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 $CH_3OOH + CH_3 = CH_3OO + CH_4$ and $CH_3OH + CH_3 = CH_3O + CH_4$, 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 as 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 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.

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] con-

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ducted 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 $CH_3OOH + CH_3 = CH_3OO + CH_4$ and $CH_3OH + CH_3 = CH_3O + CH_4$ 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 CH_4 and O_2 in N_2 (±2% uncertainty in composition) and 99.5% for pure CH_4. 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 (±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 corre-
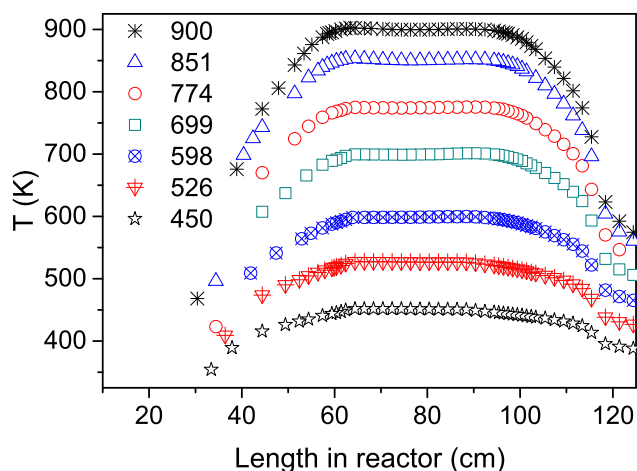

Fig. 1. Temperature profile measured inside the pressure shell wall of the reactor at different isothermal temperatures. The flow was pure nitrogen at 3.23 NL/min and 100 bar pressure.

lation. In the calculation of the thermal conductivity of formaldehyde, the employed Lennard–Jones force constants ($\sigma = 3.65$ Å, $\varepsilon/K = 313.9$ 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 $\tau[s] = 9557/T[K]$. 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 be $-7/+15$ 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