

Shock-Tube Ignition Delay Time Measurements and Chemical Kinetics Modelling for Mixtures of Dimethyl Ether and Methane in Air

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Abstract

Dimethyl ether (DME) is a potential biofuel of interest due to its low sooting potential as well as its high cetane number (~55) which makes it a potential ignition enhancer for compression ignition engines. It has been shown that the addition of even a small amount of DME to methane increases the reactivity of the system significantly [1, 2]. In this study, ignition delay times for mixtures of DME and methane in air were measured behind reflected shock waves at pressures varying from 1.3 atm to 35 atm over the temperature range 900 K to 1650 K. Eight sets of mixtures have been investigated with equivalence ratios of 0.3, 0.5, 1.0 and 2.0. The rate constant for the unimolecular decomposition reaction $\text{CH}_3\text{OCH}_3 (+\text{M}) = \text{CH}_3\text{O} + \text{CH}_3 (+\text{M})$ has been re-estimated and a nine-parameter Troe fit generated to describe the reaction as a function of temperature and pressure. The resulting rate expression agrees well with that recently reported by Cook *et al.* [3] in the temperature range 1300–1700 K at 1.5 atm. A mechanism consisting of 118 species and 667 reactions was used to simulate the experimental data. Overall agreement between the model and experiments is found to be good.

Introduction

Despite recent efforts to reduce pollutant emissions such as NO_x, soot, greenhouse gases, and toxic products, road transport vehicles and powertrains continue to be targeted by legislators with demands to meet ever lower emission targets. In order to achieve this, one strategy will be the implementation of new-generation biofuels synthesized from biomass to replace or to be blended with conventional petroleum-derived gasoline and fuel oil. A detailed understanding of the combustion characteristics of biofuels and their initial identification in terms of suitability and ultimate performance in engines is therefore fundamental. DME appears as an alternative biofuel/ignition enhancer for diesel fuel in compression ignition engines thanks to its high cetane number and low soot and particulate matter emissions.

DME has been widely investigated by many groups [3-16], and several chemical kinetic mechanisms have been developed and validated against a wide range of experimental data and conditions. Pfahl *et al.* [4] reported low-to-intermediate temperature shock tube ignition delay measurements for stoichiometric DME/air mixtures at high pressure (13 and 40 bar), and Mittal *et al.* [16] very recently reported DME auto-ignition in a rapid compression machine at compressed pressure from 10 to 20 bar, both studies showing negative temperature coefficient behaviour. Dagaut *et al.* [5,6] studied DME oxidation of dilute mixtures in a jet stirred reactor at 1 and 10 atm at low and intermediate temperatures and at equivalence ratios varying from fuel-lean to fuel-rich. Both low- and high-temperature flow reactor data have been reported on DME pyrolysis and oxidation along

with a chemical kinetic model [12, 13] also for a range of equivalence ratios and pressures up to 18 atm. Flame studies have also been conducted by a number of groups [7–11]. These include both laminar burning velocity determinations [9, 10, 11, 15] and species evolution as a function of the height above the burner [7, 8].

Various chemical kinetic mechanisms [6, 12, 13, 15] have been developed based on these studies covering both low- and high-temperature DME oxidation chemistry. Among the chemical kinetic modelling studies, only Zhao *et al.* [15] reports DME unimolecular decomposition rate constant expressions calculated at certain pressure intervals between its low- and high-pressure limits for both nitrogen and argon as diluent gases, through theoretical calculations.

Specific Objectives

This study constitutes an experimental and modelling study of ignition delay times of CH₄/DME mixtures in "air", and re-estimation of the pressure-dependant unimolecular decomposition reaction rate constant of DME, and shows that this calculation was needed to reproduce the experimental results at high pressures.

Apparatus and procedure

Two shock-tube facilities were used to measure the high-temperature reaction times at elevated pressures. Both facilities utilized are similar and are briefly described as follows. The first facility, described at length in Petersen *et al.* [17], has a driven section approximately 10.7 m long, an inner diameter of 16.2 cm, and a driver section 3.5 m in length with an internal

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diameter of 7.62 cm. The second facility, described by Aul *et al.* [18], has a driven section 4.72 m in length with an internal diameter of 15.24 cm and a driver section 4.93 m long with an internal diameter of 7.62 cm. Both facilities utilize one-dimensional shock relations along with the measured incident-shock velocity at the test region to determine the overall conditions behind the reflected shock. The incident-shock velocity is measured by using four Fluke PM 6666 timer counter boxes which are linked to five pressure transducers (PCB 113) in series located along the side of the shock tube. The counters are used to extrapolate the incident-shock velocity at the end wall.

Chemical reactions which occur behind the reflected shock wave are detected using piezoelectric pressure transducers (PBB 134A and Kistler 603B1) and photomultiplier tubes (Hamamatsu 1P21) located at the endwall and the sidewall (one cm from the endwall). The experiments conducted in this study used the time history of the activated complex CH^* . The endwall and sidewall locations were equipped with CaF_2 windows aligned with photomultipliers using 430 ± 5 nm filters to isolate the CH^* chemiluminescence near 430 nm. GaseScope oscilloscope boards and software were used for data acquisition using sampling rates of at least 1 MHz per channel and 14-bit resolution.

Ignition Time Definition

For these real fuel/air mixtures, significant pressure rises are associated with combustion. Therefore, ignition delay times are determined by measuring the pressure rise at the endwall. Endwall emission traces from the activated complex CH^* are also used to provide qualitative results for comparison. Example pressure and emission traces are provided in Fig. 1. In many of the experiments, a slight pressure rise was observed prior to the main ignition event.

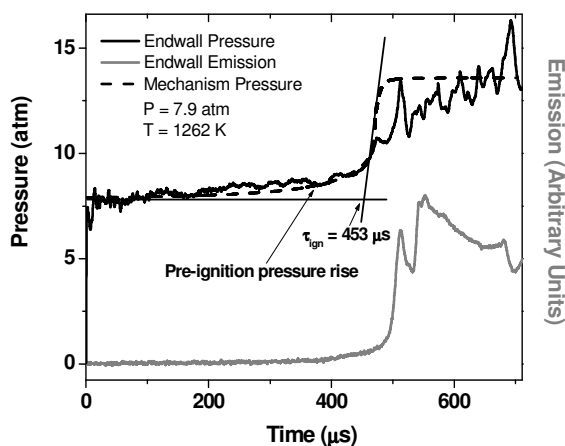


Fig. 1 Experimental and mechanism pressure traces for a typical mixture, $\phi = 0.3$, 60% v/v. CH_4 , 40% v/v. DME, $P = 7.9$ atm and $T = 1262$ K showing definition of ignition delay time. Both the measured and calculated pressure histories reveal a slight pressure rise before ignition.

As shown in Fig. 1, the chemical kinetic model described herein was run for the same conditions as the experiments assuming constant internal energy and volume conditions and shows a similar pre-ignition pressure rise. Because the pressure increase is predicted by the mechanism, the pressure rise for the mixtures and conditions herein was determined to be due to the kinetics, most likely resulting from DME decomposition, and is not due to non-ideal shock-tube effects or premature ignition that have been pointed out recently in shock-tube studies at elevated pressures and lower temperatures [19, 20].

Results and Discussion

Eight mixtures of CH_4/DME in fuel ratios of 80/20 and 60/40 by volume, and at equivalence ratios of 2.0, 1.0, 0.5 and 0.3 have been investigated and are given in Table 1. These mixtures have been simulated using NUIG C3 detailed mechanism composing of 118 species and 667 reversible reactions. Each mixture is treated at three different pressure levels between 1.5 and 30 atm.

Table 1. Methane + DME mixture compositions

Mixture	Φ in "air"	DME %	Methane %
1	2	20	80
2	1	20	80
3	0.5	20	80
4	0.3	20	80
5	2	40	60
6	1	40	60
7	0.5	40	60
8	0.3	40	60

Rate constants for the unimolecular decomposition reaction $\text{CH}_3\text{OCH}_3 (+\text{M}) = \text{CH}_3\text{O} + \text{CH}_3 (+\text{M})$ have been calculated through generation of Troe fall-off constants and are presented in a 9-parameter Troe form so as to describe it as a function of pressure as well as temperature. The rate constant of the high pressure limit has been calculated through microscopic reversibility assuming a rate expression of $2.0 \times 10^{13} \text{ cm}^3/\text{mol}\cdot\text{s}$ for the recombination of CH_3 and CH_3O .

Figure 2 is the plot of the corresponding rate constant at 1 atm pressure compared with literature and calculated in this study. In treating mixtures with Ar as diluent rather than N_2 , efficiency is taken as 0.7, and the resulting rate expression is also plotted on the same figure. This rate constant expression agrees well with that recently reported by Cook *et al.* [3], Ar being the bath gas, at 1.5 atm. in their experimental validity range of 1349–1718 K. However, in order to facilitate comparison their rate constant is plotted here between 1000 and 2000 K using their reported expression of $k = 1.61 \times 10^{79} T^{-18.4} \exp(-58600/T) \text{ s}^{-1}$. For temperatures smaller than ~ 1300 K, our rate constant is slower than that of Cook *et al.* On the other hand at temperatures up to 1700 K, our calculated rate constant is faster than the Zhao *et al.* expression.

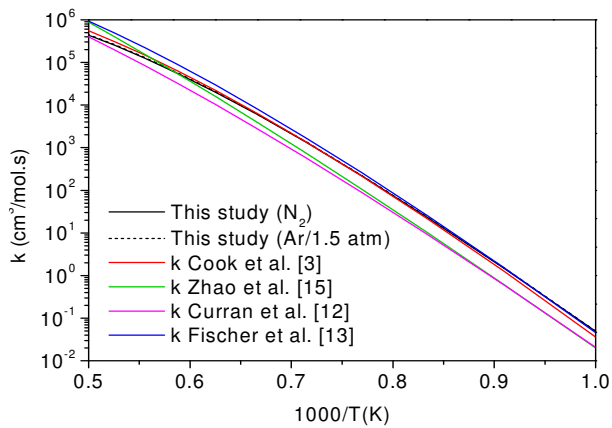


Fig. 2 Plot of reaction rate constant for $\text{CH}_3\text{OCH}_3 (+\text{M}) = \text{CH}_3\text{O} + \text{CH}_3 (+\text{M})$ at 1 atm. Comparison between the calculated rate constant in this study with literature [3, 12, 13, 15]. Cook *et al.* rate expression is plotted at 1.5 atm as given in their study.

Re-estimation of DME unimolecular decomposition rate constants

Ignition delay times of CH_4/DME mixtures are very sensitive to the unimolecular decomposition reaction of DME as given by the sensitivity analysis in Fig 3 performed at 1320 K, and equivalence ratios of 0.5 and 2.0 respectively. Experiments performed in this study range from 1.3 atm to 35 atm in pressure. Therefore an expression for the pressure dependence would be necessary. As mentioned in the introduction, Zhao *et al.* [15] computed the rate expression for pressure ranges by an order of magnitude, however that expression is slower by about a factor of two as seen in Fig 2. Integration of the calculated rate constant made it possible to calculate ignition delay times for these high pressures.

Comparisons of the simulations of all 8 mixtures with the experimental ignition delay times are shown in Fig 4, from $\phi = 2.0$ to $\phi = 0.3$, respectively. In most of the cases, calculated ignition delay times agree well with experiments, in rich cases, there is slight under-prediction of the ignition delay times.

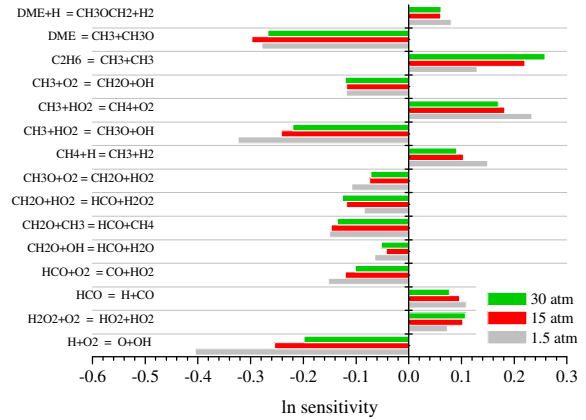
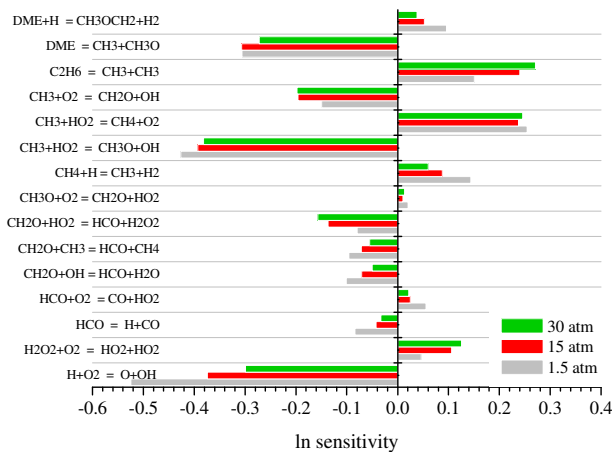
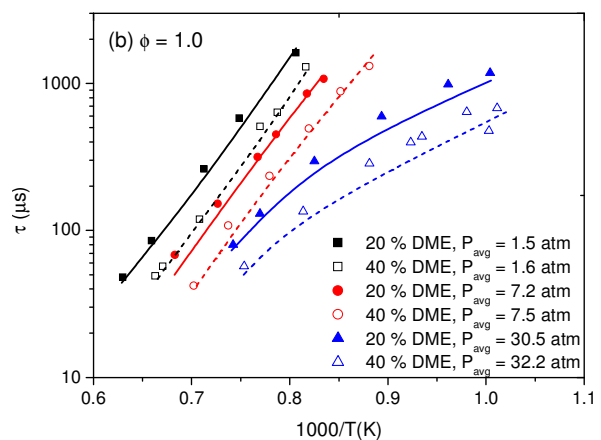
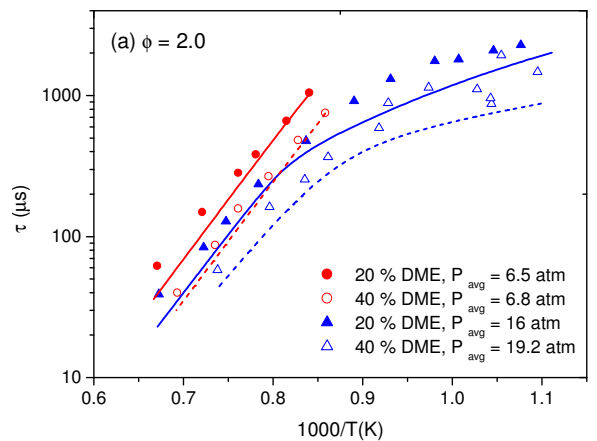


Fig. 3 Ignition delay sensitivity analysis for 20% DME in fuel CH_4/DME mixture at 1320 K for $\phi = 0.5$ and 2.0 respectively

Effect of fuel composition on ignition

In all cases, calculations confirm the experimental evidence that increasing the concentration of DME (going from 20% to 40% v/v of the fuel) in the mixture increases the reactivity of the system and eventually leads to faster ignition (by about a factor of 2) at a given temperature, pressure level and equivalence ratio.



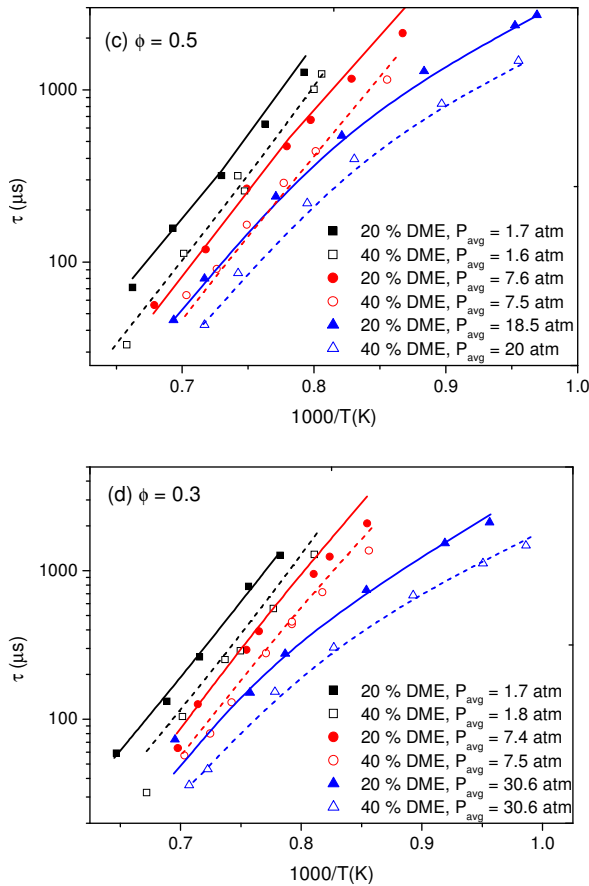


Fig. 4 Experimental and calculated ignition delay times for CH_4/DME mixtures, filled symbols and solid lines represent mixtures with 20% v/v DME while open symbols and dotted lines represent mixtures with 40% v/v DME.

Effect of pressure on ignition

For all mixtures studied, at all equivalence ratios and fuel compositions, higher pressures result in increased reactivity and therefore shorter ignition delay times were measured experimentally, and this behaviour is also captured by the model.

Effect of equivalence ratio on ignition

Figure 5 illustrates the effect of equivalence ratio on ignition time. Only equivalence ratios of 2.0, 1.0 and 0.5 are shown on the figures; $\phi = 0.3$ is omitted for the sake of clarity. The fuel lean mixtures react slightly slower than the stoichiometric ones and the fuel rich mixtures for temperatures up to roughly about 1300–1400 K. For temperatures higher than that, the trend is the reverse. This is due to the fact that the chain branching reaction $\text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH}$ dominates high-temperature chemistry. Thus, lean mixtures tend to ignite fastest and rich mixtures slowest at regions where high-temperature chemistry is dominant.

On the other hand, at relatively lower temperatures, we observe that rich mixtures tend to ignite easier than the lean. Moreover, sensitivity analysis (Fig. 3) shows that in these conditions the chain branching reaction is still effective.

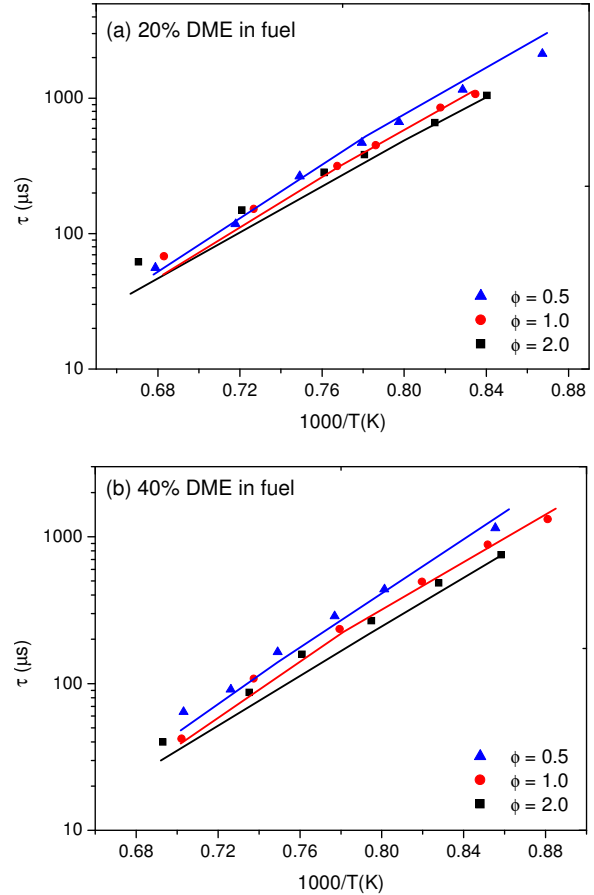


Fig. 5 Experimental and calculated ignition delay times at an average pressure of 7 atm. (a) mixture with 20% v/v DME in fuel (b) mixture with 40% v/v DME in fuel (lines are model predictions)

Simple inspection of the oxidation chemistry of the system given in Fig. 6 and the sensitivity analysis emphasize the contribution of DME to the build-up of the radical pool. CH_4 is consumed by molecular oxygen to give methyl (CH_3) and hydroperoxyl (HO_2) radicals. When there is DME in the system, its unimolecular decomposition becomes important. This brings CH_3 and CH_3O to the system, which then quickly gives CH_2O and H . Once there are enough CH_3 and HO_2 radicals, these react yielding OH and more CH_3O to the environment, which eventually enhances the chain branching reaction $\text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH}$. Therefore introduction of DME speeds up significantly the radical pool build-up. On the other hand, the chain branching reaction between CH_3O radicals with molecular oxygen also increases the reactivity of the whole system for rich mixtures (where there is more fuel and therefore more methyl and methoxy radicals), and is of nearly no effect for lean mixtures, Fig 3. These experimental trends are captured by the model as well.

In order to emphasize the dominant effect of the DME in the mixture, 20% DME in fuel mixture has been compared with pure CH_4 , pure DME and a fictional 5% DME in fuel mixtures in terms of ignition delay times, and model results are plotted on Fig. 7.

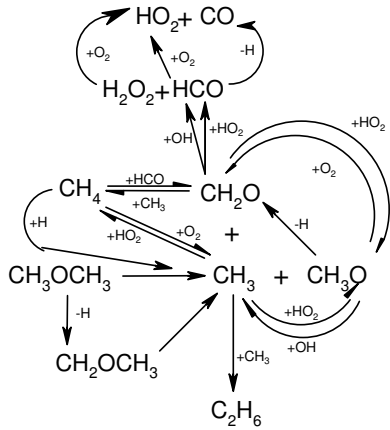


Fig. 6 Simplified oxidation route for CH₄/DME system

Ignition delay times for pure methane are considerably higher than pure DME -by two orders of magnitude- and are higher than ones of the mixtures as well. The fictional mixture with 5% v/v DME in fuel, results in a decrease of about an order of magnitude in ignition delay time compared to pure methane, this has also previously been pointed out by Chen *et al.*[3].

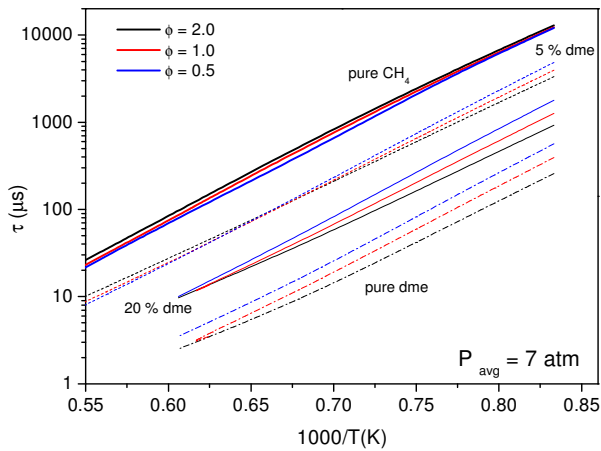
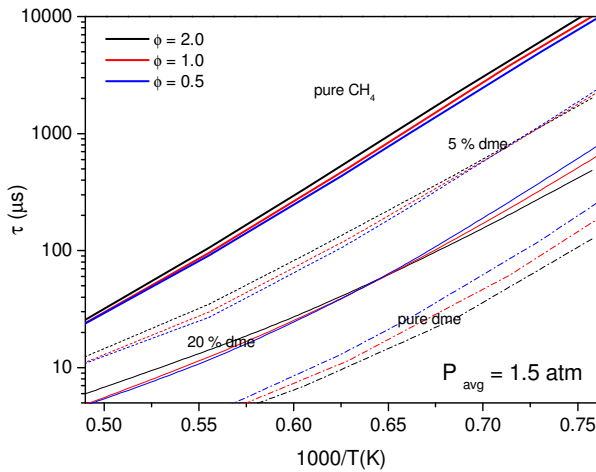


Fig. 7 Calculated ignition delay times for pure CH₄, pure DME, and 5% DME and 20% DME in CH₄ mixtures at 1.5 atm and 7 atm of average pressures respectively.

Actually, even the addition of 1% DME in the fuel (so that the fuel is 1% v/v DME and 99% v/v CH₄) causes a non-negligible reduction in ignition delay times, reducing it to about its half. Although, this has not been experimentally studied here, a modelling result is given in Fig. 8 in order to visualize this effect.

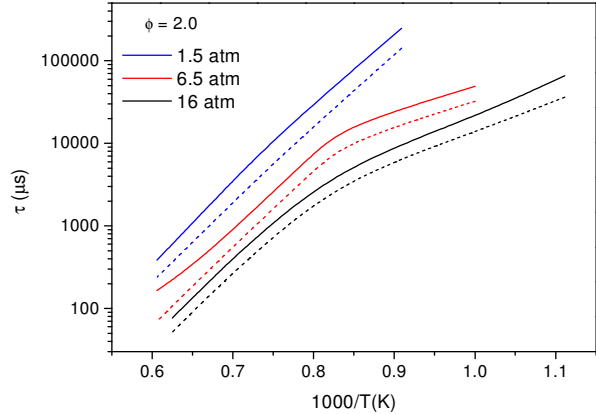


Fig. 8 Calculated ignition delay times for pure CH₄ (solid lines) and a mixture of 1% DME v/v in fuel (dashed lines) at $\phi = 2.0$

As far as the effect of equivalence ratio is concerned, pure methane shows a conventional trend where the rich mixture ignites slower than the lean mixture, in the given temperature range. Pure DME, as well as 10% and 20% v/v DME in fuel mixtures, show the inverse trend explained above. Therefore, even a small part of DME addition could lead the system to behave like pure DME at a certain temperature range, and this effect is even more pronounced at higher pressure.

Laminar flame speeds for CH₄/DME mixtures

Chen *et al.* [2] calculated laminar burning velocities for mixtures of CH₄ with DME for various blends of CH₄ showing an increase in the flame speed by addition of DME due to its contribution to the build-up of the radical pool.

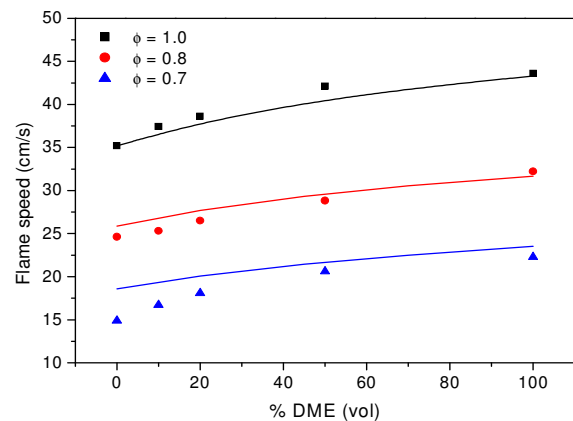


Fig. 9 Laminar flame speed of CH₄/DME blends with varying ratio of DME at 298 K, 1 atm. (Lines are model predictions)

Model calculations are performed on PREMIX module of CHEMKIN-PRO application [21] and are given in Fig 9. The model over-predicts flame speeds by a maximum of 20% on methane rich side for the leanest mixture.

Conclusions

This study deals with ignition characteristics of DME and methane mixtures in "air". It involves a wide range of shock-tube ignition delay data at pressures of approximately 1.5 - 7 - 20 or 30 atm and equivalence ratios of 0.3 - 0.5 - 1.0 - 2.0 and in the temperature range of 950-1650 K. This work also involves the re-determination of the pressure-dependent unimolecular decomposition rate constants of DME in form of Troe fit in order to be able to do calculations at high pressures. Therefore, the calculated rate constant expression can be used for a wide pressure range and also agrees well within a range with the most recent experimental unimolecular decomposition rate constant by Cook *et al.* [3]. The effect of DME addition to CH₄ is discussed, and it is experimentally and computationally shown that even small proportions of DME contribute to the build-up of the radical pool to a great extent by generating methyl and methoxy radicals. Model comparisons with the experiments are also presented. Overall, the mechanism captures the experimental trends and is mostly in good agreement with the data.

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