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Automated construction of reduced mechanisms and additive reaction modules

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ABSTRACT

A bottom-up approach to assemble reduced combustion kinetics mechanisms is proposed as an alternative to conventional reduction techniques. Rather than relying on simulations using detailed mechanisms to identify the set of species and reactions to include in the reduced mechanism, the proposed “building” algorithm follows an add-as-needed approach, in which reduced mechanisms are progressively augmented with individual reactions carefully selected among a restricted list in order to properly capture combustion dynamics in increasingly varied operating conditions. The algorithm is first described in details, and its characteristics and performance are explored through several examples. In a first example, reduced mechanisms able to capture methane/air auto-ignition in a constant volume homogeneous reactor are built, and compared to those generated with a conventional graph-based reduction technique. In the second example, the selection behavior of the algorithm is explored at the medium (methane) and large (heptane) mechanism scale, showing some computational advantage in using a building, bottom-up approach. Finally, the flexibility of the algorithm to add, onto a reduced mechanism, kinetic pathways that were initially not considered in the reduction is demonstrated, using the addition of a reduced representation of NO_x pathways on a previously obtained methane oxidation reduced mechanism as example. The algorithm is found to yield similar results compared to reduction techniques informed by detailed mechanisms, while providing increased efficiency and flexibility to the end-user.

1. Introduction

Despite advances in computational power in the past few decades, a significant disparity still exists between the size of detailed chemical kinetics models and those that can be used in computational fluid dynamics (CFD) applications. This disparity is heightened by the continued development of kinetic mechanisms that describe increasingly large molecules and a growing number of fuel components [1]. A well-known approach to lessen the computational cost associated with the chemistry description is to reduce the dimensionality of detailed mechanisms, typically an efficient solution because those mechanisms are assembled to be exhaustive and applicable over wide ranges of conditions [2], and often contain reactions and species that are overall negligible or that do not influence the dynamics of the chemical system in any significant way for the conditions of interest of the end-user. Reduced models can then, in theory, be used in lieu of detailed mechanisms to reduce CFD simulation run-time without sacrificing accuracy.

Multiple reviews [1,3,4] provide summaries of state-of-the-art kinetic mechanism reduction methodologies, showing that almost ubiquitously, reduction algorithms take a top-down approach to generating reduced mechanisms. This type of approach is characterized by the use of detailed simulation data to identify the *least important* species and reactions, which are then progressively removed until a user-defined level of error is reached. This error is typically evaluated by comparing the reduced mechanism’s predictions to those of the detailed one. Three key drawbacks to this approach can be identified:

- The first, and most apparent, disadvantage to a top-down algorithm is linked to the very nature of detailed mechanisms, which often contain an extremely large number of non-important reactions and species, and thus often yield unnecessarily expensive simulations. For example, simply by discarding reactions with a negligible rate of progress, the number of reactions in a kinetic mechanism for isooctane can be decreased by a factor of 3 (from 3606 reactions), and the number of species reduced by a factor of 2 (from 858 species), with minimal loss in accuracy [5]. In contrast, a bottom-up algorithm identifying the *most important*, rather than the least important, species and reactions would likely not have to consider those unimportant

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Nomenclature

$\boldsymbol{\phi}^{\mathcal{M}}$	Representation of gas phase composition based on mechanism $\mathcal{M}$
$\mathcal{T}$	Set of targets used in DRGEP methodology
$\mathcal{M}$	A kinetic mechanism
$n_{\mathcal{S}}^{\mathcal{M}}$	Number of species in kinetic mechanism $\mathcal{M}$
$\mathcal{S}^{\mathcal{M}}$	Set of species in $\mathcal{M}$
$n_{\mathcal{R}}^{\mathcal{M}}$	Number of reactions in kinetic mechanism $\mathcal{M}$
$\mathcal{R}^{\mathcal{M}}$	Set of reactions in $\mathcal{M}$
$\mathcal{R}^{\mathcal{M}^{\text{ref}}}$	Reference (i.e., detailed) reaction set from which reactions in the edge mechanism are identified
$\delta\mathcal{M}$	Edge of a mechanism $\mathcal{M}$
P	Thermodynamic pressure
T	Temperature
$\mathbf{Y}^{\mathcal{M}}$	Vector representing mass fractions of species in mechanism $\mathcal{M}$
$\mathbf{S}(\boldsymbol{\phi}^{\mathcal{M}})$	Chemical source term for the state vector $\boldsymbol{\phi}^{\mathcal{M}}$
K	A generic operation involving a mechanism $\mathcal{M}$ and a state vector $\phi^{\mathcal{M}}$
R^{DRGEP}	Set of DRGEP reaction coefficients
ε	User-defined cut-off used to select important reactions
$\mathcal{M}^{\star}$	Extended mechanism created from the union of $\mathcal{M}$ and $\delta\mathcal{M}$
$\delta\mathcal{M}^{+}$	A submechanism of $\delta\mathcal{M}$, containing only the most important reactions
τ_{ig}	Ignition delay time
t	Time

kinetic pathways in their entirety, potentially increasing significantly the efficiency of the process.

- A second concern stems from the fact that reduced models, whichever way they are generated, are strictly valid only for the conditions and configurations considered in the reduction. To extend the range of validity of an existing reduced model using a top-down approach, the detailed model must be reduced anew, considering the original reduction targets as well as new targets capturing the desired extended conditions. For instance, if a reduced model is generated to capture only fuel oxidation, nitrogen oxide (NO_x) chemistry will not be present in the reduced model in any significant way. To predict NO_x formation, the reduction procedure would need to be repeated, and a new reduced mechanism would need to be generated using reduction targets for both fuel oxidation and nitrogen oxide formation pathways. To the authors' knowledge, no automatic technique exists that would circumvent this requirement by directly identifying and adding to the existing reduced mechanism the set of reduced pathways pertaining to the new targets.
- The third identified drawback is the non-negligible amount of user expertise and sometimes manual labor that is often needed in top-down reduction procedures. Indeed, the majority of such algorithms require multiple stages of reduction to achieve acceptable results. Species are often removed in a primary stage and reactions are eliminated in a secondary stage. The near-ubiquitous focus on species reduction in existing methods can be explained by the significant cost saving of directly reducing the dimensionality of the system of equations. Reaction reduction, in contrast, accelerates calculations mostly through faster chemical source term evaluations and potential fast timescale removal. However, the decision to switch between species and reaction reduction techniques in a multi-stage approach remains largely empirical and driven by the user expertise.

Among the recent work in chemistry reduction exploring alternative approaches, one may note that of Nagy and Turanyi [6], who designed a hybrid reduction algorithm called SEM-CM. In this technique, species are incrementally *added* to a reduced mechanism, thereby emulating a bottom-up approach. The algorithm produces an optimally reduced mechanism for a desired level of error, but can require nearly an order of magnitude more CPU time to complete than a typical reduction algorithm because a library of mechanisms with varied selections of important species are generated and tested. More significantly here, the selection of species to include in the reduced model is still based on the analysis of detailed simulation results, and an additional, independent stage of reaction elimination is necessary after the species identification process.

To address the aforementioned shortcomings of conventional reduction techniques, we introduce here a truly bottom-up methodology to building reduced mechanisms. Rather than relying on simulations using detailed mechanisms, the proposed algorithm follows an “add-as-needed” approach, in which reduced mechanisms are progressively augmented with individual reactions carefully selected among a restricted list in order to properly capture combustion dynamics in increasingly varied operating conditions. While the philosophy behind the proposed approach may share some similarities with the well-known mechanism generation tool RMG [7–9], the focus is uniquely placed on generating reduced mechanisms, with reaction selection criteria derived from graph-based chemistry reduction techniques, here, the reaction-focused version of the Directed Relation Graph with Error Propagation (DRGEP, [10]).

The bottom-up approach avoids the computational cost associated with using detailed mechanisms to inform reduction: evaluations of reaction importance, quantified using rate-based reaction DRGEP coefficients [10], are indeed performed at the reduced mechanism level. The methodology focuses on reactions as the unit building block and proceeds in a single stage, thereby alleviating the need for user expertise in switching between reduction techniques. Most importantly, the approach also provides a convenient framework to incrementally expand existing reduced mechanisms to span wider ranges of conditions or describe new chemical features (such as the NO_x chemistry mentioned above). This attribute makes it ideally suited to complement component library approaches [11] for the generation of multi-component fuels reduced mechanisms, for example by providing an efficient way to identify and add important cross reactions between the various fuel molecules, which the component library framework is unable to handle directly.

The organization of the paper is as follows. The necessary notations are introduced in Section 2, followed by a detailed description of the algorithm in Section 4. Demonstration of the methodology and an assessment of its performances are provided in Section 5. A final summary and general conclusions are presented in Section 6.

2. Definitions and notations

Prior to describing the reduced mechanism building algorithm itself, a few definitions and notations that are used throughout this work are introduced. A kinetic mechanism $\mathcal{M}$ is defined by a set of $n_{\mathcal{S}}^{\mathcal{M}}$ chemical species, $\mathcal{S}^{\mathcal{M}}$, and a set of $n_{\mathcal{R}}^{\mathcal{M}}$ reactions, $\mathcal{R}^{\mathcal{M}}$:

$$\mathcal{M} = \left\{\mathcal{S}^{\mathcal{M}}; \mathcal{R}^{\mathcal{M}}\right\}. \tag{1}$$

A reaction in $\mathcal{R}^{\mathcal{M}}$ can only involve species that are in $\mathcal{S}^{\mathcal{M}}$. However, a species in $\mathcal{S}^{\mathcal{M}}$ does not need to participate in any reaction in $\mathcal{R}^{\mathcal{M}}$: such a species is then considered an *inert* species for the mechanism $\mathcal{M}$. We further denote by $\mathcal{R}^{\text{ref}}$ the reference set of reactions out of which a reduced mechanism is to be constructed.

While there is no restriction on what this reaction set may contain, in practice, $\mathcal{R}^{\text{ref}}$ is often simply the set of reactions contained in a detailed, or reference, mechanism describing the oxidation of a molecule of interest, which will be called $\mathcal{M}^{\text{ref}}$. In this work, reactions are assumed to be reversible, that is, a single reaction r can proceed both in the forward and backward directions. As will be detailed below, $\mathcal{M}^{\text{ref}}$ is never used directly during the construction of the reduced model, but will provide a convenient way to evaluate reduction errors to validate the approach.

We define the *edge* of a mechanism $\mathcal{M}$ with respect to a reference reaction set $\mathcal{R}^{\text{ref}}$ as the set of reactions in $\mathcal{R}^{\text{ref}} \backslash \mathcal{R}^{\mathcal{M}}$ (*i.e.*, in $\mathcal{R}^{\text{ref}}$ but not in $\mathcal{R}^{\mathcal{M}}$) satisfying at least one of the following two conditions: 1) every reactant in the reaction is an element of $\mathcal{S}^{\mathcal{M}}$, *or* 2) every product in the reaction is an element of $\mathcal{S}^{\mathcal{M}}$. In other words, a reaction belongs to the edge of $\mathcal{M}$ if it can happen based on the species included in $\mathcal{M}$. An edge mechanism will be referred to as $\delta\mathcal{M}\big(\mathcal{M}, \mathcal{R}^{\text{ref}}\big)$. Note that $\delta\mathcal{M}$ is not a stand-alone mechanism and cannot be used independently of the mechanism $\mathcal{M}$ for which it is defined. Also, since its definition is based on the selection of specific reactions, $\delta\mathcal{M}$ may contain only species already in $\mathcal{S}^{\mathcal{M}}$, or conversely, involve new species that were not included in $\mathcal{S}^{\mathcal{M}}$. We call *test mechanism*, denoted by $\mathcal{M}^{\star}$, the addition of $\delta\mathcal{M}$ onto $\mathcal{M}$, simply defined as the union of the set of species and reactions:

$$\mathcal{M}^{\star} = \mathcal{M} + \delta\mathcal{M} = \{\mathcal{S}^{\mathcal{M}^{\star}}, \mathcal{R}^{\mathcal{M}^{\star}}\},$$

where $\mathcal{S}^{\mathcal{M}^{\star}} = \mathcal{S}^{\mathcal{M}} \cup \mathcal{S}^{\delta\mathcal{M}}$ and $\mathcal{R}^{\mathcal{M}^{\star}} = \mathcal{R}^{\mathcal{M}} \cup \mathcal{R}^{\delta\mathcal{M}}$

To illustrate those various mechanism-related notations, consider a reference set of reactions that contains the following reactions:

$$\mathcal{R}^{\text{ref}} = \begin{Bmatrix} r_1 : \mathrm{A} \leftrightarrow \mathrm{B} + \mathrm{C} \\ r_2 : \mathrm{D} \leftrightarrow \mathrm{A} \\ r_3 : \mathrm{E} + \mathrm{F} \leftrightarrow \mathrm{A} + \mathrm{D} \\ r_4 : \mathrm{G} + \mathrm{H} \leftrightarrow \mathrm{I} \end{Bmatrix} \tag{2}$$

In this example, we further consider a mechanism $\mathcal{M}$ containing 4 species and one reaction, with:

$$\mathcal{S}^{\mathcal{M}} = \{A, B, C, G\} \tag{3}$$

$$\mathcal{R}^{\mathcal{M}} = \{r_1\} \tag{4}$$

G is an inert species for $\mathcal{M}$ because that species does not appear in any of the reactions currently in $\mathcal{R}^{\mathcal{M}}$. The edge of $\mathcal{M}$, $\delta\mathcal{M}$, consists of a single reaction, r_2, because every product of r_2 (here the single species A) belongs to $\mathcal{S}^{\mathcal{M}}$. Reactions r_3 and r_4 are not in $\delta\mathcal{M}$ because in both cases, at least one reactant and one product in those reactions do not belong to $\mathcal{S}^{\mathcal{M}}$.

The thermochemical state $\mathbf{\Phi}$ of a gas-phase mixture is a function of the thermodynamic pressure, P, the temperature, T, and the species composition. In practice, the representation of the latter depends on the kinetic mechanism being used. We therefore introduce the notation $\boldsymbol{\phi}^{\mathcal{M}}$ to designate the representation of $\mathbf{\Phi}$ corresponding to the kinetic mechanism $\mathcal{M}$:

$$\boldsymbol{\phi}^{\mathcal{M}} = \left\{P, T, \mathbf{Y}^{\mathcal{M}}\right\}, \tag{5}$$

where $\mathbf{Y}^{\mathcal{M}}$ is a $n_{\mathcal{S}}^{\mathcal{M}}$-vector containing the mass fractions of each species in $\mathcal{S}^{\mathcal{M}}$. The conversion between a representation $\boldsymbol{\phi}^{\mathcal{M}_1}$, associated with mechanism $\mathcal{M}_1$, to a representation $\boldsymbol{\phi}^{\mathcal{M}_2}$, associated with a *larger* mechanism $\mathcal{M}_2$ that satisfies $\mathcal{S}^{\mathcal{M}_1} \subset \mathcal{S}^{\mathcal{M}_2}$, is obtained simply by setting all species in $\mathcal{S}^{\mathcal{M}_2}$, but not in $\mathcal{S}^{\mathcal{M}_1}$, to zero, while setting all other species mass fractions in $\boldsymbol{\phi}^{\mathcal{M}_2}$ to the corresponding mass fractions in $\boldsymbol{\phi}^{\mathcal{M}_1}$, in essence padding the larger mass fraction vector with zeros.

The differential equations governing the chemical evolution of the gas-phase mixture that are solved at each step of the reduced mechanism building process are referred to as the kinetic operation K. For the homogeneous reactor used in the demonstration cases below, K is simply written as:

$$K : \frac{\mathrm{d}\mathbf{\Phi}}{\mathrm{d}t} = \mathbf{S}(\mathbf{\Phi}(t)), \tag{6}$$

where $\mathbf{S}$ is the chemical source term. K depends on the kinetic mechanism $\mathcal{M}$ used to express the equations and an initial gas-phase composition: $K\big(\mathcal{M}, \boldsymbol{\phi}_0^{\mathcal{M}}\big)$.

3. Direct relation graph with error propagation (DRGEP)

The building algorithm described below uses the DRGEP methodology to quantify the importance of any given reaction in predicting a user-defined set of targets $\mathcal{T}$, and thereby identify those reactions that need to be added to the reduced mechanism as it is being built up. The definitions and expressions are identical to those described in Pepiot and Pitsch [10] *for the selection of reactions*, and only an overview is provided here for brevity purposes.

DRGEP is based on two different measures to quantify importance. The first one, called direct interaction coefficient (DIC), measures the coupling between two directly adjacent species, say A and B, that appear in the same reaction. DIC are calculated *for a given composition state* using the following expression:

$$r_{AB} = \frac{\left|\sum_{i=1}^{n_R^{\mathcal{M}}} \nu_{i,A}\omega_i\delta_B^i\right|}{\max(P_A, C_A)}, \tag{7}$$

where δ_B^i is a Dirac Delta term, which is equal to 1 if species B is in reaction i, and 0, otherwise. P_A and C_A are the production and consumption rates of species A, respectively. The second measure applies to indirectly related species, that is, species that do not appear together in a reaction. For such pairs, we use a directed graph representation of the chemical network, identify paths in this graph that connect the two species, and define a path-dependent coefficient assuming geometric damping:

$$r_{AB,p} = \prod_{i=1}^{n_S^{\mathcal{M}}-1} r_{s_i s_{i+1}}, \tag{8}$$

where $s_1 = A$ and $s_{n_S^{\mathcal{M}}} = B$, and p denotes one of the (many) paths connecting B to A. This is the error propagation part of the DRGEP approach. Only the maximum value over all possible paths through the graph is retained, and that maximum value becomes the DRGEP species coefficient R_{AB}, which quantifies the importance of B in the prediction of A.

In a similar fashion, we quantify the importance of a reaction r_i to the prediction of a species A using:

$$r_{Ar_i} = \frac{|\nu_{r_i,A}\omega_{r_i}|}{\max(P_A, C_A)}, \tag{9}$$

where $\nu_{r_i,A}$ is the stoichiometric coefficient of A in reaction r_i, and ω is the net reaction rate. The importance of reaction r_i for the prediction of a species, or in this case, a given target T, is computed using error propagation throughout the graph using the DRGEP coefficients of the species:

$$R_{Tr_i} = \max_{S \in \{\mathcal{S}^{\mathcal{M}}\}} \left(R_{TS} r_{Sr_i}\right) \tag{10}$$

Finally, we define the DRGEP reaction coefficient, which quantifies the importance of a reaction r_i for *the set* of targets $\mathcal{T}$ as:

$$\mathbb{R}_{r_i} = \max_{T \in \{\mathcal{T}\}} \left(\alpha_T R_{Tr_i}\right) \tag{11}$$

where the scaling coefficient α_T has been introduced to weigh the relative importance of each target to the composition state under consideration. The reader is referred to [10] for a detailed description of those scaling factors. The higher the DRGEP coefficient of a reaction r_i is, the more important that reaction is for the prediction of the set of targets under consideration. In the following, the notation $\mathbb{R}^{\mathcal{M}}$ will be used to denote the $n_{\mathcal{R}}^{\mathcal{M}}$-vector containing the reaction DRGEP coefficients evaluated from composition $\boldsymbol{\phi}^{\mathcal{M}}$.

4. Algorithm and implementation

The objective of the building algorithm is to explore the regions in composition space of relevance to the application of interest, gradually expanding the kinetic mechanism needed to accurately solve the governing differential equations K over the explored regions. The process consists of an initialization stage, followed by a succession of iterative building steps. At any step during the building process, the resulting mechanism, called the "reduced" mechanism and denoted by $\mathcal{M}$, is a stand-alone, low-order mechanism that describes, with an accuracy directly function of the cut-off parameter ε, the chemical kinetics encountered prior to that step. Once all regions of interest in the composition space have been explored, the building process is complete, and the final version of $\mathcal{M}$ is recorded and stored as the final reduced, or "built", mechanism.

4.1. Initialization

The following items are to be defined at the start of the process:

- The set of governing equations to be solved, K;
- The reference set of reactions $\mathcal{R}^{\text{ref}}$;
- The set of target species whose dynamics are of interest, $\mathcal{T}$;
- The regions of composition space to be explored during the building process. Those can take the form of a series of canonical low-dimensional simulations (e.g., homogenous reactors) at various conditions;
- A starting mechanism, $\mathcal{M}_0$ and initial composition $\boldsymbol{\phi}_0^{\mathcal{M}_0}$. If the building process is used to add additional pathways directly at the reduced level on an already existing mechanism, $\mathcal{S}_0$ and $\mathcal{R}_0$ are initialized with the species and reactions from that previously generated reduced mechanism. Otherwise, $\mathcal{S}_0$ is initialized with the target species, and $\mathcal{R}_0$ is left empty:

$$\mathcal{S}_0 = \mathcal{T} \quad \text{and} \quad \mathcal{R}_0 = \emptyset \tag{12}$$

- A cut-off parameter, ε, to be used in the reaction-based procedure to identify the reactions that should be added to the mechanism;

4.2. Iterative building step

A building step is defined as a small increment in the compositions encountered by the mechanism, for example, a small time interval for an homogeneous reactor simulation, or an iteration of the Newton solver for a one-dimensional premixed flame simulation. We assume that at the end of the $(i-1)$th building step, the reduced mechanism $\mathcal{M}_{i-1}$ captures, up to the DRGEP threshold parameter ε, the kinetics necessary to obtain a solution for K for all prior steps 1 to $i-1$. The goal of the ith step is then to identify the additional set of reactions needed to solve K starting from step i initial condition $\boldsymbol{\Phi}_{0,i}$, which, by default, is taken as the solution of K from the previous building step $i-1$. This incremental reaction set is then added to $\mathcal{M}_{i-1}$ to obtain the updated mechanism $\mathcal{M}_i$. This is done according to the algorithm detailed below, the whole procedure being illustrated in Fig. 1.

At the beginning of the building step, $\mathcal{M}_i$ is initialized as the mechanism obtained at the previous step:

$$\mathcal{M}_i = \mathcal{M}_{i-1}\,. \tag{13}$$

1. The edge mechanism, $\delta\mathcal{M}_i(\mathcal{M}_i, \mathcal{R}^{\text{ref}})$ is generated by identifying those reactions in the reference set $\mathcal{R}^{\text{ref}}$ that are not in $\mathcal{M}_i$, but are satisfying one of the two conditions detailed in Section 2. This edge mechanism is then added to $\mathcal{M}_i$ to obtain the test mechanism $\mathcal{M}_i^\star = \mathcal{M}_i + \delta\mathcal{M}_i$.
2. The initial composition $\boldsymbol{\Phi}_{0,i}$ is converted to $\boldsymbol{\phi}_{0,i}^{\mathcal{M}^\star}$, the representation corresponding to $\mathcal{M}_i^\star$, and the set of equations K are solved using the test mechanism $\mathcal{M}_i^\star$. The results are used to calculate $\mathbb{R}^{\mathcal{M}_i^\star}$, the reaction-specific DRGEP coefficients for all reactions in $\mathcal{R}^{\mathcal{M}_i^\star}$. As recommended in [10], the individual weight of each target in the calculation of DRGEP coefficients is adjusted using scaling factors evaluated from all compositions encountered prior to step i, and production rates averaged over the entire building step are used instead of instantaneous ones to avoid spurious values.
3. Any reaction j belonging to the edge of $\mathcal{M}_i$ (therefore in the test mechanism $\mathcal{M}_i^\star$, but not currently included in $\mathcal{M}_i$) with a DRGEP coefficient $\mathbb{R}_j^{\mathcal{M}_i^\star}$ larger than the threshold ε is tagged. Those reactions collectively define a "sub"-edge mechanism $\delta\mathcal{M}_i^+$ deemed necessary to solve K for the DRGEP threshold ε.
4. $\mathcal{M}_i$ is updated as $\mathcal{M}_i \leftarrow \mathcal{M}_i + \delta\mathcal{M}_i^+$.

Steps 1 to 4 are then repeated with the updated $\mathcal{M}_i$ as starting point. If the algorithm returns an empty $\delta\mathcal{M}_i^+$, that is, no reaction in the edge mechanism $\delta\mathcal{M}_i$ is found to be significant in solving K, the ith building step is deemed complete, and step $i+1$ starts. The building process stops when all regions in composition space of interest have been explored. Note that consistent with conventional DRGEP-based reduction approaches, the only free parameter in the algorithm is the DRGEP threshold ε. While ε has been shown to correlate with an actual error in the prediction of the targets [10], the actual accuracy of the resulting reduced mechanisms is assessed a posteriori by comparison with detailed predictions.

The building algorithm is implemented in Python and utilizes the python-based DRGEP implementation of the ARCANE reduction package [12]. State and rate evaluations to compute the DRGEP coefficients are performed with Cantera v2.4 [13].

5. Results and discussion

In the following, various aspects of the DRGEP-based building algorithm are investigated, such as parameters selection and overall behavior. The performance of the approach in creating a reduced mechanism for methane oxidation is then compared to that of a conventional, DRGEP-based top-down reduction procedure. Finally, the capability of the building algorithm to add, directly at the reduced level, the description of chemical processes not initially included in a reduced mechanism is demonstrated, using NO_x chemistry as an example. For all cases considered below, we define K as the set of ordinary differential equations governing fuel/air ignition in an adiabatic, constant-volume homogeneous reactor.

5.1. Reduced mechanism building: methane oxidation

We first explore the behavior of the building procedure in generating reduced mechanisms for methane/air auto-ignition at high temperatures. The reference list of reactions $\mathcal{R}^{\text{ref}}$ is taken as the set of reactions included in the GRI-MECH 3.0 mechanism [14]. This mechanism, which also serves as starting point when comparing with the conventional DRGEP reduction approach, contains 53 species and 325 reactions, of which 35 species and 217 reactions directly contribute to the description of methane oxidation, the rest being associated with NO_x formation. For all cases shown in this section, we consider the regions in composition space accessed during auto-ignition simulations at atmospheric

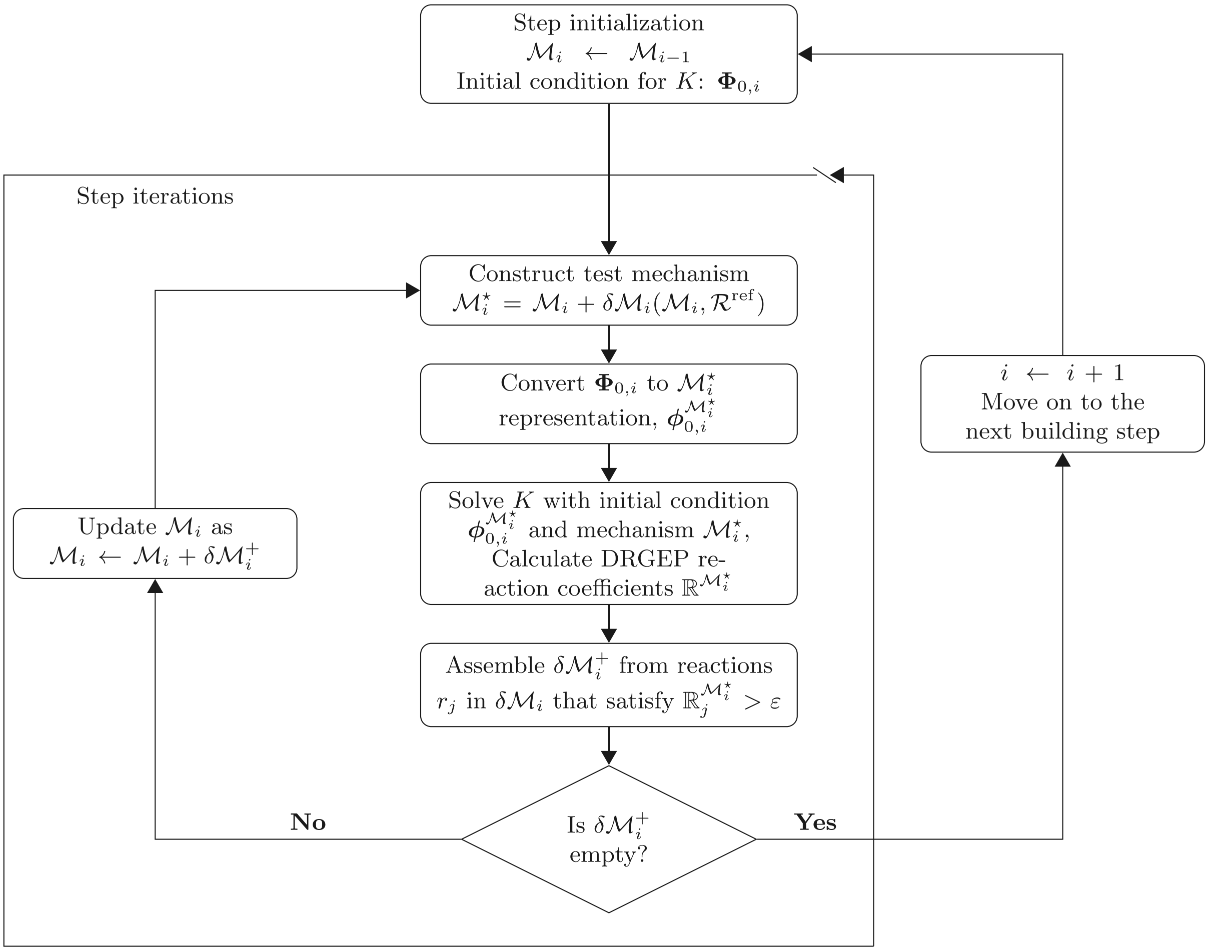


Fig. 1. Flowchart depicting actions and decision criteria for the *i*th building step and a DRGEP cut-off threshold ε.

pressure, equivalence ratios of 0.8, 1, and 1.2, and initial temperatures of 1200K and 1600K. A typical set of DRGEP targets, $\mathcal{T} = \{CH_4, \text{Heat Release (HR)}, OH, CO_2\}$, is chosen: CH_4 and HR are selected to accurately depict the fuel breakdown and ignition delay time, and OH and CO_2 are selected as a key intermediate radical and major combustion product, respectively.

5.1.1. Impact of building step duration

Given the iterative nature of the algorithm, the duration of the building step may influence which species and reactions end up being included in the mechanism at the end of each step. A sensitivity study is therefore performed first in order to determine the most appropriate time interval over which the evolution equations K should be integrated. Since the characteristic timescales in play can vary widely from one building step to another depending on their initial composition, we do not prescribe a fixed time interval. Instead, we rely on the adaptive time stepping strategy of the stiff ODE solver and aim at expressing the building step duration as a fixed number of internal time steps taken by the solver.

To that end, a series of reduced mechanisms are built by varying the number of internal integrator steps taken during each building step between 1 and 500. A single reaction selection threshold $\varepsilon = 0.01$ is applied. Results are shown in Fig. 2.

We observe that the size of the reduced mechanisms is fairly insensitive to the duration of each building step when measured in terms of internal time steps taken by the ODE solver of choice. In particular, the variations are negligible when fewer than about 175 internal time steps are taken during each building step. Consequently, we adopt a standard building step duration of 100 internal time steps for the rest of this study.

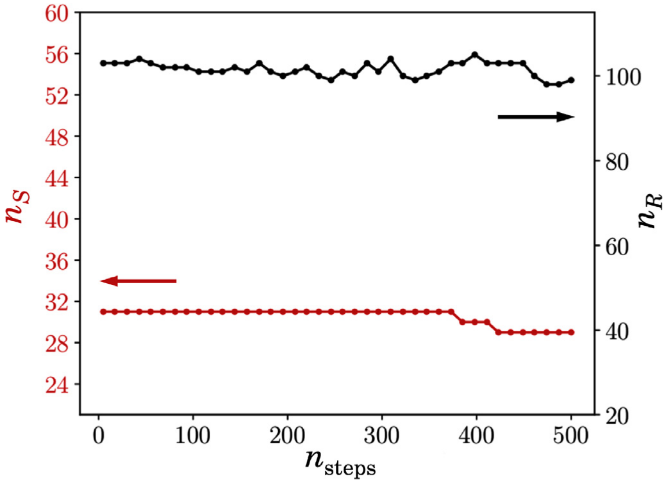


Fig. 2. Number of species (red line, left axis) and reactions (black line, right axis) included in the built reduced mechanism for methane auto-ignition using a DRGEP threshold $\varepsilon = 0.01$, displayed as a function of the number of internal time steps taken by the stiff ODE solver used to integrate K. Variability in the resulting mechanism is negligible if 175 or fewer internal times steps are taken per building step. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

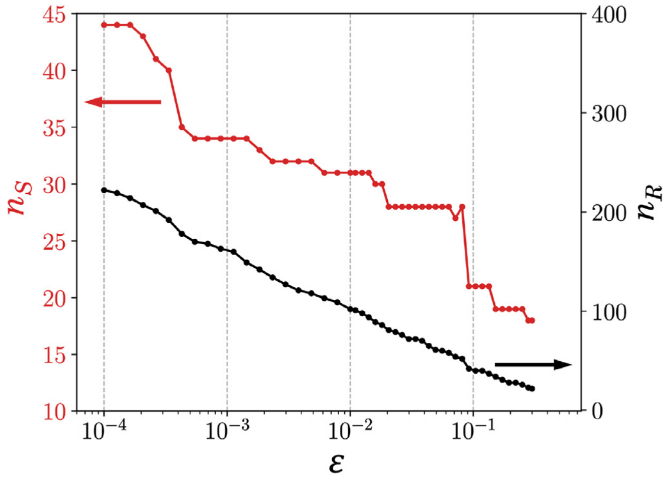


Fig. 3. Number of species, $n_{\mathcal{S}}$ (red line, left axis) and number of reactions, $n_{\mathcal{R}}$ (black line, right axis) in the reduced mechanism generated with the building algorithm, as a function of the selected DRGEP cut-off parameter ε. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

5.1.2. Impact of the DRGEP cut-off parameter, ε

The DRGEP reaction coefficient cut-off parameter, ε, directly controls the size of the final reduced mechanism. To characterize that dependence, the building process is performed for a wide range of ε values, yielding a series of reduced mechanisms with differing numbers of species, $n_{\mathcal{S}}$, and reactions, $n_{\mathcal{R}}$. The results are shown in Fig. 3.

We observe, as expected, that the number of species and reactions in the final reduced mechanism is generally a monotonic function of ε, with lower cut-off values yielding larger reduced mechanisms both in terms of number of species and number of reactions. We also find that the number of reactions in the reduced mechanisms is almost linearly related to the cut-off parameter ε, while the number of species is more sensitive to the individual reactions that are selected, and thus not as strongly correlated to ε.

Some rare exceptions to the monotonic behavior do occur. For instance, here, the species C is added for $\varepsilon = 0.06$ and $\varepsilon = 0.08$ through the addition of the reaction CH + H ↔ C + H_2, but C is not added for $\varepsilon = 0.07$. Those exceptions occur when species are added through reactions whose DRGEP coefficients are above, but very close to ε, and particularly at larger cut-off values, where reactions barely selected at an earlier step can more strongly influence the dynamics of the chemical system, and as a result, the specific species and reactions that are selected in subsequent building steps.

The choice of ε will evidently affect the accuracy of the corresponding reduced mechanism, and this aspect is investigated next.

5.1.3. Performance assessement and comparison with conventional top-down reduction approach

The performance of the building technique is assessed by comparing the building results to those of a conventional, top-down (TD) DRGEP-based species and reaction reduction strategy. Because the species and reaction reduction stages are done sequentially in the top-down approach, an error metric and an error tolerance must be provided *a priori*. Here, we choose ignition delay time to quantify the reduction error, and we consider 3 cases, with a maximum 5%, 1%, and 0.1% allowable errors in ignition delay time, respectively, evaluated over all conditions used in the building process. The resulting 3 conventionaly derived reduced mechanisms will be refered to as 'TD-5%', 'TD-1%', and 'TD-0.1%'. Mechanisms obtained using the building algorithm will follow the same naming convention, but with 'Built' as prefix.

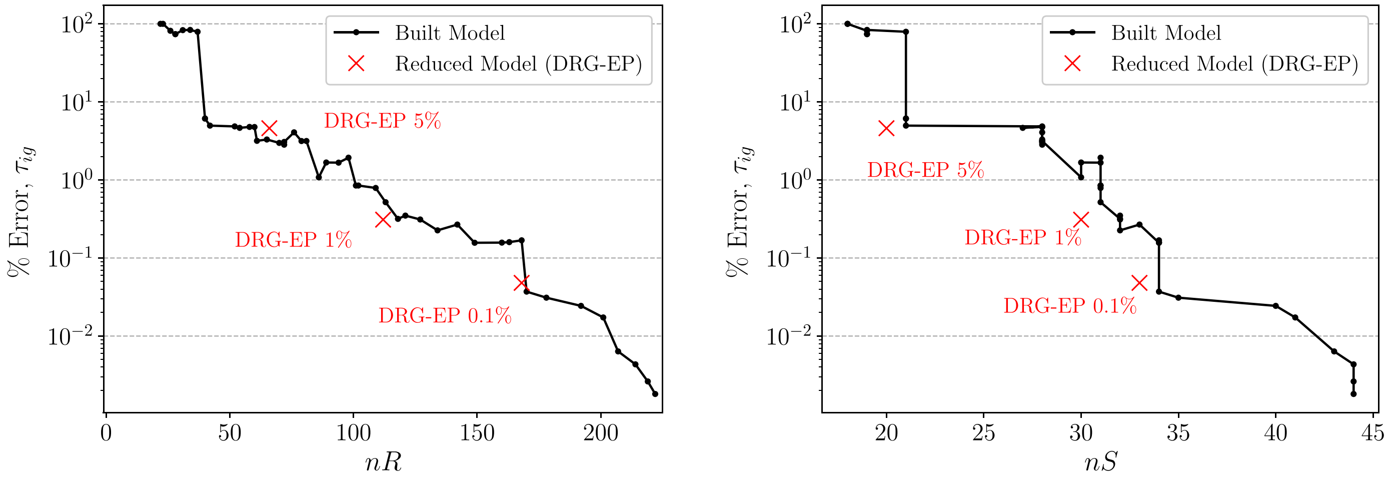
Table 1
Number of species, $n_{\mathcal{S}}$, and reactions, $n_{\mathcal{R}}$, retained in the mechanism at each stage of the top-down DRGEP reduction. Mechanisms are generated for 5%, 1%, and 0.1% allowed errors in ignition delay predictions.

		TD-5%		TD-1%		TD-0.1%	
Type of reduction	Stage	$n_{\mathcal{S}}$	$n_{\mathcal{R}}$	$n_{\mathcal{S}}$	$n_{\mathcal{R}}$	$n_{\mathcal{S}}$	$n_{\mathcal{R}}$
Species	1	21	95	30	184	33	202
Species	2	20	92	30	184	33	202
Reaction	1	20	66	30	114	33	168
Reaction	2	20	66	30	112	33	168

Ignition delay errors are evaluated with respect to the detailed mechanism, where ignition delay time is defined as the time to reach maximum heat release. As ignition delay errors are non-linearly correlated to the number of species and reactions, error may exceed the maximum allowable level at a certain degree of reduction, and become lower than the allowed level as species or reactions are subsequently removed. To select the smallest possible mechanism for each allowed error level, species reduction is performed until the ignition delay error is larger than the allowed error by a factor of 5. The smallest reduced mechanism with error below the allowed level is then selected as a starting point for the next reduction stage. Reaction elimination stages are performed in an identical fashion. For each of the allowed error levels, species and reaction reduction stages are conducted sequentially until a mechanism with a minimal number of species and reactions is found. The reduction stages and the number of species and reactions at each stage are shown in Table 1.

The mechanisms built with varying values of the cut-off parameter ε are now compared to the three top-down conventionally reduced mechanisms. Maximum errors in ignition delay time taken over all simulations used to generate the mechanisms are shown in Fig. 4a and b as a function of the number of species and reactions retained in the mechanisms. With a 0.1% maximum allowed error in ignition delay time, 'TD-0.1%' contains 33 species and 168 reactions, while the smallest built mechanism corresponding to the same threshold, 'Built-0.1%', contains 34 species and 170 reactions. Even with this small error tolerance, neither mechanism contains species or reactions related to the NO_x submechanism, as expected, and both mechanisms contain fewer reactions than the 217 detailed reactions describing methane oxidation. Following a similar trend, 'TD-1%' contains 30 species and 112 reactions, while 'Built-1%' contains 31 species and 101 reactions. 'TD-5%' contains 20 species and 66 reactions, while 'Built-5%' contains 21 species and 42 reactions. A full list of the species contained in each reduced and built model is available in Table 2, omitting targets and species with nonzero initial mass fractions, since those are automatically included in all reduced mechanisms. Species are ordered in the table from top to bottom based on their maximum DRGEP coefficients as computed from the detailed simulation data at the beginning of the first species reduction stage.

We find that at equivalent error levels, built and top-down reduced mechanisms have very similar number of reactions and species. Furthermore, the contents of built and top-down reduced mechanisms, that is, which species and reactions are in fact included, are nearly identical for all investigated cases. One potential contributor to the small discrepancies between the two approaches may be the treatment of scaling factors used in the DRGEP algorithm to weigh the relative importance of each target (denoted as α_T in [10]). In the top-down approach, the simulations are completed prior to the DRGEP coefficient evaluation, and the scaling factors can be evaluated accounting for the entire range of conditions encountered in the simulations. In contrast, scaling factors



(a) Ignition delay errors vs. number of reactions, $n_{\mathcal{R}}$.

(b) Ignition delay errors vs. number of species, $n_{\mathcal{R}}$.

Fig. 4. Comparison between conventional top down reduction strategy using DRGEP (red symbols) and built mechanisms (black lines). Ignition delay times are computed as the time of maximum rate of change in temperature, and errors are evaluated using detailed GRI-Mech simulations as reference. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
Species in built and top-down reduced methane oxidation mechanisms, generated with maximum allowed ignition delay errors of 5%, 1%, and 0.1% in constant volume configurations at atmospheric pressure, with $T_0 = \{1200, 1600\}$, and $\phi_0 = \{0.8, 1, 1.2\}$.

TD-5%	Built-5%	TD-1%	Built-1%	TD-0.1%	Built-0.1%
H_2O	H_2O	H_2O	H_2O	H_2O	H_2O
CH_3	CH_3	CH_3	CH_3	CH_3	CH_3
CO	CO	CO	CO	CO	CO
H	H	H	H	H	H
CH_2O	CH_2O	CH_2O	CH_2O	CH_2O	CH_2O
HO_2	HO_2	HO_2	HO_2	HO_2	HO_2
CH_3O	CH_3O	CH_3O	CH_3O	CH_3O	CH_3O
O	O	O	O	O	O
H_2	H_2	H_2	H_2	H_2	H_2
C_2H_6	C_2H_6	C_2H_6	C_2H_6	C_2H_6	C_2H_6
HCO	HCO	HCO	HCO	HCO	HCO
C_2H_5	C_2H_5	C_2H_5	C_2H_5	C_2H_5	C_2H_5
H_2O_2	H_2O_2	H_2O_2	H_2O_2	H_2O_2	H_2O_2
$CH_2(S)$	$CH_2(S)$	$CH_2(S)$	$CH_2(S)$	$CH_2(S)$	$CH_2(S)$
		HCCO	HCCO	HCCO	HCCO
C_2H_4	C_2H_4	C_2H_4	C_2H_4	C_2H_4	C_2H_4
		C_2H_2	C_2H_2	C_2H_2	C_2H_2
		CH	CH	CH	CH
		C	C	C	C
	CH_2	CH_2	CH_2	CH_2	CH_2
		C_2H_3	C_2H_3	C_2H_3	C_2H_3
		CH_2CO	CH_2CO	CH_2CO	CH_2CO
		CH_2CHO	CH_2CHO	CH_2CHO	CH_2CHO
		CH_2OH	CH_2OH	CH_2OH	CH_2OH
		CH_3OH	CH_3OH	CH_3OH	CH_3OH
			C_2H	C_2H	C_2H
				CH_3CHO	CH_3CHO
				C_3H_8	C_3H_8
					C_3H_7

used in the building process only account for conditions encountered up to the previous building steps. This may cause reactions to be unnecessarily added to the built reduced mechanisms when targets reach their peak production rates late in the building process. For instance, in the first interval of a constant volume methane auto-ignition building simulation, target CO_2 has a small production rate relative to its peak rate near ignition. Despite the small production rate, $\alpha_{CO_2} = 1$, because no states have previously been sampled. Reactions strongly connected to CO_2 may thus be added at this time, even though CO_2 formation is unimportant.

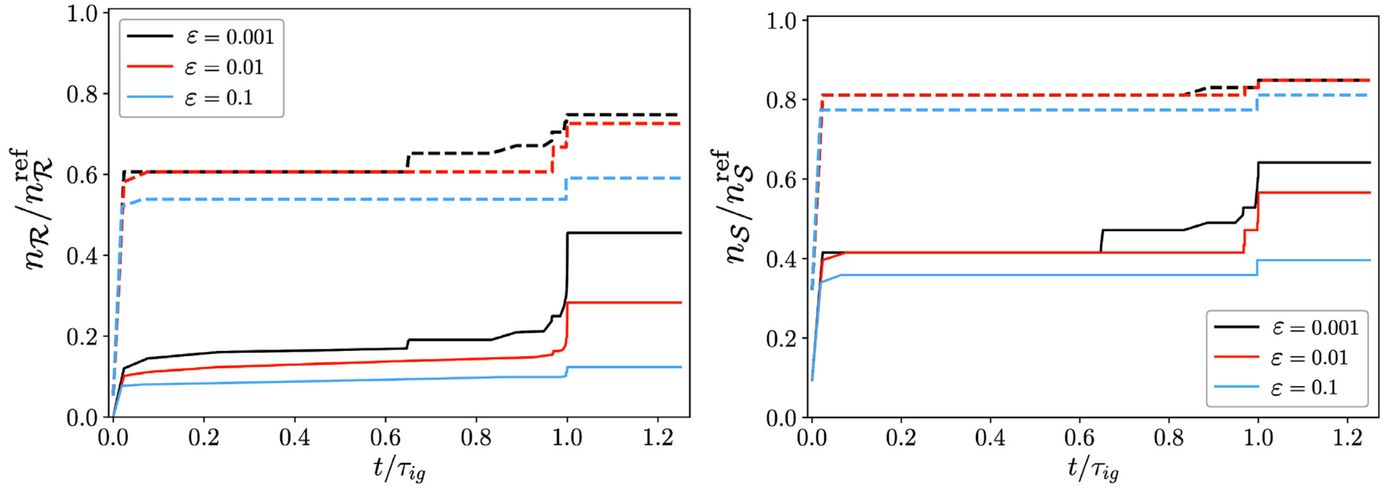
Overall, we found that the building approach, which uses a single building stage centered around reactions addition, is able to generate mechanisms comparable in size with mechanisms derived conventionally through a multi-stage top-down algorithm. The next sections now focus on the unique flexibility that this methodology affords to the reduction process.

5.2. Application to larger reference mechanisms

An advantage of the bottom-up building approach is that only the reactions directly linked (through common reactants or products) to the reduced model at step i are considered for addition at the next building step. In contrast to the conventional top-down approach in which all possible reactions are used to evaluate the detailed solution, a large fraction of the negligible reactions may therefore never be considered in the test mechanism. Here, we illustrate this characteristic by investigating the relative sizes of the reduced ($\mathcal{M}_i$) and test ($\mathcal{M}_i^\star$) mechanisms during a building process for 2 different configurations: the methane case described above, and an heptane oxidation case involving a much larger reference set of reactions. For the latter, we use the *n*-heptane mechanism from the Lawrence Livermore National Laboratory, consisting of 654 species and 4544 reactions [15]. In each case, the reduced mechanisms are built using a single constant-volume reactor simulation at atmospheric pressure and stoichiometric conditions, and with initial temperature $T = 1200$K. Selected targets include the fuel, OH, CO_2, and heat release. The cut-off parameter, ε, is varied from 10^{-3} to 0.1.

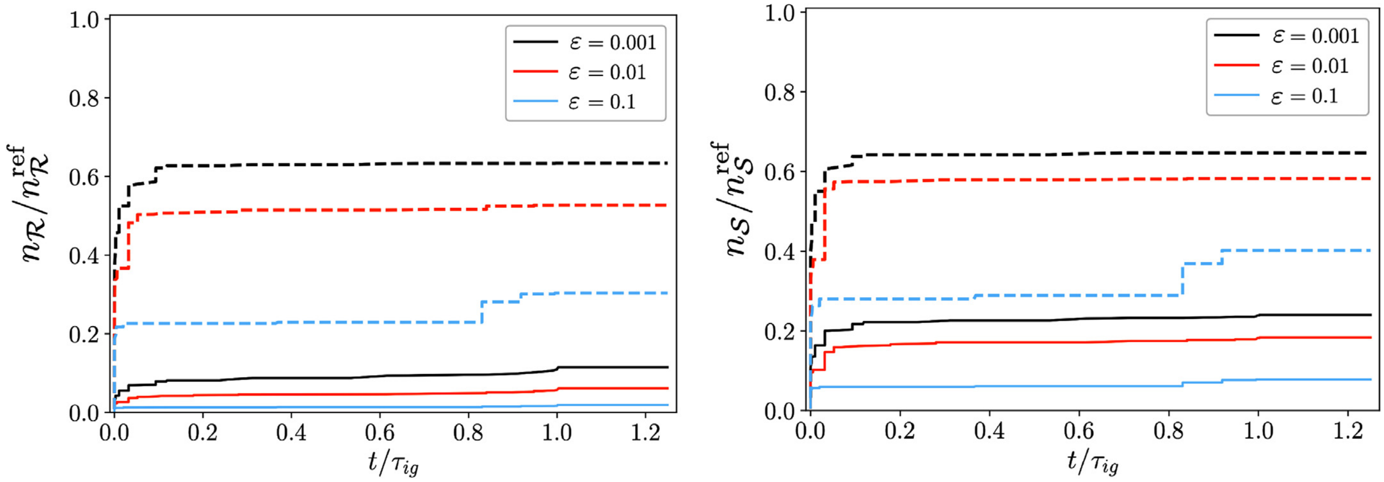
The evolution of the relative number of reactions and species included in the test and reduced mechanisms as the building progresses (simply taken here as a normalized time) is shown in Fig. 5a and b for the methane case, and in Fig. 5c and d for the *n*-heptane case.

In the *n*-heptane case, the number of species and reactions in the test mechanisms remains between 20% and 65% of those in the reference reaction set, depending on the magnitude of the selected threshold ε. Because the reference, detailed mechanism contains a large number of redundant species and reactions, the full detailed mechanism is never analyzed, even at the smallest thresh-



(a) Methane oxidation: evolution of the number of reactions in the test (dashed lines) and reduced (solid lines) mechanisms.

(b) Methane oxidation: evolution of the number of species in the test (dashed lines) and reduced (solid lines) mechanisms.



(c) n-heptane oxidation: evolution of the number of reactions in the test (dashed lines) and reduced (solid lines) mechanisms.

(d) n-heptane oxidation: evolution of the number of species in the test (dashed lines) and reduced (solid lines) mechanisms.

Fig. 5. Size of mechanisms built over the course of a single constant-volume simulation. The number of species and reactions in each mechanism, $n_{\mathcal{S}}$ and $n_{\mathcal{R}}$, respectively, are normalized by the number of species and reactions included in the reference reaction set $\mathcal{R}^{\mathrm{ref}}$. Time t is normalized by the ignition delay time τ_{ig} as obtained from the test mechanism.

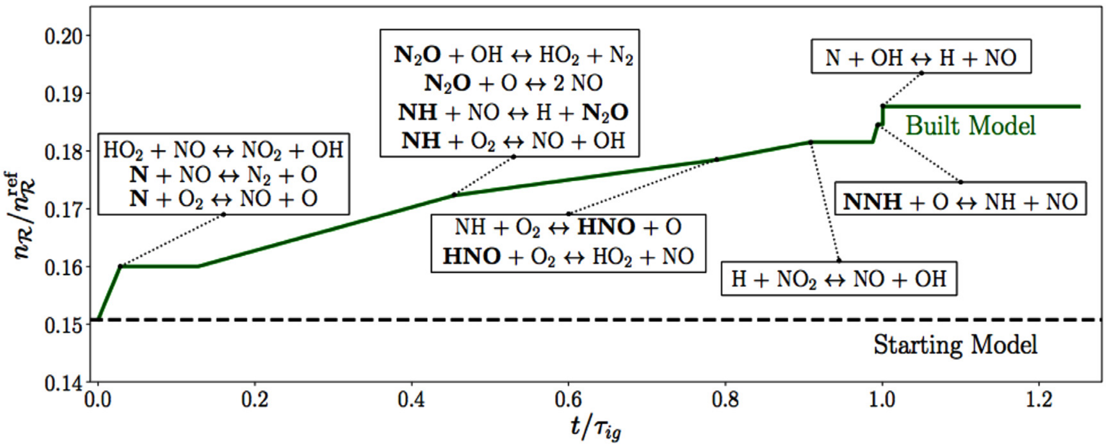
old. We also observe that the majority of species and reactions are added to the reduced mechanism during the very first building steps: capturing the fuel breakdown does in fact capture most of the kinetics leading to ignition. In contrast, the number of reactions in the test mechanism for methane oxidation varies between 50 and 80% of those in the detailed mechanism, and the number of species varies between 75 and 85%. While many species and reactions are added to both the test and reduced mechanisms in the first interval, this is not as dramatic as in the heptane case, and a significant number is also found to be important later, closer to ignition.

Each building step is by nature iterative. However, we never observed more than 3 iterations per step, and only for those few steps where reactions are added in significant numbers. The fast convergence of the set of reactions that should be added to the reduced mechanism for each step, combined with a significantly smaller number of reactions to consider in the integration of the governing equations indicates that in terms of raw computational cost, the building approach may be competitive, or at the very least comparable to the traditional reduction techniques.

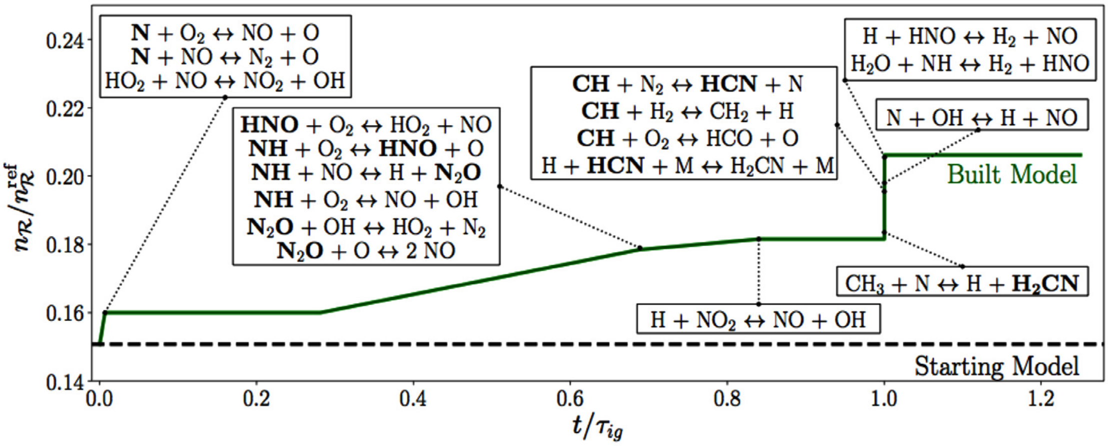
5.3. Adding onto a previously reduced mechanism: the example of NO_x formation

One of the major and key benefits of the building approach is the ability to add a reduced description of secondary pathways or kinetic features onto an existing reduced mechanism, thereby bypassing entirely the need to re-start the reduction from the detailed mechanism. We illustrate this important capability by adding a reduced description of the nitrogen oxide (NO_x) formation pathways onto a reduced description of methane oxidation.

We start from the 'Built-5%' reduced mechanism constructed in the previous section, and select all NO_x-related reactions in the GRI-MECH 3.0 mechanism [14] as our reference reaction list. We consider 2 distinct building conditions to illustrate the various NO_x formation pathways: stoichiometric and fuel-rich ($\phi = 2$) conditions. Both cases are otherwise identical, run at constant-volume, atmospheric pressure, and with an initial temperature $T_0 = 1200$K. The set of targets is $\{NO, NO_2\}$, and these species are automatically added to the reduced mechanism at the start of the building process. The DRGEP reaction selection threshold is set to a large value:



(a) NO_x pathways addition at stoichiometric conditions.



(b) NO_x pathways addition at rich conditions ($\phi = 2$)

Fig. 6. Relative number of reactions included in the reduced mechanism during the addition of NO_x formation pathways, starting from the 'Built-5%' mechanism of Section 5.1.3. Added reactions, and the time at which they are added are indicated in boxes. Species are displayed in bold when they are added to the reduced mechanism.

$\varepsilon = 0.2$, so that only the most important NO_x reactions are added. All other settings are similar to those used in Section 5.1.

At stoichiometric conditions, 12 reactions and 5 species are added to the 'Built-5%' mechanism, that itself contains 23 species and 49 reactions. Including the two target species, the final model contains 30 species and 61 reactions. Relative error in the final mass fraction of NO and NO_2, compared to the detailed mechanism results, are less than 1e−2%, and integrated errors for the same species are below 0.25%. At $\phi = 2$, 18 reactions and 7 species are added, resulting in a final reduced model with 32 species and 67 reactions. Final errors for the target species mass fractions are on the order of 1e−3%, and integrated errors for NO and NO_2 are 2.6% and 1.7%, respectively.

The size of each built methane/NO_x mechanism, normalized by the number of reactions in GRI-MECH 3.0, is plotted on the green solid curve as a function of time in Fig. 6. Reactions added over a given building step are displayed in boxes linked to the end time of that building step. The mechanism built at stoichiometric conditions is shown in Fig. 6a, while the one built at rich conditions is shown in Fig. 6b. In GRI-Mech, the NO_x sub-mechanism contains 18 species and 108 reactions, so building at the reduced level for both equivalence ratios does result in an appreciable reduction of the NO_x sub-mechanism. While the full list of reactions from GRI-MECH is provided to construct the edge models, only reactions from the NO_x sub-mechanism are identified as important in both cases.

In both cases, two thermal NO_x reactions and one catalytic NO_2 reaction ($HO_2 + NO \leftrightarrow NO_2 + OH$) are added to initiate nitrogen decomposition and NO_x formation at the end of the first building step. For the stoichiometric case, several additional N_2O reactions are added as the fuel decomposes and as temperature begins to rise. Near ignition, the OH radical becomes abundant, causing the third thermal NO_x reaction to be added. These reactions are added at similar times in rich conditions, however, the prompt NO_x formation pathway also becomes more dominant during ignition, resulting in multiple reactions added involving CH and HCN. These results display the capability to add reactions of interest onto reduced models by simply re-initializing the set of targets $\mathcal{T}$ and running the building algorithm at the conditions of interest.

6. Conclusions

A building algorithm coupled with the Direct Relation Graph with Error Propagation method has been proposed and evaluated for the systematic and fully automatic generation of reduced mechanisms. This algorithm identifies the most important reactions out of a pre-determined reference set, and adds them to the reduced mechanism when they become relevant to the solution of the governing equations of interest. Results obtained for methane and heptane oxidation in homogeneous reactors indicate that this approach can efficiently generate reduced kinetic mechanisms comparable to those produced by conventional top-down reduction strategies, with competitive computational costs. Most importantly, the building strategy also provides the flexibility to append a reduced description of reaction pathways pertaining to chemical features not originally included a reduced mechanism, without having to repeat the entire reduction process. This novel capability was demonstrated by adding a reduced NO_x submodel to a reduced mechanism for methane oxidation. Such a capability may have significant application and impact in adaptive chemistry approaches currently under development to simulate complex combustion systems.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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