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A kinetics and dynamics study on the auto-ignition of dimethyl ether at low temperatures and low pressures

Wenlin Huang\textsuperscript{a}, Qian Zhao\textsuperscript{a}, Zuohua Huang\textsuperscript{a}, Henry J. Curran\textsuperscript{b}, Yingjia Zhang\textsuperscript{a*}

*Corresponding author: Dr. Yingjia Zhang

E-mail: yjzhang_xjtu@xjtu.edu.cn

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Figure Captions

Figure 1. Experimental conditions performed using STs in the literature [3-10].

Figure 2. Comparisons of measured IDTs (symbols) with model predictions (lines) using AramcoMech 3.0 with assumption of constant $U$ and $V$ for DME/‘air’ mixtures at 3.0 atm. (a) $\phi = 0.5, 1.0$ and 2.0; (b) $\phi = 3.0$ and 5.0.

Figure 3. Typical time histories of reflected shock pressure and OH$^+$ chemiluminescence detected during the ignition of $\phi = 2.0$ mixture in region II (a) and in region IV (b).

Figure 4. Parametric study of the effect of hot spots on IDTs for DME/‘air’ mixtures at equivalence ratios of 0.5 (a), 1.0 (b), 2.0 (c) and 3.0 (d).

Figure 5. Cold side temperature dependence of laminar flame thickness at various equivalence ratios.

Figure 6. Nephogram of temperature with development of flame kernel during the ignition of $\phi = 2.0$ DME/‘air’ mixture at 960 K, where the IDT is advanced by the localized hot spot.

Figure 7. Nephogram of temperature with the dissipation of hot spot during the ignition of $\phi = 2.0$ DME/‘air’ mixture at 940 K, where IDT is not advanced by the localized hot spot.

Figure 8. Extended reaction scheme for the consumption of $\cdot O_2 CH_2OCH_2O_H$ radical. Third $O_2$ addition sub-set added in this study is annotated with a dotted box.

Figure 9. Sensitivity analysis of Aramco Mech3.0 for IDTs at 680 K and 840 K: $\phi = 2.0, p = 3.0$ atm.
Supplementary Material

Section Captions

S1. Typical time histories of reflected shock pressure and OH* chemiluminescence detected in experiments.
S2. The skeletal mechanism.
S3. Attentions
A kinetics and dynamics study on the auto-ignition of dimethyl ether at low temperatures and low pressures

Wenlin Huang\textsuperscript{a}, Qian Zhao\textsuperscript{a}, Zuohua Huang\textsuperscript{a}, Henry J. Curran\textsuperscript{b}, Yingjia Zhang\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a}State Key Laboratory of Multiphase Flow in Power Engineering, Xi’an Jiaotong University, Xi’an 710049, China; \textsuperscript{b}Combustion Chemistry Centre, School of Chemistry, Ryan Institute, MaREI, NUI Galway, Ireland.

Abstract

Though the combustion chemistry of dimethyl ether (DME) has been widely investigated over the past decades, there remains a dearth of ignition data that examines the low-temperature, low-pressure chemistry of DME. In this study, DME/air mixtures at various equivalence ratios from lean (0.5) to extremely rich (5.0) were ignited behind reflected shock waves at a fixed pressure (3.0 atm) over the temperature range 625–1200 K. The ignition behavior is different from that at high-pressures, with a repeatable ignition delay time fall-off feature observed experimentally in the temperature transition zone from the negative temperature coefficient (NTC) regime to the high-temperature regime. This could not be reproduced using available kinetic mechanisms as conventionally homogeneous ignition simulations. The fall-off behavior shows strong equivalence ratio dependence and disappears completely at an equivalence ratio of 5.0. A local ignition kernel postulate was implemented numerically to quantifiably examine the inhomogeneous premature ignition. At low temperature, no pre-ignition occurs in the mixture. A conspicuous discrepancy was observed between the measurements and constrained UV simulations
at temperatures beyond the NTC regime. A third $\text{O}_2$ addition reaction sub-set was incorporated into AramcoMech 3.0, together with related species thermochemistry calculated using the G3/G4/CBS-APNO compound method, to explore the low-temperature deviation. The new reaction class does not influence the model predictions in IDTs, but the updated thermochemistry does. Sensitivity analyses indicate that the decomposition of hydroperoxy-methylformate plays a critical role in improving the low-temperature oxidation mechanism of DME but unfortunately, the thermal rate coefficient has never been previously investigated. Further experimental and theoretical endeavors are required to attain holistic quantitative chemical kinetics based on our understanding of the low-temperature chemistry of DME.

**Keywords**

Auto-ignition; pre-ignition; hot spot; low-temperature chemistry; Dimethyl ether
1. Introduction

Dimethyl ether (DME) is an attractive renewable fuel that presents low NO\textsubscript{x} and soot emissions and a high cetane number. It has thus been proposed as a replacement for diesel fuel. To gain a better understanding of the combustion chemistry of low reactivity fuels such as ethanol and toluene, DME was used as a radical initiator by some researchers [1, 2]. This requires a clear and detailed understanding of the low-temperature chemistry of DME to decouple the chemical interaction between DME and the low reactivity fuels.

The combustion chemistry of DME has been widely investigated over the past decades based on experimental studies of DME IDTs [3-10], species profile measurements versus time and/or temperature in jet-stirred reactors (JSR) [11] and flow reactors [12, 13], and flame speeds [14, 15]. However, recently Zhao et al. [16] investigated the ozone assisted low-temperature oxidation chemistry of DME from 400–750 K using an atmospheric-pressure flow reactor coupled with molecular beam mass spectrometry, and found the existing kinetic models with an ozone sub-mechanism over-predicted DME oxidation significantly. JSR [17] and flow reactor [18] experiments have also shown that existing kinetic models tend to over-predict DME consumption. To further verify whether the DME models deviate in the low-temperature region, we collected ignition delay times (IDTs) of DME measured in shock tubes (STs) from the literature [3-10]. As shown in Fig. 1, the experimental conditions cover the range $700 \leq T \leq 1700$ K and $3 \leq p \leq 40$ atm.
However, the experimental data is lacking at pressures below 10 atm and at temperatures below 1100 K. It indicates that the current DME models have not been adequately verified for IDTs at low temperature and low pressure.

Figure 1. Experimental conditions performed using STs in the literature [3-10].

Pre-ignition, an ignition event before it is expected, is abnormal combustion that has been observed since the 1920s [19]. Recently, there have been a lot of pre-ignition studies in STs. Generally, pre-ignition hypotheses revolve around the existence of hot surfaces or hot particles that may result from shock non-uniformities [20], the interaction of the reflected shock wave with the contact surface and boundary layer, or some dust [9]. Uygun et al. [21] used schlieren imaging in ST to show the main ignition preceded by pre-ignition during the ignition of 2-methylfuran. Miguel et al. [22] measured IDTs of ethanol and illustrated the effects of pre-ignition on its auto-ignition characteristics. Javed et al. [23] reported expedited ST IDTs of n-heptane in the NTC region. Computational fluid dynamic (CFD) simulations of a randomly located hot spot in the test section showed that energy released from the hot spot can expedite IDTs, in agreement with their experimental observations. Pre-ignition occurs in the ignition of long-chain hydrocarbon NTC fuels (e.g. n-heptane) and non-NTC
fuels (ethanol) at low temperatures [22, 23]. Whether it occurs in a short-chain hydrocarbon NTC fuel needs further investigation, and DME is a representative fuel for that research.

In this work, IDTs of DME mixtures were measured in an ST at low temperatures and low pressures to enrich the database. The experimental results are also used to verify and optimize the predictions of a DME chemistry model. Through experiments, we confirmed the existence of pre-ignition for DME, similar to that of a large alkane (n-heptane) and we have analyzed its physical combustion mechanism using CFD simulations.

2. Experimental details

All the IDTs of DME/‘air’ (21% O₂/79% Ar) mixtures were measured in a variable cross-section high-pressure shock tube (HPST) at Xi’an Jiaotong University. Briefly, the ST is made of stainless steel with the internal surface honed and electro-polished (Rₐ = 0.4 μm). The 6.0 m driver section with a 75 mm bore and 7.6 m driven section with a 150 mm bore are separated by two polyethylene terephthalate diaphragms. Before each test, both the tube and the mixing tank were evacuated to below 1.0 × 10⁻⁵ bar with a normal leak rate of 2 × 10⁻⁶ bar/min. The incident shock velocity is linearly extrapolated by recording the time interval between four piezoelectric pressure transducers (PCB 113B22) and a charge output dynamic pressure transducer (PCB 113B03). The one-dimensional shock-jump equations are used to calculate the reflected shock pressures (pₛ) and temperatures (Tₛ). The largest
uncertainty in the $T_5$ is estimated to be 22 K using the standard root-sum-squares (RSS) method [24]. The end wall pressure history monitored by PCB 113B03 and excited OH$^+$ light emission (associated with $A^2 \Sigma^+ \rightarrow X^2 \Pi$ transition near 306 nm) detected by a photomultiplier tube (Hamamatsu CR131) with a narrow bandpass filter (centered at 306 nm with FWHM < 10 nm), were used to determine the IDT. Non-ideal pressure rise ($dp_5/pdt$) was observed to be less than 1%/ms, due mainly to the interaction between the reflected shock wave and the incident shock boundary layer [25]. High-purity (99.999%) helium and nitrogen were used as the driver gas, high-purity (99.9999%) oxygen and argon, and (99.9%) DME were mixed for the test mixtures.

3. Experimental measurements vs model simulations

IDTs for DME/‘air’ mixtures with various equivalence ratios ($\phi = 0.5, 1.0, 2.0, 3.0$ and $5.0$) were measured at a pressure of 3.0 atm over the temperature range 625–1200 K. The five data sets generally show conventional NTC behavior in the temperature range 770–900 K, with the expected Arrhenius-like behavior in both the high ($> 1100$ K) and low ($< 770$ K) temperature side. Interestingly, we observed experimentally an IDT transition region in the temperature range of 900–1100 K, where an odd IDT fall-off behavior was identified. A consistent trend has been found for the $n$-heptane ignition reported by Javed et al. [23] as well as in hydrogen ignition reported by Ninnemann et al. [26], but it has never been previously observed for DME ignition. The odd phenomenon appears as an intrinsic feature for the low-pressure
ignition of DME due to experimental repeatability. Based on this, the low-pressure ignition of DME can be classified by four regimes; Region I: the high-temperature ignition regime, Region II: transition-temperature ignition regime from high-temperature side to NTC side, Region III: the NTC regime and Region IV: the low-temperature regime (see Fig. 2(a)).

![Figure 2](image)

Figure 2. Comparisons of measured IDTs (symbols) with model predictions (lines) using AramcoMech 3.0 with assumption of constant $U$ and $V$ for DME/air mixtures at 3.0 atm. (a) $\phi = 0.5$, 1.0 and 2.0; (b) $\phi = 3.0$ and 5.0.

AramcoMech 3.0 [27] was employed to re-create the experimental observations. Figure 2 illustrates that the kinetic mechanism is capable of reproducing the IDTs in Regions I for all of the mixtures and in Region III for the $\phi > 2.0$ mixtures, but underestimates the reactivity in Regions II and IV. Specifically, the model predictions by AramcoMech 3.0 shows 5.7 and 3.1 times longer than the measured IDTs for the $\phi = 2.0$ mixture at 1000 K and 660 K, respectively. This discrepancy between the measurements and predictions, however, narrows with increasing $\phi$. The unexpected results, therefore, point to two remaining doubts, in that either the DME kinetic model is not valid at low-pressures or there is a fault in the numerical approach used. To resolve this, two aspects, ignition dynamics, and ignition kinetics, will be discussed in
the following sections. Note that the non-ideal facility effect is excluded in all the simulations due to the weak pressure rise \((dps/pdt < 1\%/ms)\).

4. Pre-ignition dynamics analysis

4.1 Pressure history and OH* evolution

The most prominent discrepancies in the IDT comparison of model predictions with the measurements appear in Regions II and IV. Two typical temperatures for the \(\varphi = 2.0\) mixture, 948 K and 652 K, were thus selected to characterize the ignition process by depicting the histories of reflected shock pressure and OH* light emission (see Fig. 3). In Region II, the excited OH* always begins to grow up earlier than the pressure, suggesting that pre-ignition can occur before the main ignition onset, but causes only a tiny pressure rise (see Fig. 3(a)). The pre-energy release/pre-ignition pattern has been previously observed for different fuels including \(n\)-heptane [23], \(\text{iso-octane}\) [28], methyfuran [21], toluene [29, 30] and ethanol [22]. If the temperature shifts from Region II to Region IV, however, the OH radical appears to be suppressed by the low temperature and shows excellent agreement with the pressure-time history in a homogeneous manner at the onset of ignition (see Fig. 3(b)). More experimental results are available in Figs. S1-S5 of the Supplementary Material.

Pre-ignition, the cause of inhomogeneous ignition regimes centered, has been postulated to be formed from unburned gas being ignited by small fragments of diaphragms [28]. If so, the pre-ignition pattern would be an experimentally random occurrence as observed by Shen et al. [29] in a contaminated reactor, as the
distribution of diaphragm particles cannot be the same for each run in ST experiments. Interestingly, the temperature-dependence of DME IDT with pre-ignition perturbation can be unexpectedly repeated in Region II. Figueroa-Labastida et al. [22] indicated that the pre-ignition energy release cannot be described using a typical non-ideal facility effect in an ST due to the growth and development of a localized flame kernel. Therefore, computational fluid dynamics (CFD) simulations in the growth of the flame kernel and subsequent flame propagation would be helpful to further understanding of the effect of pre-ignition.

![Figure 3](image-url)

Figure 3. Typical time histories of reflected shock pressure and OH$^*$ chemiluminescence detected during the ignition process of $\phi = 2.0$ mixture in region II (a) and in region IV (b).

### 4.2 Numerical approach

A parallel approach to that of Javed et al. [23] was used to quickly simulate the experimental observation of ignition advancement by a spherical hot spot in an inhomogeneous manner was accomplished using the CONVERGE software [31]. The computational configuration was set up as a cylinder of 50 mm in length with a 20 mm internal diameter to represent the test section near the end wall of the ST. Reynolds Average N-S equation-based turbulent models were employed throughout
the simulations, with a detailed chemistry solver (SAGE) [32]. Grid generation was performed during run-time by using both fixed imbedding of cells and adaptive mesh refinement (AMR). The mesh size was 4 mm together with a spherical fixed imbedding (diameter of 2 mm) implemented for the hot spot. The minimum cell size was 0.25 mm with a threshold valve (2.5 K) of minimum temperature, above which subgrid will be imbedded. Fully implicit time integration was used with the time step range from 10 ns to 1 μs. A reduced skeletal mechanism based on AramcoMech 3.0 was used in the CFD simulations. The comparison results are depicted Fig. S6 and the details are also available in the Supplementary material.

4.3 Effect of the hot spot on auto-ignition

Figure 4 illustrates the comparison of the measured IDTs, simulations with the assumption of constant $U$ and $V$ and simulations with a hot spot. At given energy and duration of heat release (60 mJ and 0 – 20 ms for $\varphi = 0.5$, 40 mJ and 0 – 10 ms for $\varphi = 1.0$, 12 mJ and 0 – 2 ms for $\varphi = 2.0$, and 10 mJ and 0 – 1.5 ms for $\varphi = 3.0$) (see Table S1) the localized hot spots have only a limited impact on the auto-ignition at high temperatures, whereas prominently influence it at middle temperature. The pre-ignition simulations are generally in very good agreement with the experimental IDTs over the entire temperature range except in Region IV. The simulated results substantiate the proposition that the fall-off behavior of IDT measured in the experiments is caused by localized hot spots in Region II and Region III but have also proven to be indecipherable for the discrepancy in Region IV.
Figure 4. Parametric study of the effect of hot spots on IDTs for DME/air mixtures at equivalence ratios of 0.5 (a), 1.0 (b), 2.0 (c) and 3.0 (d).

The pre-ignition energy release and time duration appear to strongly depend on equivalence ratio, and the details of various pre-ignition energy sources used in the CFD simulations are available in the Supplementary Material. In general, the energy and the duration of heat release decrease with increasing fuel concentrations. The formation of localized hot spots is likely caused by physically and chemically intertwined effects including non-ideal shock bifurcation, shock wave boundary layer, thermal diffusivity, and fuel chemistry. However, the theoretical mechanism of the formation of hot spots is still an open question.

The hot spot energy used in our CFD simulations largely refers to the work of Javed et al. [23] due to a comparable energy concern. A decrease in the selected energy with increasing fuel concentrations is due mainly to the extinction limit of
DME flame. Laminar flame thickness (thermal diffusivity divided by laminar flame speed) could represent a likelihood of the pre-ignite combustible mixture. The thinner the laminar flame is, the easier is it to generate a hot spot in shock tube due to the non-ideal boundary layer. The hot spot is, on the other hand, capable of developing a flame kernel therefore a propagating flame. It is suggested that a thinner laminar flame would more likely be affected even by a small scale inhomogeneity of temperature. It is relatively easy to gain thinner laminar flame with decreasing equivalence ratio at a given temperature (see Fig.5). Therefore, the kernel energy was set higher at a smaller equivalence ratio side, where the pre-ignition was more likely to occur.

![Figure 5. Cold side temperature dependence of laminar flame thickness at various equivalence ratios.](image)

**4.4 Growth and propagation of flame kernel**

Whether the hot spot affects IDT measurements for DME oxidation largely depends on the successful growth and propagation of a flame kernel prior to the main onset of ignition. Obviously from the experimental observation, the hot spot affects the IDTs only in Region II and III. To clarify this, simulated pressure, maximum temperature together with the corresponding nephogram of temperature at
characterized IDTs are plotted for the $\varphi = 2.0$ mixture at two typical temperatures, 960 K and 940 K, which lie in Regions II and III, respectively.

At 960 K, the IDTs of DME are advanced prominently by the localized hot spot (see Fig. 6). The hot spot does not cause a significant temperature rise before 0.7 ms, while it leads to a moderate increase in the temperature prior to 1.8 ms. Subsequently, the DME/'air' mixture is ignited with a flame kernel due to relatively higher heat accumulation than heat dissipation around 1.9 ms. Note that the temperature gradient falls to zero within a short period after 2.0 ms owing to the revocation of the hot spot. Thereafter, the temperature and pressure increase sharply because successful flame propagation caused by significant energy and radical species formation induces an inhomogeneous ignition throughout the reactor. It is therefore deduced that the competition between IDT and characteristic time \(\tau\) is crucial to determine whether the hot spot causes a pre-ignition. In Region I, however, relatively more violent molecular motion and interaction leads to a shorter IDT than the characteristic time \(\tau\), and the hot spot is too late to induce the formation of a flame kernel, and it thus maintains a homogeneous ignition (see Fig. 4).

Figure 6. Nephogram of temperature with development of flame kernel during the ignition of $\varphi = 2.0$ DME/'air' mixture at 960 K, where the IDT is advanced by the localized hot spot.
At 940 K however, the IDTs of DME cannot be influenced by the localized hot spot (see Fig. 7). The maximum temperature is increased by the hot spot but quickly falls to the initial level at the characteristic time (3). This is because a too long induced time before the main ignition removal of the radicals formed by a hot spot via collision with the reactor wall, resulting in a limited effect of the hot spot on the IDT due to greater heat dissipation than reaction heat release. The ignition of the DME/‘air’ mixture was very close to homogeneous auto-ignition due to the failure formation of flame kernel followed by flame propagation.

Figure 7. Nephogram of temperature with the dissipation of hot spot during the ignition of $\phi = 2.0$ DME/‘air’ mixture at 940 K, where the IDT is not advanced by the localized hot spot.

5. Chemical kinetics analysis

There remains a deviation between the measurements and the simulations even considering a hot spot in Region IV (see Fig. 4), implying that the chemical kinetic mechanism of DME still lacks something be it either an overlooked/inaccurate reaction pathway or inexact thermodynamic data of species involving in the low-temperature low-pressure chemistry of DME.
5.1 Third addition to O₂

A reaction class involving the third addition to O₂ was proposed by Wang et al. [33] to affect cool flame chemistry at low-temperature region, and it was thus incorporated into the AramcoMech 3.0 [27]. The detailed reaction scheme of the third addition to O₂ considered in the mechanism is depicted in Fig. 8. Glossary of the new species and the corresponding reaction rates are available in Table S2 and Table S3 of the Supplementary Material.

Figure 8. Extended reaction scheme for the consumption of \( \cdot \text{O}_2\text{CH}_2\text{OCH}_2\text{O}_2\text{H} \) radical. Third O₂ addition sub-set added in this study is annotated with a dotted box.

Rate constants for the third O₂ addition reactions were estimated by analogy with the second O₂ addition reactions in DME. Thermodynamic data of newly added species were estimated using THERM [34] based on the group additivity method employed by Benson [35]. However, the new reaction class associated with the corresponding thermochemistry has almost no effect on the low-temperature reactivity of DME. Considering uncertainty in the thermodynamic properties of \( \cdot \text{HO}_2(\cdot\text{O}_2)\text{CHOCH}_2\text{O}_2\text{H} \) (DHPR2) radical caused from the lack of a C/H/O/OO/OO group in the BD library, a quantum-chemical compound method of G3/G4/CBS-APNAO proposed by Simmie and Somers [36] was utilized to
re-calculate the standard enthalpy of formation of DHPR2 together with the atomization enthalpy method. Discrepancies of the quantum calculations and group additivity estimation are 5.5 kcal mol$^{-1}$ for enthalpy of formation and 9.6 cal mol$^{-1}$ for entropy at 298 K (see Fig. S7). This results in 22% longer IDT for $\varphi = 0.5$ DME/‘air’ mixture at 700 K and 3.0 atm relative to the original AramcoMech 3.0 (see Fig. S8). It is therefore concluded that the third O$_2$ addition reactions are unable to improve the low-temperature mechanism of DME, and more high-level ab-initio calculations of the thermochemistry of intermediates involved in the low-temperature oxidation are needed.

5.2 Sensitivity analysis

A brute-force sensitivity analysis was carried out using AramcoMech 3.0 to further identify the dominant reactions for the $\varphi = 2.0$ DME/‘air’ mixture at 3.0 atm and at 680 K and 840 K, which lie in Regions III and IV respectively (see Fig.9). Only one reaction, the decomposition of hydroperoxy-methylformate (HO$_2$CH$_2$OCHO = OCH$_2$OCHO + OH), shows a prominent promoting effect on the reactivity in the low-temperature regime but does not affect the NTC regime. The rate constant of this reaction in most kinetic models of DME is taken by analogy with ROOH decomposition [37], and the difference in reaction systems between HO$_2$CH$_2$OCHO and ROOH likely contribute to the uncertainty of available DME mechanisms.
6. Conclusions

This study provides new shock tube IDTs of DME/\textquoteleft \textquoteleft air\textquoteright \textquoteright mixtures to supplement the lack of data at low pressures and relatively low temperatures. An odd IDT fall-off behavior was found experimentally in the temperature range 900–1100 K but was blurred with increasing fuel concentrations. Based on experimental observation, the low-pressure ignition of DME was generally classified by four regimes; Region I: the high-temperature ignition regime, Region II: transition-temperature ignition regime from high-temperature side to NTC side, Region III: the NTC regime and Region IV: the low-temperature regime. An observation consistent with the \textit{n}-heptane ignition reported by Javed et al [23] was obtained experimentally. The current DME kinetic mechanism (AramcoMech 3.0) shows large discrepancies in predicting the IDTs in Regions II and IV whereas it is in excellent agreement in Regions I. A hot spot hypothesis was implemented using CFD simulations with a model configuration of post-shock conditions. In doing so, the AramcoMech 3.0 captures well the fall-off
behavior IDT in Region II and Region III. The relation of IDT and characteristic time (Fig.6.) is crucial to determine whether the hot spot causes the pre-ignition and further advances the IDTs in Region I. The successful formation and propagation of flame kernel induced by a hot spot determines the inhomogeneous ignition in Region II and III. The formation of the flame kernel is suppressed at long ignition delay times because of scavenging free radicals via collision with the wall. It thus maintains a homogeneous ignition in Region IV.

The discrepancy of experimental measurements and model predictions using AramcoMech 3.0 in Region IV is largely caused by the uncertainty in the kinetic mechanism. The third addition to O₂ reaction classes was incorporated in the current mechanism but did not show an improvement in the model performance at low temperatures. Considering the uncertainty in thermodynamic data estimated using group additivity, the thermodynamic properties of HO₂(Ö₂)CHOCH₂O₂H radical were re-calculated using the G3/G4/CBS-APNAO compound method with an atomization enthalpy approach. The ab-initio calculation shows a significant effect on the IDTs of DME/‘air’ mixtures in Region IV. A sensitivity analysis indicates that HO₂CH₂OCHO = ÓCH₂OCHO + ÓH is the only reaction showing a dominant effect on ignition in Region IV but has no effect in the other regions. An unreliable analogy to ROOH decomposition in assigning the rate constant is a potential cause for the deviation of the modeled and measured IDTs in Region IV.

Unfortunately, those who yearn for the dynamic mechanism of a hot spot and kinetic mechanism of DME low-temperature chemistry must look beyond the horizon
towards abundant experimental and theoretical studies that will be required to meet this aim.

Acknowledgments

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