Experimental and Modeling Study on Ignition Delay Times of Dimethyl Ether/Propane/Oxygen/Argon Mixtures at 20 bar

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ABSTRACT: Ignition delay times of dimethyl ether (DME)/propane/oxygen/argon mixtures at a pressure of 20 bar were measured in a shock tube at different DME blending ratios (0, 20, 50, 80, and 100%), equivalence ratios (0.5, 1.0 and 2.0), and temperatures (1100–1500 K). Validations of chemical kinetic models were made using available chemical kinetic models. A modified chemical model (Mod Mech C5) was proposed, and it can predict well the experimental ignition delay times and activation energies of pure propane, pure DME, and their blends. Both experimental and numerical results show that, with the decrease of the temperature, the logarithmic ignition delay time is increased linearly and activation energy is decreased slightly. With the increase of the equivalence ratio, the ignition delay time is increased for propane but decreased for DME. The ignition delay time is decreased with the increase of the DME blending ratio, and the reduction rate is increased with an increase in the equivalence ratio. Sensitivity analysis and radical pool analysis were performed to interpret the promoting effect of DME addition on the ignition of DME/propane mixtures.

1. INTRODUCTION

With the rapid development of the global economy, the number of vehicles has increased significantly, especially in developing countries. This increases the demand on oil supply and the burden on the environment. Therefore, use of alternative fuels and development of high-efficiency combustion technology become the important issues for engine and combustion researchers.

Homogeneous charge compression ignition (HCCI) is a promising combustion technology for internal combustion engine. Low-temperature combustion leads to low emissions of NOx and particulate matter (PM). The ignition and combustion process of a HCCI engine are controlled by chemical kinetics; therefore, the controlling of ignition timing and combustion phasing are important issues for HCCI combustion engine. There have many approaches to realize HCCI combustion. Fuel blending is one of the effective ways. Adjustment of the autoignition property of the fuel through fuel blending can match the different operation conditions of HCCI engine. The combination of a high octane number fuel with another high cetane number fuel is usually used to control the ignition chemistry of fuel mixtures.

Dimethyl ether (DME) is a promising alternative fuel because of its properties. It has good autoignition property at low-temperature ranges, and makes soot-free combustion because of its molecular structure. In the autoignition process, DME shows a two-stage chemical reaction and heat release phenomenon at low and high temperatures. This property is similar to those of higher hydrocarbons, such as diesel. To extend the operation regimes of HCCI combustion engine fueled with DME, blending of another fuel, which has high octane number, can adjust the ignition timing and combustion phasing of the HCCI combustion engine and meet various engine loads, for example, DME and hydrogen blend, DME and methanol blend, DME and methane blend, DME and liquefied petroleum gas (LPG) blend, and DME and n-butane blend.

Propane with high octane number is the major component of LPG. It can be pressurized into the liquid stage under a moderate pressure at room temperature, making the onboard storage easier. This property is very similar to that of DME. Therefore, DME/propane blends are selected as the tested fuels in this study. Results from HCCI combustion engines fueled with DME and DME–hydrocarbon blends has been studied in previous literature. Huang et al. showed that ultralow NOx emissions could be realized without smoke emission in a HCCI combustion engine fueled with DME. Sato et al. showed that DME can improve the ignition of methane in a HCCI combustion engine. Kong et al. simulated the HCCI combustion of DME and natural gas blends with the detailed chemical kinetic mechanism and showed that the ignition could be enhanced by DME addition at low-temperature oxidation. Chen et al. and Li et al. concluded that the HCCI combustion engine fueled with LPG could operate over a wide range of loads with near zero NOx emission and high efficiency in the case of DME addition. Iida et al. realized the HCCI combustion at different engine loads by controlling the DME blending ratio and exhaust gas recirculation (EGR) ratio in a HCCI combustion engine fueled with DME/n-butane blends. Previous engine studies showed that controlling of ignition timing is very important for HCCI combustion in an engine fueled with DME and hydrocarbon blends.

Ignition delay time is very important to affect the HCCI combustion engine, and it is also important to develop and validate the chemical kinetic models. Fundamental research on...
pure DME and DME/hydrocarbon blends were reported in the literature.\textsuperscript{12–17} Mittal et al.\textsuperscript{12} measured the ignition delay time of DME/O\textsubscript{2}/N\textsubscript{2} mixtures at high pressures and low temperatures. A two-step ignition phenomenon was presented, and this behavior is more obvious at low-pressure conditions. Dagaut et al.\textsuperscript{13} and Cook et al.\textsuperscript{14} studied the ignition delay times of DME/O\textsubscript{2}/Ar mixtures at high temperatures, indicating that Zhao’s DME model could predict well the experimental ignition delay times. Amano et al.\textsuperscript{15} simulated that DME could enhance the ignition of methane—air mixtures. Chen et al.\textsuperscript{16} and Tang et al.\textsuperscript{11} studied the DME addition effect on the high-temperature ignition of methane. They concluded that the addition of small amounts of DME could lead to an obvious reduction of the ignition delay time. Thus far, most studies on the ignition delay times of DME/hydrocarbon blends focused on DME/methane blends, but ignition delay times of DME/propane blends have not been investigated as much. Thus, the ignition delay times of DME/propane blends are important to control the HCCI combustion engines and develop chemical kinetic models.

In this study, ignition delay times of DME/propane/oxygen/argon mixtures were measured using a shock tube at different equivalence ratios, DME blending ratios, and elevated pressure. A modified chemical kinetic model was proposed. Additionally, chemical kinetics analysis was performed with the modified model. Sensitivity analysis and radical pool analysis were performed to well understand the ignition chemistry because of DME addition.

### 2. EXPERIMENTAL SECTION

Ignition delay times were measured in a shock tube, and the detailed experimental setup have been described in the previous literature.\textsuperscript{18,19}

Figure 1 shows the definition of the ignition delay time (\(\tau\)), the time interval between the time at incident shock wave arrived at the endwall, and the intercept of the maximum slope of the CH\(*\) signal with the baseline.

Ignition delay times of DME/propane/oxygen/argon mixtures were tested at equivalence ratios of 0.5, 1.0, and 2.0. The fuel mixtures were prepared referenced by Herzler and Naumann.\textsuperscript{20} The fuel/oxygen/argon mixtures (\(\phi = 0.5, 1.0, \text{and} 2.0; X_{O_{2}}/X_{Ar} = 21/79\%\)) were diluted with argon (20% mixture/80% argon, defined at a dilution ratio of 1:5), as shown in Table 1. The DME blending ratio (DME) is defined as \(\phi_{DME} = X_{DME}/(X_{DME} + X_{propane})\), where \(X_{propane}\) and \(X_{DME}\) are the mole fractions of propane and DME, respectively. The pressure at post-reflected shock wave (p) is set as 20 bar. Ignition temperatures (T) are calculated with Gaseq.\textsuperscript{21} Purities of DME, propane, oxygen, and argon are 99.9, 99.9, 99.995, and 99.995\%, respectively.

### Table 1. Composition of Fuel Mixtures

<table>
<thead>
<tr>
<th>mixtures</th>
<th>(X_{DME}) (%)</th>
<th>(X_{O_{2}/Ar}) (%)</th>
<th>(X_{O_{2}}) (%)</th>
<th>(X_{Ar}) (%)</th>
<th>(\phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DME00</td>
<td>0.00</td>
<td>0.41</td>
<td>4.11</td>
<td>95.48</td>
<td>0.5</td>
</tr>
<tr>
<td>DME50</td>
<td>0.26</td>
<td>0.26</td>
<td>4.09</td>
<td>95.40</td>
<td>0.5</td>
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<tr>
<td>DME100</td>
<td>0.68</td>
<td>0.00</td>
<td>4.06</td>
<td>95.27</td>
<td>0.5</td>
</tr>
<tr>
<td>DME00</td>
<td>0.00</td>
<td>0.81</td>
<td>4.03</td>
<td>95.16</td>
<td>1.0</td>
</tr>
<tr>
<td>DME20</td>
<td>0.17</td>
<td>0.70</td>
<td>4.02</td>
<td>95.11</td>
<td>1.0</td>
</tr>
<tr>
<td>DME50</td>
<td>0.50</td>
<td>0.50</td>
<td>3.99</td>
<td>95.01</td>
<td>1.0</td>
</tr>
<tr>
<td>DME80</td>
<td>0.93</td>
<td>0.23</td>
<td>3.96</td>
<td>94.88</td>
<td>1.0</td>
</tr>
<tr>
<td>DME100</td>
<td>1.31</td>
<td>0.00</td>
<td>3.93</td>
<td>94.77</td>
<td>1.0</td>
</tr>
<tr>
<td>DME00</td>
<td>0.00</td>
<td>1.55</td>
<td>3.87</td>
<td>94.58</td>
<td>2.0</td>
</tr>
<tr>
<td>DME20</td>
<td>0.33</td>
<td>1.34</td>
<td>3.85</td>
<td>94.48</td>
<td>2.0</td>
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<tr>
<td>DME50</td>
<td>0.95</td>
<td>0.95</td>
<td>3.80</td>
<td>94.30</td>
<td>2.0</td>
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<tr>
<td>DME80</td>
<td>1.76</td>
<td>0.44</td>
<td>3.74</td>
<td>94.06</td>
<td>2.0</td>
</tr>
<tr>
<td>DME100</td>
<td>2.46</td>
<td>0.00</td>
<td>3.68</td>
<td>93.86</td>
<td>2.0</td>
</tr>
</tbody>
</table>

### 3. CHEMICAL KINETIC MODEL

Calculations were performed using Senkin\textsuperscript{22} and Chemkin\textsuperscript{23} with the constant volume adiabatic model. The calculated ignition delay time is obtained by the maximum increase rate of the temperature profile (maximum \(dT/dt\)) in this study.

A well-developed binary fuel model should give good prediction on both the individual fuel and the fuel blends. Figure 2 gives the measured and calculated ignition delay times of propane, DME, and DME50 mixtures at three equivalence ratios with two available chemical models. Figure 2a gives the experimental and calculated ignition delay times of propane at equivalence ratios of 0.5, 1.0, and 2.0. Because propane is the typical hydrocarbon fuel and its chemical mechanism has been well-validated, calculations with both USC Mech 2.0\textsuperscript{24} and NUI Mech C5\textsuperscript{25} model (nC5_49) show good agreement with the experimental results. Figure 2b indicates the experimental and calculated ignition delay times of DME. Prediction with Zhao’s DME model\textsuperscript{26} shows good agreement with the experimental results at three equivalence ratios and pressure of 20 bar. The NUI Mech C5 model underpredicts the ignition delay times especially at high temperatures.

To better simulate ignition delay times of DME/propane blends, the DME submodel in NUI Mech C5 is substituted by the DME submodel from Zhao’s DME model. Thus, a modified binary fuel model named Mod Mech C5 is obtained, in which the elementary reactions of C\(_1\)–C\(_4\) hydrocarbon oxidation and their rate coefficients are totally taken from the NUI Mech C5 mechanism and the elementary reactions of DME oxidation and their rate coefficients are totally taken from Zhao’s DME model. It consists of 295 species and 1584 elementary reactions (see the Supporting Information).

The calculated ignition delay times with the Mod Mech C5 in solid lines are presented in Figure 2. Because the hydrocarbon oxidation model of the Mod Mech C5 is taken from the NUI Mech C5, the calculated values of pure propane with the two models are identical, indicating that the solid lines overlap the dotted lines. The DME submodel of Mod Mech C5 is from Zhao’s DME model, and the calculated values of DME with Mod Mech C5 and Zhao’s DME model only show a little difference when different hydrocarbon oxidation models are used.

Validation shows that the Mod Mech C5 model can predict well the experimental results on both ignition delay time and activation energy at three equivalence ratios for the pure propane, pure DME, and their blends (DME50). Therefore, the Mod Mech C5 model is used to analyze the ignition kinetics in
this study. The logarithmic ignition delay time increases linearly, and activation energy decreases slightly with the decrease of the temperature for both propane and DME. However, with an increase in the equivalence ratio, the ignition delay time of propane is increased but that of DME is decreased.

4. RESULTS AND DISCUSSION

4.1. Ignition Delay Time Measurement. Ignition delay times of DME/propane blends were measured at the temperature range from 1100 to 1500 K, DME blending ratios of 0–100%, and equivalence ratios of 0.5–2.0. The measured ignition delay times of this study are summarized in the Supporting Information. The experimental ignition delay times at high temperature show the Arrhenius dependence upon the temperature. Therefore, a fitted correlation of ignition delay times as a function of $\phi$ and $T$ can be obtained through the regression analysis

$$\tau = A\phi^n \exp\left(E/RT\right)$$

where $\tau$ is the ignition delay time in $\mu$s, $R = 1.986 \times 10^{-3}$ kcal mol$^{-1}$ K$^{-1}$ is the universal gas constant, $T$ is the temperature in kelvin, and $\phi$ is the equivalence ratio. Ignition delay times of propane give a positive dependence upon the equivalence ratio, while those of DME give a negative dependence upon the equivalence ratio, as shown in Table 2. This is consistent with the results in Figure 2. The experimental ignition delay times and fitted results with eq 1 are shown in Figure 3. It is shown that increasing the DME blending ratio can accelerate the ignition.

4.2. Effect of DME Addition on Ignition Delay Times.

Figure 4 shows the comparison of results between the experimental and calculated ignition delay times of DME/propane/oxygen/argon mixtures at lean, stoichiometric, and rich mixtures. The NUI Mech C5 underpredicts the experimental values and overpredicts the activation energy for all mixtures at different DME blending ratios. The Mod Mech C5 can predict well the ignition delay times, and it can also capture the slight variation of activation energy with the changing of the temperature and DME blending ratio. The results indicate that pure propane gives the largest ignition delay times, while pure DME gives the smallest. Ignition delay times of fuel blends have the values between those of pure propane and DME. With an increase in the DME blending ratio, the ignition delay time and activation energy are decreased at three equivalence ratios.

Table 2. Correlation Parameters for DME/Propane Mixtures

<table>
<thead>
<tr>
<th>mixtures</th>
<th>A</th>
<th>n</th>
<th>$E$ (kcal/mol)</th>
<th>$R^2$</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DME00</td>
<td>$9.95 \times 10^{-5}$</td>
<td>0.514</td>
<td>39.8 ± 1.1</td>
<td>0.984</td>
<td>0.5–2.0</td>
</tr>
<tr>
<td>DME20</td>
<td>$9.38 \times 10^{-4}$</td>
<td>0.566</td>
<td>33.3 ± 1.5</td>
<td>0.972</td>
<td>1.0–2.0</td>
</tr>
<tr>
<td>DME50</td>
<td>$2.33 \times 10^{-4}$</td>
<td>0.071</td>
<td>36.9 ± 1.1</td>
<td>0.982</td>
<td>0.5–2.0</td>
</tr>
<tr>
<td>DME80</td>
<td>$7.07 \times 10^{-4}$</td>
<td>0.111</td>
<td>33.2 ± 1.0</td>
<td>0.988</td>
<td>1.0–2.0</td>
</tr>
<tr>
<td>DME100</td>
<td>$2.66 \times 10^{-4}$</td>
<td>$-0.429$</td>
<td>35.5 ± 1.2</td>
<td>0.976</td>
<td>0.5–2.0</td>
</tr>
</tbody>
</table>

The logarithmic ignition delay time decreases linearly with an increase in the DME blending ratio at three equivalence ratios and temperatures. The logarithmic ignition delay time decreases linearly with an increase in the DME blending ratio at three equivalence ratios and temperatures, but the reduction rates at three equivalence ratios are different. These behaviors are different from those of DME/methane mixtures investigated by Tang et al. In their study, the logarithmic ignition delay time showed a nonlinear decrease dependence upon the variation of DME blending ratios.

To quantitatively understand the DME addition effect on the ignition delay time, the reduction rate of ignition delay time (RR) is defined as

$$RR = \frac{\tau_{C_3H_8} - \tau_{DME}}{\tau_{C_3H_8}} \times 100\%$$

Figure 5 gives the comparisons of the calculated ignition delay time at three equivalence ratios and temperatures. The logarithmic ignition delay time decreases linearly with an increase in the DME blending ratio at three equivalence ratios and temperatures, but the reduction rates at three equivalence ratios are different. These behaviors are different from those of DME/methane mixtures investigated by Tang et al. In their study, the logarithmic ignition delay time showed a nonlinear decrease dependence upon the variation of DME blending ratios.
where $\tau_{\text{C}_3\text{H}_8}$ is the ignition delay time of propane, $\phi_{\text{DME}}$ is the DME blending ratio, and $\tau_{\phi_{\text{DME}}}$ is the ignition delay time at $\phi_{\text{DME}}$.

Figure 6 shows the reduction rate of the ignition delay time at different DME blending ratios. The variation of the ignition delay time with an increasing DME blending ratio becomes obvious when the mixtures change from lean to rich. With an increase in the DME blending ratio, the ignition delay times decrease slightly for the lean mixtures and decrease remarkably for the rich mixtures. In other words, the variation of the ignition delay time is obvious at high fuel concentrations. This indicates that the effect of DME addition on ignition delay times of DME/propane mixtures is sensitive on the fuel concentration. The reduction rates of the ignition delay time are changed insignificantly at different temperatures.

### 4.3. Sensitivity Analysis

Sensitivity analysis on the ignition delay time is also conducted. Figure 7 gives the 10 most important sensitive reactions for the DME/propane blends at $p = 20$ bar and $T = 1350$ K. The normalized sensitivity coefficient is defined as $S = (\tau(2.0k) - \tau(0.5k))/$
1.5τ(k_i), where τ is the ignition delay time and k_i is the pre-exponential factor of the i-th reaction. A positive value of S indicates the inhibited influence on ignition and vice versa.

In the pure propane mixture (DME00), the chain-branching reaction (R1), which dominates the ignition, gives the highest negative sensitive coefficient. The ignition delay time is also sensitive to the unimolecular decomposition reaction of propane consumption (R404), which produces the reactive CH_3 and C_2H_5 radicals. Additionally, through the chain propagation reaction (R109), the CH_3 radical is consumed to generate the reactive OH radical, which increases the radical pool concentration. The propane consumption reaction by H abstraction (R409 and R410) competes with both the chain-branching reaction (R1) for the H radical and the unimolecular decomposition reaction (R404) for C_3H_8, and it gives the highest positive sensitivity coefficient. The chain termination reaction (R110) consumes the reactive HO_2 radical, produces the stable species of CH_4 and O_2, and inhibits the ignition. The chain recombination reaction (R151) is another important ignition inhibition reaction, which decreases the CH_3 radical concentration in the radical pool. Among these seven important elementary reactions, three reactions (R404, R409, and R410) relate to the propane molecule and the rest of the four reactions (R1, R109, R110, and R151) are the small-molecule participation reactions.

In the DME mixture (DME100), R1 also shows the highest negative sensitivity coefficient. The unimolecular decomposition reaction of DME (R353) is also important for promoting the ignition. R353 produces CH_3 and CH_3O, which are the major radicals of chain reactions. The CH_3 radical subsequently reacts with the DME molecule and forms the CH_3OCH_2.
radical through reaction R356. With an increase in CH3 and HO2 radical concentrations, the chain-branching reaction (R109) becomes important. The CH3O radical from R353 and R109 is very reactive, and it quickly generates the CH2O molecule by the dehydrogenation reaction. Thus, CH3O and HO2 through reaction R47 yield more reactive HCO and H2O2 radicals, and H2O2 reacts quickly to yield two OH radicals. These chain reactions have high negative sensitivity coefficients and increase the radical pool growth. The main inhibition reactions are R110 and R151.

With an increase in the DME blending ratio, the sensitivity coefficient of R1 is decreased and those of R353 and R356 related to the DME molecule are increased obviously. More CH2O radicals are generated with DME addition, indicating that R47 becomes more important in the ignition promotion. Sensitivity coefficients of R404, R409, and R410 are decreased because of the decrease of the propane fraction in DME/propane mixtures. The other small radical reactions (R109, R110, and R151) are insensitive to the DME blending ratio.

4.4. Radical Pool Analysis. The concentrations of radicals, including CH3, H, O, OH, HO2, and H2O2, are important in chain reactions during the ignition process. The sum of mole fractions of these radicals is used to interpret the effect of DME addition on the radical pool development of DME/propane oxidation in a homogeneous ignition system. Figure 8 gives the radical pool development (sum of CH3, H, O, OH, HO2, and H2O2) during the ignition of DME/propane/oxygen/argon mixtures. At the initial ignition stage, the mole fractions of the radical pool are accumulated by the initiation chain reactions and increase with the increase of DME addition. When the mole fraction reaches about $1 \times 10^{-4}$, the increase rate of the radical pool concentration is decreased and is insensitive to the DME blending ratio. When the radical pool concentration is larger than $1 \times 10^{-4}$, the radical pool concentrations increase sharply and obvious ignition occurs. Meanwhile, the mole fractions of the radical pool increase with an increase in the DME blending ratio. Moreover, the timing at the rapid increase in the radical pool concentration advances with an increase in the DME blending ratio. This is consistent with the behavior of the temperature during the ignition process, as shown in Figure 9.

5. CONCLUSION

Experimental and modeling studies on ignition delay times of DME/propane/oxygen/argon mixtures at different DME blending ratios were performed using shock tube and Chemkin at a pressure of 20 bar. The main conclusions are as follows: (1) Ignition delay times of DME—propane blends at different equivalence ratios and DME blending ratios were measured in a shock tube. Correlations of ignition delay times as a function of the equivalence ratio and temperature are obtained. Activation energies slightly decrease with the decrease of the temperature for propane, DME, and their blends. The ignition delay time of propane is increased and that of DME is decreased with an increase in the equivalence ratio. (2) A modified binary fuel model (Mod Mech C5) was obtained. The modified model can predict well the experimental ignition delay times and activation energies. The logarithmic ignition delay time decreases linearly with an increase in the DME blending ratio at high temperatures. The ignition delay time is slightly decreased for the lean mixtures and decreases remarkably for the rich mixtures with an increase in the DME blending ratio. (3) The sensitivity coefficients, which show strong dependence upon the DME blending ratio, indicate that the main chain-branching reaction (R1) and the fuel related reactions dominate the ignition delay time predictions. Further analysis of the radical pool provided evidence that the enhanced ignition of propane by DME addition is attributed to the increased radical concentrations.

ASSOCIATED CONTENT

Supporting Information

All experimental data of ignition delay times of the DME/propane/oxygen/argon mixtures and the mechanism files of Mod Mech C5. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

Figure 8. Radical pool growth in the ignition process of DME/propane/oxygen/argon mixtures.

Figure 9. Temperature profiles of DME/propane/oxygen/argon mixtures at different DME blending ratios.
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