Full Length Article

Ignition delay time measurements and kinetic modeling of CH₄ initiated by CH₃NO₂

Yanlei Shang⁵, Jinchun Shi⁵,⁎, Hongbo Ning⁵, Run tong Zhang⁶, Hongyan Wang⁵, Shengnian Luo⁵

⁵ Key Laboratory of Advanced Technologies of Materials, Ministry of Education, and Institute of Materials Dynamics, Southwest Jiaotong University, Chengdu, Sichuan 610031, PR China
⁶ School of Physical Science and Technology, Southwest Jiaotong University, Chengdu, Sichuan 610031, PR China

ARTICLE INFO

Keywords:
Shock tube
Methane
Nitromethane
Ignition delay time

ABSTRACT

Ignition delay times for methane/nitromethane binary fuels with oxygen diluted in Ar (CH₄/CH₃NO₂/O₂/Ar mixtures) are measured with a heated shock tube behind the reflected shock wave at 995–1962 K and 4–18 atm for different equivalence ratios (0.5, 1.0, and 2.0). Blending ratios for CH₃NO₂ are varied (0, 0.1, 0.2, 0.5, and 1) to investigate the promotion of CH₃NO₂ on CH₄ during the ignition process. OH* emission histories at a sidewall are used to determine the measured ignition delay times of the binary fuels mixture. Correlations for the measured ignition delay times are obtained using multiple linear regression as a function of pressure, temperature, blending ratio, and equivalence ratio. Experimental results show that a small addition of CH₃NO₂ dramatically reduces the ignition delay times of CH₄, and induces a weak two-stage ignition. Three literature mechanisms are examined and compared with the measured ignition delay times for CH₄/CH₃NO₂ binary fuels mixtures, and the mechanism from Mathieu et al. is updated and validated against the experimental data. In this mechanism, the rate constants for some important reactions are theoretically determined by quantum chemical calculation. In addition, sensitivity analysis and reaction pathway analysis as well as rate of production are carried out to further elucidate the promotion of CH₃NO₂ on ignition of the CH₄.

1. Introduction

Thermal management and heat exchange are key to combustion of fuels in engines. Poor thermal management may reduce combustion efficiency and lead to damage to engines, especially those with powerful output [1–3]. In order to improve the heat sink capability of an
endothermic hydrocarbon fuels with high density [3-8] and fuel-cooled technologies [1,9] have been proposed to achieve better thermal control. Endothermic hydrocarbon fuels can absorb heat during the transportation of fuel into a combustion chamber [10], and the reaction temperature in the chamber is reduced further due to C–C bond breaking [11]. However, the low temperature can lead to slower thermal decomposition rate and unsaturated coking deposition, which in turn result in engine knocking and lead to deteriorating heat transfer and engine damage [10,12].

Pyrolysis of a hydrocarbon fuel generally occurs at higher temperatures. To accelerate hydrocarbon pyrolysis and reduce coking deposition formation at low temperatures, several initiators are proposed to be used as additives to lower the working temperature such as nitroalkanes [13–16]. Liu et al. [14,15] investigated thermal pyrolysis of n-dodecane with additives, and found that 1-nitropropane can remarkably promote the cracking rates of n-dodecane as well as heat sink capacity. Jia et al. [13] studied the thermal cracking of n-decane initiated by nitromethane at different pressures in a flow reactor, and showed that the presence of nitromethane can reduce the initial dissociation temperature of n-decane. The promotion effect of nitromethane increases considerably as pressure increases, and the decomposition rate of n-decane is enhanced especially at low temperature [13]. The studies suggest that these nitroalkanes mentioned above can enhance the conversion rate and reduce the initial decomposition temperature of endothermic hydrocarbon fuels.

As a simple nitro containing fuel, nitromethane (CH3N02) is usually introduced to engines and blended with gasoline or alcohols [17], increasing the octane sensitivity [18] and preventing knocking [19]. Many studies on the combustion chemistry of CH3N02 have been carried out, including thermal decomposition [20–26], premixed flames [27–32], and ignition delay times [33–35]. Due to the promotion effect of CH3N02 on thermal decomposition of hydrocarbon [13,36], the combustion characteristics of fuels blended with CH3N02, such as ignition delay time and laminar burning velocity, should be examined. More recently, however, only Bhattacharya et al. [37] investigated the effects of the addition of nitromethane on the laminar burning velocity and ignition delay of syngas and air flames, and they found that the addition of nitromethane can reduce the laminar burning velocity and ignition delay of the syngas and air mixture. More experiments need to be carried out to characterize the promotion effect of CH3N02 on ignition delay times of the hydrocarbon fuels. And such a promotion effect is expected not to achieve the low temperature combustion in a conventional sense, but to lower the ignition temperature of hydrocarbon considerably via the addition of CH3N02.

In the present work, CH4 is chosen as a representative hydrocarbon for its simple structure and the existence of an accurate kinetic model, and thus appropriate for exploring the combustion characteristics of hydrocarbon/CH3N02 mixtures. The experimental data can be used to construct reliable skeletal mechanisms to model the combustion of the larger hydrocarbon and CH3N02 mixtures. CH4 in gas phase is mixed with CH4 to measure ignition delay times by using a shock tube equipped with a heating apparatus, at different blending ratios (0, 0.1, 0.2, 0.5, and 1), various temperatures (995–1962 K), pressures (3.8–17.6 atm), and equivalence ratios (0.5, 1.0, and 2.0). Three recent mechanisms [13,34,38] are examined and compared with the experimental data, and a new kinetic mechanism is updated with the reaction rate constants from literature and our quantum chemical calculations. Sensitivity analysis and reaction pathway analysis as well as rate of production (ROP) are further performed to provide more insights into the promotion effect of CH3N02 on hydrocarbon fuels.

2. Methodology

2.1. Shock tube apparatus

A heated stainless-steel shock tube is used to measure all ignition delay times for CH4/CH3N02 binary fuel mixtures. The shock tube with a 50 mm bore diameter is divided into driver and driven sections by a mylar diaphragm. The incident shock wave speed at the endwall is determined by linearly extrapolating the incident shock wave speeds measured with piezoelectric pressure transducers located at the downstream section near the endwall. (Shock wave speed is the distance between two adjacent pressure transducers divided by the time interval of shock propagation between them.) A more detailed description of the present shock tube apparatus was presented elsewhere [39,40]. In order to avoid the condensation of the gas-phase CH3N02 in the driven section, the shock tube apparatus is equipped with a heating system. The heating system consists of 12 heating tapes, which are wrapped around the whole driven section and part of the driver section near the mylar diaphragm. The temperature distribution along the driven section is monitored by ten thermocouples, and the maximum deviation is less than 2 K. An example of the temperature distributions along the driven section at 50°C is shown in Fig. 1, which demonstrates that the driven section is uniformly heated by the heating system. The experimental temperature (Td) and pressure (Pd) behind the reflected shock wave are determined by using the Gaseq package [41] with the initial temperature (Ti), pressure (Pi) in the driven section, and incident shock wave speed at endwall [39].

The test gas for CH4/CH3N02 mixtures are pre-prepared in a stainless tank (15-L) which is also heated to 50°C throughout a whole experiment. In the test gas preparation, the manifolds are also heated by the heating tapes and kept at 50°C. The purity of CH4 is >99.9% (Chengdu Jinnengda Gases Co., LTD), and those of O2 and Ar are >99.9% (Sichuan Qiaoyuan Gas Co., LTD). To ensure homogeneity, the as-prepared test gas mixture is allowed to diffuse overnight at 50°C. The blending ratio of CH3N02, XSM, is defined as:

\[ X_{SM} = \frac{n_{NM}}{n_{NM} + n_{CH4}} \]

where \( n_{NM} \) is the molar fraction of CH3N02 (NM), and \( n_{CH4} \) is the molar fraction of CH4. The compositions of the test gas mixtures and experimental conditions are listed in Table 1. In the present work, N2 is considered as the final combustion product of CH3N02 [27,28,31,34]. Therefore, the global oxidation reaction for the CH4/CH3N02 gas mixture is

\[ CH_4 + CH_3N_2 + 2.75O_2 = 2CO_2 + 3.5H_2O + 0.5N_2 \]

An OH* emission history profile, measured with a photomultiplier.
and Ar mixtures are implemented with a heated shock tube located at sidewall. This is to define the ignition delay time (τ). τ is the time interval between the arrival of the reflected shock wave and the intersection of the line along with the tangent of the OH* emission and the boundary layer effect. The overall uncertainty of ignition delay times in our work is less than 20%. In order to test the reliability of the heated shock tube, validation tests are carried out for neat CH₄ (mixture 1) and neat CH₃NO₂ (mixture 5) at an initial temperature of 50 °C. For neat CH₄, the measured ignition delay times at 8 atm are used to compare with the work of Shi et al. (Fig. 3(a)). In our neat CH₃NO₂ experiments, two definitions of ignition delay time used in the CH₃NO₂ experiments of Mathieu et al. [34] are adopted: the first one is the same as the one defined in Fig. 2 (τ₁₀⁰%), and the second one is defined as the time passage between the arrival of the reflected shock wave and the peak of the OH* emission profile (τ₁₀¹⁰⁰%). Fig. 3(b) and (c) show the comparison between the two measured ignition delay times of Mathieu et al. [34] and those from the present work at 11.5 atm, and the agreement is satisfactory.

3. Experimental results

The measurements for the ignition delay times for CH₄/CH₃NO₂/O₂/Ar mixtures are implemented with a heated shock tube at the experimental condition 995–1962 K and 4–18 atm. Varied CH₃NO₂ blending ratios (0, 0.1, 0.2, 0.5, and 1) and equivalence ratios (0.5, 1.0, and 2.0) are performed. Fig. 4 shows the measured ignition delay times at different experimental conditions. All the measured data are also summarized in the Supporting Information. Based on the measured ignition delay times, three relevant mechanisms are used to model CH₄ oxidation initiated by CH₃NO₂, i.e., Mechanism-M from Mathieu et al. [34], Mechanism-J from Jia et al. [13], and Mechanism-Z from Zhang et al. [38]. Mechanism-M from Mathieu et al. [34] consists of the submodels for the oxidation of hydrocarbons and nitrogen oxide and the subset for the oxidation of CH₃NO₂ from Brequigny et al. [31], in which the thermal decomposition rate constants of CH₃NO₂ were updated from the work of Annesley et al. [43]. Mechanism-J from Jia et al. [13] contains 266 species and 1648 elementary reactions, which was proposed and developed to model pyrolysis of n-decane initiated by CH₃NO₂. Mechanism-Z from Zhang et al. [38] was originated from the work of Mathieu et al. [44] and systematically validated against the measured ignition delay times for methane/ethane mixtures with different NOₓ additions.

Multiple regression method is used to obtain the correlations for measured ignition delay times of the neat CH₄ and CH₄/CH₃NO₂ binary fuel mixtures. For neat CH₄ (mixture 1), the obtained correlation for ignition delay times is as follows

\[
\tau = \frac{B}{T^a} + C
\]

where B, a, and C are the regression parameters to be determined. The results of the regression analysis for each test gas mixture are shown in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Mixture</th>
<th>( \phi )</th>
<th>ZNO₂</th>
<th>CH₄ (%)</th>
<th>CH₃NO₂ (%)</th>
<th>O₂ (%)</th>
<th>Ar (%)</th>
<th>( P_i ) (atm)</th>
<th>( T_s ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.0</td>
<td>1.000</td>
<td>0.000</td>
<td>4.000</td>
<td>95</td>
<td>7.9</td>
<td>1389–1962</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.1</td>
<td>0.947</td>
<td>0.105</td>
<td>3.948</td>
<td>95</td>
<td>3.8</td>
<td>1269–1722</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>0.2</td>
<td>0.889</td>
<td>0.222</td>
<td>3.889</td>
<td>95</td>
<td>9.8</td>
<td>1229–1653</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>0.5</td>
<td>0.667</td>
<td>0.667</td>
<td>3.666</td>
<td>95</td>
<td>9.8</td>
<td>1152–1488</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>1.0</td>
<td>0.000</td>
<td>2.000</td>
<td>3.000</td>
<td>95</td>
<td>11.3</td>
<td>995–1241</td>
</tr>
<tr>
<td>6</td>
<td>1.0</td>
<td>0.1</td>
<td>1.565</td>
<td>0.174</td>
<td>3.261</td>
<td>95</td>
<td>10.0</td>
<td>1229–1717</td>
</tr>
<tr>
<td>7</td>
<td>2.0</td>
<td>0.1</td>
<td>2.323</td>
<td>0.258</td>
<td>2.419</td>
<td>95</td>
<td>9.9</td>
<td>1337–1750</td>
</tr>
</tbody>
</table>

The partial pressure of CH₃NO₂ in each test gas mixture is less than 5 kPa. \( P_i \) is the average pressure for each mixture.
The effect of the blending ratio of CH$_3$NO$_2$ on the ignition process of CH$_4$ is illustrated in Fig. 4(a) at lean-fuel condition (equivalence ratio of 0.5) and 9.5 atm. A small addition of CH$_3$NO$_2$ can dramatically promote the ignition of CH$_4$, and thus the ignition delay time of CH$_4$ decreases with the increase of $X_{NM}$. It is worth noting that a weak two-stage ignition feature is observed with the addition of CH$_3$NO$_2$, and this two-stage ignition was also observed and investigated in previous studies [34,35,45]. Fig. 5(a) compares the normalized OH$^*$ emission histories of CH$_4$/CH$_3$NO$_2$ mixtures under different blending ratios for the fuel-lean case ($\phi = 0.5$) at an ignition delay time around 250 $\mu$s and pressure of 9.5 atm. The relative emission intensity during the first ignition increases with increasing CH$_3$NO$_2$ addition. To reach a similar ignition delay time, the required temperature of neat CH$_4$ exceeds that of CH$_3$NO$_2$ by 500 K, which indicates that CH$_3$NO$_2$ can be ignited at lower temperatures. Fig. 5(b) compares the normalized OH$^*$ emission histories for mixtures 2, 3, and 4 at the ignition temperature around 1317 K. With increasing CH$_3$NO$_2$ blending ratio, the ignition delay times of the mixtures decrease dramatically. Due to the low intensity of the first ignition peak at low temperatures for CH$_4$/CH$_3$NO$_2$ mixtures, only the ignition delay times of first peak ($\tau_1$) of neat CH$_3$NO$_2$ (mixture 5) are recorded for validating and comparing with mechanisms. In addition, the ignition delay times of the first peak in mixture 5 are summarized and compared with the predictions of three mechanisms to examine their reliability, as shown in Fig. 5(c). The first ignition peak seems to disappear or overlap with the major ignition peak when the ignition delay time ($\tau$) is shorter than 150 $\mu$s.

The effect of pressure on the ignition process of the CH$_4$/CH$_3$NO$_2$ binary fuel mixtures at $X_{NM} = 0.1$ and $\phi = 0.5$ is shown in Fig. 4(b). The measured ignition delay times reduce when the pressure increases, and the reduction is more obvious at low temperatures. In order to find out the influence of the addition of CH$_3$NO$_2$ on the pressure effect, the ignition delay times of neat CH$_4$ from Shi et al. [39] and a CH$_4$/CH$_3$NO$_2$ mixture (mixture 2) are used for the comparison (Fig. 6). The result indicates that the promoting effect of pressure on the CH$_4$ ignition is enhanced by the addition of CH$_3$NO$_2$, and the enhancing effect is especially evident at low temperatures. For example, the ignition delay times for neat CH$_4$ decrease by 30% as pressure increases from 4 to 8 atm, while a decrease of nearly 50% is observed for Mixture 2. Moreover, the activation energy for ignition decreases with the addition of CH$_3$NO$_2$ compared to neat CH$_4$.

The effect of equivalence ratio on the ignition process of CH$_4$ is shown in Fig. 4(c) at 10 atm and $\phi = 0.1$. The ignition delay times of CH$_4$/CH$_3$NO$_2$ mixture increase with the increase of equivalence ratios, which is consistent with the ignition behavior of CH$_4$. However, Mathieu et al. [34] found that the ignition delay times of neat CH$_3$NO$_2$ diluted in 95% Ar at medium pressures decrease with increasing equivalence ratio. Here, we compare the results from our work for CH$_3$NO$_2$/CH$_4$ mixture 2 and neat CH$_3$NO$_2$ from Mathieu et al. at around 11.5 atm diluted in 95% Ar (Fig. 7). As an oxygenated energetic material, the ignition characteristic of CH$_3$NO$_2$ is very different from those of conventional hydrocarbon fuels [34,35,45].

$$\tau = 1.724 \times 10^{-3} p^{-0.378} \exp \left( \frac{20710}{T} \right)$$

(3)

with the regression coefficient $R^2 > 0.99$. As for CH$_4$/CH$_3$NO$_2$ binary mixtures, the ignition delay times are correlated as:

$$\tau = 6.969 \times 10^{-3} p^{-0.686} e^{1.125 - \frac{14515}{T}}$$

(4)

with $R^2 > 0.94$. From the correlations, the measured ignition delay time decreases with the increase of CH$_3$NO$_2$ blending ratio and pressure, and increases as equivalence ratio increases. The results for the comparisons between measured ignition delay times of neat CH$_4$ or CH$_4$/CH$_3$NO$_2$ mixtures and the corresponding correlations are shown in Figure S1 (Supporting Information), and the results show that the multiple regression correlations can well describe the relationship between measured data and experimental parameters.
at most experimental conditions (Sensitivity analysis). Hence, the rate constants for some reactions involving HCO and HNO should be examined and re-evaluated. The rate constants of R1172, HCO + NO = HNO + CO, adopt the experimental values from Dammeier et al. [49] and are increased by a factor of 1.3 in the new mechanism. R996 HNO + NO2 = NO + HONO, which involves the conversion between NO and NO2, is important in the oxidation of neat CH3NO2. Therefore, its rate constants of R996 are theoretically determined in the present work. Furthermore, R942 CH3O2 + NO = CH3O + NO2 plays a significant role at fuel-rich conditions, and its rate constants adopt the experimental values from Bacak et al. [50]. Table 2 lists the updated rate constants of involved reactions.

4.2. Rate constants calculation

In the present work, we find that reactions R1172, R996, and R942 are significant at most experimental conditions. Considerable experimental and theoretical efforts have been devoted to determining the rate constants for R1172 and R942 [49-51]. As for R996, the direct hydrogen abstraction reaction, R996 (HNO + CH3NO2 = HNO + CH3O), is important in the inter-conversion between NO and NO2 (Sensitivity analysis; see below). However, there is only one theoretical calculation study [52] and re-assessment of its rate constants is necessary.

Here, the rate constants for R996 are theoretically determined by quantum chemical calculation. The ground geometry optimization, vibrational frequency calculation of all involved species and intrinsic reaction coordinate (IRC) calculations are performed at B3LYP/6-311 + G(d,p) level with the Gaussian 09 package [53]. In order to acquire more credible relative electronic energies to construct the potential energy surface (PES), the G4 composite method [54] is adopted. The conventional [55] and variational [56] transition state theory (CTST and VTST) as well as the 1-D asymmetric Eckart tunneling correction [57] are used to calculate the involved rate constants with the VARIFLEX code [58] in the temperature range of 500–2000 K. The calculated vibrational frequencies at B3LYP/6-311 + G(d,p) level are scaled by a factor of 0.9688 [59]. In the present work, we only consider the direct hydrogen abstractions from HNO by NO2, since it is the dominant reaction channel [52]. The reaction HNO + NO2 = NO + HNO2 is insignificantly and insensitivity to the experimental conditions, so the HNO2 channel is not considered in our calculation. The product of HONO has two conformers, i.e. trans-HONO and cis-HONO. The involved hydrogen abstraction reactions between HNO and NO2 are

\[
\text{HNO + NO2 = NO + cis-HONO (R996a)}
\]
\[
\text{HNO + NO2 = NO + trans-HONO (R996b)}
\]

The potential energy surfaces (PES) for reaction R996, HNO + NO2 = NO + HONO, are shown in Fig. 8, and the relative energies for the involved species are listed in Table 3 along with literature data from Mebel et al. [52]. In PES, the reactant complexes (RC) and product complexes (PC) are observed, and the relative electronic energies obtained with the B3LYP/6-311 + G(d,p) method are in good agreement with the work of Mebel et al. [52]. The relative energy for TSa is $-0.97 \text{kcal mol}^{-1}$ at the B3LYP/6-311 + G(d,p) level, and it seems to be unreasonable. In order to obtain more reliable relative electronic energies, we recalculate the involved values with the G4 method. At this level, the relative energy for TSa is more reasonable ($3.68 \text{kcal mol}^{-1}$).
mol$^{-1}$). However, the results of G4 and G2M(RCC, MP2) methods [52] are very different for the trans-HONO channel. In our present work, the obtained transition state geometry for R996b (to form trans-HONO) is clearly different from Mebel et al. [52], and more detailed information on the optimized geometries for involved species are available in the Supporting Information. On the basis of PES obtained with the G4 method, the high pressure limit reaction rate constants for two channels (trans- and cis-HONO) are calculated at 500–2000 K. The comparison between our calculation and literature results [34,52,60] is shown in Fig. 9. The calculated rate constants for R996 are lower than the values used by Mebel et al. [52] and Mathieu et al. [34], and the rate constants estimated by Tsang et al. [60] are lower than ours at high temperatures (above 1000 K) and higher at intermediate and low temperatures (below 1000 K). The calculated rate constants can be described with the modified three-parameters Arrhenius equation as follows

\[
k_{\text{approx}} = 2.048 \times 10^7 \mathrm{exp}\left(-\frac{4096.4}{RT}\right)
\]

(5)

\[
k_{\text{approx}} = 2.445 \times 10^7 \mathrm{exp}\left(-\frac{11328.5}{RT}\right)
\]

(6)

\[
k_{\text{approx}} = 7.847 \times 10^7 \mathrm{exp}\left(-\frac{3882.4}{RT}\right)
\]

(7)

where \(R\) is the gas constant (1.987 cal mol$^{-1}$K$^{-1}$).

\[S = \frac{\tau(2k_j) - \tau(0.5k_j)}{1.5\tau(k_j)}\]

(8)

where \(k_j\) is the rate constant for the \(j\)th elementary reaction in the updated mechanism. \(\tau(2k_j), \tau(k_j),\) and \(\tau(0.5k_j)\) are the ignition delay times obtained with the mechanism when \(k_j\) is multiplied by 2, 1, and 0.5, respectively.

Fig. 10 illustrates the sensitivity analysis for CH$_4$NO$_2$/CH$_4$ mixtures with \(\phi\) ranging from 0 to 1 at 1 atm, 1250 K, and \(\phi = 0.5\) using our updated mechanism. For neat CH$_4$, the reaction between methyl and oxygen (reaction R147, \(\text{CH}_4 + \text{O} = \text{CH}_3\text{O} + \text{OH}\)) is the most significant promoting reaction, followed by \(\text{H} + \text{O} = \text{O} + \text{OH}\) (reaction R1), \(\text{CH}_4 + \text{HO}_2 = \text{CH}_3\text{O} + \text{OH}\) (reaction R143). Subsequently, \(\text{CH}_3\text{O}\) formed from reactions R147 and subsequent reaction of R143 can be further converted to HCO. These promoting reactions contribute to the establishment of the OH radical pool which can promote the ignition of CH$_4$. The most important inhibiting reaction is the recombination of CH$_3$ to form C$_2$H$_4$ (reaction R188, \(\text{CH}_3 + \text{CH}_3\text{O} (+M) = \text{C}_2\text{H}_6\text{O} (+M)\)). In addition, the reactions consuming radicals (reaction R127, \(\text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2\), and reaction R128, \(\text{CH}_3 + \text{OH} = \text{CH}_3\text{O} + \text{H}\)) are also important in the inhibition of ignition. As for neat CH$_3$NO$_3$, the reaction R1 is the most important promoting reaction, followed by HCO + \(\text{O} = \text{CO} + \text{HO}_2\) (reaction R29), and HCO + M = H + \(\text{O} + \text{M}\) (reaction R28). Furthermore, some reactions involving NO also show a considerable promotion effect, such as \(\text{CH}_3 + \text{NO}_3 = \text{CH}_3\text{O} + \text{NO}\)

4.3. Sensitivity analysis

Using the updated mechanism, sensitivity analysis is carried out to find the significant reactions which dominate the ignition process of mixtures under different experimental conditions. A sensitivity coefficient which describes the promotion or inhibition of reactions is defined as [61]

\[S = \frac{\tau(2k_j) - \tau(0.5k_j)}{1.5\tau(k_j)}\]

(8)

Table 3

<table>
<thead>
<tr>
<th>Species</th>
<th>B3LYP/6-311 + G(dp)</th>
<th>B3LYP/6-311 + G(dp)$^*$</th>
<th>G4</th>
<th>G2M(RCC,MP2)$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO + NO$_2$</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>RCa</td>
<td>-0.83</td>
<td>-1.64</td>
<td>3.68</td>
<td>5.30</td>
</tr>
<tr>
<td>PCa</td>
<td>-2.30</td>
<td>-34.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO + cis-HONO</td>
<td>-28.20</td>
<td>-29.28</td>
<td>-31.80</td>
<td></td>
</tr>
<tr>
<td>ROc</td>
<td>-0.95</td>
<td>-3.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSc</td>
<td>5.00</td>
<td>8.57</td>
<td>20.60</td>
<td></td>
</tr>
<tr>
<td>NO + trans-HONO</td>
<td>-28.00</td>
<td>-29.88</td>
<td>-32.10</td>
<td></td>
</tr>
</tbody>
</table>

$^*$ Adopted from Mebel et al. [52].

Fig. 8. Potential energy surface for the HNO + NO$_2$ reaction at the G4 level. Energy is in kcal mol$^{-1}$.

Fig. 9. Calculated rate constants for R996 and comparison with those from literature results. Black solid line: this work; blue dashed line: Mebel et al. [52]; magenta dash-dotted line: Mathieu et al. [34]; olive short dashed line: Tsang et al. [60]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
The sensitivity coefficient of reaction R1 increases remarkably, and it has the most prominent promoting effect. Whereas, the sensitivity coefficient of reaction R147 decreases dramatically as a result of absent CH radical due to reaction R938, (CH$_3$ + NO = CH$_3$O + NO). In the mixtures of CH$_3$/NO, CH$_3$ radicals are rapidly converted to CH$_3$O via reaction R938, and CH$_3$O is further converted to CH$_3$O, leading to abundant HCO radicals. Correspondingly, the sensitivity coefficients of reaction R28 (HCO + M = H + CO + M), and reaction R29 (HCO + O$_2$ = CO + HO + H) increase considerably with increasing concentration of CH$_3$NO$_2$. Moreover, the interaction between NO$_2$ and NO, NO + HO = NO$_2$ + OH (reaction R978), further promotes the ignition process, but it is insensitive to $\chi_{OM}$.

Fig. 10. Sensitivity analysis for the CH$_3$NO$_2$/CH$_4$ mixtures with different blending ratios ($\chi_{OM}$ = 0, 0.1, 0.5, and 1) at 10 atm, 1250 K, and $\phi$ = 0.5.

The sensitivity analysis for the CH$_3$NO$_2$/CH$_4$ binary fuel mixtures at 10 atm, 1250 K, and $\chi_{OM}$ = 0.1 with different equivalence ratios ($\phi$ = 0.5, 1, and 2) is shown in Fig. 11. The reaction R1 (H + O$_2$ = O + OH) is the most promoting reaction, followed by reaction R938. R938 is sensitive to temperature, and its sensitivity coefficient dramatically decreases at high temperatures. Since R938 is an exothermic reaction [31], high temperature is not beneficial to R938. The reaction R982 (NO$_2$ + H = NO + OH) is the most inhibiting reaction, followed by reactions R128 and R188. Similar to R938, R982 is also an exothermic reaction [31], and also sensitive to temperature. For other inhibiting reactions such as recombination reaction (R188) and hydrogen abstraction reaction of CH$_4$ (R128), they are also exothermic and sensitive to temperature.

It is worth noting that CH$_3$ radical is an important intermediate species during the oxidation of neat CH$_4$ and CH$_4$/CH$_3$NO$_2$ mixtures. In the CH$_4$/CH$_3$NO$_2$ mixtures, NO$_2$ from the thermal decomposition of CH$_3$NO$_2$ is introduced and rapidly reacts with CH$_3$ to establish the radical pool; most CH$_3$ radicals are consumed by the primary reaction R938 to produce CH$_3$O which further dissociates to CH$_3$O and H radical. The C–N bond of CH$_3$NO$_2$ is easier to break [26,30,43,62] given its lower bond dissociation energy (BDE; only 61 kcal mol$^{-1}$ at 298 K) [43] than that of the C–H bond (99.24 kcal mol$^{-1}$ at 298 K) [63]. Hence, the ignition of CH$_3$NO$_2$/CH$_4$ is easier to occur at relative low temperatures due to the reactive CH$_3$ radical and NO$_2$ from the dissociation of CH$_3$NO$_2$. 

Fig. 11. Sensitivity analysis for the CH$_3$NO$_2$/CH$_4$ mixtures at 10 atm, 1250 K, and $\chi_{OM}$ = 0.1 with different equivalence ratios ($\phi$ = 0.5, 1, and 2).

Fig. 12 shows the results of the sensitivity analysis for mixture 2 ($\chi_{OM}$ = 0.1, $\phi$ = 0.5) at 10 atm, and different temperatures (1250 and 1500 K).
4.4. Reaction pathway analysis

In order to further explain the chemical kinetics of the promotion of CH3N2O on the ignition process of CH4, the reaction pathway analysis is performed for the fuel-lean CH3/CH3N2O mixtures with different blending ratios (xSNM = 0, 0.1, and 0.5) at 1250 K and 10 atm, at the reaction time of 20% CH4 consumption (Fig. 13).

For neat CH4, CH4 is mainly consumed via the hydrogen abstractions by HO2, H, O, and OH radicals, yielding CH radical which is then consumed via the self-recombination reaction (41.1%), the hydrogen abstraction by O2 (24.4%) and HO2 radical (13.2%). The main product of the hydrogen abstraction by HO2 radical on CH4 radical is CH2O radical (R143, CH3 + HO2 = CH2O + OH), which rapidly dissociates to CH2O via reaction R90. Subsequently, most of CH2O is converted to HCO. With the addition of CH3N2O, the consumption pathways of CH4 radicals in CH3/CH3N2O mixtures are different from those in neat CH4. The amount of CH3O from the reaction between CH3 and HO2 is reduced (13.2% for mixture 1, 4.7% for mixture 2, and 5.0% for mixture 4). However, the reaction between CH3 and NO2 accounts for nearly half of the consumption of CH3. The formation of CH3O from the oxidation of CH3 radical by O atom and O2 is dramatically reduced (24.4% for mixture 1, 2.9% for mixture 2, and ~0% for mixture 4). In the CH3/CH3N2O mixtures, CH3N2O rapidly dissociates to CH3 radical and NO2 behind the reflected shock wave, and most CH3 radicals are consumed via the self-recombination reaction (R188) and the reaction with NO2 (R938). In the conversion of CH3O to HCO, the importance of the reaction between CH2O and CH3 radical dramatically reduces (37.9% for mixture 1, 11.6% for mixture 2, and 4.0% for mixture 4) due to insufficient CH3 radicals consumed by reaction R938. The interaction between CH2O and HO2 radicals also becomes less important (6.5% for mixture 1, 0.8% for mixture 2, and 0.3% for mixture 4). Actually, HO2 radicals are mainly consumed through reaction R978 which yields OH radicals and recycles NO to NO2. Hence, the importance of the interaction between CH2O and OH radicals increases (23.9% for mixture 1, 41.2% for mixture 2, and 57.6% for mixture 4). The addition of CH3N2O also increases the importance of the interaction between CH2O and H atom (16.1% for Mixture 1, 33.6% for Mixture 2, and 28.2% for Mixture 4).

As discussed above, CH3 radical and NO2 play the important roles during the ignition process of the CH3/CH3N2O binary fuel mixtures. The CH3 radical from CH3N2O contributes to the establishment of the radical pools, and NO2 also has the promoting effect on the ignition of hydrocarbons [23, 38, 44, 64-68]. The CH3 radical is mainly consumed via reaction R938, forming CH2O which further decomposes to CH2O and active H radical. The interaction between NO and HO2 (R978) converts NO to NO2 and also produces active OH radical. Therefore, ROP analysis for the productions of the CH3 and OH radicals is performed for neat CH4 (mixture 1) and CH3/CH3N2O (mixtures 2 and 4) at 1250 K and 10 atm (Fig. 14).

For neat CH4, most CH3 radicals are produced from the hydrogen abstraction reactions from CH4 by H atom (R127, CH3 + H = CH2 + H2), O atom (R128, CH4 + O = CH2 + OH), and OH radical (R129, CH4 + OH = CH3 + H2O). When CH3N2O is added, CH3 radical is formed rapidly from the decomposition of CH3N2O via the dissociation of the C-N bond after the arrival of the reflected shock wave. Due to the formation of CH3, the radical pool is quickly established, and the total reaction rate of hydrogen abstraction from CH4 is also enhanced. The two-stage ignition phenomenon is also observed for OH radical (Fig. 14(b)). Reaction R1 (H + O2 = O + OH) contributes to the major proportion of the formed OH radicals (corresponding to the main ignition stage) for neat CH4, followed by reactions R11 (HO2 + H = OH + HO), R2 (O + H2 = H2 + OH), and R4 (O + H2O = OH + OH). With the addition of CH3N2O, OH radical can be produced via reactions R982 (NO2 + H = NO + OH) and R978 (NO + HO2 = NO2 + OH) during the induction period (corresponding...
to first ignition stage), while reaction R1 is still the dominant reaction for the formation of OH radicals near the main ignition stage. The production of OH radicals via reactions R982 and R978 increases dramatically with increasing concentrations of CH$_3$NO$_2$, and the roles of reactions R1 and R11 are also enhanced due to the abundant H radicals from the dissociation of CH$_2$O. Therefore, the addition of CH$_3$NO$_2$ can introduce CH$_3$ radical and NO during the induction period, which is beneficial to the establishment of the radical pool and the promoting effect on the ignition of CH$_4$.

5. Conclusions

Ignition characteristic of CH$_4$/CH$_3$NO$_2$/O$_2$/Ar mixtures is investigated behind reflected shock waves with a heated shock tube. Experimental parameters vary from 995 to 1962 K for temperature and from 4 to 18 atm for pressure. Different equivalence ratios (0.5–2) and CH$_3$NO$_2$ blending ratios (0, 0.1, 0.2, 0.5, and 1) are investigated. CH$_3$NO$_2$ can dramatically reduce ignition delay time of CH$_4$, and the reduction increases with increasing blending ratio. This promotion effect is enhanced and more pronounced at low temperatures. With the addition of CH$_3$NO$_2$, a two-stage ignition behavior is observed. The kinetic mechanism is updated based on the calculated and experimental reaction rate constants involving HCO and HNO, where the rate constants of reaction R996, HNO + NO = NO + HONO are theoretically determined from our quantum chemistry calculations. The newly updated mechanism can well reproduce the measured ignition delay times of CH$_4$/CH$_3$NO$_2$ binary fuel mixtures and capture the two-stage ignition feature accurately for neat CH$_3$NO$_2$ for comparison with our experiments. Kinetic analyses based on the newly updated mechanism are carried out to further illuminate the promotion effect of CH$_3$NO$_2$, including sensitivity analysis and reaction pathway analysis as well as rate of production analysis. For neat CH$_4$, most of CH$_3$ radicals are produced via the hydrogen abstraction reactions from CH$_3$I (R127, R128, R129), while CH$_3$ is mostly consumed by the self-recombination reaction (R188) and oxidation (R147). In the presence of CH$_3$NO$_2$, the dissociation of CH$_3$NO$_2$ has a considerable contribution to CH$_3$ formation, and most CH$_3$ are rapidly consumed by reaction R938 (CH$_3$ + NO = CH$_2$O + NO). Following R938, the reaction R90 [CH$_2$O + M = CH$_3$O + H + M] produces abundant H radicals at early induction time. On the other hand, the reactions involving the interconversion of NO$_2$ and NO (R90 and R982) can further produce reactive OH radicals. The introduced CH$_3$ radicals perturb the initial reaction process to form highly reactive OH and H radicals, and thus reduce the ignition delay times of CH$_4$.

Acknowledgement

This work is supported by the National Natural Science Foundation of China (Grant No. 11627901). Computations were performed at the Supercomputing Center of the Peac Institute of Multiscale Sciences.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.fuel.2019.01.112.

References
