Uncertainty quantification of a newly optimized methanol and formaldehyde combustion mechanism

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A B S T R A C T

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 et al. (2007) and adopting the H_2/CO base chemistry from the joint optimized hydrogen and syngas combustion mechanism of Varga et al. (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 $H\dot{O}_2$ radicals and important H-atom abstraction reactions from the methanol molecule are discussed in detail.

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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 $\dot{C}H_2OH$ and $CH_3\dot{O}$ 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

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.

Type of measurement experimental facility	References	Data sets	Data points	p (atm)	T (K)
Ignition delay times		**81**	**574**		
Shock tube[a]	[18,48–54]	67	421	0.3–51.7	963–2180
Shock tube (CH_2O)	[55]	7	99	1.6	1363–2304
Rapid compression machine	[18]	7	54	9.3–40.6	817–980
Burning velocity measurements		**87**	**632**		
Outwardly/spherically propagating flame	[56–61]	35	170	0.5–9.9	298–500
Counterflow twin-flame	[62,63]	5	90	1	298–368
Heat flux method/laminar flat flame	[64–70]	41	280	0.2–1	298–358
Flame-cone method	[71,72]	6	92	1	298–413
Concentration measurements[b]		**97**	**23,694**		
Flow reactor concentration–time profiles	[74–80]	18	1452	1–20	752–1043
Flow reactor conc.–time profiles (CH_2O)	[6,82,83]	13	462	1–6	852–1095
Flow reactor outlet concentrations	[2,7,81]	13	444	1–98.7	600–1443
Flow reactor outlet concentrations (CH_2O)	[92]	3	156	1.05	712–1279
Jet-stirred reactor outlet concentrations	[18,91]	9	711	1–20	697–1200
Shock tube concentration–time profiles[c]	[84–87]	14	12,756	0.3–2.5	1266–2100
Shock tube conc.–time profiles (CH_2O)	[88–90]	27	7713	1.5–2.0	1244–1907

[a] Fuels: CO and CH_3OH: 4 data points/1 data set, CH_3OH: 417/66.
[b] Considered species: CH_3OH, CH_2O, CO, CO_2, O_2, H_2, H_2O and CH_4.
[c] Fuels: H_2 and CH_3OH: 108/2, CH_3OH: 452/12.

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 reaction 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 are 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)