



Modeling combustion chemistry using C3MechV4.0: An extension to mixtures of hydrogen, ammonia, alkanes, and cycloalkanes

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ABSTRACT

The design of novel renewable fuel mixtures (such as hydrogen, ammonia, methanol, ethanol, and other blends) compatible with existing engine infrastructure can be greatly aided by accurate kinetic modeling of fuel surrogate mixtures. With this objective, a robust kinetic model should accurately describe the kinetics of the pure components and their mixtures at engine-relevant conditions. This work presents the results of the continued work of the Computational Chemistry Consortium (C3) to build a "universal" chemical kinetic mechanism to describe the oxidation of fuel surrogate mixtures. Our previous model, C3MechV3.3, focused on conventional fuel mixtures, i.e., the ignition behavior of *n*-alkanes up to C₁₂, as well as pollutant formation, including polycyclic aromatic hydrocarbons (PAHs) and nitrogen oxides (NO_x). To meet the needs of fast renewable fuel mixture screening, the updated model, C3MechV4.0, now also includes the combustion of carbon-free fuels, including hydrogen and ammonia; dimethyl carbonate, and ethylene carbonate, which are useful to investigate battery fires in hybrid vehicles; cyclopentane, cyclohexane, and xylene, which enrich the palette of useful conventional fuel surrogate components. Each kinetic subset was updated according to the most recent literature findings and, if needed, tuned to improve the prediction of experimental target data. The model was tested against a wide range of experimental data (some of which is new) for fuel mixtures, focusing on hydrogen, methane, and ammonia, proving the model's predictive capabilities. A hierarchical and modular mechanism structure was enforced, enabling the automatic assembly of smaller subsets of mechanisms, which can accelerate kinetic simulations of fuel mixtures.

1. Introduction

The increasing demand for sustainable energy solutions has led to a heightened interest in the kinetic modeling of fuel surrogate mixtures that include carbon-neutral alternatives, such as hydrogen and ammonia. Their practical use in existing engine infrastructure is mostly being explored in the form of mixtures with conventional fuels such as methane and heavier hydrocarbons [1–4], as well as renewable fuels and e-fuels, including alcohols [4–6] and/or ethers [7–9]. Accurate

and predictive detailed chemical kinetic models are crucial for optimizing engine performance and reducing emissions; however, developing these models requires a deep understanding of the complex chemical reactions that occur during combustion. Hundreds of papers related to kinetic modeling are published annually in leading journals such as *Fuel*, *Combustion and Flame*, and the *Proceedings of the Combustion Institute*,² highlighting the ongoing efforts and rapid advancements in this field. In this context, working towards a comprehensive, reliable,

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² Based on searches on <https://www.sciencedirect.com/search> for publications whose title, abstract, or keywords match "kinetic modeling".

Nomenclature**Abbreviations**

CSV	Comma-separated values
FR	Flow reactor
GA	Group additivity
GAV	Group additivity value
HPST	High pressure shock tube
HT	High temperature
IDT	Ignition delay time
InChI	International Chemical Identifier
JSR	Jet-stirred reactor
HACA	Hydrogen-abstraction acetylene-addition
KHP	Ketohydroperoxide
LBV	Laminar burning velocity
MAH	Monocyclic aromatic hydrocarbon
MEL	Master Equation-based Lumping
NG	Natural gas
NTC	Negative temperature coefficient
OS	Octane sensitivity
PAH	Polycyclic aromatic hydrocarbon
PES	Potential energy surface
PFR	Plug flow reactor
QCT	Quasi-classical trajectory
RCM	Rapid compression machine
RH	Alkane
RMG	Reaction Mechanism Generator
RON	Research octane number
SMILES	Simplified Molecular Input Line Entry System
ST	Shock tube
TPRF	Toluene primary reference fuel

Species

M	Inert collision partner
Ar	Argon
He	Helium
H	Atomic hydrogen
H ₂	Hydrogen
O(³ P)	Ground state atomic oxygen
O ₂	Oxygen
OH	Hydroxyl radical
HO	Hydroperoxyl radical
H ₂ O	Water
CO	Carbon monoxide
CO ₂	Carbon dioxide
CH ₂ (S)	Singlet methylene
CH ₂	Methylene radical
CH ₃	Methyl radical
CH ₄	Methane
CH ₃ OH	Methanol
CH ₂ OH	Hydroxymethyl radical
CH ₃ O	Methoxy radical
HCO	Formyl radical
C ₂ H ₂	Acetylene
C ₂ H ₄	Ethylene
C ₂ H ₆	Ethane

C ₂ H ₅ OH	Ethanol
C ₂ H ₅ OOH	Ethyl hydroperoxide
CH ₃ CH ₂ O	Ethoxy radical
CH ₃ OCH ₃ , DME	Dimethyl ether
HCCO	Ketenyl radical
C ₃ H ₃	Propargyl radical
C ₃ H ₄ -A	Allene
C ₃ H ₅ -A	Allyl radical
C ₃ H ₅ -S	1-propenyl radical
C ₃ H ₆	Propene
C ₃ H ₈	Propane
DMC	Dimethyl carbonate
EC	Ethylene carbonate
C ₄ H ₄	Vinylacetylene
C ₄ H ₅ -N	1,3-Butadienyl radical
C ₄ H ₆	1,3-Butadiene
C ₄ H ₈ -1	1-Butene
PC ₄ H ₉	1-butyl radical
SC ₄ H ₉	2-butyl radical
nC ₄ H ₁₀	n-Butane
CH ₂ CHCHCHO	3-butenal-2-yl radical
C ₅ H ₅	Cyclopentadienyl radical
C ₅ H ₆	Cyclopentadiene
CYC ₅ H ₇ 1-3/4	Cyclopentenyl radicals
CYC ₅ H ₁₀	Cyclopentane
nC ₅ H ₁₂	n-Pentane
CPTO ₂ J	Cyclopentyl-peroxy radical
CPTO ₂ H	Cyclopentyl hydroperoxide
C ₆ H ₆	Benzene
C ₆ H ₅	Phenyl radical
CYC ₆ H ₁₂	Cyclohexane
nC ₆ H ₁₄	n-Hexane
C ₆ H ₅ CH ₂	Benzyl radical
C ₆ H ₅ CH ₃	Toluene
C ₆ H ₅ CHO	Benzaldehyde
C ₆ H ₅ CH ₂ O ₂ H	Benzyl hydroperoxide
nC ₇ H ₁₆	n-Heptane
C ₆ H ₅ C ₂ H	Phenylacetylene
C ₆ H ₅ C ₂ H ₃	Styrene
C ₆ H ₅ C ₂ H ₅	Ethylbenzene
XYLENE	Xylene
RXYLENE	Xylyl radical
C ₆ H ₄ CH ₃ CHO	Methyl benzaldehyde
OC ₆ H ₄ CH ₃	Methyl phenoxy radical
HOC ₆ H ₄ CH ₂	Hydroxy benzyl radical
iC ₈ D ₃ (DIB-2)	2,4,4-Trimethyl-2-pentene
iC ₈ D ₄ (DIB-1)	2,4,4-Trimethyl-1-pentene
iC ₈ H ₁₈	iso-Octane
IND	Indene
C ₉ H ₆ O	Indenone
C ₉ H ₇	Indenyl radical
C ₉ H ₇ O	Indenoxy radical
C ₉ H ₈ O	Indenol
NAPH	Naphthalene
nC ₁₀ H ₂₂	n-Decane
C ₁₀ H ₇ CH ₃ -A	α-Methylnaphthalene
A ₂ R ₅	Acenaphthylene

A_2C_2HA	1-ethynynaphthalene
A_2C_2HB	2-ethynynaphthalene
N_2	Nitrogen
NH_3	Ammonia
$\dot{N}H$	Imidogen radical
$\dot{N}H_2$	Amino radical
NO_x	Nitrogen oxides
$\dot{O}_2QOOH$	Peroxy hydroperoxy alkyl radical
$\dot{R}O_2$	Alkyl peroxy
$QOOH$	Hydroperoxy-alkyl radical

Symbols

T	Temperature
p	Pressure
φ	Fuel-air equivalence ratio
τ_{res}	Residence time
$=$	Reversible reaction
$\Rightarrow$	Irreversible reaction

and unified model that can simultaneously predict available experimental data for a wide range of complex fuels at different operating conditions of both ignition behavior and emissions (i.e., particulate matter and NO_x) is particularly challenging. This is the primary goal of the Computational Chemistry Consortium (C3, <https://fuelmech.org>), supported by Convergent Science Inc. with contributions from research groups at universities (University of Galway, CRECK modeling Lab at Politecnico di Milano, the Institute for Combustion Technology at RWTH Aachen University), national laboratories (Argonne National Laboratory, Lawrence Livermore National Laboratory), and industrial partners (Convergent Science and others). Our first collaborative effort resulted in a robust combustion kinetic model, C3Mech version 3.3 (C3MechV3.3) [10], which was developed to simulate fuel surrogate mixtures that mimic the behavior of conventional fuels. C3MechV3.3 can reasonably predict the ignition behavior and pollutant formation of hydrogen, syngas, natural gas, gasoline surrogate mixtures, including primary reference fuels (PRFs) and toluene primary reference (TPRF) fuels. It also contains some heavier components to simulate diesel surrogate mixtures (up to C_{12}) in addition to biofuels such as dimethyl ether (DME) and alcohols, including methanol and ethanol. Specific validations of alkane/ NO_x interactions of interest to exhaust gas recirculation were also conducted.

Continuing our previous development of C3MechV3.3, we present here an updated version, C3Mech version 4.0 (C3MechV4.0), which features significant improvements, including some in the core chemistry. This updated model expands its scope by incorporating new fuels that enrich the existing palette, including renewable and carbon-free fuels, while placing particular emphasis on the study of mixtures to improve predictive accuracy in real-world combustion scenarios. Model updates mostly relate to hydrogen and the core hydrocarbon chemistry, where rate constant updates implemented in this version are predominantly based on recent theoretical studies, ensuring that the model remains state-of-the-art. Concerning carbon-free fuels, ammonia has, over the past 15 years, gained increasing interest as a direct transportation fuel rather than a simple source of hydrogen [4,11] due to its high energy density, easy storage, and well-established production and transportation processes. Hence, a kinetic model for ammonia combustion is incorporated into C3MechV4.0 to enable the simulation of both pure ammonia combustion and various mixtures with hydrogen and hydrocarbons. In addition, the pyrolysis and oxidation chemistry of dimethyl carbonate and ethylene carbonate is added. These carbonates are electrolyte solvent components in lithium-ion batteries, and their combustion kinetics are considered relevant to understanding and

investigating battery fires involving electric and hybrid vehicles [12]. Regarding alkane fuels, 2-methyl decane, cyclopentane, and cyclohexane are newly added to the fuel palette and have been tested against available ignition delay time (IDT) data. These fuels expand the palette of available hydrocarbon fuels as representative components of branched and cyclic alkanes and aromatic precursors in diesel, gasoline, and jet fuels [13–15]. Finally, among aromatic hydrocarbons, xylene chemistry is added and tested as a typical representative of the reactivity of methylated aromatics in various surrogates [14,16,17].

Similar to our previous study, we provide a wide range of validation comparisons with experimental data that include single fuel components, their mixtures, and pollutant formation under various operating conditions. Several new test cases were considered. In particular, the focus of this work concerns mixtures of carbon-free fuels (hydrogen and ammonia) with hydrocarbons (methane and larger alkanes) that ensure a reliable coverage of the combustion of mixtures of interest for practical applications. In the process of expanding this unified model, additional effort has been placed on rigorous species data modeling and accurate thermochemical properties. The kinetic mechanism is organized into different subsets to facilitate model management and flexibility. Automated tools have been developed to obtain smaller kinetic models that can reduce the computational time of kinetic simulations for light fuel mixtures. These tools should encourage the further use of C3MechV4.0 for different applications.

This work is structured as follows. Section 2 presents novelties in the hierarchical mechanism construction and species tracking. Thereafter, a summary of the main model updates for each subset, divided by species type and size, is reported. Section 3 demonstrates the predictive capabilities of the model through pure fuel validation cases, also including validation for polycyclic aromatic hydrocarbons (PAH) formation in Section 3.9, while Section 4 focuses on model validation for mixtures. The validation Sections 3 and 4 compare the performance of the current model C3MechV4.0 with the previous version C3MechV3.3 while also providing insights into the reasons for the changes in model performance. Where relevant, rate-of-production and sensitivity analyses are presented to help understand the combustion behavior of the fuels investigated.

2. Model structure and updates

Our previous work [10] extensively described the rationale behind the development of C3Mech. Hence, a description of the model development and its constitutive sub-mechanisms will only be summarized briefly here. Tables 2–4 provide a synopsis of the pure component fuel targets tested, highlighting the newly added fuels and test cases that have been included since the publication of C3MechV3.3 [10], providing the references for all cases tested. Furthermore, Table 5 lists validation targets for fuel mixtures, which is the main focus of the present work. Finally, Table 6 provides a concise summary of the validation ranges performed as a function of temperature, pressure, and fuel–air equivalence ratio for each fuel. The rationale behind the choice of the validation database is as follows. A primary motivation for stakeholders to use one kinetic model over another is the accurate prediction of global combustion properties at engine-relevant conditions for fuel components generally included in surrogate mixtures. This includes PRF and TPRF mixture validations discussed in this work. As such, the current validation effort has largely focused on IDT (at higher pressures where available) and laminar flame speed data. Thereafter, to further verify that the model appropriately reflects the fundamental chemistry we continue to build towards, some of the available speciation data are included for both pure fuels and commonly used mixtures. While the data considered do not include all relevant literature measurements, our efforts consider a range of representative mixtures and thermodynamic states relevant to a broad community. Priority is given to more recent experimental measurements. Care is taken in the inclusion of speciation measurements for fuel components used to study soot

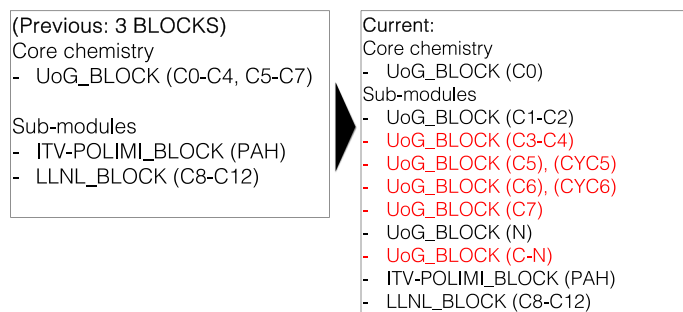


Fig. 1. Separation of the blocks in the current C3Mech structure. The red blocks indicate that these are available in both high temperature-only (HT) and low and high temperature (LT-HT) format.

precursor (e.g., polycyclic aromatic hydrocarbon, PAH) formation. This includes fuel components such as ethylene, acetylene, and unsaturated intermediates such as 1,3-butadiene. The database will be expanded in the future to add more validation targets. However, the collective set of validation data considered in this work is among the most extensive validation efforts put forth in the literature.

This work also presents new experimental data, as highlighted in green in the tables. In particular, IDT measurements of the low-temperature oxidation of methane were performed in the rapid compression machine at the University of Galway to resolve inconsistencies among different experimental datasets. Experimental data, volume histories and additional experimental details, together with uncertainty quantification are available as SM to this paper. Additionally, laminar burning velocity measurements for hydrogen, methane, and hydrogen/methane blends were newly taken at RWTH Aachen University in a spherical constant-volume combustion vessel. The approach for mixing fuel and oxidizer, tracking of flame propagation, and post-processing follows Bariki et al. [18]. Further details on the experimental setup and the determination of uncertainties are provided in the Supplementary material (SM).

C3Mech is developed by combining subsets of oxidation chemistry of different species managed by the C3 partners. In particular, the core chemistry (C₀–C₄), the large linear alkane chemistry (C₅–C₇, C₁₀–C₁₁), cycloalkane chemistry (C₅–C₆), and the non-aromatic oxygenated fuels such as methanol, ethanol, butanol, and dimethyl ether (DME) are managed by the University of Galway (UoG). Ammonia, cycloalkanes, C₁₀–C₁₁ linear alkanes, and butanol represent new fuel targets for C3MechV4.0. Other larger alkanes relevant as surrogate fuel components (C₈, C₉, and C₁₂) are managed by LLNL and are unchanged in C3MechV4.0 compared to C3MechV3.3 [10]. ITV and CRECK are responsible for developing and validating the aromatic hydrocarbon chemistry.

Given the complexity of C3MechV4.0, substantial efforts have been dedicated to the seamless and systematic merging of the different model portions and thermochemistry checks. Fig. 1 shows that in C3MechV4.0, the subsets of the model are divided into 13 separate modules, taking advantage of the hierarchical structure of combustion models [19,20]. This feature enables the flexible construction of target-specific, smaller kinetic models, which can, for example, reduce computational costs in simulations. For instance, an NH₃/H₂ subset can be compiled to simulate NH₃/H₂ flames, while for larger hydrocarbons, high- and low-temperature modules are available and combined according to the conditions of interest. Table 1 summarizes the number of species and reactions for some commonly used sub-models. All kinetic modules, thermochemistry and transport properties, as well as compilation tools to merge different blocks and species list tools (see below), are available on the public GitHub repository <https://github.com/C3Mech/C3MechV4.0>. The repository additionally includes a selection of more than 100 pre-compiled models in CHEMKIN and Cantera YAML format for direct use. The full mechanism is also available at <https://fuelmech.org/>.

The automated merging of the different subsets first requires a common definition of the species involved. The C3MechV4.0 species model collects the features of species in a table that introduces physical and chemical information in a canonical form, i.e., the international chemical identifier (“InChI”), the “excitation”, and the “multiplicity” of each entry. The set of ordered pairs $D_k = \{(\text{“InChI”}, i_k), (\text{“excitation”}, e_k), (\text{“multiplicity”}, m_k)\}$ uniquely identifies a row k in this table, where i_k is a variable length string, e_k is a boolean value, and m_k is a non-negative integer value. For each row k , additional dependent data, such as a SMILES formula, are included to improve human readability and thus increase robustness. A species j in C3MechV4.0 is identified by a set $L_j = \{D_{k_1}, D_{k_2}, \dots, D_{k_x}\}$, where x is greater than one for a lumped species and one otherwise. Each D_k must appear in at most one L_j . Each species j is then assigned a name, thermochemistry, and transport data. A Python script implementing the C3MechV4.0 species model and further details of the specification are provided on the public GitHub repository <https://github.com/C3Mech/C3MechV4.0>. In the construction of C3MechV4.0, the species model was beneficial in identifying inconsistencies between species belonging to different model subsets. Overall, the rigorously defined species model eliminates ambiguities and redundancies; it facilitates the species matching required for comparisons between computed and experimental speciation data, searches in external databases, and the generation of documentation.

Thermochemistry and transport properties were merged from the different subsets through automated protocols that select species properties by prioritizing “lower-level” species. In other words, the properties of each species are assigned from the first model subset they appear in, i.e., from the core chemistry to heavy alkanes, following the order shown in Fig. 1. The new thermochemical properties in the UoG subsets were evaluated with THERM25, a Python code developed in this study based upon THERM [21] that enables (1) the estimation of thermodynamic data based on group additivity, (2) the automated generation of thermodynamic properties in NASA polynomial format from a selected source (e.g., group additivity values implemented in the code), and (3) the analysis and comparison of thermochemical data from different sources. The code, along with the user manual, is available at <https://github.com/C3Mech/THERM25>.

Finally, each consortium partner has adopted in-house tools for the automated validation of the kinetic model against each database subset (e.g., C₀–C₃, premixed flames for the testing of PAH chemistry, etc.). Additional details are provided in the results section. The next sections provide details on model updates for each subset. A comprehensive comparison of the kinetics and thermochemical properties adopted in both C3MechV4.0 and C3MechV3.3 is available in the GitHub repository <https://github.com/C3Mech/C3MechV4.0> in the comparisons section.

2.1. Hydrogen chemistry (C₀)

The H₂ chemistry was updated to better predict the combustion characteristics of hydrogen mixtures over a wide range of conditions.

Table 1

The number of species (NS) and reactions (NR) in various C3MechV4.0 sub-models for the HT and the LT-HT range. ✓ indicates that a sub-module is included in a model, and empty cells indicate its absence. The reactions in the sub-modules are grouped based on the number of carbon atoms in the species (C_0 , C_1 – C_2 , C_3 – C_4 , C_5 , C_6 , C_7 , C_8 – C_{12} , CY_5 , CY_6), with aromatic species being managed separately. Here, CY refers to non-aromatic, cyclic fuel components. Additionally, sub-modules for dimethyl carbonate and ethylene carbonate (DMC+EC), nitrogen-containing species (N), cross-reactions between nitrogen- and carbon-containing species (C–N), and PAHs are available. Aromatic fuels include benzene, toluene, phenol, indene, naphthalene, xylene, and α -methyl-naphthalene. Toluene primary reference fuel is abbreviated as TPRF. In this table, “N” refers to the combined N and N–C sub-modules if a sub-model contains carbon atoms. Column “ C_6 – C_{12} ” indicates whether the C_6 , C_7 , and C_8 – C_{12} sub-modules are included. Each sub-model is assigned a unique model ID (MID) that encodes the specific sub-module combination used for the model compilation. This MID should be used when referencing a particular sub-model elsewhere. If a single model is used across all temperatures, the same MID is used for the HT and the LT-HT columns. All sub-models listed below, as well as additional sub-models, are provided in the public GitHub repository <https://github.com/C3Mech/C3MechV4.0>, together with a Python script for compiling custom sub-models or generating them from their MIDs.

Fuels	MID HT/LT-HT	C_0	C_1 – C_2	C_3 – C_4	C_5	C_6 – C_{12}	CY_5	CY_6	N	PAH	NS HT/LT-HT	NR HT/LT-HT
H ₂ and NH ₃	2906/2906	✓							✓		43/43	273/273
CH ₄	3DI0/3DI0	✓	✓								101/101	658/658
C_0 – C_4 fuels	3R00/4410	✓	✓	✓							374/723	2512/3952
Aromatic and cyclic fuels	3SO1/47U1	✓	✓	✓			✓	✓		✓	597/1048	5835/7623
Cyclopentadiene	3X61/4GU1	✓	✓	✓	✓		✓	✓		✓	746/1546	6738/9582
TPRF	3XQP/4HZD	✓	✓	✓	✓	✓	✓	✓		✓	1495/4874	10247/20617
Complete model	3XR9/4HZZ	✓	✓	✓	✓	✓	✓	✓	✓	✓	1604/4983	11257/21653

The new chain-branching reaction channel proposed by Klippenstein et al. [454], i.e., $HO_2 + HO_2 = OH + OH + O_2$, was included, enhancing the reactivity of hydrogen, as anticipated by sensitivity analyses, e.g., Panigrahy et al. [28]. Hence, the rate constants of several reactions of the hydrogen sub-mechanism were updated or tuned to improve model predictions for H₂ IDTs and LBVs. In particular, the rate constants for $H_2 + O(^3P) = H + OH$, $H + O_2 + N_2 = HO_2 + N_2$ and $H + O_2 + Ar = HO_2 + Ar$ were adjusted as described in the work of Zhu et al. [455] to better capture experimental microkinetic data. The PLOG format was introduced for $H + O_2 + Ar = HO_2 + Ar$ to better reproduce the experimentally measured pressure dependence at pressures above 10 atm on H₂ IDT data. The low-pressure limit of $H + O_2 + He = HO_2 + He$ was adjusted to improve the LBV predictions of H₂ mixtures in He at elevated pressures [286].

2.2. C_1 – C_2 chemistry updates

Improved C3MechV4.0 predicted combustion behavior was obtained for both C_1 and C_2 fuels, mainly due to updates in rate constants from recent literature studies. For C_1 oxidation chemistry, the rate constant for $CH_3O_2H + HO_2 = CH_3O_2 + H_2O_2$ was updated by analogy with $CH_2O + HO_2 = HCO + H_2O_2$ [456] to improve the model predictions of IDTs for CH₄ at low temperatures. This analogy was used because the bond dissociation energy of HCO (88.04 kcal mol^{−1}) is similar to CH₃O₂H (88.5 kcal mol^{−1}). A new chain-terminating channel $CH_3O_2 + HO_2 \Rightarrow CH_2O + H_2O + O_2$ based on the experimental measurements of Elrod et al. [457] was also included in competition with $CH_3O_2 + HO_2 = CH_3O_2H + O_2$ to slow down the predicted reactivity of CH₄ at low temperatures. The rate constants for $\dot{C}H_3 + HO_2 = CH_4 + O_2$ and $HCO + \dot{H} = CO + H_2$ were also updated based on the theoretical studies of Zhu and Lin [458] and Wu et al. [364]. The rate constant for $CH_3O_2 + H_2 = CH_3O_2H + \dot{H}$ was updated based on the theoretical work of Shi et al. [459]. The rate constant for the reaction $\dot{C}H_2 + \dot{H} = \dot{C}H + H_2$ was adopted from Baulch et al. [460] to improve the LBV predictions of C₂H₂. Additional information on minor rate constant tuning is found in the kinetic model attached in CHEMKIN format.

In the C_2 block, several sub-mechanisms were updated, including those for acetylene (C₂H₂), ethylene (C₂H₄), ethane (C₂H₆), and ethanol (C₂H₅OH). Minor rate constant tuning was performed for H-atom abstraction by HO₂ from ethylene as well as $\dot{O}_2C_2H_4OH$ decomposition [461] to improve predictions of C₂H₄ and C₂H₂ oxidation at high-pressure and low-temperature conditions.

Several reactions associated with C₂H₂ chemistry were updated based on theoretical studies. The multi-channel reaction of acetylene with atomic oxygen ($O(^3P)$) is the main initial reaction in acetylene oxidation and was updated using the theoretical work of Zuo et al. [462].

Compared to C3MechV3.3, the total rate constant decreases by a factor of 2–3, with a shift in the product distribution towards $\dot{C}H_2 + CO$ with respect to $H\dot{C}CO + H$. The rate constant for the reaction between acetylene and singlet methylene $C_2H_2 + CH_2(S) = \dot{C}_3H_3 + H$ was updated based on the work of Gannon et al. [463] to improve the LBV predictions of C₂H₂, while minor tuning was performed on ketenyl radical (H $\dot{C}CO$) oxidation with molecular oxygen (O₂). These combined updates improve LBV predictions but decrease propargyl radical mole fractions and, therefore, PAH concentrations in unstretched premixed acetylene flames [177,178]. Additional sensitivity analyses for propargyl formation led to the revision of the rate constant for $C_2H_2 + \dot{C}H_2 = \dot{C}_3H_3 + H$ based on new *ab initio* variational transition state theory calculations performed in this work. These calculations, which were based on CCSD(T)-cc-pVTZ-F12 frequencies and ANLO-like level energies, quantitatively reproduce the experimentally observed rate constant in the low-temperature regime [464]. The calculated rate constant is a factor of 2–4 larger than the previously adopted estimate in the 1000–2000 K range. This increase suggests a possible need to revise the rate constants for the addition of triplet $\dot{C}H_2$ to other unsaturated species. Additional reactions affecting propargyl radical consumption revised from the literature were $\dot{C}_3H_3 + O(^3P)$ [465] and $H\dot{C}CO + H = \dot{C}H_2/CH_2(S) + CO$ [466].

Finally, revisions of the ethanol (C₂H₅OH) chemistry in C3Mech were motivated by recently highlighted shortcomings in literature models [192,195]. Hence, in this work the rate constants for the decomposition channels $C_2H_5OH = C_2H_4 + H_2O$, $C_2H_5OH = \dot{C}H_3 + \dot{C}H_2OH$, and for important H-atom abstraction reactions including $C_2H_5OH + \dot{H} = \dot{S}C_2H_4OH + H_2$ and $C_2H_5OH + \dot{OH} = \dot{S}C_2H_4OH + H_2O$, were updated based on the experimental work of Choudhary et al. [193] and the theoretical work of Zheng et al. [467], respectively.

2.3. C_3 – C_4 chemistry updates

Most of the updates in the propane (C₃H₈) sub-mechanism were adopted from the recent study by Zhu et al. [232]. In addition, the rate constants for H-atom abstraction by HO₂ producing *iso*- and *n*-propyl radicals were updated based on the theoretical study of Hashemi et al. [235]. Similarly, the rate constants for H-atom abstraction by OH radicals were updated based on experimental measurements at high temperatures (895–1294 K) and fits proposed by Badra et al. [468].

In the C_4 block, the thermochemistry and kinetics of *n*-butane (nC_4H_{10}), 1-butene (C₄H₈-1), and 1,3-butadiene (C₄H₆) were updated based on the studies by Caravaca-Vilchez et al. [267,469] and Dong et al. [288]. The updated thermochemistry decreased the mechanism's reactivity in the negative temperature coefficient (NTC) and low-temperature regimes. Concerning oxidation reactivity, rate constants in the nC_4H_{10} and C₄H₈-1 sub-models were refined by applying

Table 2

C3MechV4.0 validation table for C₀–C₄ fuels. Yellow boxes indicate targets newly added to the validation database, and green boxes highlight new measurements from this work. “N.C.” indicates that experimental target data were not considered in this work (unavailable or not tested). The columns include different reactor types: shock tube (ST), rapid compression machine (RCM), jet-stirred reactor (JSR), flow reactor (FR), counterflow flame (CF), premixed flame (PF), and laminar burning velocity (LBV) measurements. The carbon stoichiometry (Carb. stoich.), common name, and mechanism name of each fuel are also indicated [22–296].

Carb. stoich.	Common name	Model name	ST	RCM	JSR	FR	CF	PF	LBV
C0	Hydrogen	H ₂	[22–30]	[28]	[31,32]	[33]	N.C.	N.C.	[34–43]
C0	Ammonia	NH ₃	[44–51]	[52–55]	[56–62]	[56,63–66]	N.C.	N.C.	[67–78]
C1	Syngas	H ₂ /CO	[22,79]	[22]	[80]	N.C.	N.C.	N.C.	[81–87]
C1	Methane	CH ₄	[25,88–97]	[25,88–97]	[100]	N.C.	N.C.	N.C.	[41,78,101] [102–121]
C1	Methanol	CH ₃ OH	[122–124]	[125]	[125]	[126]	N.C.	N.C.	[67,127–134]
C1	Formal-dehyde	CH ₂ O	N.C.	N.C.	N.C.	[135,136]	N.C.	N.C.	N.C.
C2	Ethane	C ₂ H ₆	[88,137–140]	[141,142]	[143]	[144]	N.C.	N.C.	[103–105,107] [112,145–154]
C2	Ethylene	C ₂ H ₄	[140,155–160]	[140]	[32,161]	[162]	[163][164]	[165] [166]	[103,112,145] [151,167,168]
C2	Acetylene	C ₂ H ₂	[169–172]	[173]	N.C.	[174,175]	[176]	[177,178]	[145,151,168] [173,179,180]
C2	Acetal-dehyde	CH ₃ CHO	[181–183]	[184]	[185,186]	N.C.	N.C.	N.C.	[187]
C2	Ethanol	C ₂ H ₅ OH	[123,186] [188–193]	[194,195]	[196]	[197]	N.C.	N.C.	[128,129] [67,132,198–200] [201–205]
C2	Dimethyl ether	CH ₃ OCH ₃	[90,206–212]	N.C.	[213–217]	[218,219]	N.C.	N.C.	[220–223]
C3	Propane	C ₃ H ₈	[23,224–230]	[231–233]	[234]	[235]	N.C.	N.C.	[103,107,112] [150,151,154] [225,236–242]
C3	Propene	C ₃ H ₆	[243]	[244]	[245,246]	[247]	[248]	N.C.	[112,246]
C3	Allene	C ₃ H ₄ -A	[252]	N.C.	[249]	N.C.	[250][251]	N.C.	[252]
C3	Propyne	C ₃ H ₄ -P	[253]	N.C.	[249]	[254]	[250]	N.C.	[253,254]
C3	Propanal	C ₂ H ₅ CHO	[255]	N.C.	[256,257]	N.C.	N.C.	N.C.	[256]
C3	Dimethyl carbonate	COC(VO)OC	[258,259]	N.C.	N.C.	N.C.	N.C.	N.C.	[260–263]
C3	Ethylene carbonate	CY(COCVOOC)	[264]	N.C.	N.C.	N.C.	N.C.	N.C.	[262,265]
C4	<i>n</i> -Butane	C ₄ H ₁₀	[266]	[267]	[268]	[269]	N.C.	[270]	[114,148,271,272] [112,128,273–276]
C4	<i>iso</i> -Butane	<i>i</i> C ₄ H ₁₀	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.	[148,273][275,277]
C4	1-Butene	C ₄ H ₈ -1	[278]	[279]	[280]	N.C.	[248]	N.C.	[112,273,281]
C4	2-Butene	C ₄ H ₈ -2	[282]	[282]	[283]	N.C.	N.C.	N.C.	[281]
C4	<i>iso</i> -Butene	<i>i</i> C ₄ H ₈	[282]	[282]	[284]	N.C.	N.C.	N.C.	[112,273,275] [281,285]
C4	1,3-Butadiene	C ₄ H ₆	[286]	[286]	[287,288]	N.C.	[289]	[290]	[273,275] [286,291,292]
C4	<i>n</i> -Butanol	NC ₄ H ₉ OH	[293]	N.C.	[294]	N.C.	N.C.	N.C.	[128,295,296]
C4	Vinyl-acetylene	C ₄ H ₄	N.C.	N.C.	N.C.	N.C.	[251]	N.C.	N.C.

Table 3Summary of C3MechV4.0 validation targets for pure C₅–C₁₂ non-aromatic fuels. For details on the notation, refer to Table 2 [124,129,130,133,190,200,204,212,273,297–379].

Carb. stoich.	Common name	Model name	ST	RCM	JSR	FR	CF	PF	LBV
C5	<i>n</i> -Pentane	<i>n</i> C ₅ H ₁₂	[297–299]	[298,299]	[300]	N.C.	N.C.	N.C.	[273] [301–304]
C5	<i>iso</i> -Pentane	<i>i</i> C ₅ H ₁₂	[299]	[299]	N.C.	N.C.	N.C.	N.C.	[305]
C5	Neo-pentane	NEOC ₅ H ₁₂	[299]	[299]	[306,307]	N.C.	N.C.	N.C.	N.C.
C5	1-Pentene	C ₅ H ₁₀ -1	[302,308,309]	[308]	[308]	N.C.	N.C.	N.C.	[302,310]
C5	2-Pentene	C ₅ H ₁₀ -2	[308,309]	[308]	[308]	N.C.	N.C.	N.C.	[302]
C5	Cyclopentane	CYC ₅ H ₁₀	[311–314]	[314]	[315]	N.C.	N.C.	N.C.	[273,316]
C5	Cyclopentene	CYC ₅ H ₈	N.C.	N.C.	N.C.	N.C.	[317]	N.C.	N.C.
C5	Cyclopentadiene	C ₅ H ₆	[318]	N.C.	[319]	[320][321,322]	N.C.	N.C.	[323]
C6	<i>n</i> -Hexane	<i>n</i> C ₆ H ₁₄	[324]	[324]	[325]	N.C.	N.C.	N.C.	[304,326]
C6	2-Methyl pentane	<i>i</i> C ₆ H ₁₄	[324]	[324]	[325]	N.C.	N.C.	N.C.	[327]
C6	3-Methyl pentane	I ₃ C ₆ H ₁₄	[324]	[324]	[325]	N.C.	N.C.	N.C.	N.C.
C6	2,2-Dimethyl butane	NEC ₆ H ₁₄	[324]	[324]	[325]	N.C.	N.C.	N.C.	N.C.
C6	2,3-Dimethyl butane	XC ₆ H ₁₄	[324]	[324]	[325]	N.C.	N.C.	N.C.	N.C.
C6	1-Hexene	C ₆ H ₁₂ -1	[328–330]	[330]	[329,331]	N.C.	N.C.	N.C.	[326,332]
C6	Cyclohexane	CYC ₆ H ₁₂	[311,313] [333–336]	[337]	[338]	N.C.	N.C.	N.C.	[273,316] [333,338–340]
C7	<i>n</i> -Heptane	<i>n</i> C ₇ H ₁₆	[133,190] [341–345]	N.C.	[342,346]	N.C.	[347]	N.C.	[129,200] [204,273,304] [348–353]
C8	<i>n</i> -Octane	<i>n</i> C ₈ H ₁₈	[354]	[354]	N.C.	N.C.	N.C.	N.C.	N.C.
C8	<i>iso</i> -Octane	<i>i</i> C ₈ H ₁₈	[124,355–358]	[355]	[359]	[360]	N.C.	N.C.	[130,349] [361–363]
C8	2,4,4-Trimethyl-2-pentene	<i>i</i> C ₈ D ₃ (DIB-2)	[364]	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.
C8	2,4,4-Trimethyl-1-pentene	<i>i</i> C ₈ D ₄ (DIB-1)	[365]	[365]	N.C.	N.C.	N.C.	N.C.	N.C.
C9	<i>n</i> -Nonane	<i>n</i> C ₉ H ₂₀	[366]	N.C.	[367]	N.C.	N.C.	N.C.	N.C.
C10	<i>n</i> -Decane	<i>n</i> C ₁₀ H ₂₂	[212,368,369]	[368]	[370–373]	N.C.	N.C.	N.C.	[374]
C11	2-Methyldecane	C ₁₁ H ₂₄ -2	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.
C11	<i>n</i> -Undecane	<i>n</i> C ₁₁ H ₂₄	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.	N.C.
C12	<i>n</i> -Dodecane	<i>n</i> C ₁₂ H ₂₆	[375–379]	[377]	N.C.	N.C.	N.C.	N.C.	N.C.

Table 4
C3MechV4.0 validation table for aromatic hydrocarbons. For details on the notation, refer to Table 2 [200,273,345,380–421].

Carb. stoich.	Common name	Model name	ST	RCM	JSR	FR	CF	PF	LBV
C6	Benzene	C ₆ H ₆	[380] [381]	N.C.	[380] [382–384]	[385] [386]	N.C.	[387] [388–393]	[273]
C7	Toluene	C ₆ H ₅ CH ₃	[394] [395]	[396] [397]	[398–401]	[399,402][385,403][404]	[405]	[406–408]	[200]
C6	Phenol	C ₆ H ₅ OH	[409]	[409][397]	N.C.	[410–412]	N.C.	N.C.	[413]
C9	Indene	IND	N.C.	N.C.	N.C.	[414] [415]	N.C.	N.C.	N.C.
C10	Naphthalene	NAPH	N.C.	N.C.	N.C.	N.C.	N.C.	[416]	N.C.
C8	Xylene	XYLENE	[345] [417] [418] [419]	[396]	[400]	[420]	N.C.	N.C.	[413]
C11	α -Methylnaphthalene	C ₁₀ H ₇ CH ₃	N.C.	N.C.	[421]	N.C.	N.C.	N.C.	N.C.

Table 5

C3MechV4.0 validation table for hydrocarbon blends. In each section, the blend type is specified according to the carbon stoichiometry of the components. For details on the notation, refer to Table 2. In this table, common names are omitted for simplicity, as they are the same as in the other tables. For flames, the reader is referred to Tables 2–4 [25,28,422–447].

Carb. stoich.	Model name	ST	RCM	JSR	FR	LBV
H₂/Alkanes						
C ₀ /C ₁	H ₂ /CH ₄	[25] [422,423]	[28]	N.C.	N.C.	[67,69,71] [73,75,78]
C ₀ /C ₃	H ₂ /C ₃ H ₈	[23]	N.C.	N.C.	N.C.	N.C.
C ₀ /C ₁₀	H ₂ /nC ₁₀ H ₂₂	[368]	[368]	N.C.	N.C.	N.C.
CH₄/Alkanes						
C ₁ /C ₂	CH ₄ /C ₂ H ₆	N.C.	[430]	N.C.	N.C.	N.C.
C ₁ /C ₂	CH ₄ /C ₂ H ₄	[140,158]	[140]	N.C.	N.C.	N.C.
C ₁ /C ₂	CH ₄ /C ₂ H ₆ /C ₂ H ₄	[431]	[431]	N.C.	N.C.	N.C.
C ₁ -C ₃	CH ₄ /C ₂ H ₆ /C ₂ H ₄ /C ₃ H ₈	[449]	[449]	N.C.	N.C.	N.C.
C ₁ -C ₅	CH ₄ /C ₂ H ₆ /C ₃ H ₈ /C ₄ H ₁₀ /nC ₅ H ₁₂	[432]	[432,433]	N.C.	N.C.	N.C.
C ₁ -C ₆	CH ₄ /C ₂ H ₆ /C ₃ H ₈ /C ₄ H ₁₀ /nC ₅ H ₁₂ /nC ₆ H ₁₄	N.C.	[433]	N.C.	N.C.	N.C.
C ₁ -C ₇	CH ₄ /C ₂ H ₆ /C ₃ H ₈ /C ₄ H ₁₀ /nC ₅ H ₁₂ /nC ₆ H ₁₄ /nC ₇ H ₁₆	[432,434]	[432,434]	N.C.	N.C.	N.C.
C ₁ /C ₁₀	CH ₄ /nC ₁₀ H ₂₂	[435]	[435]	N.C.	N.C.	N.C.
Heavy alkanes						
C ₂	C ₂ H ₆ /C ₂ H ₄	[140]	[140]	N.C.	N.C.	N.C.
C ₂ /C ₃	C ₂ H ₆ /C ₃ H ₈	[449]	[449]	N.C.	N.C.	N.C.
C ₂ /C ₃	C ₂ H ₄ /C ₃ H ₈	[449]	[449]	N.C.	N.C.	N.C.
C ₅ /C ₈	CYC ₅ H ₁₀ /DIB ₁	[450]	[450]	N.C.	N.C.	N.C.
C ₅ /C ₈	CYC ₅ H ₁₀ /iC ₈ H ₁₈ /DIB-1	[450]	[450]	N.C.	N.C.	N.C.
C ₇ /C ₈	nC ₇ H ₁₆ /iC ₈ H ₁₈	[124,451] [436]	N.C.	N.C.	N.C.	N.C.
Toluene blends						
C ₇	C ₆ H ₅ CH ₃ /nC ₇ H ₁₆	[437]	[437]	N.C.	N.C.	N.C.
C ₇ /C ₈	C ₆ H ₅ CH ₃ /nC ₇ H ₁₆ /iC ₈ H ₁₈	N.C.	[452]	[438]	N.C.	N.C.
C ₅ /C ₈	CYC ₅ H ₁₀ /iC ₈ H ₁₈ /C ₆ H ₅ CH ₃	[450]	[450]	N.C.	N.C.	N.C.
C ₅ /C ₇	CYC ₅ H ₁₀ /C ₆ H ₅ CH ₃	[450]	[450]	N.C.	N.C.	N.C.
DME/Alcohol blends						
C ₂	CH ₄ /CH ₃ OCH ₃	[186]	N.C.	N.C.	N.C.	N.C.
C ₂	C ₂ H ₅ OH/CH ₃ OCH ₃	[186]	[186]	N.C.	N.C.	N.C.
C ₂ /C ₅	CYC ₅ H ₁₀ /CH ₃ OCH ₃	[453]	[453]	N.C.	N.C.	N.C.
C ₂ /C ₇	C ₆ H ₅ CH ₃ /CH ₃ OCH ₃	[395]	[395]	N.C.	N.C.	N.C.
C ₁ /C ₇	CH ₃ OH/nC ₇ H ₁₆	[133]	[133]	N.C.	N.C.	N.C.
NH₃ blends						
C ₀	NH ₃ /H ₂	[44,46] [49,439]	[52,53,55]	[62]	[65]	[67,69,71] [73,75,78]
C ₀ /C ₁	NH ₃ /CH ₄	[440]	N.C.	N.C.	N.C.	[2,78,111] [441–443]
C ₀ /C ₁	NH ₃ /CH ₃ OH	[444]	[445]	N.C.	N.C.	[2]
C ₀ /C ₇	NH ₃ /nC ₇ H ₁₆	[446,447]	[446]	N.C.	N.C.	[353]
NO_x blends						
C ₁ /NO _x	CH ₄ /NO _x	N.C.	[98]	N.C.	N.C.	N.C.
C ₂ /NO _x	C ₂ H ₆ /NO _x	[142]	[142]	N.C.	N.C.	N.C.
C ₃ /NO _x	C ₃ H ₈ /NO _x	[231]	[231]	N.C.	N.C.	N.C.
C ₅ /NO _x	nC ₅ H ₁₂ /NO _x	N.C.	[298]	N.C.	N.C.	N.C.
C ₇ /NO _x	nC ₇ H ₁₆ /NO _x	[343]	[343]	N.C.	N.C.	N.C.
NO _x blend	CH ₄ /C ₂ H ₆ /C ₃ H ₈ /C ₄ H ₁₀ /nC ₅ H ₁₂ /NO _x	[298]	[298]	N.C.	N.C.	N.C.

hierarchical rate rules derived from smaller and larger structurally similar hydrocarbons (i.e., *n*-butane can be derived from propane and *n*-pentane) and tuned within the reported uncertainty limits. The most relevant update from literature studies included H-atom abstraction reactions from the fuels, β -scission of PC₄H₉ and SC₄H₉ radicals [470], tuning of C₄H₈-1 decomposition, and pathways that produce 1,3-cyclopentadiene, benzene, and furan in C₄H₆.

2.4. Cyclopentane and cyclohexane

Cyclopentane (CYC₅H₁₀) has been newly integrated into C3MechV4.0, as highlighted in Table 3. The cyclopentane model is based on the work of Patel et al. [450], with minor tuning of low-temperature oxidation reactions. The cyclopentene (CYC₅H₈) and cyclopentadiene (C₅H₆) subsets in C3MechV4.0 are derived from the combined ITV and CRECK models, as described in C3MechV3.3 [10]. This merging required adjustments to the cyclopentene and cyclopentenyl (CYC₅H₇-1-3, CYC₅H₇-1-4) sub-models and the lumping of some products such as C₅H₅O cyclic isomers. In general, the rate parameters for the primary reactions of cyclopentene and its two radicals were largely replaced by those from [396,450], especially H-atom abstraction, unimolecular decomposition, and oxygen addition reactions.

Cyclohexane was newly added in C3MechV4.0 based on the recent model of Chatterjee et al. [337]. The initial adoption of this model resulted in a significant under-prediction of IDTs. To address this, rate rules and thermochemistry data were updated, ensuring better agreement with experimental data while incorporating the latest core chemistry. In particular, thermochemical properties were updated using the group additivity values (GAVs) derived from high-level theoretical calculations proposed by Ghosh et al. [471,472] that account for the interaction between the alkyl group and the -OOH group. For the uncertainty of the associated GAVs, the authors refer to the original publications [471,472]. Furthermore, several key reaction classes proposed by Zhang et al. [324] were updated with new rate rules [473], as the original rate rules underestimated the cyclohexane IDTs with the latest core chemistry and thermochemistry.

2.5. Heavy (C>4) alkanes

In this work, both the thermochemistry and key reactions of the three pentane isomers, the five hexane isomers, *n*-heptane, *iso*-octane, and *n*-decane models were updated to adapt to the new core chemistry. Thermochemistry was updated using the STAR-1D [474] values when available or based on the GAVs recommended by Ghosh et al. [471,

Table 6

Validation ranges for each fuel. Temperature ranges ($T_{\min}$ – $T_{\max}$) consider inlet conditions or temperatures in the unburned mixture for spatially homogeneous reactors. Pressure ranges ($p_{\min}$ – $p_{\max}$) were determined from all configurations, where initial pressures were used for non-isobaric configurations. Counterflow flames were not considered when determining the equivalence ratio ranges ($\varphi_{\min}$ – $\varphi_{\max}$). No values are specified if the test cases for a fuel comprise only counterflow flames.

Common name	Model name	$T_{\min}$ [K]	$T_{\max}$ [K]	$p_{\min}$ [atm]	$p_{\max}$ [atm]	$\varphi_{\min}$ [–]	$\varphi_{\max}$ [–]
Hydrogen	H ₂	727	2696	0.3	270.6	0.1	2.5
Ammonia	NH ₃	700	2489	1	39.5	0.1	2
Syngas	H ₂ /CO	850	2246	0.9	30.9	0.1	2
Methane	CH ₄	857	2584	0.4	266.3	0.1	100
Methanol	CH ₃ OH	697	2180	1	51	0.2	6
Formaldehyde	CH ₂ O	852	1095	1	6	0.013	1.6
Ethane	C ₂ H ₆	598	1862	0.7	98.7	0.034	∞
Ethylene	C ₂ H ₄	300	2226	0.99	59.2	0.3	10
Acetylene	C ₂ H ₂	450	2319	0.03	58.8	0.1	5.6
Acetaldehyde	CH ₃ CHO	831	1703	1	9.8	0.5	3.7
Ethanol	C ₂ H ₅ OH	758	1670	1	76.7	0.03	2
Dimethyl ether	CH ₃ OCH ₃	423	1670	0.9	41.5	0.2	4.2
Propane	C ₃ H ₈	548	2615	0.8	98.7	0.02	2
Propene	C ₃ H ₆	722	1820	1	41.7	0.1	2.2
Allene	C ₃ H ₄ -A	645	1896	0.92	40.5	0.2	2
Propyne	C ₃ H ₄ -P	645	2037	0.92	40.5	0.5	2
Propanal	C ₂ H ₅ CHO	476	1607	1	16	0.35	4
Dimethyl carbonate	DMC	954	1600	1	40	0.5	2
Ethylene carbonate	EC	1228	1587	0.7	2	0.5	2
Acetone	CH ₃ COCH ₃	701	1931	1	1	0.5	2.7
<i>n</i> -Butane	C ₄ H ₁₀	300	1600	0.04	45.9	0.2	99
<i>iso</i> -Butane	<i>i</i> C ₄ H ₁₀	680	978	10	30	1	1
1-Butene	C ₄ H ₈ -1	676	1834	1	52.2	0.2	2
2-Butene	C ₄ H ₈ -2	670	1397	9.6	51.7	0.5	2
<i>iso</i> -Butene	<i>i</i> C ₄ H ₈	666	1499	10	50.2	0.3	2
1,3-Butadiene	C ₄ H ₆	300	2050	0.03	41.4	0.2	2.4
<i>n</i> -Butanol	<i>n</i> C ₄ H ₉ OH	772	1256	1	80	0.5	2
Vinyl-acetylene	C ₄ H ₄	–	–	1	1	∞	∞
<i>n</i> -Pentane	<i>n</i> C ₅ H ₁₂	500	1768	1	526.2	0.3	2
<i>iso</i> -Pentane	<i>i</i> C ₅ H ₁₂	663	1404	9.4	25.6	0.3	2
Neo-pentane	NEOC ₅ H ₁₂	500	1430	1	20	0.5	2
1-Pentene	C ₅ H ₁₀ -1	629	2374	0.4	30.5	0.4	∞
2-Pentene	C ₅ H ₁₀ -2	629	1703	1	30.1	0.5	2
Cyclopentane	CYC ₅ H ₁₀	675	1821	1	53.6	0.2	3
Cyclopentene	CYC ₅ H ₈	–	–	0.08	0.08	∞	∞
Cyclopentadiene	C ₅ H ₆	353	1800	1	2.7	0.5	∞
Pentanal	PC ₄ H ₉ CHO	500	1848	1	3	0.5	2
<i>n</i> -Hexane	<i>n</i> C ₆ H ₁₄	425	1364	1.1	15	1	1
2-Methyl pentane	<i>i</i> C ₆ H ₁₄	500	1368	1.1	15	1	1
3-Methyl pentane	<i>i</i> ₃ C ₆ H ₁₄	500	1366	1.1	15	1	1
2,2-Dimethyl butane	NEC ₆ H ₁₄	550	1297	1.1	15	1	1
2,3-Dimethyl butane	XC ₆ H ₁₄	575	1259	1.1	15	1	1
1-Hexene	C ₆ H ₁₂ -1	500	1873	1	35	0.5	2
Cyclohexane	CYC ₆ H ₁₂	500	1857	1	56.6	0.2	2
<i>n</i> -Heptane	<i>n</i> C ₇ H ₁₆	500	1411	1	55	0.2	4
<i>n</i> -Octane	<i>n</i> C ₈ H ₁₈	644	1327	20	20	0.5	1.5
<i>iso</i> -Octane	<i>i</i> C ₈ H ₁₈	500	1439	1	50	0.2	2
2,4,4-Trimethyl-2-pentene	<i>i</i> C ₈ D ₃ (DIB-2)	694	939	15	30	0.5	1.5
2,4,4-Trimethyl-1-pentene	<i>i</i> C ₈ D ₄ (DIB-1)	645	1704	1	30.3	0.2	2
<i>n</i> -Nonane	<i>n</i> C ₉ H ₂₀	684	1448	1	15	0.5	2
<i>n</i> -Decane	<i>n</i> C ₁₀ H ₂₂	500	1378	10	85.2	0.2	2
2-Methyldecane	C ₁₁ H ₂₄ -2	600	1431	13.5	30.8	0.5	2
<i>n</i> -Dodecane	<i>n</i> C ₁₂ H ₂₆	650	1408	5.7	60	0.5	2
<i>n</i> -Tetradecane	<i>n</i> C ₁₄ H ₃₀	562	1029	10	10	0.5	0.5
Benzene	C ₆ H ₆	298	1970	0.03	20	0.19	∞
Toluene	C ₆ H ₅ CH ₃	298	2050	0.04	50	0.2	∞
Phenol	C ₆ H ₅ OH	1173	1500	1	2	0.64	∞
Indene	IND	1000	1900	0.04	4	∞	∞
Naphthalene	NAPH	1850	1850	0.03	0.03	1.7	1.7
Xylene	XYLENE	838	1803	1	46.2	0.5	2
α -Methylnaphthalene	C ₁₀ H ₇ CH ₃	800	1600	1	10	0.5	1.5

472]. Table 7 summarizes the updates of the thermochemistry data for large alkanes. Thermochemistry data for all pentane isomers and most species from the 2,2- and 2,3-dimethyl butane and *iso*-octane sub-models were taken from STAR-1D, and almost all thermochemistry data for *n*-decane, 2- and 3-methyl pentane were estimated using the GA method. Overall, the thermochemical properties of 216 and 237 species were updated according to the STAR-1D and GA methods, respectively.

In addition to the thermochemistry updates, several cross-reactions between *n*C₅H₁₂ and NO₂ were updated based on the study by Pathak et al. [298].

The mechanisms for *iso*-pentane, *iso*-octane, and *n*-decane were taken directly from Refs. [355,368,475]. Moreover, the rate constants of *n*-pentane, *neo*-pentane, the five hexane isomers, and *n*-heptane were refined in the present work (PW) based on the rate rules recommended

Table 7

Overview of thermochemistry updates by STAR-1D and GA methods, respectively. Values refer to the number of species whose properties were updated. Green and blue boxes indicate thermochemistry data obtained from group additivity methods and from quantum chemistry calculations, respectively.

FUELS	SMILES	RH	$\dot{R}$	RO	RO ₂	RO ₂ H	QOOH	QOOH	SUM	
									STAR-1D	GAVs
<i>n</i> C5H12	CCCCC	1	3	3	3	3	10	10	33	0
<i>i</i> C5H12	C(C)CCC	1	4	4	4	4	13	13	43	0
<i>neo</i> C5H12	CC(C)(C)C	1	1	1	1	1	1	1	7	0
<i>n</i> C6H14	CCCCCC	1	3	3	3	3	14	14	21	20
<i>i</i> C6H14	CCCC(C)C	1	5	5	5	5	21	21	21	42
<i>i</i> 3C6H14	CCC(C)CC	1	4	4	4	4	16	16	16	33
<i>neo</i> C6H14	CCC(C)(C)C	1	3	3	3	3	7	7	20	7
<i>x</i> C6H14	CC(C)(C)C	1	2	2	2	2	7	7	16	7
<i>n</i> C7H16	CCCCCCC	1	4	4	4	4	13	13	9	34
<i>i</i> C8H18	CC(C)(C)CC(C)C	1	4	4	4	4	13	13	30	13
<i>n</i> C10H22	CCCCCCCCC	1	5	5	5	5	30	30	0	81
SUM									216	237

by Wang et al. [355] and Heng et al. [473] with some necessary adjustments within a factor of two. The mechanisms of *n*-octane, *n*-nonane, *n*-undecane, and *n*-dodecane were adopted from C3MechV3.3 without additional revisions. The 2-methyl decane sub-mechanism was taken from Sarathy et al. [354] without any adjustment, and a comparison of the C3MechV4.0 model performance compared to experimental data and C3MechV3.3 is available as SM.

2.6. Aromatic hydrocarbons

C3MechV4.0 also aims to accurately predict the formation of polycyclic aromatic hydrocarbons (PAHs) to quantify pollutant formation. In C3MechV3.3 [10], the kinetic model describing MAHs and PAHs was developed to reproduce the combustion behavior of benzene, toluene, phenol, indene, and naphthalene (see Table 4) and to estimate the formation of PAHs with up to 18 carbon atoms. In C3MechV4.0, the kinetic model describing aromatic hydrocarbons has been improved by (1) revision of the low-temperature chemistry of unsaturated C₅ species and of the high-temperature chemistry of unsaturated C₄ species and mono-aromatics ensuing changes in the core chemistry; (2) improvement in the description of the growth of 2-ring PAHs and acenaphthylene; (3) improvement in the description of toluene ignition at lower temperatures both as a neat fuel and in TPRF mixtures; (4) expansion of the fuel palette to xylene and α -methyl-naphthalene and of the PAH testing database to additional cases. A summary of the main improvements for each of the points listed above is provided in this section. The testing database for PAHs focuses on (1) aromatic species formation in flames, where unsaturated aromatic precursors (e.g., acetylene, ethylene) are used to investigate relevant pathways leading to aromatics (see premixed and counterflow flames in Table 2), (2) decomposition and oxidation of relevant aromatic species in both flow reactors and flames (Table 4), (3) ignition and laminar burning velocities of aromatic hydrocarbons present in fuel surrogate mixtures, such as toluene and xylene (Table 4). In addition, extensive validation for both global ignition properties and speciation measurements was performed for benzene, due to its relevant role as the simplest mono-aromatic species. Instead, a smaller subset was considered for, e.g., phenol, which is only tested as an intermediate and is not routinely included in the surrogate mixtures of interest in the present work. Finally, α -methyl-naphthalene also presents a reduced validation subset, as justified at the end of this section.

Concerning the revision of relevant oxidation reactions of non-aromatic species, the main updates involve addition reactions of H, OH, and HO₂ radicals with C₅H₆. Regarding the high-temperature oxidation of benzene, the products on the potential energy surface (PES) of $\dot{C}_6H_5 + O_2$ were revised according to recent theoretical calculations [476]. The performance analysis of the model also highlighted the crucial role

of $\dot{C}_4H_5$ -N as one of the main secondary oxidation products of benzene. Because of the uncertainty in the rate constants for the decomposition of CH₂CH $\dot{C}$ HCHO, i.e., one of the main oxidation products of $\dot{C}_4H_5$ -N, theoretical calculations were performed, and a new description of its decomposition to $\dot{C}_3H_5$ -A/ $\dot{C}_3H_5$ -S + CO and furan + $\dot{H}$ was implemented in the model. Rate constant calculations and post-processing were performed as described in other studies, e.g., by Pratali Maffei et al. [477].

The model development for the growth of PAHs primarily focused on the formation of pathways through indene and naphthalene and a more detailed description of the chemistry of C₁₂H₈ isomers, mainly following the analyses on PAH growth provided by Langer et al. [478, 479], thus facilitating the investigation of molecular growth processes beyond the two-ring aromatic species. The main revisions were based on literature studies and included indene formation from $\dot{C}_6H_5 + \dot{C}_3H_3$ [480], naphthalene formation from the reaction of *o*-benzyne with vinylacetylene [481] and from phenylacetylene radical and ethylene [482], scission of the five-membered ring in indenone and indenyl in the reactions with H and O(³P) atoms [483], styrene formation from $\dot{C}_5H_5 + C_3H_3$ [484] and its decomposition [485], ring-expansion from $\dot{C}_9H_7 + \dot{C}_2H_2$ [486], and reactions of ethylbenzene [487]. In some cases, automated lumping of complex sets of literature rate constants performed with MEL [488] enabled a substantial reduction in the number of reaction and intermediate species newly included in the model. In addition, the thermochemistry of several aromatic species was revised from the literature [489], while that of several oxygenated C₉ species (i.e., isomers of C₉H₈O, C₉H₇O, C₉H₆O) was newly computed in this work at the FNO-CCSD(T)/cc-pVQZ-F12// ω B97X-D/6-311+G(d,p) level of theory, with extrapolation to the complete basis set limit using the 0.69*(QZ-TZ) scheme. For the latter set, 0 K formation enthalpies were estimated from analogous reactions in MAHs. In addition, the thermochemistry data of several large aromatic species were updated with recently published literature data [489,490], as documented in the CHEMKIN files. Thermochemical properties of other aromatic species for which systematic, accurate literature studies are unavailable were not updated in this work and are mostly adopted from Burcat's thermochemical database [491].

Finally, new molecular growth pathways were added. The revisions to the kinetic model performed include analogy updates, splitting the lumped naphthyl radical into 1-naphthyl and 2-naphthyl, and updates of subsequent hydrogen-abstraction acetylene-addition (HACA) growth pathways that produce acenaphthylene (A₂R₅), 1-ethynyl-naphthalene (A₂C₂HA), and 2-ethynyl-naphthalene (A₂C₂HB) [478]. Additionally, recently investigated A₂R₅ formation pathways [492,493], initiated by radical-radical recombination reactions, have been incorporated.

The new C3MechV4.0 includes a revised version of the toluene mechanism to address the discrepancies that emerged in testing the

low-temperature ignition behavior with C3MechV3.3. First, inconsistencies among experimental datasets obtained at similar operating conditions were carefully analyzed to retain only the reliable ST and RCM experimental datasets [345,356,395–397] (where ST data points with IDTs longer than 1 ms were excluded). Then, the kinetic model was updated with recent theoretical calculations of rate constants for H-atom abstraction reactions from toluene [494], while the bibenzyl recombination reaction and benzyl oxidation with HO_2 was tuned within reasonable uncertainty factors (factor < 2) to better match toluene ignition behavior. In particular, the rate constants for $\text{C}_6\text{H}_5\dot{\text{C}}\text{H}_2 + \text{HO}_2 = \text{C}_6\text{H}_5\text{CH}_2\text{O}_2\text{H}/\text{C}_6\text{H}_5\text{CH}_2\dot{\text{O}} + \dot{\text{O}}\text{H}$ were set as pressure-independent and readjusted as in a recent version of the LLNL mechanism [495]. In the bibenzyl sub-mechanism, in addition to updating the recombination rate constants, a lumped bibenzyl radical was introduced in the model, and the corresponding oxidation mechanism was built from that of toluene. Additional modifications included ethylbenzene decomposition reactions [487], which is a relevant intermediate formed mainly from $\text{C}_6\text{H}_5\dot{\text{C}}\text{H}_2 + \dot{\text{C}}\text{H}_3$ at lower temperatures during toluene oxidation. While only neat toluene data were targeted, these changes also resulted in major improvements in the predicted ignition behavior of TPRF mixtures (see Section 4.3).

Finally, the testing database was expanded to xylene and α -methyl-naphthalene. In both cases, the chemistry was also partially present in C3MechV3.3, but it has been substantially revised and expanded in this work.

In the xylene model, the ortho, meta, and para isomers of xylene are lumped as a single isomer. In fact, the ignition behavior of the three isomers is almost identical at higher temperatures [345,413, 417–419]. Some discrepancies are found at lower temperatures ($T < 1000\text{ K}$) [396,400], where o-xylene ignites faster due to the easier $\dot{\text{O}}\text{H}$ radical production upon HO_2 recombination with o-xylyl radical. Minor differences are also found for pyrolysis conditions, where o-xylene accesses ring-closure reaction pathways to 2-ring PAHs [420] more rapidly. In the present model, no specific o-xylyl oxidation reactions were considered. The testing database reported in Table 4 includes pyrolysis and oxidation cases for all isomers, while only RCM IDT measurements for o-xylene are available in the literature.

The xylene model is developed by analogy with the toluene chemistry already included in C3Mech. Model alignment is performed for xylene and its radicals (i.e., those on the lateral groups RXYLENE and on the aromatic ring $\text{CH}_3\dot{\text{C}}_6\text{H}_4\text{CH}_3$), as well as for methylbenzaldehyde ($\text{C}_6\text{H}_4\text{CH}_2\text{CHO}$), where for simplicity only the faster reactivity of the aldehydic group is considered. Compared to the toluene sub-model, scaling factors are applied to account for the different geometry, such as the number of abstracted hydrogen atoms, number of sites for addition-elimination and hydrogen transfer reactions, including symmetry considerations for both reactants and transition state types. Xylyl decomposition kinetics is still derived by analogy with benzyl; however, additional lumped product channels are added upon appropriate scaling of the activation energy based on theoretical studies in the literature [496–498]. In addition, a lower level of detail is adopted for the description of oxidation and growth reactivity to avoid a potentially substantial increase in the number of species. In particular, the most important approximations that lead to a higher degree of uncertainty in the kinetic simulations are: (1) the $\text{HO}_2 + \text{RXYLENE}$ reaction channels, where the hydroperoxy radical is assumed to dissociate directly to products (according to the distribution already present in C3MechV3.3); (2) the RXYLENE self-recombination reaction, where the resulting isomer is assumed to grow directly to lumped PAHs (a combination of phenanthrene and pyrene) and has therefore a lower rate constant compared to the benzyl self-recombination reaction. The rate constants of a few reactions are tuned by up to 50 % to better match experimental predictions of IDT data. Finally, thermochemical properties of xylene and xylyl are computed at the $\omega\text{B97X-D}/6\text{-311+G(d,p)}$ level of theory [499]. Also in this case, minor tuning of the scaling factors used for vibrational frequencies is used to match better laminar flame speed

data, whose simulated results largely depend on the equilibrium of xylene bond-fission reactions.

For α -methyl-naphthalene, the model distinguishes between the α and β isomers. However, the sub-model of both isomers is almost identical, except for some growth pathways newly introduced in this revision (see above). The α -methyl-naphthalene sub-model is taken from the work of Nobili et al. [500] (i.e., CRECK kinetic model), who developed the methyl-naphthalene subset by analogy with toluene, with a similar approach to that described above for xylene. It should be noted that, in this case, the results of the kinetic simulations might be affected by the inclusion of soot growth. However, soot modeling is not yet coupled to C3MechV4.0. Therefore, an extensive validation subset is not deemed necessary at this stage, while soot modeling will be included in future versions.

2.7. Dimethyl ether

Dimethyl ether (DME/ CH_3OCH_3) is a promising renewable fuel with several advantages, including low NO_x and soot emissions, together with a high cetane number. Thus, DME was added to the test database of C3MechV4.0 (see Tables 3 and 5). Upon changes in the core chemistry, the DME sub-model was revised to better predict the reactivity of DME. Its decomposition reaction was updated from the combined experimental and theoretical work of Sivaramakrishnan et al. [501], while H-atom abstraction by methyl radical was updated according to the experimental measurements of Tranter et al. [502]. Concerning the reactions relevant to the NTC-region, O_2 addition to $\dot{\text{Q}}\text{OOH}$ ($\text{CH}_2\text{OCH}_2\text{O}_2\text{H} + \text{O}_2 = \dot{\text{O}}_2\text{CH}_2\text{OCH}_2\text{O}_2\text{H}$) and $\dot{\text{Q}}\text{OOH}$ β -scission ($\text{CH}_2\text{OCH}_2\text{O}_2\text{H} \Rightarrow \text{CH}_2\text{O} + \text{CH}_2\text{O} + \dot{\text{O}}\text{H}$) were updated from the theoretical calculations of Yamada et al. [503]. Regarding low-temperature reactivity, the decomposition of hydroperoxyl methylformate ($\text{HO}_2\text{CH}_2\text{OCHO}$) was updated based on the theoretical calculations of Zhao et al. [504], and a new competing pathway that produces $\text{HOCHO} + \text{CH}_2\text{OO}$ was added. Some rate coefficients were adjusted compared to the reference values in the literature to improve model predictions. The adjustments did not exceed 50 % and are all documented in the CHEMKIN files.

2.8. Direct integrations from literature works: dimethyl carbonate, ethylene carbonate, and ammonia

Two alkyl carbonate sub-models from the literature were integrated into C3MechV4.0. A dimethyl carbonate (DMC) sub-model was adopted based on the work of Sun et al. [505]. An ethylene carbonate (EC) sub-model was merged from the study of Kanayama et al. [264]. These two carbonate mechanisms were selected for integration based on their likelihood of compatibility with the current C3Mech core chemistry. This compatibility assessment was based on the fact that both carbonate mechanisms share a common core chemistry in the UoG developed AramcoMech1.3 [506] and a developmental lineage that includes contributions from LLNL and UoG researchers. Despite alterations to the core $\text{C}_0\text{--C}_5$ chemistry since the publication of their kinetic models, the studies of Sun et al. [505] and Kanayama et al. [264] required only a few formatting changes for integration. The integrated DMC and EC sub-models were then reviewed for potential sink and reservoir species (i.e., species that form – typically from irreversible reactions – but have no consumption pathways and species that form but have artificial and/or severely limited consumption, respectively). A reservoir species, COC^*OOCH , formed from the concerted elimination of molecular hydrogen from a single methyl group in DMC (reversible reaction R4 of Sun et al. [505]) was identified. This pathway is kinetically unfavorable and was, therefore, removed from the integrated DMC sub-model of this work.

Concerning ammonia, the NH_3 chemistry incorporated into C3MechV4.0 was adopted from the recently published model by Zhu et al. [455]. This chemistry includes key reaction pathways for ammonia oxidation and $\text{NO}_x/\text{N}_2\text{O}$ chemistry across different temperature regimes and is built upon the same H_2 sub-mechanism used in C3MechV4.0, ensuring identical predictions after merging.

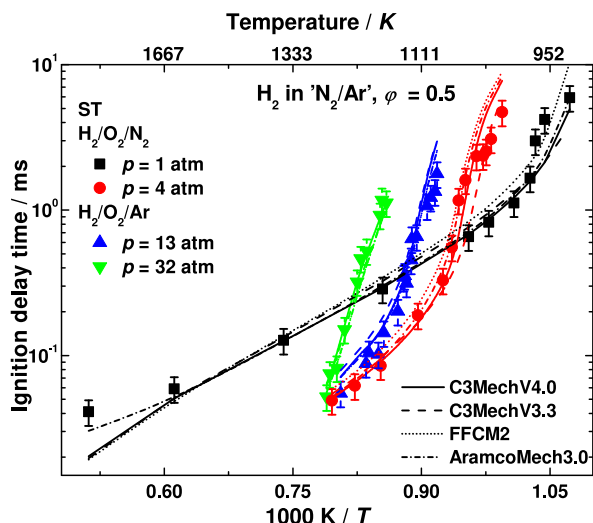


Fig. 2. Experimentally measured and model-predicted IDTs of hydrogen mixtures at pressures of 1 atm to 32 atm [22]. Measured data for 1 and 4 atm are $\text{H}_2/\text{O}_2/\text{N}_2$ mixtures, and those for 13 atm and 32 atm are $\text{H}_2/\text{O}_2/\text{Ar}$ mixtures.

3. Model validation for pure components

This section presents the predictive capability of C3MechV4.0 against relevant literature. Comparisons with the performance of C3MechV3.3 [10] are also presented. In addition, some C_0 – C_4 selected datasets are also simulated with widely adopted literature mechanisms such as AramcoMech3.0 [286] and FFCM-2 [507], where the latter is only suitable for simulations of high-temperature data.

3.1. Hydrogen

Fig. 2 presents IDTs of hydrogen mixtures in Ar (higher pressures) and N_2 (lower pressures) at pressures of 1–32 atm [22]. The predictions of H_2 IDTs with C3MechV4.0 show only slight differences compared to those with C3MechV3.3 and are in good agreement with the measurements over a wide pressure range.

Fig. 3(a) presents LBVs of hydrogen mixtures with N_2 , Ar, and He at 298 K and atmospheric pressure [22,34–37,39–43,508,509]. C3MechV4.0 shows excellent agreement with the hydrogen LBVs measured using different bath gases. C3MechV4.0 predicts increased LBVs compared to the older version, especially under stoichiometric and fuel-rich conditions. The increase in predicted LBVs with C3MechV4.0 is largely due to the updated rate constant for $\text{H}_2 + \text{O}(^3\text{P}) = \dot{\text{H}} + \text{OH}$. Finally, Fig. 3(b) presents LBVs of hydrogen mixtures with He at 298 K and elevated pressures [40]. Conversely, the updated low-pressure limit of $\dot{\text{H}} + \text{O}_2 (+\text{He}) = \text{HO}_2 (+\text{He})$ resulted in the slower LBVs of H_2 mixtures diluted with He with C3MechV4.0 at elevated pressures, while the predictions at atmospheric pressure conditions increased as presented in Fig. 3(a). C3MechV4.0 shows better agreement with the measurements at fuel-lean conditions ($\phi = 0.85$ – 1.0) and elevated pressures than C3MechV3.3, which greatly overestimates LBVs at fuel-lean conditions. Although C3MechV4.0 predicts slightly slower LBVs than the measurements at fuel-rich conditions ($\phi = 1.25$ – 2.0), the mean relative errors of the predictions from the measurements for the conditions are still less than 5%.

3.2. C_1 – C_4 pure fuels

Fig. 4 shows the current model prediction of methane (CH_4) IDTs at low temperatures in an RCM (left). The IDTs predicted with C3MechV4.0 are slower compared to C3MechV3.3, mainly due to the updates in the

hydrogen chemistry and the CH_4 sub-model. As seen in the sensitivity analysis (on the right Fig. 4), the new termination channel, $\text{CH}_3\dot{\text{O}}_2 + \text{HO}_2 \Rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} + \text{O}_2$, inhibits the reactivity of pure CH_4 as it competes with $\text{CH}_3\dot{\text{O}}_2 + \text{HO}_2 = \text{CH}_3\text{O}_2\text{H} + \text{O}_2$. In addition, the most sensitive reaction inhibiting the reactivity, $\dot{\text{C}}\text{H}_3 + \text{HO}_2 = \text{CH}_4 + \text{O}_2$, was increased as described in Section 2.2. The performance of the model improves significantly for all equivalence ratios and the entire temperature range, and it also performs quite well against the other data sets taken in ST and RCM facilities, included as SM.

Fig. 5 shows the performance of C3MechV4.0 against the low-temperature methane oxidation data from Burke et al. [90] (red points) and the new data taken at the University of Galway (black half-filled points). The experiments were repeated under consistent conditions to ensure data reliability. A detailed description of the RCM facility was previously provided [252,510,511] and in the SM, where uncertainty estimates are also discussed. Under stoichiometric conditions, the new data are considerably slower than Burke et al. [90] and agree well with the predictions of the current model at fuel-lean and stoichiometric conditions, suggesting flaws in the corresponding set previously taken as a reference.

Fig. 6 shows the model predictions for acetylene IDTs and LBVs. Overall, C3MechV4.0 captures the measured IDTs quite well over the entire range of temperature and pressure, except for the 30 atm case, where the C3MechV3.3 predictions are closer to the measurements. The improvement in the current model is primarily due to the updates in the $\text{C}_2\text{H}_2 + \text{O}(^3\text{P})$ reaction. Fig. 6(b) shows that the current model predicts acetylene LBVs from Lokachari et al. [173] well while strongly underestimating those of, e.g., Rokni et al. [512]. The latter data set was affected by the presence of acetone, as confirmed by a new set of experiments taken at the same facility by Ravi et al. [168]. HCCO is the major product of C_2H_2 oxidation and has a strong influence on LBV predictions, particularly the reaction with O_2 , as seen in Fig. 6(c). The updates in the HCCO oxidation chemistry and revised rate constant for $\text{C}_2\text{H}_2 + \dot{\text{C}}\text{H}_2 = \dot{\text{C}}_3\text{H}_3 + \dot{\text{H}}$ along with the other updates discussed in Section 2.2 helped to improve the LBV predictions.

The updated ethanol sub-model generally shows improved performance for all of the IDT targets, as shown in the SM. For the ST pyrolysis experiments [192] at 10 atm (see SM), the reactivity of the model decreases slightly, resulting in a better prediction of fuel consumption and in the product yields of methane and ethylene, as shown in Fig. 7(a). The major improvement in C_2H_4 yield prediction is due to the update of the $\text{C}_2\text{H}_5\text{OH}$ decomposition channel to C_2H_4 and H_2O (see Section 2.2), as highlighted in the sensitivity analysis presented in Fig. 7(b).

For propane oxidation, variations in IDT predictions are insignificant (see SM), while Fig. 8(a) shows that LBV predictions slightly improved for all pressures (1–4 atm), particularly at fuel-rich conditions. At 1 atm, the model shows the best agreement with the data of Kuehl [240], while it does not capture the LBV peak and rich conditions for the Dugger [236], Kuehl [240], and Goswami et al. [150] measurements. At 2 atm, the datasets of Jomaas et al. [151] and Goswami et al. [150] report different trends from the set of Shinde et al. [237]. The model predictions agree with Shinde et al. [237] measurements at fuel-lean conditions, while they agree better with the first two datasets at fuel-rich conditions. Similar considerations apply to the 4 atm datasets. The LBV increase is consistent with that observed for the CH_4 and C_2H_2 targets, owing to the core chemistry updates discussed in Section 2.2. Finally, Fig. 8(b) shows that the model predictions for He-diluted, pressure-dependent (15–30 atm) LBVs measured by Mogavhar et al. [112] also improve, reflecting the effects of changes in the C_1 core chemistry, along with a change in the He third-body collider efficiency in $\dot{\text{C}}\text{H}_3 + \text{H}$ reaction. Note that He-diluted LBVs decrease contrary to those for all of the other bath gases (see the SM), highlighting the relevance of bath gas effects.

The model performance in predicting IDT data for $n\text{C}_4\text{H}_{10}$ oxidation at 15 bar and at low temperatures in Fig. 9(a) shows improved

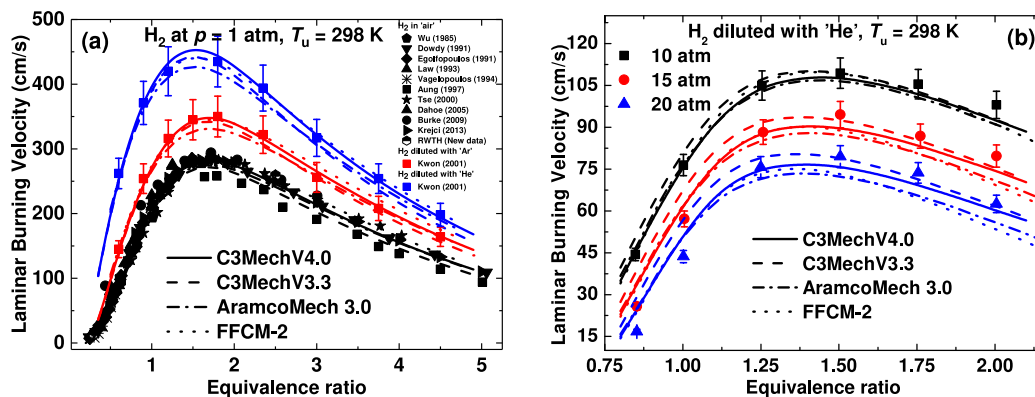


Fig. 3. Predicted and measured LBVs of hydrogen mixtures with N_2 , Ar, and He at 298 K and (a) at atmospheric pressure [22,34–37,39–43,508,509] and (b) at elevated pressures [40].

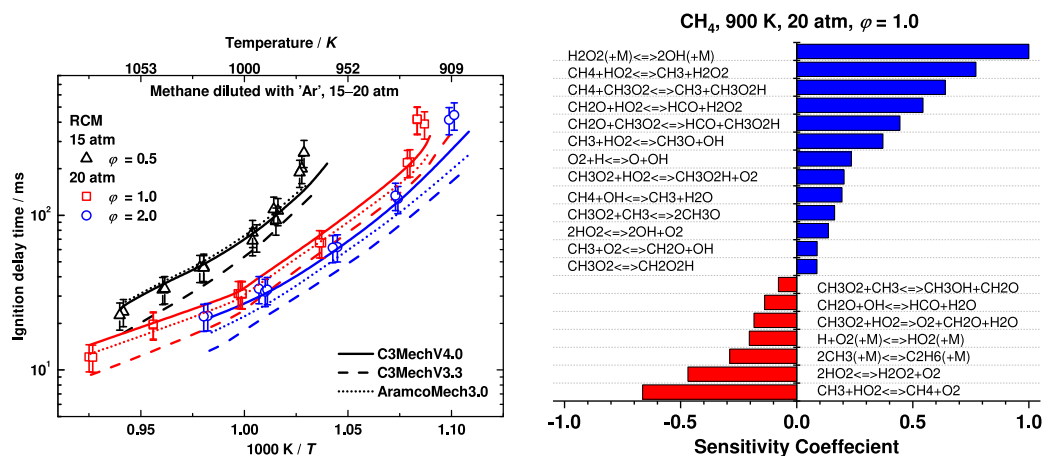


Fig. 4. A comparison of CH_4 IDTs predicted using C3MechV4.0 and C3MechV3.3 against the RCM data (left) from Sahu et al. [98] at $p = 15$ – 20 atm and $\phi = 0.5$ – 2.0 , and associated sensitivity analysis at $p = 20$ atm and $\phi = 1.0$ (right) highlighting the importance of updated reactions.

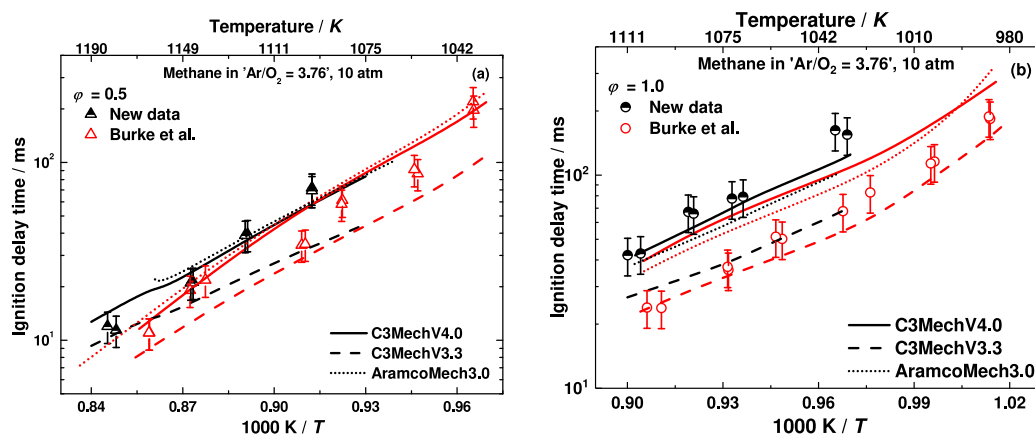


Fig. 5. A comparison of the performance of C3MechV4.0 and C3MechV3.3 with the new CH_4 IDT data (black half-filled symbols) taken under similar conditions as Burke et al. [90] (red symbols) in an RCM at (a) $p = 10$ atm and $\phi = 0.5$, and (b) $p = 10$ atm and $\phi = 1.0$. The solid and dashed lines show the model predictions considering heat loss effects, as reported in both studies.

prediction capability of C3MechV4.0 compared to C3MechV3.3 and is well within the declared experimental uncertainty of ± 15 – 20% [267]. The decrease in reactivity in the low-temperature branch is due to the updated thermochemistry, as explained in Section 2.3, and to the increase in HO_2 reactivity based on the calculations by Klippenstein et al. [454].

The updated model for 1,3-butadiene (C_4H_6) oxidation is generally slower than the previous version at high temperatures and 10 atm, while it is faster at lower temperatures and higher pressures, as shown in Fig. 10(a). The slower low-temperature reactivity is primarily due to model updates from experimental and theoretical data available for $\dot{O}H$ and HO_2 radical addition to C_4H_6 and subsequent reaction pathways [288],

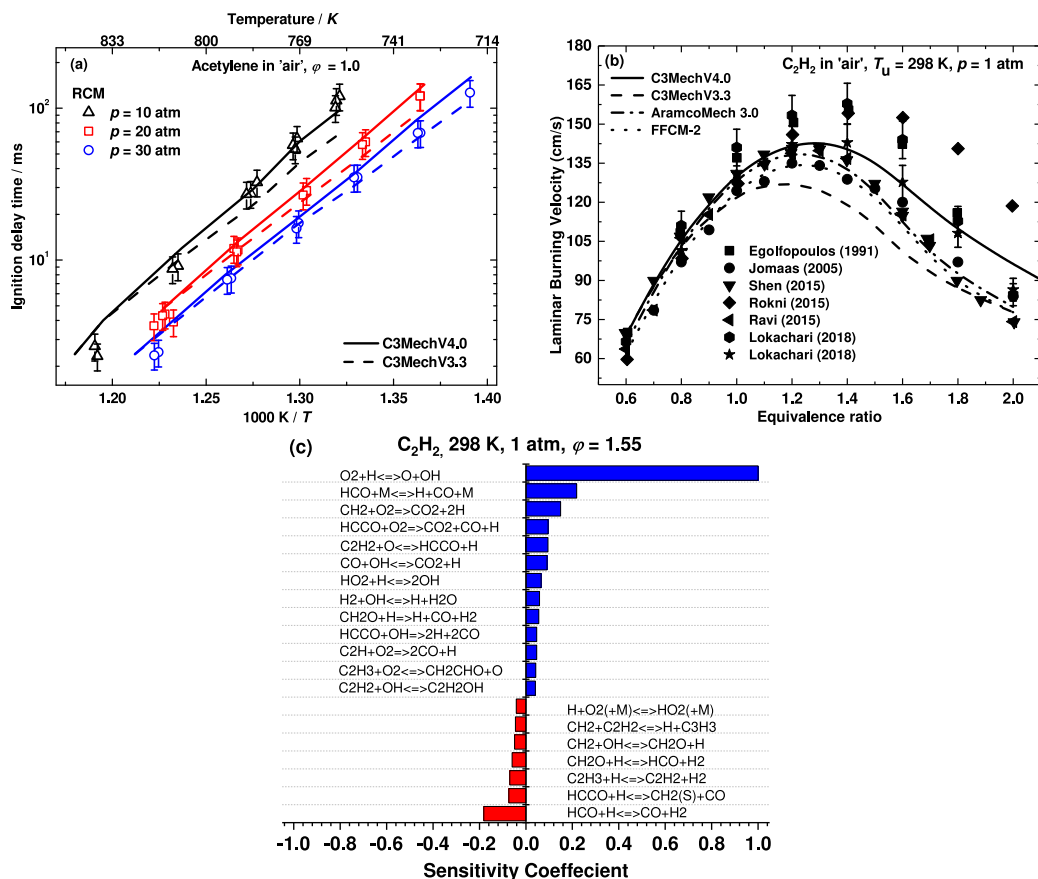


Fig. 6. The performance of C3MechV4.0 and C3MechV3.3 for acetylene (a) IDT and (b) LBV measurements. The IDTs in the RCM were measured by Lokachari et al. [173] for C_2H_2 in air at $\phi = 1.0$, $p = 10$ –20 atm. The LBV data is from multiple studies [145,151,168,173,180], measured in air and at atmospheric conditions. (c) The flow rate sensitivity analysis highlighting the series of reactions updated to improve LBV predictions.

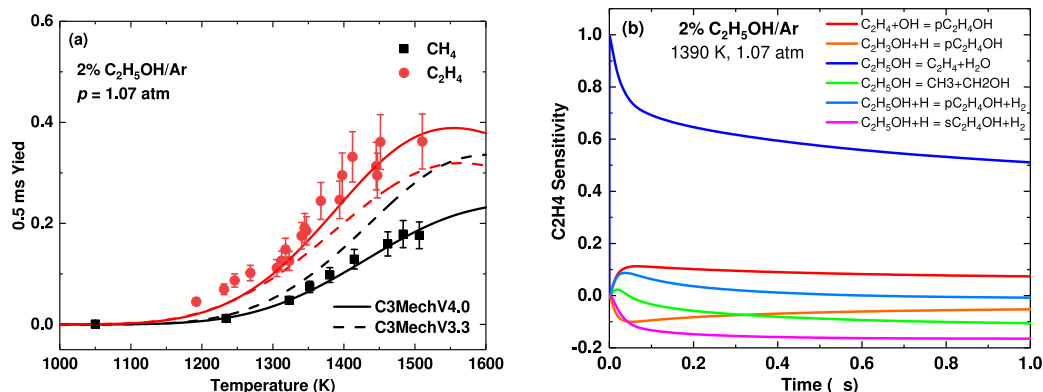


Fig. 7. The performance of the updated ethanol sub-mechanism in C3MechV4.0 compared to C3MechV3.3 at (a) $p = 1.07$ atm with methane and ethylene early-time pyrolysis yields detected during ethanol pyrolysis at 0.5 ms with 2% ethanol, and (b) C_2H_4 sensitivity against time at similar conditions.

as seen from the sensitivity analysis summarized in Fig. 10(b). Additionally, the updates in O_2 addition to 1,3-butadien-1-yl (C_4H_5-N) also played a vital role in improving the model predictions, as these are the most sensitive reactions on both sides of the sensitivity spectrum. Although the updated model reasonably predicts the trends of low-temperature reactivity, the model predictions can still be improved for these conditions. The LBV results shown in Fig. 10(c) indicate that the updated model is notably faster for fuel-rich mixtures and slightly slower for fuel-lean mixtures, resulting in better predictions. This improvement is the result of the updated core chemistry combined with the updates mentioned above, together with the updated H radical addition to C_4H_6 proposed by Dong et al. [288]. In contrast, the

previous model was only able to predict the data from Lu et al. [292], which is noticeably slower than the other measured values.

3.3. Cyclopentane and cyclohexane

Fig. 11 shows the performance of C3MechV4.0 compared to measured IDT data for cyclopentane oxidation compared to the model of Patel et al. [450]. The updated model shows faster ignition at $T > 740$ K and in the NTC region, resulting in improved predictions. The 15–20% decrease in ignition delay comes predominantly from the latest core chemistry with some improvements at $T < 700$ K due to a slower rate constant for RO_2 to $QOOH$ isomerization and KHP formation.

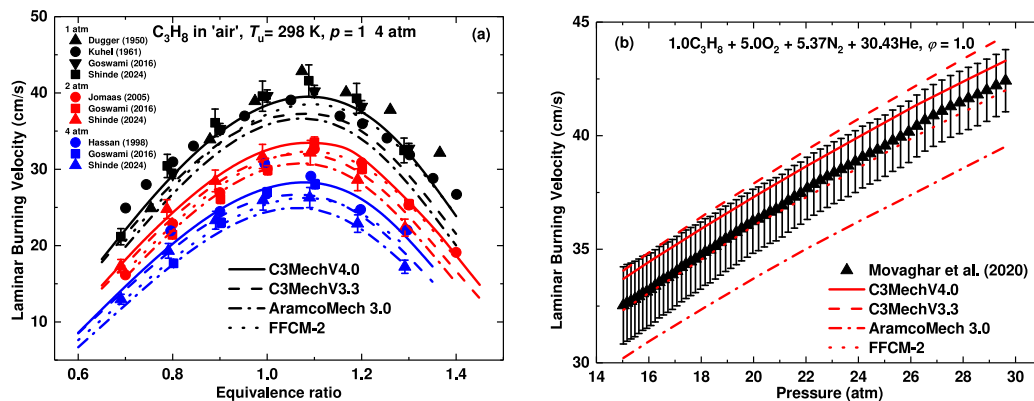


Fig. 8. A comparison of model performance for propane (C₃H₈) oxidation using C3MechV4.0 and C3MechV3.3 compared to LBV measurements at (a) $p = 1\text{--}4$ atm in air at an unburned temperature of 298 K, and (b) $p = 15\text{--}30$ atm with He dilution at $T = 410\text{--}510$ K.

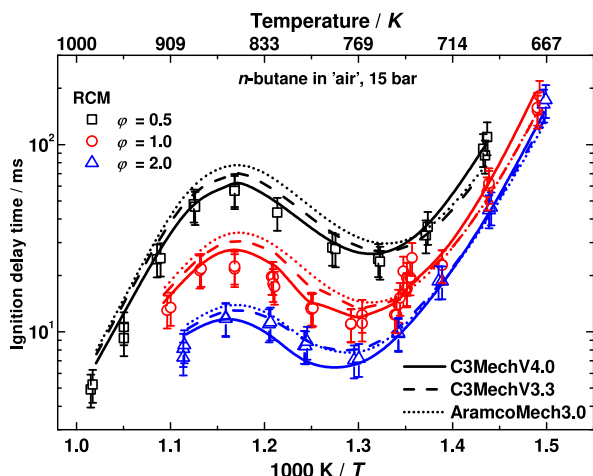


Fig. 9. The effect of model updates on the performance of *n*-butane for IDTs measured in a RCM by Caravaca-Vilchez et al. [267] at $p = 15$ bar in air and at $\phi = 0.5\text{--}2.0$.

Fig. 12 compares the performance of the cyclohexane sub-model of Chatterjee et al. [337] adopted as-is in C3MechV4.0 (dashed lines) with that of the final C3MechV4.0 (solid lines) with updated rate rules and thermochemistry compared to IDTs measured in an RCM. After updating thermochemistry and incorporating new rate rules, the updated C3MechV4.0 shows very good agreement with the low-temperature measurements, mainly due to the thermochemistry updates based on the new GAVs. The resulting increase in the enthalpy of formation for alkyl peroxy (RO_2), hydroperoxy-alkyl (QOOH), and peroxy hydroperoxy-alkyl (O_2QOOH) radicals significantly influences the predicted IDTs in the NTC region. Additionally, the group entropy values for alkyl (R) radical production are higher than those for QOOH radicals, a factor not typically addressed in conventional GAVs. As indicated by Heng et al. [473] and Wang et al. [355], these updated GAVs primarily impact the predictions in the NTC region without dramatically affecting the high- and low-temperature branches.

3.4. Heavy alkanes

The new thermochemistry data for C₅–C₁₀ alkanes generally reduce their reactivity at low temperatures, as observed by Ghosh et al. [513] and Wang et al. [355], primarily due to an increase in the Gibbs

free energy of O_2QOOH that shifts the equilibrium of the reaction $\text{QOOH} + \text{O}_2 \rightleftharpoons \text{O}_2\text{QOOH}$. Fig. 13 demonstrates the impact of subsequently improving the core chemistry, thermochemistry, and rate rules (in C3MechV4.0) on the reactivity of *iso*-octane. Compared to C3MechV3.3, the updated core chemistry produces an increase in the reactivity due to the new $\text{HO}_2 + \text{HO}_2 \Rightarrow \text{OH} + \text{OH} + \text{O}_2$ channel [454]. The update of the thermodynamic data offsets this effect at high and intermediate temperatures, but it leads to an overestimation of the reactivity in the low-temperature branch. Finally, updating the rate rules for the kinetics of *iso*-octane according to Wang et al. [355] and Heng et al. [473] led to a substantial improvement in the IDT predictions at lower temperatures, highlighting the relevance of the consistency between the thermodynamics and the kinetic sets.

Fig. 15 shows the validation of C3MechV4.0 against IDT data for heavy alkanes updated in the present model. In the high-temperature regime, C3MechV4.0 generally aligns with C3MechV3.3, while in the NTC regime, the present model is usually slower than C3MechV3.3 and is in better agreement with the experimental data. In the case of the pentane isomers, thermochemistry played the most significant role in improving model predictions in the NTC region, Fig. 14(a). For the hexane isomers and *n*-heptane, combined updates of thermochemistry and kinetics has led to substantial improvements, especially in IDT predictions for 2,3-dimethylbutane, where the IDT increases by more than a factor of three in the NTC region, as shown in Figs. 14(b) and 14(c). The performance of the *iso*-octane and *n*-decane submodels has also improved. The model shows good agreement with recent literature IDT data and performs well for larger alkanes such as *iso*-octane and *n*-decane, as shown in Figs. 14(d) and 14(e).

3.5. Toluene and xylene

Fig. 15 shows C3MechV4.0 model performance against IDTs of neat toluene measured in STs and RCMs at higher pressures, closer to engine conditions [345,395–397]. Literature data were filtered to exclude data deemed unreliable. In particular, lower temperature shock tube IDT data with measured times above 1 ms (i.e., low-temperature data in Refs. [356,357]) were neglected. Furthermore, the RCM data of Mittal et al. [514] was not considered due to the unavailability of volume traces necessary to account for facility effects in the simulations. Concerning the high-temperature ST measurements, the model correctly reproduces the pressure trends, capturing quantitatively the 50 bar data of Shen et al. [345] while underestimating the IDTs of Zhang et al. [395] within reasonable uncertainties (i.e., up to a factor of 1.7 at 1400 K). Fig. 15 also shows that the model agrees well with the low-temperature RCM measurements of Kukkadapu et al. [396] and

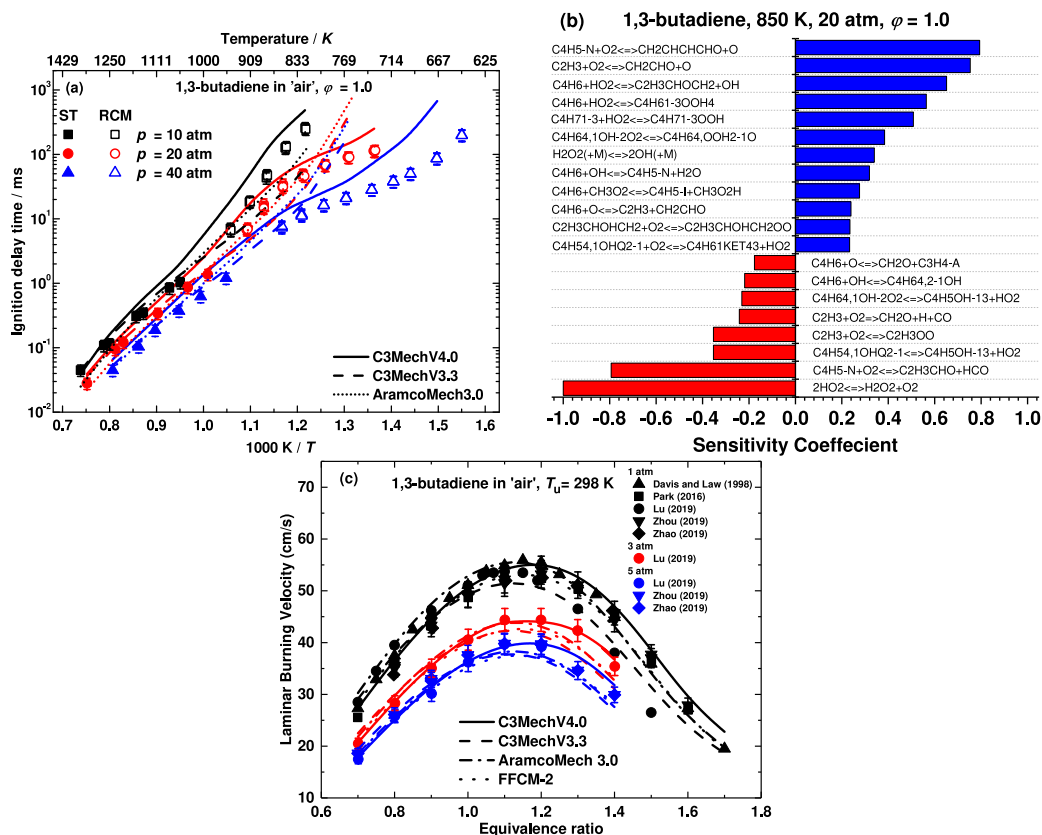


Fig. 10. The performance of the updated 1,3-butadiene model against (a) the IDT data from Zhou et al. [286] at $p = 10\text{--}40$ atm in air and at $\phi = 1.0$ taken in a ST (solid symbols) and in an RCM (hollow symbols), (b) the constant volume sensitivity analysis at 298 K depicting the reactions updated to improve the model performance, and (c) LBV data from multiple studies [273,275,286,291,292] at $p = 1\text{--}5$ atm in air at an unburned gas temperature of 298 K.

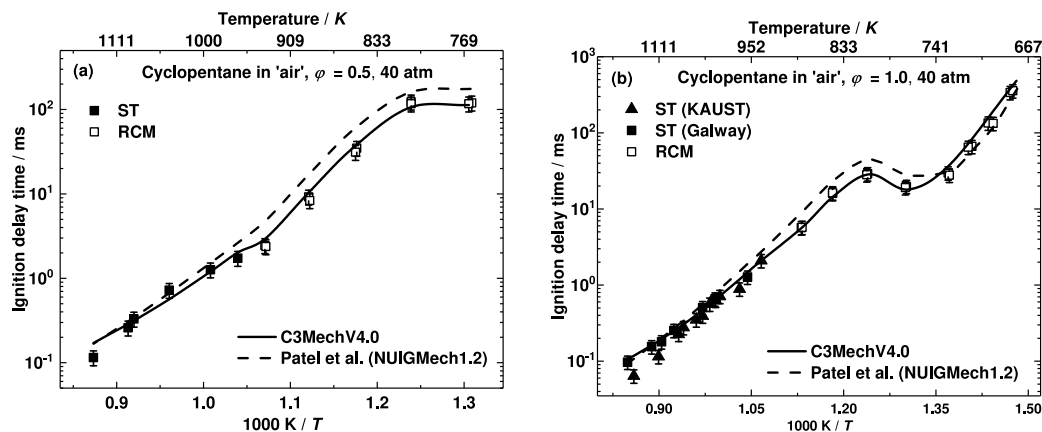


Fig. 11. A comparison between the model of Patel et al. [450] and C3MechV4.0 at (a) 40 atm, $\phi = 0.5$, and (b) 40 atm, $\phi = 1.0$. The experimental data is taken from Al Rashidi et al. [314].

Büttgen et al. [397]. Fig. 16 shows that, for the RCM cases, substantial improvement in model performance is observed using C3MechV4.0 compared to C3MechV3.3, especially at temperatures below 1000 K, where the predicted IDTs decrease by up to a factor of six.

To better understand the reasons behind the changes in model performance, Fig. 17 compares the reaction rates of the benzyl radical – which largely controls the reactivity of the system – close to ignition at $p = 25$ bar and $\phi = 1$ when the end of compression temperature is ~ 975 K. The most striking difference between the two models is that in C3MechV4.0 the $C_6H_5\dot{C}H_2 + HO_2 \rightarrow \dot{O}H + C_6H_5CH_2\dot{O}$ reaction is responsible for 25 % of benzyl radical consumption, as opposed to $\sim 10\%$ in C3MechV3.3. In fact, the rate constant for this reaction in

C3MechV4.0 has been increased by a factor of 1.5–2.0 in the temperature range of interest, thus strongly fostering the production of $\dot{O}H$ radicals and therefore an increase in the rate of fuel ignition, while the rate constant for the termination channel producing BZCOOH has been decreased by approximately 40 %. Consequently, the reaction rate of H-atom abstraction by $\dot{O}H$ from the fuel also increases. Finally, while the rate constant for benzyl radical self-recombination is about a factor of 1.2–1.5 higher than the one adopted in C3MechV3.3, the contribution of this reaction to benzyl radical consumption decreases, due to the greater relevance of benzyl consumption by reaction with HO_2 . Note that the rate constants for H-atom abstraction reactions from toluene underwent only minor changes compared to those used in C3MechV3.3

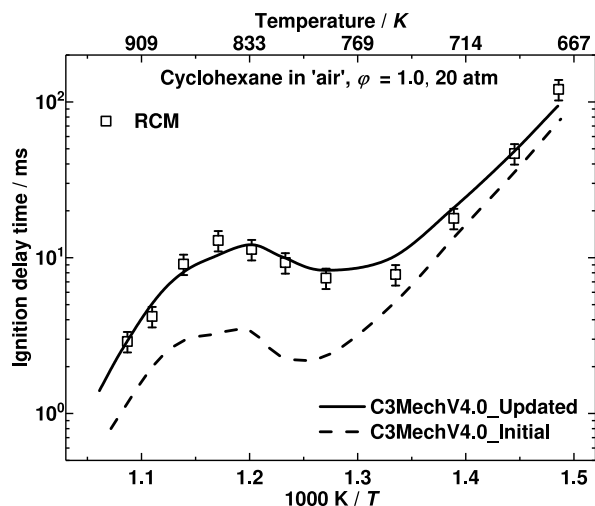


Fig. 12. A comparison of the initial and updated C3MechV4.0 models, both of which incorporate the cyclohexane model from Chatterjee et al. [337]. The updated model includes modifications to the thermochemistry and rate rules of the cyclohexane sub-model.

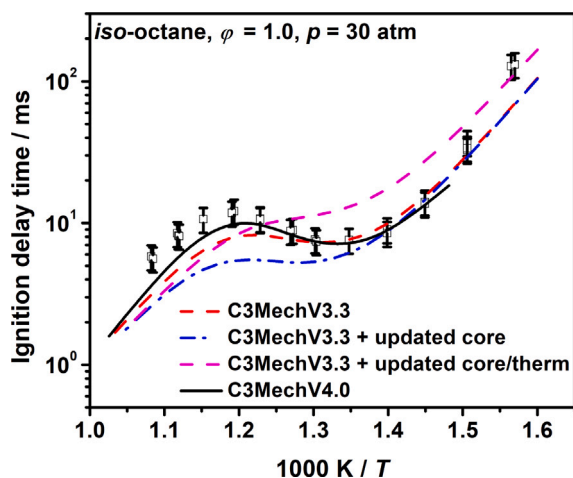


Fig. 13. Influence of updating core chemistry and thermochemistry data in iso-octane sub-mechanism. Experiments are taken from Wang et al. [355]. Lines are constant volume simulations.

except for those by HO_2 (increased by a factor of 2.5), hence the differences in the cumulative contribution of the respective reaction rates are due to the changes in the simulated radical concentrations.

The updated xylene subset was tested against IDT measurements. Fig. 18 shows the model performance for the IDT measurements of xylene at $p = 8\text{--}40\text{ atm}$ against the experimental measurements of Battin-Leclerc et al. [418] (with initial xylene mole fraction $X_0(\text{XYL}) = 0.004\text{--}0.006$) and Shen et al. [345] (less diluted conditions with $X_0(\text{XYL}) = 0.02$) for the high-pressure range, while model predictions of the experimental measurements of Gail et al. [417,419] are plotted for atmospheric conditions (with $X_0(\text{o-XYL}) = 0.004$, $X_0(\text{p-XYL}) = 0.0004\text{--}0.001$). It is noted that experimental measurements are available for all three xylene isomers (ortho, meta, para), while the current model presents only one lumped species. The current model reproduces the IDT data of Shen et al. [345] well at stoichiometric and fuel-lean conditions and high pressures while slightly overestimating the reactivity at $T > 1300\text{ K}$ and $p = 10\text{ atm}$. An opposite trend is observed in the model predictions of the IDT measurements at the dilute conditions studied by Battin-Leclerc et al. [418], where over-predictions of up to a factor of two are observed at fuel-rich conditions. Less substantial

over-predictions are also found in model predictions of IDTs for p-xylene at atmospheric pressure and $T > 1650\text{ K}$ measured by Gail et al. [417], while the agreement with measured IDTs for o-xylene at similar conditions is almost perfect [419]. Note that Battin-Leclerc et al. [418] reported that the large scatter in their IDT measurements might be due to reactants condensation caused by the low volatility of xylenes. Hence, while the authors do not declare the uncertainty of their measurements, it is expected that these may be larger than 20%, and the reliability the lower pressure data of Gail et al. [417,419] may be higher.

To understand the potential reasons for model discrepancies, a sensitivity analysis was performed at $p = 8\text{ atm}$, $\phi = 1$ and $T = 1650\text{ K}$ for the diluted conditions [418] (where the experimental data are overestimated) and at $p = 10\text{ atm}$, $\phi = 1$ and $T = 1330\text{ K}$ for the less diluted conditions [345] (where experimental data are underestimated), respectively. The results are reported in Figs. 18(c) and (d), respectively. At lower temperatures and higher concentrations (Fig. 18(d)), the reactivity is largely controlled by fuel-specific reactions, and in particular it is enhanced by the H-atom abstraction reaction by O_2 and the recombination of HO_2 . In contrast, the fuel bond-fission reaction decreases the reactivity as it occurs mainly as a recombination with H prior to ignition, as well as H-atom abstraction by OH radicals. The reaction classes involved in xylene ignition are similar to those found in the analysis of low-temperature toluene reactivity, as is expected due to the analogies of the two fuels. Instead, the most sensitive reactions at higher temperatures and more diluted conditions, Fig. 18(c), involve the isomerization and oxidation of methyl-phenyl radical $\dot{\text{C}}_6\text{H}_4\text{CH}_3$, where the former reaction suppresses the reactivity while the latter enhances it. In addition, xylyl radical decomposition also accelerates the reactivity. The main source of $\dot{\text{C}}_6\text{H}_4\text{CH}_3$ is $\text{C}_6\text{H}_4\text{CH}_3\text{CHO}$ decomposition reaction, similar to the low-temperature case; however, at higher temperatures, the main sources of $\text{C}_6\text{H}_4\text{CH}_3\text{CHO}$ are xylene or xylyl oxidation reactions with $\text{O}(^3\text{P})$. Hence, future model improvements will address the development of more accurate analogy rules between toluene and xylene, focusing on oxidation reactions with $\text{O}(^3\text{P})$ and HO_2 that should enable improving the model performance at both low- and high-temperature conditions.

Regarding other datasets tested, the SM reports also results of simulations of RCM ignition delay time data for o-xylene [396], LBVs for all xylene isomers at both 358 K and 398 K inlet temperatures [515], and temperature-dependent species profiles from both pyrolysis (ST, 20 bar [420]) and oxidation (JSR, 1 bar [400]) conditions. Overall, the model captures both LBV data and fuel conversion under pyrolysis conditions well (Figure 18 and 66 of Section 7 of the SM). The model also reasonably captures the trends of the product distributions in pyrolysis. It should be mentioned that in this case the severe lumping of large PAH species affects the interpretation of the results, such that e.g., C_{15} and C_{16} products generated from the recombination of fuel radicals are absent in the model and directly form condensed isomers such as phenanthrene and pyrene (see Figure 66 of Section 7 of the SM). Conversely, the model requires some improvement for oxidative conditions and lower temperatures. In fact, C3MechV4.0 mildly overestimates o-xylene ignition at $T < 900\text{ K}$ for the RCM experiments reported by Kukkadapu et al. [396]. At these conditions, sensitivity analyses highlight the relevance of the oxidation by HO_2 of relevant radicals in the system such as RXYLENE , $\dot{\text{O}}\text{C}_6\text{H}_4\text{CH}_3$, and $\text{HOC}_6\text{H}_4\dot{\text{C}}\text{H}_2$, as well as of H-atom abstractions by HO_2 and O_2 . Interestingly, recombination reactions among the resonance-stabilized radicals mentioned above also play a role. However, the rate parameters for most of these reactions are currently based on analogy estimates and should be refined in future studies.

Finally, the model overall reproduces the main trends and product profiles in the JSR experiments of Meziane et al. [400] ($T = 800\text{--}1100\text{ K}$, $p = 1\text{ atm}$, $\phi = 0.5, 1, 2$, see Figure 65 of Section 7 of the SM). However, fuel conversion is underestimated at fuel-lean conditions. In this case, similar reactions as those mentioned for the RCM experiments appear in the sensitivity analysis, such that it is hard to reconcile the agreement with both the JSR and RCM datasets through adjustments in the rate constants.

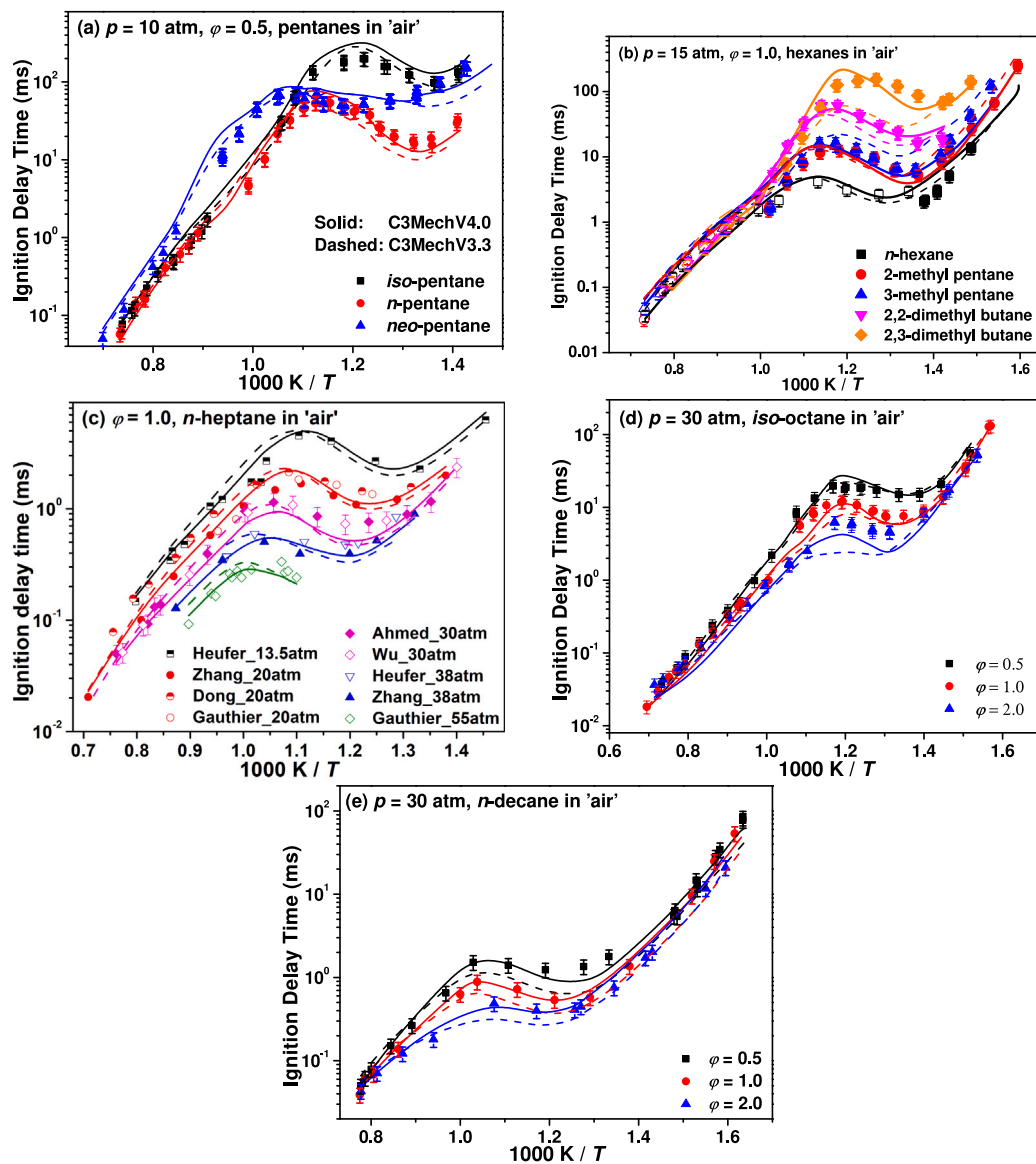


Fig. 14. Simulated IDTs with C3MechV4.0 (solid lines) and C3MechV3.3 (dashed lines) against the experimental data (points) of pentane isomers, hexane isomers, *n*-heptane, *iso*-octane, and *n*-decane over a wide range of conditions. Experiments are taken from Refs. [133,190,299,324,341,342,368,475].

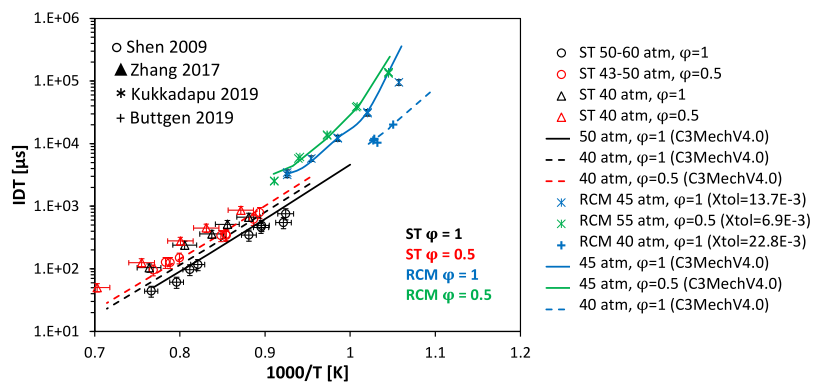


Fig. 15. Main sets of IDT data from ST and RCM experiments considered reliable for the model validation of neat toluene compared to C3MechV4.0 model results [345,395–397]. In the legend, Xtol indicates the initial toluene mole fraction (where deemed relevant).

Note: uncertainty bars not reported for the RCM experiments as the declared uncertainty of 10% in the published works corresponds to the size of the data points.

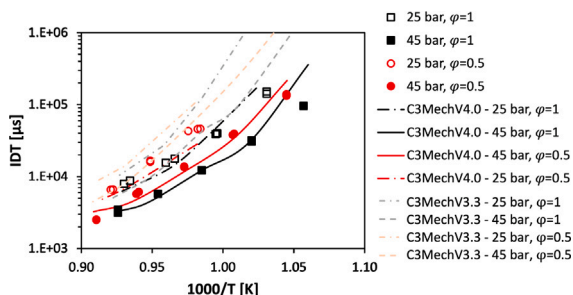


Fig. 16. Experimental IDTs for neat toluene measured by Kukkadapu et al. [396] compared to C3MechV4.0 model simulations (solid/dash-dotted black and red lines) and to C3MechV3.3 (shaded lines).

Note: uncertainty bars not reported as the declared experimental uncertainty of 10 % corresponds to the size of the data points.

3.6. Dimethyl ether

In the updated DME sub-model, we aimed to decrease reactivity in the NTC region and at lower temperatures to improve IDT predictions compared to C3MechV3.3. Fig. 19(a) shows a noticeable improvement in C3MechV4.0 model performance at $T < 1100$ K, while the model maintains the previous performance at $T > 1100$ K at both 10 atm and 23 atm and at fuel-lean and fuel-rich conditions. As anticipated in Section 2.7, lower reactivity in the NTC region was obtained by tuning the reactivity of O_2 addition to $QOOH$, which is –together with $QOOH$ β -scission– the most inhibiting reaction in DME ignition, as highlighted in the sensitivity analysis shown in Fig. 19(b). Additional future revisions for lower temperature chemistry might include KHP decomposition ($HO_2CH_2OCHO \Rightarrow \dot{O}CH_2OCHO + \dot{O}H$), which is an extremely sensitive reaction at low temperatures $T = 600$ – 700 K [516]. For LBV simulations, the SM reports that the updated model has a faster flame speed that better captures the data over a wide pressure range (1–10 atm).

3.7. Dimethyl carbonate and ethylene carbonate

This version of C3Mech is the first to contain models for a linear (DMC) and cyclic (EC) alkyl carbonate, albeit leveraging previous literature efforts [264,505]. As such, the initial verification and validation efforts of the integrated kinetic model focused on: (1) simulations of neat components rather than mixtures with fuel components (e.g., H_2 , NH_3 , CH_3OH , gasoline/jet/diesel-range fuel components) that may be present in hybrid powertrains or more complex mixtures representing battery vent gases, (2) IDTs, and (3) LBVs. For DMC, measurements of IDTs, species, and LBVs are available in the literature. Perhaps the most comprehensive publication of IDT measurements for DMC was reported by Alexandrino et al. [258]. An example of validation for the neat DMC sub-model integrated into this version of C3Mech is provided in Fig. 20(a). Simulations of the ignition delay times using the integrated DMC model are generally in acceptable agreement (within a factor of 2) with the reported measurements. Another set of DMC IDT simulations corresponding to the mixtures and conditions of Luo et al. [265] are presented in the SM. Validation comparisons of DMC LBVs, show that the simulations are generally within 10 % of the literature measurements, and are also provided as SM. Two validation sets, one for IDTs and one for LBVs, for EC are provided in Figs. 21(b) and 22(a). Simulations of EC IDTs are in acceptable agreement with the experimental measurements. While the simulations show very similar IDTs for the three equivalence ratios, the measurements of Kanayama et al. [264] exhibit a slight trend of increasing reactivity as the mixtures become richer. However, due to scatter in the IDT measurements, which is of similar magnitude to the influence of the equivalence ratio observed, no definitive claims can be made in terms of trends. In contrast, the LBVs

predicted by the integrated model are significantly slower (8 cm s^{-1} or 10 %) than the measurements reported by Feng et al. [262], in contrast to measurements from [265], which the simulations match or over predict by as much as 5 %. The sensitivity of LBVs to reaction rate constant pre-exponential factors was evaluated at three equivalence ratios ($\phi = 0.5, 1.0, 2.0$) and presented in Fig. 22(b) based on the average ranking of each reaction step in the respective sensitivity analysis. As expected, reactions containing EC are not among the most sensitive steps. The most sensitive fuel-containing reaction was found to be the H-atom abstraction reaction from EC by $\dot{H}$. In flames, sensitive reactions for LBV simulations tend to be $\dot{H} + O_2 = O(^3P) + \dot{O}H$ and other C_0 – C_1 reactions as shown in this work. Of the ten reactions highlighted in Fig. 22(b), there are two C_2 species that are closely related intermediates of EC, i.e., acetaldehyde (CH_3CHO) and its alkyl radical (CH_2CHO). In particular, the main products of the unimolecular decomposition of EC adopted in this work are acetaldehyde, oxirane (C_2H_4O 1-2), and vinyl alcohol (C_2H_3OH). Oxirane and vinyl alcohol can both further react to form acetaldehyde and shared intermediates (e.g., CH_2CHO). Additional efforts to improve the simulated LBVs may benefit by focusing on the modeled reactions of this C_2H_4O potential energy surface and relevant experimental measurements. Future work may be directed at improving the performance of neat EC, mixtures of DMC and EC with additional components, and theoretical studies of DMC- and EC-relevant reactions.

3.8. Ammonia

In the last few years, numerous detailed NH_3 combustion kinetic models have been published [47,60,63,71,75,455,517–532], indicative of the considerable complexity of NH_3 combustion and significant progress in this field. The NH_3 sub-model adopted in C3MechV4.0 was quantitatively evaluated alongside sixteen recent literature models [60,63,71,75,455,517–526] by Girhe et al. [533], using an extensive experimental database for pure NH_3 and NH_3/H_2 fuel mixtures. They showed that the UoG_2023 model [455] (adopted in C3MechV4.0) achieved the highest overall performance score averaged across key targets, including species concentrations, IDTs, and LBVs. As two representative examples, comparisons of model predictions of C3MechV4.0 and UoG_2023 [455] against IDTs [53] and jet-stirred reactor (JSR) speciation measurements [523] are depicted in Fig. 22 and Fig. 23, respectively. The predictions remain identical, ensuring the same accuracy of C3MechV4.0 as the source model. Similar validation plots for NH_3/H_2 mixtures as well as LBVs are provided as SM.

3.9. Model validation for aromatic species

Model testing for PAH chemistry considered predictions of aromatic species in various configurations and for numerous fuels (C_2 – C_7), as summarized in Tables 2 and 4. Testing targets included reactor and unstretched laminar flame data available as SM to this paper (see POLIMI validation section of the attached report) and the counter-flow flame data compiled by Langer et al. [478] (also available as SM). This section evaluates model predictions of species mole fractions for mono-aromatic and poly-aromatic hydrocarbons in jet-stirred reactors, flow reactors, burner-stabilized premixed flames, and counterflow flames. Further speciation data, LBVs, and IDTs are presented in the SM. The complete database comprised 73 global combustion datasets (IDTs and LBVs), 59 flow reactor speciation measurements, 27 premixed laminar flame speciation measurements, and 31 counterflow flame speciation measurements, including several new test sets compared to C3MechV3.3 for small hydrocarbons (e.g., C_3H_4 -A/P and C_4H_4), previously tested unsaturated cyclic species (cyclopentadiene, benzene, toluene) and newly introduced aromatics (xylene, α -methylnaphthalene).

Figs. 24 and 25 show parity diagrams for various cyclic and aromatic hydrocarbons, including mean factors of the deviations between the measured and computed species peak mole fractions [478].

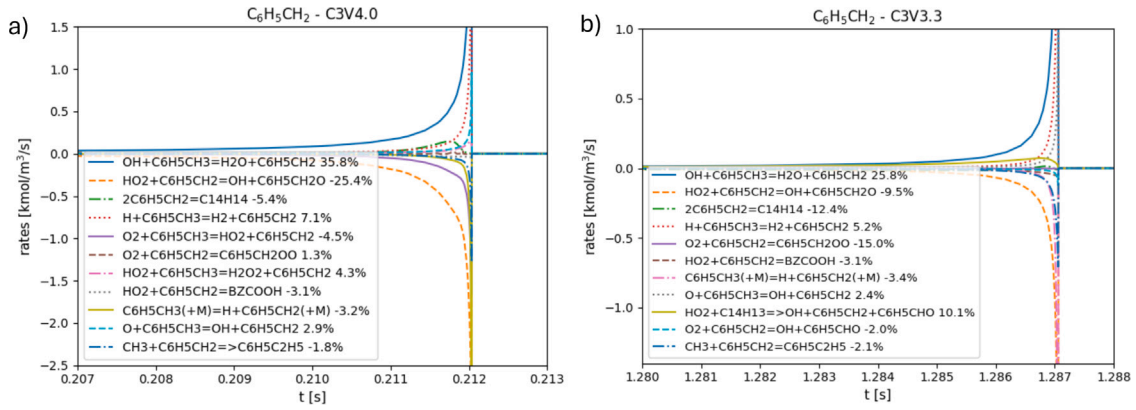


Fig. 17. Reaction rates for benzyl production and consumption along the reactor coordinate close to ignition at the conditions of the toluene RCM experiments of Kukkadapu et al. [396] ($p = 25$ bar, $\phi = 1$, T at end of compression = 975 K) obtained with (a) C3MechV4.0 and (b) C3MechV3.3. The legend shows integrated %-contributions to the consumption or production of the species.

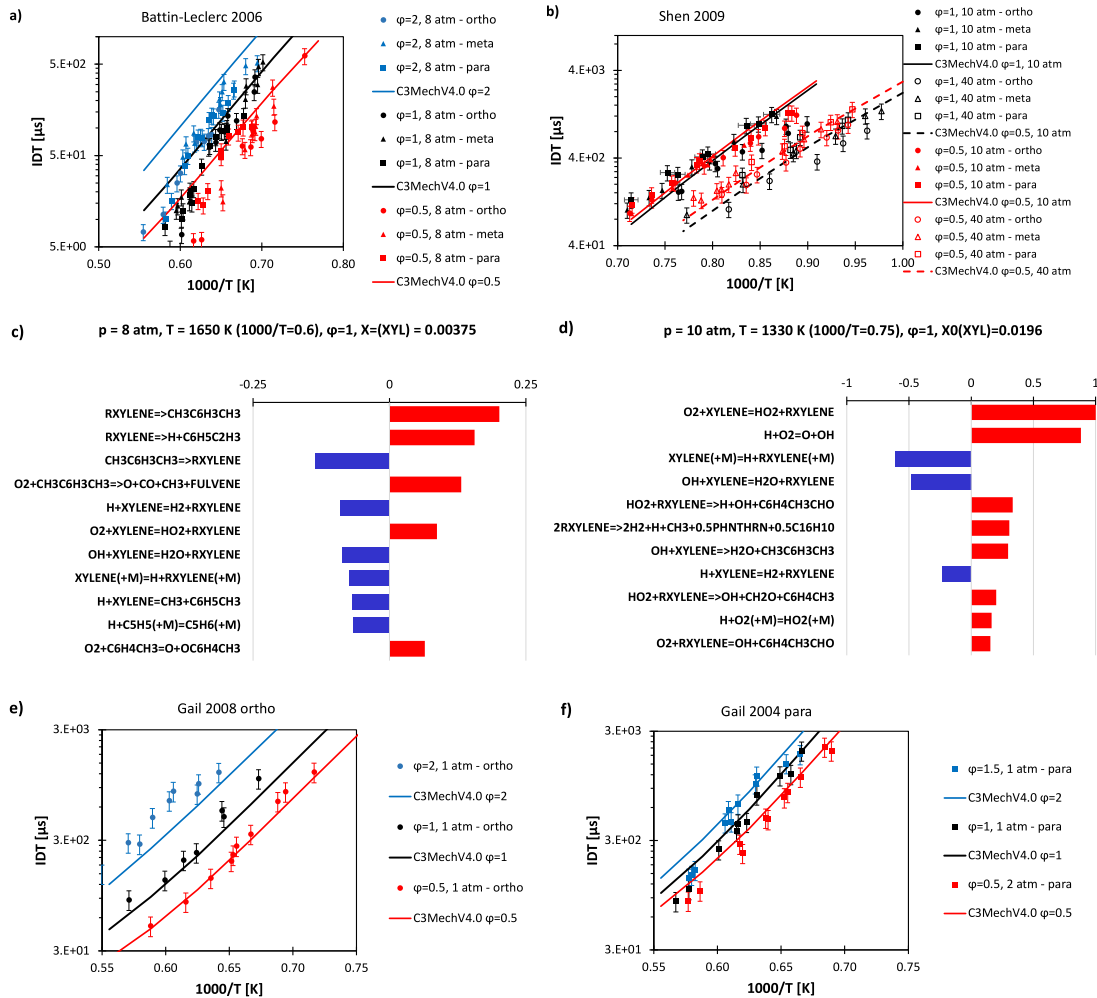


Fig. 18. C3MechV4.0 model performance for the IDT measurements of different xylene isomers (ortho, meta, para) according to the experimental measurements of (a) Battin-Leclerc et al. [418], (b) Shen et al. [345], (e), (f) Gail et al. [417,419]. In the legend, X0(XYL) refers to the initial mole fraction of xylene used in the experiments. (c) and (d) present normalized integrated sensitivity coefficients for temperature at the conditions specified in the plots, corresponding to cases within sets (a) and (b), respectively. The first reaction $H + O_2 = \dot{O} + OH$ in (c) was omitted to improve readability.

Note: In panel (a), the uncertainty in the experimental measurements was set to 20% (as common in several literature ST experiments) as it was not declared by the authors; in panel (b), only one dataset presents uncertainty bars for temperatures to improve readability. In panel (e,f), the error bars were set to 15% as declared by the authors in [419].

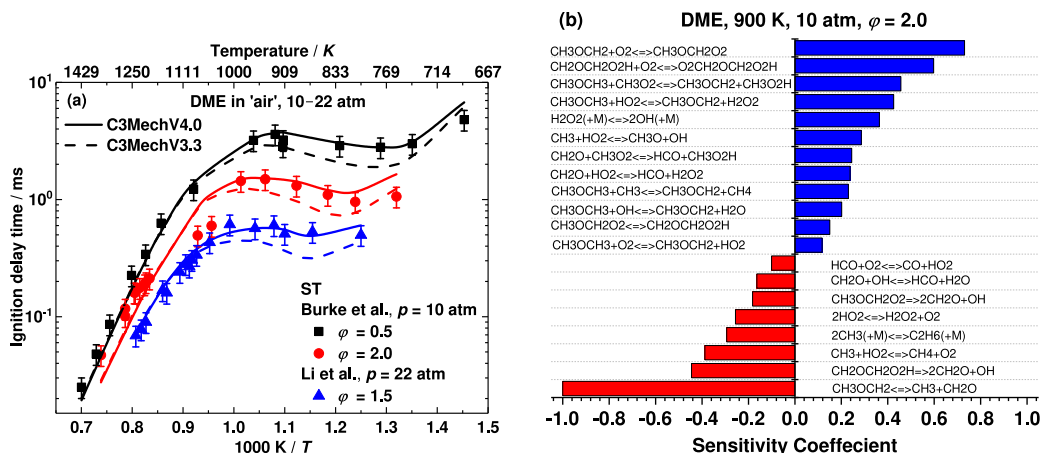


Fig. 19. The performance of the updated DME sub-model in C3MechV4.0 compared to C3MechV3.3 in simulating IDT data measured in a ST at (a) $p = 10$ atm in air and at $\phi = 0.5$ –2.0 by Burke et al. [90], and $p = 23$ atm in air at $\phi = 1.5$ by Li et al. [210] and (b) the sensitivity analysis at $p = 10$ atm in air at $\phi = 2.0$.

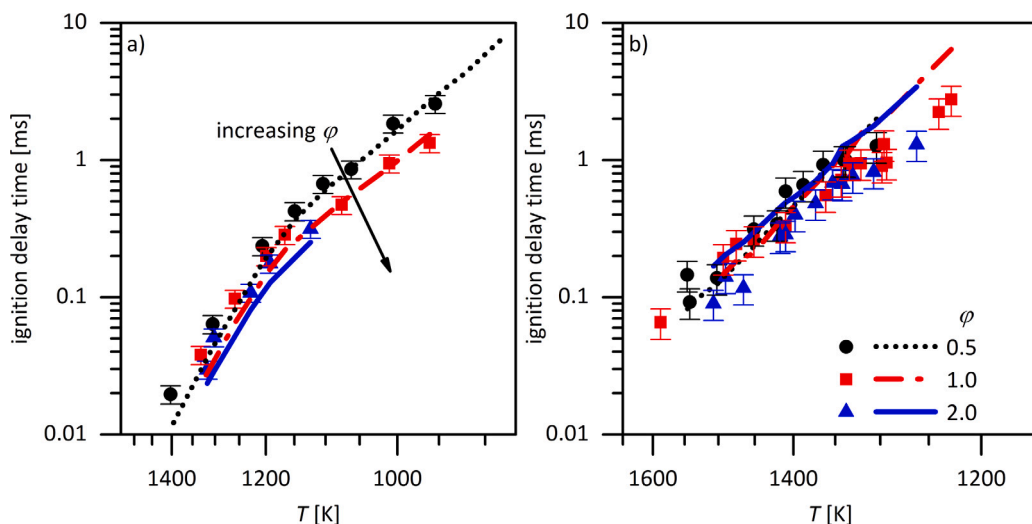


Fig. 20. Ignition delay time measurements (symbols) from [258,264] with zero-dimensional homogeneous batch reactor simulations (lines) using the current version of C3Mech across $\phi = (0.5, 1.0, 2.0)$ mixtures and conditions of: (a) 3.4–12.3 % DMC in O_2/N_2 at 40 atm; (b) EC in 95 % Ar dilution at 1 atm.

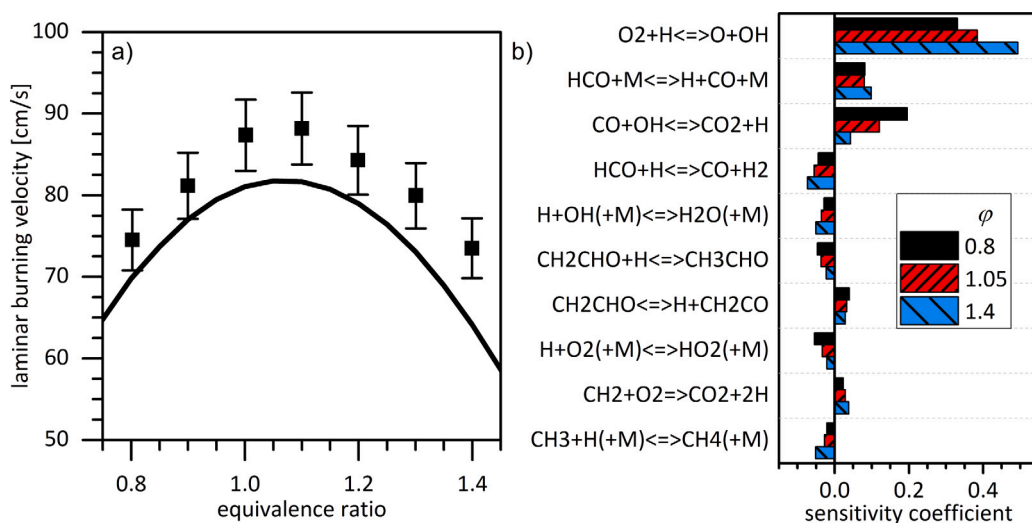


Fig. 21. Simulations (lines) of EC using the current version of C3Mech compared to: (a) LBV measurements (symbols) from [262] at $T = 543$ K and $p = 1$ atm; (b) sensitivity coefficients with respect to rate constant pre-exponential factors from the LBV simulations at $T = 543$ K and $p = 1$ atm.

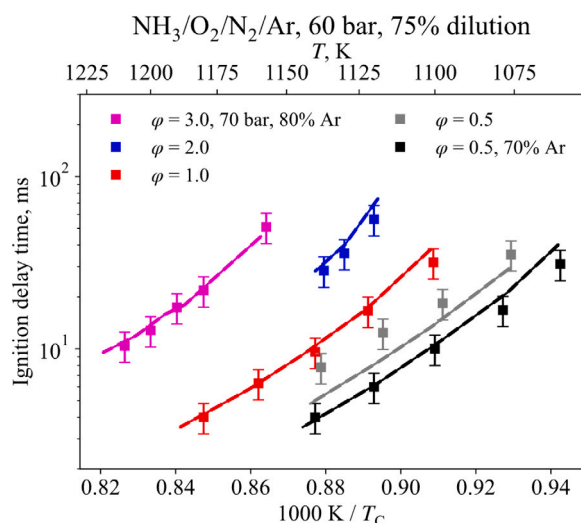


Fig. 22. NH_3 IDTs in RCM experiments from Dai et al. [53]. Solid lines: C3MechV4.0, dashed lines: UoG_2023 [455].

When calculating the mean values, outliers were ignored for toluene ($\text{C}_6\text{H}_5\text{CH}_3$), styrene ($\text{C}_6\text{H}_5\text{C}_2\text{H}_3$), indene (IND), and naphthalene (NAPH), i.e., for these species, cases where the deviations between experiment and simulation exceeded a factor of 15 for both model versions were ignored. It should be noted that outliers occur due to data from only four experimental studies [177,178,319,385]. The associated operating conditions and experimental data are recommended for detailed examination in future work.

Compared to C3MechV3.3 [10], Fig. 24 shows slight improvements in the predicted C_5H_6 peak mole fractions for C3MechV4.0. These enhancements are primarily due to the updated core chemistry, particularly affecting 1,3-butadiene and 1-butene flames. While deviations between experiments and simulations remain almost unchanged for benzene (C_6H_6 in Fig. 24) and increase for phenylacetylene ($\text{C}_6\text{H}_5\text{C}_2\text{H}$ in Fig. 25), they decrease significantly for the other substituted monoaromatic species ($\text{C}_6\text{H}_5\text{CH}_3$, $\text{C}_6\text{H}_5\text{C}_2\text{H}_3$, $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$ in Fig. 24). The predictions for phenylacetylene peak mole fractions generally decrease in the updated model, resulting in improved performance in benzene flames. However, under-predictions occur for the premixed configurations when cyclopentadiene, toluene, or C_2 species are used as fuels, indicating areas where future model improvements are necessary. Fig. 25 shows that while the average deviation between experiment and simulation remains almost unchanged for indene (IND), the average deviation factor decreased slightly for naphthalene (NAPH) and substantially for the C_{12}H_8 isomers (C_{12}H_8 isomers in C3MechV4.0 are acenaphthylene (A_2R_5), 1-ethynynaphthalene ($\text{A}_2\text{C}_2\text{HA}$), and 2-ethynynaphthalene ($\text{A}_2\text{C}_2\text{HB}$)). This trend extends to larger PAHs (fluorene and phenanthrene), as shown in the SM.

Due to the large variety of fuels, reactor types, and experimental conditions tested, only a few cases are analyzed in detail in the following. First, the model performance in simulating the acetylene premixed flame of Bierkandt et al. [178] at 40 mbar is presented. Note that this dataset may show a large uncertainty due to the approximate estimation of the exhaust temperature and temperature profile performed by the authors [178]. Hence, the discussion focuses mainly on the observed changes with respect to C3MechV3.3. This is one of the few cases where the model predictions of PAHs dramatically worsen compared to C3MechV3.3. Fig. 26 depicts the main simulated species profiles together with sensitivity and rate of production analyses to guide the understanding of the model and future improvements. Additional reaction rate of production analyses are plotted in the SM. Starting from the fuel conversion, C_2H_2 plateau concentration increases compared to

C3MechV3.3, increasing the discrepancy with experimental data due to its lower consumption by the revised $\text{O}(^3\text{P}) + \text{C}_2\text{H}_2$ channels. The mole fraction of C_4H_2 decreases by almost a factor of two, in much better agreement with experimental measurements, mainly due to the newly added $\text{O}(^3\text{P}) + \text{C}_4\text{H}_2 \Rightarrow \text{C}_3\text{H}_2 + \text{CO}$ reaction [534]. Note that at a low pressure of approximately 0.3 mbar, the channel producing $\text{C}_3\text{H}_2 + \text{CO}$ was experimentally found to be among the dominant ones for this reaction [535]. Nonetheless, $\text{C}_4\text{H}_2\text{O}$ may also be formed [535], and it was indeed detected in the flame investigated by Bierkandt et al. [178]. With the currently assumed products this reaction causes (1) a larger fraction C_3H_2 , resulting in more reasonable trends at least for the onset of C_3H_2 formation; (2) lower concentration of C_4H_4 , due to the negligible contribution of the formation channel $\text{H} + \text{C}_4\text{H}_3 - \text{I}$, where $\text{C}_4\text{H}_3 - \text{I}$ mainly derives from $\text{H} + \text{C}_4\text{H}_2$. Additional plots and rate analyses for C_4 species are provided as SM. Concerning the formation of aromatic species, benzene is formed mostly from propargyl radical self-recombination or conversion from fulvene via H-assisted isomerization, where the same pathway also forms the latter. Benzene is under-predicted by the updated C3MechV4.0 model, with predicted concentrations at the lower boundary of the estimated experimental uncertainties. The sensitivity analysis of Fig. 26 confirms the relevance of propargyl radical formation pathways in benzene formation. In particular, $\text{C}_3\text{H}_2 + \text{C}_2\text{H}_2 \Rightarrow \text{H} + \text{C}_3\text{H}_3$ is the most sensitive reaction, and it was increased compared to the previous model, as described in Section 2.2. Nevertheless, this effect is more than compensated by the other sensitive reactions, i.e., $\text{H} + \text{HCC} = \text{CO} + \text{CH}_2(\text{S})$, $\text{O}(^3\text{P}) + \text{C}_2\text{H}_2 = \text{H} + \text{HCCO}$, and $\text{CH}_2(\text{S}) + \text{C}_2\text{H}_2 = \text{H} + \text{C}_3\text{H}_3$, whose rate constants all decrease compared to the previous version – sometimes by up to a factor of five, as in the latter. Hence, overall, the concentration of benzene decreases. As for this main precursor, the mole fractions also tend to decrease for PAHs, as in the case of phenylacetylene and naphthalene. Instead, the mole fraction of indene remains almost identical. In fact, in this case the newly added pathways $\text{C}_6\text{H}_5 + \text{C}_3\text{H}_3 = \text{C}_6\text{H}_5\text{C}_3\text{H}_3$ on the PES [536] (see Section 2.6) leads to a direct precursor of indene, as highlighted by the reaction rates in Fig. 26(d). While $\text{C}_6\text{H}_5\text{C}_3\text{H}_3$ also acts as a precursor of phenylacetylene (about 3.4 % of phenylacetylene formation, as shown in Fig. 26(c), its contribution is insufficient to compensate for the lower concentration of phenyl. Finally, naphthalene formation becomes almost negligible and dramatically worsens with respect to the previous model version. The reaction rates in Fig. 26(e) highlight methylene-indenyl decomposition and $\text{C}_7\text{H}_5 + \text{C}_3\text{H}_3$ as the main formation pathways. While the former was newly added in C3MechV4.0 and is part of the reaction network of $\text{C}_7\text{H}_7 + \text{C}_3\text{H}_3$, the latter substantially decreased its contribution compared to C3MechV3.3 due to (1) the updated rate parameters, which are lower than the previously adopted analogy, (2) the mild decrease in C_3H_3 and substantial decrease in C_7H_5 fractions. Rate of production analyses reveal that the latter is due to the updated reactivity of C_7H_5 , including recombination with H, oxidation, and decomposition. These findings highlight the need to revise C_7H_5 reactivity in kinetic models and encourage further studies on formation and oxidation reactions of aromatic precursors (i.e., C_3H_3 , C_3H_2) in acetylene flames.

The effects of revisions in the acetylene and PAH chemistry are further analyzed based on an atmospheric $\text{C}_2\text{H}_2/\text{O}_2/\text{Ar}$ counterflow diffusion flame that Baroncelli et al. [176] investigated experimentally. Fig. 27 shows that deviations between measured and predicted mole fractions also tend to increase with C3MechV4.0 for this non-premixed flame. However, changes are less severe than for the low-pressure premixed flame discussed above, especially for naphthalene. Sensitivity analysis highlights that the above-discussed reactions involving oxygen have a much smaller impact on the prediction of aromatic species, as shown in Fig. 28. Hence, although predictions also deteriorate for the considered counterflow flame with C3MechV4.0, the effects are less pronounced compared to the premixed flame and predicted mole fractions of aromatic species are still close to the lower boundary of the estimated uncertainty of the measured data. The decreased sensitivity

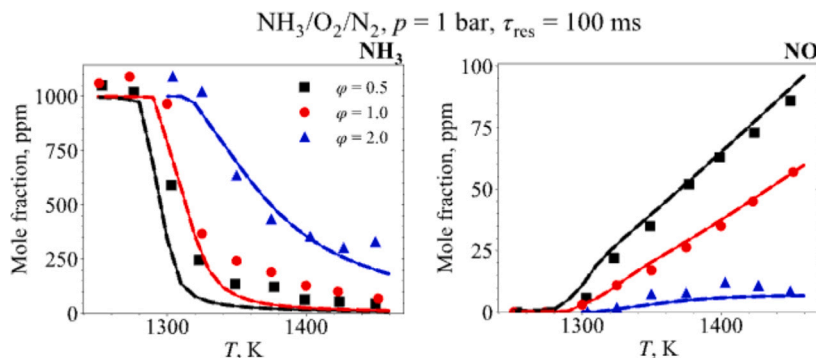


Fig. 23. NH_3 oxidation speciation in the JSR experiments from Dagaut et al. [61]. Solid lines: C3MechV4.0, dashed lines: UoG_2023 [455].

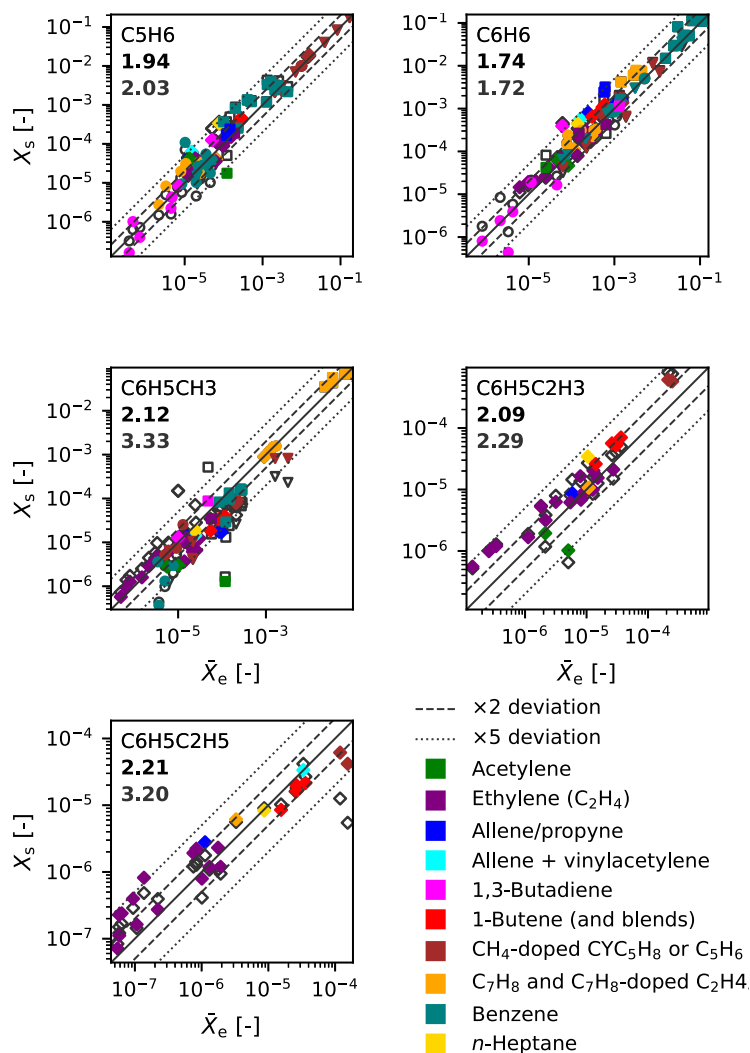


Fig. 24. Parity diagrams comparing peak mole fractions from experimental measurements to simulation results, where single species or isomer mole fractions were selected as appropriate for the respective experiment. Results obtained with C3MechV3.3 [10] are shown as empty symbols in gray. The symbol shape represents the configuration: ■ burner-stabilized premixed flames, ◆ counterflow flames, ● flow reactors, ▼ jet-stirred reactors. Values in the top left are the average deviation factor for C3MechV4.0 (upper row) and C3MechV3.3 [10] (lower row), respectively. Cases where the deviation between experiments and simulations exceeded a factor of 15 for both models were excluded from the computation of means.

to oxygen-involving reactions in this flame, along with the less severe change in naphthalene, confirms that the under-prediction of aromatic species, especially naphthalene, is partly caused by the base chemistry revisions introduced in C3MechV4.0.

The reaction flux analysis in Fig. 28 shows that naphthalene formation is dominated by HACA pathways in the counterflow flame.

Although phenyl radical addition to diacetylene (C_4H_2) and ring-enlargement pathways contribute to naphthalene formation, a sensitivity analysis highlights the importance of the Bittner–Howard HACA route [539], in which a second acetylene molecule adds to the styryl radical $\text{C}_6\text{H}_5\text{CHCH}$. In contrast to the premixed low-pressure flame, naphthalene formation pathways involving C_7H_5 are negligible.

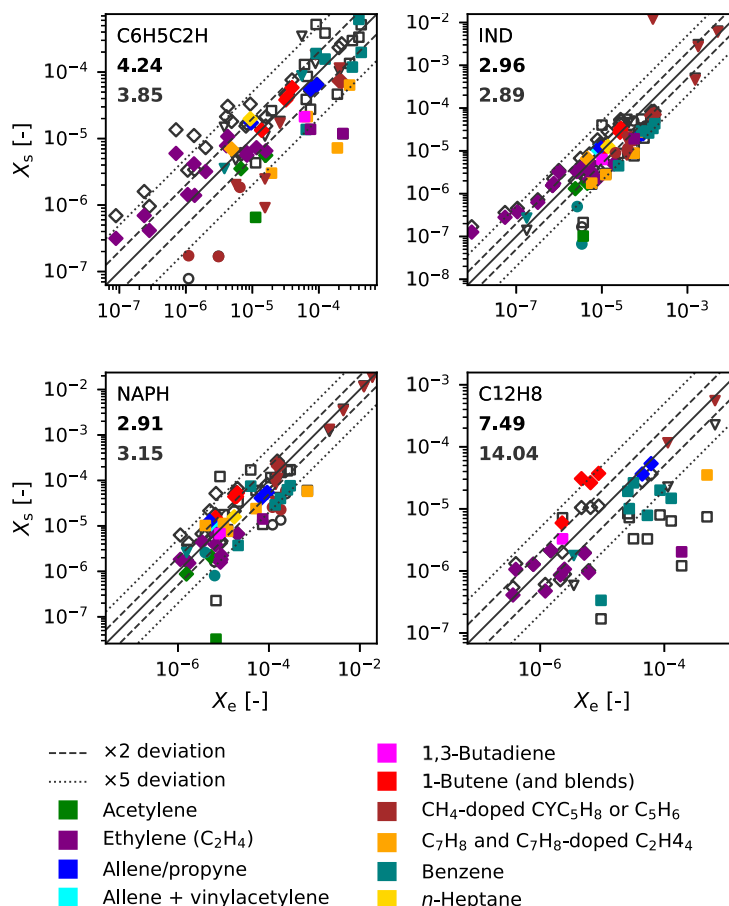


Fig. 25. Parity diagrams comparing peak mole fractions from experimental measurements to simulation results, where single species or isomer mole fractions were selected as appropriate for the respective experiment. Results obtained with C3MechV3.3 [10] are shown as empty symbols in gray. The symbol shape represents the configuration: ■ unstretched premixed flames, ◆ counterflow flames, ● flow reactors, ▼ jet-stirred reactors. Values in the top left are the average deviation factor for C3MechV4.0 (upper row) and C3MechV3.3 [10] (lower row), respectively. Cases where the deviation between experiments and simulations exceeded a factor of 15 for both models were excluded from the computation of means for all species except phenylacetylene and $C_{12}H_8$ isomers. “ $C_{12}H_8$ ” refers to the mole fraction of acenaphthylene or the sum of the $C_{12}H_8$ isomers in C3MechV4.0 (acenaphthylene, 1-ethynynaphthalene, and 2-ethynynaphthalene) as appropriate for the respective experimental data.

4. Fuel mixtures validation

One of the major aims of C3MechV4.0 was to extend the model's capability in accurately predicting various fuel mixtures, including n -alkanes, cyclic alkanes, and aromatics. A wide range of blends was validated, including binary and ternary blends containing H_2 , NH_3 , CH_4 , C_2H_6 , C_2H_4 , iC_8H_{18} (iso-octane), CH_3OH (methanol), CYC_5H_{10} (cyclopentane), and $C_6H_5CH_3$ (toluene). The C_1 – C_8 blends are defined based on the fuel with the highest carbon number. For example, C_1 blends include H_2/CH_4 , and C_3 blends include H_2/C_3H_8 .

4.1. Hydrogen/methane blends

The performance of C3MechV4.0 against IDT and LBV measurements for hydrogen/methane (C_1) blends in various proportions is shown in Fig. 29. Compared to C3MechV3.3, the model's reactivity decreases at both low and high temperatures, leading to improved predictions. A significant improvement is observed against the RCM data of Panigrahy et al. [28], shown in Fig. 29(a). The decrease in the model's reactivity is in line with the predictions for the pure CH_4 IDTs, Fig. 4. As noted by Petersen et al. [423], small or moderate additions of other fuel species to methane primarily add extra radicals to the pre-ignition radical pool. However, the main radicals involved remain the same as in pure methane oxidation. On the other hand, the concentration of CH_3O_2H and CH_3O_2 radicals decreases in mixtures

compared to pure CH_4 . However, the higher H_2 concentration in the blends prompted us to update the rate constant of $CH_3O_2H + H_2$ (see Section 2.2), which led to a noticeable improvement in the predictions of the IDTs of the mixtures. Concerning the LBV predictions, Fig. 29(b) shows an improvement over C3MechV3.3 at both fuel-lean and fuel-rich conditions. Fig. 29(b) also shows the new experimental data taken at RWTH Aachen University as part of this project for blends containing 20 % and 60 % hydrogen (black filled and blue half-filled squares, respectively; 40 % are not shown in the plot and reported as SM). The new data for 20 % and 60 % hydrogen blends agree well with the existing data and with the current predictions. The model is still slow against the peak velocity for a 50 % hydrogen blend, especially with the dataset of Kim et al. [448]. However, the latter dataset overlaps approximately with the new data taken for the 60 % hydrogen blend, thus highlighting an inconsistency between the two sets. The overall predictions demonstrate the positive impact of the updated hydrogen and methane chemistry on both the pure fuels and their blends.

Regarding C3MechV4.0 model performance against IDT measurements for light alkane blends at 40 bar, e.g., CH_4/C_2H_4 , propane/ethylene, the model shows small differences from the previous version. A detailed discussion is provided in recent publications [140,449], while plots are available as SM.

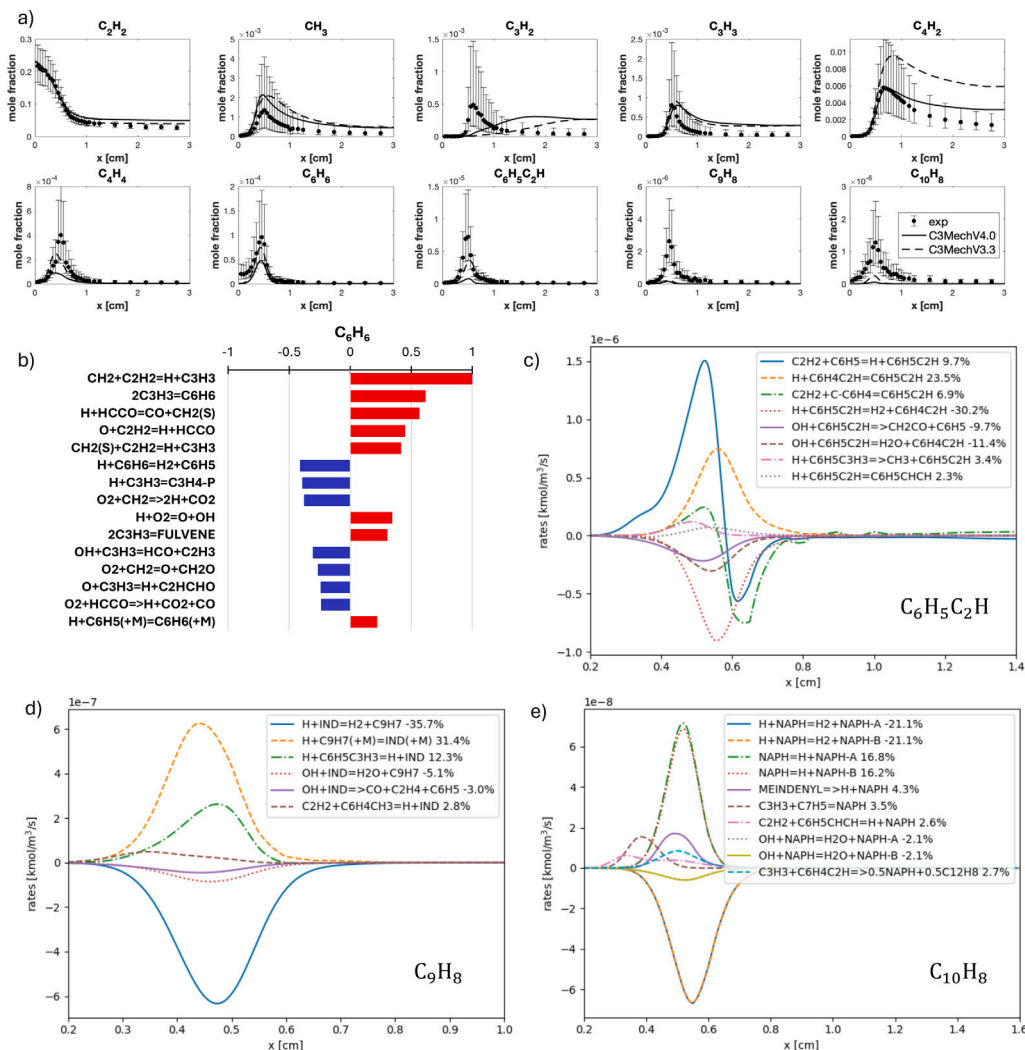


Fig. 26. (a) Experimental (points) and simulated (solid lines: C3MechV4.0, dashed lines: C3MechV3.3) profiles of the main species involved in PAH formation in the acetylene laminar premixed flame of Bierkandt et al. [178]; error bars in experimental measurements were not reported in the original work, however estimates were derived as detailed in [537] (i.e., the reference for uncertainty estimate within the original publication [178]); (b) sensitivity analysis for C_6H_6 mole fraction in the flame (global sensitivity coefficients computed as in [538]); (c)–(e) reaction rates along the flame axis for the main production and consumption pathways of $C_6H_5C_2H$, C_9H_8 , $C_{10}H_8$ (percentages indicate the total contribution of the reaction rate integrated over the reactor coordinate with respect to the total sum of reaction rates).

4.2. Heavier alkane blends

Comparisons of C3MechV4.0 predictions of large alkane blends are shown in Fig. 30. As discussed in Section 2.5, the large n -alkanes were updated in C3MechV4.0, obtaining good predictions for the ignition behavior of pure n -alkanes (see Section 3.4). These improvements are also reflected in the predictions of the blends. Fig. 30(a) shows noticeable model improvements in predicting IDTs for the primary reference fuel (PRF80, 80 % iso-octane with 20 % n -heptane by volume) at $T > 950$ K, especially at lower pressures. Compared to neat n -heptane IDTs, a higher content of iso-octane in the blend decreases the overall reactivity because of the competition for $\dot{O}H$ radicals, as observed by AlAbbad et al. [451]. As shown in Fig. 30(b), iC_8H_{18} decomposition plays a crucial role in controlling the reactivity at higher temperatures. The updates in the high-temperature mechanism of iC_8H_{18} combined with core chemistry updates have improved the model predictions. For the other blends with higher nC_7H_{16} content, the decrease in IDT in the updated model at higher temperatures is consistent with that observed for n -heptane (see Section 3.4, Fig. 14c and the SM).

Similarly, the model reactivity decreases for hydrogen and n -decane ($nC_{10}H_{22}$) blends, as shown in Fig. 30(c), resulting in improved predictions, similar to that observed for neat n -decane (see Section 4.2, Fig. 14(e)). In fuel blends, both hydrogen and $nC_{10}H_{22}$ kinetics play a vital role in controlling the reactivity of the blend. As seen in Fig. 30(d), at 900 K, the blend reactivity is influenced by H-atom abstraction from $nC_{10}H_{22}$ by HO_2 radicals. The rapid decomposition of H_2O_2 produces $\dot{O}H$ radicals, further enhancing the blend reactivity. These $\dot{O}H$ radicals can also react with H atoms, which inhibits reactivity. At these lower temperatures, there is a significant contribution from low-temperature chain branching pathways. At temperatures close to 1500 K, chain branching is limited because the reactivity is primarily controlled by the $H + O_2$ reaction in pure fuel and blends, leading to similar IDTs at higher temperatures.

4.3. Toluene blends

The model's improved predictions of neat toluene IDTs also substantially improved the predicted ignition behavior of toluene primary

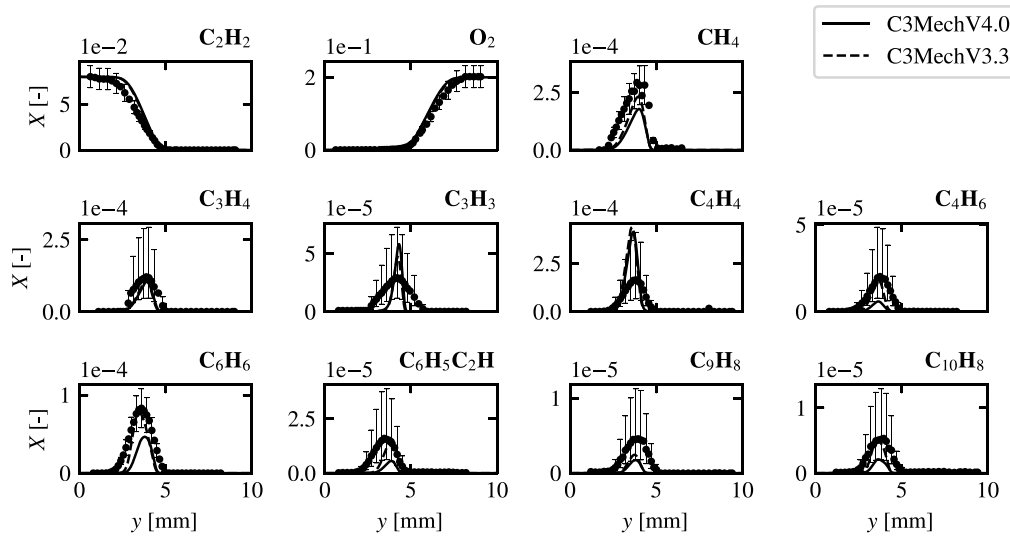


Fig. 27. Measured and predicted species mole fractions as a function of distance from the fuel nozzle for an atmospheric, argon-diluted acetylene counterflow diffusion flame. Lines show simulation results, and symbols are experimental data from Baroncelli et al. [176]. The uncertainty in the species mole fractions is up to 15% for C_2H_2 and O_2 , up to 30% for CH_4 and C_6H_6 , and approximately a factor of 2–3 for all other species [176].

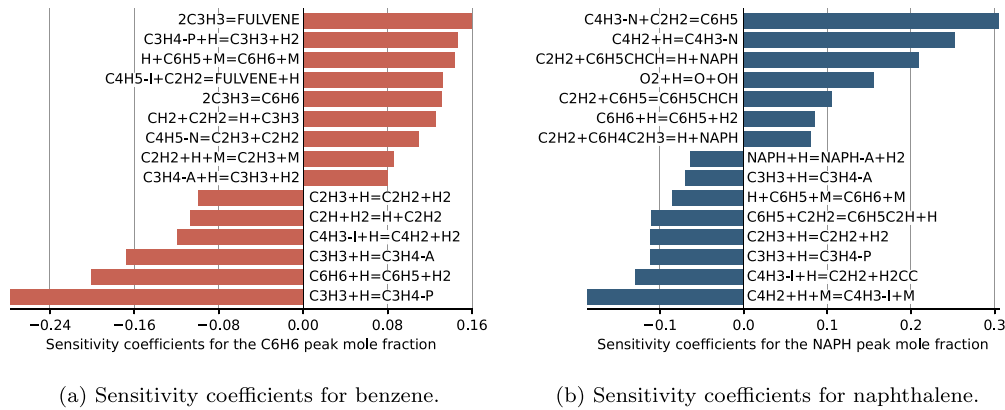


Fig. 28. (a) and (b) Logarithmic sensitivity coefficients for the benzene and naphthalene peak mole fraction with respect to the frequency factors of the shown reactions. (c) Reaction flux analysis for naphthalene. Numbers next to the arrows are relative contributions to the formation of the respective species, and species names next to the arrows are other reactants involved in the formation reactions. Colors represent the number of carbon atoms in the consumed species.

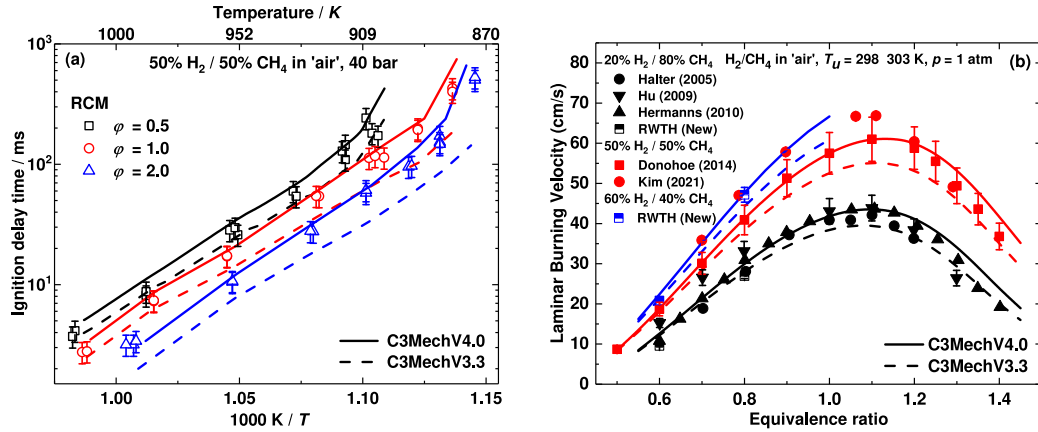


Fig. 29. The performance of C3MechV4.0 in simulating hydrogen and methane blends compared with C3MechV3.3 for (a) IDTs at $p = 40$ bar in air and at $\phi = 0.5-2.0$ measured in an RCM by Panigrahy et al. [28] for 50/50 H_2/CH_4 blends, and (b) LBVs at atmospheric pressure and unburned temperatures of 298–303 K in air with blends containing 20% [424,425,540] (black filled squares: new data from this work), 50% [422,448], and 60% H_2 (blue half-filled squares: new data from this work).

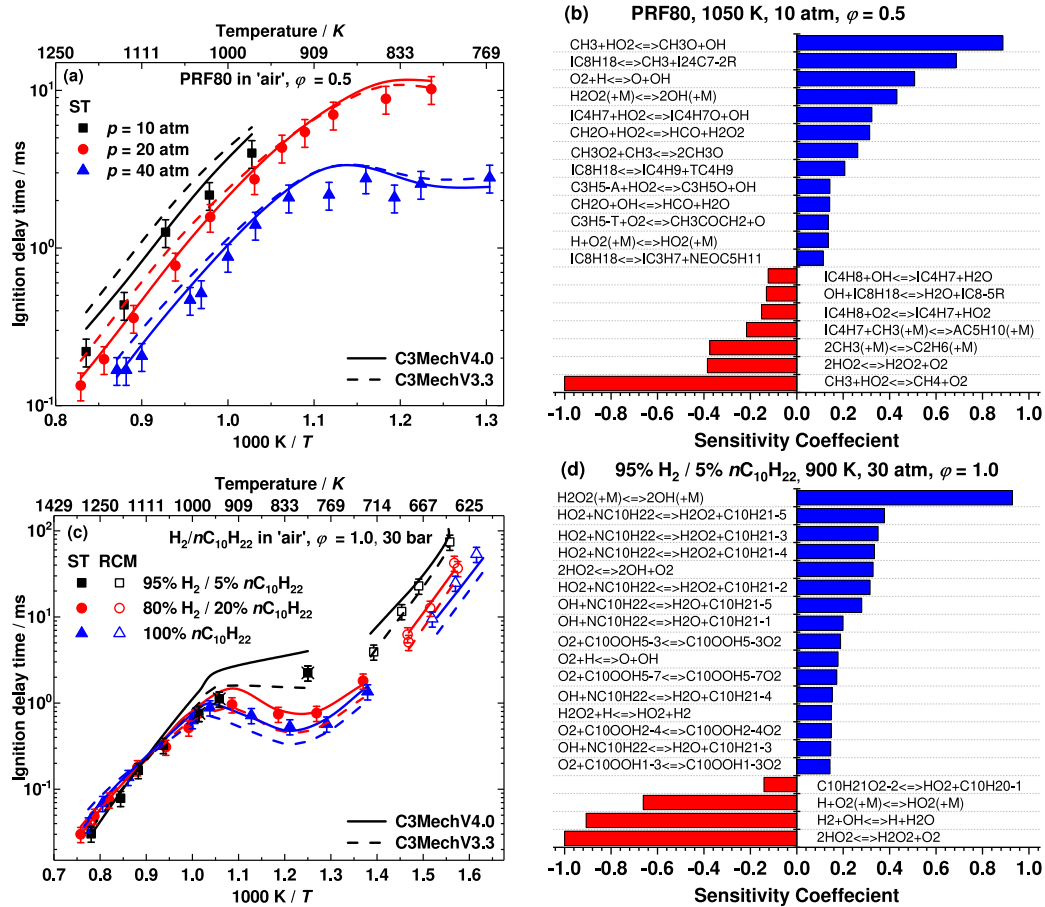


Fig. 30. Predictions using C3MechV4.0 and C3MechV3.3 for (a) primary reference fuel (PRF80) blend shock tube (ST) data from Alabbad et al. [451] at $p = 10-40 atm$ and $\phi = 0.5$ in air, (b) sensitivity analysis of PRF80 blend showing the importance of updated iso-octane sub-model (c) hydrogen blended with 5–20% $nC_{10}H_{22}$ at $p = 40 bar$ and $\phi = 1.0$ in air, against the ST and RCM data from Zhou et al. [368]. The crossed-out symbols indicate data affected by pre-ignition in an ST, and (d) sensitivity analysis of $H_2/nC_{10}H_{22}$ blend showing the dominating effect of $nC_{10}H_{22}$ in controlling low-temperature reactivity.

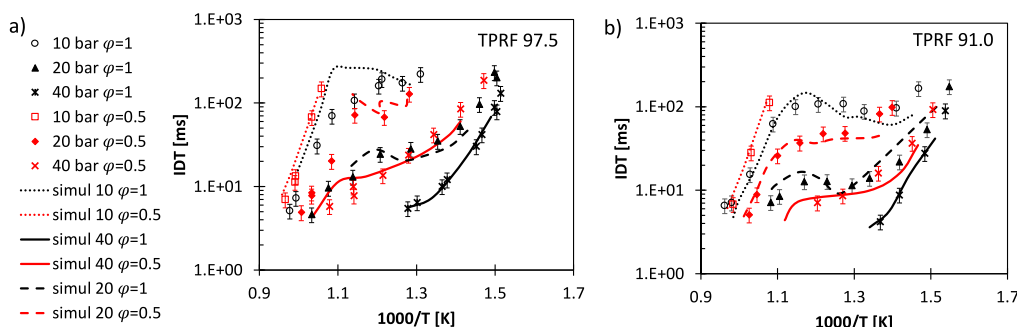


Fig. 31. IDTs of a TPRF mixture (toluene/*iso*-octane/*n*-heptane) with (a) 70.4% toluene and (b) 44.1% toluene (by volume) measured in the RCM by Javed et al. [452] compared with kinetic simulations performed using C3MechV4.0. The details of the experimental conditions and the IDT profiles simulated with C3MechV3.3 are available as SM. In “TPRF 97.5/91”, the number indicates the estimated RON.

reference fuels (TPRFs) mixtures. Fig. 31(a) compares the results of C3MechV4.0 with high-pressure RCM data for the ignition of two toluene-rich mixtures from the experimental work of Javed et al. [452]. For the sake of simplicity, the results obtained with the previous model version C3MechV3.3 are reported in the SM. Whereas C3MechV3.3 strongly overestimated IDT predictions from this dataset, the performance of C3MechV4.0 is satisfactory, despite the over-prediction of the experimental IDTs at stoichiometric conditions in the 800–1000 K temperature range, especially at lower pressure, and an under-prediction at fuel-lean conditions in the 650–750 K range. The model agreement with this dataset is strongly controlled by the competition between the benzyl radical oxidation (mostly by HO_2) and self-recombination, as highlighted in the analyses on the ignition of pure toluene in Section 3.5. Hence, it is unsurprising that predicted IDTs decrease compared to C3MechV3.3.

Since cyclic alkanes were also added to C3MechV4.0, the model was also tested against available IDT data for cyclopentane mixtures with toluene and other alkanes. Fig. 32 shows that the model can reasonably predict IDTs for ternary blends of $\text{C}_6\text{H}_5\text{CH}_3$, $\text{C}_6\text{H}_5\text{CH}_3$, and $i\text{C}_8\text{H}_{18}$. As observed by Patel et al. [450], $\text{C}_6\text{H}_5\text{CH}_3$ dominates the reactivity for ternary blends mostly due to its high concentrations in them, ranging from 60% to 90%. $\text{C}_6\text{H}_5\text{CH}_3$ also plays a role in scavenging HO_2 radicals produced by $\text{C}_6\text{H}_5\text{CH}_3$ through both abstraction reactions from toluene and recombination reactions with benzyl radicals, forming benzyl hydroperoxide $\text{C}_6\text{H}_5\text{CH}_2\text{O}_2\text{H}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{O}$, thus the presence of $\text{C}_6\text{H}_5\text{CH}_3$ in binary blends with $\text{C}_6\text{H}_5\text{CH}_3$ promotes reactivity. The addition of $i\text{C}_8\text{H}_{18}$ promotes reactivity in the ternary blends at both high and low temperatures. At low temperatures, H-atom abstraction reactions by HO_2 radicals from $i\text{C}_8\text{H}_{18}$ are more dominant than in pure $i\text{C}_8\text{H}_{18}$ because $\text{C}_6\text{H}_5\text{CH}_3$ scavenges OH radicals. At high temperatures, the unimolecular decomposition of $i\text{C}_8\text{H}_{18}$ produces CH_3 radicals that decrease the ignition time of the ternary blend [450].

4.4. DME blends

The dimethyl ether (DME) model updates are also reflected in the prediction of the IDTs of the blends, as shown in Fig. 33. For IDT predictions of CH_4/DME blends, Fig. 33(a), compared to C3MechV3.3, the reactivity slightly decreases for the 80/20 blend at 7 atm and for 60/40 and 80/20 blends at 20 atm and higher temperatures. In general, C3MechV4.0 captures the IDTs well, with some overestimation of the IDTs below 1000 K. This general trend of decrease in reactivity highlights the effect of updates in the DME model. As shown in the sensitivity analysis (top right), DME chemistry controls ignition with H-atom abstraction from DME by OH and O_2 addition to QOOH ($\text{CH}_2\text{OCH}_2\text{O}_2\text{H} + \text{O}_2 = \text{O}_2\text{CH}_2\text{OCH}_2\text{O}_2\text{H}$), promoting reactivity, and QOOH β -scission ($\text{CH}_2\text{OCH}_2\text{O}_2\text{H} \Rightarrow \text{CH}_2\text{O} + \text{CH}_2\text{O} + \text{OH}$) inhibiting reactivity. On the contrary, at higher temperatures, the unimolecular

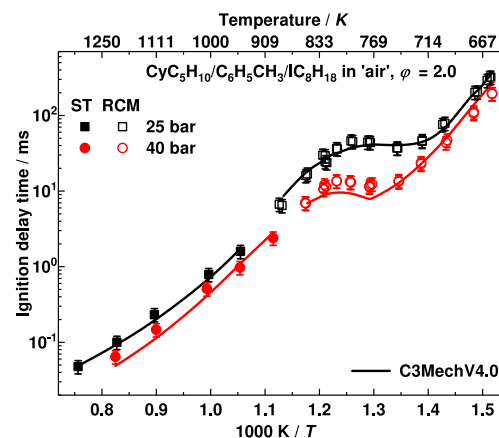


Fig. 32. The performance of C3MechV4.0 in predicting IDTs of $\text{C}_6\text{H}_5\text{CH}_3$ blended with approximately 60% $\text{C}_6\text{H}_5\text{CH}_3$ and 30% $i\text{C}_8\text{H}_{18}$ at $p = 25\text{--}40$ bar and $\phi = 2.0$ in air compared to the data from Patel et al. [450]. The blend also contains traces of other components between 2–3% of the total blend volume.

decomposition of DME and reactions of methyl radicals drive the ignition process [90]. The updates in these reactions are discussed in Section 2.7.

Concerning DME blends with ethanol, Fig. 33(b) shows that the updated model captures the ethanol/DME blends quite well, with a noticeable improvement in predicting the RCM data, in line with current updates for pure ethanol. In blends, the H-atom abstraction by OH from the alpha site (updated in this work) is more sensitive, as shown in the sensitivity analysis of the 70/30 ethanol/DME blend (bottom right). It further shows that ethanol dominates the ignition of the 70/30 blend, which points to the impact of the pure ethanol updates in improving the predictions of the blends at low temperatures. The addition of DME accelerates blend ignition because it favors low-temperature chain branching, leading to the formation of OH radicals. The sensitivity analysis also reveals the dominance of the chemistry of the pure fuels in controlling the reactivity (see right panel of Fig. 33(b)) with no contribution from the cross-reactions added based on the work by Zhang et al. [186].

The performance of the current model in predicting the IDTs of the 70/30 and 30/70 cyclopentane/DME blends against the data from Lokachari et al. [453] is shown in Fig. 34. The model shows overall good IDT predictions. However, it slightly underestimates the reactivity of blends at temperatures between 750 K and 900 K, similar to the behavior observed for neat $\text{C}_6\text{H}_5\text{CH}_3$ (Fig. 11), and for the 80/20 CH_4/DME blends. $\text{C}_6\text{H}_5\text{CH}_3$ consumption is initiated through H-atom abstraction by OH and HO_2 radicals. The concerted elimination reaction of cyclopentyl peroxy (CPTO_2) radicals producing cyclopentene

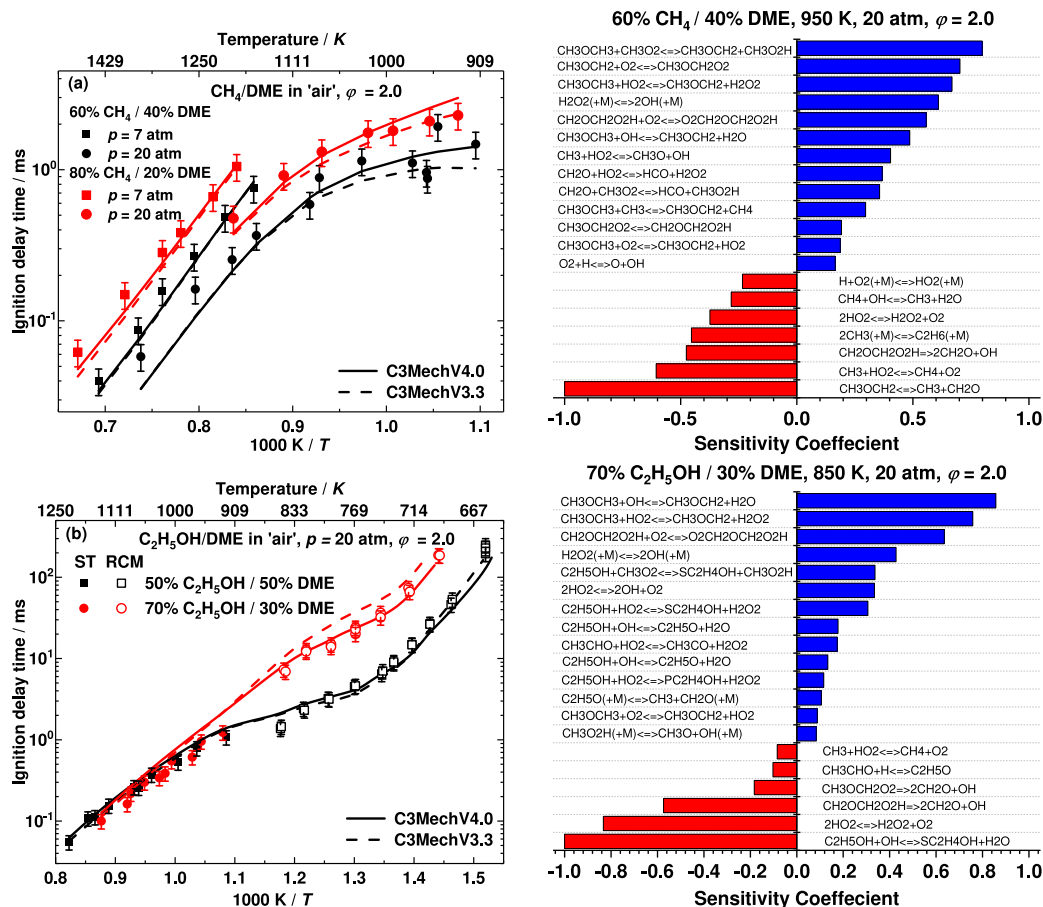


Fig. 33. IDT predictions of DME blends using C3MechV4.0 and C3MechV3.3 for (a) 20% and 40% DME blended with CH₄ measured in a shock tube (ST) at 7 atm and 20 atm and $\phi = 2.0$ in air by Burke et al. [90] along with the sensitivity analysis (top right), and (b) 30% and 50% DME blended with ethanol measured in an ST and in an RCM at $p = 20$ atm and $\phi = 2.0$ in air by Zhang et al. [186] and sensitivity analysis (bottom right) for 30% DME blended with ethanol.

(CYC₅H₈) and HO₂ radicals prevails over RO₂ radical isomerization and suppress the reactivity, as shown in the sensitivity analysis in Fig. 33. However, due to the addition of DME to the binary blend, more OH radicals are generated in the pool from low-temperature DME pathways, and H + O₂ dominates HO₂ radical production. As a result, CYC₅H₁₀ consumes OH radicals, while HO₂ radicals mostly react with CPT₂O₂J (CPT₂O₂J + HO₂ = CPT₂O₂H + O₂) and other species. Eventually, the ring-opening products from the latter pathway lead to low-temperature chain branching, significantly affecting the reactivity of CYC₅H₁₀ and its blends.

4.5. No_x effect on fuel mixtures

Understanding NO_x interactions with hydrocarbon fuels is vital in reducing emissions and developing efficient combustors. Considering this, the model was tested in its ability to predict the effect of NO_x interactions with natural gas, primarily CH₄. As shown in Fig. 35, there is a general decrease in the model reactivity compared to C3MechV3.3. The model performs quite well in predicting the CH₄/NO_x interactions, with 15–20% improvement noticed for the blends with 400 ppm N₂O dilution. As described in the work of Sahu et al. [98], adding 0–1000 ppm of N₂O has a negligible effect on the IDTs of CH₄. So, the model shows a similar improvement in the predictions as observed for pure CH₄, Fig. 5. Hence, the model generally shows a good performance for NG3 (CH₄, C₂H₆, C₃H₈, nC₄H₁₀, nC₅H₁₂) blended with NO₂, as shown in Fig. 35(b). Both models depict a similar performance, except for 5–10% faster reactivity observed with the latest model at high-pressure conditions. The sensitivity analysis showed that the reactivity is primarily

controlled by H-atom abstraction from large alkanes (C₃–C₅) as they produce propyl, butyl, and pentyl radicals that participate in chain branching and promote reactivity.

5. Conclusions

Herein, the Computational Chemistry Consortium (C3) presents a new version of C3Mech (C3MechV4.0), a global unified combustion kinetic model used to reproduce the ignition, combustion, flame behavior and pollutant formation of surrogate mixtures for both conventional and renewable fuels. Compared to C3MechV3.3, the new kinetic model includes substantial updates: from recent literature studies in the description of the core chemistry (hydrogen and C₂ in particular); rate rule updates for heavy alkane chemistry; inclusion of recent literature calculations for PAH growth, focusing on 2-ring PAH formation and growth; new kinetic subsets to describe the combustion of ammonia, cyclopentane and cyclohexane, dimethyl carbonate and ethylene carbonate, and xylene.

C3MechV4.0 was validated against a wide range of experimental data, showing excellent predictive capabilities. Compared to C3MechV3.3, the validation dataset was expanded for both the new fuel components and their mixtures. This work focused on the model performance against data for mixtures of carbon-free fuels (hydrogen, ammonia) and hydrocarbons (especially methane), which are interesting for short-term practical applications in existing engines.

In addition to routine model updates, the next steps for model development will consider additional fuel components for biodiesel fuel surrogate mixtures, renewable fuel components such as oxymethylene

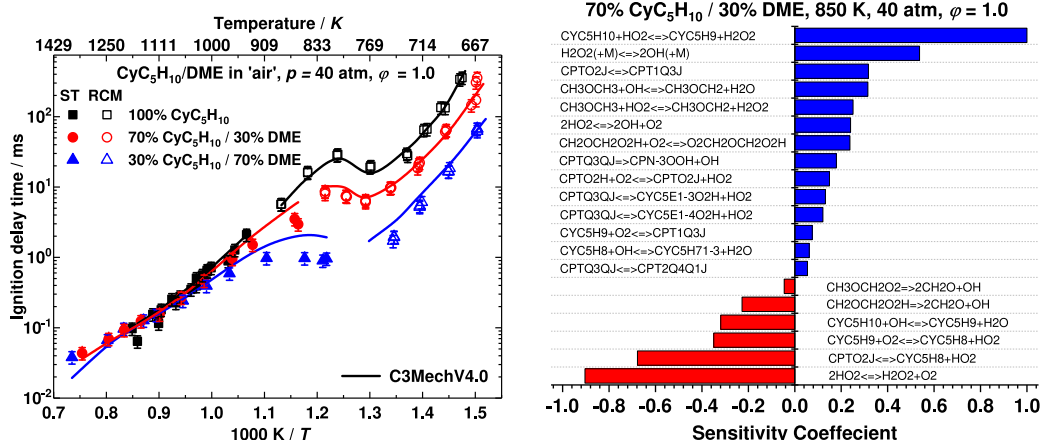


Fig. 34. Experimental data measured in a ST and in a RCM from Lokachari et al. [453] and model predictions using C3MechV4.0 for 30–100% $\text{CYC}_5\text{H}_{10}$ blended with DME at $p = 40\text{ atm}$ and $\phi = 1.0$ –2.0 and sensitivity analysis at similar conditions (on right) depicting the influence of $\text{CYC}_5\text{H}_{10}$ on the blend's reactivity.

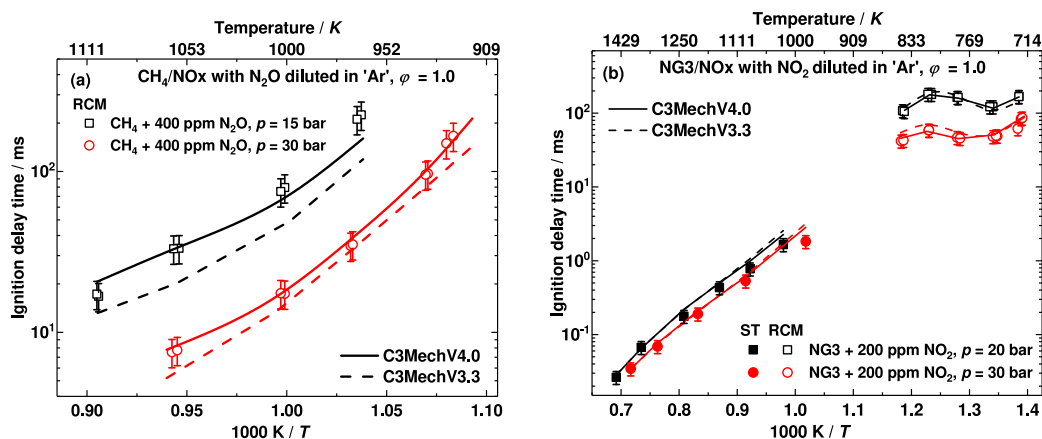


Fig. 35. A comparison of the performance of C3MechV4.0 and C3MechV3.3 in predicting IDTs in a ST and in a RCM for (a) a CH_4/NO_x blend measured by Sahu et al. [98] at $p = 15$ –30 bar with 400 ppm of N_2O , and (b) a $\text{NG3}/\text{NO}_x$ blend measured by Pathak et al. [298] at $p = 20$ –30 bar diluted with 200 ppm of NO_2 .

ethers, and more complex aromatic structures such as alkyl aromatics, with a continued effort towards a global, unified, reliable, and an easy to manage kinetic model to study practical applications in the combustion sector.

CRediT authorship contribution statement

Luna Pratali Maffei: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Raymond Langer:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Yuki Murakami:** Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Scott W. Wagnon:** Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation. **Pengzhi Wang:** Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Data curation. **Jiaxin Liu:** Writing – original draft, Validation, Software, Investigation, Formal analysis, Data curation. **Mohsin Raza:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation. **Yuxiang Zhu:** Writing – original draft, Validation, Investigation, Formal analysis, Data curation. **Sanket Girhe:** Writing – original draft, Validation, Investigation, Formal analysis, Data curation. **Christian Schwenzer:** Writing – original draft, Formal analysis, Data curation.

Joachim Beeckmann: Supervision. **Stephen J. Klippenstein:** Investigation, Formal analysis, Data curation. **Tiziano Faravelli:** Writing – review & editing, Supervision. **Heinz Pitsch:** Writing – review & editing, Supervision. **Peter Kelly Senecal:** Resources, Project administration, Funding acquisition. **Henry J. Curran:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the authors used generative AI to proofread the article. After using this tool/service, the author(s) reviewed and edited the content as needed, and take full responsibility for the content of the publication.

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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Appendix A. Supplementary data

- New experimental data (ignition delay times and laminar burning velocities)
- Detailed descriptions of the experimental setups
- Additional details and validation in a PDF file:
 1. Instructions for access and use of the model, of THERM25 software, and of new experimental data (Sec. 1, 2)
 2. Description of experimental data and uncertainty quantification (Sec. 3–5)
 3. Comparison of most important updated rate constants (core chemistry) with microkinetic data (Sec. 6)
 4. Complete model validation (Sec. 7–10)

Users of C3MechV4.0 can download all required files from this repository: <https://github.com/C3Mech/C3MechV4.0>. The repository contains:

- All sub-modules maintained by the C3 consortium in CHEMKIN format
- A species directory (CSV & PDF), along with a Python script for checking species data and converting them from CSV format to a PDF
- A compiler script to generate CHEMKIN mechanisms from user-selected sub-modules
- Several precompiled sub-models, including the complete model (in CHEMKIN and Cantera YAML) for direct use
- Plots with comparisons of rate constants and thermochemical properties between C3MechV3.3 and C3MechV4.0.

The group additivity code THERM25 is available at <https://github.com/C3Mech/THERM25>.

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.jaecs.2025.100385>.

Data availability

Research data are attached and available online.

[Kinetic model \(Original data\) \(GitHub\)](#)

[Thermochemistry code \(Original data\) \(GitHub\)](#)

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