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Shock Tube Measurements and Kinetic Study on Ignition Delay Times of Lean DME/*n*-Butane Blends at Elevated Pressures

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S Supporting Information

ABSTRACT: In this study, the ignition delay times of lean DME/*n*-C₄H₁₀ fuel blends diluted with argon were measured behind reflect shock waves over a wide range of conditions: pressures from 0.2 to 2.0 MPa, temperatures from 1100 to 1600 K, and DME blending ratios from 0 to 100%. The results show that for all of the mixtures, an increase in pressure significantly promotes the ignition of the fuel blends. An empirical Arrhenius correlation with high fidelity was proposed and was used to calculate the ignition delay times of DME/*n*-C₄H₁₀. Under fuel-lean conditions, both neat DME and neat *n*-C₄H₁₀ present almost uniform global activation energies. For a given temperature and/or pressure, the ignition delay time is considerably insensitive to changes in the DME blending ratio. Comparisons of the predictions by five available kinetic mechanisms with the measured ignition delay times were made, and NUIG Aramco Mech 1.3 was found to give excellent predictions for all of the tested mixtures. Hence, NUIG Aramco Mech 1.3 was used to make the kinetic analysis, including fuel flux analysis, sensitivity analysis, and mole fraction analysis of key radicals, and to interpret the effect of DME addition on the ignition chemistry of *n*-C₄H₁₀.

1. INTRODUCTION

The homogeneous charge compression ignition (HCCI) engine has attracted much attention because it can simultaneously achieve higher thermal efficiency and extremely low NO_x and particulate emissions. However, the too-narrow operating range of the HCCI engine, which is limited by knocking at high load and misfire at low load, is the main obstacle to its commercial use.¹ Many techniques have been tested to extend the operating range of the HCCI engine, such as cooled exhaust gas recirculation (EGR), intake pressure boosting, and variable valve actuation maintaining hot EGR.² Besides these techniques, study of fuel design is a promising approach to extend the HCCI engine operating limits.

It is well-known that the ignition and combustion characteristics of the HCCI engine are mainly controlled by the fuel chemistry during compression, and fuel blending is an efficient way to control the HCCI ignition and combustion. Thus, changing the fuel octane number and/or cetane number can meet the requirements under different operation conditions. In this study, dimethyl ether (DME) and *n*-butane blends were chosen as the testing fuels. As an alternative to diesel, dimethyl ether (DME) with a high cetane number can achieve soot-free combustion because DME includes an oxygen atom but no C–C bonds in its structure. As an important component of natural gas, *n*-butane (*n*-C₄H₁₀) with four carbon atoms has a high octane number. Thus, it is expected that the ignition of the HCCI engine can be controlled through the blending of DME and *n*-C₄H₁₀.

Some research on engines fueled with blends of high octane fuel and high cetane fuel have been made. Iida and co-workers^{3–7} conducted a series of experimental and numerical studies on combustion and emission characteristics of DME/hydrocarbon fuel blends under HCCI engine operating conditions. The tested hydrocarbon fuels included methane, propane, and *n*-butane. Additionally, Tsutsumi et al.⁸ and

Konno et al.⁹ studied the effects of the mixing ratio and the absolute quantity of DME/methane blends on the ignition timing and rapidity of combustion. They suggested that the ignition kinetics of DME has the dominant influence on the ignition timing, whereas methane exhibits only a small observed effect. However, they found that the rapidity of combustion could not be controlled even by varying the DME/methane mixing ratio. Kong¹⁰ numerically investigated the combustion characteristics of natural gas/DME blends using a computational fluid dynamics (CFD) model. The numerical results showed that the ignition of fuel blends was mainly dominated by DME oxidation. With an increase in the DME concentration, the low-temperature heat release of DME was increased, resulting in the promotion of the ignition process. Yao and co-workers^{11–14} conducted both experimental and numerical studies on the HCCI combustion of DME/methanol dual fuel. They suggested that the combustion efficiency mainly depends on the DME concentration and that the ignition timing and combustion duration could be adjusted effectively by adjusting the DME percentage and EGR rate.

Fundamentally, both neat DME and neat *n*-C₄H₁₀ have been extensively investigated. For neat DME fuel, for example, Pfahl et al.¹⁵ studied the autoignition of DME/air by shock tube measurements at high pressure (1.3 MPa) and low to intermediate temperatures (840–1300 K) and found a two-stage autoignition behavior for the DME fuel. Dagaut et al.¹⁶ developed a kinetic mechanism for DME oxidation and validated the model against both JSR data (550–1275 K, 0.1–1.0 MPa) and shock tube data (650–1600 K, 0.35–4.0 MPa). Curran and co-workers^{17–19} also developed a chemical kinetic model of DME and validated the model with

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experimental data from burner-stabilized flame, flow reactor, stirred reactor, and shock tube measurements. Cook et al.²⁰ measured the ignition delay and OH concentration time histories of argon-diluted DME and validated several existing models.

For neat butane fuel specifically, Gersen et al.²¹ studied the autoignition delay times of *n*-butane and isobutane using a rapid compression machine. Their results revealed that both *n*-butane and isobutane presented significant negative temperature coefficient (NTC) ignition behavior at low temperature. Recently, Curran and co-workers^{22–26} measured the ignition delay times of methane, *n*-butane, isobutane, and their blends and developed a kinetic model against the measured data. In general, this model can well capture the experimental observations at high, intermediate, and low temperatures. To date, only one available study of the autoignition characteristics of DME/*n*-C₄H₁₀ blends has been reported. Hu et al.²⁷ measured the ignition delay times of stoichiometric DME/*n*-C₄H₁₀ blends with varied DME blending ratios (0, 30, 70, and 100%) at high temperatures (1200–1600 K) and relatively low pressures (0.12–0.53 atm) using a shock tube. Their study showed that ignition could be significantly promoted by DME addition.

It is well-known that high-pressure ignition data are very important for both HCCI engine control and chemical kinetic development. Thus, it is necessary to measure the ignition delay time of DME/*n*-C₄H₁₀ fuel blends over a wide range of experimental conditions. Thus, one objective of this study was to measure the shock tube ignition delay times of DME/*n*-C₄H₁₀ blends at higher pressures and wider blending ratios. The previous study suggested that if a kinetic model can well predict the ignition delay time for the neat fuel, it can also give a good prediction for the fuel blends.^{28,29} Thus, the second objective was to evaluate the adaptability of currently available kinetic mechanisms for the neat fuel and fuel blends against the data measured. Currently, the kinetic interaction mechanism of the fuel blend is unclear, and this needs to be investigated further. Therefore, the third objective was to perform chemical kinetic analyses for various DME/*n*-C₄H₁₀ blends to identify the dominant reactions and clarify the enhanced and/or inhibited effect on the autoignition of *n*-C₄H₁₀ when DME is added.

2. EXPERIMENTAL AND NUMERICAL APPROACHES

2.1. Experimental Setup. In this study, all of the experiments were performed in a shock tube that has been described in detail in previous publications.^{29,30} Here, only a brief description is given. The shock tube is separated into a 2 m long driver section and a 7.3 m long driven section with an internal diameter of 11.5 cm using double poly(ethylene terephthalate) (PET) diaphragms. High-purity helium and nitrogen mixtures were used as the driver gas. Test mixtures were prepared in a 128 L stainless steel tank according to Dalton's law of partial pressures and allowed to settle for 12 h to ensure sufficient mixing. The driven section can be evacuated to a pressure below 1 Pa using a Nanguang vacuum system (2ZX-30D rotary vane vacuum pump and ZJP-150 Roots vacuum pump). The incident shock velocity at the end wall was determined by linear extrapolation using four fast-response piezoelectric pressure transducers (PCB 113B26) with three time interval counters (Fluke PM6690) located at fixed intervals along the driven section. The temperature and pressure behind the reflected shock wave were calculated using the Gaseq chemical equilibrium software.³¹ The typical uncertainty in the temperature was ± 15 K.

The CH* chemiluminescence selected by a narrow-bandpass filter centered at 430 ± 10 nm was measured with a photomultiplier (Hamamatsu CR131) located at the end wall. All of the experimental

data were acquired and recorded using a digital recorder (Yokogawa DL750). The ignition delay time is defined as the time interval between the arrival of incident shock wave at the end wall and the onset of end-wall CH* chemiluminescence as determined by extrapolation of the steepest rise of the CH* chemiluminescence curve to the zero baseline, as shown in Figure 1.

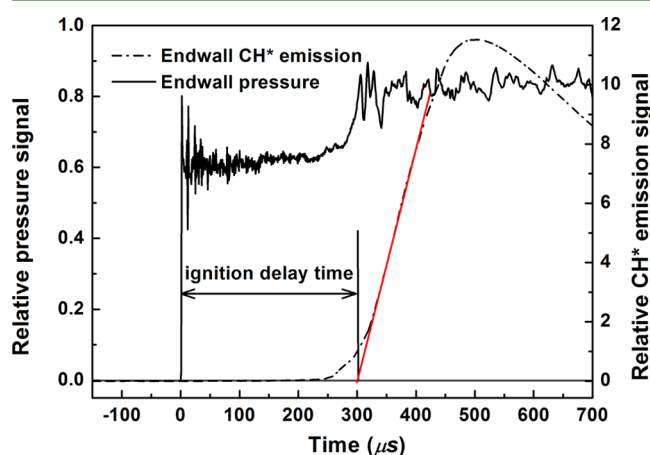


Figure 1. Measurement of the ignition delay time from the end-wall pressure and CH* emission data (the curve is for mixture 2 at $p = 1.95$ MPa, $T = 1293$ K, and an equivalence ratio of 0.5).

The detailed test mixture compositions are listed in Table 1. The purities of DME, *n*-butane, oxygen, and argon were higher than 99.999%. Fuel mixtures were prepared according to the method in the previous studies.^{29,32} The fuel/oxygen/argon mixtures ($\phi = 0.5$, $X_{O_2}/X_{Ar} = 21\%/79\%$) were diluted with argon (20% mixture/80% argon). In this study, all of the fuel mixtures were diluted with the same dilution ratio.

2.2. Kinetic Simulations. It is well-known that nonideal effects arising from the interaction between the boundary layer and the reflected shock wave significantly influence the prediction of the ignition delay time, especially for longer ignition times at relatively low temperature. In this study, an obvious pressure rise ($dp/dt = 4\% \text{ ms}^{-1}$) was observed experimentally and was taken into account in the numerical simulations. Previously, Li et al.³³ developed a simple gas dynamic model called CHEMSHOCK and Chaos and Dryer³⁴ proposed the SENKIN/VTIM approach to include the nonideal effects. In general, these two methods are applicable under highly diluted gas conditions. In this study, the SENKIN code in the CHEMKIN II package, which employs the SENKIN/VTIM approach, was used to calculate the ignition delay times of the DME/*n*-C₄H₁₀ blends.

For numerical simulations of neat *n*-butane fuel, three available chemical kinetic mechanisms were used to represent the autoignition delay characteristics:

- ◆ LLNL C₄ Mech,³⁵ which was developed in 1998 by Lawrence Livermore National Laboratory and involves 155 species and 689 elementary reactions;
- ◆ USC Mech 2.0,³⁶ which was developed in 2007 by the Combustion Kinetics Laboratory at the University of Southern California and consists of 111 species and 784 elementary reactions;
- ◆ NUIG Aramco Mech 1.3,³⁷ which was developed in 2013 by the Combustion Chemistry Center of the National University of Ireland and consists of 253 different chemical species and 1542 elementary reactions.

Figure 2a shows comparisons between the measured and predicted ignition delay times using the above three kinetic mechanisms for neat *n*-butane fuel at different pressures. NUIG Aramco Mech 1.3 gave good predictions over whole range of experimental conditions, while LLNL C₄Mech and USC Mech 2.0 underpredicted the ignition delay

Table 1. Test Mixture Compositions in This Study

mixture		ϕ	X_{DME} (%)	$X_{\text{C}_4\text{H}_{10}}$ (%)	X_{O_2} (%)	X_{Ar} (%)
no.	composition					
1	100% DME	0.5	0.676	0	4.056	95.268
2	80% DME/20% $n\text{-C}_4\text{H}_{10}$	0.5	0.442	0.110	4.084	95.364
3	60% DME/40% $n\text{-C}_4\text{H}_{10}$	0.5	0.280	0.186	4.100	95.434
4	40% DME/60% $n\text{-C}_4\text{H}_{10}$	0.5	0.161	0.242	4.110	95.487
5	100% $n\text{-C}_4\text{H}_{10}$	0.5	0.000	0.318	4.134	95.548

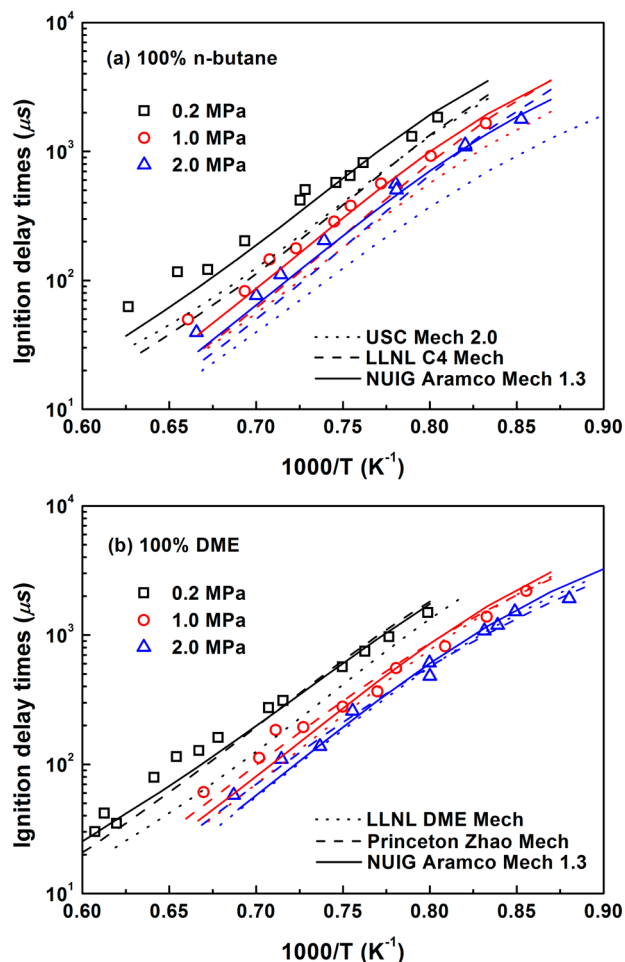


Figure 2. Comparisons between the measured and model-predicted ignition delay times using different mechanisms for neat $n\text{-C}_4\text{H}_{10}$ and DME at pressures of 0.2, 1.0, and 2.0 MPa.

times. This is reasonable since LLNL C₄ Mech was validated only by some small hydrocarbon flames under fuel-rich conditions while USC Mech 2.0 was examined against only 1,3-butadiene oxidation at high temperatures among C₄ fuels.

For numerical simulations of neat DME fuel, NUIG Aramco Mech 1.3 was again used along with two other kinetic mechanisms:

- ◆ LLNL DME Mech,^{38–40} which was developed in 2000 by Lawrence Livermore National Laboratory and involves 80 species and 351 elementary reactions;
- ◆ Princeton-Zhao Mech,⁴¹ which was developed in 2008 by Dryer's group at Princeton University and includes 55 species and 290 elementary reactions.

Figure 2b shows the comparison between the measured and model-predicted ignition delay times. Both NUIG Aramco Mech 1.3 and Princeton-Zhao Mech gave moderately good predictions, while LLNL DME Mech underpredicted the ignition delay time at a low pressure of 0.2 MPa.

In general, NUIG Aramco Mech 1.3 could predict well the ignition delay times of either neat DME or neat $n\text{-butane}$ under all of the experimental conditions. Therefore, this mechanism was used to calculate the ignition delay times and conduct the sensitivity analysis and fuel flux analysis for the DME/ $n\text{-C}_4\text{H}_{10}$ fuel blends examined in this study.

3. RESULTS AND DISCUSSION

3.1. Ignition Delay Times. **3.1.1. Measurement, Empirical Correlation, and Numerical Simulation.** DME/ $n\text{-C}_4\text{H}_{10}$ fuel blends with DME fractions of 0%, 40%, 60%, 80%, and 100% were studied under pressures of 0.2, 1.0, and 2.0 MPa. All of the experimental data and simulation results under the current test conditions are provided in the Supporting Information and are also presented in Figure 3. Under the whole range of test conditions, the ignition delay times of both the neat fuels and the fuel blends exhibit the typical Arrhenius dependence on the temperature. Multiregression analysis was used to obtain the empirical correlation of eq 1:

$$\tau = Ap^{\beta} \exp\left(\frac{E_a}{RT}\right) \quad (1)$$

where τ is ignition delay time in seconds, p is the pressure in atmospheres, T is the temperature in kelvins, E_a is the activation energy in kilocalories per mole, and $R = 1.986 \times 10^{-3}$ kcal mol⁻¹ K⁻¹ is the universal gas constant. The correlation parameters under each mixture condition are given in Table 2, and the residual squares of all correlations are over 0.98. It is interesting that the activation energy of neat DME is almost consistent with that of neat $n\text{-butane}$ as well as those of the DME/ $n\text{-C}_4\text{H}_{10}$ blends at different pressures. This allows reference to the study of Cheng and Oppenheim⁴² on methane and hydrogen mixtures to obtain a heuristic formula based on the correlations of neat DME and neat $n\text{-C}_4\text{H}_{10}$ using the blending ratio of the DME/ $n\text{-C}_4\text{H}_{10}$ fuel blend. The expression is

$$\tau = \tau_{n\text{-C}_4\text{H}_{10}}^{(1-\zeta)} \tau_{\text{DME}}^{\zeta} \quad (2)$$

where ζ is the mole fraction of DME in the fuel blend and τ_{DME} and $\tau_{\text{C}_4\text{H}_{10}}$ are the ignition delay times of DME and $n\text{-C}_4\text{H}_{10}$, respectively. That is,

$$\begin{aligned} \tau &= \left[2.0 \times 10^{-4} p^{-0.43} \exp\left(\frac{40.5 \pm 0.8}{RT}\right) \right]^{(1-\zeta)} \\ &\quad \times \left[5.0 \times 10^{-4} p^{-0.44} \exp\left(\frac{37.8 \pm 0.7}{RT}\right) \right]^{\zeta} \\ &= (2.0 \times 10^{-4})^{(1-\zeta)} (5.0 \times 10^{-4})^{\zeta} \\ &\quad p^{(-0.43-0.01\zeta)} \exp\left(\frac{40.5 - 2.8\zeta}{RT}\right) \end{aligned} \quad (3)$$

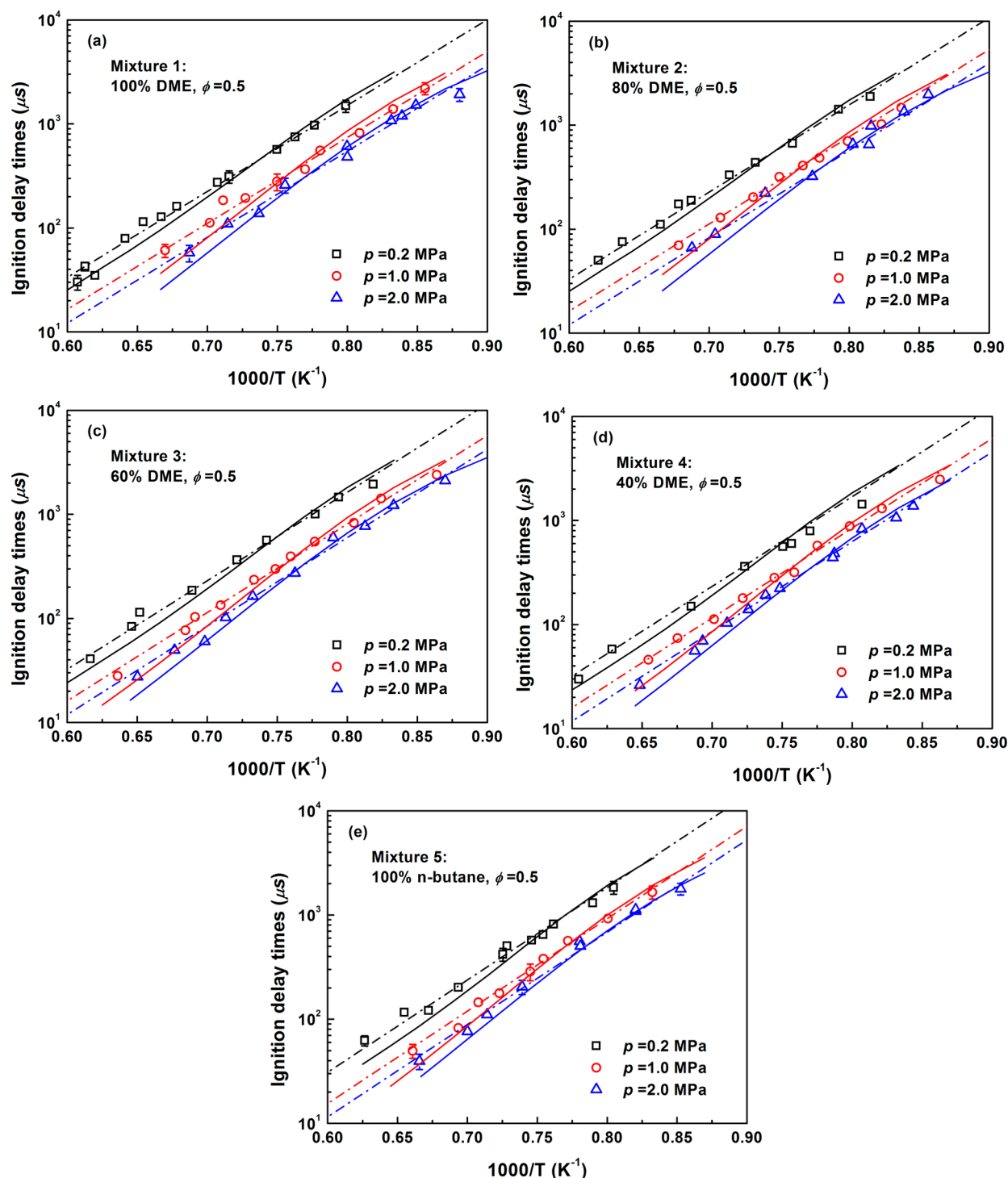


Figure 3. Measured and simulated ignition delay times of DME, $n\text{-C}_4\text{H}_{10}$, and their blends at elevated pressures: (a) 100% DME; (b) 80% DME/20% n -butane; (c) 60% DME/40% n -butane; (d) 40% DME/60% n -butane; (e) 100% n -butane. Symbols, experiment; solid lines, numerical simulation using NUIG Aramco Mech 1.3; dash-dot lines, correlation using eq 3.

Generally, the experimental data exhibit good Arrhenius exponential dependence on the reciprocal temperature, and they decrease with increasing pressure. The correlations well reproduce the measured ignition delay times both qualitatively and quantitatively for both the neat fuels and the fuel blends.

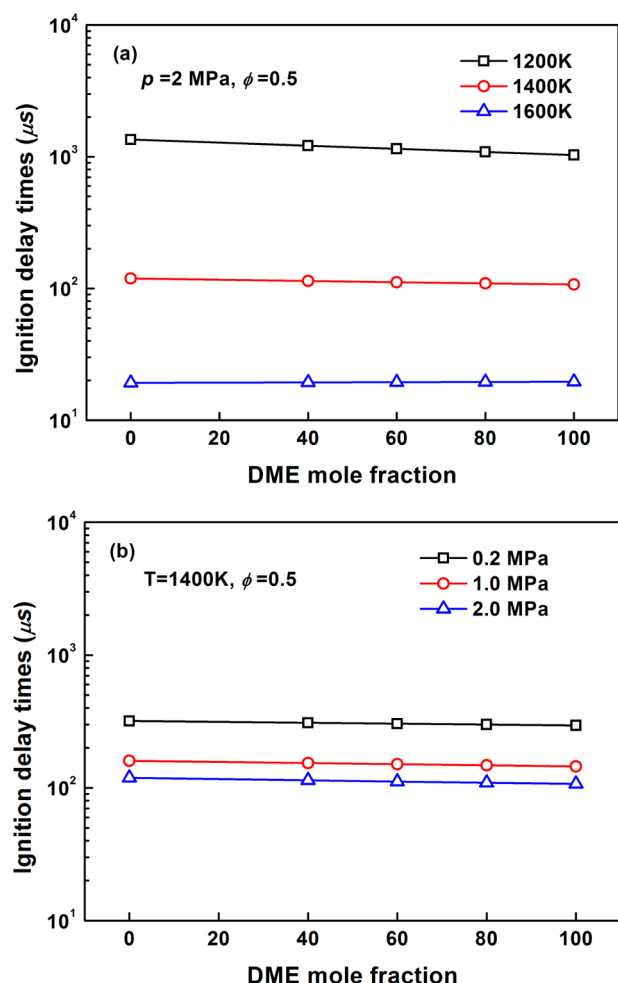
Moreover, from the comparisons between the measured and numerical ignition delay times for the five fuel blends at different pressures it can be seen that the ignition delay times obviously decrease with increasing pressure. This reason for this

is that the collision probability between the molecules of fuel and oxygen is enhanced under elevated pressures. Furthermore, the effect of increasing pressure on the global activation energy is considerably weak under the current experimental conditions. As expected, NUIG Aramco Mech 1.3 can well capture the ignition delay characteristics for both neat DME and neat $n\text{-C}_4\text{H}_{10}$ as well as for the DME/ $n\text{-C}_4\text{H}_{10}$ blends over the range of test temperatures and pressures in this study.

Table 2. Correlation Parameters from Equation 1 for DME/ n -C₄H₁₀ Fuel Blends

mixture	A	β	E_a (kcal/mol)	R^2
1	5.02×10^{-4}	-0.440	37.78 ± 0.73	0.989
2	5.25×10^{-4}	-0.421	37.70 ± 0.71	0.991
3	3.31×10^{-4}	-0.458	39.12 ± 0.64	0.982
4	2.70×10^{-4}	-0.387	39.21 ± 0.59	0.994
5	2.00×10^{-4}	-0.428	40.53 ± 0.78	0.990

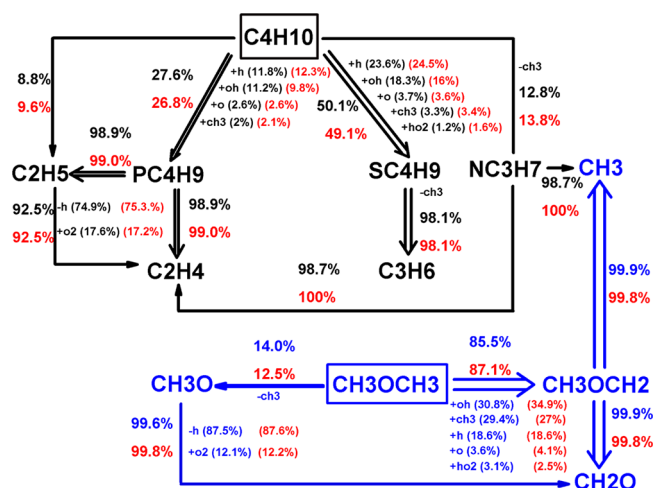
3.1.2. Effect of the Fuel Blending Ratio. Figure 4 shows the ignition delay time as a function of the DME blending ratio at

**Figure 4.** Effect of blending ratio on the ignition delay time for the DME/ n -butane fuel blends at different temperatures and pressures.

temperatures of 1200, 1400, and 1600 K and pressures of 0.2, 1, and 2 MPa. It is noted that the experimental schemes do not cover all of the data in the isothermal curves in Figure 4, so all of the data in Figure 4 were calculated using eq 3. The results indicate that the ignition delay times exhibit a negligible dependence on the DME mole fraction as it varies from 0% to 100% at all temperatures and pressures. This means that at high temperature the addition of DME cannot significantly promote and/or inhibit the ignition behavior of n -C₄H₁₀. In other words, DME exhibits almost consistent ignition delay characteristic to that of n -C₄H₁₀ under the current experimental conditions. This is different from the results of the previous study on the ignition of DME/methane blends.⁴³ They suggested that an

increase in DME blending ratio could remarkably decrease the ignition delay time of methane. Hu et al.²⁷ believed that the addition of DME could remarkably promote the ignition of n -C₄H₁₀ under low-pressure and fuel-stoichiometric conditions. The differences from those of the current study are the difference in equivalence ratio and component of the test mixtures.

3.2. Chemical Kinetic Analysis. **3.2.1. Fuel Flux Analysis.** Figure 5 shows the results of the fuel flux analysis for neat

**Figure 5.** Reaction pathway diagram for DME/ n -butane in a shock tube at $p = 20$ atm, $T = 1300$ K, and 20% DME consumption, obtained using NUIG Aramco Mech 1.3. Black, neat n -C₄H₁₀; red, 60% DME/40% n -C₄H₁₀ blend; blue, neat DME.

DME, neat n -C₄H₁₀, and the 60% DME/40% n -C₄H₁₀ blend obtained using NUIG Aramco Mech 1.3 under the shock tube conditions ($T = 1300$ K and $p = 2.0$ MPa). The analysis provides a snapshot of the reaction flux when 20% DME is consumed, as in the literature.⁴⁴

The scheme shows that neat DME presents almost the same consumption pathway as the 60% DME/40% n -C₄H₁₀ blend. Moreover, neat n -C₄H₁₀ also exhibits consumption similar to that of the 60% DME/40% n -C₄H₁₀ blend. For neat n -C₄H₁₀, the fuel undergoes hydrogen abstraction by free radicals, including H radical (23.6%), OH radical (18.3%), and O radical (3.7%) and small contributions from CH₃ (3.3%) and HO₂ (1.2%). This accounts for 50.1% of the total n -C₄H₁₀ consumption and forms *sec*-butyl radical (SC₄H₉). Furthermore, approximately 27.6% of the n -C₄H₁₀ consumption produces *n*-butyl radical (PC₄H₉) via hydrogen abstraction by H radical (11.8%), OH radical (11.2%), and O radical (2.6%) and a small contribution from CH₃ (2%). Since primary hydrogen atoms have a higher bond dissociation energy (101.5 kcal/mol) than secondary ones (98.5 kcal/mol), SC₄H₉ is formed in greater abundance than PC₄H₉.²³ In addition to fuel consumption via hydrogen abstraction reactions, a small amount of n -C₄H₁₀ fuel directly undergoes molecular pyrolysis to form propyl radical (NC₃H₇, 12.5%) through β C–C bond dissociation and ethyl radical (C₂H₅, 8.6%) through β C–C bond dissociation. It is clear that the consumption of n -C₄H₁₀ is mainly dominated by the hydrogen abstraction reactions (in which the H and OH radicals give the primary contributions while O, CH₃, and HO₂ radicals give relatively smaller effects) rather than direct decomposition. NC₃H₇ is consumed by β -scission reactions to form ethylene (C₂H₄). SC₄H₉ forms

propene (C_3H_6) through β -scission reactions. Through the decomposition reaction, PC_4H_9 yields the C_2H_5 and C_2H_4 . C_2H_5 is consumed by hydrogen abstraction reactions and generates C_2H_4 . For the 60% DME/40% n - C_4H_{10} blend, the reaction pathway of n - C_4H_{10} does not make any obvious change.

The flux analysis for neat DME shows that 85.5% of DME consumption proceeds mainly through hydrogen abstraction by small radicals. Most of these hydrogen abstractions are by OH (30.8%), CH_3 (29.4%), H (18.6%), O (3.6%), and HO_2 (3.1%) to form methoxymethyl radical (CH_3OCH_2), all of which subsequently decomposes to form methyl radical and formaldehyde (CH_2O). Furthermore, approximately 14% of the DME directly decomposes through unimolecular decomposition to produce the methoxyl radical (CH_3O) and methyl radical. The relatively instable methoxyl radical then loses a hydrogen atom either through direct reaction with molecular oxygen (12.1%) or hydrogen elimination (87.5%) to form formaldehyde. For the 60% DME/40% n - C_4H_{10} blend, the reaction pathway of DME does not make any obvious change.

It is interesting that the 60% DME/40% n - C_4H_{10} blend exhibits oxidation pathways similar to those of neat DME and neat n - C_4H_{10} . This suggests that addition of DME does not affect the kinetic regime of n - C_4H_{10} under the current conditions.

3.2.2. Sensitivity Analysis. Sensitivity analyses were performed to identify the most important reactions in the ignition kinetics of DME/ n - C_4H_{10} blends. The normalized sensitivity of the ignition delay time was determined at the same temperature as in the fuel flux analysis. The sensitivity coefficient is defined as

$$S = \frac{\tau(2k_i) - \tau(0.5k_i)}{1.5\tau(k_i)} \quad (4)$$

where τ is the ignition delay time of the mixture and k_i is the specific rate coefficient. Reactions with a positive rate coefficient inhibit the reactivity, while those with a negative coefficient promote the reactivity. In this study, NUIG Aramco Mech 1.3 was used to obtain the sensitivity coefficients.

Figure 6 depicts the sensitivity coefficients of DME/ n - C_4H_{10} fuel blends with different DME mole fractions at $T = 1300$ K

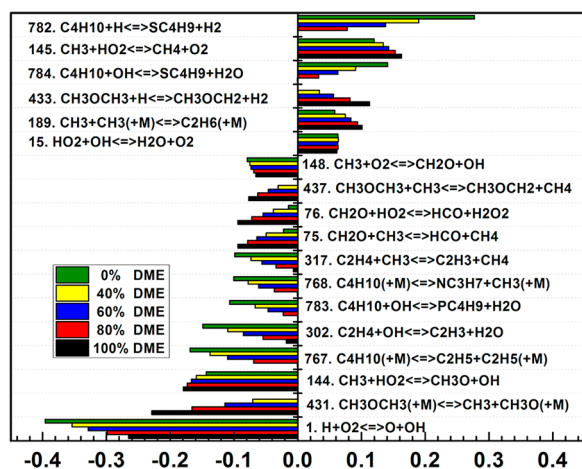
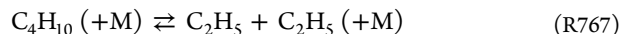


Figure 6. Normalized sensitivity analysis of the ignition delay time for the DME/ n -butane blends at $p = 2.0$ MPa, $T = 1300$ K, and DME mole fraction from 0% to 100%.

and $p = 2.0$ MPa. Among the 18 high-sensitivity elementary reactions, the most important reaction that promotes the reactivity of neat n - C_4H_{10} is the chain-branching reaction R1,



Another important reaction is the decomposition reaction of n - C_4H_{10} to produce two ethyl radicals (reaction R767):

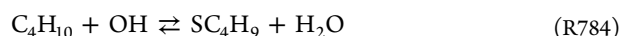
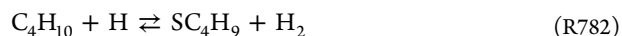


This chain-branching reaction is important promoting the reaction because ethyl radicals can subsequently form the active the free radical H via direct H-elimination reactions. Also, the chain-propagation reaction of CH_3 and HO_2 radicals to form CH_3O and OH,



is of considerable importance because the CH_3O radical subsequently decomposes to form CH_2O and H radicals and promotes the global reaction rate.

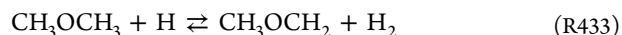
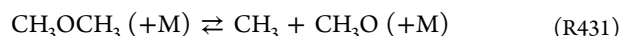
The most important reactions that inhibit the reactivity of neat n - C_4H_{10} under these conditions are the formation of *sec*-butyl radical through the reactions of n - C_4H_{10} with H and OH via hydrogen abstraction:



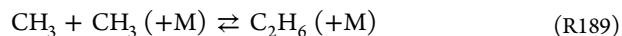
Moreover, the chain-termination reaction of methyl and hydroperoxyl radicals to produce methane and oxygen is also considerably important:



For neat DME, reactions R1 and R144, which promote the reactivity, and reaction R145, which inhibits the reactivity, still dominate the ignition kinetics under the current conditions. Additionally, the ignition delay time of DME is also considerably sensitive to fuel-molecule-related reactions such as the following:



Reaction R189 is another important ignition-inhibiting reaction because it is a third-order radical–radical recombination reaction:



With the addition of DME, the production of CH_3 radical and CH_2O will be obviously increased through direct decomposition reactions of DME and CH_3OCH_2 radical, and this behavior can be also seen in Figure 7 in section 3.2.3 below. The effect of increasing CH_3 is twofold. First, increasing CH_3 increases the sensitivity coefficient of reactions R189 and R145, resulting in an increase of ignition-inhibiting tendency. Second, the sensitivity coefficient of reaction R144, which occurs in parallel with reaction R145, is also increased with increasing CH_3 , resulting in an increase of ignition-promoting tendency. Furthermore, the sensitivity coefficient decreases for reactions R782 and R1 but increases for reaction R433 when DME is increased. This indicates that DME gives stronger competitiveness with H radical compared with n - C_4H_{10} and reaction R1.

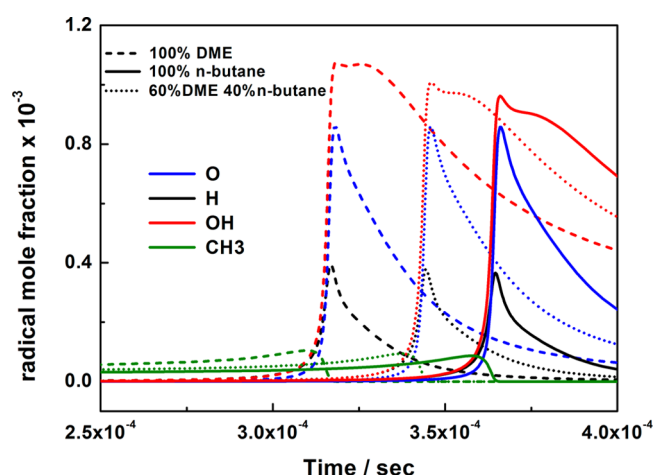


Figure 7. Mole fractions of free radicals and CH_3 radical at different DME blending ratios with $\phi = 0.5$, $T = 1300$ K, and $p = 2.0$ MPa.

These opposite effects determine the global reaction rate, and the ignition delay times do not exhibit any obvious change when DME is added. The results also show agreement with the experimental observations.

3.2.3. Small-Radical Mole Fraction Analysis. Through above flux analysis it was found that free radicals such as H, O, and OH are the important radicals for $n\text{-C}_4\text{H}_{10}$ ignition at high temperature. Additionally, CH_3 and CH_2O are the major products during the oxidation of DME. Therefore, a study of the mole fractions of key radicals can help provide further understanding of the effect of DME addition on the ignition chemistry of $n\text{-C}_4\text{H}_{10}$. Figures 7 and 8 show the effect of DME addition on the mole fractions of H, O, OH, CH_3 and CH_2O for the DME/ $n\text{-C}_4\text{H}_{10}$ blends at a temperature of 1300 K and pressure of 2.0 MPa.

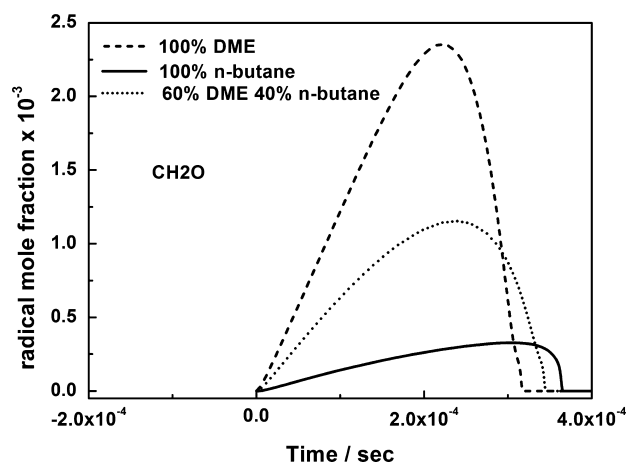


Figure 8. Mole fraction of CH_2O radical at different DME blending ratios with $\phi = 0.5$, $T = 1300$ K, and $p = 2.0$ MPa.

For free radicals and CH_3 (Figure 7) at different DME blending ratios, in general, DME addition exhibits only a negligible effect on the maximum concentrations of H, O, and OH radicals, especially for the H and O radicals. It is well-known that the consumption of $n\text{-C}_4\text{H}_{10}$ mainly proceeds through hydrogen abstraction by these free radicals. Thus, the ignition delay time presents a slight reduction with an increase in DME mole fraction. However, this discrepancy of ignition

between DME and $n\text{-C}_4\text{H}_{10}$ is small from the experimental results of this study, as shown in Figure 4.

Moreover, with an increase of the DME blending ratio, the mole fraction of CH_3 does not exhibit an obvious change. The CH_3 radicals produced from DME via direct pyrolysis or indirectly by hydrogen abstraction reactions mainly feed DME oxidation through reaction R437, whereas the CH_3 radicals have only a relatively small impact on the ignition of $n\text{-C}_4\text{H}_{10}$.

Since CH_2O radical is the key decomposition production of DME, the addition of DME results in a sharp increase of CH_2O concentration (Figure 8). However, the CH_2O radicals have little effect on promoting or inhibiting ignition of DME/ $n\text{-C}_4\text{H}_{10}$ blends. As a result, DME addition does not affect the ignition delay time under the current conditions but does lead to higher pollution of CH_2O emission.

4. CONCLUSIONS

Ignition delay times of lean DME/ $n\text{-C}_4\text{H}_{10}$ fuel blends with various DME blending ratios were measured using a shock tube. A kinetic study was conducted to interpret the ignition chemistry and the effect of DME addition on the ignition kinetics of $n\text{-C}_4\text{H}_{10}$. The main conclusions are summarized as follows:

(1) An empirical correlation of the ignition delay times at various DME blending ratios was obtained through regression analysis against the measured ignition delay times. The correlation parameters show that the global activation energy of DME is almost equal to that of $n\text{-C}_4\text{H}_{10}$, so DME addition does not change the activation energy of the fuel blends in this study.

(2) The measured ignition delay times were compared with the numerical predictions from five available kinetic models, and only NUIG Aramco Mech 1.3 gave good agreement for both the neat fuels and the fuel blends. In addition, NUIG Aramco Mech 1.3 also captured well the ignition-promoting behavior and global activation energy with increasing pressure.

(3) The ignition delay time is insensitive to the DME blending ratio at different temperatures and pressures for the fuel-lean DME/ $n\text{-C}_4\text{H}_{10}$ blends.

(4) Chemical kinetic analysis showed that DME addition induces a discernible change in the oxidation pathway of $n\text{-C}_4\text{H}_{10}$ under the fuel-lean conditions. The effects of DME addition on the ignition kinetics of fuel blends are attributed to the competition of the elementary reactions with H radical and CH_3 radical. The sensitivities of the dominant reactions exhibit the opposite response, and this leads to the insensitivity of the ignition delay time to DME addition. DME addition remarkably increases the emission of CH_2O .

■ ASSOCIATED CONTENT

Supporting Information

Ignition delay times of the dimethyl ether/ n -butane blends. 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.

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