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<th><strong>Title</strong></th>
<th>Uncertainty quantification of a newly optimized methanol and formaldehyde combustion mechanism</th>
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Uncertainty quantification of a newly optimized methanol and formaldehyde combustion mechanism

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Abstract

A detailed reaction mechanism for methanol combustion that is capable of describing ignition, flame propagation and species concentration profiles with high accuracy has been developed. Starting from a modified version of the methanol combustion mechanism of Li \textit{et al.} (\textit{Int. J. Chem. Kinet.} 2007) and adopting the H\textsubscript{2}/CO base chemistry from the joint optimized hydrogen and syngas combustion mechanism of Varga \textit{et al.} (\textit{Int. J. Chem. Kinet.}, 2016), an optimization of 57 Arrhenius parameters of 17 important elementary reactions was performed, using several thousand indirect measurement data points, as well as direct and theoretical determinations of reaction rate coefficients as optimization targets. The final optimized mechanism was compared to 18 reaction mechanisms published in recent years, with respect to their accuracy in reproducing the available indirect experimental data for methanol and formaldehyde combustion. The utilized indirect measurement data, in total 24,900 data points in 265 datasets, include measurements of ignition delay times, laminar burning velocities and species profiles captured using a variety of experimental techniques. In addition to new best fit values for all rate parameters, the covariance matrix of the optimized parameters, which provides a quantitative description of the temperature-dependent ranges of uncertainty for the optimized rate coefficients, was calculated. These posterior uncertainty limits are much narrower than the prior limits in the temperature range for which experimental data are available. The uncertainty of the self-reaction of HȮ\textsubscript{2} radicals and important H-atom abstraction reactions from the methanol molecule are discussed in detail.

\textbf{Keywords:} Methanol combustion; formaldehyde combustion; chemical kinetic mechanisms; mechanism optimization; parameter uncertainty
1. Introduction

Methanol is widely used as an alternative automotive fuel, as an octane-boosting fuel additive in gasoline and as a feedstock in various industrial processes. It is regarded as a model fuel in chemical kinetic studies of C\(_1\) combustion, with ČH\(_2\)OH and CH\(_3\)ČO being additionally important radicals in this system. Substantial efforts have been made to elucidate the combustion chemistry of methanol, which has led to the development of several kinetic mechanisms in recent years [1-7]. Large differences in the reactivity predictions of these reaction mechanisms can be observed. Other mechanisms primarily developed to describe the combustion of larger oxygenated and hydrocarbon fuels [8-18] may also be chosen for methanol combustion simulations. The prevailing lack of agreement between experimental data and many model simulations using detailed kinetic mechanisms motivated us to develop a new, systematically optimized methanol combustion mechanism built upon our previously published optimized hydrogen and syngas combustion mechanisms [19, 20].

In the context of the development of reaction mechanisms, the term “optimization” refers to a systematic search of parameter values (typically rate parameters, but in principle also thermodynamic properties or transport data) of a combustion model within their physically realistic domain of uncertainty in order to achieve the best possible reproduction of selected experimental data.

The use of mechanism optimization techniques to improve detailed combustion models follows the ideas of Frenklach and Miller [21-23], who later developed their methods towards data collaboration [24-28]. Further extensions were introduced by Wang and co-workers [29-33] that lead to the development of the Method of Uncertainty Quantification and Minimization using Polynomial Chaos Expansion (MUM-PCE) [33]. This method was, for instance, applied in studies of the kinetics of some important radical reactions [34, 35]. In these optimization methods, typically a limited number of optimization targets based on representative indirect measurement data were defined, and the most influential rate parameters at these conditions (“active parameters”, such as frequency or A-factors, third body collision efficiencies, and selected enthalpies of formation) were identified using local sensitivity
analyses. To avoid that the optimized $A$-factors approach the edges of their assigned uncertainty intervals, deviations from the initial values were penalized in more recent works [28, 32, 33, 36].

Another approach was suggested by Cai and Pitsch [37]. Their method includes the optimization of rate rules, which can reduce the dimensionality of the task for larger combustion systems, while ensuring the consistency of rate coefficients of kinetically similar reactions. Several other authors used genetic algorithms (GAs) for parameter optimizations of reaction mechanisms [38-44]. A discussion of the GA approach can be found in the textbook of Turányi and Tomlin [45].

An alternative optimization methodology was developed by Turányi and co-workers [19, 46], which differs from the methods above as follows: (i) much larger number of indirect and direct experimental data is used as optimization targets, (ii) all Arrhenius parameters ($A, n, E$) of the important reactions are optimized instead of $A$-factors only, (iii) polynomial surrogate models (“response surfaces”) are utilized to replace flame calculations only; the more accurate direct integration is used for the spatially homogeneous simulations, (iv) new algorithms are used for the generation of response surfaces and for the global parameter estimation and (v) the temperature-dependent uncertainties of the optimized rate coefficients are determined. Penalization of the deviation from the recommended values was replaced by the inclusion of direct measurements of rate coefficients as optimization targets.

The present article describes the development of an optimized methanol combustion mechanism and compares its accuracy in reproducing experimental data to other published mechanisms. The main goal of this work is to quantify the uncertainty in the rate coefficients of reactions crucial for modeling methanol and formaldehyde combustion. In addition to this a new, improved model is developed, which is largely based on the previous best model available from the literature.

In Section 2, the collection of indirect experimental data is detailed, followed by a description of the initial mechanism for optimization (Section 3) and the reasoning behind the selection of the rate parameters to be optimized (Section 4). Direct measurements and theoretical determinations of reac-
tion rate coefficients used in this work are summarized in Section 5. The method of parameter optimization and the determination of parameter uncertainties are explained in Section 6. Thereafter, Sections 7 and 8 deal with the calculation of response surfaces and the optimization strategy, respectively. The uncertainties of the rate coefficients obtained are described in Section 9, a comparison to other published reaction mechanisms can be found in Section 10. A discussion of the quantification of rate coefficient uncertainties and branching ratio uncertainties can also be found in this section, with the conclusions provided in Section 11.

2. Collection of indirect experimental data

Experimental data related to combustion studies include measurements of fundamental combustion properties such as ignition delay times, laminar burning velocities and concentration profiles measured in various types of facilities. Such measurements are considered “bulk” or “indirect” ones, since the results are not directly related to the rate parameters of a single elementary reaction in a mechanism. These experimental data can be interpreted via comparison with simulation results using detailed reaction mechanisms.

On the contrary, rate coefficients of elementary reactions for a given temperature, pressure and bath gas can be determined directly, either via experiments or theoretical calculations. It is common practice in such experimental studies to publish the determined rate coefficients only. The rate coefficient values so derived usually have a high uncertainty. Therefore, detailed reaction mechanisms primarily based on direct measurements are unlikely to reproduce well the results of indirect measurements. In addition to this, many elementary reactions cannot be studied experimentally, or only in narrow ranges of temperature and pressure. Extrapolations from these measured rate coefficients is subject to considerable uncertainty in addition to the inherent experimental uncertainty. In practice, all combustion mechanisms use rate parameters based on direct measurements or theoretical considerations, but these are modified (manually or systematically) to permit the reproduction of indirect experimental data.

This section deals with the collection of indirect measurements for methanol and formaldehyde combustion. In the present study, a total of 24,900 data points in 265 data sets (i.e. a group of data
points that were measured consecutively on the same equipment, often by varying just one parameter within the experiments) were gathered, starting from (but not limited to) the methanol combustion data reviewed by Sarathy et al. [47] and Christensen et al. [3]. Further details of the data collection can be found in the Supplementary Material (Tables A.1 to C.7); an overview is provided in Table 1. Ignition delay times were measured in shock tubes [18, 48-55] (520 data points in 74 data sets, including 99/7 for CH₂O fuel) and a rapid compression machine [18] (“RCM”, 54/7). For the majority of shock tube ignition delay measurements behind reflected shock waves, pressure–time profiles, which can be used to account for facility effects, were not reported. In these cases, data recorded at temperatures below 1000 K were excluded. Methanol laminar burning velocity measurements were carried out in spherical bombs [56-61] (170/35), using the counterflow twin-flame technique [62, 63] (90/5), in laminar, flat, adiabatic flames of heat flux burners/matrix burners [64-70] (280/41) or were measured in conical flames [71, 72] (92/6). Note that the laminar burning velocities of Sileghem et al. [67] and Nauclé et al. [69] measured using the heat flux method were modified in accordance with the recommendations of Alekseev et al. [73]. If a linear extrapolation method was used to account for stretch correction in the determination of laminar burning velocities for spherical bomb or counterflow measurements [55-58, 60], these data (208 of the 632 laminar burning velocity measurements) were excluded as potential optimization targets, but were used for the comparison of the investigated mechanisms. However, these laminar burning velocities are reproduced by the optimized mechanism within their uncertainties. 

Species profiles have been recorded using flow reactors (1896/31 for CH₃OH fuel [2, 7, 74-81], 618/16 for CH₂O fuel [6, 82, 83] and for CH₃OH/CH₄ fuel [76]), shock tubes [84-87] (12756/14 for CH₂O fuel [84-87], 7713/27 for CH₂O fuel [88-90]) and jet-stirred reactors [18, 91] (“JSR”, 711/9). 

The collected data cover a wide range of operating conditions (ignition data: \(T_s = 817–2304 \text{ K}, p_s = 0.3–51.7 \text{ atm}, \varphi = 0.17–5.9\); flames: \(T_{\text{preheat}} = 298–500 \text{ K}, p = 0.2–9.9 \text{ atm}, \varphi = 0.50–2.23\); speciation data: \(T = 600–2100 \text{ K}, p = 0.3–98.7 \text{ atm}, \varphi = 0.004–36.7\)) and diluent mixtures (N₂, N₂/H₂O, Ar, Ne/Ar, CO₂). In the majority of the experiments methanol was the fuel investigated, although a limited amount of data using other fuels or fuel mixtures (CH₂O in [6, 55, 82, 83, 88-90, 92], H₂+CH₃OH in [86],
CO+CH₃OH in [48]) was also included. In addition to oxidation experiments, shock tube measurements of characteristic times [55] and speciation profiles [88-90] for the pyrolysis of formaldehyde, and speciation data from methanol pyrolysis experiments in shock tubes [85-87] are used here, since these experiments describe other important aspects of the conversion of methanol for which CH₂O is a key intermediate. As for species profiles, the numbers above include measurements of CH₃OH, CH₂O, CO, CO₂, O₂, H₂, H₂O and CH₄ concentrations. Additional species may have been measured experimentally (C₂H₂, C₂H₄, C₂H₆, HCOOH), but are not included in several of the investigated mechanisms, which is why they were omitted here.

It has been noted by Burke et al. [93] that, in the case of H₂ combustion, speciation measurements in premixed flames cannot be utilized well for optimization, since all simulation results are far more sensitive to the temperature profile than they are to the kinetic parameters used in the simulations. A recent study of Li et al. [94] found that in two investigated methanol flames, the maximum mole fractions of ÕH and ÕH are affected by the uncertainties in the temperature measurements, while the temperature profile only has a minor effect on other C₀/C₁ intermediates. In light of these partially ambiguous results, we decided not to use premixed flame speciation measurements (e.g. [6, 95, 96]) in the present work. Simulated counterflow flame speciation data (e.g. [97-99]) are less affected by uncertainties caused by the temperature profiles. A discussion of other – potentially large – sources of uncertainty in counterflow flame measurements was provided by Ju [100]. For the purpose of this work, we have also decided not to consider counterflow flame speciation data.

All experimental data were encoded into the ReSpecTh Kinetics Data format (RKD format) [101], which is an extended version of the PrIME XML format [102]. These XML files provide all measured values and experimental conditions as well as the metadata required for simulations (e.g. the exact definition of ignition delay or the time-shift criterion) and are available on the ReSpecTh webpage [103].

A pre-selection of the data was carried out before optimization (see Supplementary Material, Part 1 for details). Experimental data that could not be reproduced within 3σ of their experimental scatter
by any of the mechanisms and data generated using outdated experimental techniques were excluded from the evaluation of the error function, in order to both compare the agreement between simulation results and the available experimental data, and to perform the optimization process. The excluded data sets are indicated by dark gray shading in the Tables of the Supplementary Material.

3. The initial mechanism

Based on a preliminary study of the performance (i.e. an evaluation of the agreement between the simulation results and the available experimental data, see Section 6 for a quantitative description) of published methanol combustion mechanisms, the mechanism of Li et al. [6] was selected for further improvement by means of optimization. An initial mechanism for subsequent optimization was developed based on this mechanism. This section describes the modifications carried out to ensure that the initial mechanism contains all species and reactions that are chemically relevant in the combustion of methanol and formaldehyde.

The H₂/CO sub-mechanism was replaced by our previously optimized joint hydrogen and syngas mechanism [20]. The noble gases Kr and Ne were added to the mechanism so that they could be included as possible third body collision partners with unit collider efficiencies, as they were used in some experimental studies. Thermochemical data of the species not appearing in the H₂/CO sub-mechanism were updated using the values from Goos et al. [104] (for the species CH₃OH, ĖH₂OH, CH₃Ȯ, CH₂O, CH₄, ĖH₃). The thermochemical data of ethane was adopted from Burke et al. [105], to maintain consistency with our optimized ethanol combustion mechanism [106], while the data for species H₂O₂ found in the mechanism of Li et al. [6] were retained. An additional pathway of the reaction of CH₃OH with HȮ₂ radicals yielding CH₃Ȯ and H₂O₂ was added to the mechanism, using the rate coefficient recommended by Klippenstein et al. [5]. After all modifications, the initial mechanism for optimization consisted of 24 species and 102 reactions (compared to 21 species/ 93 reactions in the Li et al. mechanism).
It will be shown in Section 9 that the above described modifications did not substantially alter the performance of the mechanism. Table 4 introduced in Section 10 furthermore shows that a modification of the rate coefficient of the other H-atom abstraction branch, CH$_3$OH+HȮ$_2$ = ĈH$_2$OH+H$_2$O$_2$, in favor of the theoretical values reported by Klippenstein et al. negatively affects the agreement between simulation results and experimental data, particularly ignition delay times. In light of the factor of 2 uncertainty estimated by the authors [5], we decided to keep the previous values used in the mechanism of Li et al. for the construction of the initial mechanism.

As completeness of a detailed mechanism is an important issue, we investigated the effect of including further species and reaction steps. Ren et al. [87] suggested the consideration of ĈH$_2$/ĈH$_2$(S) chemistry in combustion simulations of the methanol system. While some effect is observed, due to the inclusion of the corresponding reactions, the modifications did not improve the agreement between simulation results and experimental data.

We acknowledge the significance of the prompt dissociation of weakly bound radicals (e.g. HĈO) that was recently discovered by Labbe et al. [107, 108], and which is particularly important at low pressures and high temperatures. In their work, HĈO prompt-dissociation probabilities were calculated up to 10 atm. Unfortunately a large amount of experimental data used in this work was obtained at pressures above 10 atm, and the uncertainty of the rate parameters proposed by Labbe et al. was not described. Furthermore, dissociation probabilities for further radicals relevant to methanol and formaldehyde combustion (e.g. CH$_3$Ȯ) are yet to be published. We expect that the above listed models, including the optimized model presented in this work, can be modified and re-fit easily as soon as the dissociation probabilities of all important radical species become available over a wide pressure range.

Li et al. [94] reported that high concentrations of C$_2$ species were observed in low-pressure methanol flames, which may affect the predictions at these specific conditions. This aspect, although not covered by the present work, should receive further attention in the development of more comprehensive methanol combustion models.
4. Selection of rate parameters to be optimized

A brute-force first-order local sensitivity analysis (see e.g. [45], Chapter 5.2) was carried out at the conditions of the collected indirect experiments, with respect to the A-factors of each reaction in the initial model, including low pressure A-factors for pressure dependent reactions. For each simulated data point, the sensitivities corresponding to 5% changes of the A-factors were calculated. The relative importance of rate coefficients was classified based on the investigation of the average local sensitivity coefficients for subsets of data, e.g. for ignitions, flames or species profiles only. Table F in the Supplementary Material, Part 1, shows an overview of the most sensitive reactions for five different subsets of data.

Based on this analysis, 57 rate parameters of 17 reactions important in methanol and formaldehyde combustion and pyrolysis were selected for optimization (see Table 2). For the investigated methanol combustion system, the self-reaction of HȮ₂ radicals (R14/R15) is sensitive over a much wider range of temperature compared to the H₂/CO system investigated by Varga et al. [19, 20]. The rate coefficient of this reaction is given by the sum of two Arrhenius expressions (i.e. duplicate reactions in the CHEMKIN notation), where the rate parameters of R14 and R15 are important at lower and higher temperatures, respectively. For this reason and in contrast to the previous studies [19, 20] in which only the high-temperature branch was optimized, we decided to re-optimize both the low and high temperature branches of this reaction: R14 and R15.

Further reactions involving CH₂O, ĈH₂OH and H₂/CO species were also observed to be sensitive under certain conditions. Many of them were optimized by Varga et al. [20] against a large set of hydrogen and syngas experimental data. Unlike for R14/R15, there was no necessity to re-optimize these reactions. Other sensitive reactions, such as CH₂O + Ĉ = HĈO + ĈH (R39), CH₂O + HȮ₂ = HĈO + H₂O₂ (R42) and CH₃OH + ĈH₃ = ĈH₂OH + CH₄ (R89), were included in a trial optimization, but the calculated posterior uncertainty ranges of the corresponding optimized parameters were very large. This indicates that the included targets (described in Sections 2 and 5) do not contain enough information to characterize these reactions quantitatively. Therefore, they were not optimized in the
final round (see Section 8). On the contrary, the minor branch of CH$_3$OH + HȮ$_2$, yielding CH$_3$Ȯ and H$_2$O$_2$ (R88) proved to be well quantifiable in the trial optimization, despite not being amongst the most important reactions based on the sensitivity analysis results. Another justification for adding R88 to the list of optimized reactions, despite its relative insensitivity, was that exclusion of this branch would have led to an inadequate description of the branching ratio of the CH$_3$OH + HȮ$_2$ reaction.

All three Arrhenius parameters ($A$, $n$ and $E$) were optimized for all selected rate coefficients. In one case (R77, ṘH + ĈH$_3$ + M = CH$_3$OH + M), both the high- and low-pressure limit rate parameters were selected for optimization. Rate parameters of the pressure dependence (i.e. Troe parameters) or third body collision efficiency parameters reaction steps and were not optimized.

5. Selection of rate determinations used as optimization targets

Direct measurements and theoretical studies of the rate coefficients at conditions relevant in methanol and formaldehyde combustion were collected for the selected reactions and used as additional optimization targets. If the accuracy of a direct measurement or a theoretically obtained rate coefficient was in doubt, usually due to inconsistencies with other rate determinations of the same elementary reaction, it was not used as an optimization target.

For H-atom abstraction from CH$_3$OH by ṘH radicals (reactions R83/R84 in the initial mechanism), in total 79 data points in 7 data sets were used [109-115], alongside the theoretical results of Jodkowski et al. [116], and Xu and Lin [117]. One data set containing 5 direct rate coefficient measurements [118] was included for the CH$_3$OH + Ṛ abstraction reactions (R80/R81); theoretical calculations of Meana-Pañeda et al. [119], Carvalho et al. [120], Kerkeni and Clary [121] and Jodkowski et al. [116] were also considered. The decomposition of methanol was studied in the fall-off region by several groups [86, 113, 122, 123] (89/7), while others [124-126] focused on the investigation of the low-pressure limit reaction CH$_3$OH + M = ĈH$_3$ + ṚH + M (R77 LPL; 56/4). The reverse direction, i.e. ĈH$_3$ + ṚH = products, which comprises other elementary reactions besides R77, was discussed in several experimental studies [125, 127-132] (143/9, of which 135/7 was used here). Fundamental theoretical work on this system was published by Jasper et al. [133]. Further H-atom abstraction reactions from
the CH₃OH molecule were only studied theoretically. Abstraction via O₂ (R85) was investigated by Klippenstein et al. [5]; H-atom abstraction via HȮ₂ (R87/R88) by Klippenstein et al. [5], Alecu and Truhlar [134] and Altarawneh et al. [135].

The low-pressure limit of the decomposition reaction of CH₃Ȯ radicals yielding Ḥ + CH₂O (R67) was measured [136] (58/2) and studied theoretically by Hippler et al. [137] and Dames and Golden [138]. Formaldehyde decomposition was investigated experimentally [89, 139, 140] (sum of the product branches: 4/1; CO + H₂ branch (R37): 29/2) and theoretically by Troe [141] and Friedrichs et al. [142]. The reaction of ĈH₂OH radicals with molecular oxygen (R60, 17/2) was studied by Schocker et al. [143] and Grotheer et al. [144].

The optimized H-atom abstraction reactions from CH₂O were studied extensively. For the reaction CH₂O + Ḥ = HĈO + H₂ (R38), experimental data [145-152] over a wide temperature range (143/8) and theoretical calculations of Wang et al. [151] and Irdam et al. [152] were used. Only direct measurements [140, 153] were available for the H-atom abstraction reaction via O₂ (R41; 59/3), while the reaction CH₂O + ȮH = HĈO + H₂O (R40) was studied both experimentally [114, 129, 154-157] (63/6) and theoretically [154, 158, 159]. The theoretical results of Jasper et al. [160] and direct measurements of rate coefficients [161-164] for the ĈH₃ + HȮ₂ reaction (R47/R53) were considered (sum of the two branches: 3/1, branch-specific: 57/5, including one direct measurement of R53 in reverse direction). Note that in our previous ethanol mechanism optimization study [106], only the ĈH₃ + HȮ₂ = CH₃Ȯ + ḤOH reaction was optimized, while in the present work the CH₄ + O₂ branch was also included.

In addition to the direct measurements [165-167] (72/4) that were utilized in our previous studies [19, 20, 168] for the reaction HȮ₂ + HȮ₂ = H₂O₂ + O₂ (R14/R15), now also measurements at lower temperature [169-174] (57/6) as well as the theoretical calculations of Zhou et al. [175] were considered.

A summary of all of the direct measurements and theoretical rate determinations collected and used in the present work can be found in Table 3, which also includes the ranges of temperature covered by the assembled data. Tables D.1 to D.12 (direct measurements) and Table E (theoretical determinations)
of the Supplementary Material, Part 1, provide more details. The collected data were also encoded in the RKD format [101, 103] and are available on the ReSpecTh webpage [103].

6. Parameter optimization method

The global parameter optimization algorithm applied here has been described by Turányi et al. [46] and has been utilized for various combustion systems [19, 20, 106, 176-178]. The optimal set of parameters was obtained by minimizing the following objective function:

$$ E(p) = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{N_i} \sum_{j=1}^{N_i} \left( \frac{Y_{ij}^{\text{mod}}(p) - Y_{ij}^{\exp}}{\sigma(Y_{ij}^{\exp})} \right)^2, $$

(1)

Here $N$ is the number of data sets and $N_i$ is the number of data points in the $i$-th data set. The value $Y_{ij}^{\exp}$ is the $j$-th measured data point in the $i$-th data set. For the indirect measurement data, the modeled value is $Y_{ij}^{\text{mod}}$, obtained from a simulation using an appropriate detailed mechanism, which belongs to a given set of rate parameters $p$. For direct measurement data and theoretically determined rate coefficients, $Y_{ij}^{\text{mod}}$ corresponds to the calculated rate coefficient. During the global minimum search, multiple random parameter sets $p$ are created within the uncertainty domain of the parameters, the corresponding $E(p)$ values are evaluated and the minimum search is continued in the neighborhood of the point having the lower $E(p)$ value [46].

The standard deviation of an experiment was determined for each data set separately, based on the scatter of the data and experimental uncertainties, if reported. Details on their determination can be found in the Supplementary Material, Part 1, as well as the calculated standard deviations for each data set. Constant absolute error ($\sigma(Y_{ij}^{\exp})$ is identical for all data $j$ within data set $i$) was assumed for the measured laminar burning velocities and species profiles, in this case $Y_{ij} = y_{ij}$ applies. Constant relative error, implying identical $\sigma(\ln Y_{ij}^{\exp})$ values for all data $j$ within data set $i$, was assumed for the ignition delay data and the reaction rate coefficients; thus $Y_{ij} = \ln Y_{ij}$. Explanations for these choices were provided in a previous study [179]. The estimated standard deviations for each data set are listed
in Tables A.1 to D.12 of the Supplementary Material, Part 1. Constant relative $\sigma(\ln \gamma_{ij}^{exp})$ values were used for theoretical rate determinations (see Table E of the Supplementary Material, Part 1).

Following the method described by Nagy et al. [168], temperature-dependent uncertainty limits were calculated from direct rate coefficient measurements and theoretical studies of the rate coefficient of each selected reaction. This method provides the prior uncertainty limits which represent the range in which the rate coefficients can still be considered physically meaningful. Therefore, these uncertainty limits can be used as boundaries for the optimization method, ensuring that only physically feasible random parameter sets are tested.

The uncertainty parameter $f$ is defined as [180]:

$$f = \log_{10} \left( \frac{k^0}{k_{\text{min}}} \right) = \log_{10} \left( \frac{k_{\text{max}}}{k^0} \right)$$

where $k^0$ is the nominal value of the rate coefficient based on an assessment of available experimental and theoretical studies, and $k_{\text{min}}$ and $k_{\text{max}}$ are the extreme, but not excludable values. A discussion of the uncertainty parameter $f$ and its relation to other representations of uncertainty can be found in Chapter 5.6.1 of the book by Turányi and Tomlin [45].

The method of Nagy et al. [168] for the determination of the prior uncertainty domain of the Arrhenius parameters was applied to the reactions selected for optimization in this work. Direct measurements and theoretical determinations of the rate coefficient were collected for each of the elementary reactions investigated from the NIST Chemical Kinetics Database [181] and from review articles. These carefully examined data outlines an uncertainty band of the rate coefficient $\ln k$ on an Arrhenius plot, which can be described by the temperature-dependent uncertainty parameter $f$. The $f(T)$ points were converted to the prior covariance matrix of the Arrhenius parameters for each investigated reaction step [45, 46, 182] that characterizes the prior uncertainty domain of the parameters. The extrema of the uncertainty band were used as the limiting values of the acceptable rate coefficients during the optimization. In this way, reactions R38, R40, R67, R77 HPL, R80, R81 and R84 could be treated and
a normal probability distribution was assumed for these reactions. For all other reactions too few literature data were available, and thus temperature-independent prior \( f \) values were estimated based on these scarce data and assuming a uniform probability distribution of the rate coefficients. The prior uncertainty limits were determined by using the computer codes [168, 182] \( u-Limits \), UBAC and JPDAP, which are available online [103]. Values of the prior \( f(T) \) limits for each optimized reaction can be found in Table 2. During the optimization, the estimated uncertainty ranges were enforced by discarding all rate parameter sets that result in a rate coefficient outside the corresponding uncertainty domain in the respective temperature range.

An overview of the uncertainty limits determined for the reactions optimized in this work is provided in the Supplementary Material, Part 2. Note that the prior uncertainty limits for the self-reaction of \( \text{HO}_2 \) radicals (R14/R15) were revised as compared to Nagy et al. [168] and now also include the theoretical calculations of Zhou et al. [175].

The posterior covariance matrix of the optimized parameters can be determined as described by Turányi et al. [46] and transformed to the temperature-dependent uncertainty limits of the rate coefficients. Since the optimization presented here is based on experimental data collected from many independent sources, un-correlatedness of the systematic errors can be assumed [20, 106].

If two duplicate branches of the same reaction (e.g. \( \text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2 \), described by R14 and R15) are optimized, it is useful to characterize the joint uncertainty of the sum of the two reaction rate coefficients. This can be given as:

\[
\sigma^2(\ln(k_{14} + k_{15})) = \frac{k_{14}}{k_{14} + k_{15}} \sigma^2(\ln k_{14}) + \frac{k_{15}}{k_{14} + k_{15}} \sigma^2(\ln k_{15}) + 2 \frac{k_{14}k_{15}}{(k_{14} + k_{15})^2} \text{cov}(\ln k_{14}, \ln k_{15})
\]

(3)

with

\[
\text{cov}(\ln k_{14}, \ln k_{15}) = r_{\ln k_{14}, \ln k_{15}} \sigma(\ln k_{14})\sigma(\ln k_{15}).
\]

(4)

The joint uncertainty parameter \( f \) can be obtained from the relation:

\[
\sigma^2(\ln(k_{14} + k_{15})) = \left(\frac{f_{k_{14}+k_{15}}}{3 \ln 10}\right)^2
\]

(5)
In the equations above, $\text{cov}(\ln k_{14}, \ln k_{15})$ is the covariance of the natural logarithms of the reaction rate coefficients and $r_{\ln k_{14}, \ln k_{15}}$ is their correlation. Both quantities are temperature-dependent and can be obtained from the joint covariance matrix of the Arrhenius parameters. Equation (2) is based on linear error propagation. The derivation of Eqs. 2–4 and an extension for the sum of $N$ Arrhenius expressions can be found in the Supplementary Material, Part 1.

The evaluation of the error function requires simulations of the experiments. Simulation codes of the CHEMKIN-II package [183] were used. The integrator tolerances were set to strict values for all simulations. In flame simulations, the mixture-averaged diffusion model was used and thermal diffusion was accounted for. In the CHEMKIN-II premixed flame solver PREMIX [184], the flame grid was set to contain at least 600 points, the gradient and curvature settings were always less than 0.1, and typically around 0.02. At this level of refinement, the influence of further increasing the grid size has a negligible effect on the simulated value of the laminar burning velocity [106]. For five mechanisms investigated in Section 10, simulation results could not be obtained at certain experimental conditions using PREMIX due to convergence problems. Therefore, analogous simulations were carried out using the FlameMaster [185] or OpenSMOKE [186] codes instead of PREMIX. As FlameMaster supports the PLOG formalism, it was used for all simulations with the mechanisms that employ this format. While the agreement between CHEMKIN-II and FlameMaster in the results of 0D simulations is excellent, some discrepancies (up to a few cm/s) were observed between the laminar burning velocity results using the three different solvers.

7. Calculation of response surfaces

Due to the high computational costs of direct flame simulations during the global minimum search outlined in the previous section, the utilization of polynomial surrogate models ("response surfaces") was the method of choice in many previous optimization studies (e.g. [187, 188]), including those performed by our group [19, 20, 106]. A general overview of response surface methods and their applications has been provided by Turányi and Tomlin [45], Chapter 5.5.5. It has also been shown
that the approach of calculating laminar burning velocities via response surfaces, and direct simulation of all other experimental data represents a good compromise between a favorable speed of computation and goodness of the obtained optimal fit of parameters. However, as explained below, most of the flame calculations in this work were carried out via direct simulations and not using response surfaces.

Similar to [106], 9500 uniformly distributed samples of the active parameters were generated for each laminar burning velocity data point within their joint domain of uncertainty using the SAMAP algorithm [168]. All other parameters remained unchanged. Simulations were performed at all experimental conditions using each generated parameter set. The simulation results were fitted by orthonormal polynomials using the method described by Turányi [189]. The polynomials obtained were tested against simulation results generated from 5% of the simulated sets of parameters. The maximum allowed difference between the test set of simulation results and the polynomial was 1 cm/s. When the laminar flame velocities were calculated using response surfaces, the corresponding average deviations were typically below 0.4 cm/s.

The rationale behind limiting the number of reactions included in the response surface generation was discussed in a previous article [106]. This article also outlined possible ways to overcome an insufficient coverage of laminar burning velocity data if many of the response surface calculations fail or do not provide sufficient accuracy to justify their use instead of direct simulations for each sampled set of parameters. High-quality response surfaces could only be obtained for a subset of the flames featured in the present work. For this reason, additional flames were selected for direct simulations that supplement the available response surface for an optimal coverage of operating conditions. In total, 153 flames were used as optimization targets, and during the optimization calculations 55 flame velocities were calculated using response surfaces and 98 via direct simulations. In the testing of the reaction mechanisms (see Section 10), all flame calculations were carried out using direct simulations.
8. Optimization strategy

In the final optimization round 153 flames velocity data points, 517 shock tube ignition data points, 59 RCM data points and species concentration points from flow reactors, JSRs and shock tubes (2,508, 706 and 20,460 points, respectively) were used. Details on the selection of targets used in the optimization process can be found in Tables B1 to B4 of the Supplementary Material.

The results of turbulent flow reactor experiments were interpreted by shifting the simulated species profiles to match the simulated half depletion time of the fuel (methanol or formaldehyde) as recommended by Dryer et al. [190]. In a few cases where the half fuel depletion point was not reached, a smaller degree of conversion was used as the matching point. As outlined by Varga et al. [20], this introduces a free parameter. Consequently, the uncertainties of rate parameters would be under-predicted, as most of the systematic discrepancies between the experimental data and the simulation results are eliminated by the shifting of the concentration profiles. For this reason, flow reactor concentration–time profiles were omitted from the calculation of the covariance matrix, but are still used as optimization targets.

A systematic hierarchical optimization strategy was devised as in [19, 20, 106]. In the first optimization step those experimental data that were sensitive only to the parameters of a small number of reactions were selected as optimization targets. In the next step, more experimental data and the corresponding influential reactions were included and all parameters considered up to that point were optimized. The inclusion of the new reactions was performed in such a way that the amount of newly added experimental data points was always the maximum possible.

9. Uncertainties of the rate coefficients obtained

Table 2 compares the optimized values of the rate parameters with the values in the initial mechanism. In this table, the values of the posterior uncertainty parameters are listed for the temperature range of 500–2500 K (R14/R15: from 300 K, R37 LPL and R81: from 800 K, R41: from 1000 K).
Note that the temperature ranges in which optimal parameter values were actually sought was somewhat wider, so that direct rate determinations (see Section 5) could be included that fall outside the above ranges.

Combustion data used as targets during the optimization of this mechanism are in a temperature range of 750 – 2400 K, \((i.e. \ 1000 \ K/T \approx 0.42 – 1.33)\) and cover pressures up to almost 100 atm, although the majority of data was obtained at lower pressures. The temperature-dependent uncertainty of the optimal rate coefficients can be obtained from the calculated covariance matrix of the optimized parameters. The posterior uncertainty limits represent how precisely the rate coefficients can be determined from the available data. They can be considered meaningful only in the temperature range for which data were included in the optimization. If at the extremes of this temperature range none of the experimental data is sensitive to a certain reaction, the posterior uncertainty limits (which are calculated from the posterior covariance matrix of the Arrhenius parameters) can be wider than the prior ones (which are estimated based on direct measurement data, theoretical rate determinations and review articles). The reason for this is that the posterior covariance matrix not only includes contributions from direct measurements and theoretical results, but also from indirect measurements, if these are sensitive to some of the reactions.

For almost all of the reactions optimized, the uncertainties of \(k\) could be effectively reduced over the entire temperature range of interest as a result of optimization (see Figs. 1, 2 and 5 and also the corresponding \(f\) values in Table 2). The posterior uncertainty parameter \(f\) value of \(\text{CH}_3\text{OH} + \text{O}_2 = \text{CH}_2\text{OH} + \text{HO}_2\) (R85) is somewhat larger compared to the corresponding prior \(f\) value, and increases with temperature. Figure 1 furthermore shows that the optimized rate coefficients of several reactions are close to the respective prior limits: the rate coefficients of \(\text{CH}_2\text{O} + \text{OH} = \text{HCO} + \text{H}_2\text{O}\) (R40) and \(\text{CH}_2\text{O} + \text{O}_2 = \text{HCO} + \text{HO}_2\) (R41) at the lower end of the optimized temperature range, the rate coefficients of \(\text{CH}_3 + \text{HO}_2 = \text{CH}_3\text{O} + \text{OH}\) (R47) and \(\text{CH}_3\text{OH} + \text{OH} = \text{CH}_3\text{O} + \text{H}_2\text{O}\) (R83) at high temperatures. These trends were observed throughout the whole optimization process, which indicates that a
good reproduction of the included targets can only be achieved with rate coefficients close to the reported optimal values.

A possible concern is that the posterior uncertainties calculated from the covariance matrix of the optimized parameters will be under-estimated as the Arrhenius parameters of H\textsubscript{2}/CO reactions were not re-optimized in this study and therefore not taken into account at the quantification of posterior uncertainties. This issue was addressed by carrying out an additional covariance matrix calculation, including all sensitive H\textsubscript{2}/CO reactions (see Table F in the Supplementary Material, Part 1), together with all indirect and direct measurement data used for the optimization of the H\textsubscript{2}/CO sub-mechanism [20]. The posterior uncertainties of several rate coefficients were affected by the inclusion of additional reactions and targets (containing more chemical information that can aid the quantification of parameter uncertainties). Results are shown in Fig. S.1, Supplementary Material, Part 1. The uncertainty of the self-reaction of H\textsubscript{Ȯ}\textsubscript{2} radicals (R14/R15) was reduced from $f_{\text{posterior}} = 0.71$ at high temperatures to 0.57. Through correlation effects, several reactions benefitted from the reduced uncertainty of R14/R15, mostly (but not only) the reactions involving H\textsubscript{Ȯ}\textsubscript{2} radicals such as R47/R53 ($\text{CH}_{3} + \text{H}\text{Ȯ}\text{2} = \text{products}$), R87/R88 ($\text{CH}_{3}\text{OH} + \text{H}\text{Ȯ}\text{2} = \text{products}$) as well as $\text{CH}_{3}\text{OH} + \text{O}_{2} = \text{CH}_{2}\text{OH} + \text{H}\text{Ȯ}\text{2}$ (R85) that was found to have the highest remaining uncertainty when only considering the optimized parameters for the calculation of the covariance matrix. It can be concluded that the posterior uncertainties calculated from the optimized parameters serve as a safe upper estimate of the uncertainties obtained from a full covariance matrix calculation.

The red shading in Fig. 2 represents the probability density function (pdf) of the sum of the optimized rate coefficients R14 and R15 calculated using a Monte Carlo sampling technique at temperatures between 300 K and 2500 K. The rate coefficients were sampled $10^5$ times from the posterior covariance matrix assuming multivariate normal distribution and using a temperature interval of 0.02 on a 1000 K/$T$ scale in order to obtain a smooth density function at each temperature. Figures 3, 4 and 6 visualize the temperature dependence of the branching ratios for the H-atom abstraction reactions from the CH\textsubscript{3}OH molecule via ŌH, Ũ and H\textsubscript{Ȯ}\textsubscript{2}, respectively. The uncertainty ranges shown in these
figures were calculated using the same Monte Carlo sampling technique, this time with a 10 K resolution on a normal scale. It can be seen that the highest probabilities are found close to the median of the respective ranges of uncertainty. The *pdfs* of the other optimized reaction rate coefficients (see Figs. 1 and 5) were not plotted as they should always follow a normal distribution if the Arrhenius parameters are sampled normally [46], while the sum of two normally distributed random variables does not necessarily follow a normal distribution due to correlations.

\[
\text{H}_2\text{O}_2 + \text{H}_2\text{O}_2 = \text{H}_2\text{O}_2 + \text{O}_2 \quad (\text{R14/R15})
\]

Compared to previous optimization studies [19, 20], the optimized rate coefficient values for R14/R15 are closer to the theoretical results of Zhou *et al.* [175] (see Fig. 2). While direct rate coefficient measurements carried out by Hong *et al.* [165] and Kappel *et al.* [167] are captured well by the optimized model, it deviates from the older measurements of Hippler *et al.* [166] by almost half an order of magnitude at high temperatures. The posterior uncertainty is of the same order of magnitude as the prior one at the upper end of the optimized temperature range, and approaches substantially smaller values as the temperature decreases. It can be shown that the uncertainties of certain reactions are correlated, *e.g.* reactions involving H\(\text{O}_2\) radicals (R14/R15, R85, R87 and R88), which has to be taken into account for the interpretation of their respective uncertainty limits.

The modification of the rate parameters of R14/R15 based on the methanol experimental data only has a small effect on the simulation results for hydrogen and syngas combustion. Compared to the joint optimized hydrogen and syngas mechanism of Varga *et al.* [20], the overall *E* values changed only slightly, from 6.48 to 6.85 for hydrogen combustion (Table II in [20]) and from 8.43 to 9.22 for syngas combustion (Table III in [20]). Some subsets of data, such as hydrogen speciation profiles and syngas flames, are actually predicted more accurately as a result of the re-optimization of the H\(\text{O}_2\) radical self-reaction, while the opposite can be observed *e.g.* for very lean flames and some ignition delay times obtained in RCMs. Overall, the present mechanism is still well applicable for hydrogen and syngas combustion simulations, and the optimized rate of reaction R14/R15 is more consistent with the majority of direct measurement data and theoretical rate determinations.
CH$_3$OH + ÓH = CH$_3$Ö + H$_2$O (R83) and CH$_3$OH + ÓH = ĖH$_2$OH + H$_2$O (R84)

The CH$_3$OH+ÖH reaction has been discussed extensively by Metcalfe et al. [17], who recommend using the reaction rates calculated by Xu and Lin [117]. As it has been noted by Xu and Lin [117], there is a considerable discrepancy between the branching ratios of the CH$_3$OH + ÓH reactions predicted by their theoretical calculations, and those found in kinetic models. Xu and Lin compare their results to the branching ratios calculated from the rates found in the Marinov [13] ethanol combustion mechanism, which used data from a review article of Tsang [191]. In that review, the accepted branching ratio dates back to Hägele et al. [192], who performed direct measurements at low temperatures. It is stated in [191] that “the branching ratio is subject to considerable uncertainty”. Many mechanisms, including the one of Leplat et al. [12], adopted rates that were refitted to the experimental data of Hess and Tully [111] during the creation of the GRI-mechanism [193]. The corresponding branching ratios follow a similar trend as Tsang’s recommended rates.

It can be seen in Fig. 3 that the optimization favors branching ratios that are qualitatively similar to the rates found in the above mentioned mechanisms and review articles (i.e. a strong temperature dependence is observed), despite the fact that they were also constrained by the inclusion of theoretical data of Xu and Lin [117] and Jodkowski et al. [116], which change much less with temperature. The constant 85%/15% (R84/R83) branching ratio used in the mechanism of Rasmussen et al. [7] to reproduce their flow reactor measurements agrees with the optimized values below 900 K. The strongly temperature dependent branching ratios obtained during the optimization are close to the theoretical values at low temperatures, but the importance of the two branches relative to each other switches at higher temperatures. This qualitative behavior was also observed by Bott and Cohen [114], who carried out TST calculations. Note that the latter theoretical rate determinations, which were adopted by Li et al. [6] and therefore also appear in the initial mechanism, could not be used as optimization targets in the present work as the valid temperature range of these calculations was not reported. Apart from the 95% confidence intervals and red shading that illustrates the pdf of the branching ratios obtained via sampling, distribution plots at selected temperatures are shown in Fig. 3 (upper part). If both branches
are similarly important, then the distribution of the branching ratio can be well approximated using a normal distribution. As the histograms indicate, the assumption of a normal distribution is only approximate for branching ratios close to 0% or 100%. In a temperature range of roughly $T = 1500–2200$ K, the CH$_3$OH + ÕH branching ratios implemented in the Marinov [13] and Leplat et al. [12] mechanisms are within the confidence interval of the optimized ratios.

**CH$_3$OH + ÕH = ČH$_2$OH + H$_2$ (R80) and CH$_3$OH + Ħ = CH$_3$Ô + H$_2$ (R81)**

At temperatures up to $T = 1400$ K, the temperature dependence of the optimized branching ratios of CH$_3$OH + ÕH (Fig. 4) is similar to those suggested by the theoretical work of Kerkeni and Clary [121] and Meana-Pañeda et al. [119], but differs by more than 15% from those of Jodkowski et al. [116] and Carvalho et al. [120] as the temperature increases. Only in a temperature range of 1400–1800 K, the branching ratios obtained agree with the fixed 80%/20% (R80/R81) ratio defined in the mechanisms of Leplat et al. [12], Marinov [13] and Li et al. [6]. In accordance with all theoretical predictions, the importance of the secondary CH$_3$Ô + H$_2$ channel (R81) increases at higher temperatures. The optimum favors a branching ratio of 55%/45% at $T = 2500$ K as opposed to 80%/20% predicted in some of the most recent theoretical studies. However, this deviation is put into perspective by the increased uncertainties of the simulated branching ratios (more than ±15%) at high temperatures and the uncertainties inherent to theoretical calculations. For the reasons discussed above and despite the observed discrepancies, we discourage the use of constant branching ratios for the CH$_3$OH + ÕH reaction.

**CH$_3$OH + HÔ$_2$ = ČH$_2$OH + H$_2$O$_2$ (R87) and CH$_3$OH + HÔ$_2$ = CH$_3$Ô + H$_2$O$_2$ (R88)**

Klippenstein et al. [5] performed a global uncertainty analysis of methanol combustion at elevated pressures, and highlighted the importance of the CH$_3$OH + HÔ$_2$ reaction (R87/R88) for reducing the uncertainty of ignition delay time predictions. Theoretical calculation results for the rate coefficients of CH$_3$OH + HÔ$_2$ were published not only by Klippenstein et al. [5], but also by Alecu and Truhlar [134] and Altarawneh et al. [135] in the same year. While the theoretical calculations and the optimized
rate coefficients of the minor branch, \( \text{CH}_3\dot{\text{O}} + \text{H}_2\text{O}_2 \) (R88) do not differ substantially, optimized values for the other branch, yielding \( \dot{\text{CH}_2\text{OH}} + \text{H}_2\text{O}_2 \) (R87), were obtained that are about one order of magnitude higher than those calculated by Klippenstein et al. [5] at combustion temperatures, Fig. 5. The optimization results for R87 are, however, in reasonably good agreement with Alecu and Truhlar [134] and Altarawneh et al. [135]. The latter values were also chosen in a recent experimental and modeling study of Burke et al. [18] and an enhancement of their model’s predictive performance was observed by the authors as a consequence of this decision.

All three theoretical determinations of rate coefficients were used as optimization targets for this reaction, with equal weights through the assigned uniform standard deviations. As the Arrhenius plots in Fig. 5 show, Klippenstein et al.’s rate coefficient values were not approached during the iterative optimization process, most certainly to ensure a sufficient accuracy in describing ignition delay time measurements. Figure 6 illustrates the temperature dependence of the branching ratios for this pair of reactions. The optimized branching ratios are in good qualitative agreement with all theoretical calculations and mechanism predictions, with the exception of Klippenstein et al. [5]. The uncertainties of the branching ratios again increase with temperature, and the 95% confidence intervals comprise all displayed branching ratios at temperatures above 2000 K (above 1600 K if Klippenstein et al.’s values are disregarded).

10. Mechanism comparison results and discussion

Several mechanisms developed to simulate the combustion of methanol were collected. The mechanisms of Zabetta and Hupa [1] (published in 2008, “AAU-2008”), Alzueta et al. [2] (2001), Christensen et al. [3] (2016; a version with updated \( \dot{\text{CH}_2} \) chemistry was published later by Fomin et al. [194]), Hamdane et al. [4] (2012), Li et al. [6] (2007), Rasmussen et al. (2008) [7] were developed primarily for methanol combustion. Klippenstein et al.’s [5] (2011) modifications to the Li et al. mechanism were taken into consideration here as they were often adopted in the literature. Larger schemes such as the CaltechMech v2.3 [8] (2015, developed for several fuels up to \( \text{C}_{12} \)); those of Johnson et al.

For easier referencing, mechanism identifiers such as “Alzueta-2001” for the Alzueta et al. [2] mechanism will be used from this point onwards (see Table 4). Inert species Kr and Ne were added to all mechanisms, assuming unit third body collision efficiencies for all low-pressure reactions. Similarly, Ar was added to the Marinov-1999 mechanism. In the USC-II-2007 mechanism, different reaction rate coefficients were included for a subset of reactions depending on the pressure. The set of rate parameters was chosen which matched the pressure in an individual experiment the closest on a logarithmic scale. Both, Li-2007 and the subsequently developed Klippenstein-2011 mechanism use a bath gas-dependent parametrization of the \( \cdot H + O_2 (+M) = H\cdot O_2 (+M) \) reaction, which was also taken into account.

Table 4 contains two additional lines containing error function values for two modifications of the initial mechanism: one in which the \( \cdot CH_3/\cdot CH_3(S) \) chemistry and further recommended changes were implemented in accordance with Ren et al. [87], and another modification which contains the reaction rates of \( CH_3OH + O_2 = \cdot CH_2OH + H\cdot O_2 \) and \( CH_3OH + H\cdot O_2 = \cdot CH_2OH + H_2O_2 \) as published by Klippenstein et al. [5]. The effect of these modifications has been discussed in Section 3.

Figures 7–9 illustrate the ability of the optimized mechanism to describe selected experimental data in comparison to three published mechanisms (Li-2007, Rasmussen-2008 and SanDiego-2014) and the initial mechanism. The uncertainties in the optimized rate coefficients were propagated to an uncertainty of the simulations through sampling using the calculated posterior covariance matrix merged with the covariance matrix of the Arrhenius parameters of H2/CO reactions as published by Varga et
al. [20]. Correlation coefficients between these H₂/CO reactions and reactions optimized in this work were assumed to be zero. 10,000 samples were calculated at each measured data point, the means and standard deviations were interpolated between these. The propagation of rate coefficient uncertainties to simulation uncertainties and the description of the latter with the help of a pdf follows the ideas of Sheen and Wang [33], although a different method was chosen here.

Figure 7 shows a comparison of typical shock tube and RCM cases. It can be seen that the uncertainties in RCM simulations are much larger than in shock tube simulations. For the investigated series of RCM measurements, all data points lie within the range of simulation uncertainties, unlike for some of the other mechanism predictions. As for the plotted shock tube data set, most data points are outside the corresponding uncertainty range of the simulations using the optimized mechanism.

The performance of the mechanisms for atmospheric methanol/air flames measured without pre-heating, i.e. at room temperature is shown in Fig. 8. Measured laminar burning velocities differ by up to 7 cm/s, the plotted mechanism predictions are within 3 cm/s, with the notable exception of the Rasmussen-2008 mechanism, that strongly under-predicts lean and near-stoichiometric flames, but captures the rich side fairly well. It can be seen that the optimized mechanism, similarly to the Li-2007 mechanism, represents a good compromise between the partially contradictory experimental results. The uncertainty of the simulation results increases with the equivalence ratio, coincidentally with typical measurement uncertainties. The better agreement of the optimized mechanism with heat-flux burner measurements is apparent. The standard deviation of the simulated burning velocities obtained from the Monte Carlo sampling procedure can be as high as 2.4 cm/s at rich conditions, and is 0.4 cm/s at lean conditions, and results in a simulation uncertainty that is comparable to the scatter of the available experimental data. The uncertainty of the most sensitive H₂/CO reactions has the most significant contribution to the simulation uncertainty for flames.

For a CH₃OH/O₂/N₂ oxidation case at 10 atm, a comparison between simulation results and experimental data obtained in a jet-stirred reactor is shown in Fig. 9. The optimized mechanism approaches the measured O₂ mole fractions at lower temperatures the closest, but fails to match them perfectly.
Other species profiles can be captured more accurately by the simulations; the measurement points are often found within the respective simulation uncertainty ranges. The uncertainty of the simulation depends on the species examined, which indicates that e.g. some of the more uncertain reactions have a stronger impact on the simulated mole fraction of CO, but not on CH$_2$O.

Table 4 shows the average error function values for these mechanisms, calculated using the sum-of-squares error function (Eq. 1) that provides a quantitative description of the agreement of experimental and simulation data; lower numbers representing a better agreement. Among the previously published mechanisms, Li-2007 has the lowest average $E$ value overall, which was the reason for choosing this mechanism as a starting point for optimization in Section 3. Despite the changes of the Li-2007 mechanism during the development of this initial mechanism, its performance remained comparable. The optimized mechanism performs better than any of the 18 mechanisms collected from the literature, both overall and separately for each type of data (exception: formaldehyde ignition data, for which SanDiego-2014 and SaxenaWilliams-2007 mechanisms are slightly more accurate). While this new mechanism is only marginally better than the Li-2007 mechanism for laminar burning velocity data, its major strength is the highly improved accuracy in 0D simulations, since ignition delay times and particularly species concentration profiles are predicted much more accurately. The new rate parameters of the 17 optimized reactions can be considered the best representation of the overall kinetic information that can be extracted from the utilized experimental data. The average error function value of the optimized mechanism, the initial mechanism and the Li-2007 mechanism are well below the threshold value of $E = 9$. This means that, on average, the data can be described well within a 3$\sigma$ uncertainty by these mechanisms.

A detailed analysis of the behavior of the investigated mechanisms as a function of temperature, pressure and equivalence ratio was carried out following the scheme of previous studies on hydrogen and syngas combustion [179, 195]. The results of this analysis and a discussion can be found in Figs. S.2 to S.8 of the Supplementary Material, Part 1, and prove that simulations performed with the mechanism optimized in this work are accurate over a wide range of experimental conditions.
11. Conclusions

The optimization of a detailed methanol combustion mechanism starting from an updated version of the kinetic scheme of Li et al. [6] is discussed in the present article. A large amount of experimental data was collected from the literature including ignition delay times, laminar burning velocities, speciation data and direct measurements of rate coefficients. As a result of a local sensitivity analysis, 57 Arrhenius parameters of 17 elementary reactions were selected for optimization. All available direct measurements and theoretical determinations related to these reactions were used to outline the respective temperature-dependent prior uncertainty domain of the rate coefficients. The procedure provided optimized values for all rate parameters and posterior uncertainty bands for the rate coefficients. The optimized mechanism was compared in detail to 18 published mechanisms.

If the parameters for all of the important rate coefficients are optimized, then the obtained rate coefficients will not be bound by the kinetic scheme or, in other words, they will not be model-dependent. In this case, the exact values of the other, non-optimized rate parameters can be assumed to have a negligible influence on the optimized parameter values and the posterior covariance matrix calculated.

Some cautionary notes: The above statement is true if the underlying kinetic mechanism is complete, that is, important reaction pathways are not missing. Also, it is assumed that the rate parameters of these unimportant reaction steps have “good” estimates, e.g., within an order of magnitude of the real values, at the investigated conditions. Both assumptions are valid for relatively well-known systems such as the one studied in this work and the initial mechanism that is based on the one published by Li et al. [6].

The key result of this work is a mechanism that not only provides the overall best description of the currently available experimental data for methanol and formaldehyde combustion, but also features optimized rate parameters consistent with the respective literature values. The rate coefficient uncertainties of the self-reaction of HȮ₂ and the H-atom abstraction reactions from methanol via ȮH atoms and ṅH and HȮ₂ radicals were discussed in detail. In the present work, the optimization method of
Turányi et al. [46] was extended by the propagation of rate coefficient uncertainties onto simulation results, which adds further insights to the behavior of the optimized model.

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Table 1. Overview of the indirect measurements used in this work by the type of measurement and the experimental facility. Pure methanol was used as fuel, unless otherwise stated. The numbers of included data sets and data points as well as the temperature and pressure ranges are indicated.

<table>
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<tr>
<td></td>
<td>Counterflow twin-flame</td>
<td>[62, 63]</td>
<td>5</td>
<td>90</td>
<td>1</td>
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<tr>
<td></td>
<td>Heat flux method / laminar flat flame</td>
<td>[64-70]</td>
<td>41</td>
<td>280</td>
<td>0.2–1</td>
<td>298–358</td>
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<tr>
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<td>Flame-cone method</td>
<td>[71, 72]</td>
<td>6</td>
<td>92</td>
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<td>298–413</td>
</tr>
<tr>
<td>Concentration measurements</td>
<td></td>
<td>[97]</td>
<td>97</td>
<td>23,694</td>
<td></td>
<td></td>
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<tr>
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<td>Flow reactor conc.–time profiles</td>
<td>[74-80]</td>
<td>18</td>
<td>1,452</td>
<td>1–20</td>
<td>752–1043</td>
</tr>
<tr>
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<td>Flow reactor conc.–time profiles (CH$_2$O)</td>
<td>[6, 82, 83]</td>
<td>13</td>
<td>462</td>
<td>1–6</td>
<td>852–1095</td>
</tr>
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<td>Flow reactor outlet concentrations</td>
<td>[2, 7, 81]</td>
<td>13</td>
<td>444</td>
<td>1–98.7</td>
<td>600–1443</td>
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<tr>
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<td>Flow reactor outlet concentrations (CH$_2$O)</td>
<td>[92]</td>
<td>3</td>
<td>156</td>
<td>1.05</td>
<td>712–1279</td>
</tr>
<tr>
<td></td>
<td>Jet-stirred reactor outlet concentrations</td>
<td>[18, 91]</td>
<td>9</td>
<td>711</td>
<td>1–20</td>
<td>697–1200</td>
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<tr>
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<td>Shock tube conc.–time profiles</td>
<td>[84-87]</td>
<td>14</td>
<td>12,756</td>
<td>0.3–2.5</td>
<td>1266–2100</td>
</tr>
<tr>
<td></td>
<td>Shock tube conc.–time profiles (CH$_2$O)</td>
<td>[88-90]</td>
<td>27</td>
<td>7,713</td>
<td>1.5–2.0</td>
<td>1244–1907</td>
</tr>
</tbody>
</table>

---

*a* Fuels: CO and CH$_3$OH: 4 data points/1 data set, CH$_3$OH: 417/66.

*b* Considered species: CH$_3$OH, CH$_3$O, CO, CO$_2$, O$_2$, H$_2$, H$_2$O and CH$_4$.

*c* Fuels: H$_2$ and CH$_3$OH: 108/2, CH$_3$OH: 452/12.
Table 2. Reactions selected for optimization, the rate parameters in the initial mechanism and the optimized values of the parameters. Units are in cm, mol, K and s. Values of the prior and posterior uncertainty parameters are given for the temperature range of 500–2500 K (except for R14/R15: 300–2500 K, R37 LPL/R81: 800–2500 K, and R41: 1000–2500 K).

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$f_{\text{prior}}$</th>
<th>$f_{\text{posterior}}$</th>
<th>$A_{\text{orig}}$</th>
<th>$n_{\text{orig}}$</th>
<th>$E_{\text{orig/R}}$</th>
<th>$A_{\text{opt}}$</th>
<th>$n_{\text{opt}}$</th>
<th>$E_{\text{opt/R}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R14</td>
<td>HO$_2$ + HO$_2$ = H$_2$O$_2$ + O$_2$</td>
<td>0.30–0.70</td>
<td>0.08–0.71</td>
<td>1.300E+11</td>
<td>0</td>
<td>-820.33</td>
<td>1.214E+10</td>
<td>0.422</td>
<td>-745.03</td>
</tr>
<tr>
<td>R15</td>
<td></td>
<td></td>
<td></td>
<td>1.605E+15</td>
<td>0</td>
<td>7825.60</td>
<td>1.688E+16</td>
<td>-0.681</td>
<td>6507.48</td>
</tr>
<tr>
<td>R37 LPL</td>
<td>CH$_2$O + M = CO + H$_2$ + M</td>
<td>0.50</td>
<td>0.09–0.12</td>
<td>3.100E+45</td>
<td>-8.00</td>
<td>49073.98</td>
<td>1.840E+45</td>
<td>-7.886</td>
<td>49051.2</td>
</tr>
<tr>
<td>R38</td>
<td>CH$_2$O + H = HCO + H$_2$</td>
<td>0.60</td>
<td>0.08–0.10</td>
<td>5.740E+07</td>
<td>1.90</td>
<td>1383.29</td>
<td>3.621E+02</td>
<td>3.407</td>
<td>401.868</td>
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<tr>
<td>R40</td>
<td>CH$_2$O + OH = HCO + H$_2$O</td>
<td>0.34–0.43</td>
<td>0.22–0.30</td>
<td>3.430E+09</td>
<td>1.18</td>
<td>-224.96</td>
<td>4.440E+10</td>
<td>0.906</td>
<td>85.318</td>
</tr>
<tr>
<td>R41</td>
<td>CH$_2$O + O$_2$ = HCO + H$_2$O</td>
<td>1.20</td>
<td>0.19–0.20</td>
<td>1.230E+06</td>
<td>3.00</td>
<td>26170.11</td>
<td>1.592E+18</td>
<td>-1.218</td>
<td>19847.2</td>
</tr>
<tr>
<td>R47</td>
<td>CH$_3$ + HO$_2$ = CH$_3$O + OH</td>
<td>0.46–0.76</td>
<td>0.26–0.49</td>
<td>2.410E+10</td>
<td>0.76</td>
<td>-1170.11</td>
<td>5.019E+09</td>
<td>1.066</td>
<td>-405.13</td>
</tr>
<tr>
<td>R53</td>
<td>CH$_3$ + HO$_2$ = CH$_4$ + O$_2$</td>
<td>1.00</td>
<td>0.25–0.45</td>
<td>3.160E+12</td>
<td>0</td>
<td>0.00</td>
<td>6.895E+18</td>
<td>-1.923</td>
<td>888.181</td>
</tr>
<tr>
<td>R60</td>
<td>CH$_2$OH + O$_2$ = CH$_2$O + HO$_2$</td>
<td>0.50</td>
<td>0.27–0.38</td>
<td>2.410E+14</td>
<td>0</td>
<td>2524.91</td>
<td>1.701E+16</td>
<td>-0.606</td>
<td>2845.39</td>
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<tr>
<td>R67 LPL</td>
<td>CH$_3$O + M = CH$_2$O + H + M</td>
<td>0.84–1.24</td>
<td>0.16–0.26</td>
<td>8.300E+17</td>
<td>-1.20</td>
<td>7800.70</td>
<td>6.815E+18</td>
<td>-1.269</td>
<td>9539.55</td>
</tr>
<tr>
<td>R77 HPL</td>
<td>OH + CH$_3$ = CH$_2$OH</td>
<td>0.34–0.84</td>
<td>0.20–0.31</td>
<td>2.790E+18</td>
<td>-1.43</td>
<td>669.35</td>
<td>5.489E+12</td>
<td>0.300</td>
<td>-430.96</td>
</tr>
<tr>
<td>R77 LPL</td>
<td>OH + CH$_3$ + M = CH$_3$OH + M</td>
<td>1.20</td>
<td>0.07–0.39</td>
<td>4.000E+36</td>
<td>-5.92</td>
<td>1580.30</td>
<td>1.056E+54</td>
<td>-10.920</td>
<td>5610.96</td>
</tr>
<tr>
<td>R80</td>
<td>CH$_3$OH + H = CH$_2$OH + H$_2$</td>
<td>0.44–1.07</td>
<td>0.18–0.27</td>
<td>3.200E+13</td>
<td>0</td>
<td>3067.44</td>
<td>8.266E+09</td>
<td>1.072</td>
<td>2461.34</td>
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<tr>
<td>R81</td>
<td>CH$_3$OH + H = CH$_3$O + H$_2$</td>
<td>1.70</td>
<td>0.24–0.38</td>
<td>8.000E+12</td>
<td>0</td>
<td>3067.44</td>
<td>2.818E+07</td>
<td>1.900</td>
<td>5104.69</td>
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<tr>
<td>R83</td>
<td>CH$_3$OH + OH = CH$_3$O + H$_2$O</td>
<td>0.70</td>
<td>0.13–0.44</td>
<td>1.000E+06</td>
<td>2.10</td>
<td>249.97</td>
<td>1.043E–02</td>
<td>4.502</td>
<td>-941.06</td>
</tr>
<tr>
<td>R84</td>
<td>CH$_3$OH + OH = CH$_2$OH + H$_2$O</td>
<td>0.46–0.87</td>
<td>0.19–0.41</td>
<td>7.100E+06</td>
<td>1.80</td>
<td>-299.95</td>
<td>7.323E+09</td>
<td>0.845</td>
<td>172.944</td>
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<tr>
<td>R85</td>
<td>CH$_3$OH + O$_2$ = CH$_2$OH + HO$_2$</td>
<td>0.80</td>
<td>0.78–1.01</td>
<td>2.050E+13</td>
<td>0</td>
<td>22596.88</td>
<td>8.907E+13</td>
<td>-0.043</td>
<td>22904.2</td>
</tr>
<tr>
<td>R87</td>
<td>CH$_3$OH + HO$_2$ = CH$_2$OH + H$_2$O$_2$</td>
<td>1.10</td>
<td>0.20–0.25</td>
<td>3.980E+13</td>
<td>0</td>
<td>9763.46</td>
<td>7.619E+05</td>
<td>2.284</td>
<td>8116.24</td>
</tr>
<tr>
<td>R88</td>
<td>CH$_3$OH + HO$_2$ = CH$_3$O + H$_2$O$_2$</td>
<td>0.70</td>
<td>0.15–0.42</td>
<td>3.336E–02</td>
<td>4.12</td>
<td>8170.00</td>
<td>2.703E–03</td>
<td>4.576</td>
<td>8245.84</td>
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</table>
Table 3. Overview of the direct measurements and theoretical rate determinations used in this work. The numbers of included data sets and data points as well as the temperature ranges are indicated. Note that some of the listed measurements describe multiple reactions, not just the one in the first column.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Direct measurements of rate coefficients</th>
<th>Theoretical rate determinations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>References</td>
<td>Data sets</td>
</tr>
<tr>
<td>R37</td>
<td>CH₂O + M = products</td>
<td>[89]</td>
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<tr>
<td></td>
<td>CH₂O + M = CO + H₂ + M</td>
<td>[139, 140]</td>
<td>2</td>
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<tr>
<td>R38</td>
<td>CH₂O + H = HCO + H₂</td>
<td>[145-152]</td>
<td>8</td>
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<tr>
<td>R40</td>
<td>CH₂O + OH = products</td>
<td>[114, 129, 155]</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>CH₂O + OH = HCO + H₂O</td>
<td>[154, 156, 157]</td>
<td>3</td>
</tr>
<tr>
<td>R41</td>
<td>CH₂O + O₂ = HCO + HO₂</td>
<td>[140, 153]</td>
<td>3</td>
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<tr>
<td>R47 &amp; R53</td>
<td>CH₃ + HO₂ = products</td>
<td>[163]</td>
<td>1</td>
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<tr>
<td>R47</td>
<td>CH₃ + HO₂ = CH₃O + OH</td>
<td>[161, 162]</td>
<td>2</td>
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<tr>
<td>R53*</td>
<td>CH₃ + HO₂ = CH₄ + O₂</td>
<td>[161, 162, 164]</td>
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<tr>
<td>R60</td>
<td>CH₂OH + O₂ = CH₂O + HO₂</td>
<td>[143, 144]</td>
<td>2</td>
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<tr>
<td>R67</td>
<td>CH₂O + M = CH₂O + H + M</td>
<td>[136]</td>
<td>2</td>
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<tr>
<td>R77 HP**</td>
<td>CH₃OH = OH + CH₃</td>
<td>[125, 127, 129-132]</td>
<td>7</td>
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<tr>
<td>R77 (fall-off)</td>
<td>CH₃OH+(M) = products</td>
<td>[86, 113, 122, 123]</td>
<td>7</td>
</tr>
<tr>
<td>R77 LP*</td>
<td>CH₃OH + M = OH + CH₃ + M</td>
<td>[124-126]</td>
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<tr>
<td>R80</td>
<td>CH₂OH + H = CH₃O + H₂</td>
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<tr>
<td>R81</td>
<td>CH₂OH + H = CH₂OH + H₂</td>
<td>[118]</td>
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<tr>
<td>R85</td>
<td>CH₃OH + O₂ = CH₂OH + HO₂</td>
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<td>–</td>
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<tr>
<td>R87</td>
<td>CH₃OH + HO₂ = CH₂OH + H₂O₂</td>
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<td>–</td>
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<tr>
<td>R88</td>
<td>CH₃OH + HO₂ = CH₂O + H₂O₂</td>
<td>–</td>
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</table>

*Includes rate determinations for the reaction in reverse direction (and determinations of the sum of multiple channels)
Table 4. Comparison of error function values calculated for the optimized mechanism and the mechanisms collected from the literature. The values are averaged over each experimental category, the overall value is the average over all categories weighted by the number of data sets within each category. Solver packages used for the simulations: not bracketed: CHEMKIN-II [183], round brackets: FlameMaster [185], square brackets: OpenSMOKE [186]. The last column containing overall results was calculated from the three preceding ones. The corresponding number of data sets and data points for each column are denoted below the double solid line.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Ref.</th>
<th>Ignition delay times</th>
<th>Average error function value</th>
<th>Overall</th>
</tr>
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<td></td>
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<td>CH₃OH</td>
<td>CH₃O</td>
<td>Burning velocities</td>
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<td>28.4</td>
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<tr>
<td>Alzueta-2001</td>
<td>[2]</td>
<td>103.9</td>
<td>11.3</td>
<td>no transport</td>
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<tr>
<td>Christensen-2016</td>
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<td>Hamdane-2012</td>
<td>[4]</td>
<td>41.2</td>
<td>6.4</td>
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<tr>
<td>Li-2007</td>
<td>[6]</td>
<td>7.6</td>
<td>3.4</td>
<td>1.9</td>
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<tr>
<td>Rasmussen-2008</td>
<td>[7]</td>
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<td>8.2</td>
<td>[3.0]</td>
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<td>[11]</td>
<td>54.6</td>
<td>7.5</td>
<td>[76.0]</td>
</tr>
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<td>Leplat-2011</td>
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<td>6.1</td>
<td>22.2</td>
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<tr>
<td>Marinov-1999</td>
<td>[13]</td>
<td>260.7</td>
<td>20.7</td>
<td>(14.1)</td>
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<tr>
<td>SanDiego-2014</td>
<td>[14]</td>
<td>24.7</td>
<td>1.6</td>
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<tr>
<td>SaxenaWilliams-2007</td>
<td>[15]</td>
<td>86.2</td>
<td>1.7</td>
<td>2.3</td>
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<tr>
<td>USC-II-2007</td>
<td>[16]</td>
<td>602.8</td>
<td>2.3</td>
<td>(8.5)</td>
</tr>
<tr>
<td>Aramco1.3-2013</td>
<td>[17]</td>
<td>(41.3)</td>
<td>(11.1)</td>
<td>(4.3)</td>
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<tr>
<td>NUIG-16.09-2016</td>
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<td>(51.6)</td>
<td>(11.0)</td>
<td>(4.2)</td>
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<td>2.5</td>
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<td>Optimized mechanism</td>
<td></td>
<td>6.8</td>
<td>2.0</td>
<td>1.6</td>
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</tbody>
</table>

a CH₃/CH₃(S) chemistry and further recommended changes according to Ren et al. [87].

b With reaction rates of CH₃OH + O₂ = CH₂OH + HO₂ and CH₃OH + HO₂ = CH₂OH + H₂O₂ from Klippenstein et al. [5].

c Some RCM simulation results could not be obtained. Numbers shown are for the remaining data.

d CH₃ profiles cannot be captured well by the mechanism. Results shown do not include those profiles.

– Some simulation results could not be obtained or transport data were not available. Overall results were not calculated.
Figure 1. Arrhenius plots of the initial and optimized rate coefficients with their prior and posterior uncertainty ranges for the optimized $\text{C}_1$ reactions (except for R14/R15: $\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$, shown Fig. 2, R87: $\text{CH}_3\text{OH} + \text{HO}_2 = \text{CH}_2\text{OH} + \text{H}_2\text{O}_2$ (R87) and R88: $\text{CH}_3\text{OH} + \text{HO}_2 = \text{CH}_3\text{O} + \text{H}_2\text{O}_2$ shown in Fig. 5). The unit of $k$ is cm$^6$ mol$^{-2}$ s$^{-1}$ for the LPL of R77, otherwise cm$^3$ mol$^{-1}$ s$^{-1}$. If no solid black line is plotted, the solid blue line corresponds to the chosen mean rate coefficient (see Supplementary Material, Part 2). If the chosen mean differs from the values of Li et al. [6], these are shown using a solid black line. The area shaded gray signifies the temperature range that was not optimized for the respective reaction.
Figure 2. Arrhenius plot for the sum of the two H\(\dot{O}2\) + H\(\dot{O}2\) = H\(_2\)O\(_2\) + O\(_2\) branches, including initial and optimized rate coefficients with their prior and posterior uncertainty ranges. Direct measurement data shown: purple squares – Hippler et al. [166], turquoise triangles – Kappel et al. [167], orange circles – Hong et al. [165], gray inverse triangles – Patrick and Pilling [172], burgundy diamonds – Lii et al. [174]. If available, error bars are plotted. Rate recommendations shown: dashed black lines – Zhou et al.[175], solid green lines – Varga et al. [20], solid blue lines – Varga et al. [19] for the high-temperature and Baulch et al. [180] for the low-temperature branch. At each temperature, the red shading represents the pdf of the sum of the rate coefficients calculated from the posterior covariance matrix (see Section 9 for details).
Figure 3. Temperature dependence of the branching ratios of reactions \( \text{CH}_3\text{OH} + \text{OH} = \text{CH}_2\text{OH} + \text{H}_2\text{O} \) (R84) and \( \text{CH}_3\text{OH} + \text{OH} = \text{CH}_3\text{O} + \text{H}_2\text{O} \) (R83). Branching ratios recommended by Xu and Lin [117] (black lines), Jodkowski et al. [116] (purple) and Bott and Cohen [114] (blue) are compared to those found in the Leplat-2011 mechanism [12] (cyan), the Marinov-1999 mechanism [13] (orange), the initial mechanism/Li-2007 mechanism (adopted from Bott and Cohen [114], blue), the Rasmussen-2008 mechanism [7] (green) and the optimized mechanism (thick red). The thin red lines signify the respective 95% confidence intervals of the optimized branching ratios. At each temperature, the red shading represents the \text{pdf} of the branching ratios calculated from the posterior covariance matrix (see Section 9 for details). Distribution plots of the sampled branching ratios at selected temperatures are shown above the main plot.
Figure 4. Temperature dependence of the branching ratios of reactions $\text{CH}_3\text{OH} + \text{H} = \text{CH}_2\text{OH} + \text{OH}$ (R80) and $\text{CH}_3\text{OH} + \text{H} = \text{CH}_3\text{O} + \text{OH}$ (R81). Branching ratios recommended by Meana-Pañeda et al. [119] (black lines), Carvalho et al. [120] (orange), Kerkeni and Clary [121] (green) and Jodkowski et al. [116] (purple) are compared to those found in the Leplat-2011 and Marinov-1999 mechanisms [12, 13] (cyan), the initial mechanism/Li-2007 mechanism (blue) and the optimized mechanism (thick red). The thin red lines signify the respective 95% confidence intervals of the optimized branching ratios. At each temperature, the red shading represents the pdf of the branching ratios calculated from the posterior covariance matrix (see Section 9 for details). Distribution plots of the sampled branching ratios at selected temperatures are shown above the main plot.
Figure 5. Arrhenius plots for CH$_3$OH + HȮ$_2$ = CH$_2$OH + H$_2$O$_2$ (R87) and CH$_3$OH + HȮ$_2$ = CH$_3$Ȯ + H$_2$O$_2$ (R88), including initial and optimized rate coefficients with their prior and posterior uncertainty ranges. Theoretical calculations shown: dash-dotted green lines – Klippenstein et al. [5], orange dashed lines – Alecu and Truhlar [134], dash-dot-dotted black lines – Altarawneh et al. [135].
Figure 6. Temperature dependence of the branching ratios for \( \text{CH}_3\text{OH} + \text{H}_2\text{O}_2 = \text{CH}_2\text{OH} + \text{H}_2\text{O}_2 \) (R87) and \( \text{CH}_3\text{OH} + \text{H}_2\text{O}_2 = \text{CH}_2\text{O} + \text{H}_2\text{O}_2 \) (R88). Branching ratios recommended by Klippenstein et al. [5] (green lines), Alecu and Truhlar [134] (orange) and Altarawneh et al. [135] (black) are compared to those found in the initial mechanism (blue) and the optimized mechanism (thick red). The thin red lines signify the respective 95% confidence intervals of the optimized branching ratios. At each temperature, the red shading represents the pdf of the branching ratios calculated from the posterior covariance matrix (see Section 9 for details). Distribution plots of the sampled branching ratios at selected temperatures are shown above the main plot.
Figure 7. Simulation results vs. experimental data of Burke et al. [18] for selected shock tube and RCM ignition delay time measurements: Comparison of the optimized and initial mechanisms against three published mechanisms [6, 7, 14]. At each temperature, the gray shading represents the pdf of the branching ratios calculated from the posterior covariance matrix, and the color black represents the maximum of the pdf across all temperatures. The uncertainty of the measurements was estimated to be 20% [18], which is represented by the error bars shown.
Figure 8. Simulation results vs. experimental data for methanol/air flames at $T = 298$ K and $p = 1$ atm: Comparison of the optimized and initial mechanisms against three published mechanisms [6, 7, 14]. Measurements: #1 – Egolfopoulos et al. [62]; #2 – Saeed and Stone [56] (at a differing pressure of 1 bar); #3 – Gülder [59] (at $p=1$ bar and $T_{\text{preheat}}=300$ K), #4 – Metghalchi and Keck [60]; #5 – Vancoillie et al. [70]; #6 – Voss et al. [68]. At each temperature, the gray shading represents the pdf of the branching ratios calculated from the posterior covariance matrix, and the color black represents the maximum of the pdf across all temperatures. The maximum uncertainties of the Gülder [59] and Metghalchi and Keck [60] measurements were estimated to be $\pm 2$ cm/s. The accuracy the Vancoillie et al. [70] measurements was reported to be better than $\pm 0.8$ cm/s (2$\sigma$), although Alekseev et al. [73] state that these may have a higher uncertainty of about $\pm 2$ cm/s. Voss et al. [68] reported that the laminar burning velocities measured in different laboratories are reproducible with $\pm 0.2$ cm/s. Their average $S_L$ values are shown here.
Figure 9. Simulation results vs. experimental data of Burke et al. [18] for selected JSR species concentration measurements: Comparison of the optimized and initial mechanisms against three published mechanisms [6, 7, 14]. Species CH₄ is not shown here. At each temperature, the gray shading represents the pdf of the branching ratios calculated from the posterior covariance matrix, and the color black represents the maximum of the pdf across all temperatures. Thin solid lines of the respective color are used for the 1% and 99% quantiles corresponding to the displayed uncertainty ranges.
List of Supplementary Materials

Supplementary Material, Part 1: Data collection, local sensitivity analysis results and additional plots

Supplementary Material, Part 2: Data used for the estimation of the prior uncertainty limits

Supplementary Material, Part 3: Covariance matrices

Supplementary Material, Part 4: New reaction mechanism in CHEMKIN format, including thermochemical and transport data