Methane/propane mixture oxidation at high pressures and at high, intermediate and low temperatures

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Abstract

The oxidation of methane/propane mixtures in “air” has been studied for blends containing 90% CH₄/10% C₃H₈ and 70% CH₄/30% C₃H₈ in the temperature range 740–1550 K, at compressed gas pressures of 10, 20 and 30 atm, and at varying equivalence ratios of 0.3, 0.5, 1.0, 2.0 and 3.0 in a high-pressure shock tube and in a rapid compression machine. These data are consistent with other experiments presented in the literature for other alkane fuels in that, when ignition delay times are plotted as a function of temperature, a characteristic negative coefficient behavior is observed, particularly for mixtures containing 30% propane. In addition, the results were simulated using a detailed chemical kinetic model. The model reproduces correctly the effect of change in equivalence ratio and pressure, predicting that fuel-rich, high-pressure mixtures ignite fastest while fuel-lean, low-pressure mixtures ignite slowest. Moreover, the reactivity as a function of temperature is well captured with the model predicting negative temperature coefficient behavior similar to the experiments. Quantitatively the model is faster than experiment for all mixtures at the lowest temperatures (740–950 K) and is also faster than experiment throughout the entire temperature range for fuel rich mixtures.

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1. Introduction

Fuel-flexible gas turbine engines are presently of interest to the power generation and combustion re-
day and is expected to be so until 2030. Natural gas has a low greenhouse gas signature, is energy efficient and is easy to use, in that the infrastructure needed is already in place. Although natural gas is mostly methane (CH$_4$), higher-order hydrocarbons such as ethane (C$_2$H$_6$) and propane (C$_3$H$_8$) can be present depending on its origin, extraction, and transport processes [2].

In this paper, we are concerned with methane-based fuels with even greater levels of hydrocarbons than what is typically found in natural gas. Such fuel blends can come from a variety of non-traditional sources. The resulting fuel compositional variations can impact the performance of dry low emission (DLE) industrial gas turbine engines through variations in the autoignition delay time, flame dynamics, and flame speed [3–5]. For example, in pre-mixed systems, the fuel and air are mixed prior to entering the main combustion chamber. To avoid combustion events in the pre-mixing section, the mixture’s autoignition delay time must be longer than a prescribed limit, which is design-dependent. Knowledge of a fuel–air mixture’s ignition time at engine-relevant pressures and temperatures is therefore crucial. From a fundamental perspective, ignition delay time information is also needed for the optimization of chemical kinetics models.

Some studies on the ignition of methane/propane mixtures exist in the literature [2,6–12]. While the majority of these studies considered only lower-pressure experiments, Huang and Bushe [12] considered CH$_4$/C$_3$H$_8$ ignition at pressures up to 40 atm. However, all of these past studies considered mostly mixtures near stoichiometric and with propane levels much less than 10% of the fuel blend by volume. In a recent study, the present authors considered one methane/propane blend with an 80/20 volume ratio at a pressure of 12 atm and a fuel-to-air equivalence ratio (φ) of 0.5 [13]. Even more recently, Petersen et al. [14] presented an experimental shock-tube and chemical kinetic modeling study of methane/propane/air ignition delay times over a considerably wider range of percent C$_3$H$_8$ (10–40%), stoichiometry (φ = 0.5–3.0), temperature (1042–1615 K), and pressure (6–28 atm) than previously covered.

In the present work, we extend the range of the study presented by Petersen et al. [14] to include data recorded in a rapid compression machine to lower temperatures (740–1136 K) and pressures in the range 10–40 atm. These data complement the results of the shock-tube tests, and serve to further test and validate the detailed kinetic model.

2. Experimental

2.1. Rapid compression machine

Detailed descriptions of both the rapid compression machine [15–17] and the shock tube [14,18] have been provided previously. Briefly, the NUI Galway RCM (formerly the Shell–Thornton RCM [19]) has a twin-opposed piston configuration, resulting in a fast compression time of a little more than 16 ms. Thus, heat losses during compression are low but do exist, mainly corresponding to the last 2–3 ms of compression in which most of the rapid rise in pressure and temperature takes place. In addition, creviced piston heads are used to improve the post-compression temperature distribution in the combustion chamber [15,16], but we do observe our greatest heat losses in this period and these are accounted for in our simulations, discussed below.

Experiments were carried out at a compression ratio, defined as the ratio between the volume before compression and at the end of compression, of approximately 10:1. The “effective” compression ratio was observed to be lower using pure argon as the diluent gas compared to that using pure nitrogen, due to argon’s higher thermal diffusivity. In order to vary the compressed gas temperature, $T_C$, two approaches were used: (i) the proportions of the diluent gases (N$_2$, Ar) were varied, to alter the overall heat capacity of the fuel and “air” mixture, and (ii) an electrothermal, digitally controlled heating blanket surrounds the combustion chamber of the machine such that the initial temperature is varied from ambient to a maximum operating temperature of 393 K. Sufficient time is allowed for the chamber temperature to stabilize after a change is made to the thermostat setting.

Gases used were supplied by BOC Ireland—nitrogen (CP Grade) 99.95%, argon (Research Grade) 99.9995%, oxygen (Medical Grade) 99.5%—and were used without further purification. Methane and propane gases were obtained from Aldrich at 99% purity and were used without further purification. Test mixtures were prepared manometrically in a stainless steel container and allowed to homogenize. The mixtures, Table 1, were left overnight before use, allowing on average 10 h to ensure homogeneity. The equivalence ratio given in Table 1 is defined in terms of the fuel to “air” ratio; the actual diluent composition is given in the tables of experimental results provided as supplemental material.

Pressure–time data were measured using a pressure transducer (Kistler 603B) with a response time of 1 µs and transferred via an amplifier to an oscilloscope and ultimately recorded digitally on computer. The ignition delay time, defined as the time from the end of compression to the maximum rate of pressure rise
Table 1
Molar compositions and conditions of CH₄/C₃H₈ mixtures tested

<table>
<thead>
<tr>
<th>Mix</th>
<th>% CH₄</th>
<th>% C₃H₈</th>
<th>% O₂</th>
<th>% Diluent</th>
<th>φP</th>
<th>T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90/10</td>
<td>2.40</td>
<td>0.27</td>
<td>20.44</td>
<td>76.89</td>
<td>0.3</td>
<td>10, 20, 30, 40</td>
</tr>
<tr>
<td>90/10</td>
<td>3.93</td>
<td>0.44</td>
<td>20.08</td>
<td>75.55</td>
<td>0.5</td>
<td>10, 20, 40</td>
</tr>
<tr>
<td>90/10</td>
<td>7.53</td>
<td>0.84</td>
<td>19.24</td>
<td>72.39</td>
<td>1.0</td>
<td>10, 20</td>
</tr>
<tr>
<td>90/10</td>
<td>13.90</td>
<td>1.54</td>
<td>17.76</td>
<td>66.80</td>
<td>2.0</td>
<td>30</td>
</tr>
<tr>
<td>90/10</td>
<td>19.35</td>
<td>2.15</td>
<td>16.48</td>
<td>62.01</td>
<td>3.0</td>
<td>30</td>
</tr>
<tr>
<td>70/30</td>
<td>1.49</td>
<td>0.64</td>
<td>20.55</td>
<td>77.32</td>
<td>0.3</td>
<td>30, 40</td>
</tr>
<tr>
<td>70/30</td>
<td>2.44</td>
<td>1.05</td>
<td>20.27</td>
<td>76.24</td>
<td>0.5</td>
<td>10, 20, 40</td>
</tr>
<tr>
<td>70/30</td>
<td>4.73</td>
<td>2.03</td>
<td>19.58</td>
<td>73.67</td>
<td>1.0</td>
<td>10, 20, 30</td>
</tr>
<tr>
<td>70/30</td>
<td>8.86</td>
<td>3.80</td>
<td>18.34</td>
<td>69.01</td>
<td>2.0</td>
<td>30</td>
</tr>
<tr>
<td>70/30</td>
<td>12.49</td>
<td>5.35</td>
<td>17.25</td>
<td>64.90</td>
<td>3.0</td>
<td>20, 30</td>
</tr>
</tbody>
</table>

2.2. Shock tube

Each of the shock-tube experiments was conducted in the high-pressure shock-tube facility described by Petersen et al. [18]. The mixtures and the measured data are presented in [14]. These included equivalence ratios of 0.5, 1.0, and 3.0 and CH₄/C₃H₈ splits of 90/10, 80/20, 70/30, and 60/40% by volume. The gases were mixed in a separate mixing tank using partial pressures to an accuracy of better than 1% of each volume fraction numerical value. Gas purities were ultra high purity (99.9995%) for N₂, Ar and O₂, and research grade (99.95%) for the CH₄ and C₃H₈. Further details on the experimental apparatus pertaining to the present study can be found in Petersen et al. [14].

In most cases, the shock-tube ignition delay times were derived from chemiluminescence emission from excited CH* radicals as monitored from a window located in the endwall of the shock tube. The CH* emission passed through a narrow-band filter centered at 430 nm and onto a Hamamatsu 1P21 photomultiplier tube in a homemade housing. In general, the onset of rapid CH* formation, delineated by the intersection of the steepest slope of the CH* increase with the initial (i.e., zero) value of CH*, defined the ignition delay time, as in Petersen et al. [13]. It has been shown by the authors in previous papers that the chemiluminescence diagnostic applied to the endwall location provides a reliable measurement of the ignition delay time [13,21] for undiluted mixtures such as the ones of interest herein. Simultaneous endwall pressure measurements were also taken using a microsecond-response piezoelectric transducer from PCB. Because of the large exothermicity of the ignition event, the ignition was clearly evident as a rise in endwall pressure, so the pressure measurements were used to corroborate the CH* emission measurements.

3. Computational modeling

The chemical kinetic mechanism was developed and simulations performed using the HCT (Hydrodynamics, Chemistry and Transport) program [22]. The detailed chemical kinetic model is based on the hierarchical nature of hydrocarbon combustion mechanisms containing the H₂/O₂ submechanism [23], together with the CO/CH₄ and larger hydrocarbon submech-
anisms and is based on that published in our previous work on methane/propane mixtures [14], but some changes have been made and these are discussed here. DeSain et al. [24] carried out a detailed analysis of the C$_2$H$_5$ + O$_2$ system and we have adopted their rate constant recommendations at 10 atm. We have adopted the rate constant of Hessler [25] for H + O$_2$ → O + OH, but this has had little effect on the predictions. You et al. [26] have recently reported on the rate constant for CO + HO$_2$ → CO$_2$ + OH and we have adopted their value.

Recently, Srinivasan et al. [27] studied the reaction CH$_4$ + O$_2$ → CH$_3$ + HO$_2$, and using both experimental results and calculations provided a rate constant in the temperature range 1655–1822 K. Jasper et al. [28] have calculated a rate constant expression for CH$_3$ + HO$_2$ → CH$_3$O + OH which we have also adopted. The rate constant expression for C$_2$H$_6$ + H → C$_2$H$_5$ + H$_2$ was taken from GRI-Mech 3.0 [29]. Moreover, sensitivity analysis has shown that for the prediction of ignition delay times for methane, and for ethane in particular, there is very sensitive to the rate constant of ethyl radical decomposition to ethylene and a H atom, C$_2$H$_5$ + M → C$_2$H$_4$ + H + M. We have adopted the rate constant expression recommended in GRI-Mech 3.0 [29], which is approximately a factor of two slower than the rate constant in our previous paper [14].

Other minor changes have been made to the mechanism, but the preceding description details the most significant changes. A complete listing of the detailed kinetic mechanism together with thermochemical parameters and transport data are available on the NUI Galway combustion chemistry website at http://c3.nuigalway.ie/naturalgas2.html.

3.1. Simulations

Petersen et al. [30] conducted an analytical study to supplement extreme shock-tube measurements of CH$_4$/O$_2$ ignition at elevated pressures (40–260 bar), high dilution (fuel plus oxidizer ≤30%), intermediate temperatures (1040–1500 K), and equivalence ratios as high as 6. Overall, good agreement is observed between model and experiment, although the model is slower than experiment for the highest-pressure (260 atm) measurements. This comparison was presented as part of our previous work on methane/propane mixtures [14] and even though some changes have made to the mechanism these did not adversely affect the performance of the model for these extreme mixtures.

Moreover, in this previous work we presented comparisons of shock tube experimental results versus model predictions for CH$_4$/C$_3$H$_8$ splits of 90/10, 80/20, 70/30, and 60/40% by volume in air at equivalence ratios from lean (φ = 0.5) through stoichiometric to rich (φ = 3.0) at test pressures from 5.8 to 27.5 atm, and in the temperature range 1042–1550 K. Overall, good agreement was observed between the model and the experiment.

Below we present our most recent results obtained in the RCM which complement our previous shock tube results and extend the range of study to lower temperatures. The RCM experiments by their nature involve heat losses, and it is necessary to account for these in performing model simulations. Therefore, a series of experiments was undertaken whereby oxygen was replaced by nitrogen in the test mixture in order to record pressure profiles for “unreactive” mixtures. We observed that, because the thermal diffusivities of nitrogen and argon are different (and also for CH$_4$ and C$_3$H$_8$), heat losses using various compositions of these diluent gases are also different, with those in pure argon greater than in pure nitrogen.

Thus, in performing our simulations using HCT, we treat the RCM as a homogeneous reactor (zone) with a rigid left boundary and a right boundary that can move at any specified velocity (piston velocity). A positive piston velocity is used to simulate compression and a decrease in volume, while a negative velocity is used to simulate an expansion process in which the volume increases. Experiments were simulated in three phases: (i) the compression phase, (ii) a phase immediately after the end of compression where the greatest decrease in pressure was observed in each experiment, and (iii) a phase after this to infinite time with a more constant, and lesser, pressure decrease. In simulating the compression phase we use the initial experimental mixture composition, temperature and pressure and the experimentally observed/measured compression ratio. The constant volume phases (ii) and (iii) were simulated as an adiabatic expansion process, with a greater expansion in phase (ii) compared to phase (iii). This type of simulation was proposed and used by Mittal et al. [31] in simulating their H$_2$/CO RCM experiments. We have also applied this same methodology to our recent work on propane oxidation in an RCM with reasonable success [17], in that the model was reasonably accurate in reproducing the experimental results, but there was still some disagreement between experiment and model. Comparisons of experimental results and model simulations of unreactive mixtures are provided in the supplemental material.

A series of conditions of initial pressure and temperature were tested using (i) pure argon diluent, (ii) 66% argon/33% N$_2$ diluent, (iii) 33% argon/66% N$_2$ diluent, and (iv) pure nitrogen diluent. It was found that the different input parameters to HCT had to be employed in the simulation depending on the diluent composition used, and on the initial conditions of
pressure and temperature. A comprehensive comparison of simulations versus experimental measurements of unreactive mixtures was undertaken in order to successfully simulate the pressure profiles of “unreactive” mixtures. Thereafter, the same procedure was applied to reactive mixtures. Although this simulation is physically unrealistic this treatment allows for heat losses using a zero-dimensional simulation and a more realistic simulation of the experimental conditions within the RCM.

4. Results

All ignition delay times measured in the RCM are provided in the supplemental material. Figs. 1–9 present the results of the experiments in comparison to the predictions of the detailed mechanism. For all mixtures and conditions, the effect of propane addition was to speed up the ignition process, thus producing shorter ignition delay times. As anticipated, increasing pressures also led to decreasing ignition times (Figs. 1–4).

4.1. Effect of pressure on ignition

Figs. 1–4 show comparisons of experimental results versus model predictions for methane/propane mixtures. Fig. 1 includes data for a 90% CH$_4$/10% C$_3$H$_8$ mixture at $\phi = 0.5$ in “air” at pressures of approximately 10, 20, and 40 atm. The RCM data extend the temperature range of study from 1200 K in the shock tube to approximately 850 K. A direct comparison of shock tube and RCM experimental results is available at 10 atm only, and although there is no data point at a common temperature, it is clear that both the RCM and shock tube data sets are consistent. The mechanism is also in good agreement with experiment at all conditions.

Fig. 2 shows the effect of pressure for a 90% CH$_4$/10% C$_3$H$_8$ mixture at $\phi = 1.0$ in “air” at pressures of approximately 10 and 20 atm. The RCM data show that reactivity starts at 950 K in the case of the 10 atm data but starts at 900 K at the higher pressure of 20 atm. Moreover, there is a marked change in “activation energy” as a function of temperature in the region of transition from intermediate- to high-temperature chemistry (900–1050 K at 20 atm and 950–1100 K at 10 atm). The model correctly reproduces this behavior and is in excellent agreement with the experimental results.

Similar comparisons depicting the effect of pressure are shown for 70/30 CH$_4$/C$_3$H$_8$ mixtures at $\phi = 1.0$ in “air” at 10 and 30 atm pressure, Fig. 3, and at $\phi = 3.0$ in “air” at pressures of approximately 7, 20 and 30 atm, Fig. 4. For the 70/30 mixtures we observe more pronounced low- to intermediate-temperature chemistry particularly at higher pressures, due to the higher concentration of propane.

In Fig. 3 the model is in excellent agreement with the experimental results at 10 atm. However, at 30 atm the model is consistently faster compared to experiment but does correctly capture the global features of the reactivity, predicting a rapid increase in reactivity from 720 to 780 K, the plateau in reactivity from 780 to 860 K and a rapid rise in reactivity at temperatures above approximately 880 K. Furthermore, the simulation predicts a transition from intermediate-
Fig. 2. Effect of pressure on ignition delay times for 90% CH₄/10% C₃H₈ oxidation, \( \phi = 1.0 \) in “air.” (□) RCM 10 atm, (■) shock tube 10 atm, (○) RCM 20 atm, (●) shock tube 20 atm. Solid line, HCT 10 atm; dashed line, HCT 20 atm.

Fig. 3. Effect of pressure on ignition delay times for 70% CH₄/30% C₃H₈ oxidation, \( \phi = 1.0 \) in “air.” (□) RCM 10 atm, (■) shock tube 10 atm, (○) RCM 30 atm, (●) shock tube 30 atm. Solid line, HCT 10 atm; dashed line, HCT 30 atm.

temperature to high-temperature kinetics at approximately 1000 K for the 10 atm data and at about 850 K for the 30 atm data, where we see a marked change in activation energy.

A similar comparison is shown in Fig. 4 for a fuel-rich equivalence ratio of 3.0 for a 70% CH₄/30% C₃H₈ mixture at three different average pressures: 7, 20 and 30 atm. Here we observe that at the lower pressure the model predicts longer ignition delay times and is slower compared to the high-temperature shock tube measurements. However, at the higher pressures of 20 and 30 atm the model is consistently faster compared to the RCM experiments but again it does correctly capture the global features of the reactivity, predicting a rapid increase in reactivity from 760 to 800 K, a plateau in reactivity from 800 to 860 K and a rapid rise in reactivity at temperatures above approximately 860 K. Furthermore, the simulation predicts a transition from intermediate-temperature to high-temperature kinetics at approximately 780 K for the 20 atm data and at about 820 K for the 30 atm data.

4.2. Effect of equivalence ratio on ignition

Figs. 5 and 6 illustrate the effect of equivalence ratio on ignition delay times. Fig. 5 shows data recorded for 90% CH₄/10% C₃H₈ mixtures in air at a pressure
Fig. 4. Effect of pressure on ignition delay times for 70% CH$_4$/30% C$_3$H$_8$ oxidation, $\phi = 3.0$ in “air.” (■) Shock tube 7 atm, (□) RCM 20 atm, (□) RCM 30 atm, (●) shock tube 30 atm. Solid line, HCT 7 atm; dashed line, HCT 20 atm; solid line, HCT 30 atm.

Fig. 5. Effect of equivalence ratio on ignition delay times for 90% CH$_4$/10% C$_3$H$_8$ oxidation in “air,” $\rho = 20$ and 30 atm. (□) RCM $\phi = 0.5$ (20 atm), (■) shock tube $\phi = 0.5$ (30 atm), (○) RCM $\phi = 1.0$ (20 atm), (●) shock tube $\phi = 1.0$ (20 atm), (△) RCM $\phi = 2.0$ (30 atm), (▲) shock tube $\phi = 2.0$ (30 atm), (○) RCM $\phi = 3.0$ (30 atm), (●) shock tube $\phi = 3.0$ (30 atm). Lines: HCT simulations; solid line, $\phi = 0.5$ (20 atm); dashed line, $\phi = 1.0$ (20 atm); thick solid line, $\phi = 0.5$ (30 atm); solid line, $\phi = 2.0$ (30 atm); dashed line, $\phi = 3.0$ (30 atm).

of approximately 30 atm (some data were recorded at 20 atm). It is evident that fuel-lean mixtures react most slowly, while as the mixtures become stoichiometric and more and more rich ignition occurs faster. This is due to the fact that under these conditions, low- and intermediate-temperature kinetics are controlling the oxidation process, where chain branching depends on fuel concentration. One interesting point to note in this figure is that at the highest temperatures ignition delay times for all equivalence ratios converge at approximately 1350–1400 K. This is the point at which high-temperature kinetics start to take over where the reaction $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ becomes the most important chain branching reaction and the system reactivity no longer depends on the fuel concentration but rather depends on oxygen concentration.

Fig. 5 also shows that there is excellent agreement between the model and experiment at $\phi = 0.5$ and 1.0, but for fuel rich mixtures ($\phi \geq 2.0$) at temperatures below 900 K, the model tends to under-predict ignition delay times and thus predicts a greater reactivity.
than that measured experimentally, in some cases by about a factor of two.

Fig. 6 shows data recorded for 70% CH\textsubscript{4}/30% C\textsubscript{3}H\textsubscript{8} mixtures in air at 30 atm pressure. There is overall good agreement between the mechanism and the data for these mixtures, but again the model predicts a higher degree of reactivity than that measured experimentally at low temperatures. Nonetheless, the relative effect of fuel addition is still captured very well and these results also mirror those for the 90% CH\textsubscript{4}/10% C\textsubscript{3}H\textsubscript{8} mixture in that the richer mixtures are faster to ignite compared to leaner ones.

4.3. Effect of dilution on ignition

Figs. 7–9 illustrate the effect on dilution on ignition delay time. Fig. 7 compares the effect for stoichiometric 90/10 and 70/30 CH\textsubscript{4}/C\textsubscript{3}H\textsubscript{8} mixtures in air at 10 atm. The 70/30 mixture is faster to ignite compared to the 90/10 mixture at all temperatures due to the higher concentration of propane which shows more low-temperature oxidation chemistry. For both mixtures, the chemical kinetic mechanism accurately captures the reactivity, which starts at approximately 965 K for the 90/10 mixture but at the lower temperature of 915 K for the 70/30 mixture. Moreover,
there is a marked change in activation energy at approximately 1040 K for the 90/10 mixture, while this change occurs at approximately 1000 K for the 70/30 mixture.

Fig. 8 compares the effect of dilution for rich (\(\phi = 2.0\)) 90/10 and 70/30 CH\(_4\)/C\(_3\)H\(_8\) mixtures in air at 30 atm. Again, the 70/30 mixture is faster to ignite compared to the 90/10 mixture. For both mixtures, the chemical kinetic mechanism captures the relative reactivities of these mixtures very well, but does over-predict the reactivity of the 70/30 mixture at low temperatures. Reaction starts at approximately 800 K for the 90/10 mixture but at the lower temperature of 740 K for the 70/30 mixture. Note that these mixtures show a greater amount of reactivity at lower temperature compared to the stoichiometric mixtures depicted in Fig. 7 due to both the higher fuel concentrations and higher pressure. Moreover, there is a negative temperature coefficient (NTC) region or at least a region of no dependence on temperature observed for the 70/30 mixture in the temperature range 760–820 K. This is due to the relatively high concentration of propane present which exhibits low-temperature kinetics.
Finally, Fig. 9 compares the effect of dilution for rich (\(\phi = 3.0\)) 90/10 and 70/30 CH\(_4/\)C\(_3\)H\(_8\) mixtures in air at 30 atm. Here again, the 70/30 mixture is faster to ignite compared to the 90/10 mixture and these mixtures are also relatively more reactive compared to those depicted in Fig. 8 at \(\phi = 2.0\). For both mixtures, the chemical kinetic mechanism accurately captures the reactivity, which starts at approximately 750 K for the 90/10 mixture but at the lower temperature of 730 K for the 70/30 mixture. There is also a region of no dependence on temperature observed for both mixtures; in the range 770–830 K for the 90/10 mixture and in the range 750–800 K for the 70/30 mixture. Simulations do capture the global features of the fuel mixture reactivities but tend to be faster compared to experimental measurements.

5. Conclusions

This paper presents an extensive range of experimental data for methane/propane mixtures in the temperature range 740–1550 K, at compressed gas pressures of 10, 20 and 30 atm, and at varying equivalence ratios of 0.5, 1.0, 2.0 and 3.0 in a high-pressure shock tube and in a rapid compression machine. The RCM data presented here extend the temperature window of observation of a previous study [14] to lower temperatures. In addition, a detailed chemical kinetic model which has been published previously [14] has been modified and used to simulate the data herein. Overall, the mechanism performs excellently in qualitatively capturing the major features of relative reactivities of various fuel mixtures. Moreover, in many cases there is excellent quantitative agreement between model and experiment but there is a general trend in that, for data recorded at lower temperatures (700–900 K) the model is generally faster than experiment, sometimes by up to a factor of two.

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Supplementary material

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