Low to intermediate temperature oxidation studies of dimethoxymethane/\(n\)-heptane blends in a jet-stirred reactor

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Kinetic research concerning fuel blends of ethers or dithers and larger alkanes at low temperatures is extremely scarce. In this work, a study of the oxidation of dimethoxymethane (DMM)/\(n\)-heptane fuel blends (neat \(n\)-heptane, 25/75, 50/50, neat DMM) was performed using an atmospheric pressure jet-stirred reactor over the temperature range of 500–1100 K, at a residence time of 2.0 s, at three equivalence ratios (0.5, 1.0, and 2.0), and at a constant fuel inlet mole fraction of 0.005 (with high dilution in argon). The reliability of the newly built JSR setup was validated against literature data. A chemical kinetic model capable of describing the low temperature chemistry of the fuel blends was constructed. The effect of using AramcoMech 1.3 and AramcoMech 2.0, respectively, as the base-mechanism has been tested and some important reactions such as \(H + O_2 \rightarrow HO_2 + M\) have been found to be responsible for their different performances. Not unexpectedly, the reactivity of DMM is remarkably enhanced in the fuel blends and correspondingly, that of \(n\)-heptane is inhibited. To quantify the degree to which the reactivity of \(n\)-heptane is inhibited, an inhibiting coefficient was introduced. It is interesting that the correlation between the inhibiting intensity and equivalence ratio is non-monotonic. Rate of production analysis was conducted to investigate the chemical interaction effect on their respective decomposition pathways at lower temperatures. Kinetic analysis combined with the experimental observations indicate that the rate coefficients for \(H\)-abstraction reactions by \(OH\) from DMM were overestimated. Possible modifications to the reaction rate of this reaction type were suggested, leading to a better prediction. Three intermediate representatives were discussed in detail to elucidate the chemical interactions between the two fuel components.

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1. Introduction

Depletion of fossil energy reserves and the problem of environmental pollution have motivated research of alternative fuels and novel concepts for cleaner combustion. Blending conventional diesel fuels with oxygenated compounds has been widely demonstrated to be capable of effectively reducing emissions [1–4]. Dimethoxymethane (DMM) is a promising additive due to its high miscibility with diesel fuels and the absence of carbon–carbon (C–C) bonds from the molecular structure. Engine studies [2,5,6] have proved its soot-inhibition ability, positive influence on the soot-NO\(_x\) tradeoff and other good combustion characteristics. As an advanced low temperature combustion (LTC) technique, RCCI combustion offers prominent benefits in terms of simultaneous reduction of NO\(_x\) and particulate matter (PM) [7]. This combustion strategy is realized by using a combination of high- and low-reactivity fuels to achieve efficient ignition timing control. Diesel is usually used as the high-reactivity fuel for RCCI combustion research [8–10]. While for DMM, which shows considerably less reactivity under low temperatures, it can be a potential candidate of the low-reactivity fuel in such a LTC combustion concept. Hence, fundamental knowledge of the combustion chemistry which drives the low temperature reactivity of their fuel mixtures is needed. Due to the complexity of the components of commercial diesel fuel, \(n\)-heptane has been widely used as a diesel surrogate in fundamental combustion research.

Well-developed chemical kinetic mechanisms for both \(n\)-heptane and DMM are prerequisites to elucidate the synergistic combustion behaviors of their fuel blends. As a primary reference fuel (PRF), \(n\)-heptane has been extensively studied in a range of experimental facilities, such as shock tubes [11–16], rapid compression machines (RCM) [17–20], as well as jet-stirred reactors (JSR) [21–25]. Continuous effort has been devoted into the development of its kinetic model to gain a better understanding of its oxidation chemistry at both high and low temperatures since 1979 [11]. A kinetic model for the oxidation of iso-octane and \(n\)-heptane...
was developed by Westbrook et al. [26]. This model was validated against a series of experimental data over a wide range of conditions including data from JSR. Curran et al. [27] conducted a systematic study on the oxidation of n-heptane. A new kinetic model was built and a satisfactory agreement between the model predictions and measured data was obtained. Further refinement was made to this model by Mehlt et al. [28] on the basis of quantum chemical calculations and literature reviews. As a part of a gasoline surrogate model in their work, ignition delay times of PRFs, 1-hexene, toluene and their mixtures in a RCM as well as a JSR can be well simulated by this model. More effort has been devoted to the low temperature oxidation of n-heptane by Herbinet et al. [24]. By using synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS), important unstable intermediates such as keto-hydroperoxides were observed, thus a deeper insight into the low temperature oxidation of n-heptane was obtained. An improved model for the low-temperature oxidation of n-heptane was proposed by Pelucchi et al. [29] by introducing new reaction classes and good agreements between model predictions and measured data were achieved. Recently, a comprehensive study on the oxidation of n-heptane was performed by Zhang et al. [30] and a detailed kinetic model was constructed. One of the most significant features about this model is the implementation of the rate rules used for pentane isomers [31,32] and n-hexane [33] modeling. Many of the rate constants adopted in the rate rules for the low temperature reaction classes are from quantum chemical calculations [34–38] with proper modifications. Validation against data sets from various experimental facilities over a wide range of conditions showed a good agreement between the model predictions and the experimental data.

Compared with n-heptane, the kinetics of DMM especially at lower temperatures are less explored. Daly et al. [39] developed the first detailed DMM kinetic model. The rate constants of most reactions specific to DMM oxidation in this model are obtained by analogy with similar reactions of dimethyl ether (DME) and di-ethyl ether (DEE). JSR experiments were performed over a temperature range of 800K–1200K. Reasonable agreement was achieved between the measured products mole fractions and model simulations although some important reaction pathways for low temperature are missing in this model. This is due to the less importance of low temperature chemistry in such an intermediate temperature range. Dias et al. [40] studied the rich and lean premixed DMM/O2/Ar flame structure and a kinetic model was built to reproduce the experimental results, with most kinetic parameters directly taken from the model developed by Daly et al. [39]. Marrodán et al. [41,42] performed atmospheric and high pressure (20–60 bar) flow reactor studies on the oxidation of DMM with an extended temperature range of 373K–1073K. A kinetic model was proposed based on the model of Dias et al. [40]. The experimental data was not well captured by the model, indicating that the oxidation chemistry of DMM is not fully understood.

Meanwhile, new experimental facilities and theoretical methods are being used to further explore the mechanism of DMM combustion. Ignition delay times of DMM were measured in a shock tube by Zhang et al. [43]. Recently, for the first time, \textit{ab initio} methods was used to elucidate the kinetics and thermochemistry of DMM by Kopp et al. [44]. Some key reactions for DMM oxidation were computed. Results of this work presented new insights into the oxidation of DMM with a more accurate method. However, only several important reactions were calculated and the reactions involved in the low-temperature chemistry were not included. More recently, the low temperature chemistry of DMM was investigated in detail both theoretically and experimentally by Vermeire et al. [45]. By using the software Genesys [46,47] and the calculated rate expressions for main reactions, a comprehensive kinetic model was built.

With regard to fuel blends of ethers or diethers and larger alkanes, a combination of low- and high-reactivity fuels, the kinetic research remains extremely scarce, especially at lower temperatures [48]. Due to the chemical stability of DMM, not much low-temperature reactivity has been observed in the study of Vermeire et al. [45]. In their study, only methyl formate and formaldehyde were used as indicative species of the low temperature oxidation as the changes of DMM concentration were negligible. It is to be expected that by blending n-heptane with DMM, the low temperature oxidation of DMM will be significantly promoted, and therefore new experimental data can be obtained and used for validation of kinetic models and further refinements, which is another important motivation of this work. Similar method can be found in recent work [49] in which DME was used as a radical initiator to induce low temperature ignition in toluene.

In general, the present work focuses on both experimental and simulation results for DMM/n-heptane blends at different conditions. In addition to providing new insights into the oxidation of this fuel blend, the abundant new experimental data for DMM low-temperature oxidation also contributes to its model validation and refinement.

2. Experimental methods

2.1. Setup and procedures

The oxidation of DMM, n-heptane as well as their dual-fuel mixtures was investigated in a newly built JSR setup. Rules established by Matras and Villermaux [50] and David and Matras [51] were followed during the design of the reactor. Figure 1 shows the schematic of the experimental system. The reactor consists of a fused silica sphere (volume of 87 cm$^3$) and an injection cross made of 4 nozzles at its center. Stirring is achieved by turbulent jets flowing through the nozzles since homogeneity in both temperature and composition of the gas phase is of importance in such reactors. An electrical furnace (SK-G05123K, ZHONGHUAN) operating within ±1.0°C of its set value is used to heat the reactor. The reaction temperature is measured using an Omega K-type thermocouple (the extremity of the thermocouple is located at the center of the reactor in a glass finger in the injection cross, as illustrated in Fig. 1.). The uncertainties in the measurements are ±0.4%. The liquid fuel is delivered by a syringe pump (LONGER, LSP01-1A) to a vaporization chamber maintained at 30°C above the boiling point of the fuels, producing a homogenous dilute (Ar) fuel gas mixture. Both n-heptane and DMM were supplied by Energy Chemical in high purity (99%). Uncertainties in the flow rate are below 0.5%. All the high purity gases (Ar and O2 with a purity of 99.999%) are regulated by thermal mass-flow controllers (MKS) with a maximum uncertainty of 0.5%. Reactant mixtures are preheated before entering the reactor to minimize the thermal gradients within the reactor.

Reaction products are analyzed using online gas chromatography (GC). The heated transfer line between the outlet of the JSR and the analytic equipment ensures good vaporization of the products. As shown in Fig. 1, two GCs (Agilent 7890B) are used to detect a wide range of species. The first one equipped with 3 packed columns (1 Molecular Sieve 5A and 2 Haysep Q packed columns) and a thermal conductivity detector (TCD) is used to determine the concentration of light species such as O2, CO, CO2, and H2. The second one fitted with two flame ionization detectors (FID) and two capillary columns (HP-5 and Plot Q) is used for the quantification of C7 hydrocarbons and lighter species including oxygenated compounds, respectively.

In this work, atmospheric-pressure oxidation experiments were conducted for DMM/n-heptane fuel blends by varying the mole
Percentage of DMM (0%, 25%, 50%, 100%) at temperatures from 500 to 1100 K, at different equivalence ratios (0.5, 1.0, 2.0), at a constant residence time of 2.0 s and fuel inlet mole fraction of 0.005 (diluted in argon). Based on the fixed initial pressure of 1.0 atm, the residence time \( \tau \) is calculated through the following equation:

\[
\tau = \frac{V}{\nu \times \frac{T}{298.15}} \quad (1)
\]

where \( V \) is the volume of the reactor, \( \nu \) is the inlet (the whole fuel/O\(_2\)/Ar mixture) volume flow rate at 298.15 K, \( T \) is the reactor temperature (reaction temperature). The inlet flow rate needs to be recalculated at different temperatures to keep the residence time constant.

The inlet conditions are given in Table 1. The following species were quantified: DMM, n-heptane, oxygen, carbon monoxide, carbon dioxide, hydrogen, methane, ethylene, acetylene, ethane, propane, propene, methanol, acetaldehyde, acrolein, propanal, methyl formate, butanal, butane, butene, 1,3-butadiene, 1-pentene, 1-hexene. All the species were calibrated using standard gas mixtures provided by Air Products.

2.2. Validation of the experimental setup

In this work, a JSR experimental setup was built to perform the low-temperature oxidation study. The reliability of this system was validated by comparing the stoichiometric neat n-heptane data obtained from this JSR setup with the work of Herbinet et al. [24]. Noted that helium was used for the fuel dilution by Herbinet et al. while argon was employed in this study. Apart from this, other experimental conditions such as the residence time, pressure and the fuel mixture composition are identical between the two studies. Figure 2 displays the comparison results for the reactants and major products. “CNRS” and “USTC” in the legend represent experimental data from the study of Herbinet et al. [24] obtained by GC and SVUV-PIMS, respectively. “XJTU” represent experimental data obtained in this study. More detailed validation results are provided in the Supplement material (Figs. S1–3).

According to Fig. 2 and Figs. S1–3, good consistency between the two sets of data is achieved. In specific, the mole fractions of reactants and major products (CO and CO\(_2\)) obtained from this JSR agree fairly well with that of Herbinet et al. [24] from CNRS. The agreement of major hydrocarbons, especially olefins between the two datasets is also pretty good. Some deviations (not significant) are observed for acetylene. For oxygenate species, most of them achieve good agreement except for methanol and acrolein. Note that methanol was measured using SVUV-PIMS by Herbinet et al. [24] and obvious deviations between data sets obtained using SVUV-PIMS and GC were also observed for many species in their study. In general, the reliability of this experimental setup is fairly good. In addition, this setup also showed a good repeatability under all conditions. Based on the repeatability of the experiments, the estimated error on the obtained mole fractions is ±5%. To guarantee the reliability of the quantification, the carbon balance was checked for every sample in our experiments and the agreement was found to be within 10%.

3. Chemical kinetic modeling

3.1. Evaluation of the implementation of different base mechanisms

A detailed chemical kinetic model capable of describing the chemistry of the fuel blend is needed to kinetically interpret their
synergistic oxidation behaviors. The blend model was created by coupling the two individual models for each of the fuel components. In this work, the n-heptane model developed by Zhang et al. [30] was adopted for its overall good performance, especially its superiority in terms of predicting the JSR species compared with other published models. For DMM, the model developed by Vermeire et al. [45] was used since this is the only model which contains the complete low temperature reaction network in present literatures. However, different base mechanisms were used in the two models. AramcoMech 2.0 [52,53] was used for describing the C0-C4 chemistry in the n-heptane model of Zhang et al. [30], while AramcoMech 1.3 [54] was chosen in the DMM model of Vermeire et al. [45]. This raises questions about the ability of the merged blend model to predict species for each pure component when a different base mechanism is adopted compared with the corresponding original model.

The effect of using different base mechanisms in the blend model was evaluated, as shown in Fig. 3(a). Blend models using AramcoMech 1.3 and AramcoMech 2.0 as the base mechanism respectively are named as BLmech 1.3 and BLmech 2.0, respectively. The most significant difference between them was found to be their predictions on methyl formate (MF) for pure DMM oxidation at \( \phi = 0.5 \). As shown in Fig. 3(a), the experimentally measured MF below 800 K (the only intermediate detected at this temperature range) indicates some low-temperature reactivity under this condition. Both the original DMM model, namely Vermeire model, and BLmech 1.3 are able to predict this low-temperature reactivity with the formation peak close to experimental values, although the start of the reactivity is not accurately captured. However, BLmech 2.0 fails to predict the low-temperature reactivity under this condition. It should be noted that when the low-temperature oxidation occurs at this condition, the corresponding maximum DMM conversion is around 5%, according to Vermeire model or BLmech 1.3. This slight change was not reflected by the experimental DMM concentration profile because it is within the uncertainty of the experimental values. Several reactions have been found to be responsible for yielding different predictions when using different base mechanisms. The reaction \( \text{H} + \text{O}_2 (+\text{M}) \leftrightarrow \text{HO}_2 (+\text{M}) \) has a different enhanced third-body efficiency for Ar in the two base mechanisms (0 in AramcoMech 1.3, 0.5 in AramcoMech 2.0) and it gains importance with Ar being used as the dilution in this study. Detailed comparisons of the rate expressions for this reaction in different mechanisms are listed in Table 2.

A second rate expression for \( \text{H} + \text{O}_2 (+\text{M}) \leftrightarrow \text{HO}_2 (+\text{M}) \) with the third body specified to be Ar (\( \text{H} + \text{O}_2 (+\text{Ar}) = \text{HO}_2 (+\text{Ar}) \)) is used in Aramco 1.3. While in the Vermeire DMM model [R8], only the rate expression \( \text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2 (+\text{M}) \) was retained even though the whole DMM model is based on Aramco 1.3. Since BLmech 1.3 uses the same base-mechanism as the Vermeire DMM model, the rate expression for \( \text{H} + \text{O}_2 (+\text{Ar}) = \text{HO}_2 (+\text{Ar}) \) was not included either, as shown in Table 2.

To investigate the sensitivity of this reaction to the low-temperature reactivity of DMM, BLmech 1.3 was compared with two modified BLmech 1.3 as shown in Fig. 3(b). Modification 1 stands for replacing the rate coefficient for \( \text{H} + \text{O}_2 (+\text{M}) \leftrightarrow \text{HO}_2 (+\text{M}) \) in BLmech 1.3 with the one from Aramco 2.0. Modification 2 stands for adding the rate expression of \( \text{H} + \text{O}_2 (+\text{Ar}) = \text{HO}_2 (+\text{Ar}) \) in Aramco 1.3 to BLmech 1.3.

It can be seen that by solely replacing the rate constant for \( \text{H} + \text{O}_2 (+\text{M}) \leftrightarrow \text{HO}_2 (+\text{M}) \) in BLmech 1.3 with the one from Aramco 2.0, BLmech 1.3 produces similar prediction with that of BLmech 2.0 (the blue line in Fig. 3(a)). This is because the first-step decomposition of DMM is dominated by H-abstraction by H.

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**Fig. 2.** Comparison results for the reactants and major products.
radical. The higher reaction rate for \( H + O_2 (\pm M) \rightarrow H O_2 (\pm M) \) in AramcoMech 2.0 promotes the consumption of \( H \) radical and thus the decomposition of \( DMM \) is inhibited. After adding the rate expression of \( H + O_2 (\pm Ar) = H O_2 (\pm Ar) \) in Aramco 1.3 to BLmech 1.3 (modification 2), the model gives almost the same results as modification 1. From the comparison results, BLmech 1.3 gives the most reasonable simulations. More detailed discussion about this reaction is provided in the SM.

For AramcoMech 2.0 system, besides the reaction discussed above, other important reactions such as \( CH_3OH + O_2 \rightarrow CH_3O + HO_2, CH_3O_2 + H \rightarrow CH_3O + HO_2 \) whose rate constants differ in the two base mechanisms, also play a significant role in determining the reactivity under low temperatures. For the reason explained above, AramcoMech 1.3 was finally selected as the base mechanism in the blend model. Note that the latest version of the AramcoMech, namely AramcoMech 3.0, has been developed by Zhou et al. [55] by updating the 1,3-butadiene mechanism. However, the rate constants of the abovementioned reactions remain the same as those in AramcoMech 2.0. Therefore, AramcoMech 3.0 was not considered in this work.

### 3.2. Validity of the blend model for pure fuel components

Not unexpectedly, BLmech 1.3 gives almost the same predictions as that of the original DMM model. However, since it uses a different base mechanism (AramcoMech 1.3) than the one used (AramcoMech 2.0) in the original \( n \)-heptane model, its validity for pure \( n \)-heptane oxidation needs to be tested. The comparisons between the calculated results of neat \( n \)-heptane oxidation using the blend model and the original \( n \)-heptane model are displayed in Figs. S3–6. In short, no significant deteriorations are observed except for acerolin (\( C_2H_7CHO \)), which is not unexpected due to that many reactions involving unsaturated C3 species differ in AramcoMech 1.3 and AramcoMech 2.0.

### 3.3. Cross reactions

For multi-component fuel mixtures, their chemical interactions are considered to be limited to the effect of small radicals [56,57]. Nevertheless, cross reactions in which a fuel derived radical abstracts hydrogen from the other fuel were also included in some studies [58,59]. Andrae et al. [60] suggested that cross reactions should be considered for two fuels with similar
molecular structures. However, they become less important if the fuels are substantially different since their consumption processes are not synchronous. Furthermore, once the pool of small radicals has developed, hydrogen abstraction by small radicals other than fuel derived radicals will dominate the fuel consumption. Cross reactions were also not considered in recent n-heptane-containing fuel mixture studies [61]. More recently, Zhang et al. [49] added some potential important cross reactions during the modeling of DME/toluene mixtures. However, they found that these new reactions have little or no impact on the mixture consumption pathway. Hence, cross reactions are not introduced in this work.

4. Results and discussions

4.1. General performance of the blend model

Comparisons between the BLMech1.3 predicted and measured species mole fractions under different equivalence ratios and DMM blending ratios are given in Figs. 4–6. The qualitative conversions of both DMM and n-heptane can be reasonably predicted by the model under all conditions. Particularly, the concentration of O₂ is in good agreement with the model simulations. Main products such as hydrogen, CO₂ and CO are also well predicted. For some light hydrocarbons such as methane and ethane, obvious deviations are observed as the DMM blending ratio increases. This is due to the underperformance of the DMM sub-mechanism on predicting the formation of these species, which has also been pointed out by Vermeire et al. [45]. Detailed discussions about other important intermediates are presented in the next sections. Generally, the agreements between the experimental and computed data are satisfactory.

4.2. Influence of DMM addition on fuel reactivity

The interaction effect between the two fuels is presented in more detail by normalizing their fuel consumptions, as shown in Fig. 7.

N-heptane shows typical two-stage oxidation behaviors under all investigated conditions. The conversion of n-heptane under neat fuel conditions starts around 525 K and no obvious delay of this low temperature reactivity with the addition DMM is observed. For φ = 0.5, φ = 1.0 and φ = 2.0, the maximum low temperature conversion of n-heptane is 71%, 52% and 43% respectively, as seen in Fig. 7a–c. While for pure DMM, the experimental data measured at φ = 1.0 and 2.0 indicates that its consumption starts only above 800 K. As previously mentioned, the experimentally detected formation of methyl formate during the oxidation of pure DMM at φ = 0.5 (see Fig. 4i) shows some low temperature reactivity. This is not clear from the mole fraction profile of DMM due to that the change is too small. Both DMM and n-heptane in this study suggest that fuel lean mixtures are more reactive. In some low-temperature studies [62,63], the opposite conclusion is drawn because the way the reactant mixtures were prepared is different. In this study, the concentration of the fuel remains constant while that of O₂ varies to meet the desired equivalence ratio. Thus the fuel lean mixtures with a higher O₂ concentration exhibit a higher reactivity. Noting that in the study of Vermeire et al. [45], for φ = 2.0, φ = 1.0 and φ = 0.25, the conversion of DMM was observed around 650 K, 650 K and 550 K respectively. This is because of the longer residence time and higher inlet fuel mole fraction employed in their study.

The enhanced reactivity of DMM by n-heptane can be clearly seen from Fig. 8d–f. In their fuel blends, DMM exhibits a similar two-stage oxidation behavior. The blend model gives satisfactory predictions on the enhancement effect for the fuel blend of D50. As the replacement of n-heptane increases in the blends (from D100 to D25), the enhancement effect tendency to be over-predicted but the shape of the simulated conversion profiles corresponds well to that of the experimental data. Accordingly, the reactivity of n-heptane is inhibited by the addition of DMM as seen from Fig. 8a–c. The inhibiting effect is found to be most pronounced at ϕ = 0.5 indicated by the significantly reduced low temperature fuel conversion. Apart from that, DMM addition also advances the start of the NTC region at ϕ = 0.5. Specifically, the NTC region of pure n-heptane starts at 690 K. With 25% and 50% addition of DMM, it is advanced to 635 K and 600 K, respectively, as seen from Fig. 8a. Unlike the stoichiometric and rich mixtures, the conversion of n-heptane at ϕ = 0.5 does not return to zero at the end of the NTC region (around 750 K). While as the mole fraction of DMM increases, the NTC effect is progressively enhanced and the conversion eventually returns to zero at the end of the NTC region when DMM blending ratio reaches 50% (D50). Although the inhibiting effect is qualitatively predicted by BLMech1.3, it fails to quantitatively capture the effect on the NTC behavior. The primary reason is that at ϕ = 0.5, the performance of the n-heptane sub-model developed by Zhang et al. [30] is not as good as other equivalence ratios, which has also been pointed out in their paper.

It can be roughly seen from Fig. 7a–c that at different equivalence ratios, the DMM addition exhibits different inhibiting intensities (the degree to which the reactivity of n-heptane is inhibited). To quantitatively evaluate this inhibition as a function of equivalence ratio, an inhibiting coefficient (I) is introduced. It is defined as follows:

\[
I = 1 - \frac{c_{\text{blend}, i}}{c_{\text{pure}, i}}
\]

(2)

where \(c_{\text{blend}, i}\) and \(c_{\text{pure}, i}\) represent the maximum n-heptane conversion during the first-stage oxidation under blended and pure n-heptane condition respectively, at equivalence ratio of \(i = 0.5, 1.0, 2.0\).

From the definition above, it can be concluded that a higher inhibiting coefficient means that the addition of DMM suppresses the conversion of n-heptane to a larger extent. Figure 8 depicts the inhibiting coefficients with corresponding uncertainties calculated based on the uncertainty in the experimental data for the fuel blends of D25 and D50 at different equivalence ratios. It is interesting that the correlation between the inhibiting intensity and the equivalence ratio is non-monotonic. For both D25 and D50, the maximum inhibiting effect is observed upon \(\phi = 2.0\) while \(\phi = 1.0\) has the smallest inhibiting coefficient. This can be seen directly from Fig. 8b that at \(\phi = 1.0\) the addition of DMM leads to a relatively unnoticeable change of the n-heptane conversion.

The rate of production analysis highlighting the primary decomposition pathways for DMM and n-heptane was performed at \(T = 600\) K to investigate the effect of the chemical interactions on their respective consumption pattern, as shown in Figs. 9 and 10. The values besides the arrows in different color represent the percent contribution of the species on the source side of the arrow. For pure DMM, as shown in Fig. 9, the H-abstraction by O₂ shows the maximum contribution to the first-step consumption (35.2% +1.6%). This is because the reactivity of DMM is so low at this temperature that the consumed amount of DMM is negligible according to the simulation results. Before the radical pool (such as CH₃, H, OH) is fully developed, O₂ plays an important role in initiating the oxidation of DMM. For D50, H-abstraction by OH dominates the consumption of DMM with the contributions of O₂ and H₂O drastically drop below 1%. A further increase in the n-heptane mole fraction (D25) enhances its dominance by increasing the contribution from 90% (39.2% +50.8%) to 95.3% (41.5% +53.8%), as seen in Fig. 9. Abstraction from the terminal carbon site and the central carbon site lead to the formation of dimethoxymethyl radical (CH₂–O–CH₂–O–CH₃) and methoxymethoxymethyl radical
Fig. 4. Measured (symbols) species mole fractions together with simulation results (lines) for the oxidation of DMM/n-heptane blends at 1.0 atm with residence time = 2 s, $\phi = 0.5$, 0.5% fuel diluted by Ar.
Fig. 5. Measured (symbols) species mole fractions together with simulation results (lines) for the oxidation of DMM/n-heptane blends at 1.0 atm with residence time = 2 s, $\phi = 1.0$, 0.5% fuel diluted by Ar.
Fig. 6. Measured (symbols) species mole fractions together with simulation results (lines) for the oxidation of DMM/n-heptane blends at 1.0 atm with residence time = 2 s, $\phi$ = 2.0, 0.5% fuel diluted by Ar.
(CH$_3$–O–CH–O–CH$_3$) respectively, with the formation of the latter being favored in the three fuel mixtures. The decomposition of dimethoxymethyl radicals proceeds predominantly by $\beta$-scission while methoxymethoxymethyl radicals prefers the addition of molecular oxygen. The addition of $n$-heptane in the fuel blends shows a slight impact on the decomposition pathways of the abovementioned two fuel radicals. The fate of their subsequently formed products is hardly influenced by DMM addition indicated by the kinetic analysis.

Figure 10 displays the main decomposition pathways during the oxidation of $n$-heptane. Without the addition of DMM, $n$-heptane is mainly consumed through H-abstraction by OH, accounting for 91% of its first-step consumption. This consumption pathway is perturbed by DMM addition with its branching ratio decreases to 87.3 and 69.5 respectively for D25 and D50 fuel mixtures. Almost 100% of the heptyl radicals (R) converts to peroxyalkyl radicals (ROO) via O$_2$ addition for all the fuel mixtures. The DMM addition effect on the fate of ROO is negligible, most of which undergoes isomerization reaction to produce hydroperoxyalkyl radicals (QOOH). While a more obvious (not significant) impact on the consumption pattern of QOOH is observed. Specifically, the branching ratio of the cyclic ethers formation increases with the increase in DMM mole fraction. Noting that this is an important source of OH radical. The OH produced from this reaction is consumed by DMM, resulting in the equilibrium being shifted toward the products and finally the branching ratio of this reaction is increased. Accordingly, the contribution of its competing channel, the second addition to O$_2$ giving peroxyhydroperoxyalkyl radicals (OOQOOH) reduces as DMM content increases. OH radicals generated from both the formation and decomposition of keto-hydroperoxides are the other two important OH sources and according to the reaction path analysis, these conversions are not influenced by DMM addition.

Due to the overwhelming significance of H-abstraction by OH for the two fuels in their blends, a better understanding of their
Competitiveness in terms of producing and consuming $\cdot OH$ radicals will help to explain their synergistic oxidation behaviors. Figure 11 depicts the contributions of the primary pathways to the formation and consumption of $\cdot OH$ at 600 K and $\phi = 0.5$. The bars represent the normalized rate of productions of $\cdot OH$ radical. The reactions in the upper part of Fig. 11 produce $\cdot OH$ while those in the lower part consume $\cdot OH$. It can be seen that without DMM addition, $\cdot OH$ is mainly consumed by $n$-heptane by $H$-abstraction from different carbon sites (R3, R4). Upon 25% DMM addition, the $H$-abstractions from DMM (R1, R2) show comparable contributions with R3 and R4. For D50, in which DMM and $n$-heptane are equal in mole fraction, R1 and R2 consume much more $\cdot OH$ radicals than R3 and R4. A large amount of $\cdot OH$ radical is produced during the formation and decomposition of keto-hydroperoxides (R7, R8, R9, 10), which is the main source of $\cdot OH$ for pure $n$-heptane. With an increase in DMM content, R6 shows important contributions to the $\cdot OH$ production. Noting that R6 is the only highlighted $\cdot OH$ production pathway in Fig. 9, deriving from the hydroperoxide formed during the consumption of DMM fuel radical. When DMM content reaches 50%, R6 becomes the major $\cdot OH$ source in the fuel blend.

In short, according to the model, $n$-heptane provides $\cdot OH$ as the reactivity initiator for DMM. Compared with $n$-heptane, DMM is much more competitive in terms of reacting with $\cdot OH$ and its low temperature $\cdot OH$ producing pathway (R6) is significantly promoted. When the two fuels have equal mole fractions in their blends (D50), DMM becomes the major producer and consumer of $\cdot OH$. Considering the fact that the model over-predicts the consumption of DMM (correspondingly under-predicts that of $n$-heptane) especially at a higher DMM blending ratio (see Fig. 7), it is very likely that the rate constants for DMM + $\cdot OH$ were overestimated. After decreasing the rate coefficients of the two reactions (R1 and R2)
by a factor of 3, the model gives much better predictions on the fuel consumptions, especially for DMM, as seen in Fig. 12 (Fig. 12 only focuses on low temperatures since no significant changes are observed at higher temperatures). Specific assessment of the uncertainty on theoretical calculations for the calculated reactions is not done by Vermeire et al. [40] as it is too computationally intensive. Instead, they performed a general assessment based on previous studies [37, 64–67]. The uncertainty on the kinetic data was eventually assumed to be within a factor of 2–4. Thus, a factor of 3 should be acceptable.

4.3. Important intermediate species

As previously mentioned, the formation of CH$_3$–O–CH–O–CH$_3$ by H-abstraction from the central carbon in DMM molecule is always favored over its isomer radical (CH$_3$–O–CH$_2$–O–CH$_3$). Reaction path analysis in Fig. 9 indicates that over 90% of CH$_3$–O–CH–O–CH$_3$ is consumed via β–scission, leading to the formation of an important intermediates during DMM oxidation–methyl formate (See Fig. 10). Since methyl formate was not experimentally observed during the oxidation of n-heptane, it can be considered as an intermediate specific to DMM. Figure 13 shows the experimentally measured and predicted methyl formate concentration at different inlet conditions. All the profiles are normalized by their respective inlet mole fractions of DMM. By normalization, it becomes possible to compare the production rate of methyl formate among fuel blends with different DMM initial mole fractions, and thus the interactive effects in the mixtures on the formation of this species can be investigated. As seen in Fig. 13, methyl formate shows two formation peaks. The model also gives good predictions with respect to the peak locations and values. The first peak around 600 K corresponds well to the first stage consumption of n-heptane and at this stage, more DMM in D25 compared with D50 is converted into methyl formate. This is because the formation of CH$_3$–O–CH–O–CH$_3$ is favored with a higher mole fraction of n-heptane in the blend. In fact, the branching ratio of the pathway that directly forms methyl formate, namely the β–scission of CH$_3$–O–CH–O–CH$_3$, is reduced as n-heptane mole fraction increases, as indicated in Fig. 9. The peak concentration of methyl formate at the first stage decreases with an increase in equivalence ratio. This is clearly due to the decrease in the low-temperature reactivity of n-heptane as equivalence ratio increases. For the second peak around 850–900 K, methyl formate exhibits comparable mole fractions in different fuel blends and at different equivalence ratios, suggesting that the pathway of DMM is less perturbed by n-heptane.

Keto-hydroperoxides are important intermediate species in the low temperature oxidation of n-alkanes. These large unstable species can easily decompose into smaller oxygenated species, primarily aldehydes. In this study, acetaldehyde is experimentally detected with a higher concentration compared with other types of aldehydes, such as butanal, propanal and acrolein. Since acetaldehyde is not detected in the oxidation of DMM, it can be considered as an intermediate specific to n-heptane.

Figure 14 shows the concentration of acetaldehyde together with simulation results. Similarly, both the experimental data and simulations are normalized by their respective initial mole fraction of n-heptane. It can be seen that DMM addition inhibits the formation of acetaldehyde and this inhibiting effect is limited to the low temperatures (below 700 K). The model can qualitatively capture the addition effect on the formation of acetaldehyde at lower temperatures for φ = 0.5 and gives better predictions for φ = 1.0 and φ = 2.0. However, it notably under-predicts the formation of acetaldehyde at higher temperatures (the second peak) for all equivalence ratios. Reaction analysis reveals that at low temperatures, C$_7$KET42 (one of keto-hydroperoxide isomers) decomposes to OH and C$_7$KET42O by breaking the O–O bond. The sequent β–scission of C$_7$KET42O leads to the formation of acetaldehyde, which is the primary source of acetaldehyde. Figure 10 has shown that the low temperature branching path of n-heptane is barely perturbed by DMM addition, thus the main reason for the reduced formation of acetaldehyde is the reduction in n-heptane consumption.

As one of the key precursors of PAH and soot, acetylene is formed in the oxidation of many hydrocarbons, especially under fuel-rich conditions. Due to the absence of C–C carbon, DMM produces almost no soot precursors during its oxidation. To evaluate the effect of DMM addition on the acetylene production rate, normalized (by inlet mole fraction of n-heptane) acetylene concentration with simulations are plotted in Fig. 15.

As seen from Fig. 15, the formation of acetylene is favored at higher temperatures. Despite that the model predicts a small amount of acetylene at 600–700 K especially for φ = 0.5 and φ = 1.0, no acetylene was detected below 800 K at all investigated inlet conditions during experimental measurements. A remarkably
Fig. 12. DMM and *n*-heptane conversion profiles together with model predictions. Solid lines are predictions obtained using BLmech1.3. Dash dot lines are obtained after decreasing the rate coefficients of DMM + OH by a factor of 3. Blue: D25; Red: D50; Green: D100. *n*-heptane Data of D25 is multiplied by a factor of 2 to avoid overlapping with that of D50. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 13. Measured (symbols) and predicted (lines) methyl formate concentration at different DMM addition levels and equivalence ratios. Each profile is normalized by the respective inlet mole fractions of DMM.

A larger concentration of acetylene is observed at φ = 2.0. Unlike the trends at φ = 0.5 and φ = 1.0, the amount of acetylene produced at φ = 2.0 keeps increasing with temperature. According to the model, at high-temperature and fuel-rich conditions, acetylene is mainly produced from the decomposition of propene. The normalized experimental data shows similar peak concentrations as well as the onset temperatures of the formation of acetylene, suggesting that the conversion of *n*-heptane to acetylene is not perturbed by DMM addition to a great extent. Noting that above simulations were performed using BLmech 1.3.
5. Conclusion

The oxidation of DMM/n-heptane binary fuel blends was firstly investigated in an atmospheric pressure JSR, over a wide range of equivalence ratios. The newly built JSR setup was validated against literature data [24] and good consistency was achieved. A blend kinetic model capable of describing the low-temperature chemistry of the fuel blends was constructed. The sub-mechanisms of n-heptane and DMM were taken from the work of Zhang et al. [30] and Vermeire et al. [45], respectively. The effect of the implementation of different base-mechanisms (AramcoMech 1.3 and AramcoMech 2.0) has been carefully evaluated. It was found that reactions $\text{H} + \text{O}_2 (+\text{M}) \leftrightarrow \text{HO}_2 (+\text{M})$, $\text{CH}_3\text{OH} + \text{O}_2 \leftrightarrow \text{CH}_3\text{O} + \text{HO}_2$, $\text{CH}_3\text{O}_2 + \text{H}_2 \leftrightarrow \text{CH}_3\text{O}_2\text{H} + \text{O}_2$, and $\text{CH}_3\text{O} + \text{O}_2 \leftrightarrow \text{CH}_2\text{O} + \text{HO}_2$, whose rate coefficients differ in the two base-mechanism are primarily responsible for yielding different performances when using the two base-mechanisms. Generally, the agreements between the experimental and computed data are satisfactory.

The inhibiting effect of DMM addition on the reactivity of n-heptane at low temperatures was quantified by introducing an inhibiting coefficient [1]. The correlation between the inhibiting intensity and equivalence ratio is found to be non-monotonic. For both 25% and 50% DMM addition levels, the most inhibiting effect is observed upon $\phi = 2.0$ while 1.0 has the smallest inhibiting coefficient. Rate of production analysis was performed to investigate the chemical interaction effect on their respective decomposition pattern at lower temperatures. The ROP analysis indicates that the OH radical produced from n-heptane acts as a reactivity initiator for DMM and the addition effect is mainly limited to the initial decomposition path for both fuels.

The H-abstraction from DMM by OH at both the terminal and central carbon sites is unimportant for pure DMM oxidation. However, it plays a significant role in the consumption of DMM for DMM/n-heptane fuel blends. According to the kinetic analysis and the experimental observations, it is very likely that the rate coefficients for the DMM+OH reactions are overestimated. Kinetic parameters of the two reactions are theoretically calculated in the DMM sub-model [45]. Other available kinetic parameters are mostly obtained by analogy with DME [39–42], while Kopp et al. [44] recently pointed out the unreasonableness of this analogy in their high level ab initio study of DMM. Simply reducing the rate coefficients of the two reactions by a factor of 3 can lead to remarkably better predictions on the fuel conversions. A theoretical re-evaluation at a higher level of theory with proper uncertainty analysis for the two reactions is also suggested due to their overwhelming significance in such fuel mixtures.

Three important intermediates were discussed to investigate the interactive effect. At low temperatures, the formation of methyl formate is enhanced by n-heptane and that of acetaldehyde is suppressed by DMM, while their formation at higher temperatures is less perturbed. The formation of acetylene is observed only above 800 K. The normalized experimental profiles suggest that the conversion of n-heptane to acetylene is not affected by DMM addition to a great extent.

The large data set obtained in this work can be used for the validation and further refinement of DMM models considering the dearth of related species information at low temperatures. It is also believed that the improvement on the n-heptane model
performance at fuel lean conditions and a higher level calculation for abovementioned DMM related reactions will be beneficial to the predictions on the oxidation of such fuel blends, which is also the focus of our future work.

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Supplementary materials

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References


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