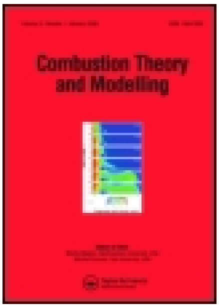

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An automatic chemical lumping method for the reduction of large chemical kinetic mechanisms

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A novel approach to the lumping of species in large chemical kinetic mechanisms is presented. Species with similar composition and functionalities are lumped into one single representative species. Simulations using the detailed scheme are used to gather statistical information on the distribution of the isomers within each lump group. These distributions are functions of space and time. Closure is performed in state space by approximating these distribution functions as the conditional averages depending on the independent state space variables of the lumped scheme. This approach is simplified further, so that the resulting chemical mechanisms can be used directly in standard chemistry packages. For this purpose, only the dependence of the isomer distributions on the temperature is retained, and optimal correcting factors are incorporated into the Arrhenius form of the rate coefficients of lumped reactions. Validation is performed using two comprehensive mechanisms for *n*-heptane and iso-octane oxidation. In all cases, a very good agreement is observed between the predictions obtained using the detailed and the lumped mechanisms. Effects of the lumping procedure on sensitivities of the kinetic scheme and on isomer concentrations are studied. Also, integration of this lumping approach into a multi-stage reduction strategy is discussed and illustrated.

Keywords: chemical lumping; kinetics;p reduction; iso-octane; *n*-heptane

1. Introduction

Systems modelled by elementary chemical reactions are found in many scientific fields, from combustion problems to atmospheric chemistry or biology. For most applications, however, the complete and accurate description of the system would involve an extremely large number of participating species, leading to prohibitive computational costs in numerical simulations. Therefore, developing reliable, systematic reduction methods that ideally require minimum user input is necessary, and major advancements have been made on this topic recently.

Reduction of chemical mechanisms can be achieved through several types of techniques. An overview of these methods can be found in a number of references [1–3]. The most straightforward strategy is to identify, then explicitly remove from the mechanism species and reactions that have a negligible contribution to the phenomena of interest [3–9].The resulting skeletal mechanisms, usually of moderate sizes, are suitable for other techniques introducing model assumptions to further accelerate the computation. These techniques are usually based on time scale analysis, such as Quasi-Steady State Assumption (QSSA) [10], Intrinsic Low-Dimensional Manifolds (ILDM) [11] or Computational Singular Perturbation (CSP) [12]. The present work complements

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another important aspect of kinetic reduction that aims to describe the system in terms of a reduced number of variables, called lumped variables, through a linear or non-linear transformation.

1.1. *Background*

Depending on the applications, lumping can be either an essential modelling tool or a convenient reduction technique. For instance, the extremely large number of molecules in hydrocarbon feedstocks renders the task of developing a comprehensive model for fuel conversion very difficult. To model feedstock pyrolysis, Nigam and Klein [13] proposed to lump all the molecules into compound classes, e.g., normal and iso-paraffins, alkylbenzenes, alkylnaphthenes or alkylhydroaromatics, and the typical pyrolysis reactions into four families: bond homolysis, H atom abstraction, β-scission, and recombination reactions. Corresponding rate coefficients for this two-level lumping approach were obtained from available experimental data using Quantitative Structure-Reactivity Relationships (QSRR). To achieve a more detailed representation of the pyrolysis problem, Fake et al. [14] developed a mechanism-based lumping, in which all molecules in the mixture are described individually. However, the large number of radicals produced by these molecules were reduced to a mere 42-member lump subset representative of the current mixture. Reaction rates were expressed in terms of those lumped radicals using quasi-steady state and long chain [15] approximations, and the rate constants were estimated through QSRR. Systems involving infinite reaction sequences also require lumping as a numerical modelling tool. For example, Frenklach [2,16] developed a lumping procedure for polymerization processes and applied it to polycyclic aromatic hydrocarbon growth in flames. The lumped solution of the chemical system was expressed in terms of moments of the species distribution function.

On the other hand, lumping can be a very efficient tool to reduce the computational burden of detailed models that can be formulated and solved. A significant effort was done in an attempt to find a mathematical procedure that could be applied to any general reaction system to reduce the number of variables. Conditions for the exact and approximate linear [17,18] or non-linear [19,20] lumping of a system of ordinary differential equations (ODEs) have been established and subsequent studies show various successful applications and developments of the mathematical approach [21,22]. However, although an optimal non-linear mathematical lumping would certainly provide the largest reduction potential for a given system of ODEs, no systematic procedure exists to find that optimal lumping transformation, and other more practical solutions have been sought, that exploit the specific features and topology of the system to lump.

Significant simplification can be achieved by constraining the lumping procedure to linear transformations. This is easily demonstrated through the following simple reaction mechanism:

$$\begin{aligned}
&(R_1) A_1 \xrightarrow{k_1} L_1 \quad \omega_1 = k_1[A_1] \\
&(R_2) A_2 \xrightarrow{k_2} L_2 \quad \omega_2 = k_2[A_2] \\
&(R_3) L_1 \xrightarrow{k_3} P_1 \quad \omega_3 = k_3[L_1] \\
&(R_4) L_2 \xrightarrow{k_4} P_2 \quad \omega_4 = k_4[L_2]
\end{aligned} \tag{1}$$

Suppose we want to lump L_1 and L_2 together. The representative species L, lump of species L_1 and L_2, can be defined simply as:

$$[L] = [L_1] + [L_2], \tag{2}$$

where [·] represents a concentration. The lumped mechanism:

$$
\begin{aligned}
&(\widetilde{R}_1)\quad A_1 \xrightarrow{\widetilde{k}_1} L \quad \widetilde{\omega}_1 = \widetilde{k}_1[A_1]\\
&(\widetilde{R}_2)\quad A_2 \xrightarrow{\widetilde{k}_2} L \quad \widetilde{\omega}_2 = \widetilde{k}_2[A_2]\\
&(\widetilde{R}_3)\quad L \xrightarrow{\widetilde{k}_3} P_1 \quad \widetilde{\omega}_3 = \widetilde{k}_3[L]\\
&(\widetilde{R}_4)\quad L \xrightarrow{\widetilde{k}_4} P_2 \quad \widetilde{\omega}_4 = \widetilde{k}_4[L]
\end{aligned}
\tag{3}
$$

is equivalent to mechanism (1) provided that the rate coefficient of the reactions are modified adequately to account for the larger concentration of the lumped species L compared to the original species L_1 and L_2. Production reactions are left unchanged, as their rates do not involve the lumped species concentration, i.e. $\widetilde{k}_1 = k_1$ and $\widetilde{k}_2 = k_2$. The rate coefficients of the consumption reactions, however, must be decreased by a factor proportional to the respective contribution of each original species to the lumped species concentration:

$$\widetilde{k}_3 = k_3 \frac{[L_1]}{[L]} \quad \text{and} \quad \widetilde{k}_4 = k_4 \frac{[L_2]}{[L]} . \tag{4}$$

This result, easily extended to any lump group and reaction mechanism, shows that two different aspects have to be considered for linear lumping, that are not independent from one another. The first one is an appropriate definition of the lump groups, the second one is an accurate evaluation of the quantitative contribution of each species to its lump group. Whitehouse et al. [23] and Huang et al. [24] showed that if the groups of species to lump are carefully chosen, the species distribution can be evaluated directly from the individual production rates of the species, which are available from the lumped scheme since the species production reactions are not modified by the lumping process. Whitehouse et al. [23] lumped species with comparable time-scale and chemical behaviour for the reduction of a mechanism describing atmospheric chemistry. Huang et al. [24] formalized the choice of the groups by introducing a numerical criterion based on local concentrations and formation rates obtained using the detailed mechanism. This criterion was applied successfully in the context of isothermal conversion of methane. The lumping was done on the fly, with the rate-correcting factors evaluated at each time step. However, this approach prevents the lumping to be embedded directly into a stand-alone mechanism suitable for use in standard chemistry solvers. Moreover, the lump groups are chosen on numerical considerations, and thus, have little chemical meaning.

The oxidation chemistry of large hydrocarbon molecules suggests another natural way to define lump groups. Indeed, hydrocarbon oxidation involves a large number of functional isomer species, that is, species with similar composition and structure, but whose chemical functionalities such as radical sites or oxygenated groups are distributed differently on the molecule. Such species usually are formed through analogous chemical channels but may lead to different kinetic behaviours depending on the chain branching, propagating or breaking nature of their decomposition pathways. Several approaches to the lumping of these isomers can be found in the literature that use different simplifying assumptions. In the case of high-temperature kinetics, Zeppieri et al. [25] and Chaos et al. [26] assume pseudo-equilibrium of the isomerization reactions to estimate the relative distribution of the isomers. While Zeppieri et al. [25] use empirical considerations to define appropriate rate constants for the lumped reactions, Chaos et al. [26] fit the temperature-dependent distributions to an Arrhenius-type law, so that the correcting factors can be directly incorporated into the reaction rate constants. Recently, Lu and Law [27] have used a method where the relative distribution of the isomers was assumed constant over a wide range of conditions, and evaluated these constants based on numerical simulations using the original detailed mechanism.

Isomer lumping is also widely used during the automatic generation of mechanisms for hydrocarbon oxidation, that proceeds hierarchically by adding the description of increasingly longer molecules to a basis mechanism. An efficient way to limit the size of the growing mechanism is to lump the isomer species appearing in the primary mechanism, that is, the part of the mechanism that converts the long fuel molecules into smaller ones already described in the basis scheme. In this context, the full detailed mechanism is not used in the solution. Instead, assumptions are made at the level of the primary mechanism to determine the correcting factors. Ahmed et al. [28] suppose an equi-repartition of the primary isomers and modify the pre-exponential factor of the lumped reactions accordingly. Bounaceur et al. [29] and Fournet et al. [30] express the reaction rates of the lumped mechanism in terms of the radical species distributions, and evaluate those rates at a given temperature by applying quasi-steady state assumptions and long chain approximation to the primary mechanism. Also using QSSA, Ranzi et al. [31–34] evaluate the rate constants of the lumped primary mechanism through least-square optimization of the primary product selectivity over a range of pressure and temperature. Additionally, parallel reactions with identical reactants are lumped together, the stoichiometry of the corresponding products being estimated at a given temperature using the detailed description of the reactions.

1.2. *Proposed approach*

The lumping approaches mentioned above involve assumptions that may not be valid for all desired conditions. In this work, a general automatic lumping approach is derived, that directly uses simulation results obtained from the detailed mechanism to generate a lumped scheme valid over a user-specified range of conditions. The method, applied here to isomer lumping in hydrocarbon oxidation kinetic schemes, does not rely on equilibrium or quasi-steady state assumptions. In addition, the resulting lumped mechanisms are suitable for direct use in standard chemistry softwares. In the following, the proposed lumping procedure will be detailed, and compared to some of the techniques outlined above. The quality of the resulting lumped schemes will be assessed. Finally, the integration of the lumping procedure into a multi-stage reduction strategy will be discussed and illustrated.

2. Model

2.1. *General considerations*

Suppose the original set of species $\mathcal{S} = \{S_{i,i=1,\ldots,N_S}\}$ is sub-divided into $\widetilde{N}_S$ lumped groups $\mathcal{L}^S_{I,I=1,\ldots,\widetilde{N}_S}$. For each lumped group $\mathcal{L}^S_I$, a representative species is defined as a linear combination of the species of this group, such that:

$$\left[\widetilde{S}_I\right] = \sum_{i \in \mathcal{L}^S_I} [S_i] \,. \tag{5}$$

We define the relative contribution of species S_i to its group as:

$$\alpha_i = \frac{[S_i]}{\left[\widetilde{S}_I\right]} \,. \tag{6}$$

The reaction rate of a reaction j, is defined as:

$$\omega_j = k_j \prod_{i=1}^{N_S} [S_i]^{\nu'_{i,j}} , \tag{7}$$

where $\nu'_{i,j}$ is the stoichiometric coefficient of species S_i on the reactant side of reaction j and k_j is the rate coefficient of reaction j. Forward and backward reactions are considered separately. Defining $\widetilde{\nu}'_{I,j} = \sum_{i \in \mathcal{L}_I^S} \nu'_{i,j}$ and using the fact that $\mathcal{L}^S_{I,I=1,\ldots,\widetilde{N}_S}$ is a partition of $\mathcal{S}$, the reaction rate can be expressed using the lumped variables:

$$\begin{aligned}
\omega_j &= k_j \prod_{i=1}^{N_S} \left(\alpha_i \left[\widetilde{S}_I\right]\right)^{\nu'_{i,j}} \\
&= k_j \prod_{i=1}^{N_S} \alpha_i^{\nu'_{i,j}} \prod_{I=1}^{\widetilde{N}_S} \prod_{i \in \mathcal{L}_I^S} \left[\widetilde{S}_I\right]^{\nu'_{i,j}} \\
&= k_j \prod_{i=1}^{N_S} \alpha_i^{\nu'_{i,j}} \prod_{I=1}^{\widetilde{N}_S} \left[\widetilde{S}_I\right]^{\sum_{i \in \mathcal{L}_I^S} \nu'_{i,j}} \\
&= k_j \prod_{i=1}^{N_S} \alpha_i^{\nu'_{i,j}} \prod_{I=1}^{\widetilde{N}_S} \left[\widetilde{S}_I\right]^{\widetilde{\nu}'_{I,j}} .
\end{aligned} \tag{8}$$

At this stage, the reactions that have become identical after the lumping of species can also be lumped together. The set of reactions $\mathcal{R} = \{R_{j,j=1,\ldots,N_R}\}$ is sub-divided into $\widetilde{N}_R$ lumped groups $\mathcal{L}^R_{J,J=1,\ldots,\widetilde{N}_R}$ that combine identical reactions. Most lumped reaction groups are trivial, that is, contain a single reaction. The reaction rate for each lumped reaction becomes, as $\widetilde{\nu}'_{I,j} = \widetilde{\nu}'_{I,J}$ for each $j \in \mathcal{L}_J^R$:

$$\widetilde{\omega}_J = \sum_{j \in \mathcal{L}_J^R} \omega_j = \widetilde{k}_J \prod_{I=1}^{\widetilde{N}_S} \left[\widetilde{S}_I\right]^{\widetilde{\nu}'_{I,J}} , \tag{9}$$

with

$$\widetilde{k}_J = \sum_{j \in \mathcal{L}_J^R} \left(k_j \prod_{i=1}^{N_S} \alpha_i^{\nu'_{i,j}} \right) . \tag{10}$$

This transformation corresponds to an exact linear lumping if $\widetilde{k}_{J,J=1,\ldots,\widetilde{N}_R}$, and therefore, the relative contributions $\alpha_{i,i=1,\ldots,N_S}$, are known functions of time and space. Unfortunately, these functions usually are unknown and a closed form has to be assumed. In this work, rather than specifying the relative distributions as functions of physical space and time, models for these distributions will be formulated in terms of the state space:

$$\left\{ T, P, [\widetilde{S}_I]_{I=1,\ldots,\widetilde{N}_S} \right\} . \tag{11}$$

Suppose that a subset Π of the state space variables is chosen to parameterize a set of data σ. In our case, σ refers to the relative distributions $\alpha_{i,i=1,\ldots,N_S}$ or to the lumped rates $\widetilde{k}_{J,J=1,\ldots,\widetilde{N}_R}$. In most cases, there is no explicit relationship between the data and the chosen state parameters. Therefore, a model $f^{\sigma}(\Pi)$ has to be formulated, that will approximate the actual data by a function of the parameters included in Π. Both the choice of the set of parameters and the definition of the function f will impact the quality of the model. To assess the accuracy of the model function f, an error measure can be defined as the L^2 norm of the difference between the data σ and the model $f^{\sigma}(\Pi)$:

$$\epsilon = \langle (\sigma - f^{\sigma}(\Pi))^2 \rangle , \tag{12}$$

where $\langle \cdot \rangle$ denotes statistical averaging.

For a given set Π, the function f must be chosen so that it will minimize the error ϵ. A procedure to construct such a function has been provided by Moreau et al. [35] in the context of sub-grid scale models for large eddy simulations. They demonstrated that if Equation (12) is used to measure the error, the best possible representation of a set of data σ is given by the conditional mean with respect to the parameters used to describe σ, that is,

$$f^{\sigma}_{\text{opt}}(\Pi) = \Omega^{\sigma}(\Pi) = \langle \sigma | \Pi \rangle \ . \tag{13}$$

$\Omega^{\sigma}(\Pi)$ is called the optimal estimator of the data σ given the set of parameters Π. The error introduced by using the optimal estimator instead of the actual data σ corresponds to the minimum amount of error a model based on Π can possibly introduce, and thus, is called the irreducible error.

The concept of optimal estimator provides a convenient tool to assess the relevance of the chosen set of parameters. Indeed, it is expected that the more parameters are used, the smaller the error will be. However, some parameters might be more relevant than others in describing a particular set of data. This is demonstrated here for a practical case. A skeletal mechanism for iso-octane oxidation was derived from the comprehensive mechanism by Curran et al. [36] using the Directed Relation Graph with Error Propagation (DRGEP) reduction procedure [4]. Using this mechanism, a large number of simulations of homogeneous reactors at various pressures, initial temperatures, and equivalence ratios have been run. For each simulation, the evolution of the ratios between the four iso-octyl radicals and the corresponding full state space have been recorded. This can be seen as a statistical database for the relative contributions α_i of the iso-octyl isomers. Figure 1 shows the quadratic errors ϵ obtained using the optimal estimator based on conditional averages for the four isomers, for different sets of variables Π. These errors correspond to the minimal error level introduced in the representation of the relative contributions by assuming that they can be expressed as functions of the given state space. As expected, the error decreases as the number of variables used increases, and the overall error level remains small, even when a single parameter is used. But the results also show that different sets of variables produce different levels of error. For example, representing α_i using temperature, pressure and HO_2 is better than using the fuel or a progress variable as the third independent coordinate. A possible explanation is that the fuel is depleted when the intermediate iso-octyl species reach their peak concentrations, and the major products are produced only when the iso-octyl radicals are already present in large quantities. Thus, neither of these variables can provide a good representation of the evolution of the radicals over their entire production and consumption cycle. The evolution of HO_2 concentration, on the other hand, roughly follows that of the iso-octyl radicals, which explains the small error obtained when using it as the third parameter.

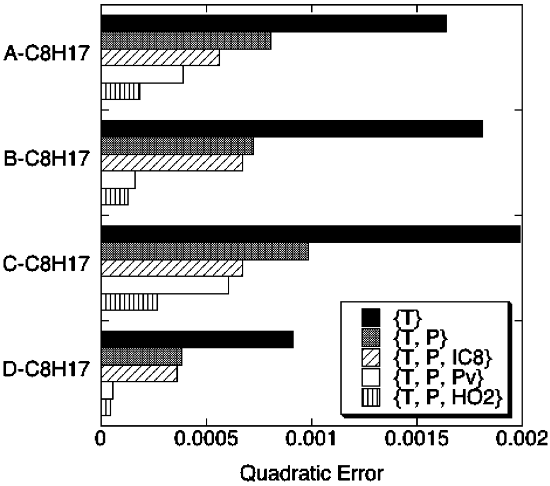


Figure 1. Quadratic error $\epsilon_i = \langle(\alpha_i - \langle\alpha_i|\Pi\rangle)^2\rangle$ in the representation of the relative contributions α_i for iso-octyl radicals in homogeneous reactors for different sets of parameters Π. P_v is a progress variable defined as the sum of CO, CO_2, H_2O and H_2.

2.2. *Evaluation of the model function*

Now that we have seen that the optimal estimator provides a convenient procedure to choose the most adequate set of parameters Π, the next step is to find practical ways to evaluate the model function $f^{\sigma}(\Pi)$, so that it accurately represents the conditional expectation. A promising approach is to use non-linear data modelling tools such as artificial neural networks, which can be seen as parametric functions whose weights are adjusted by training the network to minimize errors [37]. This technique allows to retain the dependence of the data on a large number of state variables, thus introducing very little error in the model. However, the training process is not an easy and straightforward procedure, and extra routines need to be provided to evaluate the lumped rate constants. A possible simplification consists in restricting the resulting lumped mechanism to an elementary form. This simplification is very convenient, first in term of portability from one kinetic code to another, but also if other reduction techniques are further applied to the lumped scheme. Therefore, for practical reasons, the approach will be demonstrated and analysed by considering only constant values or temperature dependent values of α_i. To increase accuracy, the modelling procedure will be applied directly to the lumped rate coefficients $\widetilde{k}_J$, instead of the relative contributions α_i. Then, the lumped rate coefficients can be expressed in Arrhenius form and the lumped reactions readily incorporated into the lumped mechanism that retains the same format as the detailed mechanism. Accordingly, $\widetilde{k}_J$ will be modelled using a basis function of the form:

$$f^{\widetilde{k}_J}(T) = \beta T^{\gamma} e^{-\frac{\delta}{RT}} . \tag{14}$$

The determination of the unknown coefficients β, γ, and δ is done using the detailed simulation data. Identical fall-off reactions are not lumped together, and the modelling function in Equation (14) is applied to both low and high pressure limit rate coefficients. The Troe parameters, if any, can be taken from the original reaction without modifications. To illustrate the soundness of this simplifying assumption, the data for the iso-octyl isomers obtained in the example above are projected onto the temperature and shown in Figure 2. An important observation is that the role played by these isomers in the overall dynamics of the system might be more or less

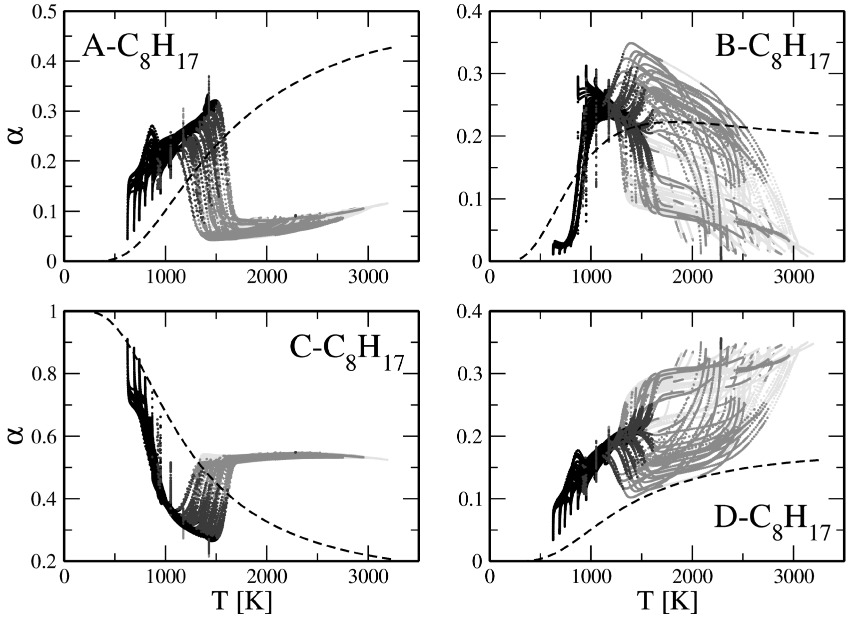


Figure 2. Iso-octyl radical distribution as function of the temperature for homogeneous and flame configurations. Darker colours mean higher DRGEP coefficients. Dashed lines correspond to thermodynamic equilibrium ratios.

important depending on the configurations. A global interaction coefficient was defined as part of the DRGEP methodology presented in [4], that quantifies the impact of a species on major parameters such as ignition delay time, laminar burning velocities or fuel consumption. This DRGEP coefficient R is computed for all cases and used as a weighting factor to analyse the relative contribution of each iso-octyl isomer. In Figure 2, darker colours mean larger coefficients R, that is, a higher importance of the radicals in the mechanism. These data demonstrate that keeping only the temperature dependence of the distribution functions α is a good approximation at low temperatures, whereas some scatter is observed at higher temperatures. However, less accuracy in the isomers distribution will have little impact on the prediction of the targets, as indicated by smaller DRGEP coefficients. Also shown in Figure 2 are the relative contributions computed using the equilibrium constants of the isomerization reactions. Although the trends are similar, using the pseudo-equilibrium assumption to evaluate α might introduce large inaccuracies in the reaction rates. This will be demonstrated in more detail below.

3. Technical description

3.1. *Choice of groups of isomers*

The identification of the potential lump groups can be based on mathematical criteria such as the one developed by Huang et al. [24]. Two intermediate species were included in the same lump group if their concentration over formation rate ratios evolved similarly. Such criterion ensures that the lumping transformation gives accurate results. However, it was designed so that the relative contribution of each species inside a lump group could be computed explicitly at run time from the kinetic parameters of the original scheme, which can be an overly restrictive selection procedure. Moreover, especially in the case of hydrocarbon oxidation mechanisms, it is desirable to keep in the lump mechanism the overall organization of the detailed scheme, with representative elementary steps for each specific class of reactions. In that case, the reduced mechanism can still be used to get insight into the dynamic chemical processes occurring during combustion. A simple way to achieve that is to lump together chemical isomers, as these species have potentially similar formation and decomposition pathways. Mauss et al. [28] further refined this approach by subdividing isomers depending on the type of intermediate chemical complex appearing during the formation of the species and the primary or secondary position of the radical site on the molecules. With this definition, the lump groups are more consistent in terms of energy levels and reactivity, which may lead to a more accurate lumping, at the expense of larger lumped mechanisms. In the present work, the lump groups consist of chemical isomer species. It was found in the mechanisms used as examples, that the distinction between primary and secondary radical sites was not important, but that for some cases, taking into account the size of the ring in the transition states, as suggested by Ahmed et al. [28], improved results dramatically with a small loss in the degree of reduction.

3.2. *Procedure*

The first step is to define the physical space, for which the lumping process will be performed and the validity of the reduction tested. Then, this domain is densely sampled so that if the lumped mechanism is a good approximation to the detailed mechanism at each sample point, it can be reasonably assumed that it will be valid also between sampled points. Solutions using the detailed mechanism are computed at each of the sample points. From these solutions, statistical data on the relative contribution of the isomers and the corresponding temperature are gathered at each computational step, each data point being weighted by the corresponding DRGEP coefficient of the isomers. This comprehensive treatment of the detailed solutions ensures that all reaction states relevant to the domain of applicability of the mechanism are included. Contributions from regions of the state space unimportant for the considered group of isomers are damped by small DRGEP coefficients. The definition of the lump groups determines the list of lump reactions $\mathcal{L}^R_{J,J=1,\ldots,\widetilde{N}_R}$, and the value of their rate coefficients $\widetilde{k}_J$ are evaluated at each sample point, forward and backward reactions being treated separately, using the previously obtained values for α. A least-square regression algorithm is applied to the set of $\widetilde{k}_J$ values using the logarithm of the Arrhenius-like model function shown in Equation (14) and the optimal pre-exponential factor, temperature exponent, and activation energy of each of the lumped reactions are determined. However, if the fitted data as function of temperature exhibits a large curvature, the three-parameter fitting procedure may result in very large fitting parameters, causing numerical overflow. On the other hand, a two-parameter fit that considers only pre-exponential factor and activation energy is less accurate, but always well defined, provided that the fitted data span a reasonable range of temperatures, which is the case for combustion applications. Therefore, a two-parameter fit is chosen when the exponent of the pre-exponential factor obtained with a three-parameter fit is larger than a certain threshold, here chosen to be 100. Although this simplification might affect the accuracy, it applies only to a few percent of the lumped reactions and was found not to affect the quality of the results. The resulting kinetic mechanism will have less species and less reactions. A few comments can be made at that point. First, as the obtained rate coefficients are solutions of a fitting process, they are not chemically meaningful. Then, backward rates are not determined using thermodynamic data anymore, but must be explicitly specified in the lumped mechanism as output from the algorithm.

3.3. *Thermodynamic data*

The issue of thermodynamic data for the representative species in each lump group was not studied in details in previous work. Two reasons can be found for this. The first one is that some of the lumping methods detailed above were used in situations for which thermodynamic properties of the lumped species mattered very little, such as iso-thermal conditions with irreversible reactions, or lumped species that have identical thermodynamic properties. In other cases, the thermodynamic data were taken as the ones of the first species appearing in the lumped group. In the current approach, because the rate coefficients of the lumped backward reactions are specified explicitly, thermodynamic data for the lumped species appear only in the energy equation. To keep a more consistent approach to the overall lumping procedure, the same treatment was applied to the thermodynamic data as for the species themselves. However, to avoid any fitting problems, the relative contribution of each species in the lump was averaged over the range of temperature relevant to the domain of applicability of the lumped mechanism, and the thermodynamic coefficients were computed as the weighted average of the coefficients of each species. In the context of large hydrocarbon molecules oxidation mechanism, this procedure was found to have very little consequence on the lumping accuracy.

4. Results and validation

The skeletal mechanism for iso-octane oxidation derived in [4] is used as starting mechanism to demonstrate the efficiency of the lumping approach. This mechanism contains 195 species and 802 reactions, backward and forward reactions counted separately. Among those species, 27 lump groups involving 88 chemical isomer species can be identified, leading to a reduction of the number of species from 195 to 135 if all groups of isomers are lumped, and a reduction of the number of reactions to 611.

4.1. *Evaluation of the relative contributions* $\alpha(T)$

The accuracy of the lumping procedure depends on the quality of the model $f^{\widetilde{k}_J}(T)$ describing the lumped rate coefficients. In Equation (10) defining $\widetilde{k}_J$, all the terms are known analytically except the α functions that need to be estimated. The current approach, in which the α values are taken directly from simulations using the detailed mechanism, can be compared to three other methods. The first one follows Lu and Law's method [27] and assumes constant α values, computed as the average over all sample point of the actual ratio of isomers. The second one assumes a pseudo-equilibrium of the isomerization reactions to compute temperature-dependent values for α based on thermodynamic data [26]. Finally, following the equi-repartition approach by Ahmed et al. [28], α can be defined as the reciprocal of the number of isomers in the lump. For this comparison, the thermodynamic data of the representative species were chosen as those of the isomer present in largest concentration. Lumping was performed for isochoric homogeneous auto-ignition cases in engine-relevant conditions, that is, with initial pressures ranging from 1 to 40 bar, equivalence ratios varying from lean ($\phi = 0.5$) to rich ($\phi = 2$), and temperatures between 600 K and 1500 K. No simulation was included that led to ignition delay times larger than a couple of seconds. The procedure detailed in Section (3.2) is followed for the proposed lumping approach. For each initial configuration, the solution is computed and the value of $\widetilde{k}_J$ is recorded at each time step, which corresponds to a different advancement of the oxidation process. The determination of β, γ, and δ from Equation (14) is done using the entire set of $\widetilde{k}_J$ data obtained in this process. For each of the other approaches, the α_i values are evaluated independently using the detailed simulations if necessary, Equation (10) is computed for each lumped reaction, and the resulting $\widetilde{k}_J$ are fitted using the model function from Equation (14). Results for ignition delay times of stoichiometric mixtures are shown in Figure 3. As logarithmic plots are misleading in estimating the error level, Figure 4 shows as an example the differences in percent between detailed and lumped schemes on a linear scale for a pressure of 13 bar. From these two figures, it

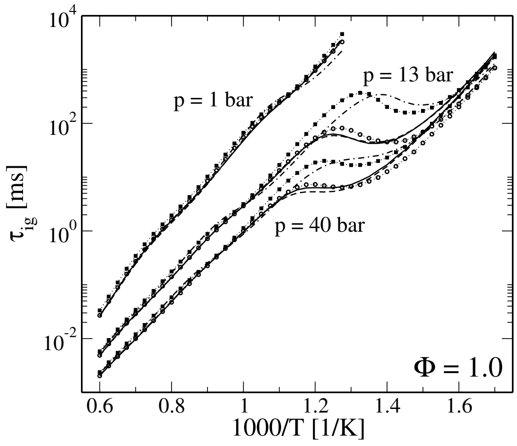


Figure 3. Ignition delay times obtained using different explicit methods. Comparison between the skeletal mechanism (solid lines), and lumped mechanisms obtained using fitted ratios (dashed lines), constant ratios (circles), thermodynamic equilibrium (filled squares) and equi-repartition (dash-dotted lines).

is apparent that all methods give an accurate representation of the high temperature chemistry, but perform very differently around the Negative Temperature Coefficient (NTC) region and for low temperatures. The method proposed here is the most accurate, with only a small under-prediction of the ignition delay time at high pressure around the NTC region. At $\phi = 1$ and $p = 13$ bar, the maximum error between the skeletal mechanism and the lumped mechanism is always smaller than 8%. On the other hand, approximating the isomer distribution by constants is a correct approximation for high to medium temperatures, but the solutions divert significantly in the low temperature regime, with errors up to 50%. The other two methods perform extremely poorly in the NTC region, both predicting the roll-over of the ignition delay time at too low temperatures.

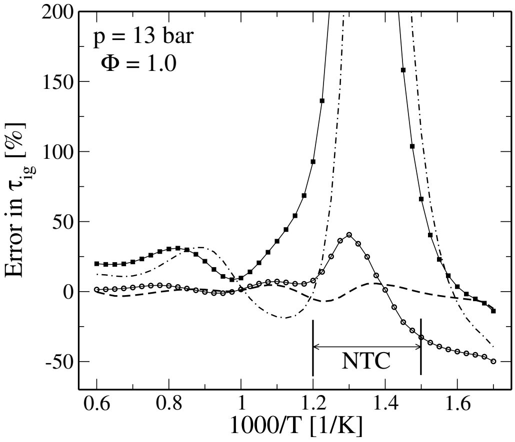


Figure 4. Error in ignition delay times when compared to the skeletal mechanism: Lumped mechanisms obtained using fitted ratios (dashed lines), constant ratios (circles), thermodynamic equilibrium (filled squares) and equi-repartition (dash-dotted lines).

This proves that an accurate fitting of the ratio as function of temperature is an essential step to correctly reproduce the temperature selectivity of the original mechanism.

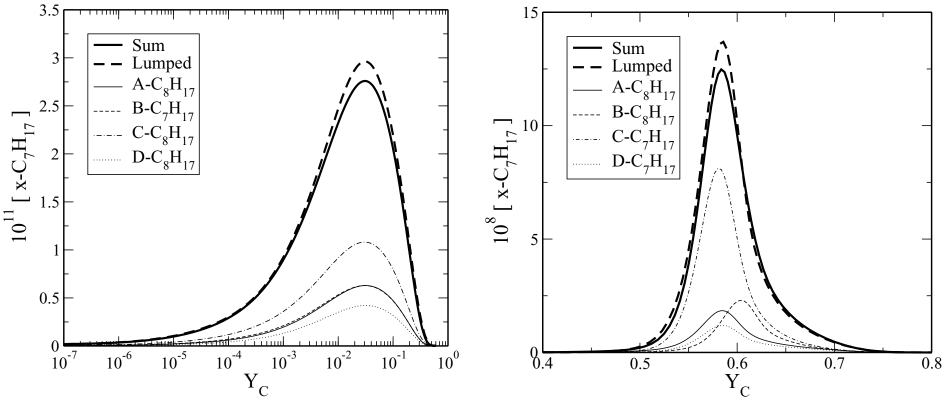
4.2. *Impact on chemical and dynamic characteristics of the mechanism*

In addition to the auto-ignition configurations used to generate Figure 2, the lumped mechanism obtained above with the proposed method was used to simulate atmospheric plug flow reactors, modelled by isobaric homogeneous systems, and atmospheric one-dimensional laminar premixed flames. It is important to note that in the present lumping approach only the chemical source terms are analysed and modified. This approach is directly applicable to typical diffusive systems such as laminar flames, provided that the lumped species have identical diffusion coefficients and no production source other than chemical reactions. If these two conditions are satisfied, which is the case in this study, the linearity of the governing equation for species conservation indicates that the only term that needs modelling is indeed the chemical source term, as is described in [27]. Table 1 provides the errors obtained over all conditions between skeletal and lumped schemes for ignition delay times and laminar burning velocities, which are two parameters describing the global behaviour of the considered systems. Virtually no error on the final concentration of the products was observed.

The small errors show that the prediction of global parameters are quite accurate. More remarkable is the fact that even though the lumped rate coefficients were modelled using homogeneous reactor data only, the resulting scheme is applicable to different configurations such as flames. However, additional comparisons are required to ensure that the lumping does not affect fundamental aspects of the original mechanism, for example, mass fluxes between species and dynamic properties such as reaction classes sensitivities [28]. Mass conservation can be assessed by comparing the sum of the concentration of isomers of the lump group to the actual concentration of the representative species. For an accurate lumping, these two quantities should be equal, as indicated by the fundamental definition of the representative species in Equation (5). This is demonstrated for the iso-octane lumped mechanism, in a few representative configurations: in a PFR simulation at atmospheric pressure, $\phi = 0.5$ and initial temperature of 945 K (case *a*), in a premixed stoichiometric flame, for which the discrepancy with the skeletal mechanism was the largest (case *b*), and for auto-ignition, by selecting the worst case (case *c*) and some initial conditions corresponding to the average error over all cases included in the lumping process (case *d*). The concentration of the representative octyl radical is compared to the sum of the four octyl radicals lumped together. Results are shown in Figure 5. Because of the unsteady character of the cases studied, instead of considering those concentrations in physical space (time or space coordinates), the comparison is done with respect to a progress variable [4]. This progress variable is composed of the main products, that is H_2O and CO_2 for cases *a* and *b*, H_2O, CO_2, H_2, and CO in cases *c* and *d*. Good agreement is obtained for cases *a* and *b*, and excellent agreement is obtained for the representative average ignition configuration. In the worst possible case for ignition, there

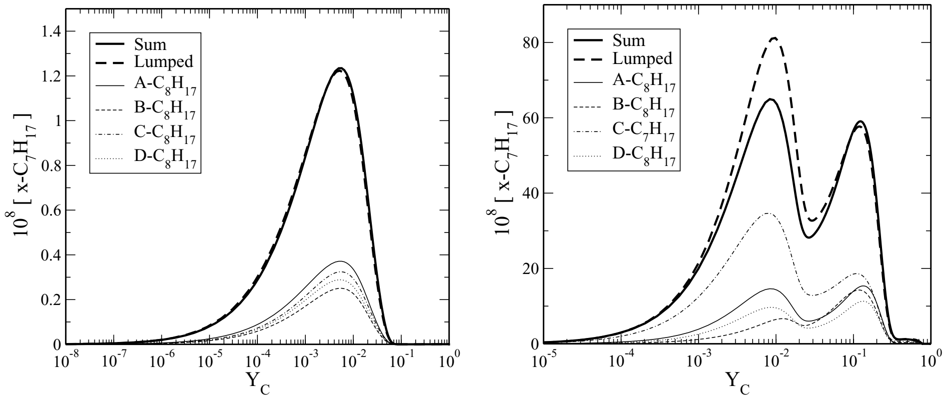
Table 1. Comparison of global parameters between skeletal and lumped iso-octane mechanisms.

Error in τ_{ig} [%]	
Max	16.19
Avg	4.75
Error in S_L [%]	
Max	1.05
Avg	0.67



(a) Plug-flow reactor.

(b) Stoichiometri premixed flame.



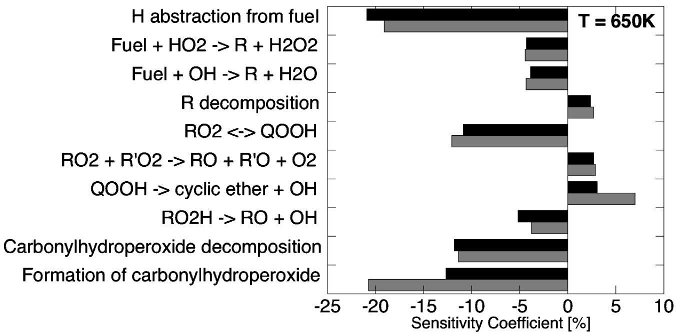
(c) Average auto-ignition case.

(d) Worst auto-ignition case.

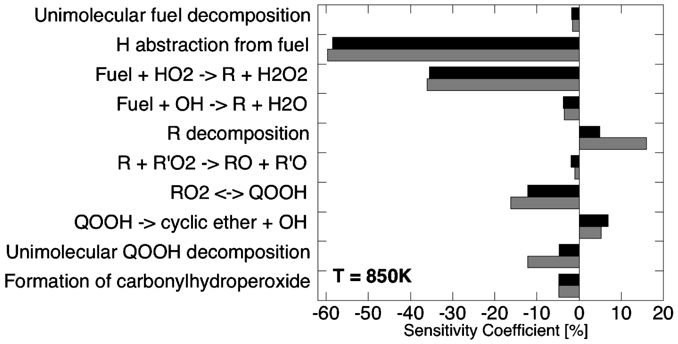
Figure 5. Comparison of iso-octyl isomers and lumped representative species concentrations in selected configurations.

is an over-prediction of the total iso-octyl concentration around the first stage ignition, which leads to an under-prediction of the main ignition delay time. However, the iso-octyl concentration is very well reproduced at ignition.

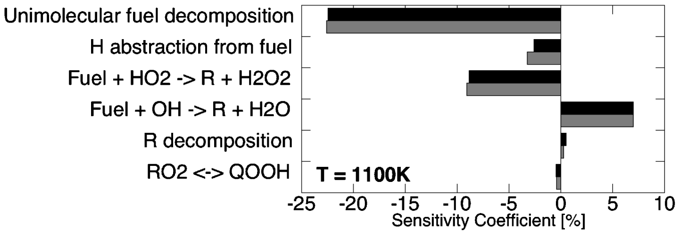
The impact of lumping on the main dynamics of the reactive system can be quantified by the changes introduced by the lumping process on the original sensitivities of the system, as suggested by Ahmed et al. [28]. Kinetic mechanisms for alkane pyrolysis and oxidation, including the one used in this example, are usually built hierarchically by defining a number of reaction classes that are applied to each size of alkane molecules. For iso-octane, 25 reaction classes were defined in [36] to generate the comprehensive iso-octane mechanism, but only 20 of them are still present in the skeletal mechanism. The sensitivity of the system to each class of reactions can be evaluated by comparing the solution obtained with the original rates to the one obtained using a mechanism in which forward and backward rate coefficients of the reactions are multiplied by a factor of 2. Sensitivity of the most important classes of reactions on ignition delay time for auto-ignition of a stoichiometric mixture of iso-octane and air at 13 bar and various initial temperatures are shown in Figure 6. The most sensitive classes of reactions change as the initial temperature increases, as expected. Unimolecular fuel decomposition, negligible at low temperatures, become more and more important as the temperature increases. H atom abstraction from the fuel is important in



(a) 650 K



(b) 850 K



(c) 1100 K

Figure 6. Sensitivities of the most important classes of reactions. Comparison between the skeletal (dark bars) and the lumped (light grey bars) iso-octane mechanisms.

all cases, but with various intensity. Ignition delay time is very sensitive to low temperature-type chemical reactions, especially those producing small radicals or OH. Good agreement is observed between the lumped mechanism and the skeletal mechanism, proving that the lumping procedure did not affect too much the natural dynamics of the system.

5. Integration into a multi-stage reduction strategy

5.1. *Influence of the ordering of the reduction techniques*

The next step is to integrate the lumping procedure into a more comprehensive, multi-stage reduction strategy. Recently, Lu and Law [27] proposed to combine several techniques, such as the Directed Relation Graph (DRG) and DRG Aided Sensitivity Analysis methods, an isomer lumping technique using constant intra-group isomer fractions, QSSA using a CSP-based criterion, and diffusive species bundling. They illustrated their approach with the reduction of the detailed Lawrence Livermore National Laboratories mechanism for *n*-heptane oxidation by Curran et al. [38]. The strategy described here includes explicit removal of species and elementary reactions using the DRGEP method [4], chemical lumping, and introduction of quasi-steady state assumptions. At that point, it is necessary to determine if the order in which the various reduction techniques are applied has an impact on the final degree of reduction and error levels achieved. To answer this question, the detailed mechanism for *n*-heptane oxidation by Curran et al. [38] has been reduced for auto-ignition configurations in two different ways: first DRGEP, then the chemical lumping, and the reverse, first chemical lumping, then DRGEP. The sample state space is similar to the one used for the lumping of the iso-octane mechanism. In the first case, the comprehensive mechanism is reduced until the maximum error on ignition delay time over all initial conditions is around 15%. Then, all possible isomer groups are lumped together. For this example, the Ahmed et al. [28] criterion to select groups of isomers was applied for the two groups of heptyl oxygenated radicals QOOH and O_2QOOH, the molecule names being taken from the Curran et al. [38] nomenclature. Instead of lumping all isomers into a single group, distinction between isomers is made depending on the size of the transition state ring involved in the isomerization reactions, resulting in four smaller lumped groups and significantly lower errors in the predictions made using the lumped mechanism. In the second case, the isomer groups are lumped first, then DRGEP is used to remove species and reactions, so that the final reduced mechanisms obtained from both combinations have similar sizes: 127 species and about 600 reactions. The intermediate mechanisms contain 177 and 252 species in the first and second cases, respectively. Comparisons of ignition delay times obtained from the reduced mechanisms are shown in Figure 7, while error levels are displayed in Table 2. Each reduction technique

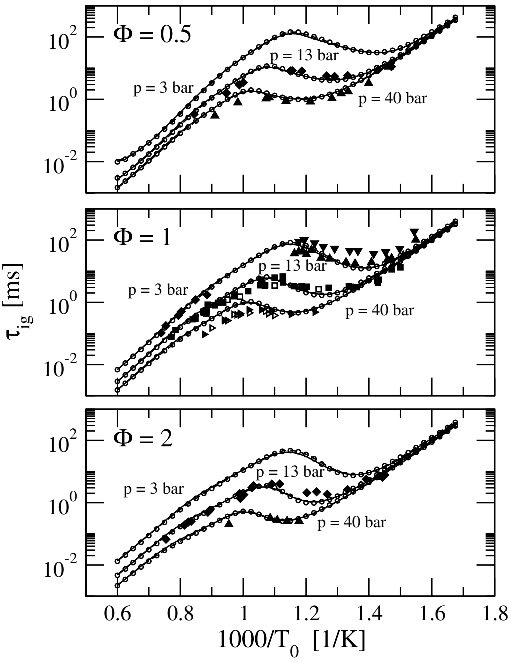


Figure 7. Ignition delay times for *n*-heptane. Comparison between experiments [39–41] (symbols), detailed mechanism (solid lines), mechanism lumped at the detailed level (dashed lines), and at the skeletal level (dotted lines with circles).

Table 2. Ignition delay times of *n*-heptane. Comparison between two different reduction strategies that differ in the order in which the individual reduction techniques are applied. The 'Reference Mechanism' column defines the mechanism against which the reduced schemes are compared.

Reduction Stage	Reference Mechanism	Type of Error	DRGEP → Lumping	Lumping → DRGEP
Stage I	Detailed	Max	15.17%	9.45%
		Avg	6.19%	3.14%
Stage II	Stage I	Max	10.81%	13.32%
		Avg	2.64%	4.52%
	Detailed	Max	16.70%	18.83%
		Avg	5.66%	6.42%

introduces roughly the same amount of error, regardless of their order in the reduction procedure. Lumping isomers first decreases slightly the accuracy of the final mechanism, but the difference is not significant, which suggests that both approaches are valid. Moreover, the chemical pathways retained in both reduced mechanisms are very similar. However, removing first from the mechanism the isomers that have negligible contributions might, in general, prevent more important regression error in the lumping stage. In the next example, the DRGEP technique will be applied first.

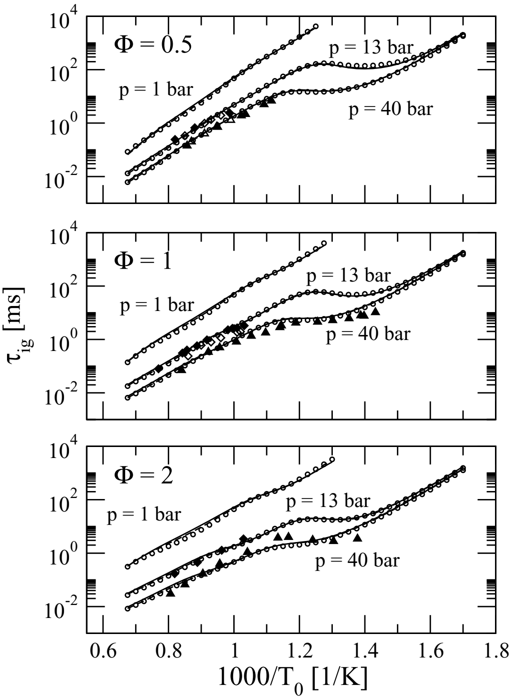


Figure 8. Ignition delay times for iso-octane. Comparison between experiments [43–45] (filled symbols), detailed (solid lines), skeletal (dashed lines), and reduced (open circles) mechanisms. Maximum error in ignition delay time is 34.94%, average error is 10.86%. Errors in the final concentration of the major products H_2O and CO_2 do not exceed 0.5%.

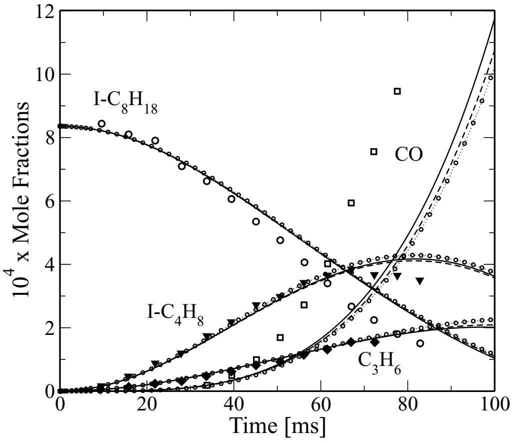


Figure 9. Very lean iso-octane oxidation in an atmospheric plug-flow reactor at 945 K. Experiments [46] (symbols), detailed (solid lines), skeletal (dashed lines), and reduced mechanism (dotted line with circles).

5.2. *Full reduction of a comprehensive iso-octane mechanism*

As a final example, the three reduction techniques are applied successively to reduce the LLNL comprehensive iso-octane oxidation mechanism by Curran et al. [36]. The sample state space includes auto-ignition, plug-flow reactors, and premixed flames. The order of the reduction techniques is as follows. First, DRGEP removes negligible species and reactions until some error tolerance of about 15% for the chosen targets is reached. Removing more species at this stage would bring the error up considerably, as parts of some important parallel pathways would be removed. Although each channel individually does not contribute much to the global fluxes, discarding too many of them ends up introducing a lot of error. These pathways are lumped together in the next stage of reduction using the method presented in this paper. These first two stages have been

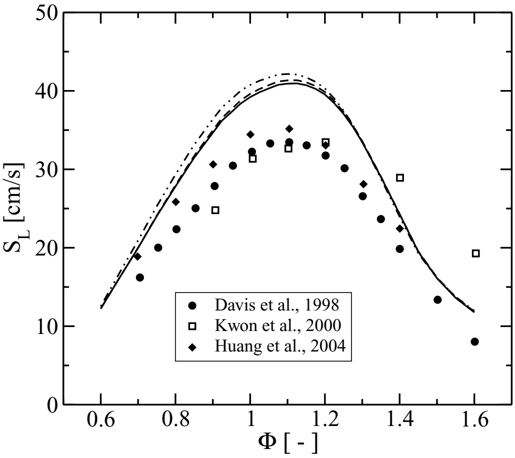


Figure 10. Atmospheric laminar burning velocity for iso-octane and air mixtures at 298 K. Experiments [47, 48, 49] (symbols), skeletal mechanism (solid line), lumped (dashed line), and reduced mechanisms (dash-dotted line). Maximum error with respect to the skeletal mechanism is 5.45%, average error is 2.81%.

described in detail above. Then, an additional stage of DRGEP can be applied to bring the number of species further down. Finally, QSSA are introduced to speed-up the computational process. Suitable QSS species are identified using the procedure described in Pepiot-Desjardins et al. [4], which is based on a life time analysis combined with DRGEP weighting factors. A final reduced mechanism is obtained, that consists of 109 species and 504 reactions, among which 52 can be set in steady-state. An electronic version of the reduced mechanism can be downloaded online [42]. Comparison of the results at various stages of reduction are shown in Figures 8–10. Overall, the reduced mechanism reproduces correctly the detailed results for ignition timing, very lean oxidation in PFR and flame propagation. The errors introduced are everywhere negligible compared to the discrepancies with experimental data. For comparison, Lu and Law [27] reduced a 558 species mechanism to 55 species and 13 QSS species. The present method reduced an 850 species mechanism to 57 species and 52 QSS species, leading to similar computational gains. However, it should be noted that the present approach only requires one single evaluation of the detailed solution for each stage of reduction, whereas the DRGASA method from Lu and Law based on sensitivity analysis requires a large number of such evaluations, which is computationally intensive.

6. Conclusion

A lumping method has been devised, that leverages information from the detailed mechanism to accurately derive kinetic rate coefficients for the lumped scheme. It was applied to the reduction of large hydrocarbon oxidation mechanisms, by replacing chemical isomers by one single representative lump. The rate optimization procedure was shown to be more accurate than other existing methods, especially in the very sensitive NTC region typical of low temperature ignition of large alkane molecules. Mass fluxes through the isomers and dynamic properties of the system were conserved satisfactorily. The lumping technique was incorporated into a more general multi-stage reduction strategy. The quality of the results was fairly insensitive to the order in which the reduction techniques were applied. Whereas one single technique is not powerful enough to reduce comprehensive mechanisms to a practical size, the combination of several methods has been shown to achieve such reduction levels. As an example, an 850 species mechanism was reduced to a 57 species scheme that still has excellent predictive capabilities.

Acknowledgments

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