High-Pressure Oxidation of Methane

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Abstract

Methane oxidation at high pressures and intermediate temperatures was investigated in a laminar flow reactor and in a rapid compression machine (RCM). The flow-reactor experiments were conducted at 700–900 K and 100 bar for fuel-air equivalence ratios (Φ) ranging from 0.06 to 19.7, all highly diluted in nitrogen. It was found that under the investigated conditions, the onset temperature for methane oxidation ranged from 723 K under reducing conditions to 750 K under stoichiometric and oxidizing conditions. The RCM experiments were carried out at pressures of 15–80 bar and temperatures of 800–1250 K under stoichiometric and fuel-lean ($\Phi=0.5$) conditions. Ignition delays, in the range of 1–100 ms, decreased monotonically with increasing pressure and temperature. A chemical kinetic model for high-pressure methane oxidation was established, with particular emphasis on the peroxide chemistry. The thermodynamic properties of CH_3OO and CH_3OOH , as well as the rate constants for the abstraction reactions $\text{CH}_3\text{OOH} + \text{CH}_3 = \text{CH}_3\text{OO} + \text{CH}_4$ and $\text{CH}_3\text{OH} + \text{CH}_3 = \text{CH}_3\text{O} + \text{CH}_4$, were calculated at a high level of theory. Model predictions were evaluated against the present data as well as shock tube data (1100–1700 K, 7–456 bar) and flame speeds (1–10 bar) from literature. The model yielded satisfactory predictions for the onset temperature as well for most major species upon ignition in the flow reactor, but the concentration of particularly CH_3OH was severely underpredicted, indicating that further work is desirable on reactions of CH_3O and CH_3OO . Measured ignition delay times from the RCM tests were reproduced well

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by the model for high pressures, but underpredicted at 15 bar. For the shock tube and flame conditions, predictions were mostly within the experimental uncertainty. Prompt dissociation of HCO increased predicted flame speeds by up to 4 cm s^{-1} but had little impact under flow reactor, RCM or shock tube calculations.

Keywords:

Methane, Ignition, High pressure, Reaction kinetics

1. Introduction

Liquefied (LNG) and compressed (CNG) natural gas are becoming attractive alternatives for traditional transportation fuels such as diesel and heavy fuel oil. To guarantee safe and efficient operation of gas engines, insight in the autoignition and flame properties of methane, which is the main component of LNG and CNG, is needed. Furthermore, insight in the combustion properties of methane is important for premixed gas turbines.

Ignition is mainly governed by reaction kinetics. A reliable chemical kinetic model for methane as the major component of natural gas is important in design and optimization of combustion devices. Oxidation mechanisms for methane are available [1–5], but they have mostly been verified at lower pressure and/or higher temperature. In shock tubes, ignition delays for CH_4 have been obtained over a wide pressure range, recently by Levy et al. [6] (7–9 atm), Huang et al. [7] (16–39 atm), Merhubi et al. [8] (10–40 atm), Davidson and Hanson [9] (48–156 atm), and Zhukov et al. [10] (156–456 atm). However, shock tube studies are generally restricted to temperatures above 1100 K. Even at high temperatures, autoignition depends not only on chemical processes at the time of ignition, but also on the earlier, lower temperature chemistry creating the necessary conditions for ignition [11]. The relatively long residence times, which are required to study combustion at high pressures and temperatures of 600–1100 K can be realized in static reactors and flow reactors. Melvin [12] measured the ignition delay time of methane for pressures of 58–110 atm and temperatures around 623 K inside a steel static reactor. Dagaut et al. [13] conducted experiments in a jet-stirred reactor at 900–1300 K and 1–10 atm. High-pressure flow reactor studies have been reported by Hunter et al. [14] (930–1000 K and 3–10 atm), Rytz and Baiker [15] (698–773 K and 20–50 bar), Amano and Dryer [16] (860–1060 K and 10–18 bar), and Rasmussen et al. [1] (700–900 K and 50–100 bar).

Rasmussen et al. [1] pointed to important uncertainties in our understanding of the high-pressure, intermediate-temperature oxidation chemistry for methane, in particular related to reactions involving alkylperoxyl radicals such as CH_3OO . In the present work we conduct methane oxidation experiments in a laminar flow reactor at 700–900 K and 100 bar and in a Rapid Compression Machine (RCM) at 800–1250 K and at 15–80 bar. The thermodynamic properties of CH_3OO and CH_3OOH are reevaluated and the abstraction reactions $\text{CH}_3\text{OOH} + \text{CH}_3 = \text{CH}_3\text{OO} + \text{CH}_4$ and $\text{CH}_3\text{OH} + \text{CH}_3 = \text{CH}_3\text{O} + \text{CH}_4$ are studied at a high level of theory. A detailed chemical kinetic model is established, drawing on the theoretical work as well as previous high-pressure work [1, 17–21], and modeling predictions are compared with the present measurements as well as data from shock tubes and flames at the highest pressures reported.

2. Experimental

2.1. The laminar flow reactor

The experimental setup was a laboratory-scale, high-pressure laminar flow reactor designed to approximate plug flow. It has been described in detail elsewhere [17] and only a brief description is provided here. The system was used to investigate methane oxidation chemistry at 100 bar pressure and temperatures up to 900 K. The reactions took place in a tubular quartz reactor (inner diameter of 8 mm), enclosed in a stainless steel tube that acted as a pressure shell. Using a quartz tube and conducting the experiments at high pressure ensured a minimal contribution from heterogeneous reactions at the reactor wall. The steel tube was placed in a tube oven with three individually controlled electrical heating elements that produced an isothermal reaction zone (± 6 K) of 37–39 cm. A moving thermocouple was used to measure the temperature profile inside the pressure shell wall after stabilizing the system. The system was pressurized from the feed gas cylinders. The reactor pressure was monitored upstream of the reactor by a differential pressure transducer and controlled by a pneumatically actuated pressure-control valve positioned after the reactor. The pressure fluctuations were less than 0.2 % during the experiments. The reactant gases were premixed before entering the reactor. The flow rate was 3.23 Nl/min (STP; 1 atm and 273 K). All gases were certified; 99.999%

for CH₄ and O₂ in N₂ ($\pm 2\%$ uncertainty in composition) and 99.5% for pure CH₄. GC measurements did not indicate impurities.

Downstream of the reactor, the system pressure was reduced to atmospheric level prior to product analysis, which was conducted by an on-line 6890N Agilent Gas Chromatograph (GC-TCD/FID from Agilent Technologies). All GC sampling and measurements were repeated at least twice to reduce uncertainties in measurements.

For gaseous compounds the GC peak areas were related to concentrations by calibration against certified gas mixtures ($\pm 2\%$ from AGA A/S). For liquid compounds, usually the calibration was based on gas mixtures prepared by injecting a known quantity of the liquid component into a known volume of nitrogen in a Tedlar bag and allowing the liquid to evaporate. To avoid difficulties in handling formaldehyde, its calibration was provided by correlating TCD response factors for other components to calculated thermal conductivities estimated from the Chapman-Enskog kinetic theory [22]. The TCD response factor for formaldehyde was then determined by using a calculated thermal conductivity with this correlation. In the calculation of the thermal conductivity of formaldehyde, the employed Lennard-Jones force constants ($\sigma = 3.65 \text{ \AA}$, $\varepsilon/\text{K} = 313.9 \text{ K}$) were in turn estimated from the critical properties [23], using the method of Satterfield [24]. A general uncertainty of 6% is estimated for measurements by GC. However, a larger uncertainty (up to 10%) is estimated for both methanol and formaldehyde measurements due to the calibration process.

The plug flow assumption was shown by Rasmussen et al. [17] to be a good approximation for the present operating conditions. Figure 1 shows the measured temperature profiles for different isotherms with a flow of pure nitrogen. The residence time of gases in the isothermal zone of the reactor can be estimated as $\tau[\text{s}] = 9557/T[\text{K}]$. However, it was found that using a full temperature profile improved the accuracy of the simulation. Therefore, a plug flow reactor with a fixed temperature profile and constrained pressure was used for modeling in CHEMKIN [25]. The profiles used in modeling were based on the measured values, interpolating between data when required.

The uncertainty in the gas temperature due to the effect of heat release from combustion was limited by a high level of dilution. Simulations with a constant pressure and enthalpy (adiabatic) model lead to a maximum 21 K temperature rise. However, because

of the fast heat transfer from the hot gases to the pressure shell, augmented by the small dimensions of the reactor, we estimate the deviation of the gas temperature from the measured temperature to be considerably smaller. Measurement of the wall temperature in real experiments did not reveal any deviation beyond ± 2 K. The overall uncertainty in the temperature, including interpolation, was estimated to $-7/+15$ K.

2.2. The rapid compression machine (RCM)

Autoignition delay times of methane were measured in a Rapid Compression Machine (RCM), whose details were described elsewhere [26]. The gas mixtures studied were compressed in a short time (~ 10 – 20 ms) to moderate temperature ($T_{max}=1250$ K) and high pressure ($P_{max}=80$ bar) by the motion of the piston. The compression and ignition processes were monitored by measuring the pressure in the combustion chamber of the machine using a Kistler quartz pressure sensor with a thermo-shock optimized construction.

As discussed in the literature, measures should be taken to avoid deviation from ideal behavior such as those caused by heat loss and complex fluid dynamics [27–30] during the RCM experiments. In [27, 31] it has been shown that vortices created by the motion of the piston causes unwanted mixing of cold boundary-layer gas into the compressed core gas, destroying the adiabatic core. CFD calculations [30, 31] and experiments [27] showed that the incorporation of a specially designed crevice on the piston head successfully suppresses the vortex formation, and preserves the well-defined homogeneous core region after compression. Towards this end we used in this study a creviced piston head designed for this machine [31] to maintain a homogeneous adiabatic core gas during the measurements in the combustion chamber. Furthermore, to prevent breakdown of the adiabatic core during the post-compression period due to heat loss and the subsequent increase of the thermal boundary layer [29] we increased the volume to surface ratio by increasing the clearance height of the combustion chamber for longer autoignition delay times. Additionally, as described in [28] we increased the crevice volume for the measurements at low pressures and large ignition delay times. However, no significant differences were observed with the original crevice design [31]. A typical measured pressure trace is presented in Fig. 2.

The gas mixtures presented in Table 1 were prepared in a 10-liter gas bottle and allowed to mix statically during 72 hours before performing measurements in the RCM to ensure their homogeneity. All test gases used in the experiments had purities greater than 99.9%. The desired range of studied temperatures (800–1250 K) and pressures (15–80 bar) at the end of compression was controlled by varying the initial pressure, the compression ratio, the clearance height of the combustion chamber and the N₂/Ar ratio of the mixture (Table 1). The pre-ignition peak temperature (T_c) was derived from the measured pre-ignition peak pressure (P_c) by using the isentropic relations for an ideal gas. The uncertainty of the calculated core gas temperatures (T_c) was less than ± 3.5 K for all measurements and the reproducibility of the measured ignition delay time was in general within 5%.

To account for the effects of compression and heat loss that occurred during the measurements, the changes in the specific volume of the assumed adiabatic core were used in the simulations. Since no multistage ignition phenomena were observed in this study, we derived the specific volume directly from the measured pressure trace for the reactive mixture in the period between compression and the moment that substantial heat release begins by using the isentropic relations for an ideal gas. Subsequently, we extrapolated the time dependence of the measured pressure to the region in which substantial heat release begins, as described in detail in [32, 33]. The derived specific volume was used together with the measured initial temperature and pressure of the mixture as input to the SENKIN code [34]. Figure 2 shows the measured pressure trace for mixture C and the computed pressure trace (red dotted line) by using the procedure described above.

3. Theory

At the conditions of the present study ($T \geq 600$ K and high pressure), hydrogen abstraction from CH₄ by radicals such as CH₃OO and CH₃O,

is potentially important. Neither of these steps are well characterized. For reaction (R34) only an estimate from Tsang [35] is available. Reaction (R39b) was identified by Rasmussen et al. [1] as the key step in forming CH_3OH from CH_4 under conditions similar to those of the present flow reactor experiments. To explain the observed CH_3OH formation, they adopted the rate constant measured by Wantuck et al. [36]. However, theoretical studies of the reverse reaction (R39) [37, 38] imply a significantly lower rate constant. In this section the rate constants for (R34) and (R39) are calculated from high-level theory. Furthermore, the thermodynamic properties for CH_3OO and CH_3OOH are recalculated, with special emphasis on the corrections for the CH_3 and OH hindered rotational modes.

3.1. Methodology

The CCSD(T) [39] and B2PLYPD3 [40–42] methods were used to determine the rovibrational properties of the stationary points for the $\text{CH}_3\text{OOH} + \text{CH}_3=\text{CH}_4 + \text{CH}_3\text{OO}$ (R34) and $\text{CH}_3\text{OH} + \text{CH}_3=\text{CH}_4 + \text{CH}_3\text{O}$ (R39) abstraction reactions. Both calculations employed the correlation-consistent polarized-valence triple-zeta (cc-pVTZ) basis of Dunning [43]. High level (HL) energy estimates were obtained from a sequence of single point calculations at the CCSD(T)/cc-pVTZ geometries consisting of (i) evaluation of the CCSD(T)-F12b [44] complete basis set (CBS) limit from extrapolation of calculations for the cc-pVTZ-F12 and cc-pVQZ-F12 basis sets [45], (ii) a correction for higher order excitations from CCSDT(Q)/cc-pVDZ calculations, (iii) a core-valence correction from CCSD(T,full)/CBS calculations based on extrapolation of results for the cc-pcVTZ and cc-pcVQZ basis sets [46], (iv) a relativistic correction from CI/aug-cc-pcVTZ calculations, and (v) an anharmonic zero-point energy (ZPE) correction calculated from second order spectroscopic perturbation theory [47] at the B3LYP/cc-pVTZ level [48].

Each of the CBS extrapolations were based on a two-point $1/(l+1)^4$ formula [49]. The CCSD(T) calculations generally employed RHF wavefunctions within the UCCSD(T) formalism implemented in MOLPRO [50], which was used for the majority of the calculations. The CCSDT(Q) calculations instead employed UHF wavefunctions as required by the MOLPRO implementation of Kallay’s MRCC code [51]. For the saddle points the contribution from the imaginary mode anharmonicity was excluded. The B2PLYPD3

calculations were performed with GAUSSIAN09 [52].

The present HL methodology is closely related to other high level methods such as the popular HEAT [53] and W4 [54, 55] methods. An extensive unpublished comparison of closely related calculations with Active ThermoChemical Tables [56, 57] values indicates 2σ uncertainties of 0.2–0.3 kcal/mol for stable species [58].

Kinetic predictions were obtained with variational transition state theory (TST) employing asymmetric Eckart tunneling corrections and 1-dimensional hindered rotor treatments for the torsional modes (1 in CH_3OO and CH_3OH , 2 in CH_3OOH and the TS for reaction (R39), and 3 in the TS for reaction (R34)) [59]. The remaining vibrational modes were treated as harmonic oscillators and the overall rotation was treated as a rigid body. Multidimensional torsional effects are expected to be negligible since for each stationary point at most one mode is not a methyl rotor. Variational effects are obtained from B2PLYPD3 evaluations of the intrinsic reaction path variations and a scaling of the B2PLYPD3 calculated minimum energy path energies to the CCSD(T) calculated imaginary frequencies. Such variational effects are small ($< 10\%$ for T in the 300 to 2000 K range) because both reactions have a large imaginary frequency.

For CH_3OO and CH_3OOH these calculations are also used to predict the 0 K heat of formation. These predictions are obtained by using CH_4 , H_2 , and H_2O as reference species whose heats of formation are taken as those in the current version of the ATcT of Ruscic [60]. Temperature dependent thermodynamic quantities are also obtained from the partition functions employed in the rate analysis and this data is fit with standard NASA polynomials. Notably, this analysis includes corrections for the CH_3 and OH hindered rotational modes.

3.2. Results

For both reactions the CCSD(T)/cc-pVTZ and B2PLYPD3/cc-pVTZ predicted rovibrational properties are remarkably consistent. The product of the frequencies differs by only 2 and 12% for the transition states in reaction (R34) and (R39), respectively. Furthermore, CCSD(T)-F12/CBS calculated saddle point energies for the two optimization methods differ by only 0.10 and 0.01 kcal/mol for reactions (R34) and (R39b), respectively. Most importantly, the torsional frequencies differ by 5 cm^{-1} or less for all but the

lowest mode in (R39), where the two values still differ by only 9 cm^{-1} . Thus, our use of the B2PLYPD3 method to map the torsional potentials and the minimum energy path should be more than adequate.

There is, however, one significant difference between the CCSD(T) and B2PLYPD3 rovibrational analysis. In particular, the imaginary frequencies predicted by the B2PLYPD3 method are about 15% lower (1880, 1772) than those predicted with the CCSD(T) method (2228, 2031). As a result, there is a difference of about 5–10% in the predicted tunneling corrections near 1000 K.

The predicted high level barrier heights are summarized in Table 2. The CBS correction to the energies is seen to be large, while the T(Q) correction is also significant. The remaining corrections are small enough that they have little impact on the kinetic predictions. Note that we do not provide a prediction for reaction (R39b) relative to $\text{CH}_3\text{O} + \text{CH}_4$ because an accurate treatment of the effect of Jahn-Teller distortions in CH_3O is difficult and beyond the scope of the present work.

The present predictions for the rate coefficients for reactions (R34), (R34b), and (R39) are reported in Table 3, where parameters for modified Arrhenius representations of the calculations are provided. A very rough estimate of the 2σ uncertainty in these rate predictions is a factor of 1.3 for temperatures near 1000 K. The predictions are also compared with the available literature data in Figures 3 and 4. For reaction (R34) the only literature data appears to be the review based estimate of Tsang and Hampson [35]. The present predictions are of similar magnitude to the Tsang and Hampson estimate near 1000 K, but have a quite different activation energy.

For reaction (R39b) the present predictions are in good agreement with the low temperature data of Shannon and Harrison [61] and Shaw and Thynne [62], and with the early TST calculations of Jodkowski et al. [37], while our rate constant is higher than that obtained in the literature review of Tsang [63] and the recent theoretical study of Alecu and Truhlar [38]. However, it still falls significantly below the value inferred from measurements of the reverse reaction by Wantuck et al. [36]. It should be noted that under the conditions of Wantuck et al., $\text{CH}_3\text{O} + \text{CH}_4$ competed with thermal dissociation of CH_3O and their value of k_{39b} has a comparatively high uncertainty. In related work, various experimental studies have determined the rate constant for the overall reaction of

CH₃OH with CH₃, but that rate constant appears to be dominated by a different channel: the production of CH₂OH + CH₄ [37].

The thermodynamic properties for CH₃OO and CH₃OOH, which are of particular interest for modeling CH₄ oxidation at high pressure and low to intermediate temperatures, were also predicted. The ratios of the hindered rotor partition function to the harmonic partition function for CH₃OO, CH₃OOH, and for the abstraction transition state for reaction (R34) are plotted in Fig. 5. As expected, the ratios all approach unity at low temperature, but deviations already start to be significant by 100 K. At slightly higher temperatures the hindered rotor partition functions become larger due to the decreased repulsiveness of the bending potential, while at even higher temperature the ratio decreases due to the inappropriate assumption of an infinite range of coordinates for the harmonic description. The use of harmonic partition functions would lead to errors in the predicted rate constant of up to a factor of 3. Of course, it is important to include these corrections not only in the rate coefficients but also in the thermodynamic properties. For example, over the 1000 to 1500 K temperature range, harmonic to hindered rotor deviations of about 1 cal mol⁻¹ K⁻¹ are observed for the entropy and the heat capacity and about 1 kcal mol⁻¹ for the enthalpy.

Polynomial fits for thermodynamic properties of CH₃OO and CH₃OOH are provided in the supplementary material. The thermodynamic data for the two species are shown in Table 4. The heats of formation for CH₃OO and CH₃OOH are calculated to be $\Delta_f H_0(\text{CH}_3\text{OO}) = 5.39 \text{ kcal mol}^{-1}$ and $\Delta_f H_0(\text{CH}_3\text{OOH}) = -27.45 \text{ kcal mol}^{-1}$. These values correspond to $\Delta_f H_{298}(\text{CH}_3\text{OO}) = 3.06 \text{ kcal mol}^{-1}$ and $\Delta_f H_{298}(\text{CH}_3\text{OOH}) = -30.51 \text{ kcal mol}^{-1}$.

The present value for $\Delta_f H_{298}(\text{CH}_3\text{OO})$ is slightly lower than other recent theoretical values of 3.4 kcal mol⁻¹ from Janoschek and Rossi [64] and 3.3 kcal mol⁻¹ from Goldsmith et al. [65]. It is in excellent agreement with the experimental value of 3.0±1.2 kcal mol⁻¹ from Meloni et al. [66] and in between other experimental determinations of 2.1±1.2 kcal mol⁻¹ [67] and 4.8±1.2 kcal mol⁻¹ [68]. For CH₃OOH, the present calculation of $\Delta_f H_{298}(\text{CH}_3\text{OOH})$ is in excellent agreement with recent theoretical values of -30.4±1 kcal mol⁻¹ [69] and -30.7±0.9 kcal mol⁻¹ [65].

4. Chemical kinetic model

A chemical kinetic model for methane oxidation was established, with emphasis on reactions important at high pressure. Thermodynamic and transport data were mainly taken from Rasmussen et al. [1]. Important components were checked for any refinement in renowned databases (e.g. Burcat et al. [70]). The reaction mechanism was based on earlier work on oxidation of H_2 [71], CO/H_2 [17], C_1 - C_2 hydrocarbons, [1, 19, 21], and CH_3OH [20, 72]. However, the C_1 subset reactions were reviewed in this work and more accurate rate constants were implemented when available. The full mechanism is available as Supplementary Material.

A special feature of the mechanism is that it takes into account the prompt dissociation of the weakly bound radical HCO , based on the recent work of Labbe et al. [73]. Weakly bound free radicals have low dissociation thresholds, facilitating dissociation during the vibrational-rotational relaxation process at high temperatures where the timescales for dissociation and collisional relaxation become comparable. The prompt dissociation of HCO yields atomic hydrogen, promoting the radical pool. We adopt the method of Labbe et al. [73] to derive prompt dissociation fractions of important reactions involving HCO .

The fraction of HCO dissociating directly increases with temperature. However, at high temperatures, thermal dissociation of HCO is favored anyway compared to reaction with, for instance, O_2 . For this reason, prompt dissociation of HCO is important only in a specific temperature window. During the course of the present work, we found that HCO prompt dissociation had a considerable impact on prediction of flame speeds, while it did not show up as sensitive for flow reactor and ignition delay calculations.

The combustion chemistry of hydrocarbons is generally more complicated at intermediate temperatures (500–1000 K) than at higher temperatures, partly due to the importance of peroxy radicals [11]. For methane oxidation in particular, reactions of methylperoxy (CH_3OO) are important [1], but our understanding of these steps is limited. The methylperoxy radical is formed by recombination of CH_3 and O_2 ,

This step is barrierless; we have adopted the rate constant from Fernandes et al. [74].

For most alkanes, isomerization of the alkylperoxyl radical to the hydroperoxide radical ($\text{ROO} \longrightarrow \text{QOOH}$) is known to be an important step in fuel conversion at lower temperatures. However, isomerization of the methylperoxyl radical, $\text{CH}_3\text{OO}(+\text{M})=\text{CH}_2\text{OOH}(+\text{M})$ is insignificant due to a high energy barrier of $\sim 38 \text{ kcal mol}^{-1}$ [75]. Consequently, dissociation of CH_3OO (R24b) with an endothermicity of about 32 kcal mol^{-1} is favored compared to isomerization to hydroperoxide.

Only a few CH_3OO reactions have been studied experimentally, and even for reactions with measured rate constants, extrapolation to combustion related temperatures is uncertain [35]. The most important reactions of CH_3OO under the present conditions are hydrogen abstraction from stable species to form CH_3OOH , and the reactions with CH_3 and HO_2 radicals. The rate constant for $\text{CH}_4 + \text{CH}_3\text{OO}=\text{CH}_3 + \text{CH}_3\text{OOH}$ (R34) was calculated in the present work, as discussed above. In addition, the methylperoxyl radical can abstract hydrogen from CH_2O ,

The rate constant for this reaction was estimated by analogy to $\text{HO}_2 + \text{CH}_2\text{O}$. For the reactions of CH_3OO with the radical pool, rate constants were mostly adopted from Rasmussen et al. [1]. The rate constant for $\text{CH}_3\text{OO} + \text{CH}_3$ was measured at temperatures up to 530 K by Keiffer et al. [76], while that of $\text{CH}_3\text{OO} + \text{HO}_2$ was drawn from the evaluation of Tyndall et al. [77], based on measurements below 700 K. The reaction $\text{CH}_3\text{OO} + \text{OH} = \text{CH}_3\text{OH} + \text{O}_2$ (R29) is known to be very fast [35, 78].

The reaction between hydroperoxyl (HO_2) and methyl (CH_3) is important at intermediate temperatures and high pressures where both radicals attain considerable concentrations during oxidation of methane. The reaction can proceed as either a chain-propagating step,

or as a chain-terminating step,

The competition between these channels has a considerable impact on ignition delay calculations for methane. The rate constant for reaction (R22) has been measured by Sangwan and Krasnoperov [79] at 295 K and by Hong et al. [80] at 1054–1249 K. The theoretical study by Jasper et al. [81] agrees well with both sets of measurements and their rate constant is adopted here. For (R23), we have adopted the rate constant from Srinivasan et al. [82], based on measurements in the temperature range 1655–1822 K and extrapolation to 200–2000 K by theory. Their rate constant is in agreement within the uncertainty with the more recent measurements of Hong et al. [80] for temperatures of 1000–1200 K.

Under the conditions of this work, formaldehyde is mainly consumed by reactions with OH (R8) or HO₂ (R9). For reaction (R8), the total rate constant is now taken from the recent shock tube study of Wang et al. [83] while the branching to H+CO instead of HCO is estimated following the method suggested by Labbe et al. [73]. The competition between dissociation of the formyl radical (R3),

and its reaction with molecular oxygen (R4),

is important for modeling at higher temperatures, in particular for flame speed predictions [84]. For both reactions, the rate constants are still in discussion. To determine k_3 , Hippler et al. [85] and Krasnoperov et al. [86] did measurements over a wide pressure range, 1–140 bar (590–800 K) and 0.8–100 bar (498–769 K), respectively. For most conditions, the rate constant derived from Krasnoperov et al. is considerably lower than that of Hippler et al. More recently, Yang et al. [87] studied the rate of HCO dissociation theoretically over temperatures of 300–2700 K and pressures of 0.01–1000 atm. At

atmospheric pressure and medium temperatures, their rate constant is in between the values from Hippler et al. and Krasnoperov et al., while at high temperatures, where this reaction is important for flame speed calculations, it agrees better with the results of Krasnoperov et al. Here we adopt the rate constant from Yang et al. [87], noting that further study of this reaction is desirable. Most experimental results for k_4 have been obtained at low temperature. However, Friedrichs and coworkers [88, 89] have derived values for the rate constant over the temperature range 739–1705 K. We have adopted the recommendation from Faßheber et al. [89], which involves a stronger temperature dependence than previous determinations.

5. Results and discussion

5.1. Oxidation in the flow reactor

In this section, the results from the laminar flow reactor at 100 bar and 700–900 K are presented. Figure 6 presents the gas composition at the reactor outlet under reducing conditions ($\Phi=19.7$) for different isotherms. The consumption of reactants starts at 725 K, and the major product of the partial oxidation of methane is CO at all investigated temperatures. Upon ignition, considerable amounts of formaldehyde and methanol are formed but their fractions gradually decline at higher temperatures. Above 750 K, C_2H_6 and C_2H_4 are formed to greater extents. At 900 K, the major products are CO and C_2H_6 . The model predicts the onset of reaction as well as the concentrations of CH_4 , O_2 , CO, and C_2H_6 very well. However, CO_2 and in particular CH_3OH are underpredicted while CH_2O is overpredicted. The discrepancies for these species cannot be explained by the experimental uncertainties (shown as error bars in the figure). The observed levels of CH_3OH are in agreement with the measurements under similar conditions by Rasmussen et al. [1].

Under stoichiometric conditions, the fuel conversion starts at a slightly higher temperature of 750 K (see Fig. 7). The major products are CO and CO_2 , with trace amounts of C_2H_4 and C_2H_6 . Above 800 K, further conversion of fuel is retarded and the methane conversion is limited to 88% at 900 K. The model reproduces accurately the onset of reaction as well as the relative changes in the fractions of stable components. However, it

underpredicts the conversion of methane and oxygen at high temperatures, accompanied by an underprediction of CO_2 .

The methane oxidation under very oxidizing conditions ($\Phi=0.06$) starts at 750 K. The major products are CO and CO_2 (Fig. 8). The CO concentration peaks at 775 K but declines gradually at higher temperatures where CO is oxidized to CO_2 . The model predicts well the onset of reaction and the methane consumption upon ignition, but above 775 K CO is slightly overpredicted while again CO_2 is underestimated.

The results of a reaction path analysis for oxidation of methane are shown in Fig. 9. At a very early stage of reaction, oxidation of methane is initiated by its reaction with molecular oxygen, $\text{CH}_4 + \text{O}_2 = \text{CH}_3 + \text{HO}_2$ (R23). The methyl radical then reacts with molecular oxygen to form either CH_3OO (R24) or $\text{CH}_2\text{O} + \text{OH}$ (R26). The branch to CH_3OO is dominant under these conditions, resulting in an accumulation of CH_3OO radicals. However, reaction (R26) is important, since it is the main source of OH radicals at early stages of reaction. The OH from (R26) and HO_2 from (R23) attack CH_4 (R13 and R14) and start the main path of the fuel oxidation.

Upon initiation, the peroxide radicals are mainly consumed by reaction with other peroxide radicals or with CH_3 ,

or by abstracting a hydrogen atom from a stable species, mainly CH_2O ,

When a sufficient concentration of radicals is established, consumption of methane proceeds by reaction with OH (R13). The required OH radicals are provided by the dissoci-

ation of H_2O_2 and CH_3OOH ,

The CH_3O radical mainly decomposes to $\text{CH}_2\text{O} + \text{H}$ (R37). The major sink of formaldehyde under stoichiometric conditions is its reaction with OH (R8).

At higher temperatures (~ 900 K) reaction with HO_2 (R22) becomes the dominant path for removal of methyl radicals, as well as a major source of OH . In fact, the shift from the low-temperature to the high-temperature pathways is mainly controlled by the competition for methyl radicals between reactions (R22) and (R24).

Under reducing conditions, methanol is formed via the reactions $\text{CH}_3\text{O} + \text{CH}_4 = \text{CH}_3\text{OH} + \text{CH}_3$ (R39b) and $\text{CH}_3\text{O} + \text{H}_2\text{O}_2 = \text{CH}_3\text{OH} + \text{HO}_2$ (R42b), while $\text{CH}_3\text{OH} + \text{OH} = \text{CH}_2\text{OH} + \text{H}_2\text{O}$ (R40) and $\text{CH}_2\text{OH} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$ (R41) constitute the main oxidation sequence of methanol for all investigated conditions, in line with previous findings for high-pressure oxidation of CH_3OH [20].

The sensitivity of modeling predictions towards rate constants is analyzed using a brute-force method in which the sensitivity coefficient for the predicted concentration of component 'X' toward reaction 'i' is calculated as

$$S_{X,i} = \frac{\Delta[X]/[X]}{\Delta k_i/k_i} \quad (1)$$

A positive coefficient displays a promoting effect of the reaction on the species mole fraction.

The results of the analysis are shown in Figs. 10 and 11. In line with findings of earlier studies [1, 90–92], reactions of methylperoxyl radicals are found to be important. The methane oxidation rate and even more so the formation of methanol and formaldehyde are sensitive to the reactions of CH_3OO with both stable species (CH_2O , CH_4) and radicals (HO_2 and CH_3). The competition between the terminating (R23b) and propagating (R22) channels of the $\text{CH}_3 + \text{HO}_2$ reaction is important for the oxidation rate of methane. Also formaldehyde reactions show considerable sensitivity coefficients, with H-abstraction by

HO₂ (R9) promoting reaction, while the reaction with OH (R8) inhibits oxidation.

Methanol is severely underpredicted while formaldehyde is overpredicted by the model upon onset of reaction (723 K) under reducing conditions. According to the sensitivity analysis, the methanol prediction is quite sensitive to the rate of $\text{CH}_3\text{O} + \text{CH}_4 = \text{CH}_3\text{OH} + \text{CH}_3$ (R39b), which is the main path of methanol formation. The use of our calculated value of k_{39} , instead of the experimental determination of k_{39b} from Wantuck et al. [36] used in our earlier work [1], has detrimental effects on the prediction of CH₃OH, leading to a larger underprediction. However, both this step and the other reaction forming methanol (R42b) has been characterized at a high level of theory and rate constants should be accurate within a factor of two.

Prediction of the methanol yield is also sensitive to reactions of the methylperoxyl radicals with CH₂O (R35), CH₄ (R34), HO₂ (R30), and CH₃ (R31), in agreement with the results of Arutyunov et al. [90]. These reactions also show up in the sensitivity analysis for formaldehyde. In particular (R35) is important for the prediction of methanol, but its rate constants is a rough estimate based on analogy to $\text{CH}_2\text{O} + \text{HO}_2 = \text{HCO} + \text{H}_2\text{O}_2$.

A major discrepancy under stoichiometric and oxidizing conditions is the underprediction of carbon dioxide. For both conditions, also the fuel conversion was underpredicted and the discrepancy is attributed to deficiencies in the fuel oxidation chemistry rather than specific CO oxidations steps. The sensitivity analyses (Fig. 11) emphasizes the role of CH₃OO reactions in predicting CO₂. Further work on the methylperoxyl chemistry is required to improve the accuracy of key reaction rate constants and improve modeling predictions under the present conditions.

5.2. Ignition in the RCM

The measured and simulated autoignition delay times for the RCM conditions are presented in isobars (Figs. 12 and 14) and isotherms (Figs. 13 and 15). Figure 12 shows the computed autoignition delay times at a peak pressure of 40 bar for the stoichiometric mixtures; they agree within 10% with the measurements. However, at a peak pressure of 15 bar a systematic underprediction, up to a factor of two, is observed for all stoichiometric mixtures studied. As can be seen in Fig. 13 the predictions agree within 10% with the measurements for all measured pressures (25–50 bar) at a fixed peak temperature of

1010 K.

Figure 14 shows that the computed autoignition delay times for the fuel-lean ($\Phi = 0.5$) mixtures at 50 and 30 bar agree within 20% with the measurements. In contrast, the model at 15 bar again systematically underpredicts the measured ignition delay by up to a factor of two. For the two isotherms at $T_c \sim 970$ K and 1010 K, presented in Fig. 15, very good agreement (within 17%) is observed between the measurements and computations over the entire measured pressure regime (30–80 bar).

Figure 16 shows a sensitivity analysis for methane ignition under RCM conditions. The sensitivity coefficients were calculated as

$$S_{\tau,i} = \frac{\Delta\tau/\tau}{\Delta k_i/k_i} \quad (2)$$

Consequently, a positive coefficient indicates that the reaction prolongs the ignition delay time. The analysis was conducted for pressures of 15 and 80 bar. The model underestimates the ignition delay at 15 bar, but predicts the delay time at 80 bar accurately. Similar to the flow reactor conditions, reactions of CH_3OO are important for the modeling predictions, especially at high pressures; at lower pressures other reactions are more active. Hydrogen abstraction by CH_3OO from stable species such as methane (R34) and formaldehyde (R35) promotes ignition.

The chain-terminating reaction $\text{CH}_3\text{OO} + \text{OH} = \text{CH}_3\text{OH} + \text{O}_2$ (R29), which was unimportant under flow-reactor conditions, inhibits ignition in the RCM considerably, especially at the high pressure of 80 bar. Another important inhibiting reaction is the terminating step $\text{CH}_3 + \text{HO}_2 = \text{CH}_4 + \text{O}_2$ (R23b). The reaction of methyl radicals with molecular oxygen, $\text{CH}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{OH}$ (R26) accelerates ignition, especially at lower pressures, in line with the analysis for the flow-reactor conditions at 900 K (figures 10 and 11). The sensitivity towards k_{26} decreases considerably at higher pressure (80 bar).

5.3. Comparison with literature data

The present chemical kinetic model is further evaluated by comparison to high-pressure data from literature. In our earlier work [1], high-pressure oxidation of methane was investigated at 700–900 K and 50–100 bar. A detailed comparison between these data and the present model is shown in Supplemental Material. The modeling predictions are

in good agreement with the ignition temperatures from the present study, while they slightly underestimate the values reported by Rasmussen et al. [1]. Overall, we find the level of agreement satisfactory. It is worth noting that Rasmussen et al. [1] introduced a terminating reaction for the CH_3OO radical at the reactor wall to avoid premature ignition in their simulations. However, in our subsequent high-pressure work [18–20] we have found no indications of surface activity in the reactor and the present model does not include any heterogenous reactions.

In the following, predictions with the present model is compared to ignition delay times and flame speeds, reported in literature for increased pressure.

5.3.1. Ignition delay time in shock tubes

The oxidation of methane has been investigated extensively in shock tubes [6, 7, 9, 10, 93–104]. The gas residence time in shock tubes is relatively short, making it difficult to study ignition at low temperatures. Consequently, most of the measurements have been conducted at temperatures higher than those of this study.

Davidson and Hanson [9] measured the ignition delays of methane at pressures up to 156 atm and temperatures of 1137–1536 K. A selection of their results is shown in Fig. 17. As expected, the ignition delay decreases with increasing pressure or temperature, being most sensitive to temperature. The ignition is faster for fuel-lean mixtures although those mixtures had a slightly higher dilution (77% Ar) compared to the fuel-rich mixtures (67% Ar). The predictions compare well with the experimental results, especially at higher pressures. The model is also accurate in simulating the results by Petersen et al. [104] who measured the ignition delays at pressures up to 261 atm (see Fig. 18).

In Fig. 19, modeling predictions are compared to ignition delay data obtained at very high pressure by Zhukov et al. [10]. As shown the modeling results agree well with the measured data at 156 and 456 atm. The figure also includes ignition delays measured at much lower pressures (6.9–8.0 atm) by Levy et al. [6]. Here, ignition is promoted by increasing the oxygen fraction in the mixture, consistent with the results of Davidson and Hanson [9]. Levy et al. [6] argued that excess oxygen accelerates the ignition by promoting the chain-branching sequence, $\text{CH}_3 + \text{O}_2 = \text{CH}_3\text{O} + \text{O}$ (R25), $\text{CH}_4 + \text{O} = \text{CH}_3 + \text{OH}$. In contrast, excess CH_4 inhibits ignition by promoting reaction (R11),

CH₄ + H=CH₃ + H₂, which competes for H radicals with the branching reaction H + O₂ (R1). Although the model overpredicts the ignition delays slightly, it reflects well the sensitivity to stoichiometry.

The model is assessed at lower pressures versus data reported more recently by Merhubi et al. [8]. The comparison can be found in *Supplementary materials*. The model slightly overpredicts ignition delays at pressures of 10–40 bar and temperatures of 1400–1900 K.

The model is assessed at lower temperatures by comparing with data reported by Huang et al. [7] from shock-tube measurements over 1000–1350 K. Contrary to the predictions for the present RCM experiments, the model here overpredicts the ignition delays, especially at lower temperatures (see Supplementary Material). Measurements of long ignition delay times (of the order of milliseconds) in shock tubes are vulnerable to non-idealities arising from flow compression and mixing [105–107]. Usually pressure and temperature increase gradually behind the shock wave as a result of fluid dynamic non-idealities; they have been observed even for non-reactive mixtures [108]. To compensate for these device-dependent variations, the measured pressure history behind the shock wave should be included in simulations [108], similarly to what is done in RCM studies. However, this information is not available for the measurements in [7].

5.3.2. Flame speed

The laminar burning velocity of methane has been measured in several studies [109–115], but most of the published data are limited to low pressure. Figure 20 compares simulations with the experimental data. The solid lines denote calculations with the full model while the dashed line corresponds to modeling without inclusion of the prompt dissociation of HCO. As expected, the flame speed decreases at elevated pressures. The predicted flame speeds agree well with the measurements at pressures of 1, 5, and 10 atm. It should be noted that the inclusion in the mechanism of prompt dissociation of HCO leads to an increase in the predicted flame speed of 3.7 cm s⁻¹ (at $\Phi=1$), increasing the accuracy of the predictions. For flow reactor and shock tube conditions, the prompt HCO dissociation has a negligible effect on the model predictions.

To identify reactions sensitive for predicting the flame speed, the sensitivity of the

mass flow rate is calculated using the built-in functions of CHEMKIN [25] (see Supplemental Material). Since the conditions at the inlet of the system are fixed, the mass flow rate sensitivity is linearly related to the flame speed sensitivity. Typical for flame speed predictions, the most important step is the main chain-branching reaction $\text{H} + \text{O}_2 = \text{O} + \text{OH}$ (R1). This step controls the prediction of the methane flame speed to a great extent. Reactions competing for H radicals exhibit negative sensitivities. In particular, the terminating reaction $\text{CH}_3 + \text{H} (+\text{M}) = \text{CH}_4 (+\text{M})$ (R10) exhibits a high negative sensitivity coefficient. The decomposition of HCO (R3) promotes the flame speed whereas its reactions with H, OH, and O_2 slow down flame propagation since they terminate the radical chain. Also the oxidation of CO by OH (R44) is among the reactions controlling the flame speed. A fraction of the HCO radicals from $\text{CH}_2\text{O} + \text{H} = \text{HCO} + \text{H}_2$ (R7) dissociate promptly to $\text{H} + \text{CO}$ (R7p), and accelerates the flame propagating due to radical branching. The competition between the two channels are important for the predicted flame speed.

6. Conclusion

Methane oxidation at high pressures and intermediate temperatures has been investigated in a flow reactor and in a rapid compression machine. Under the flow reactor conditions (100 bar pressure), the onset temperature of methane reaction was found to be 725–750 K, slightly dependent on stoichiometry. Ignition delay times in the RCM at 15–80 bar and 800–1250 K were in the range 1–100 ms, decreasing with increasing pressure or temperature. The thermodynamic properties of CH_3OO and CH_3OOH , as well as the rate constants for the abstraction reactions $\text{CH}_3\text{OOH} + \text{CH}_3 = \text{CH}_3\text{OO} + \text{CH}_4$ and $\text{CH}_3\text{OH} + \text{CH}_3 = \text{CH}_3\text{O} + \text{CH}_4$, were calculated at a high level of theory. A chemical kinetic model was developed and tested against the measurements. It predicts well the onset temperature of reaction in the flow reactor and the concentrations of major stable species upon ignition, but the methanol yield under reducing conditions was underpredicted. The model reproduces the ignition delay measured at high pressure in the RCM very well, but it underpredicts values at 15 bar. Sensitivity analyses showed that modeling predictions for both the flow reactor and the RCM are sensitive to the methylperoxyl chemistry and further studies on methylperoxyl reactions are desirable

to improve our understanding of methane oxidation at high pressures and intermediate temperatures. Model predictions were in satisfactory agreement with measured ignition delay times and flame speeds from literature over a wide range of conditions.

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Table 1: Studied mixture compositions in RCM tests (mole fractions)

No.	Φ	CH ₄	O ₂	N ₂	Ar
A	1.0	0.09091	0.1818	0.3	0.4273
B	1.0	0.09091	0.1818	0	0.7273
C	0.5	0.04762	0.1905	0.3	0.4619
D	0.5	0.04762	0.1905	0	0.7619

Table 2: Barrier Height Energies^a.

Geometry	High Level	CCSD(T)/cc-pVTZ ^b	CBS Corr. ^c	T(Q) Corr. ^d	Core-Val. ^e	Rel. Corr. ^f	Anh. Corr. ^g	B2PLYPD3
TS34 ^h	6.39	5.65	1.13	-0.39	0.07	-0.01	-0.05	3.13
TS34 ⁱ	25.29	22.26	2.85	-0.14	0.15	0.07	0.0	24.14
TS39 ^j	12.6	11.53	1.23	-0.21	0.09	-0.08	0.04	8.81

^a All energies are in kcal/mol.^b Including CCSD(T)/cc-pVTZ ZPE correction.^c CCSD(T)-F12/CBS relative to CCSD(T)/cc-pVTZ.^d CCSDT(Q)/cc-pVDZ relative to CCSD(T)/cc-pVDZ.^e Core-valence correction^f Relativistic correction.^g Anharmonicity correction.^h Relative to CH₃OOH + CH₃.ⁱ Relative to CH₃OO + CH₄.^j Relative to CH₃OH + CH₃.

Table 3: Modified Arrhenius Representations of TST Predicted Rate Constants^a

Reaction	A ^b	n	E _a ^c	T-Range ^d
R34) CH ₃ OO + CH ₄ =CH ₃ OOH + CH ₃	4.45×10^{-3}	4.691	19868	400–2000
R34b) CH ₃ OOH + CH ₃ =CH ₃ OO + CH ₄	1.62×10^{-3}	4.322	-235	300–2000
R39) CH ₃ OH + CH ₃ =CH ₃ O + CH ₄	1.25×10^{-2}	4.161	6002	400–2000

^a $k = A T^n \exp(\frac{-E_a}{RT})$
^b Units of cm³ mole⁻¹ s⁻¹.
^c Units of cal mole⁻¹.
^d Temperature range (K) over which fit is valid.

Table 4: Thermodynamic properties for CH₃OO and CH₃OOH. Units are kcal mol⁻¹ for H, and cal mol⁻¹ K⁻¹ for S and C_p. The temperatures for C_p are in K.

Species	ΔH _{f298}	S ₂₉₈	C _{p300}	C _{p400}	C _{p500}	C _{p600}	C _{p800}	C _{p1000}	C _{p1500}
CH ₃ OO	3.06	64.45	11.91	14.01	15.98	17.78	20.72	22.83	26.15
CH ₃ OOH	-30.51	67.13	14.49	16.98	19.22	21.18	24.31	26.58	30.27

Table 5: Selected reactions from the chemical kinetic model. The rate constants are in the form of $k = A T^n \exp(-E/(RT))$. Units are *mol*, *cm*, *K*, *s*, and *cal*.

	Reaction	A	n	E	Note/Ref.
R1	$\text{H} + \text{O}_2 = \text{O} + \text{OH}$	1.0E14	0.000	15286	[116]
R2	$\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$	1.2E9	0.770	-1825	[117]
	duplicate rate constant	1.3E12	0.295	7397	
R3	$\text{HCO}(+ \text{M}) = \text{H} + \text{CO}(+ \text{M})$	4.9E16	-0.930	19724	^a , [87]
	Low-pressure limit:	7.4E21	-2.360	19383	
	Troe parameters: 0.103 139.0 10900.0	4550.0			
R4	$\text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2$	6.9E6	1.900	-1369	[89]
R5	$\text{CH}_2\text{O}(+ \text{M}) = \text{HCO} + \text{H}(+ \text{M})$	8.0E15	0.000	87726	[118]
	Low-pressure limit:	1.3E36	-5.500	93932	
R6	$\text{CH}_2\text{O}(+ \text{M}) = \text{CO} + \text{H}_2(+ \text{M})$	3.7E13	0.000	71969	[118]
	Low-pressure limit:	4.4E38	-6.100	93932	
R7	$\text{CH}_2\text{O} + \text{H} = \text{HCO} + \text{H}_2$	4.2E09	1.294	3591	^b , [73, 119]
	duplicate rate constant	7.3E23	-2.665	17635	
R7p	$\text{CH}_2\text{O} + \text{H} = \text{H} + \text{CO} + \text{H}_2$	1.2E09	1.812	13163	^b , [73, 119]
R8	$\text{CH}_2\text{O} + \text{OH} = \text{HCO} + \text{H}_2\text{O}$	1.1E09	1.330	-392	^b , [73, 83]
R8p	$\text{CH}_2\text{O} + \text{OH} = \text{H} + \text{CO} + \text{H}_2\text{O}$	8.4E10	0.879	9843	^b , [73, 83]
R9	$\text{CH}_2\text{O} + \text{HO}_2 = \text{HCO} + \text{H}_2\text{O}_2$	4.1E04	2.500	10206	^b , [73, 120]
	duplicate rate constant	-2.5E14	0.027	30133	
R9p	$\text{CH}_2\text{O} + \text{HO}_2 = \text{H} + \text{CO} + \text{H}_2\text{O}_2$	2.5E14	0.027	30120	^b , [73, 120]
R10	$\text{CH}_3 + \text{H}(+ \text{M}) = \text{CH}_4(+ \text{M})$	2.3E14	0.030	144	^a , [121]
	Low-pressure limit:	2.7E35	-5.350	3380	
	Troe parameters: 0.395 163.5 4250.3	1253676.0			
R11	$\text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2$	4.1E03	3.160	8755	[1]
R12	$\text{CH}_4 + \text{O} = \text{CH}_3 + \text{OH}$	4.4E05	2.500	6577	[122]
R13	$\text{CH}_4 + \text{OH} = \text{CH}_3 + \text{H}_2\text{O}$	1.0E06	2.180	2506	[123]
R14	$\text{CH}_4 + \text{HO}_2 = \text{CH}_3 + \text{H}_2\text{O}_2$	4.7E04	2.500	21000	[122]
R15	$\text{CH}_3 + \text{OH} = \text{CH}_2 + \text{H}_2\text{O}$	4.3E04	2.570	3997	[124]
R16	$\text{CH}_3 + \text{OH} = \text{CH}_2(\text{S}) + \text{H}_2\text{O}$	6.1E10	0.600	2923	^c , [124]
R17	$\text{CH}_3 + \text{OH} = \text{CH}_3\text{OH}$	1.3E22	-2.660	2451	^c , [124]
R18	$\text{CH}_3 + \text{OH} = \text{CH}_2\text{OH} + \text{H}$	2.5E10	0.910	6402	^c , [124]
R19	$\text{CH}_3 + \text{OH} = \text{CH}_3\text{O} + \text{H}$	3.1E09	0.920	12981	^c , [124]
R20	$\text{CH}_3 + \text{OH} = \text{H}_2 + \text{HCOH}$	9.4E07	1.290	2423	^c [124]
R21	$\text{CH}_3 + \text{OH} = \text{H}_2 + \text{CH}_2\text{O}$	2.4E09	0.450	3791	^c , [124]
R22	$\text{CH}_3 + \text{HO}_2 = \text{CH}_3\text{O} + \text{OH}$	1.0E12	0.270	-687	[81]
R23	$\text{CH}_4 + \text{O}_2 = \text{CH}_3 + \text{HO}_2$	2.0E05	2.750	51714	[82]
R24	$\text{CH}_3 + \text{O}_2 = \text{CH}_3\text{OO}$	1.1E19	-2.300	1800	^d , [74]
	duplicate rate constant	4.1E30	-5.700	8750	
R25	$\text{CH}_3 + \text{O}_2 = \text{CH}_3\text{O} + \text{O}$	7.5E12	0.000	28297	[125]
R26	$\text{CH}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{OH}$	1.9E11	0.000	9842	[125]
R27	$\text{CH}_3\text{OO} + \text{H} = \text{CH}_3\text{O} + \text{OH}$	1.0E14	0.000	0	[35]
R28	$\text{CH}_3\text{OO} + \text{O} = \text{CH}_3\text{O} + \text{O}_2$	2.9E10	1.000	-724	$\text{HO}_2 + \text{O}$
R29	$\text{CH}_3\text{OO} + \text{OH} = \text{CH}_3\text{OH} + \text{O}_2$	1.7E14	0.000	0	[78]
R30	$\text{CH}_3\text{OO} + \text{HO}_2 = \text{CH}_3\text{OOH} + \text{O}_2$	2.5E11	0.000	-1490	[77]

Continued on next page

Table 5 – continued from previous page

		Arrhenius data			
R31	$\text{CH}_3\text{OO} + \text{CH}_3=\text{CH}_3\text{O} + \text{CH}_3\text{O}$	5.1E12	0.000	-1411	[76]
R32	$\text{CH}_3\text{OO} + \text{CH}_3\text{OO}=\text{CH}_3\text{O} + \text{CH}_3\text{O} + \text{O}_2$	1.1E18	-2.400	1800	[77]
	duplicate rate constant	7.0E10	0.000	800	
R33	$\text{CH}_3\text{OO} + \text{CH}_3\text{OO}=\text{CH}_3\text{OH} + \text{CH}_2\text{O} + \text{O}_2$	2.0E11	-0.550	-1600	[77]
R34	$\text{CH}_3\text{OO} + \text{CH}_4=\text{CH}_3\text{OOH} + \text{CH}_3$	4.5E-3	4.690	19868	p.w.
R35	$\text{CH}_3\text{OO} + \text{CH}_2\text{O}=\text{CH}_3\text{OOH} + \text{HCO}$	4.1E04	2.500	10206	$\text{HO}_2 + \text{CH}_2\text{O}$, [73]
	duplicate rate constant	-2.5E14	0.027	30133	
R35p	$\text{CH}_3\text{OO} + \text{CH}_2\text{O}=\text{CH}_3\text{OOH} + \text{H} + \text{CO}$	2.5E14	0.027	30133	$\text{HO}_2 + \text{CH}_2\text{O}$, [73]
R36	$\text{CH}_3\text{OOH} (+ \text{M})=\text{CH}_3\text{O} + \text{OH} (+ \text{M})$	4.1E19	-1.153	44226	[81]
	Low-pressure limit:	3.9E42	-7.502	46730	
	Troe parameters: 0.8375 36562 498.8 9990				
R37	$\text{CH}_3\text{O} (+ \text{M})=\text{CH}_2\text{O} + \text{H} (+ \text{M})$	1.1E10	1.210	24069	[126]
	Low-pressure limit:	6.0E16	-0.547	18012	
	Troe parameters: 0.341 28 1000 2339				
R38	$\text{CH}_3\text{O} + \text{O}_2=\text{CH}_2\text{O} + \text{HO}_2$	4.8E-1	3.600	-1055	[20]
R39	$\text{CH}_3\text{OH} + \text{CH}_3=\text{CH}_3\text{O} + \text{CH}_4$	1.3E-2	4.161	6002	p.w.
R40	$\text{CH}_3\text{OH} + \text{OH}=\text{CH}_2\text{OH} + \text{H}_2\text{O}$	1.5E08	1.440	113	[72, 127]
R41	$\text{CH}_2\text{OH} + \text{O}_2=\text{CH}_2\text{O} + \text{HO}_2$	7.2E13	0.000	3736	[122]
	duplicate rate constant	2.9E16	-1.500	0	
R42	$\text{CH}_3\text{OH} + \text{HO}_2=\text{CH}_3\text{O} + \text{H}_2\text{O}_2$	1.5E-3	4.610	15828	[38]

^a : for enhanced third-body efficiencies see the mechanism file in the supplementary materials.

^b : at 10 atm pressure, for other pressures see the mechanism file in the supplementary materials.

^c : at 132 atm pressure, for other pressures see the mechanism file in the supplementary materials.

^d : at 100 atm pressure, for other pressures see the mechanism file in the supplementary materials.

Figure 1: Temperature profile measured inside the pressure shell wall of the reactor at different isothermal temperatures. The flow was pure nitrogen at 3.23 NL/min and 100 bar pressure.

Figure 2: Measured and calculated pressure history for mixture C (RCM experiments, table 1) at 968 K, with the definitions autoignition delay time, peak pressure and compression time.

Figure 3: Plot of the temperature dependence of the rate coefficient for $\text{CH}_3\text{OO} + \text{CH}_4 \longrightarrow \text{CH}_3\text{OOH} + \text{CH}_3$. The line labeled Tsang & Hampson is a literature review based estimate [35].

Figure 4: Plot of the temperature dependence of the rate coefficient for $\text{CH}_3\text{OH} + \text{CH}_3 \longrightarrow \text{CH}_3\text{O} + \text{CH}_4$ (R39). The symbols represent the experimental data of Shannon and Harrison [61], Shaw and Thynne [62], and Wantuck et al. [36]. The latter data are derived from measurements of the reverse step, using the present thermodynamic data. The lines show calculated rate constants from Tsang [63] (BEBO, adjusted to experimental results), Jodkowski [37], Alecu and Truhlar [38], and the present work.

Figure 5: Plot of the ratio of the hindered rotor partition function to the harmonic oscillator partition function for CH_3OO , CH_3OOH , and for the abstraction transition state.

Figure 6: Results of experiments under reducing conditions (0.18% O_2 and 1.75% CH_4 in N_2 , $\Phi=19.7$) at 100 bar pressure. Symbols mark the experimental results and lines denote the predictions of the present model. The temperature profile was implemented in the simulations. Considering only the isothermal zone of the reactor (± 6 K, residence time= $9586/T$ [s]) deteriorates slightly the agreement.

Figure 7: Results of experiments under stoichiometric conditions (0.31% O_2 and 0.16% CH_4 in N_2 , $\Phi=1.0$) at 100 bar pressure. Symbols mark the experimental results and lines denote the predictions of the present model. The temperature profile was implemented in the simulations. Considering only the isothermal zone of the reactor (± 6 K, residence time= $9586/T$ [s]) deteriorates slightly the agreement.

Figure 8: Results of experiments under oxidizing conditions (3.96% O₂ and 0.11% CH₄ in N₂, $\Phi=0.06$) at 100 bar pressure. Symbols mark the experimental results and lines denote the predictions of the present model. The temperature profile was implemented in the simulations. Considering only the isothermal zone of the reactor (± 6 K, residence time= $9586/T$ [s]) deteriorates slightly the agreement.

Figure 9: Reaction pathways for methane consumption and methanol formation at conditions investigated in the flow reactor. The dashed lines are active only under specific conditions, see the text for more details.

Figure 10: Sensitivity of predictions for different components under reducing conditions. The pressure was 100 bar and only the isothermal part of the reactor was considered in the simulations. The residence time was adjusted to achieve 25% conversion of CH₄ or O₂.

Figure 11: Sensitivity of predictions for different components under stoichiometric conditions. The pressure was 100 bar and only the isothermal part of the reactor was considered in the simulations. The residence time was adjusted to achieve 25% conversion of CH₄ or O₂.

Figure 12: Measured (symbols) and calculated (line) autoignition delay times (RCM experiments) at a fixed pressure of 40 bar (mixture A: 9/18/30/43% of $\text{CH}_4/\text{O}_2/\text{N}_2/\text{Ar}$) and 15 bar (mixture B: 9/18/73 % of $\text{CH}_4/\text{O}_2/\text{Ar}$). Both mixtures are stoichiometric ($\Phi=1.0$). Polynomial fits to the modeling results are shown above.

Figure 13: Measured (symbols) and calculated (line) autoignition delay times (RCM experiments) at a fixed temperature of 995 K and for a stoichiometric mixture (mixture A: 9/18/30/43 % of $\text{CH}_4/\text{O}_2/\text{N}_2/\text{Ar}$). Polynomial fits to the modeling results are shown above.

Figure 14: Measured (symbols) and calculated (line) autoignition delay times (RCM experiments) at a fixed pressure of 15 bar (mixture D: 5/19/76 % of $\text{CH}_4/\text{O}_2/\text{Ar}$), 30 bar (mixture D) and at 50 bar (mixture C: 5/19/30/46% of $\text{CH}_4/\text{O}_2/\text{N}_2/\text{Ar}$). All mixtures are fuel-lean ($\Phi=0.5$). Polynomial fits to the modeling results are shown above.

Figure 15: Measured (symbols) and calculated (line) autoignition delay times (RCM experiments) at a fixed temperature of 970 K and 1010 K an equivalence ratio of $\Phi=0.5$, mixture C (5/19/30/46 % of $\text{CH}_4/\text{O}_2/\text{N}_2/\text{Ar}$). Polynomial fits to the modeling results are shown above.

Figure 16: Sensitivity of ignition delay time of methane (RCM experiments) for fuel-lean mixtures (mixture C, $\Phi = 0.5$) at 1010 K.

Figure 17: Ignition delay times of fuel-lean (3.8% CH_4 +19.2% O_2 in Ar, $\Phi=0.4$) and fuel-rich (20.0% CH_4 +13.3% O_2 in Ar, $\Phi=3$) mixtures. Symbols mark experimental results from Davidson and Hanson [9] and lines denotes the predictions of the present model. The simulations are conducted at fixed pressures while the pressure in the experiments fluctuated within $\pm 10\%$.

Figure 18: Ignition delay times of fuel-rich ($\Phi=3$) mixtures of CH_4/O_2 in inert gases (55–67% of Ar or N_2). Symbols mark experimental results from Petersen et al. [104] and lines denotes the predictions of the present model. The simulations are conducted at fixed pressures while the pressure in the experiments fluctuated within $\pm 10\%$.

Figure 19: Ignition delay times of CH_4/air ($\Phi=0.5$, from Zhukov et al. [10]) and CH_4/O_2 mixtures (from Levy et al. [6], mix 4: 3.53% CH_4 in N_2 , 8 atm, $\Phi=1.01$; mix 7: 4.0% CH_4 in N_2 , 6.9 atm, $\Phi=1.33$; mix 11: 1.99% CH_4 + 3.72% CO_2 in N_2 , 7.7 atm, $\Phi=0.32$). The simulations are conducted at fixed pressures while the pressure in the experiments fluctuated within $\pm 10\%$.

Figure 20: Laminar burning velocity of methane/air mixture at 1, 5, and 10 atm and initial temperature of 298–300 K. Symbols mark experimental results from Gu et al. [109], Dirrenberger et al. [110], Rozenchan et al. [111], Varea et al. [112], Goswami et al. [113], Tahtouh et al. [114], and Lowry et al. [115]. Lines denote the model prediction at specified pressures. The dashed line corresponds to modeling without inclusion of the prompt dissociation of HCO .