

Auto-ignitions of methane at intermediate and high temperatures

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Introduction

Chemical kinetic mechanisms together with CFD codes are used for optimizing practical devices such as internal combustion engines, gas turbines and other systems. However, in order to produce and validate kinetic mechanisms experimental data generated under well-controlled conditions (temperature, pressure, equivalence ratio and dilution) are needed.

Methane auto-ignition has been extensively studied for the last forty years [1–12]. Early shock tube ignition delay time measurements were conducted under low pressures (0.5–15 atm) and high temperatures (1200–2500) [1, 2]. Recent shock tubes studies covered the wide range of pressures (up to 450 atm) and equivalence ratios ($\varphi = 0.5$ –4) [3–10]. The temperature range was generally extended by achieving tailored-interface conditions in the test volume. The researchers observed very weak ignition at the intermediate temperatures and suggested that further study is needed in this regime to validate the current kinetics models. The rapid compression machine (RCM) can provide a platform for combustion studies at intermediate temperatures from 600 K to 1100 K. This temperature range is generally outside of the observable region in most shock tubes. Only a small number of studies on methane were found in literature [11–13]. Moreover majority of them related to the influence of hydrogen or heavier hydrocarbons (ethane, propane, butane, and pentane) on the oxidation of methane and a little data have been reported for pure methane oxidation.

An obvious lack of experimental data exists over the range of temperatures from 900 to 1400 K and elevated pressures, because previous intermediate temperature shock tube measurements were carried out under not well-controlled tailored-interface conditions at which boundary layer effects and shockwave bifurcation can effect the induction time and cause significant errors. On the other hand the available RCM data are too sparse and presented for narrow range of conditions

In the present work we developed a rapid compression machine in order to extend the typical temperature range for RCM measurements and to perform a comprehensive methane auto-ignition study at elevated pressures and intermediate-to-high temperatures. New experimental data provide the continuous overlapping with high temperature data points previously obtained in shock tube facility [10].

Experimental setup

The essential features of shock tube and diagnostic equipment have been described previously [10]. The main feature of the RCM used in this study is a high compression ratio (up to 80), which provides both high pressure and high temperature at the end of compression stroke. Fig. 1 shows the general layout of the compression cylinder and measurement setup. The test chamber (4) has diameter 48 mm and height about 12 mm. It is equipped with a high-temperature quartz pressure sensor Kistler 6031U18 (8) combined with a Kistler 5015A charge amplifier (9), a gas inlet/outlet valve (6) and quartz window (10). For recording the luminescence at ignition and combustion the bifurcated optical fiber light guide was connected to the mandrel of the quartz window. Doubled narrowband interferometric filters installed in front of the photomultiplier photocathodes (11) passed only emissions of OH radicals at $\lambda = 308.9$ nm (transitions $A^2\Sigma - X^2\Pi$) and CH radicals at $\lambda = 431.5$ nm (transitions $^2\Delta - ^2\Pi$). An optical reflection probe (7) was used for measuring positions of the compression piston and hence the current gas volume during the compression.

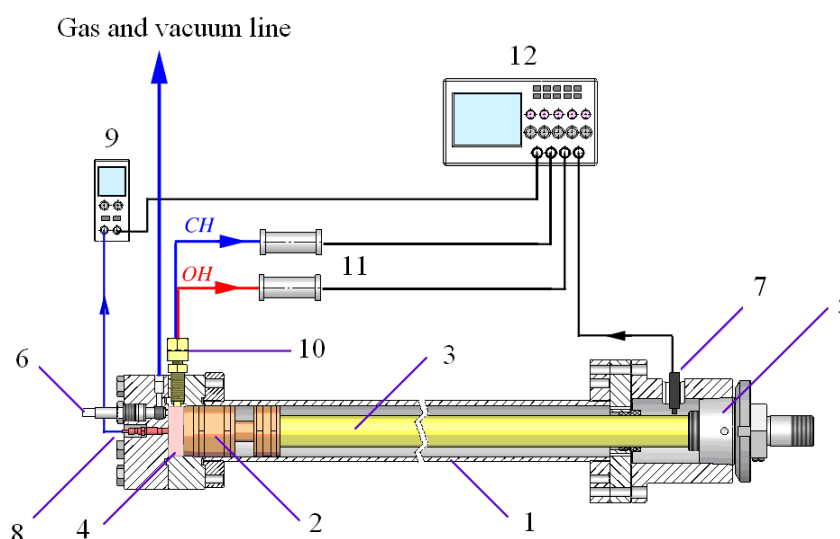


Figure 1. The layout of the compression cylinder and measurement system: 1 – compression cylinder, 2 – doubled compression piston with conical head, 3 – pushing rod, 4 – test chamber, 5 – conical stopper, 6 – inlet gas and vacuum valve, 7 – optical reflection probe, 8 – pressure sensor, 9 – charge amplifier, 10 – quartz window, 11 – photomultipliers, 12 – digital oscilloscope.

The gas temperature was calculated using pressure measurements as in other RCM studies [11-13] with the assumption that compression is adiabatic and isentropic and heat losses effects only on thin boundary layer. Runs were performed in stoichiometric $\phi = 1$, lean $\phi = 0.5$, and rich $\phi = 2$ $\text{CH}_4/\text{O}_2/\text{N}_2/\text{Ar}$ mixtures within the range of post-compression pressures of 10–20 atm and temperatures of 700–1400 K. The ratio of total inert gases to oxidizer was similar to that of nitrogen to oxygen in air, while the N_2/Ar ratio was chosen for obtaining different post-compression gas temperatures for the same compression ratios. The N_2/Ar mixtures containing 0, 25, 50, 75 and 100 % of argon were used as diluents. All studied compositions were mixed by the method of partial pressures within the ten-liter gas vessel and kept for two days before use.

The ignition or induction time of the mixture was defined as the time difference between pressure peak at the end of compression stroke and the onset of emission and pressure rising (5 % of maximal rise) within the measuring gas volume. The compression time in this study was in range of 45–60 ms. It depended on compression ratio which was varied from 20:1 to 60:1.

Results and discussion

To obtain the correct temperature dependences of ignition times all comparative shock-tube and RCM experimental series were performed at constant density (2 and 4 kg/m³) of compressed gas mixtures. It means that fuel, oxygen, and dilution concentrations were kept nearly constant within a studied temperature range.

For high- and low-density stoichiometric CH₄/O₂/N₂/Ar mixtures the results of induction time measurements performed in the RCM and corresponding data points obtained in the shock tube [10] for equivalent post-shock densities are plotted in Fig. 2. Ignition times in the shock tube were also controlled by ion current measurements at the reflecting wall and auto-ignitions in boundary layer were detected by emission C₂ radicals (516.3 nm, $\Delta\lambda = 4.6$ nm). These data are also plotted on Fig. 3. As one can see we combined together the regions with high and intermediate temperatures. The low temperature RCM data exhibit much lower activation energies 8.59 and 11.67 kcal/mole in comparison with corresponding shock-tube plots. At the same time, the linear Arrhenius approximations of RCM data demonstrate reasonable intersections with a high-temperature induction time plots. Experimental measurements from the RCM suggest, that for high- and low-density stoichiometric mixtures the ignition limits are close to the temperature of $T = 936$ K and 1190 K, respectively. At lower temperatures than those critical one's there were not auto-ignitions of methane at RCM compression.

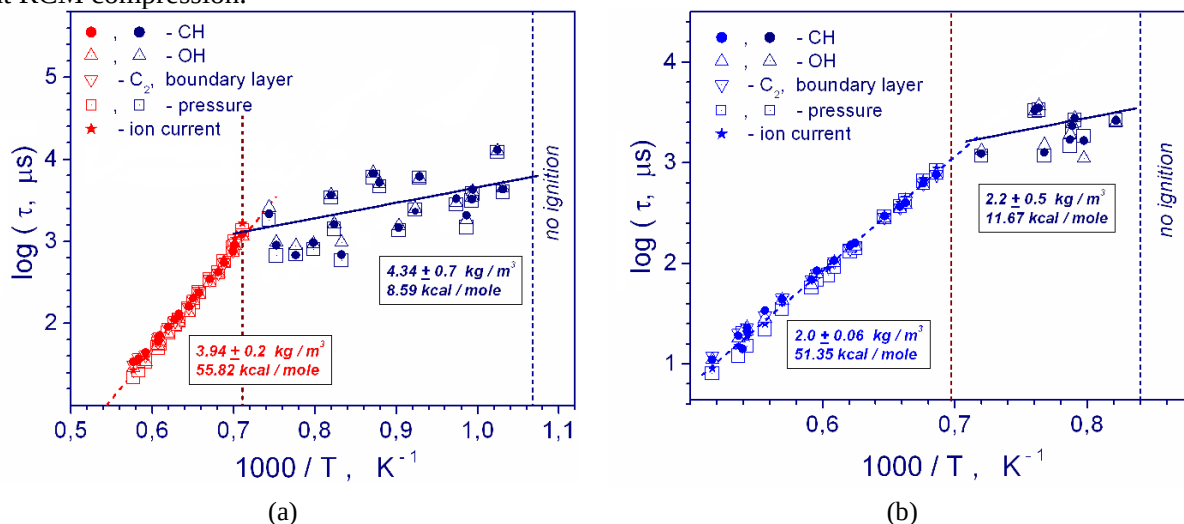


Figure 2. Ignition delay time vs. reciprocal temperature in stoichiometric CH₄/O₂/N₂/Ar mixtures at compression density of $4.34 \pm 0.7 \text{ kg/m}^3$ (a) and $2.2 \pm 0.5 \text{ kg/m}^3$ (b).

Some problems are visible from experimental observations. It is a big experimental uncertainty of measured induction times for the same initial and final conditions (Fig. 2, a). The reason is that during the compression stroke the long pushing rod (approximately 1 m) experiences the transverse vibrations affecting on the dynamic contact of the compression piston with the fixing conical part of the test chamber. Any misalignment during this contact can cause: 1) local metal-to-metal collisions ejecting small metal particles into the gas volume; 2) primary gas over compressions in formed gas pockets within the conical clearance. These factors can produce the local hot spots, which can strongly influence on the ignition timing. In the further experimental series we have tested different non-metal materials for the conical piston head in order to reduce the role of metal particle formation. But application of plastic materials also causes some problems. The collision of the plastic piston head with a fixing cone is unpredictable. Therefore the combustion chamber height is not constant and can vary from 12 to 13.5 in different experiments. This produces a big experimental scatter of the data. So, to obtain good dependence a huge amount of experiments is required. Nevertheless, application of plastic piston conical head improved repeatability in further experiments.

Experiments for rich mixtures (Fig. 3) show reasonable combining of the shock-tube and RCM induction time measurements as well as for stoichiometric mixtures. Similarly, low temperature RCM data exhibit lower activation energy of 21.67 kcal/mole in comparison with the shock-tube Arrhenius approximation with global activation energy of 49.5 kcal/mole. For rich high-density mixture, the ignition limits are close to the temperature of $T = 1105$ K. This value is much higher than corresponding one $T = 936$ K for stoichiometric mixture. For low-density mixture the ignition limit is nearby of $T = 1347$ K and only few auto-ignitions were observed. That is why Arrhenius approximation was not made.

Results of induction time measurements for lean mixtures are plotted in Fig. 4. As for stoichiometric and rich mixtures, experiments show good overlapping of the shock-tube and RCM induction times. Like for other stoichiometries, the low temperature RCM data exhibit lower activation energies of 15.03 and 18.45 kcal/mole for high- and low-density mixtures correspondingly in comparison with shock-tube Arrhenius., the ignition limits are close to the temperature of $T = 1075$ K for lean high-density mixtures and $T = 1020$ for low-density mixtures.

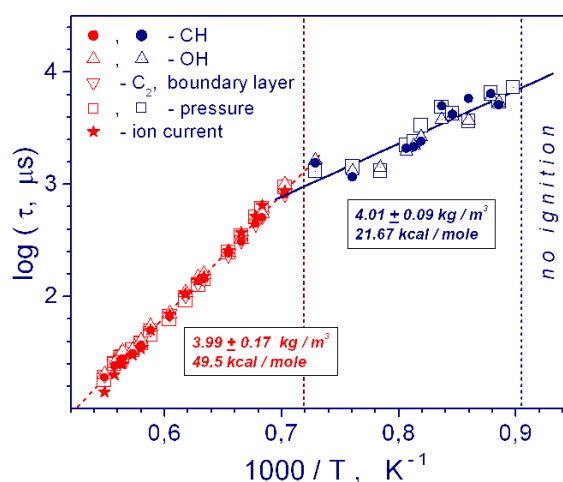


Figure 3. Ignition delay time vs. reciprocal temperature in rich $\text{CH}_4/\text{O}_2/\text{N}_2/\text{Ar}$ mixtures at compression density of $4.01 \pm 0.09 \text{ kg/m}^3$.

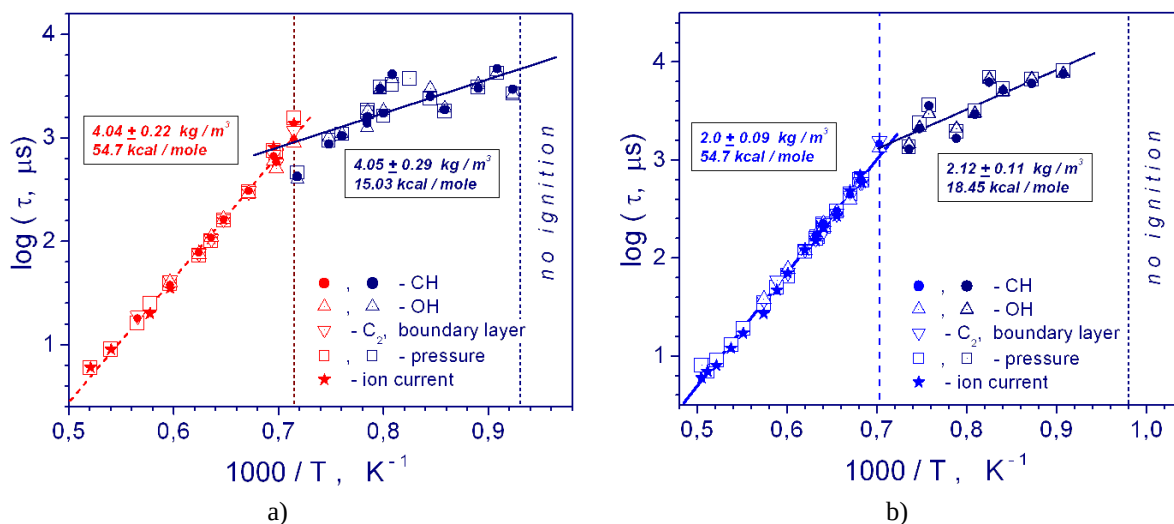


Figure 4. Ignition delay time vs. reciprocal temperature in lean $\text{CH}_4/\text{O}_2/\text{N}_2/\text{Ar}$ mixtures at compression density of $4.05 \pm 0.29 \text{ kg/m}^3$ (a) and $2.12 \pm 0.11 \text{ kg/m}^3$ (b).

In comparison with usual auto-ignition behavior of the mixture in RCM at low temperatures for compression temperatures higher than 1200 K a standard knocking phenomena in the end gas were observed in experiments. Knocking produced stable self-oscillations with amplitude approximately equal to the half height of the pressure rise induced by the normal combustion. The minimal temperature at which knocking was observed is different for stoichiometric (1200 K), lean (1250 K) and rich mixtures (1375 K).

After the induction time data for all equivalence ratios were collected the data processing algorithm was built to produce a correlation equation for shock-tube and RCM ignition delay times at studied range of conditions. This algorithm bases on the elementary model, which explains the existence of two branches of the induction time curve by the presence of two parallel processes controlling the production of initial radicals with different activation energies. Within the framework of such model it is assumed, that density of an initial radical $N_{radical}$ [mol/cm³] varies proportionally to the sum of two exponents, controlling the process rate and density of components, used at radical production (see equation 1).

$$\frac{dN_{radical}}{dt} = N_{react_component} \left(A_1 \exp\left(-\frac{U_1}{T}\right) + A_2 \exp\left(-\frac{U_2}{T}\right) \right) \quad (1)$$

Depending on the composition of the reacting mixture $N_{react_component}$ is either fuel density N_{fuel} or density of oxygen N_{O_2} (in case of rich mixtures). In order to take into account all possible situations for stoichiometric range from lean up to rich mixtures, it is possible to use interpolating dependence for effective density:

$$N_{ef} = \frac{N_{fuel} N_{O_2}}{N_{fuel} + N_{O_2}} \quad (2)$$

Having integrated the equation (1) induction time τ is determined as:

$$\tau N_{ef} = \frac{N_{A1}^* \exp\left(\frac{U_1}{T}\right)}{\left(A_{21} \exp\left(\frac{U_1 - U_2}{T}\right) + 1\right)} = \frac{2.7 \cdot 10^{-18} \exp\left(\frac{31481}{T}\right)}{\left(9.565 \cdot 10^{-9} \exp\left(\frac{31481 - 4747}{T}\right) + 1\right)} \quad (3)$$

where, τ is the ignition time in (sec), T is the temperature in (K), and N_{eff} is effective concentration in (mol/cm³), $N_{A1}^* = N_{radical}^* / A_1$ and $A_{21} = A_2 / A_1$. Unknown values in (4) were obtained by minimization procedure, which requires the best coincidence of an analytical curve with the experimental data (Fig.5).

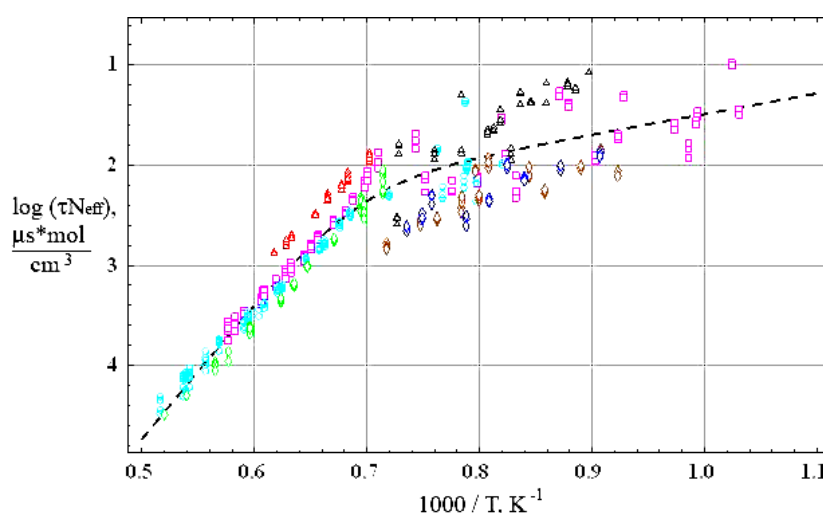


Figure 5. Normalized dependence of induction time on reciprocal temperature for high- and low-density CH₄/O₂/N₂/Ar mixtures (lean rhombi; stoichiometric squares and circles, rich triangles) and found approximation (dashed curve).

Conclusions

Ignition times of $\text{CH}_4/\text{O}_2/\text{N}_2/\text{Ar}$ mixtures for pressures of 3.8–22 atm, temperatures of 900–2100 K and stoichiometries of $\phi = 0.5$ –2 were measured in the shock tube and rapid compression machine. The RCM runs were performed for overlapping of shock-tube and RCM induction periods obtained at equivalent densities of the mixture. For studied range of conditions, the RCM runs show the significant reduction of mean activation energy of $\text{CH}_4/\text{O}_2/\text{N}_2/\text{Ar}$ mixtures up to 8.6 kcal/mol in comparison with shock-tube tests at high temperatures. Linear Arrhenius approximations of RCM results demonstrate reasonable coincidence with a high-temperature induction time curves obtained by using shock-tube techniques. For lean high-density mixture the ignition limit in the course of RCM tests was close to the temperature of $T = 1075$ K, for stoichiometric one – $T = 936$ K, and for rich one – $T = 1105$ K. The overall ignition time correlation equation for equivalence ratios $\phi = 0.5$ –2 with two activation energies of the mixture for high- and intermediate temperature regions in shock tube and rapid compress machine was proposed.

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