propene flame speeds for $\phi \leq 1$ but underestimates flame speed quite strongly above this point. The model predicts much shorter values of ignition delay than those determined by Burcat and Radhakrishnan [256], but these latter results have been called into question. Sensitivity studies reveal that the following reactions, as well as the usual $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$, are most important in the oxidation of propene at 1200 K:



Propene ignition was studied behind reflected shock waves by Qin et al. [257] at postshock temperatures ranging from 1270 to 1820 K and postshock pressures from 95 to 470 kPa, when reactant concentrations were varied from 0.8 to 3.2% propene and from 3.6 to 15.1% oxygen diluted in argon, giving equivalence ratios ranging from 0.5 to 2.0. The measurements were not in good agreement with the previous results of Burcat and Radhakrishnan [256]. The data could be accounted for using a reaction mechanism with 463 elementary reactions [141].

The computer code EXGAS was used to generate detailed mechanisms for the oxidation and combustion of alkenes [258]. An analysis of the elementary reactions from the literature allowed the definition of new specific generic reactions involving alkenes and their free radicals, as well as correlations to estimate the related rate constants. The corresponding generic rules were then implemented in the EXGAS code and a mechanism for the oxidation of propene involving 262 species and including 1295 reactions was generated. The predictions of this mechanism were compared with two sets of experimental measurements: the first obtained in a static vessel between 580 and 740 K; the second used a jet-stirred reactor between 900 and 1200 K. If one takes into account that no fitting of individual rate constants was done, the mechanism reproduces correctly both the NTC observed at ~ 630 K and the variations of the concentrations with residence time of C_3H_6 , CO, CO_2 , CH_4 , C_2H_2 , C_2H_4 , C_3H_4 , H_2CO , CH_3CHO , CH_2CHCHO , and cyclic ethers, especially the general shape of these curves and their minima, maxima, and inflection points. In a later paper [259] they use the same mechanism to match

experimental ignition delays for propene obtained in shock tubes [256,257].

Flux and sensitivity analyses were performed to get insight into the kinetic structure of the mechanism explaining the observed characteristics, such as the NTC or the autocatalytic behaviour of the reaction. At low temperatures, these analyses showed that the NTC is mainly due to the reversibility of the addition of oxygen to the adducts which yield degenerate branching agents. At high temperatures, in both kind of reactor, the determining role of termination reactions involving the very abundant allyl radicals has been emphasized, especially the recombination of allyl and hydroperoxy radicals, which is the main source of acrolein.

Reactivity experiments on propene oxidation at 1.3 MPa from 500 to 860 K in a variable pressure flow reactor were carried out by Zheng et al. [260] as well as species times histories for reactants, intermediates and products. A detailed mechanism based on propane work by Qin et al. [141] gave a better account of the experiments than the Heyberger et al. model [258], including correctly predicting the absence of an NTC region.

3.3. Butenes

Iso-butene oxidation and ignition has been studied by Dagaut and Cathonnet [261] in a jet-stirred reactor from 800 to 1230 K and at 100, 500 and 1000 kPa pressure; their results for species concentration profiles and earlier ignition delay measurements of Curran et al. [262,263] were modelled with a 110 species, 743 reactions mechanism. The species profiles are reasonably well simulated although 2-methyl-1 and 2-methyl-2-butenes, acrolein and isoprene are underpredicted.

Baugé et al. [264] describe an experimental and modelling study of the oxidation of *iso*-butene. The low-temperature oxidation was studied in a continuous-flow stirred-tank reactor operated at constant temperature (from 833 to 913 K) and 100 kPa pressure, with fuel equivalence ratios from 3 to 6 and space times ranging from 1 to 10 s corresponding to *iso*-butene conversion yields from 1 to 50%. The ignition delays of *iso*-butene–oxygen–argon mixtures with $1 \leq \phi \leq 3$ were measured behind shock waves from 1230 to 1930 K and pressures from 950 to 1050 kPa. A mechanism is able to reproduce moderately well the profiles obtained for the reactants and the products during the slow oxidation; however, the stoichiometric ignition delays are not well fitted. The main reaction paths have been determined for both series of measurements by both sensitivity and rate of production analysis.

The lean oxidation of *iso*-butene has been studied in a high pressure, plug flow reactor by Chen et al. [265] at 920 K and 600 kPa; the concentrations of 15 intermediates were quantified and compared to the predictions of a mechanism comprised of 3570 reactions of some 850

species on the assumption of isobaric plug flow with no axial diffusion of species or energy. Overall the mechanism underestimated the concentrations of most of the intermediates.

Chen and Bozzelli [266] have analysed the kinetics for the reactions of allylic isobutenyl radical $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2$ with molecular oxygen by using quantum Rice–Ramsperger–Kassel theory for $k(E)$ and master equation analysis for falloff. Thermochemical properties and reaction path parameters were determined by ab initio and density functional calculations and an elementary reaction mechanism constructed to model experiments [267] in *iso*-butene oxidation.

Heyberger et al. [259] have modelled the jet-stirred reactor oxidation [268] and ignition in shock waves of 1-butene with 377 reactions of 180 species valid only above 900 K. The predictions of the mechanism produced for the oxidation of 1-butene compared successfully with both sets of experimental results: the first obtained in a jet-stirred reactor between 900 and 1200 K; the second being new measurements of ignitions delays behind reflected shock waves from 1200 up to 1670 K, pressures from 670 to 900 kPa, equivalence ratios from 0.5 to 2, and with argon as bath gas. Flux and sensitivity analyses show that the role of termination reactions involving the very abundant allylic radicals is less important for 1-butene than for propene.

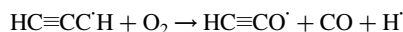
3.4. Higher alkenes and dienes

The autoignition of 1-pentene has been studied by Ribaucour et al. [164] in a rapid compression machine between 600 and 900 K and at 600–900 kPa. The main features are an ignition limit at ~ 700 K, a cool flame region between 700 and 800 K and an NTC near 760–800 K; 1-pentene is less reactive than pentane under the same conditions. The authors discuss their results in terms of a generalised mechanism of 888 reactions between 179 species and focus attention on the formation of cyclic ethers of which propyloxirane is predominant.

A fuel-rich, non-sooting 1-pentene–oxygen–argon low-pressure flame was studied by Alatorre et al. [269] who measured species profiles mass spectroscopically and modelled the results; the authors conclude that pentene consumption to propene and ethene is the dominant reaction and draw parallels with their previous work on propene–oxygen–argon flames [270] whilst benzene formation is governed by propargyl radical recombination.

A low-temperature oxidation and modelling study of cyclohexene by Ribaucour et al. [271] explored the temperature range from 650 to 900 K and pressures of 760–1580 kPa and measured autoignition delay times in a rapid compression machine compared with the predictions of a mechanism comprising 136 species and 1024 reactions.

The oxidation of allene, CH_2CCH_2 , has been studied by Pauwels et al. [272] at 1% concentration in a rich, low-pressure hydrogen/oxygen/argon flame and stable species profiles and OH concentrations measured. Their detailed kinetic model, based on earlier work by Miller and Melius [273], identifies the reaction of C_3H_2 with oxygen as of paramount importance:



The oxidation of 1,3-butadiene has been investigated by Dagaut and Cathonnet [274] in a jet-stirred reactor at high temperature (750–1250 K), variable pressure (100 and 1000 kPa) and variable equivalence ratio ($0.25 \leq \phi \leq 2$). Molecular species concentration profiles for O_2 , H_2 , CO , CO_2 , H_2CO , CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_4 , C_3H_6 , acrolein, 1- and 2-butenes, butadiene, vinylacetylene, cyclopentadiene, and benzene were obtained by probe sampling and GC analysis. The oxidation of butadiene was modelled using a detailed kinetic reaction mechanism (91 species and 666 reactions, most of them reversible) which is able to predict the experimental results reasonably well. Sensitivity analyses and reaction path analyses, based on species net rate of reaction, are used to interpret the results. The routes to benzene formation have been delineated: At low fuel conversion and low temperature, benzene is mostly formed through the addition of vinyl radical to 1,3-butadiene, yielding 1,3-cyclohexadiene, followed by two channels: (a) elimination of molecular hydrogen to yield benzene and (b) decomposition of 1,3-cyclohexadiene yielding cyclohexadienyl followed by its decomposition into benzene and H atom; at high fuel conversion and higher temperature, (c) the recombination of propargyl radicals and (d) the addition of vinyl to vinylacetylene increasingly yield to benzene formation.

Fournet et al. [275] have determined ignition delays for 1,3-butadiene (also acetylene, propyne and allene) at 1000–1650 K and reflected shock pressures of 850–1000 kPa; under similar conditions they find that acetylene is the most reactive followed by butadiene and with allene as reactive as propyne. Their model was also compared to stable and radical species profiles for laminar premixed butadiene flames [276] and acetylene flames [277].

Laskin et al. [152] have studied the high-temperature oxidation of 1,3-butadiene in a flow reactor at 1035–1185 K and at atmospheric pressure. Their kinetic model of 92 species and 613 reactions [278] was validated against shock-tube ignition data [275], laminar flame speeds [234] and pyrolytic work. Three separate pathways for butadiene oxidation were identified with the chemically activated reaction of H-atom with butadiene producing ethylene and vinyl, Fig. 9, radical

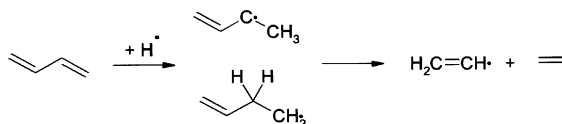


Fig. 9. H-atom addition to butadiene.

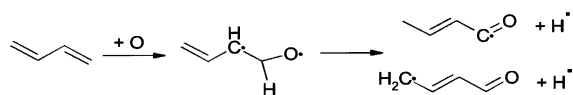


Fig. 10. O-atom addition to butadiene.

being the most important channel of consumption (once the radical pool is established) than the O-atom addition, Fig. 10, over all experimental conditions.

The model is a good fit to the flow reactor data, albeit that the latter are time-shifted, but does not match the ignition delay data that well and it underpredicts the maximum flame speed by $\sim 4 \text{ cm s}^{-1}$.

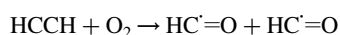
4. Alkynes

4.1. Ethyne

Peeters and Devrient [279] reacted ethyne or acetylene, $\text{HC}\equiv\text{CH}$, and oxygen with O and H-atoms in a fast-flow reactor at 600 K, at a total pressure of 270 kPa and flow times of 1–5 ms. Mass spectrometric sampling determined the concentrations of reactive species such as $\text{C}'\text{H}$, CH_2 , $\text{HC}'\text{CO}$ and HCC' and compared these with a detailed kinetic model which could be simplified by using the measured reactant concentration profiles for C_2H_2 , O, H and O_2 as a given. An additional experiment in which the usual diluent helium was replaced by methane served to confirm the good agreement between the model and experiment.

Hidaka and co-workers [280] studied the oxidation (and pyrolysis) of acetylene behind reflected shocks from 1100 to 2000 K at pressures of 110–260 kPa by analysing reacted gas mixtures and from measurements of ignition delay times. The mixture compositions ranged from 0.5 to 4.0% for ethyne, 0.4–5.0% for oxygen with the balance argon. Existing mechanisms did not give a good fit to the data and so they propose a 103 reaction/38 species model which does.

Ryu et al. [281] studied the detonation characteristics of ethyne behind reflected shock waves from 800 to 1350 K over a very wide range of mixture compositions ($\text{C}_2\text{H}_2:\text{O}_2:\text{Ar} = 2-10:5-32:60-93\%$) and simulated their data with a mechanism of 33 reactions based on earlier work by Hidaka et al. [282]. They identify the formation of formyl as a key step:



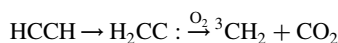
They report that their ignition delay times have essentially zero dependence on oxygen, $\tau \propto [\text{O}_2]^{-0.1}$ and a high dependence on argon, $\tau \propto [\text{Ar}]^{1.33}$; these are not in accord with the Hidaka data, Fig. 8 of [280].

Fournet et al. [275] have measured ignition delays of ethyne (allene, propyne and 1,3-butadiene were also studied under identical conditions) from 1010 to 1380 K and

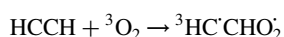
pressures of 850–1000 kPa for three different mixtures whose fuel:oxygen:argon ratios were 1:4:95, 1:8:91 and 3:12:85. As expected the ignition delay times decrease with increasing O_2 content; acetylene is the most reactive fuel followed by butadiene and then propyne = allene (all at a constant O_2), Fig. 11.

Laskin and Wang [283] analysed the reaction between molecular oxygen and acetylene and concluded that isomerisation to vinylidene precedes reaction. Detailed kinetic models which included this initiation process did match experimental [280,282] ignition delays quite well.

The exact routes traced by the direct reaction between acetylene and oxygen have been computed by Sheng and Bozzelli [284] who conclude that at 1000 K and high-pressures Laskin and Wang's isomerisation pathway is viable:



but that another initiation also contributes to acetylene oxidation, namely:



Ethyne oxidation has been addressed numerically with a 114 step mechanism involving 28 species by Varatharajan and Williams [285] who also usefully summarise ignition delay times measured over the years in shock waves.⁸ At high temperatures the ketyl radical, $\text{HC}'=\text{C}=\text{O}$, dominates with the vinyl radical, $\text{H}_2\text{C}=\text{C}'\text{H}$ becoming more important at lower temperatures.

4.2. Propyne

The ignition and oxidation of propyne (and allene) has been studied by Curran et al. [286] in a single-pulse shock-tube from 800 to 2030 K, 200–500 kPa and for $\phi = 0.5 \rightarrow 2$, and, in a jet-stirred reactor from 800 to 1260 K, 100 and 1000 kPa pressure and $\phi = 0.2 \rightarrow 2$. A detailed model provides good agreement for the ignition delay times and for the concentration profiles, obtained with a range of residence times from 20 to 2.4 s in the reactor, for a wide range of intermediates.

Propyne or methylacetylene, $\text{H}_3\text{C}-\text{C}\equiv\text{CH}$, has been studied by Davis and co-workers [287] in the Princeton turbulent flow reactor at atmospheric pressure, at $\sim 1170 \text{ K}$ and for a number of stoichiometries (0.7, 1.0 and 1.4). In addition they measured the laminar flame speeds from $\phi = 0.7-1.7$ in nitrogen-diluted air using the counterflow twin flame technique with corrections for flame-stretch effects. Their detailed kinetic model of 69 species and 437 reactions [288] provides good agreement not just for the flow reactor data but also for ignition

⁸ But not those of Ref. [281].

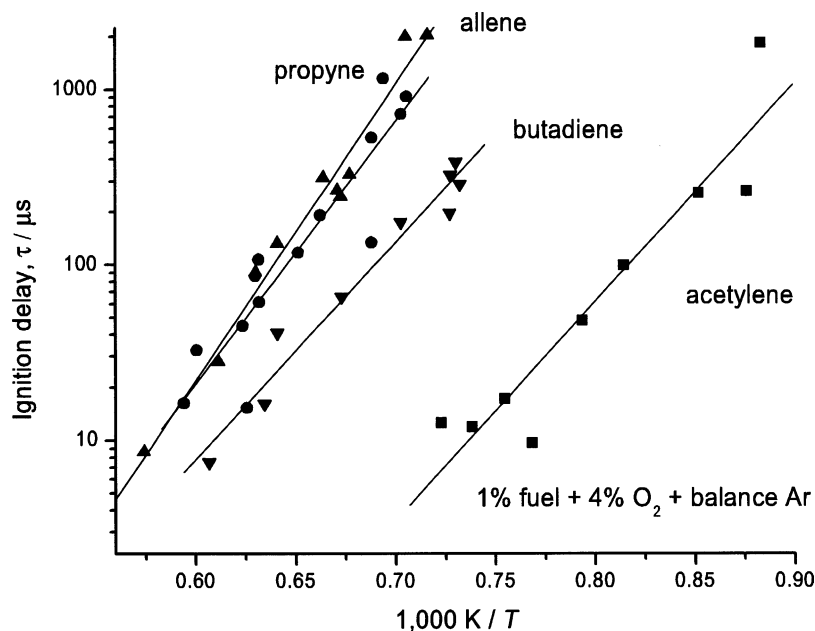
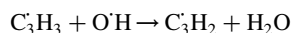
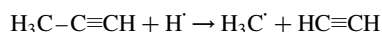


Fig. 11. Propyne, allene, butadiene and acetylene; data from Ref. [275].

delay times obtained previously by Curran et al. [286]; the comparison of flame speeds shows that the model predicts faster flame speeds ($\sim 2 \text{ cm s}^{-1}$) than that observed, fairly uniformly over the whole range of equivalence ratios used. Only the following reactions, involving C_3 species, influence the computed flame speed to any extent:

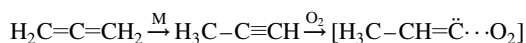


Fournet et al. [275] have measured ignition delays of propyne and allene (acetylene and 1,3-butadiene were also studied under identical conditions) from 1200 to 1720 K and pressures of 850–1000 kPa for three different mixtures whose fuel:oxygen:argon ratios were 1:4:95, 1:8:91 and 3:12:85. As expected the ignition delay times decrease with increasing O_2 content; as found previously [286], the behaviour of allene (technically not an alkyne) is hardly distinguishable from that of methylacetylene. Modelling the results shown in Fig. 11 with Konnov's mechanism [69] gives good qualitative agreement for propyne, allene and butadiene except that the mechanism predicts 10-fold slower ignition delay times but there is good quantitative agreement for acetylene [289].

Data for propyne and allene oxidation was obtained by Faravelli et al. [290] in a jet-stirred reactor at 800–1200 K at 100 and 1000 kPa for different fuel/oxygen equivalent ratios from 0.2 to 2.0. Experiments clearly indicate

the different oxidation behaviour of the two isomers with allene being more reactive than propyne at 1000 kPa and producing more benzene and other hydrocarbons except for acetylene. No O-containing compounds were detected save for CO, CO_2 and H_2CO . Critical reactions are presented and discussed together with extended comparisons of model predictions with their experiments, with Princeton turbulent flow reactor data for propyne [287], with higher temperature shock-tube experiments [286], and with species profiles in an allene-doped fuel-rich acetylene premixed flame [291]. Isomerization reactions proceeding via direct and H addition routes are significant in the oxidation. As a result of H-abstraction reactions, both propyne and allene form the resonance-stabilized propargyl radical. These species are important intermediates in all combustion processes, and their successive reactions are relevant candidates in explaining the formation of aromatic and polyaromatic species, possible precursors of particulate and soot.

Wang [246] has explored the importance of carbenes as free-radical chain initiators in the oxidation of propyne and allene (and ethylene) by combined DFT calculations and kinetic modelling of ignition delay measurements [286] and concludes that a carbene pathway dominates the initial radical pool production. Thus for allene, which isomerises rapidly to propyne, the route is



→ free radicals

with the formation of $\text{H}_3\text{C} + \text{CHO} + \text{CO}$ as the likely outcome. His proposed mechanism is a very good fit to the allene and propyne data, and, quite good for the ethylene results.

4.3. Butynes

An experimental and modelling study of the high-temperature oxidation of both butynes has been carried out from 1100 to 1600 K at pressures of 630–9100 kPa and for equivalence ratios of 0.5–2 by Belmekki et al. [292]; they find that 1-butyne is more reactive than 2-butyne and attribute the difference to the easier formation of $\text{HC}\equiv\text{C}-\text{C}\equiv\text{H}_2$ radicals from 1 than $\text{CH}_3-\text{C}\equiv\text{C}$ from 2. Their mechanism is also used to simulate thermal decomposition species profiles obtained in shock waves by Hidaka et al. for 1-butyne [293] and 2-butyne [294] with reasonable agreement.

4.4. Diynes

A shockwave and modelling study of diacetylene, $\text{HC}\equiv\text{CC}\equiv\text{CH}$, oxidation and pyrolysis by Hidaka et al. [295] was carried out from 1100 to 2000 K and 110–260 kPa for mixtures with $0.5 \leq \phi \leq 2$. Species profiles were obtained for the parent itself, ethyne, CO, CO_2 and H_2 for reaction times of ~ 2 ms as well as induction times at a constant initial (preincident shock) pressure of 6670 Pa. The mechanism of 466 reactions involving 83 species which could be condensed down to 174 reactions of 51 species accounted reasonably well for their data.

5. Aromatics

The modelling of aromatic compounds present special difficulties and kinetic complexities beyond those of most other hydrocarbons; for example, modelling of benzene oxidation is inextricably linked with the formation of higher polycyclic aromatic hydrocarbons and soot [12,13]. Some of the work in this area has been described, in a telling phrase, as ‘an extensive literature of bad assumptions’ caused no doubt by the paucity of experimental data and the lack of theoretical models to guide the researcher.

5.1. Benzene

Zhang and McKinnon [296] have developed an elementary reaction mechanism containing 514 reactions without adjusted parameters for the low-pressure flaming rich combustion of benzene. Key features of the mechanism are accounting for pressure-dependent unimolecular and bimolecular (chemically activated) reactions using QRRK, inclusion of singlet methylene chemistry, and phenyl radical oxidation and pyrolysis reactions. The results are compared to earlier detailed molecule and free-radical profiles

measured using a molecular beam mass spectrometer by Bittner and Howard [297]. In general, the mechanism does a good job of predicting stable species and free-radical profiles in the flame. The computed profiles of small free radicals, such as H-atom or OH, match the data quite well. The largest discrepancies between the model and experiment are phenyl radical and phenoxy radical concentrations.

A detailed comprehensive kinetic mechanism has been developed through reaction path flux and sensitivity analysis by Tan and Frank [298] to model species profiles in a rich, near-sooting benzene–oxygen–argon flame [297], speeds of freely propagating benzene–oxygen–nitrogen flames [299] and ignition delays of a mixture of 1.69% benzene + 12.7% oxygen with the balance argon [300]. Although generally speaking good agreement was obtained, the reactions of C_5 species are not satisfactory.

Benzene–air flame speeds were measured by Davis et al. [301] in an atmospheric pressure counterflow flame for $0.8 \leq \phi \leq 1.4$ and compared to predictions from mechanisms due to Emdee et al. [302] and Lindstedt and Skevis [303]; a modified version of the Emdee mechanism not only gave good agreement with the flame speeds but also retained the ability to give a good fit to atmospheric pressure flow reactor data for benzene oxidation at temperatures of 1000–1200 K [302].

Benzene oxidation at two equivalence ratios ($\phi = 0.19$ and 1.02) was studied by Chai and Pfefferle in a well-mixed reactor with a 50 ms mean residence time at 350 Torr and 900–1300 K [304]. Acetylene was the major hydrocarbon intermediate for both stoichiometries with phenol ($\text{C}_6\text{H}_5\text{OH}$) and acrolein ($\text{H}_2\text{C}=\text{CH}-\text{CHO}$) reaching significant concentrations for the lean condition, while at the stoichiometric condition C_4H_4 is more than twice as abundant compared to the lean case, and phenol and acrolein are minor intermediates. The predominant radical species for both conditions is cyclopentadienyl while cyclopentadienonyl and phenoxy ($\text{C}_6\text{H}_5\text{O}$) are the next most abundant radical species detected in the lean condition.

Marinov et al. [110] studied the chemical structure of an opposed-flow methane diffusion flame operated in such a way as to highlight the routes to mono and polycyclic aromatic hydrocarbons and modelled the results with a methane mechanism of 156 species participating in 680 reactions. They found good agreement for the large hydrocarbon aliphatic compounds, aromatics (benzene, toluene, phenylacetylene, styrene), two- and three-ring polycyclics (naphthalene, acenaphthalene, phenanthrene, anthracene) but not with four-membered rings (pyrene and fluoranthene).

Alzueta et al. [305] have carried out an experimental study of benzene oxidation in a plug-flow reactor at 900–1450 K and residence times of ~ 150 ms; they reacted 107 ppm of benzene with between 830 and 491,000 ppm of

O₂ in the presence of 0.5–2% H₂O. They compared their detailed kinetic model to data from turbulent flow [306] and jet-stirred [304] reactors studies (but not to any flame data), and, conclude that the flow and stirred reactor data are incompatible.

Schöbel [307] has studied the oxidation of benzene in a plug-flow reactor at intermediate temperatures, 850–960 K, and at atmospheric pressure with a view to understanding the fate of benzene in the burnout zones of waste incinerators. He measured species profiles as a function of residence time, temperature and oxygen concentration and compared the results with simulations based on detailed models from Zhang and McKinnon [296], Emdee et al. [302] and Zhong and Bozzelli [308]. The generally poor agreement with these existing models necessitated extensive modifications to the Zhang and McKinnon model which then gave satisfactory agreement.

Ristori et al. [309] have studied benzene oxidation in a jet-stirred reactor at atmospheric pressure from 1010 to 1295 K for $0.3 \leq \phi \leq 2$. They have also modelled shock tube and flame experiments [301], well-mixed reactor data [304] and their own perfectly stirred reactor results at 1000 kPa. The mechanism is a particularly good fit to the benzene–air flame speed data and it performs reasonably well for other simulations thus laying the foundations for modelling the kinetics of more complex aromatics. Sensitivity analysis reveals that reactions of the cyclopentadienyl, phenyl and phenoxy radicals are important, Fig. 12.

Lindstedt et al. [310] highlight some current issues in the formation and oxidation of aromatics in the context of detailed kinetic modelling of benzene and butadiene flames and stirred reactors featuring ethylene and mixed aromatic–ethylene–hydrogen fuels. In particular, uncertainties pertaining to the rates and product distributions of a range of possible naphthalene and indene formation sequences are discussed from the basis of improved predictions of key intermediates. The naphthalene formation paths considered include initiation via cyclopentadienyl radicals, phenyl + vinylacetylene, and benzyl + propargyl recombination. It is shown that a number of possible formation channels are plausible and that their relative importance is strongly dependent upon oxidation conditions. Particular emphasis is placed on the investigation of formation paths leading to isomeric indene, C₉H₈, structures. The latter are typically ignored despite measured concentrations similar to those of naphthalene. The rates of formation of C₉H₈ compounds are consistent with sequences initiated by reactions of phenyl with propargyl, C₆H₅ + C₃H₃, and with allene,

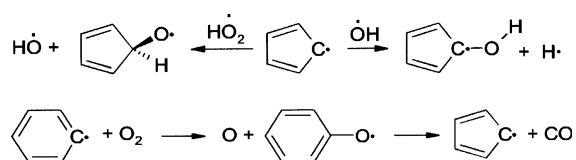


Fig. 12. Reactions of phenyl and cyclopentadienyl radicals.

C₆H₅ + C₃H₄, leading to indene through repeated isomerisation reactions. The current work also shows that reactions of the indenyl radical with methyl and with triplet methylene provide a mass growth source that link five- and six-member ring structures.

Richter and Howard in a very long paper discuss the formation and consumption of single-ring aromatic hydrocarbons and their precursors in premixed laminar benzene, acetylene and ethene low-pressure flames [311] with the predictive ability of their detailed model [312] ranging from excellent to fair for the consumption of reactants, formation of major combustion products and formation/destruction of intermediates. Self-combination of propargyl, H₂C=C=C·H, followed by ring closure and rearrangement is shown to be the dominant route for benzene formation in rich acetylene and ethylene flames whilst phenoxy radical overprediction is still a problem in determining the fate of phenyl radical oxidation.

5.2. Other aromatics

Although benzene is the archetypal aromatic, work on toluene and on other aromatics is probably more representative of the chemistry that will be encountered in the study of real fuels, from which of course benzene has been excluded by regulatory authorities.

A detailed chemical kinetic mechanism for the combustion of toluene has been assembled and evaluated by Lindstedt and Maurice [313] for a wide range of oxidation regimes including counterflow diffusion flames [176], plug flow reactors [314] and premixed flames (more accessible from [234]), and, for shock-tube pyrolytic experiments [315, 316]. The reaction mechanism features 743 elementary reactions and 141 species and represents an attempt to develop a chemical kinetic mechanism applicable to intermediate and high-temperature oxidation. Toluene thermal decomposition and radical attack reactions leading to oxygenated species are given particular attention. The benzyl radical sub-mechanism is expanded to include isomerisation and thermal decomposition reactions, which are important at flame temperatures, and a molecular oxygen attack path to form the benzylperoxy radical, which is found to be relevant at lower temperatures. The final toluene kinetic model results in excellent fuel consumption profiles in both flames and plug flow reactors and sensible predictions of the temporal evolution of the hydrogen radical and pyrolysis products in shock-tube experiments. The structures of toluene/*n*-heptane, toluene/*n*-heptane/methanol and toluene/methanol diffusion flames are predicted with reasonable quantitative agreement for major and minor species profiles. Furthermore, the evolution of major and intermediate species in plug flow reactors is well modelled and excellent laminar burning velocity predictions have also been achieved.

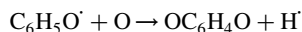
A chemical kinetic model was developed by Klotz et al. [317] to predict the high-temperature oxidation of neat

toluene, neat butane, and toluene–butane blends in an atmospheric-pressure flow reactor at 1170 K. The focus of this study was on the behaviour of the blended fuel but extensive validation of the toluene mechanism was also undertaken during which it emerged that improvements were needed in the toluene model of Emdee et al. [302]. The changes include addition of *iso*-butyl reactions, which significantly improved predictions for 1,3-butadiene and acetylene. Additionally, improvements were made in the modelling of benzaldehyde since the experimentally measured benzaldehyde profiles were obtained with a gas chromatograph better configured to separate polar compounds than in previous experimental toluene studies, and these better profiles led to the adoption of a more appropriate rate constant for the overall reaction that accounts for the formation of benzaldehyde during the oxidation of toluene, $C_6H_5CH_2 + HO_2 \rightarrow C_6H_5CHO + OH + H$. The modelling results presented demonstrate that when the chemical interactions between the various fuel components are limited to radical pool effects, the blended fuel oxidation process is more likely to be predicted when the blend model is properly configured to predict the oxidation processes of the neat fuel components.

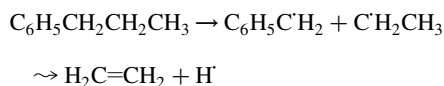
The oxidation of toluene at high dilution in nitrogen was studied in a jet-stirred reactor at 100 kPa by Dagaut and co-workers [318] over the temperature range 1000–1375 K, 70–120 ms residence times and variable equivalence ratios, $0.5 \leq \phi \leq 1.5$. Concentration profiles of reactants, stable intermediates and final products were measured by probe sampling followed by on-line and off-line GC analyses. These experiments were modelled using a detailed kinetic reaction mechanism (120 species and 920 reactions) and, used to simulate the ignition of toluene–oxygen–argon mixtures [319] and the burning velocities of toluene–air mixtures [301,234]; there is good agreement with ignition delay data and with flame speeds for $\phi \leq 1.2$. Sensitivity analyses and reaction path analyses, based on species rates of reaction, were used to interpret the results. The routes involved in toluene oxidation have been delineated: toluene oxidation proceeds via the formation of benzyl, by H-atom abstraction, and the formation of benzene, by H-atom displacement yielding methyl and benzene; benzyl oxidation yields benzaldehyde, that further reacts yielding phenyl whereas benzyl thermal decomposition yields acetylene and cyclopentadienyl; further reactions of cyclopentadienyl yield vinylacetylene.

Shock-tube measurements of species profiles obtained in toluene/oxygen/argon mixtures ($\phi = 1$ and 5) at very high pressure, over 60 MPa, from 1250 to 1450 K have been made by Sivaramakrishnan et al. [320] and modelled against the mechanisms of Klotz et al. [317] and of Dagaut et al. [318]. The latter model severely underpredicts the rate of toluene decay as well as the concentrations of benzene and carbon monoxide so the former mechanism was chosen for slight modifications; the addition of *para*-quinone channels,

inter alia, improved the fit:



In the case of propylbenzene [321] concentration profiles for 23 species were obtained at atmospheric pressure over the temperature range 900–1250 K for 70 ms dwell time and at three stoichiometries (0.5, 1.0 and 1.5). *n*-Propylbenzene is more reactive than toluene with the production of ethyl radicals identified as the key early step in the production of reactive H-atoms:



The low-temperature oxidation of butylbenzene was studied at temperatures between 640 and 840 K by Ribaucour et al. [322] in a rapid compression machine. They measured delay times of one- and two-stage autoignitions and intermediate species concentrations after the cool flame and modelled the results with a mechanism of 1149 reaction and 197 species.

Autoignition data for 11 alkylbenzenes was collected by Roubaud et al. [323] from 600 to 900 K and at compressed gas pressures up to 2500 kPa. Toluene, *m*- and *p*-xylenes and 1,3,5-trimethylbenzene ignite only above 900 K and 1600 kPa whilst *o*-xylene, ethyl, propyl and *n*-butylbenzenes, 1,2,3- and 1,2,4-trimethylbenzenes and 2-ethyltoluene ignite at much lower temperatures and pressures. A more detailed study by the same group [324] concentrated on *o*-xylene, *o*-ethyltoluene and *n*-butylbenzene and obtained samples of the intermediates formed at 10, 20 and 35% fuel consumption, respectively.

Work on 1-methylnaphthalene by Pitsch [325] and Shaddix et al. [326] is indicative of the complexity that awaits when multi-cyclic aromatics are tackled—a daunting prospect.

6. Conclusions

The ultimate goal of chemical kinetic modelling is to develop an ideal set of thermodynamic data and a 'perfect' reaction mechanism which will describe all the essential details of the physical reality, specifically the combustion of a hydrocarbon in the gas-phase. Some sense of how far we have progressed can be gleaned from the preceding text.

A series of cooperative efforts are required to progress the field, unless there are some dramatic developments on the theoretical side which enable both the calculation of reaction pathways and rate coefficients of individual reactions with reasonable precision. Great strides have been made of late in the computation of rate constants (a masterly summary by Wagner [327] on the challenges of combustion for chemical theory is available) but it can be an acronymic nightmare for the unwary. Since

individual rate constants, k , are required as functions of temperature and of pressure, $k = f(T, p)$, this adds substantially to the burden. Initiatives such as CSEO [328] which provide, inter alia, online computations of rate constants are most welcome and are a signpost for the future.

On the experimental side a number of different approaches are required including the measurement of a few selected critically important rate coefficients, the measurement of concentration profiles (not just for stable species but also for such species as O'H, H, HO₂, etc.) in flow reactors, shock waves and burners, the determination of complex parameters such as laminar flame velocities, ignition delay times, et cetera. Since this variety of experimental techniques is rarely, if ever, available in one laboratory, it reinforces the notion that co-operative research is essential.

Once all of this hard-won data has been gathered it must be properly accessible. A substantial effort is required to render known data into more useful formats which will eliminate the problem of nomenclature, encourage data mining techniques, enhance portability and reduce wheel re-invention. In particular the archiving of data needs to be made more rigorous; many of the links mentioned here have very short time spans.

Finally, modelling just your own experiments with your own mechanism is scientifically worth very little (unless there is no other data of course) and one would hope that journal editors and referees would discourage researchers from such excessive introspection.

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