AIAA JOURNAL
Vol. 41, No. 9, September 2003

Development of Comprehensive Detailed and Reduced Reaction Mechanisms for Combustion Modeling

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Presented as Paper 2002-0331 at the AIAA 40th Aerospace Sciences Meeting, Reno, NV, 14–17 January 2002; received 5 December 2002; revision received 6 March 2003; accepted for publication 10 March 2003.

Introduction

HISTORICALLY, the role of chemistry in the modeling of combustion processes was handled in a rather rudimentary manner. For example, chemical equilibrium was assumed in the analysis of internal combustion engine cycles, whereas infinitely fast chemistry was used in the study of diffusion flames. In situations where finite-rate chemistry was intrinsically important, as in premixed flame propagation, the one-step overall, Arrhenius-sensitive, reaction was frequently used.

Since the late 1970s, however, the fundamental importance of chemical kinetics in combustion phenomena, beyond the one-step description and frequently involving chain mechanisms, has been gradually appreciated by those whose technical background is not in chemical kinetics. Meanwhile, there has been a tremendous growth of detailed chemistry knowledge (e.g., Refs. 1–6) that started as well as built upon the pioneering work of Dixon–Lewis[7] in flame simulation. Consequently, at present it is a fairly routine matter to describe laminar flames of simple configurations with detailed chemistry and to model turbulent flames and engine combustion processes with mechanisms consisting of several semiglobal steps. These reduced mechanisms are substantially simpler than the detailed mechanisms, but nevertheless embody some essential elements of the kinetic pathways, and as such can be sufficiently descriptive. Notable among them are the celebrated four-step mechanism of Peters and Williams[8] and the recently proposed 12-step mechanism of Sung et al.[9] for methane oxidation. These simplifications are necessary because of the simultaneous demand of computational capability to describe the complex flowfields associated with realistic and practical combustion phenomena.

This heightened awareness of the importance of chemical kinetics in combustion has led to a corresponding proliferation in the development of detailed and reduced mechanisms and in studies in which these mechanisms are incorporated. Although this increased activity has yielded significant advance in fundamental and practical combustion, there has also been increasing concern over the adequacy of some of the mechanisms proposed, as well as the appropriateness in applying mechanisms beyond their parametric ranges of validity. The controlling issue here is the comprehensiveness of a given mechanism.[2] That is, because of the coupled and nonlinear nature of the chemical reaction rates and pathways with respect to temperature, pressure, and species composition, and the extended ranges over which these parameters can vary, say either locally within a flame structure or globally through the operating conditions of an engine, a mechanism is considered to be adequate only if it can describe all relevant chemical responses over the diverse ranges of parametric and system variations that are expected to occur.

In view of the preceding considerations, the objectives of the present paper are the following. We shall first demonstrate the inadequacy of the one-step overall reaction in describing some well-known combustion phenomena and thereby the need for kinetic mechanisms beyond such a simplified description. We shall then show that mechanisms with sufficient comprehensiveness, however, do not exist, even for the simplest fuel, hydrogen, and the relatively simple hydrocarbon fuels, methane and benzene. Strategies towards systematic development of detailed kinetic mechanisms are subsequently presented.

We shall then discuss the approaches towards developing reduced mechanisms from detailed mechanisms, with minimal loss of comprehensiveness. The performance of the 12-step reduced mechanism for methane oxidation[9] will be demonstrated.

The last topic to be covered is the role of the transport coefficients in combustion modeling. Inaccuracies and uncertainties in these coefficients could exert influences of the same order of magnitude as those imposed by kinetics on the calculated flame responses. Indeed, such influences can be masqueraded as those caused by kinetics, and consequently mislead the direction in mechanism development and thereby contaminate the eventual simulation.

The present paper is an updated and condensed version of Ref. 10, which was presented at the 40th Aerospace Sciences Meeting of the AIAA in January 2002. It is also to be noted that the primary aim of this paper is to advocate the importance of fidelity in the chemical representation in combustion modeling to those whose research focus is not on chemical kinetics. Because it is not the aim of the paper to provide a review on the merits of various mechanisms in the literature for the chemistry community, mechanisms from and studies by various research groups on chemical kinetics may not be specifically referenced and discussed.

Role of Complex Chemical Kinetics in Combustion Phenomena

H_2/O_2 Kinetics

To demonstrate the intrinsic nonlinear and nonmonotonic influence of chemical kinetic mechanisms on the response of transport-affected combustion phenomena, we first consider the three explosion limits of the hydrogen/oxygen system, as shown in Fig. 1. Because hydrogen is the smallest of the fuel molecules, and because its oxidation does not involve carbon-related species as would the hydrocarbons, its response to the intricate chain pathways can be sharply expressed and readily identified. Furthermore, because hydrogen oxidation constitutes a major building block for hydrocarbon oxidation, its influence is expected to be carried over to the response of hydrocarbons.

Referring to Fig. 1, we see that for a fixed mixture temperature which is not too high the mixture becomes explosive, nonexplosive, and explosive again as its pressure is gradually increased from a low, nonexplosive value and crosses the first, second, and third limits, respectively. Kinetically, it is well established that as the pressure crosses the first limit, diffusive loss of the key radicals responsible for chain branching, namely H, O, and OH, is diminished such that the chain branching cycle

$$H + O_2 \rightarrow O + OH \tag{R1}$$

$$O + H_2 \rightarrow H + OH \tag{R2}$$

$$OH + H_2 \rightarrow H_2O + H \tag{R3}$$

proceeds uninhibited. With further increase in pressure, the three-body termination reaction

$$H + O_2 + M \rightarrow HO_2 + M \tag{R9}$$

becomes important, removing H from the radical pool until the net reaction is terminated at the second limit.

It can also be readily shown that the second limit can be approximated by

$$p_C = \frac{2k_1(T_C)}{k_9(T_C,\, p_C)} \tag{1}$$

where p_C and T_C are respectively the crossover pressure and temperature defining this relation, $k_1(T_C)$ and $k_9(T_C, p_C)$ are the reaction-rate constants of (R1) and (R9), and the dependence of k_9 on p_C signifies the influence caused by pressure fall-off. This relation is shown in Fig. 2.

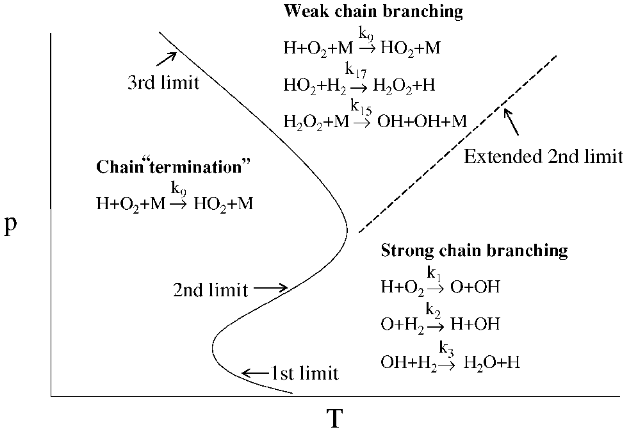

Fig. 1 Schematic of the three explosion limits of homogeneous hydrogen/oxygen mixtures, showing their nonmonotonic behavior and the extended second limit.

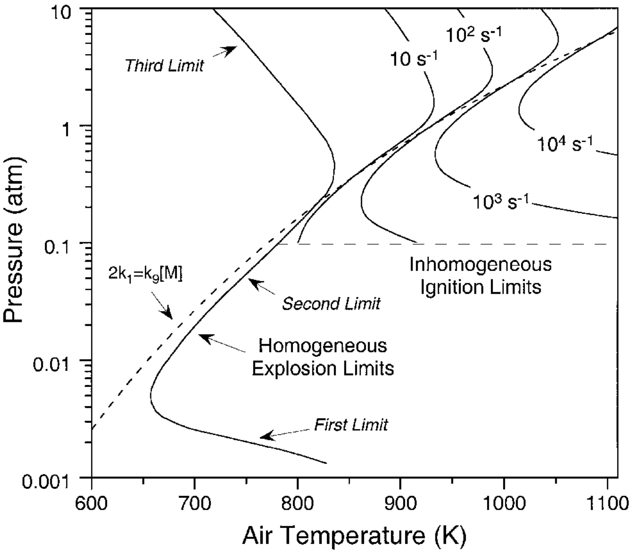

Fig. 2 Ignition–extinction S curves of counterflowing 60% H_2-in-N_2 vs heated air for different pressure-weighted strain rates, superimposed on the homogeneous explosion limit curve.[17]

At the third limit reactions involving the HO_2 and H_2O_2 radicals

$$HO_2 + H \rightarrow OH + OH \qquad (R11)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (R14)$$

$$H_2O_2 + M \rightarrow OH + OH + M \qquad (R15)$$

$$HO_2 + H_2 \rightarrow H_2O_2 + H \qquad (R17)$$

constitute a high-pressure chain branching cycle, releasing the reactive radicals H and OH.

For mixtures at higher temperatures, the third limit is not distinctively exhibited, although reactivity of the mixture is still governed by the gradual transition from the strong H-O_2 branching at lower pressures to the weaker HO_2-H_2O_2 branching at higher pressures, traversing a regime identified as the extended second limit.[11]

Chain-branching reactions, say (R1), frequently involve two-body collisions that are highly temperature sensitive, characterized by large activation energies. On the other hand, many termination reactions, say (R9), involve three-body collisions that are temperature insensitive, characterized by zero activation energies. Thus, increasing temperature and pressure respectively facilitate the branching and termination reactions.

In view of the highly nonmonotonic dependence of the reaction rates with pressure and temperature, it is a futile effort to attempt to approximate the reaction rate w by that of a one-step overall reaction

$$w = AC_F C_O p^n \exp(-E_a/RT) \qquad (2)$$

with constant values of the overall reaction order n and activation energy E_a, which respectively measure the system sensitivity to variations in pressure and temperature. In particular, we expect that n will change from positive, to negative, and to positive again as a homogeneous mixture traverses the three explosion limits. Thus n not only is not a constant, it also does not assume the value of two, which is frequently used to represent the two-reactant nature of a global fuel-oxidizer reaction. Furthermore, E_a should also increase with increasing pressure towards the second limit, as the progress of the overall reaction is slowed down, and subsequently decrease as it traverses through the third limit.

In the presence of diffusive and convective transport, and for hydrocarbon fuels, elements of these trends are expected to be preserved, though at levels which are not as sharp. We shall demonstrate in the following how the nonmonotonic nature of the H_2/O_2 kinetic mechanism exerts its influence on the behavior of several combustion phenomena.

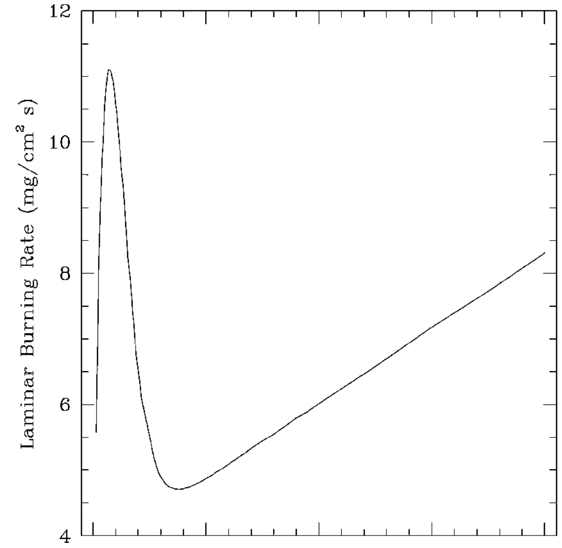

Fig. 3a Nonmonotonic variation of the laminar burning rates of hydrogen/air mixtures (ϕ = 0.35) with pressure, reflecting the corresponding nonmonotonic influence of the homogeneous mixture shown in Fig. 1.[12]

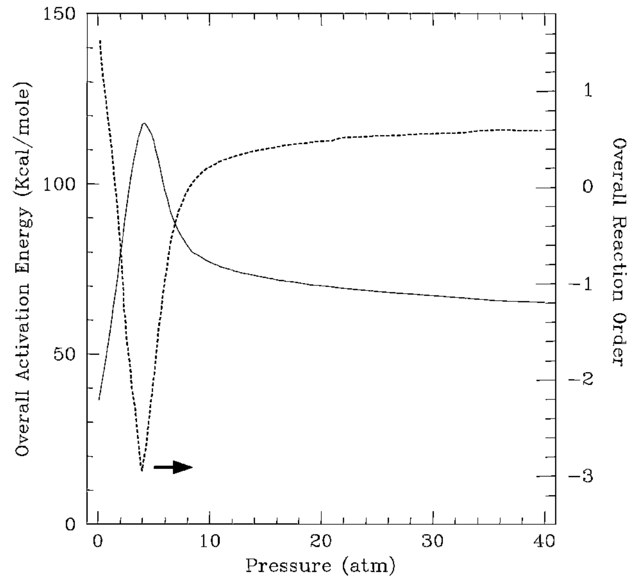

Fig. 3b Overall reaction orders and overall activation energies extracted from the laminar burning rates of Fig. 3a. The overall reaction order can assume negative values, and the overall activation energies show substantial variations with pressure.[12]

Global Kinetic Parameters for Flame Propagation

Figure 3a shows the computed laminar burning rates (per unit area) of the adiabatic, one-dimensional, planar, freely propagating flame, $m^o = \rho_u s_L$, vs the system pressure, for hydrogen/air mixtures with equivalence ratio of $\phi = 0.35$, where ρ_u is the density of the freestream and s_L the laminar flame speed.[12] The kinetic mechanism used is that of Mueller et al.[11] It is seen that, with increasing pressure, m^o first increases, then decreases, and finally increases again. This behavior is consistent with the trend shown in Fig. 1 for the homogeneous system. Specifically, the initial increasing segment is controlled by the fast branching cycle of (R1–R3). At higher pressures the rate of (R9) becomes greater than that of (R1) because of the pressure-sensitive nature of the three-body reaction. This results in the decrease of the burning rate with increasing pressure, which is an outcome not anticipated from a one-step overall reaction description. Finally, the burning rate increases with pressure again when the HO_2-H_2O_2 branching cycle becomes active at even higher pressures.

Because the burning rate of the flame varies with the reaction rate through $m^o \sim w^{1/2}$, the overall reaction order n as a function of pressure can be extracted[13] from the computed results of Fig. 3a based on Eq. (2),

$$n = \frac{2\partial \ln(m^o)}{\partial \ln(p)} \tag{3}$$

Figure 3b shows its decreasing and increasing trends with increasing pressure, and the attainment of negative values over a substantial range in pressure, as anticipated from Fig. 3a. Furthermore, n appears to approach a value around two as the pressure steadily decreases. This is reasonable because the influence of the three-body reactions decreases with decreasing pressure while reactions that exhibit (pseudo) first-order behavior at higher pressures would revert back to their true second-order behavior according to the concept of the Lindemann mechanism. Consequently, all elementary reactions of importance are second order, resulting in a corresponding second-order response for the global reaction.

The overall activation energy can also be extracted[13] from Eq. (2) through the relation

$$E_a = -\frac{2R\partial \ln(m^o)}{\partial(1/T_{\mathrm{ad}})} \tag{4}$$

where T_{ad} is the adiabatic flame temperature. The numerical differentiation can be conducted by substituting a small portion of N_2 by Ar so as to effect a small change in T_{ad} without affecting the reactant concentrations. Figure 3b then shows that E_a first increases and then decreases, demonstrating the initial progressive importance of the termination reaction (R9) and the subsequent emergence of the HO_2-H_2O_2 branching cycle. Considering the sensitive nature with which the reaction rate varies with E_a, the adoption of a constant E_a can therefore greatly falsify the actual progress of the reaction, especially within the highly nonmonotonic regime in which E_a exhibits a prominent peak.

Although we have demonstrated the sensitive variations of n and E_a with pressure, Fig. 3b also shows that these sensitivities are significantly diminished at higher pressures such that n and E_a appear to assume fairly constant values for pressures higher than about 10 atm. This result indicates that the pressure-dependent transition is over and the chemistry has now settled to that of HO_2-H_2O_2 branching. It further suggests that there do exist situations under which the one-step overall reaction with constant kinetic parameters could be possibly used. For the present example, they involve hydrogen flame propagation in sufficiently lean, elevated pressure environments.

We next demonstrate that the highly nonmonotonic response of the hydrogen oxidation mechanism is indeed carried over to the response of hydrocarbon flames.[14] Figure 4 shows the calculated m^o, n, and E_a of methane/air flames at $\phi = 0.67$. The kinetic mechanism used was GRI-Mech 3.0 (Ref. 15). Figure 4a shows the decreasing and increasing trend of n with increasing pressure, in qualitative agreement with the hydrogen case. The limiting value of n approaching two at low pressures is again noted. The effects of the three-body termination reactions, however, are not sufficiently strong to produce negative values of n, hence the absence of the decreasing portion of the burning-rate curve in Fig. 4a. A nonmonotonic and significant variation of E_a over the pressure range is also noted in Fig. 4b.

The preceding results demonstrate conclusively the inadequacy of the one-step overall reaction with constant kinetic parameters for applications with extensive parametric ranges of variation. A viable approach that could take care of this difficulty is to use variable kinetic parameters, say $n = n(p, \phi)$ and $E_a = E_a(p, \phi)$. However, there exist other situations indicating that even this modification is not adequate. This then brings us to consider a second manifestation of the limitation of the one-step overall reaction.

Kinetically Controlled Ignition in Diffusive-Convective Systems

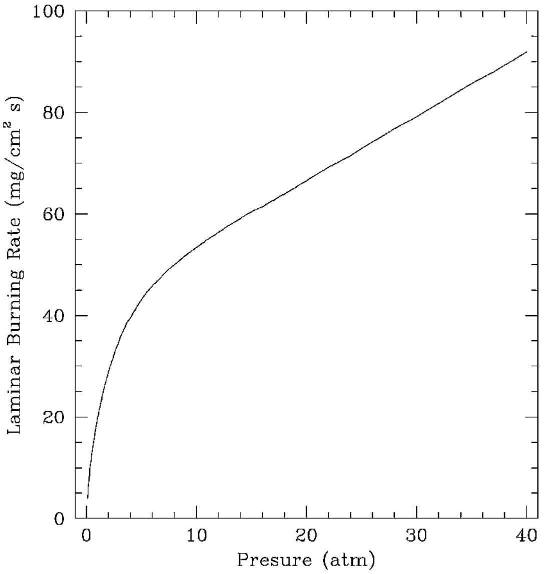

Fig. 4a Nonlinear variations of the laminar burning rates of methane/air mixtures (ϕ = 0.67) with pressure, reflecting the nonmonotonic influences of the homogeneous hydrogen/oxygen mixture shown in Fig. 1.[12]

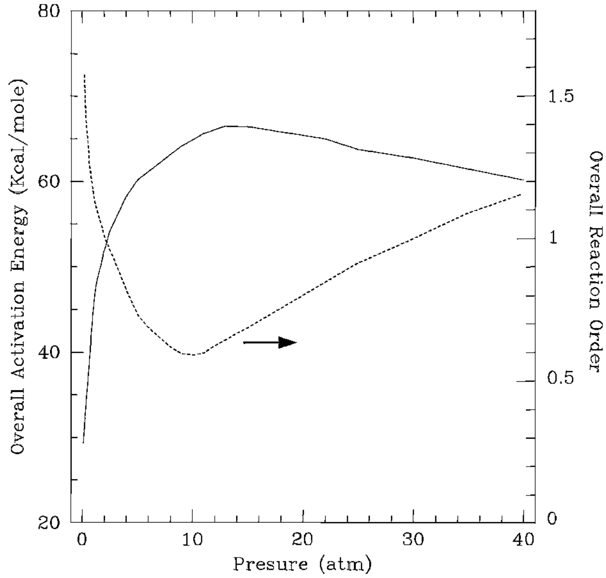

Fig. 4b Overall reaction orders and overall activation energies extracted from the laminar burning rates of Fig. 4a.[12]

We now extend the homogeneous ignition system of Fig. 1 to a nonhomogeneous one, involving convection and diffusion. The specific problem considered is the ignition of a cold hydrogen/inert jet by a counterflowing hot air jet.[16–18] The presence of the flow imposes a characteristic timescale on the system, namely, the inverse of the flow strain rate. It is therefore reasonable to expect that by either increasing the air temperature or decreasing the flow strain rate a state is reached at which the system runs away. This is shown in Fig. 5, in which the peak hydrogen mole fraction and the maximum temperature are plotted vs the strain rate, at a state that is close to the second limit, with $p = 1$ atm and $T_{\mathrm{air}} = 930$ K. The peak hydrogen concentration profile clearly exhibits the characteristic ignition and extinction turning points. From these ignition turning points the states of ignition can be mapped as functions of the system pressure and the air temperature for given strain rates. These stretch-affected ignition boundaries are plotted in Fig. 2. It is seen that they retain the same Z-shaped response as the homogeneous explosion limits, but are displaced to higher values of temperature and pressure with increasing strain rate. The extent of displacement of the different segments of the Z curves, however, depends on the pressure. To demonstrate this point, we first note from Fig. 5b that the maximum temperature in the flow for the lower, ignition branch is basically a constant, independent of the strain rate, and thereby exhibiting a cusped ignition turning point. The ignition event therefore involves

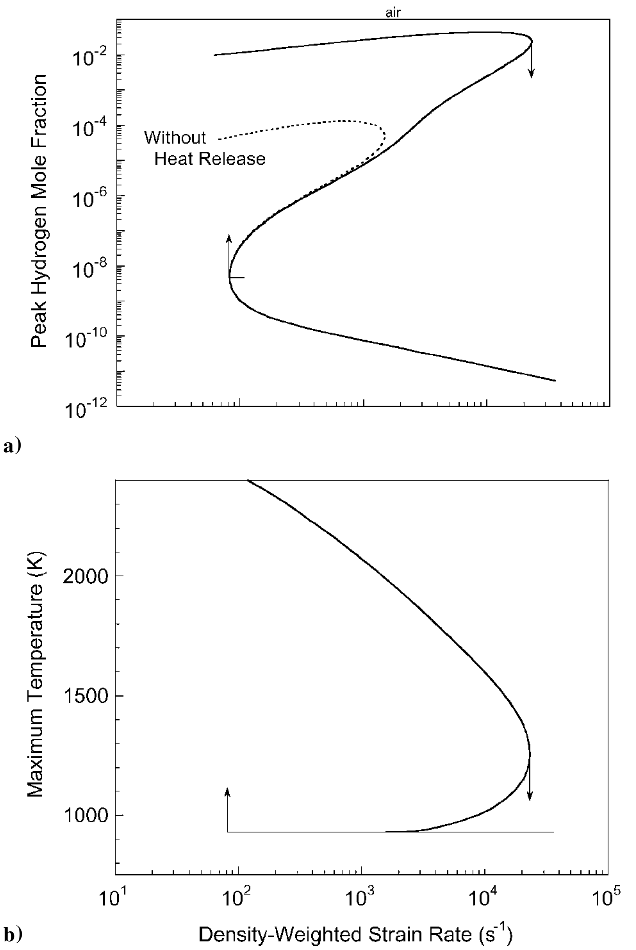

Fig. 5 Ignition–extinction S curves of counterflowing 60% H_2-in-N_2 vs heated air for the second ignition limit ($p = 1$ atm, $T_{air} = 930$ K) obtained by plotting a) the maximum H mole fraction and b) the maximum temperature, as functions of the strain rate.[16]

minimal amount of heat release. Indeed, a similar calculation with all chemical heat-release terms suppressed yielded almost identical results for the lower and middle segments of the ignition–extinction response curve in Fig. 5a. Thus, ignition for this case is kinetically controlled, involving radical instead of thermal runaway. To further demonstrate this unique behavior, Fig. 6 plots the ignition temperature as a function of the strain rate. It is then quite remarkable to note that, over a wide range of strain rate variations, the ignition temperature at one atmosphere pressure is almost independent of the flow strain rate. This is completely contrary to the expectation based on a one-step overall reaction. The fundamental reason here is that the controlling reactions occur so fast that their progress is independent of the flow rate. In other words, the reactions are basically decoupled from the flow, behaving like a pure chemical system.

Ignition Distance in Supersonic Mixing Layers

The influence of complex chemistry becomes particularly significant for systems with short residence times such as those involving supersonic combustion. As an example, consider the numerically calculated ignition distance x_{ig} in a supersonic laminar mixing layer of nonpremixed hydrogen and high-temperature air as a function of the system pressure, for given freestream air temperatures,[19] as shown in Fig. 7. It is seen that with increasing pressure the ignition distance first decreases, then increases, and then decreases again, with the increasing segment being rather abrupt and substantial. Such a nonmonotonic behavior again reflects the explosion limit behavior of the hydrogen-oxygen system. Attempts towards describing this behavior with one-step overall reaction are obviously futile.

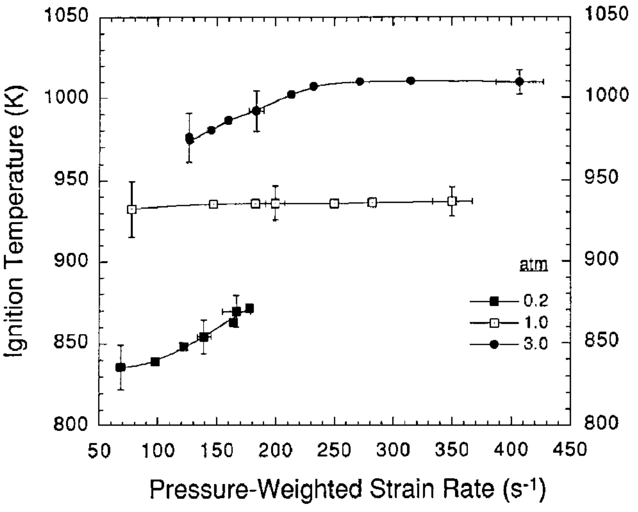

Fig. 6 Experimental ignition temperature as function of the pressure-weighted strain rate for three different pressures, showing regimes within which it is remarkably insensitive to strain rate variations.[18]

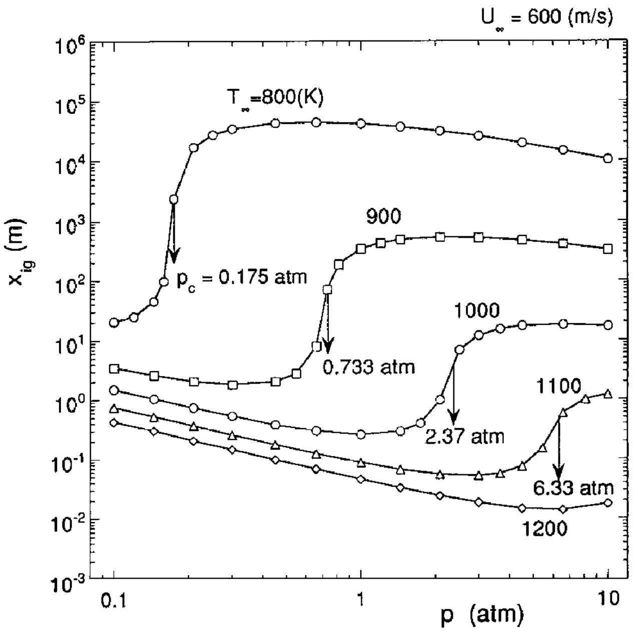

Fig. 7 Ignition distance as a function of ambient pressure, for different hot stream temperatures, showing the nonmonotonic and substantial influence of pressure.[19]

Comprehensiveness of Kinetic Mechanisms

Performance Requirements of Kinetic Mechanisms

Now that we have demonstrated the importance of kinetic mechanisms in combustion phenomena, it is appropriate to ask what constitutes a satisfactory mechanism for a fuel/oxidizer system. Because there is no theory that would indicate whether a certain kinetic mechanism is complete at the level of elementary reactions, the relevant question to ask instead is whether the mechanism can describe all classes of combustion phenomena over all possible ranges of thermodynamic and system parametric variations. The more phenomena it can describe, and over as wide a range of parametric variations as possible, the more complete, or comprehensive, it is. The cost of making the mechanism as complete as possible is the increase in its size in terms of the number of species and reactions and the correspondingly increased demand on the computation time and storage. Because of the need to perform matrix inversion in the process of numerically solving for the species concentration field, to the leading order of estimation the computation time varies quadratically with the number of species. Thus there exists much incentive to reduce the number of species whose concentrations need to be solved through differential equations.

In terms of thermodynamic parametric variations in considering the comprehensiveness of a mechanism, we note that at the molecular level the outcome of an elementary reaction depends on the energetics and frequency of the collision between the molecules. The effects of these two molecular parameters are respectively manifested through the global parameters of temperature and molar concentrations of the fuel and oxidizer reactants, with the concentrations also dependent on the system pressure. Consequently, a comprehensive study must include extensive and possibly independent variations in the system pressure, the characteristic temperature such as the ignition temperature or the adiabatic flame temperature, and concentrations of the reacting mixture through, say, the equivalence ratio, ϕ. Frequently independent variations in the reactant concentration and flame temperature can be achieved through the judicious addition and/or substitution of inerts with different specific heats and molecular weights, as in the cases of nitrogen vs argon for the former and argon vs helium for the latter.

An assessment of comprehensiveness also requires consideration of the hierarchy nature of the fuel oxidation process. For example, because H_2 is an intermediate in the oxidation of a hydrocarbon, the H_2 oxidation mechanism must constitute a submechanism of the hydrocarbon mechanism. Consequently, a comprehensive mechanism for the hydrocarbon must degenerate to that for H_2 when all elementary reactions not related to H_2 oxidations are stripped away. Alternately stated, mechanisms for mixtures of H_2 and the hydrocarbon must exhibit the appropriate limiting behavior for pure H_2 and pure hydrocarbon.

The comprehensiveness of a kinetic mechanism in terms of combustion phenomena can be investigated at two levels of complexity. Ideally, studies of chemical kinetics should be conducted in systems involving homogeneous mixtures such as shock tubes, perfectly stirred reactors (PSR), laminar and turbulent flow reactors, and rapid compression machines. The results are uncomplicated by transport effects and, through extensive experimentation, should cover all ranges in temperature, pressure, and concentrations of interest.

These homogeneous studies, however, are usually not sufficiently extensive in terms of the parametric ranges of variation to ensure comprehensiveness, and as such must be complemented by studies involving inhomogeneous systems such as flames. Furthermore, the performance of a mechanism must be eventually judged by its ability to describe different combustion phenomena, which frequently involve flames.

Flame-based kinetics studies are fundamentally affected by flow and diffusion effects. Extraction of kinetic information is therefore indirect in nature, through assessment of the adequacy and validity of proposed mechanisms in describing certain flame phenomena. Ideally, because a flame structure spans extensive ranges of temperature and composition variations, although the flame can also be subjected to wide ranges of variation in terms of the system pressure, reactant concentration, and flame temperature, studies involving flames impose stringent and extensive constraints on the extraction and validation of the kinetic information. In reality, however, the extensive variations within the flame structure and the use of global flame response parameters tend to smear out the kinetic information, whereas the presence of convective and diffusive transport could also impose considerable inaccuracy and uncertainty on such information. Furthermore, because most practical and laboratory flames are usually highly contorted and situated in spatially and temporally complicated flowfields it is essential that mechanism extraction and validation be conducted on flames that are as configurationally simple and aerodynamically clean as possible.

Based on the preceding considerations, the following phenomena and system parametric dependence should be taken into account to ensure comprehensiveness: 1) ignition (homogeneous and diffusive); 2) steady burning; 3) extinction; 4) premixed flames, nonpremixed flames, detonation waves; 5) pressure effects; 6) equivalence ratio and concentration effects; 7) global responses: laminar flame speeds, extinction strain rates, detonation induction lengths; 8) detailed flame and detonation structures: thermal and major/minor species; 9) unsteady effects: oscillatory and pulsed; and 10) pollutant chemistry.

The preceding phenomena and parameters should impose a reasonably comprehensive scrutiny of the influence of the various aspects of a kinetic mechanism, such as intermediate- vs high-temperature reactions, the presence of oxygen in the fuel stream through either premixing or flame leakage, the scarcity or abundance of one of the reactants, the relative importance of the temperature-sensitive two-body chain branching reactions vs the pressure-sensitive three-body chain terminating reactions, near-limit phenomena, and residence time limitations.

Validation of a proposed mechanism can be conducted by comparing calculated and experimental results at three levels of detail. At the global level we can compare, for example, the laminar flame speeds of premixed flames, the ignition and extinction strain rates of premixed and diffusion flames, the ignition delays of homogeneous mixtures obtained from shock tube and flow reactor studies, and the induction lengths of detonation waves. At the detailed level we can compare the evolution of the temperature and concentrations of the homogeneous mixtures and the thermal as well as the concentration structures of the major and minor species for the steadily burning and the near-ignition and near-extinction states of laminar flames. At the third level unsteadiness of various characteristic timescales should be imposed onto the system in order to examine the adequacy of the reactions at the correspondingly different chemical timescales.

Because the comprehensiveness of a kinetic mechanism is validated through comparison with experimental data, it is then equally important that experimental data of high fidelity be acquired. Indeed, the lack of accurate/meaningful experimental data has in the past hampered the progress in the development of accurate kinetic mechanisms. The most well-known example is the determination of laminar flame speeds. Figure 8, reproduced from Ref. 20, shows the experimentally determined laminar flame speeds of stoichiometric methane/air mixtures as a function of the year in which the individual datum was reported. The data clearly exhibit large scatters, which also do not reduce with time. Because experimental instrumentation and methodology are supposed to improve with time, the persistence of the scatters then indicates the existence of systematic errors in the determination and/or interpretation of the experimental data. It was not until the mid-1980s that flame stretch was identified as the primary cause that led to such persistent and significant scatters.[21] It was somewhat fortuitous that earlier attempts at developing kinetic mechanisms for methane oxidation had selected values around the middle of the range of scatters that turned out to be close to the stretch-free value.

Because the comprehensiveness of a kinetic scheme depends on the phenomena and parameters of interest, the size of a mechanism can be reduced by restricting the extent of comprehensiveness, as suggested by the plateauing behavior in the high-pressure regime of Fig. 3b. As a further example, if NO_x is not of interest then nitrogen chemistry might not need to be considered. In making simplifications of this nature, however, care should be exercise lest some other subprocesses be inadvertently deleted. For the NO_x example eliminating nitrogen chemistry would suppress the catalyzing effect of NO on the ignition of both hydrogen and hydrocarbons. As such, it is prudent to be as comprehensive as possible when simulating combustion processes. We therefore advocate the development and application of detailed mechanisms that are as general as possible.

Current State of Comprehensiveness of Kinetic Mechanisms

Over the past two decades, we have seen a large number of reaction mechanisms published in the literature. These reaction mechanisms were built on the success of early studies of flame chemistry and modeling (e.g., Refs. 1–6) and incorporated elementary kinetics and thermochemical properties made available in more recent years. Because the list of available reaction mechanisms is quite extensive, a review of these models is beyond the scope of the current paper.

Let us, however, now consider the current state of predictability of some of the simplest fuels in terms of the laminar flame speed, which is perhaps one of the most important global properties of

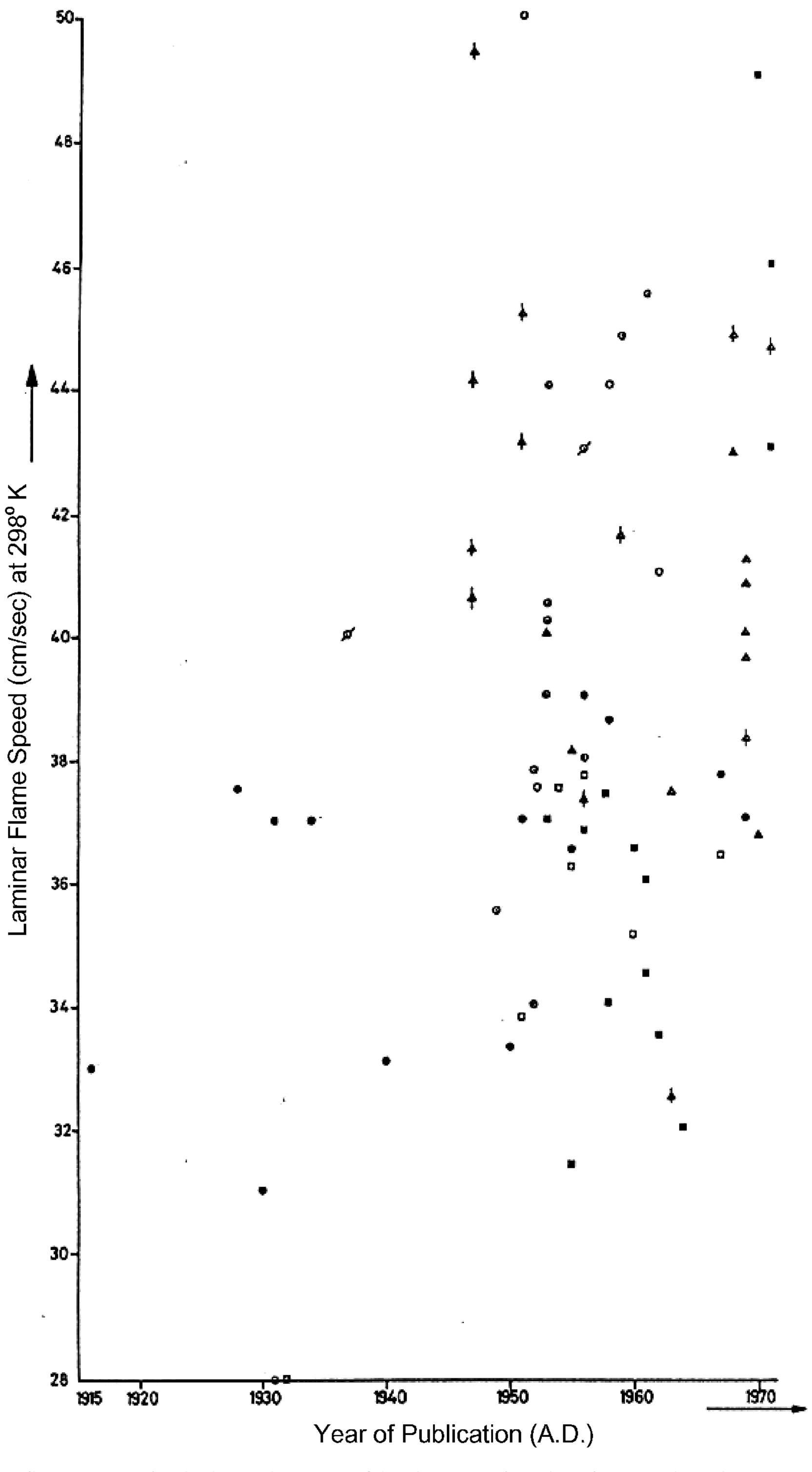

Fig. 8 Experimental laminar flame speeds of stoichiometric methane/air mixtures as function of the year in which they were determined, showing that the scatters not only are substantial, but they also do not diminish with time, implying the presence of some systematic errors in the determination.[20]

a combustible. Figure 9 compares the predicted atmospheric laminar flame speeds of hydrogen/air mixtures, using the most recent kinetic mechanism of Mueller et al.,[11] with the experimentally determined, stretch-corrected values using the constant-pressure, outwardly propagating spherical flames.[22] The comparison clearly shows that the predictions become increasingly inaccurate for rich mixtures. Such a disagreement not only suggests the possible deficiency of the hydrogen oxidation chemistry, but it also highlights the potential inaccuracy in the evaluation of the transport coefficients which could be a cause for the disagreement. Although research is currently underway to improve the accuracy in the evaluation of transport coefficients, as will be discussed later, it is nevertheless sobering to realize that at present we cannot even predict the global flame property of such a simple and essential fuel.

Figure 10 compares the calculated and measured laminar flame speeds of atmospheric methane/air flames.[14] It is seen that the deviations now span throughout the equivalence ratio, having relative magnitudes that are comparable to those of the hydrogen/air flames. Furthermore, although one might consider the degree of comparison to be satisfactory it must be cautioned that the methane mechanism used[15] was developed with the stoichiometric value as one of the optimization points. In other words, the mechanisms have been “calibrated” or “tuned.” Consequently, the observed agreement is to be expected.

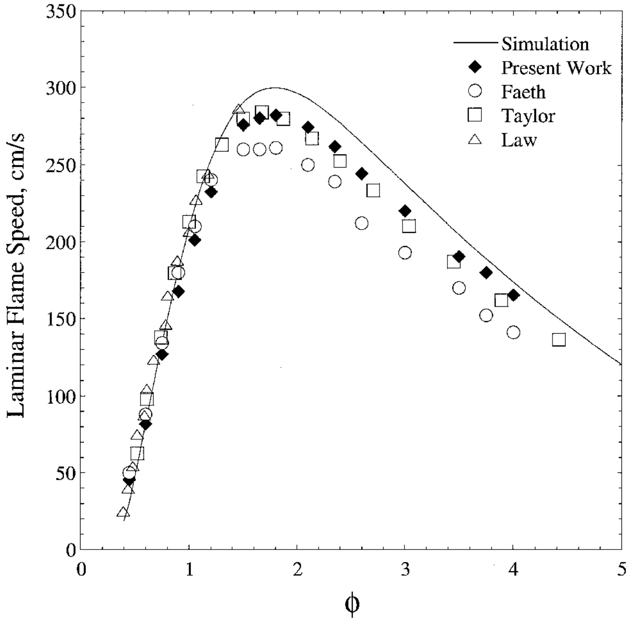

Fig. 9 Experimental and calculated laminar flame speeds of hydrogen/air mixtures at atmospheric pressure, showing the discrepancy for the rich mixtures.[22]

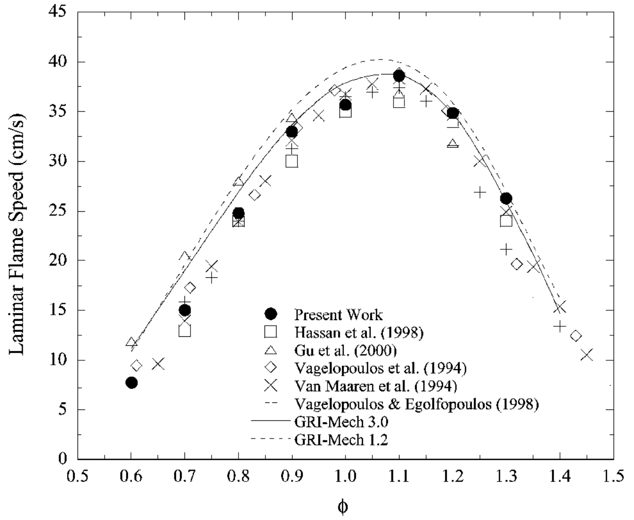

Fig. 10 Experimental and calculated laminar flame speeds of methane/air mixtures at atmospheric pressure.[14]

Recognizing that the methane mechanisms used were calibrated at atmospheric pressure, it is then of interest to note that there is substantial disagreement when the pressure is increased to 60 atm (Fig. 11). Such degradation is not surprising because development of the kinetic mechanism has not utilized any stretch-free data at high pressures. Substantial disagreements between experimental and calculated values have also been reported for high-pressure hydrogen flames.[22]

In Fig. 12 the measured laminar flame speeds of benzene/air mixtures are compared[23] with the calculated ones using the mechanism of Ref. 24, developed from flow reactor studies. It is seen that the experimental values are consistently much higher than those of the computed ones. This result is again not surprising because the laminar flame speed is a parameter of high-temperature phenomenon, whereas flow reactor studies involve lower temperatures. The agreement was improved[23] by adopting a recently measured rate constant of phenyl + $O_2 \rightarrow$ phenoxy + O and incorporating the pressure fall-off of rate constants for key reactions that are relevant to high-temperature oxidation. Despite this improvement, there might still be reactions unaccounted for in the mechanism of aromatics oxidation at high temperatures.

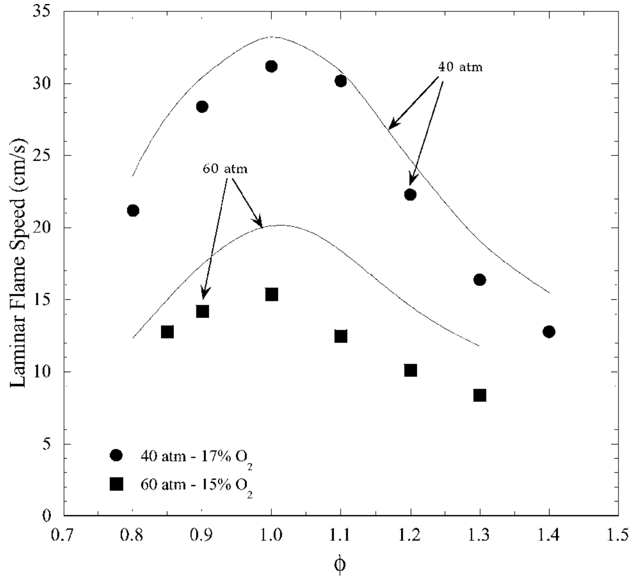

Fig. 11 Experimental and calculated laminar flame speeds of diluted methane/air mixtures at elevated pressures, showing their disagreements.[14]

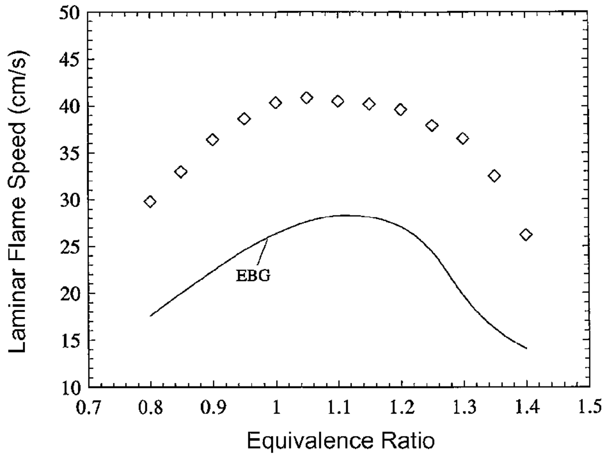

Fig. 12 Experimental and calculated[23] laminar flame speeds of benzene/air mixtures, showing substantial disagreement because the chemical mechanism lacked appropriate pressure dependence of rate constants for reactions relevant to high-temperature chemistry.

Other instances of discrepancy abound. Based on the preceding observations, we are thus led to the following observations of the state of the art concerning the oxidation mechanisms of hydrogen and hydrocarbons. First, it is not always appropriate to use kinetic mechanisms developed from one type of phenomenon in the simulation of another type of phenomenon. Second, a kinetic mechanism cannot be considered to be comprehensive without having it validated against experimental data from all relevant combustion phenomena. Third, the validation is meaningful only if the experimental data are of high quality. Fourth, because there does not exist a comprehensive mechanism even for such simple fuels as hydrogen, methane, and benzene, we are faced with the sobering reality that there is no comprehensive mechanism for all hydrocarbon fuels. Fifth, in view of the preceding comment all simplified and reduced mechanisms derived from existing "complete" kinetic mechanisms can only be considered as efforts of limited utility at best, at least quantitatively. Sixth, the need for accurate, comprehensive kinetic mechanism requires a corresponding level of fidelity in the description of the transport coefficients.

Although the preceding assessment seems to be rather pessimistic, the prospect of developing comprehensive kinetic mechanisms for hydrocarbon oxidation is actually quite promising. The reason is that, based on the lessons we have learned and the present state of knowledge in the experimental and computational aspects of mechanism development, we now largely know what to do to achieve the goal. The task is still daunting, but it is mostly a matter of effort and time. Serious conceptual roadblocks are not anticipated.

In the following we shall present systematic approaches towards development of detailed and reduced mechanisms.

Development of Detailed Mechanisms

Overall Approach

Mechanism development often starts with a careful evaluation of thermochemical and elementary-reaction kinetic data. A large body of these data has been periodically reviewed (e.g., Refs. 25–29). The chemistry of major chain branching processes and small hydrocarbon species in flames is quite well understood, both qualitatively and quantitatively, although uncertainties still exist in the rate constants of many reactions. Some of these uncertainties stem from the difficulties associated with an accurate determination of the rate parameters, whereas others come from a lack of data over a wide range of temperature and pressure. For large species the assignment of elementary reaction-rate parameter often relies on the knowledge of the reaction kinetics of small species.

There has been significant progress in the development of computational methods that can be used to predict the potential energy of interactions and reaction kinetics. In particular, advances in computational quantum chemistry tools in the past two decades have allowed the determination of the potential energy of interactions with some degree of accuracy. Reaction-rate theories have been brought to a level that accurate predictions of the temperature and pressure dependence of reaction-rate constants are now possible.[30–33] Advances have also been made in the area of computer algorithms of mechanism generation and management.[34] These algorithms use empirical kinetic rules, for example, group-additivity-based methods, as well as computational chemistry tools.

The aforementioned theoretical and computational advances offer exciting possibilities that a vast amount of kinetic data and knowledge can be intelligently utilized in reaction mechanism development and management. Yet the ever-expanding kinetic knowledge and the nearly infinite chemical complexity require the general rules implemented in the computer algorithm be continuously updated. To illustrate this point, it has been shown very recently that the initial radical pool during the homogeneous oxidation of simple hydrocarbons like acetylene and ethylene is generated by a class of reactions not previously considered.[35] We should also recognize that it is still not possible to determine a priori a potential energy surface that is accurate and, more importantly, complete for the prediction of the reaction kinetics of large molecules. Experimental validation of reaction-rate constants and mechanisms remains a necessary element in the development of reaction models for combustion simulations.

The preceding discussion points to the fact that a comprehensive mechanism must be developed with a careful evaluation of relevant reaction kinetics, aided with quantum chemistry tools and application of reaction-rate theories. The validity of the reaction mechanism must be scrutinized and verified using reliable combustion data. When the reaction mechanism becomes sufficiently comprehensive, the joint kinetic uncertainty space is then reduced by the numerical techniques of response surface development and systematic optimization.[36]

Finally, because of the hierarchy nature of hydrocarbon combustion chemistry a comprehensive mechanism can be and should be developed sequentially, starting from small hydrocarbon species and then extending to large compounds.[2] Yet it was shown recently[37] that a well-developed and optimized reaction mechanism of small hydrocarbon combustion might not be sufficiently accurate as a secure foundation for building a comprehensive mechanism for large hydrocarbon combustion. This result has led to the suggestion that the development of a comprehensive reaction mechanism requires a joint optimization for a large number of hydrocarbon compounds.

In the following we shall discuss initial steps in the development of a comprehensive reaction mechanism of hydrocarbon combustion. A hierarchy of hydrocarbon fuels of increasing molecular weights and complexity will be used to provide different kinetic components that constitute the mechanism.

Target Hydrocarbon Fuels for Mechanism Development

The selection of target compounds is based mainly on two considerations. First, the selected hydrocarbon must be a dominant component of practical fuel blends or its suitable surrogate. These compounds include straight-chain, branched-chain, and cyclic paraffinic hydrocarbons, methanol and ethanol, and aromatic species. The following is a suggested list of these hydrocarbons: propane, *n*-butane, *i*-butane, pentane, 2-methylbutane, hexane, cyclohexane, methylcyclohexane, heptane, octane, iso-octane, methanol, ethanol, benzene, ethylbenzene, toluene, and xylene(s). Methanol and ethanol are included for their role in the kinetics of oxygenated intermediates. Larger hydrocarbons are not included because their kinetic behavior is expected to be similar to those of the lower ones.

Because the oxidation mechanism of the target fuels is based on the fundamental knowledge of reaction kinetics and thermodynamics, the components of such an oxidation mechanism must be self-consistent and must be based on a single mechanism consisting of the oxidation kinetics of the intermediate hydrocarbon species of higher hydrocarbon combustion. It is well established that the initial aliphatic fuel breakdown yields mainly unsaturated ethylenic species, including ethylene, propene, and under certain conditions allene and butene. These unsaturated hydrocarbon species are known to be produced via the β-scission process of alkyl radicals. In the case of fuel-rich combustion, highly unsaturated species like acetylene and propyne are produced as dominant intermediate species of combustion. For aromatic compounds, the initial reactions lead to the breaking of the aromatic ring structure and produce unsaturated C_4 species, for example, vinylacetylene and butadiene.[24] Because most of the intermediate species are stable fuels themselves, a predictive kinetic model for the combustion intermediates can be and should be established first. Such a kinetic model then serves as the foundation or the submechanism for building a predictive kinetic model for higher paraffinic and aromatic fuel combustion. A suggested list of the relevant species is given here: ethylene, acetylene, ethane, allene, propyne, propene, vinylacetylene, 1-butene, 2-butene, and 1,3-butadiene. We note that the flame characteristics of many species just listed have not been adequately studied. Hence, not only will such data facilitate the development of the comprehensive reaction mechanism proposed here, but they will also help to establish a quantitative understanding of the effect of fuel structure on the combustion characteristics of hydrocarbons.

Mechanism for C_2-C_4 Fuels

As an example, we demonstrate here a detailed reaction mechanism of C_2-C_4 fuel combustion[38] based on the approach outlined earlier. The mechanism was compiled on the basis of a critical review of literature kinetic data and extensive ab initio quantum mechanical and Rice–Ramsperger–Kassel–Marcus calculations for the determination and/or extrapolation of reaction-rate coefficients. The small-species chemistry is largely based on the GRI-Mech 1.2 (Ref. 29). Troe's fall-off formalism[30] was used to describe the pressure dependence of the rate coefficients for unimolecular dissociation and bimolecular combination reactions. The reaction kinetics of acetylene and ethylene is based on a series of works reported previously.[35,39–41] The propyne, allene, propene, and propane submodels were taken from Davis et al.[42–44] Finally, the chemistry of 1,3-butadiene was compiled and verified against available data.[45] The kinetic model retains a reasonable number of C_5-C_6 species to ensure proper simulation under fuel-rich conditions and to make it possible for expansion to include large hydrocarbon chemistry. The thermochemical data of H/O/C_1-C_2 species were taken from the GRI-Mech compilation, and those of $C_{>2}$ have been documented.[35,39–45]

The resulting mechanism, although not optimized, has been subjected to extensive validation tests against a wide range of combustion data, over 100 sets in all, covering the combustion properties of acetylene, ethylene, propyne, allene, propene, propane, and 1,3-butadiene from ignition in shock tubes,[46–55] to laminar flame

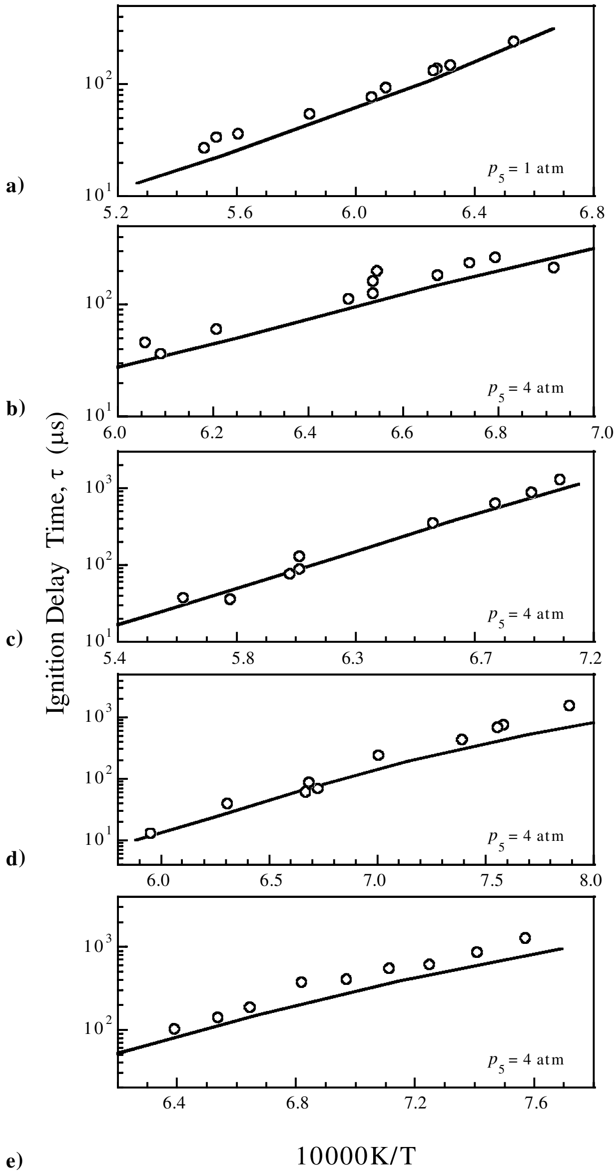

Fig. 13 Experimental[53] (○) and computed (——) ignition delay times, determined by the maximum pressure gradient. Shock mixtures (in argon): a), b) 1.6% C_3H_6-7.2% O_2, c) 1.59% C_3H_6-3.58% O_2, d) 1.6% C_3H_6-14.4% O_2, and e) 3.17% C_3H_6-7.83% O_2.

speeds,[56–58] and to detailed major and minor species profiles in flow reactors[44,45] and burner-stabilized flames.[59,60] Figures 13–16 respectively show the representative results from these four classes of phenomena. Results from the extensive comparisons are given in Ref. 10. The comparisons are considered to be satisfactory in general, lending support to the viability of the present approach toward the development of detailed mechanisms.

Development of Reduced Mechanisms

Methodologies of Mechanism Reduction

Although in theory accurate results and comprehensive responses can be obtained by using detailed mechanisms in simulating combustion phenomena, in practice this is feasible only for very simple situations such as the structure and laminar flame speeds of the one-dimensional planar flame and the induction lengths of the planar detonation wave. The reason being either the heavy demand of computation, considering that even a moderately detailed mechanism for hydrocarbon fuels would consist of tens of species and hundreds of elementary reactions, and/or the stiffness resulting from the significantly disparate timescales associated with different species and reactions. There is therefore the need to develop reduced mechanisms from detailed mechanisms, without losing comprehensiveness.

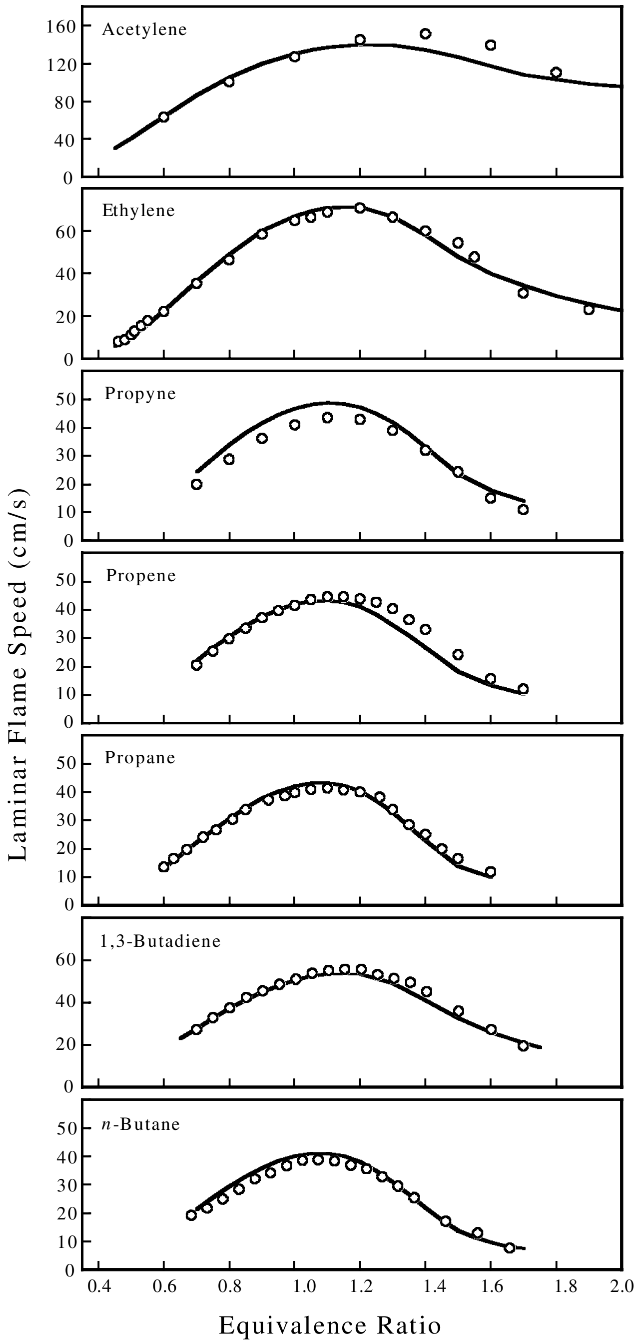

Fig. 14 Experimental (○, acetylene and ethylene,[56] propyne,[42] propene,[44] propane,[57] 1,3-butadiene and n-butane[58]) and computed (——) laminar flame speeds of fuel-air mixtures at 1 atm.

The first level of reduction is from detailed mechanism to skeletal mechanism and is achieved by eliminating species and elementary reactions that are not important to any major parameters of interest such as the heat release and major species production rates. The unimportant species and reactions can be identified by using sensitivity analysis,[61] detailed reduction,[62,63] or computational singular perturbation (CSP).[64–70] The size of a skeletal mechanism depends on the complexity of the detailed mechanism as well as the required accuracy and comprehensiveness. Because the skeletal mechanism is simply a subset of the detailed mechanism, it can be applied in the same manner as the detailed mechanism without any additional work in the modification of computer codes.

Depending on the extent of simplification, sometimes substantial facilitation in computation can be accomplished even at the skeletal level. Thus for sufficiently simple flows, such as those involving steady-state, two-dimensional, laminar flames, it might be possible

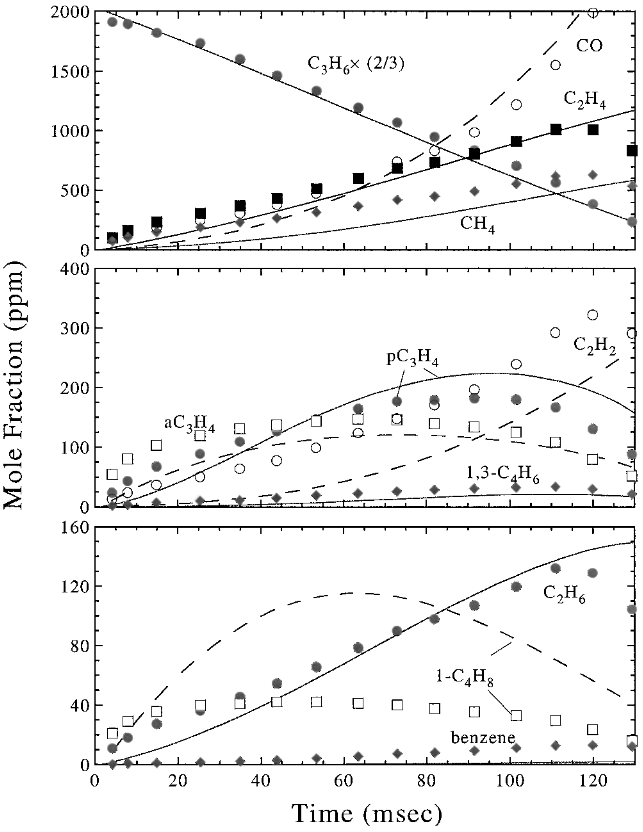

Fig. 15 Experimental[44] (symbols) and computed (lines) mole fraction profiles of species during propene oxidation (ϕ = 0.7) in an atmospheric pressure flow reactor at an average temperature of 1170 K.

to stop at this level and proceed with computation. This would avoid making additional assumptions and encountering possible computational difficulties of different natures. However, if further simplification is desired, fairly systematic procedures of reduction have been developed, to be discussed next.

Further reduction starting from the skeletal mechanism is based on two assumptions, namely quasi-steady state (QSS) for species and partial equilibrium for elementary reactions. A species can be approximated as QSS if its characteristic destruction time is much shorter than that of formation, and if both of their rates are much faster than its net creation rate such that its concentration is very low. A reaction is considered to be in partial equilibrium if its forward and backward rates are much faster than those of other reactions involving related species. Each of these assumptions yields an algebraic relation between the concentration of one species and those of the others and hence reduces the species number by one.

The two major approaches for mechanism reduction that implicitly embody the concepts of QSS and partial equilibrium are intrinsic low-dimensional manifold (ILDM)[71] and CSP. The approaches are based on Jacobian matrix analysis through which the dimension of the parametric space is reduced. The species lifetime analysis[72] is somewhat less rigorous and hence could be more restrictive in its applicability.

Once the QSS species are identified, reduced mechanisms can be generated through algebraic manipulation.[73] For large mechanisms such algebraic manipulations can be performed by the computer. Various reduced mechanisms for hydrogen and hydrocarbon oxidation have been developed.[9,74]

Reductions based on the preceding techniques exploit internal algebraic iterations to evaluate the concentrations of QSS species that are required to calculate the production rates of the non-QSS species. However, substantial difficulties usually occur in the iteration procedure as a result of the deterioration or failure of the QSS assumption, for example, as consequences of evaluation in the low-temperature zone of the flame or in situations where the intermediate compositions depart substantially from the correct solution. The failure of the QSS assumption generally results in abnormally high concentrations of the QSS species and/or the difficulty to converge. An approach to deal with this problem is truncation, which involves either eliminating the terms that result in the failure or setting an upper bound for each QSS species. However, truncation cannot guarantee acceptable results, and the induced discontinuities can cause difficulties in the convergence of the outer solver. The extra time spent on the unsuccessful iterations could cancel much of the time saved from the reduction and render the reduced mechanism less effective.

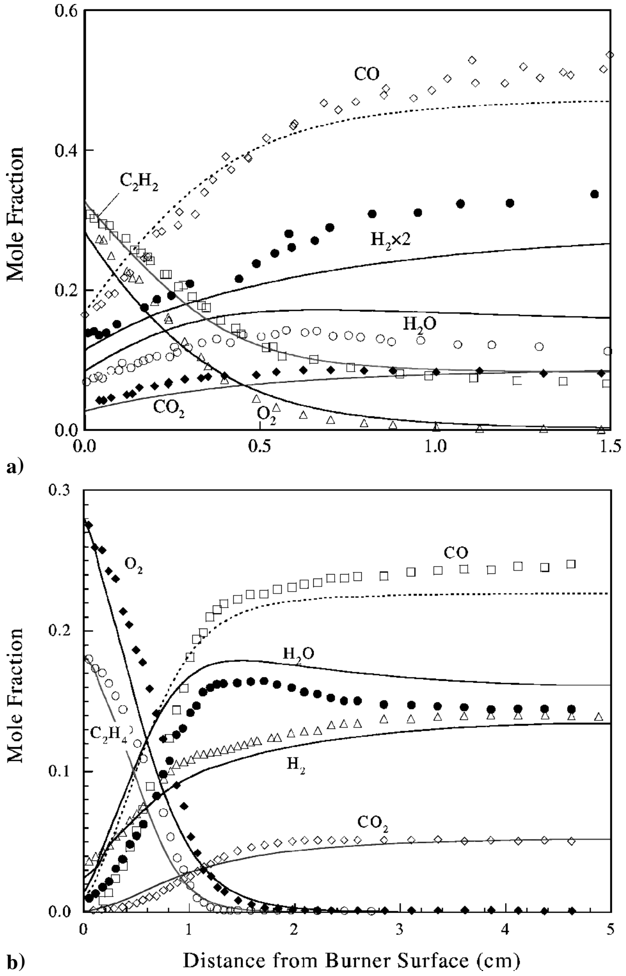

Fig. 16 Comparison of computed (lines) major species profiles of a burner-stabilized flame at 20 torr, with a) experimental results in Ref. 59 (symbols), for acetylene–oxygen–5%argon (ϕ = 2.4), and b) experimental results in Ref. 60 (symbols), for ethylene–oxygen–50%argon (ϕ = 1.9).

To improve the computational efficiency, an in situ adaptive tabulation (ISAT) method[75] can be applied to ILDM in order to eliminate the need for internal algebraic iteration by tabulating possible species concentrations with respect to the combinations of major species concentration. However, failure of the QSS assumptions can still result in the difficulty of convergence of the outer solver. Furthermore, when the accuracy requirement is high and the size of the mechanism is large, implementation of the tabulation becomes more demanding in terms of storage requirement and searching time.

Reduced Mechanisms

The class of reduced mechanisms for hydrocarbon oxidation that currently enjoys extensive usage typically consists of four to five steps. These mechanisms have led to considerable simplification and advance in theoretical and computational developments. Valuable as they are, it has however also been found that their comprehensiveness can be quite restricted in terms of the combustion phenomena they describe and the parametric ranges of simulation.

If one takes the viewpoint that because the hydrogen/oxygen system forms an essential building block for hydrocarbon oxidation and that the existing hydrogen oxidation mechanism is the simplest possible, then it is reasonable to expect that the level of simplification for a hydrocarbon oxidation mechanism must not be less than that of the hydrogen mechanism, with appropriate additional descriptions for CO oxidation as well as those that are specific to the hydrocarbons. Because there are eight species (H, O, OH, H_2, O_2, H_2O, HO_2, H_2O_2) and two elements (H, O) involved in hydrogen oxidation, the minimum number of lumped steps needed to describe hydrogen oxidation should be about six. If we further allow a minimum of one step each for CO oxidation and the characterization of the specific hydrocarbon, then the minimum number of steps in a reduced mechanism should be about eight. As such, some degree of compromise in terms of comprehensiveness must have been made for the four- to five-step reduced mechanisms.

Having examined these four- to five-step reduced mechanisms in detail, especially those on methane oxidation, it was recognized that some of the crucial intermediate species indeed might not exist in steady state over extensive thermodynamic parametric ranges as assumed. On the other hand, it was also realized that the number of species involved with these assumptions is not large, and it is therefore reasonable to expect that relaxation of these assumptions could lead to substantial improvements in the comprehensive nature of their descriptive capability. Particularly, it was suggested[9] that reduced mechanisms consisting of 10 to 20 lumped reactions, with the corresponding number of species, could be adequate to meet such an objective, at least for the smaller alkanes whose reaction kinetics have acquired a moderate degree of understanding.

Although a mechanism of this size might not be feasible for current implementation in the computational simulation of many complex chemically reacting flows, especially those involving turbulent flames, advances in the computational capability in the foreseeable future, say within the next 5 to 10 years, could obviate such a limitation. Therefore it is prudent to initiate development of mechanisms of this size in anticipation of the corresponding advances in the computing capability.

The potential of such an augmented reduced mechanism (ARM) was explored, using methane as the vehicle for investigation. Specifically, a recently developed automatic numerical algorithm[74] was used to generate reduced mechanisms from GRI-Mech at various levels of detail. The capabilities of these reduced mechanisms to describe extensive kinetically affected combustion phenomena were then tested by comparing their predictions against those determined from the detailed GRI mechanism. Validation comparisons were conducted for various combustion phenomena traditionally employed for kinetics studies, as mentioned earlier. These include S curves of perfectly stirred reactors, autoignition and shock-tube ignition delays, laminar flame speeds over wide range of equivalence ratios, and S curves for nonpremixed flames. The comparisons were conducted at two levels of stringency, namely, the global response parameters such as the laminar flame speeds and the ignition delays, and the time and space resolved temperature and species structures. A 12-step ARM was found to be comprehensively adequate. This reduced mechanism consists of 16 species (H_2, H, O_2, OH, H_2O, HO_2, H_2O_2, CH_3, CH_4, CO, CO_2, CH_2O, C_2H_2, C_2H_4, C_2H_6, and N_2), which includes some crucial C_2 species and is listed here:

$$CH_4 + H = CH_3 + H_2 \tag{r1}$$

$$CH_3 + OH = CH_2O + H_2 \tag{r2}$$

$$CH_2O = CO + H_2 \tag{r3}$$

$$C_2H_6 = C_2H_4 + H_2 \tag{r4}$$

$$C_2H_4 + OH = CH_3 + CO + H_2 \tag{r5}$$

$$C_2H_2 + O_2 = 2CO + H_2 \tag{r6}$$

$$CO + OH + H = CO_2 + H_2 \tag{r7}$$

$$H + OH = H_2O \tag{r8}$$

$$2H_2 + O_2 = 2H + 2OH \tag{r9}$$

$$2H = H_2 \tag{r10}$$

$$HO_2 + H = H_2 + O_2 \tag{r11}$$

$$H_2O_2 + H = H_2 + HO_2 \tag{r12}$$

The rate expressions for the preceding reactions can be found in Ref. 76. With the QSS species identified, reduced mechanisms consisting of different linearly independent lumped reactions, but with equal size, performance, and accuracy, can be deduced. The choice of a particular combination is therefore somewhat arbitrary and can be based more on an aesthetic reason in that the individual lumped reactions would convey the meaning of some specific aspects of the mechanism. Consequently, in the preceding reduced mechanism (r1–r3) represent the conversion of $CH_4 \rightarrow CH_3 \rightarrow CH_2O \rightarrow H_2$ and CO, (r4–r6) account for the formation of C_2 species, such as C_2H_6, C_2H_4, and C_2H_2, and their subsequent oxidation, (r7) and (r8), respectively, correspond to CO_2 and H_2O formation, and (r9–r12) relate to the submechanism of H_2 oxidation including the chemistry of HO_2 and H_2O_2.

A 15-step ARM[76] based on GRI-Mech 3.0 (Ref. 15) has also been developed to account for NO formation. This 15-step ARM is basically the 12-step ARM plus three additional steps

$$N_2 + O_2 = 2NO \tag{r13}$$

$$HCN + H + O_2 = H_2 + CO + NO \tag{r14}$$

$$NH_3 + 3H + H_2O = 4H_2 + NO \tag{r15}$$

to include the description of NO, HCN, and NH_3 chemistry. Specifically, reaction (r13) includes the NO formation reactions corresponding to thermal NO, prompt NO, and the $N_2O \rightarrow NO$ mechanisms. In addition, reactions between nitrogen-related radicals and N/NO, converting N and NO back to N_2, are also accounted for. Reaction (r14) involves the prompt and reburning reactions, whereas reaction (r15) accounts for the conversion of NH_3 to NH_2 through reactions with OH, O, and H. The important reactions of $NH_2 + NO$ leading to thermal De-NOx processes are not included in the GRI-Mech 3.0; this chemistry can be added when it becomes available in future releases of GRI-Mech or its equivalents.

Validation Procedure

Whereas the comprehensiveness of a detailed mechanism is established through its comparison with either experimental data or first-principle calculations, the comprehensiveness of a reduced mechanism is validated against the detailed mechanism from which it is deduced. In the following we shall demonstrate the performance of the reduced mechanisms just mentioned. Results from extensive comparisons are given in Refs. 9, 76, and 77.

Global Response

For comparison, we used a four-step mechanism deduced from GRI-Mech with a form similar to that of Peters and Coworkers,[8,78,79] the 10-step mechanism of Chen,[74] and the 12-step ARM.[9,76,77]. The 10-step mechanism is the 12-step mechanism with the additional assumption that HO_2 and H_2O_2 are steady-state species. The four-step mechanism is given by

$$CH_4 + 2H + H_2O = CO + 4H_2 \tag{rI}$$

$$CO + H_2O + 2H = CO_2 + 2H_2 \tag{rII}$$

$$2H = H_2 \tag{rIII}$$

$$4H_2 + O_2 = 4H + 2H_2O \tag{rIV}$$

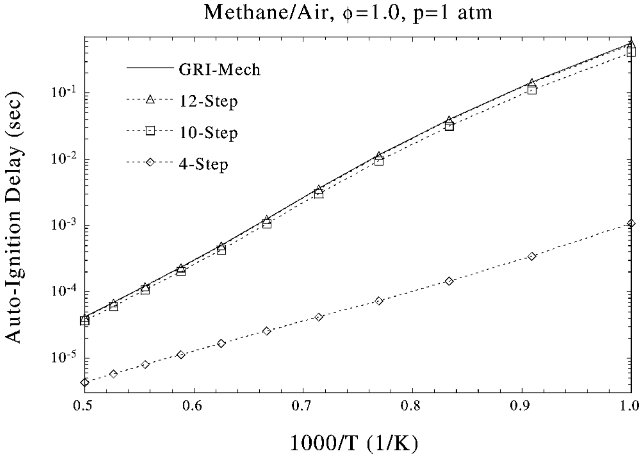

Fig. 17 Comparison of predicted autoignition delay times of atmospheric, stoichiometric methane/air mixtures using various reduced mechanisms and the detailed mechanism showing improvements in the descriptive capability of the reduced mechanism with increasing numbers of lumped reaction steps.[9]

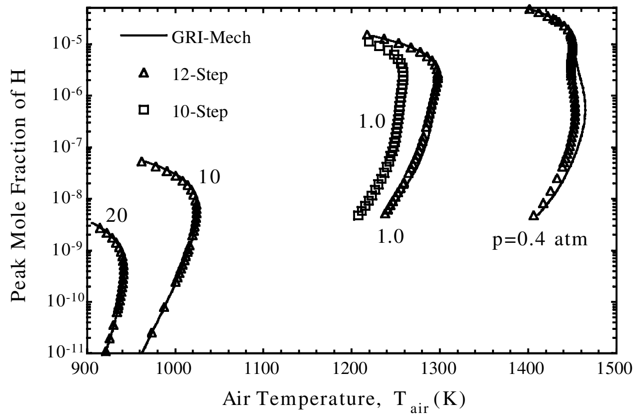

Fig. 18 Predicted peak mole fraction of H as a function of air temperature for 80% methane in nitrogen vs heated air counterflowing systems at various pressures. The boundary temperature of the fuel stream is 300 K. The turning points define the corresponding ignition temperatures. The underprediction of the ignition temperature by the 12-step mechanism is less than 0.8%, and its performance is much better than that of the 10-step mechanism.[9]

Figure 17 compares the performance of the 4-, 10-, and 12-step mechanisms in predicting the autoignition delay times of atmospheric, stoichiometric methane/air mixtures at various initial temperatures. It is seen that the four-step mechanism is inadequate in predicting the ignition delay. Subsequent relaxation of quasi-steady-state species leads to significant improvements in the descriptive capability of the corresponding reduced mechanism. The errors in the predicted delay times by the 10-step reduced chemistry are within 15%. The 12-step mechanism further reduces the discrepancy.

The adequacy of the 10-step mechanism was further tested. Comparisons between the 10-step and detailed mechanisms over a wide range of atmospheric flame conditions, including PSR, one-dimensional flame propagation, opposed flow flames, transient PSR, autoignition delays, transient well-mixed reactor, and partially stirred reactor, showed very satisfactory agreement.[9] However, extension of the test to counterflow nonpremixed ignition involving impinging a cold methane/inert jet against a heated air jet showed an order of magnitude overprediction in the size of the radical pools, as depicted in Fig. 18, which compares the ignition response curves at various pressures, for 80% methane in nitrogen, with a fixed pressure-weighted strain rate $p\kappa$, 300 atm/s. Further scrutiny led to the recognition that the QSS assumptions of HO_2 and H_2O_2 need to be relaxed. Therefore, with the addition of HO_2 and H_2O_2 the 12-step mechanism emerges. It is seen that the ignition (boundary) temperature, as given by the turning point, steadily decreases with increasing pressure. Moreover, the performance of the reduced chemistry improves significantly with increasing pressure. It is seen that although the size of the ignition kernel is relatively overpredicted by the 12-step reduced mechanism for subatmospheric conditions the error in predicting the ignition temperature in general is much less than 1%.

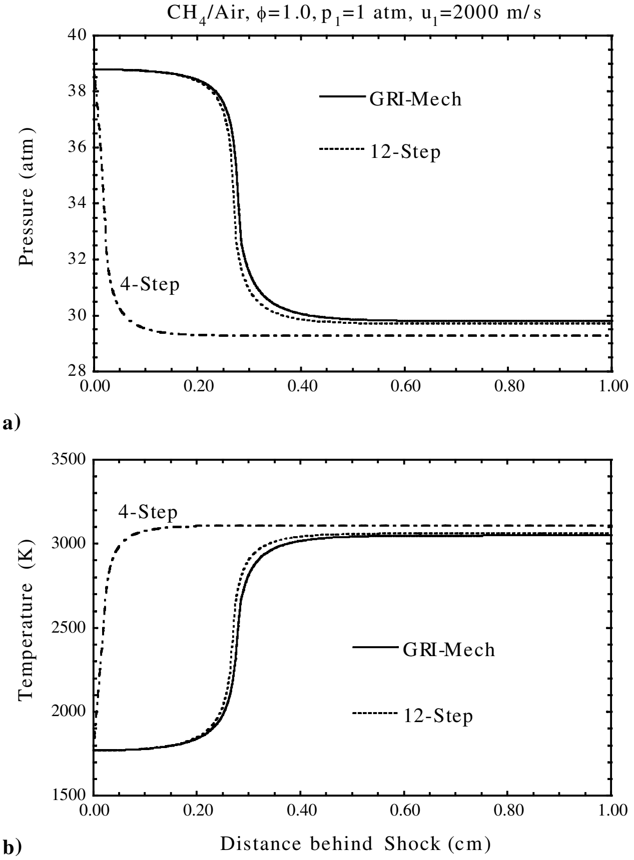

Fig. 19 Comparison of predicted ZND structure of atmospheric, stoichiometric methane/air mixtures using various reduced mechanisms and the detailed mechanism for a) pressure profiles and b) temperature profiles.

The performance of the 4- and 12-step mechanisms in detonations was examined by comparing the ZND structure of the one-dimensional detonation wave for a stoichiometric methane/air mixture (Fig. 19). Consistent with the autoignition validation, the 12-step mechanism yields very close agreement with the detailed mechanism in the predicted induction length, whereas the four-step mechanism misses this important parameter by substantial amounts.

Figure 20 presents calculated laminar flame speeds of methane/air mixtures over equivalence ratios from 0.7–1.3, with pressure ranging from 0.25–20 atm. The agreement is generally quite good. For the pressure range of 0.25–1 atm, the discrepancy is within 4%, whereas the use of the 10-step reduced mechanism yields 10–15% overprediction near stoichiometric conditions and at atmospheric pressure. With increasing pressure the performance of the 12-step reduced mechanism is further improved.

Detailed Flame Structure

Figure 21 compares the spatially resolved thermal structure, including temperature and heat-release profiles, for freely propagating stoichiometric methane/air flames at pressures of 1–20 atm. For the atmospheric condition the thermal structure is shown to be well resolved by reduced chemistry, except that the peak heat release is slightly overpredicted by the 12-step ARM. With increasing

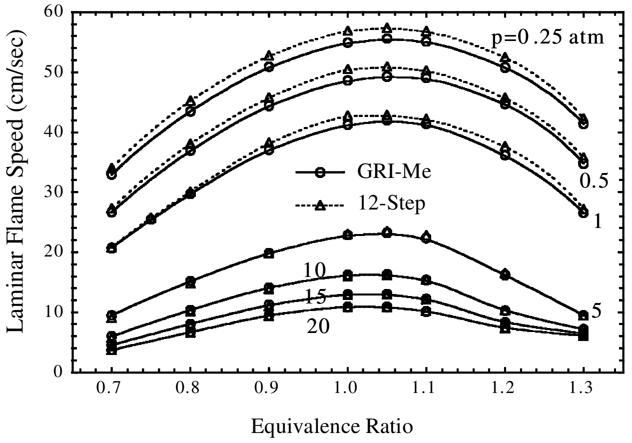

Fig. 20 Predicted laminar flame speeds of methane/air mixtures over a wide range of equivalence ratios at various pressures. The flame speeds are overpredicted within 4% by the reduced mechanism at subatmospheric conditions.[9]

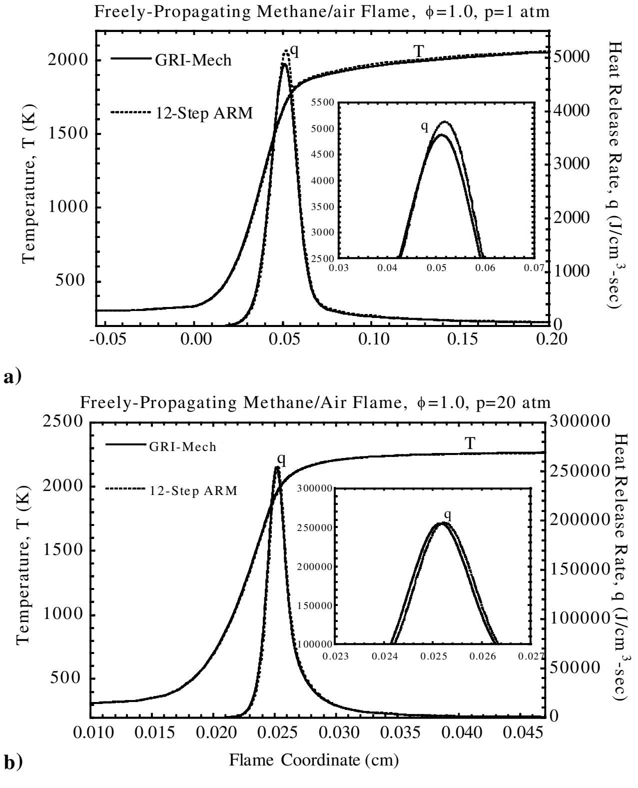

Fig. 21 Comparison of predicted thermal structure, including spatially resolved profiles of temperature and heat-release rate, of stoichiometric, freely propagating, methane/air mixture with 300 K initial temperature, using GRI-Mech and 12-step ARM for a) 1 atm and b) 20 atm. The flame coordinate is determined by spatially collating the temperature of 500 K (Ref. 77).

pressure the thermal structure is still well predicted. The corresponding structures of the major and minor species for the 20-atm flame are compared in Fig. 22, and the predictability of the 12-step ARM is again demonstrated.

Figures 23 and 24 show similar comparisons and agreements for the thermal and concentrations structures of a methane/air diffusion flame at 1 and 20 atm. Recognizing the fundamentally different structures of premixed and diffusion flames, the ability of the reduced mechanism to simulate both types of flames is particularly noteworthy in terms of its comprehensiveness.

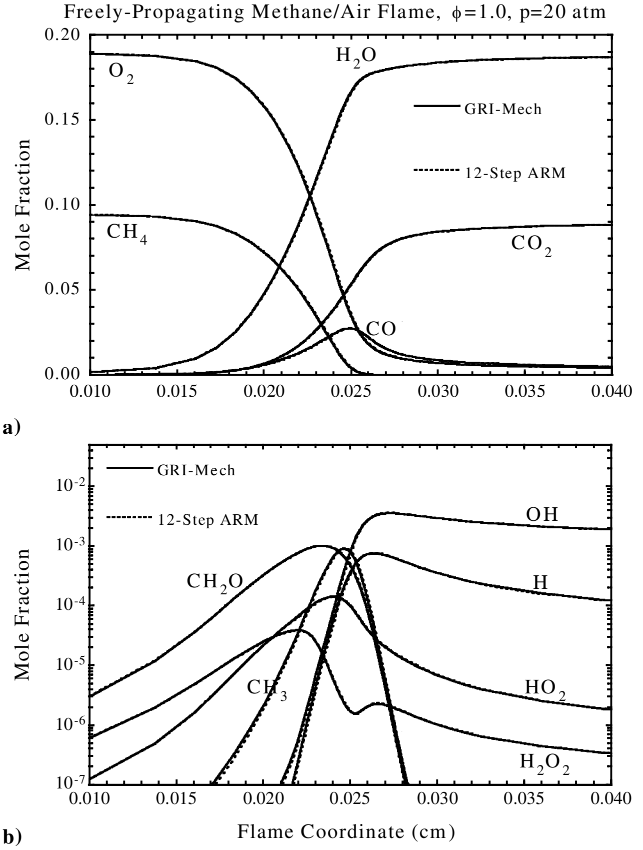

Fig. 22 Comparison of predicted profiles of a) major species and b) minor species for stoichiometric, freely propagating, methane/air mixture with 300 K initial temperature and 20 atm, using GRI-Mech and 12-step ARM. The flame coordinate is determined by spatially collating the temperature of 500 K (Ref. 77).

NO Formation

Because pollutant formation is an important measure of the performance of practical combustors and processes, it is essential that the predictive capability of a detailed mechanism in terms of pollutant chemistry is not compromised in mechanism reduction. Figure 25 compares the exit NO mole fraction as a function of residence time for a PSR at 1 and 20 atmospheric pressures, obtained with the GRI-Mech 3.0 and the present 15-step mechanisms for stoichiometric mixture. The inlet temperature is kept constant at 300 K. The turning points represent the critical residence times for extinction, and hence the lower branches are unstable solutions. Excellent agreement between the detailed and reduced mechanisms is again demonstrated.

Comparison with Skeletal Mechanism

Comparisons have been conducted on the relative merits of reduced and skeletal mechanisms.[77] Regarding the CPU time, because it scales with the square of the total number of species, and because the size of a skeletal mechanism (23 species) that has the same degree of comprehensiveness as the 12-step ARM (16 species) is larger, using the 12-step ARM would speed up the calculation by a factor of two. However, evaluation of the steady-state species in the reduced mechanism would require additional CPU time. As a result, the CPU time could be arguably reduced by 20% by using the 12-step ARM. Regarding the memory requirement, which scales with the cube of the total number of scalars and is an important consideration, for example, in ISAT,[75] the use of the 12-step ARM reduces this requirement by a factor of three. All of these savings could be meritorious considerations in the simulation of turbulent flames[80] and other complex combustion phenomena.

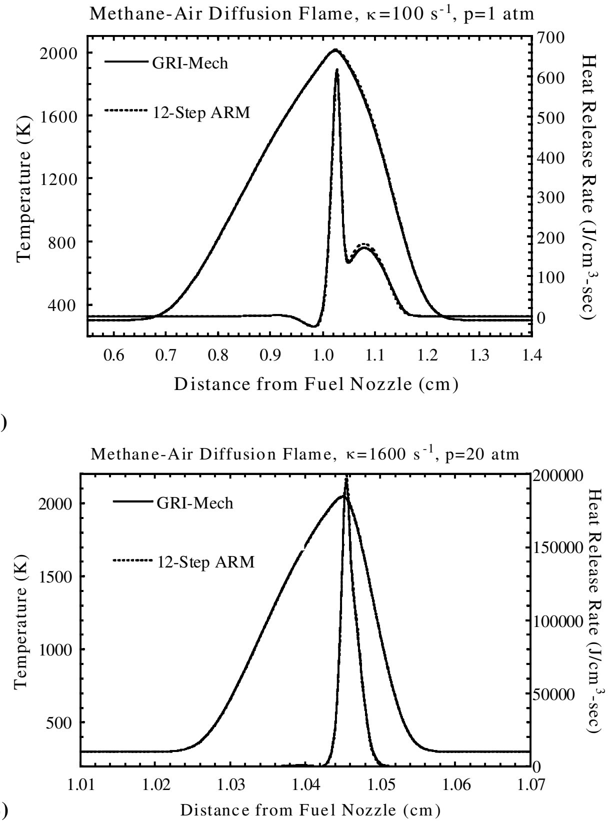

Fig. 23 Comparison of predicted thermal structure, including spatially resolved profiles of temperature and heat-release rate, of counterflowing, nonpremixed, methane-air flame with 300 K boundary temperatures, using GRI-Mech and 12-step ARM for a) κ = 100 s^{-1} and 1 atm and b) κ = 1600 s^{-1} and 20 atm (Ref. 77).

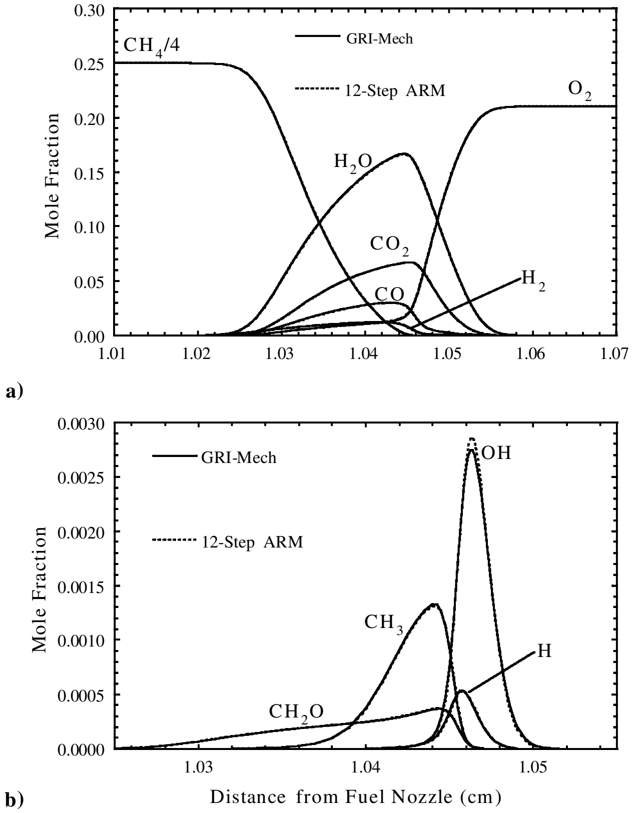

Fig. 24 Comparison of predicted spatially resolved profiles of a) major species and b) minor species, for counterflowing, nonpremixed, methane-air flame with 300 K boundary temperatures, κ = 1600 s^{-1} and 20 atm, using GRI-Mech and 12-step ARM.[77]

Uncertainties of Transport Properties

The discussion has so far been on the adequacy of chemical reaction mechanisms. However, because most combustion phenomena take place in nonhomogeneous media, adequate specification of the transport properties could be equally important in the satisfactory description of these phenomena. In combustion simulation most of the transport properties are based on the work of Marrero and Mason,[81] Dixon-Lewis,[82] and Warnatz.[83] For work discussed in the current review paper in particular, we have used the transport database of Kee et al.[84] Multicomponent transport formalism and thermal diffusion were considered where appropriate.

In general, the transport properties of many stable molecular species are accurate owing to the Chapman–Enskog theory and the large number of data available for these species. The uncertainty in transport parameters is thus primarily associated with the free radicals and mainly stems from the difficulties in experimental measurement. Of particular concern is the recognition that there have been only several measurements reported for the diffusion coefficient of the H atom in inert gases, with all of them carried out at or near room temperature. For other radicals the transport properties have been largely approximated by those of their parent molecules.

Because free-radical species usually have low concentrations in flames, the uncertainties in their conductivity and viscosity present very little effect on flame simulation. The diffusion coefficients, however, play a more important role, as demonstrated in a recent study.[85] It was shown that in the simulation of laminar flame speeds of hydrogen/air mixtures the sensitivity coefficients computed for the binary diffusion coefficients of H-N_2 are larger than those computed for the rate constant of the $H + O_2 \rightarrow O + OH$ chain branching reaction. For hydrocarbon flames the influence of the diffusion rate of the H atom was found to be comparable to the rate constant of the same chain branching process.[86]

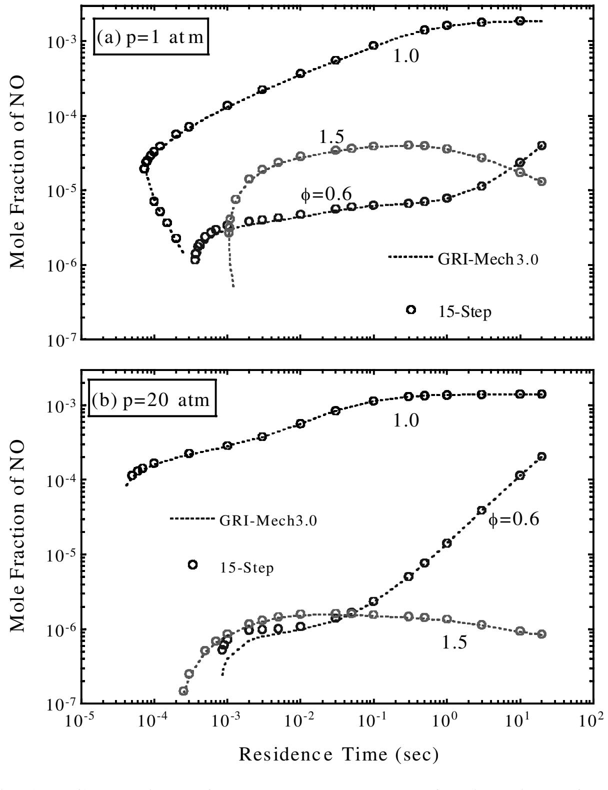

Fig. 25 Comparison of calculated responses of adiabatic perfectly stirred reactor with reduced and detailed mechanisms, showing excellent agreement for lean, rich, and stoichiometric methane/air mixtures over a wide range of residence times. The inlet temperature (T_{inlet}) is 300 K: a) 1 atmospheric pressure and b) 20 atmospheric pressure.[76]

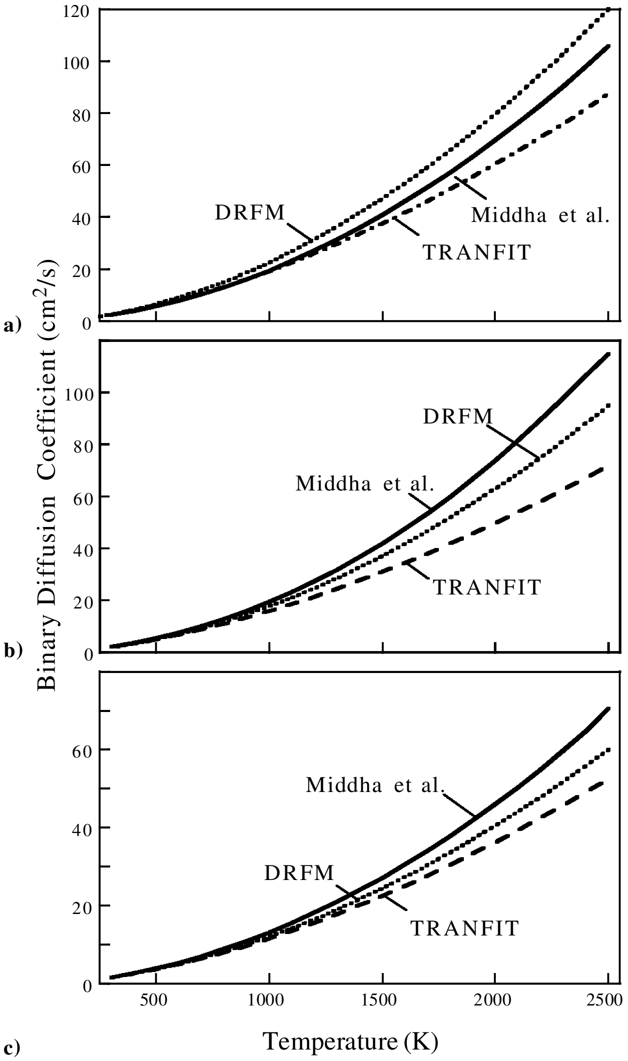

Fig. 26 Comparison of the binary diffusion coefficient of a) H-He, b) H-H_2, and c) H_2-He at the pressure of 1 atm, obtained from first-principle calculation[89] and semi-empirical predictions of TRANFIT[84] and DRFM.[88]

In flame simulation extrapolation to high temperatures has been made semi-empirically using the Chapman–Enskog equation and the Lennard–Jones (L-J) 12-6 potential energy function.[84] With a limited number of low-temperature data, this extrapolation is highly unreliable at high temperatures. This point has recently been demonstrated by Paul and Warnatz.[87,88] Because the repulsive part of the L-J 12-6 potential is too stiff, for small species the use of the L-J potential results in underprediction of binary diffusion coefficients by as much as 30% at high temperatures. They suggested that a more accurate extrapolation of the transport data might be achieved by switching to an exponential repulsive potential when $k_B T/\varepsilon > 10$.

Given the large sensitivity of laminar flame speeds with respect to the diffusion coefficients of the H atom, and recognizing that the discrepancy between experimental and computed laminar flame speeds of H_2-O_2-He mixtures[22] could be a result of uncertainties in the H-atom diffusion coefficients, a first-principle calculation was carried out recently to determine the diffusion coefficients of simple pairs H-He, H-H_2, and H_2-He.[89] These calculations were conducted using the quantum close-coupling scattering method and accurate potential energies recently published in the literature. Figure 26 shows that large discrepancies exist between the first-principle results[89] and the semi-empirical extrapolations[84,88] at high temperatures. The use of the first-principle results led to even a large discrepancy between aforementioned experimental and computed H_2-O_2-He laminar flame speeds at high pressures.

In addition to the problems caused by the lack of diffusion data and the inaccuracy of semi-empirical extrapolation, the Chapman–Enskog theory might not be adequate for pairs that can undergo inelastic collision, as demonstrated recently.[86] At flame temperatures the collision dynamics of a large number of binary pairs, including H-O_2, H-CO, H-CO_2, are expected to be highly inelastic. This situation leads to even large uncertainties in the diffusion coefficients. The preceding results clearly demonstrate that significant attention must be paid to the transport properties when developing detailed and reduced reaction mechanisms and that concerted experimental and theoretical efforts are required to improve their accuracy.

Conclusions

This paper reviews the state of the reaction mechanisms used in the simulation of combustion phenomena and processes and advocates the adoption of a systematic strategy and program toward the development of detailed and reduced mechanisms that are both chemically comprehensive and computationally adaptable. Our advocacy was motivated by the recognition that existing detailed kinetic mechanisms for the modeling of hydrocarbon oxidation are far from being comprehensive to describe the diverse thermochemical conditions and combustion situations within complex flames and practical combustors, that such a deficiency could be further compromised through the use of reduced mechanisms with insufficient number of steps, and that, in spite of their limited comprehensiveness, they are increasingly being integrated into the simulation of combustion phenomena and combustor performance characterized by extensive variations in the thermodynamic and system parameters. It is thus advocated that a concerted experimental and modeling effort be implemented to develop detailed, comprehensive mechanisms that are capable of describing diverse combustion and flame phenomena, including homogeneous and diffusive ignition, steady burning and extinction, premixed and nonpremixed flames, pressure and concentration effects, global responses including the laminar flame speeds and extinction strain rates, thermal and the major and minor species structures, and pollutant chemistry. Furthermore, it is emphasized that systematic, mathematically rigorous procedures exist for the reduction of detailed mechanisms to simplified ones with specified level of comprehensiveness, and that satisfactory description of hydrocarbon oxidation of sufficiently large size could possibly be achieved with reduced mechanisms consisting of semiglobal steps whose number is in the low tens instead of hundreds and thousands. This is illustrated by the comprehensively satisfactory performance of a 12-step mechanism for methane oxidation.

The need to acquire data of sufficient accuracy for the description of transport properties, especially those associated with the diffusion of the free radicals, is also advocated.

Acknowledgments

This work was initiated and primarily supported by the New World Vista Program of the U.S. Air Force Office of Scientific Research under the technical monitoring of Julian M. Tishkoff, to whom we express our appreciation for his vision and support. Additional support from the U.S. Army Research Office under David Mann and the NASA Microgravity Combustion Program under Merrill K. King, on chemistry-related projects have also contributed to our study on combustion chemistry. C. J. Sung and H. Wang were also supported by the National Science Foundation under the technical monitoring of Farley Fisher.

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