Experimental and kinetic comparative study on ignition characteristics of 1-pentene and \(n\)-pentane

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HIGHLIGHTS

- Ignition delay times of 1-butene and \(n\)-pentane were measured in a shock tube.
- NG model, JetSurF2.0 model and Touchard model were validated.
- NG model was updated to form Aramco-NG model.
- Ignition delay times of 1-pentene and \(n\)-pentane were compared and the crossover of ignition delay times were explained.

ABSTRACT

Ignition delay times of 1-pentene and \(n\)-pentane were measured using a shock tube at pressures from 0.12 MPa to 1.0 MPa, at equivalence ratios from 0.5 to 2.0 with 0.5% and 1.0% fuel concentrations, in the temperature range of 1040–1880 K. Correlations of 1-pentene and \(n\)-pentane ignition delay times were deduced from the experimental data using a multiple linear regression. A NG model, JetSurF2.0 model and Touchard model were used to simulate the experiments but the performance was not good for all data. The C1–C4 sub-model of the NG model was updated using Aramco Mech 1.3, forming the Aramco-NG model, which conformed closely to the experiments. A crossover of the ignition delay times of 1-pentene and \(n\)-pentane can be observed in the correlations and calculations as well as in the experimental data. The shorter ignition delay times of 1-pentene in the relative low temperature region can be explained by the abundant H atom producing channels and the higher rate constant of the unimolecular decomposition reaction in this region. In the relative high temperature region, the higher amount of allyl radical formed through the breakage of the \(C_C\) bond and lower concentration of oxygen may contribute to the longer ignition delay times for 1-pentene compared with \(n\)-pentane.

1. Introduction

Ignition delay time, which can affect the performance and operation of the combustion equipment, is one of the most important parameters in the combustion process. Furthermore, it can be used to validate and establish the chemical kinetic models, which could help to ascertain the detailed combustion process, evaluate the impact on the environment and develop new combustion strategies. Up to now, many studies have been carried out on the auto-ignition of hydrocarbons, but most of them have been focused on the C1–C4 hydrocarbons, especially on the alkenes. While larger hydrocarbons are the important constituents of the real fuels which are widely used in combustion devices, such as internal combustion engines. Specifically, alkenes are the important component of the real gasoline compositions [1–4] and the proportion of them can be up to 20% [5]. Due to their higher octane number compared with the paraffins, the existence of olefins may contribute to the auto-ignition chemistry. Besides, they also affect the formations of pollutants, especially soot formation in engines [6–8] due to their unsaturation. In recent studies [9,10], four-component gasoline surrogate models including iso-octane, \(n\)-heptane, toluene and pentene have been formulated. Kukkadapu et al. [11] reported that the four-component models had the closer ignition delay times to the gasoline when compared with three-component models without pentene.

For many years, the studies of alkenes have been limited to the lighter ones such as ethylene [6,12–18], propene [19–23] and butene [24–28]. For pentene, the oxidation of 1-pentene was experimentally studied by Prabhu et al. [29] in a plug flow reactor between 657 K and 714 K. Alatorre et al. [30] conducted
experiments of the fuel rich 1-pentene–O₂–Ar flame at 50 mbar and simulated their own work. Subsequently, an experimental comparison study of the ignition delay time of 1-pentene and pentane between 600 K and 900 K was carried out by Minetti et al. [31] in a rapid compression machine (RCM) and 1-pentene presented less reactivity in this region. In the following work by Ribaucour et al. [32], these data were used to develop a chemical kinetic model. Later, Touchard et al. [33] investigated the high temperature (from 1130 K to 1620 K) auto-ignition of 1-pentene in a shock tube with equivalence ratios of 0.5 to 2.0 and pressures from 0.73 to 0.95 MPa. A detailed high temperature kinetic model was generated by a mechanism producing software EXGAS. A low temperature kinetic model for the oxidation of 1-pentene and 1-hexene was also proposed by Touchard et al. [34] using the same software EXGAS. Mehl et al. [1] explored the ignition behaviors of the unsaturated hydrocarbons with shock tube and a kinetic model was also developed. Recently, Westbrook et al. [35] studied the oxidation of 2-methyl-2-buten in shock tube and jet-stirred reactor (JSR), and a detailed chemical kinetic model was established based on these experimental data. N-pentane, which is the saturated hydrocarbon in the same carbon number with 1-pentene, is also a component of gasoline. Several research has been performed on n-pentane using RCMs [31,36,37], shock tubes [37–39], a well-stirred reactor [40] and a flow reactor [29].

Both 1-pentene and n-pentane are linear hydrocarbons with 5 carbons and the only difference between them is that 1-pentene has a C–C double bond between the α and β carbon (Cα = Cα–Cα–Cα–Cα–Cα). Thus, the difference between 1-pentene and n-pentane is only produced by the double bond and the comparison between them can help to clarify the property of the double bond. Additionally, the comprehension of the double bond could help to understand the characteristics of unsaturated fatty acid esters, which are the major components of biodiesels. Although some research has been conducted on the ignition characteristics of 1-pentene and n-pentane, the data are still limited. Besides, the comparison study of 1-pentene and n-pentane is limited to the low temperature region and the mechanism used is not a fully developed one which lacks some reactions such as abstractions of alkyllic H-atoms [34]. To further understand the ignition characteristics introduced by the double bond and provide more experimental data to establish the accurate model, the experimental and chemical kinetic modeling studies have been conducted on 1-pentene and n-pentane in a shock tube at different equivalence ratios, pressures and temperatures.

2. Experimental section

The experiments were conducted on a shock tube with an effective diameter of 11.5 cm and detailed description of this experimental facility has been reported in the previous literature [41–43]. Thus only a brief introduction of the experimental apparatus and data processing is provided here. The shock tube includes a 4 m long driver part and 5.3 m long driven part, separated by the different thicknesses of polyester terephthalate diaphragms to achieve different reflected pressures. Four fast-response pressure transducer (PCB 113B26) are installed along the last 1.5 m side wall of the driven part with equal spacing and three timers (FLUKE, PM6690) are used to determine the endwall incident shock velocity by linear extrapolation. The endwall pressure and local OH* chemiluminescence are detected by a piezoelectric pressure transducer (PCB113B03) and a photo multiplier (Hamamatsu, CR 131), respectively. In this study, 1-pentene (analytical standard, supplied by Fluka), n-pentane (99.5% pure, supplied by Energy Chemical), oxygen (99.99% pure) and argon (99.99% pure) were prepared in a 128 L stainless steel tank with the partial pressures method and at least 12 h was left for homogenous mixing.

The interval between the shock wave arrival and the extrapolation of the maximum slope line of the OH* signal to the baseline is defined as the measured ignition delay time. A example of ignition delay time definition is shown in Supplementary Material 1. The temperature behind the reflected shock wave was calculated with the reflected shock model by Gaseq [44]. Besides, the uncertainty of temperature in this study is less than 23.7 K and that of the measured ignition delay times is within 15.6%.

3. Results and discussions

3.1. Measurements and correlations

For 1-pentene, ignition delay times were measured at two pressures (0.12 MPa and 1.0 MPa) and three equivalence ratios (0.5, 1.0 and 2.0) behind reflected shock waves in temperature range of 1040–1880 K with a fixed fuel concentration of 0.5%. In addition, experiments were also carried out at the stoichiometric equivalence ratio and 0.1 MPa with fuel concentration of 1.0% for the experimental validation. Prior to current experiments, reproducing experiment was conducted for 1-pentene ignition at 0.1 MPa and good consistency of current data and data from Mehl [1] validate our facility. For n-pentane, experiments were conducted at three equivalence ratios (0.5, 1.0 and 2.0) additionally with the stoichiometric equivalence ratio at 0.12 MPa. The compositions of the test fuel mixtures are listed in Table 1. All the raw data and the validation results are also provided in the Supplementary Material 1 and 2. For all the test fuel mixtures, the ignition delay times exhibit a strong Arrhenius temperature dependence and correlations of the ignition delay time as a function of the equivalence ratio, pressure and temperature are given through the multiple linear regression, with the following form:

\[ \tau = A \phi^{a} p^{b} \exp(E_{\alpha}/RT) \]  

(1)

where \( \tau \) is the ignition delay time (\( \mu s \)), \( \phi \) is the equivalence ratio, \( p \) is the pressure (MPa), \( E_{\alpha} \) is the global activation energy (kJ/mol), \( T \) is the temperature (K) and \( R = 8.314 \times 10^{-3} \) kJ mol\(^{-1}\) K\(^{-1}\) is the universal gas constant. The parameters (\( A, \alpha, \beta, E_{\alpha} \)) in the correlations and the fitting factors (\( R^{2} \)) for 1-pentene and n-pentane are given in Table 2.

Fig. 1 shows the experimental data and fitted values calculated by Eq. (1). It can be seen that the correlations agree well with the experimental data. As expected, for both 1-pentene and n-pentane, ignition delay times increase with the equivalence ratio and decrease with pressure, indicating plus and minus sign of their index, respectively. Furthermore, compared with n-pentane, 1-pentene exhibits longer ignition delay times at higher temperatures and shorter ignition delay times at relative low temperatures. The crossover of the ignition delay time results in the lower activation energy of 1-pentene (as shown in Table 2).

3.2. Chemical kinetic model validation

Simulations were carried out with the Chemkin II package [45], using the Senkin code [46] with a zero-dimensional and constant

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Compositions and pressure conditions of test mixtures in this study.</th>
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<tbody>
<tr>
<td>Fuel</td>
<td>Fuel (%)</td>
</tr>
<tr>
<td>1-pentene</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
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<tr>
<td></td>
<td>0.5</td>
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<tr>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>n-pentane</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
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volume adiabatic model. In the calculation, the time interval between the simulation starting point and the maximum temperature rise (maximum \( \frac{dT}{dt} \)) timing is defined as the ignition delay time and a pressure rise (\( \frac{dp}{dt} \)) of 4%/ms is taken into consideration. Three kinetic models available for 1-pentene, namely the NG model [47–50], JetSurF2.0 [51], Touchard model [33], were adopted. The NG model, which was developed by the Combustion Chemistry Centre of National University of Ireland in 2010, contains 293 species and 1593 reactions. This mechanism has been validated by the C1–C5 \(- \)alkanes in both a rapid compression machine and a shock-tube facility. The JetSurF2.0 model, which was developed by Prof. Wang’s Group and is based on USC-Mech II and contains 348 species and 2163 reactions and includes the high-temperature pyrolysis and oxidation of \(- \)alkanes from \(- \)pentane to \(- \)dodecane. The Touchard model was developed for 1-pentene using the mechanism generating EXGAS system, and has been validated with the shock tube, RCM and plug flow reactor data. The NG model and JetSurF2.0 contain both 1-pentene and \(- \)pentane while the Touchard model doesn’t contain the \(- \)pentane species. Fig. 2(a) and (b) shows the comparison between measured ignition delay times and simulations for 1-pentene using NG model, JetSurF2.0, Touchard model. It can be seen that for 1-pentene, the NG model doesn’t agree well at all conditions; JetSurF2.0 shows good predictions of the ignition delay times at 0.12 MPa, however, it underestimates the ignition delay times for the fuel-lean condition at 1.0 MPa; the Touchard model shows a good performance in the fuel-lean condition, but underestimates ignition delay times in the fuel-rich and stoichiometric conditions. For \(- \)pentane, the comparison between the experimental data and simulations using NG model and JetSurF2.0 are presented in Fig. 2(c) and (d). The NG model exhibits quite a good performance at 1.0 MPa but discrepancies exist between the calculations and measurements at 0.12 MPa. JetSurF2.0 always underpredicts the measured data at all test conditions. In general, none of the three available models could perform good predictions of all of the current data. Note that the NG model was developed in 2010, and a new C1–C4 submodel, namely Aramco Mech 1.3 [52], was developed by NUIG in 2013 and has revised many rate constants for the C0–C2 submechanisms. The Aramco Mech 1.3 has been validated using abundant data and a good performance has been observed. The C1–C4 submechanisms in the NG model was thus replaced by the Aramco Mech 1.3 model, forming the Aramco-NG model with 316 species and 1805 reactions. The calculation results of Aramco-NG model are also presented in Fig. 2. It can be seen that the predictions for 1-pentene are significantly improved under all conditions. For \(- \)pentane, the simulations with Aramco-NG model at 0.12 MPa agree better with the experimental data than those using the original NG model and good performance is also observed at 1.0 MPa since the original NG model predicts pretty well and the Aramco-NG model doesn’t change much. The

<table>
<thead>
<tr>
<th>Fuel</th>
<th>( A \times 10^3 )</th>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>( E_a ) (kJ/mol)</th>
<th>R-square</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-pentene</td>
<td>2.35 ± 0.49</td>
<td>1.51 ± 0.04</td>
<td>−0.53 ± 0.02</td>
<td>130.13 ± 2.07</td>
<td>0.986</td>
</tr>
<tr>
<td>(- )pentane</td>
<td>0.56 ± 0.19</td>
<td>1.27 ± 0.07</td>
<td>−0.42 ± 0.03</td>
<td>147.74 ± 3.26</td>
<td>0.984</td>
</tr>
</tbody>
</table>

Fig. 1. Comparison between ignition delay times for 1-pentene and \(- \)pentane at (a) 0.12 MPa (b) 1.0 MPa and (c) \( \phi = 1.0 \). (Point: experiments; lines: correlations.)
Aramco-NG model shows a good performance at all tested conditions for both 1-pentene and n-pentane. Therefore, the following analysis is conducted using this model.

3.3. Comparison of 1-pentene and n-pentane

Fig. 3 shows the comparison of ignition delay times between 1-pentene and n-pentane. It can be seen that the predictions of the Aramco-NG model conform well to the experimental data. Similar to the experimental data and correlation values, the simulation results of 1-pentene and n-pentane also exhibits a crossover in test conditions, that is 1-pentene shows shorter and longer ignition delay time compared with n-pentane in the relative low and high temperature region respectively.

3.4. Reaction pathway analysis

To seek out the main reaction pathways and find the reason for the crossover of the ignition delay time, a reaction pathway analysis of 1-pentene and n-pentane was conducted at a pressure of 1.0 MPa and at an equivalence ratio of 1.0, as shown in Fig. 4. The time of 20% fuel consumption is chosen for analysis and temperature region respectively.

3.5. Chemical kinetic interpretation

3.5.1. Relative low temperature region

Fig. 5 shows the mole fractions and temperature profiles of 1-pentene and n-pentane at 1.0 MPa for the stoichiometric mixture. As shown in Fig. 5(a) and (b), the increase timing of the...
temperature, which is the sign of ignition, is close to the rising of H, OH and O radicals at both 1200 K and 1600 K. This indicates that the accumulation of these chain branching active radicals can provide some key information in the fuel oxidation process and the ignition behaviors can be explained by these active radicals. It can also be seen that fuel consumption is faster for 1-pentene at 1200 K and n-pentane at 1600 K, respectively. Furthermore, the ignition delay time is fully close to the end time of fuel consumption at 1200 K, while a time interval can be observed between the two timings for both 1-pentene and n-pentane at 1600 K. Mole fractions of ethyl radical, allyl radical and a hydrogen atom are displayed in Fig. 5 (c) and (d). The ethyl radical can easily generate ethylene and a H atom. At 1200 K, the mole fraction of ethyl radical remains almost the same until the time of ignition and the peak timing of ethyl radical appears much earlier than that of H atom. This is due to the quick consumption of the fuel in the high temperature region. Because of the high percentage of unimolecular decomposition of 1-pentene at high temperature, the amount of allyl radical of 1-pentene at high temperature shows obvious increase compared with that of n-pentane at high temperature and that of 1-pentene at low temperature.

Since the ignition timing is consistent with the change of H atom, which has great influence on the global activity and ignition delay, the major reactions responsible for the production of H atom for the both 1-pentene and n-pentane at 1200 K, 80 μs are shown in Fig. 6. As can be seen in Fig. 6(a), there are four main reactions contributing to the generation of H atom for 1-pentene. The primary H atom producing path is R201 (C5H10(\(+M\)) \(\rightleftharpoons\) C5H9\(+\)H\(+M\)), which accounts for 30.7% in H atom production, while a time interval can be observed between the two timings for both 1-pentene and n-pentane at 1600 K. Mole fractions of ethyl radical, allyl radical and a hydrogen atom are displayed in Fig. 5 (c) and (d). The ethyl radical can easily generate ethylene and a H atom. At 1200 K, the mole fraction of ethyl radical remains almost the same until the time of ignition and the peak timing of ethyl radical appears much earlier than that of H atom. This is due to the quick consumption of the fuel in the high temperature region. Because of the high percentage of unimolecular decomposition of 1-pentene at high temperature, the amount of allyl radical of 1-pentene at high temperature shows obvious increase compared with that of n-pentane at high temperature and that of 1-pentene at low temperature.

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It can be concluded that 1-pentene has three more ways to produce H atom than n-pentane and this may result in the larger net ROP of H atom for 1-pentene.

As mentioned above, R201 is an important H producing path for both 1-pentene and n-pentane. Therefore, the ROP of H by R201 for the auto-ignition of 1-pentene at 1200 K, 1.0 MPa and $\phi = 1.0$ is given in Fig. 7. Despite the long ignition delay time of 1-pentene and n-pentane (beyond 1000 $\mu$s) because both of the two fuels are in similar period in this early age of the pre-ignition region and the differences in the late age basically result from the differences in the early age. The ROP of H by R201 for 1-pentene is obviously higher than that for n-pentane, indicating more H atom producing for 1-pentene in this path. Considering the larger account of this reaction of about 90.0% for n-pentane compared with that of only 30.7% for 1-pentene, the net ROP of H atom is much higher for 1-pentene in this temperature region. The higher ROP of H by R201 can be explained by the higher mole fraction of ethyl radical for 1-pentene in this region. The ROP of C$_2$H$_5$ radical by the main C$_2$H$_5$ radical generating reactions (R1589 and R1594 for 1-pentene, R1589 and R1547 for n-pentane) at 1200 K, 1.0 MPa and $\phi = 1.0$ are plotted in Fig. 6. Major H atom producing path in auto-ignition of 1-pentene and n-pentane at 1200 K, 1.0 MPa, 80 $\mu$s and $\phi = 1.0$. 

![Fig. 6](image_url)
3.5.2. Relative high temperature region

As seen from Fig. 9, the rate constant of R1594 is higher than that of R1547 in the relative low temperature region while smaller in the high temperature region. As mentioned above, calculation with replacing rate constant of R1594 with that of R1547 for 1-pentene partly slows down the ignition of 1-pentene due to the smaller rate constant of R1547 in the relative low temperature region. However, there is not an evident change in the ignition delay time for 1-pentene when replacing the lower rate constant of R1594 with the higher one of R1547 in the relative high temperature region, as shown in Fig. 9. Besides, as mentioned above, the ignition delay time is fully close to the fuel consumption ending time at 1200 K, while a time interval can be observed between the two timings for both 1-pentene and n-pentane at 1600 K (see in Fig. 5). These findings suggest that the fuel consumption rate has a crucial effect on the ignition delay time in the relative low temperature region but is not the only factor for ignition in the high temperature region. At 1200 K, according to the high activation energy for the unimolecular decomposition reaction, the ignition is largely affected by the fuel consumption rate because other oxidation reactions are easier compared with the fuel decomposition reactions and the fuel decomposition is the rate-controlled factor in this region. However, at 1600 K, the effect of the higher activation energy for the unimolecular decomposition reaction is compromised because of the high temperature. On the other hand, the following oxidation of hydrocarbon intermediates and the accumulation of the active radicals, which reflected in the time interval between the fuel consumption and the ignition, are important factors for ignition. Thus, the replacement of the rate constant changes the ignition delay time in the relative low temperature region but has little effect in the high temperature region.

To further illustrate the difference of 1-pentene and n-pentane in the oxidation of hydrocarbon intermediates and the accumulation of the active radicals in the high temperature region, the normalized rate of consumption of H atom (NROC) of 1-pentene and n-pentane at the stoichiometric equivalence ratio and 1600 K, 1.0 MPa is presented in Fig. 10. For both 1-pentene and n-pentane, the fuel consumption reactions are the main H consumption paths at the early age of the pre-ignition region due to the abundance of fuel and lack of intermediate radicals; in the late age of the pre-ignition region, the chain branching reaction R1 (H + O₂ → H₂O + O) plays the main role in H consumption. However, in the middle age of the pre-ignition region, R540 (C₃H₅-1 + H → C₃H₄ + H₂) dominates the H consumption for 1-pentene and R1 has the highest NROC for n-pentane. This is understandable because of the higher mole fraction of the resonantly stabilized allyl radical (C₃H₅-1) of 1-pentene (as shown in Fig. 5(d), which is produced by fuel unimolecular decomposition reaction R1594. At 1600 K, compared with n-pentane, the higher mole fraction of the allyl radical of 1-pentene inhibits the}

Fig. 7. ROP of H by R201 for the auto-ignition of 1-pentene and n-pentane at 1200 K, 1.0 MPa and φ = 1.0.

Fig. 8. ROP of the unimolecular decomposition reaction R1594 for 1-pentene is higher than that of R1547 for n-pentane, and ROP of R1589 for 1-pentene is higher than that of n-pentane. The higher rate constant of the unimolecular decomposition reaction R1594 than that of R1547 (see in Fig. 9) in this temperature may be partly responsible for the higher rate of production (ROP) of C₂H₅ at 1200 K, 1.0 MPa and φ = 1.0.

Fig. 9. Rate constant of unimolecular decomposition reaction R1594 and R1547 and ignition delay time for 1-pentene and n-pentane in a shock tube at p = 1.0 MPa, and φ = 1.0.
accumulation of H atom because allyl radical will consume the H atom to form propene through R540, which would regenerate the allyl radical through R549 (C3H5-A+H(+M)⇌C3H6(+M)) and R555 (C3H6+H⇌C3H5-A+H2). Furthermore, the n-pentane mixture contains more oxygen at the same equivalence ratio than 1-pentene, which promotes the important chain branching reaction R1, further facilitating R2 (O+H2⇌H+OH) and R3 (OH+H2⇌H+H2O), indicating the acceleration in ignition. Thus the shorter ignition delay time of n-pentane in the high temperature region can be explained by the dominant role of R1 compared with R540 in the H atom competition.

Generally speaking, 1-pentene exhibits longer ignition delay time in the relative high temperature region for the more allyl radical and less oxygen compared with n-pentane; and its higher reactivity in the relative low temperature region can be interpreted by the various H generating ways and higher unimolecular decomposition reaction rate.

3.6. Sensitivity analysis

To further understand the role of each reaction in the 1-pentene and n-pentane ignition, the sensitivity analysis of 1-pentene and n-pentane in a shock tube at T=1200 K and T=1600 K, 1.0 MPa and φ=1.0 is conducted. The sensitivity coefficient 

\[
S_i = \frac{\tau (2.0k_i) - \tau (0.5k_i)}{1.5\tau (k_i)}
\]

where \(\tau\) is the ignition delay time and \(k_i\) is the rate constant of the \(i^{th}\) reaction. A positive sensitivity coefficient indicates the ignition delay time becomes longer with the increase of this rate constant, suggesting an inhibiting effect on ignition and vice versa.

Fig. 11 shows the top 14 reactions enhancing and inhibiting the ignition of 1-pentene and n-pentane at stoichiometric equivalence ratio, 1.0 MPa, 1200 K and 1600 K. It can be seen that both the small radical reactions and the fuel-related reactions have influence on the ignition of 1-pentene and n-pentane. As expected, the important chain branching reaction R1 has the largest negative sensitivity coefficient in all the conditions, indicating a remarkable acceleration in ignition. Besides, the dominance of R1 is reduced with the decrease of temperature and at 1200 K, the fuel-related reactions, such as R1602 (C6H12-OH→C6H11-A+H2O), R1596 (C6H12-H+→C6H11-A+H2), R1594 and R1547, show considerable promoting effect on ignition. For the ignition-inhibiting reactions, reactions related to the resonantly stabilized allyl radical (C6H12-A) play important roles. Both of the reaction R549 and R555 have positive sensitivity coefficients because they...
consume the reactive radicals (OH, H) and produce the stabilized allyl radical. Consistent with our previous analysis, R540 shows significant inhibition effect on the ignition of 1-pentene, especially at 1600 K, in which condition allyl radical can be easily produced by 1-pentene directly through the unimolecular decomposition reaction R1594. Different from 1-pentene, for n-pentane, the chain termination reactions R189 (2CH3( +M) ⇔ C2H6( +M)) and R145 (CH3 + HO2 ⇔ CH4 + O2) perform relatively strong repressive effect on ignition at 1200 K. Interestingly, R577 (C3H3A + HO2 ⇔ C3H6O + OH) shows large negative sensitivity coefficient at 1200 K, because it consumes the relative stable radical C3H3A and HO2 and produces the active H atom. Besides, the produced C3H6O could further generate H atom through R747 (C3H2O ⇔ C3H2CHO + H). This is consistent with our previous analysis, acting as the third H producing path in 1200 K for 1-pentene (shown in Fig. 10). Similarly, R330 (C3H3 + O2 ⇔ CH3CHO + O) promotes the overall reactivity since it produces reactive O radical and CH2CHO, which could produce H atom through R269 (CH3CHO( +M) ⇔ CH2CO + H( +M)). It can be noted that the unimolecular decomposition reactions R1547 and R1594 exhibit negative sensitivity coefficient, showing positive effect on ignition. This is understandable because these unimolecular decomposition reactions consume the fuel and produce relative active radicals, serving as chain branching reactions. While for the H-abstraction reactions, which are also very important in ignition, the signs of their sensitivity coefficients are different, indicating their different roles in the overall reactivity. Taking 1-pentene at 1200 K for example, H abstractions from the σ–H bond (R1596, R1602) expedite the ignition, on the contrary, H abstractions from the γ and ε–C–H bond (R1595, R1597, R1601) have negative effect on ignition.

4. Conclusions

Ignition delay times of 1-pentene and n-pentane were measured in a shock tube at three equivalence ratios (0.5, 1.0 and 2.0) with 0.5% and 1.0% fuel concentrations, pressures from 0.12 MPa to 1.0 MPa and temperature from 1040 K to 1880 K. Ignition delay times were correlated with the equivalence ratio, pressure, and temperature in the tested conditions for both 1-pentene and n-pentene by multiple linear regression. Three models (NG model, JetSurf2.0, Touchard model) were validated, however, none of them could present good performance in all test conditions. The Aramco-NG model, in which the C1–C4 submodel was updated by the Aramco Mech 1.3 based on the NG model, showed good prediction on the ignition delay times of both 1-pentene and n-pentane. Both the correlations and simulations captured the ignition character of the 1-pentene and n-pentane experimental data, and that is 1-pentene shows shorter and longer ignition delay times in the relative low and high temperature region, respectively.

In the relative low temperature region, the fuel consumption rate was found to be a crucial factor on ignition. Due to the various H generating ways and higher rate constant of unimolecular decomposition reactions, 1-pentene shows shorter ignition delay time in this region. While in the relative high temperature region, the fuel consumption only make part contribution to ignition and the following oxidation of hydrocarbon intermediates and the accumulation of the active radicals have great effect on the ignition. In this region, R540 (C3H3A + H( +M) ⇔ C3H6( +M)) make competition with R1 (H + O2 ⇔ O + OH) for H atom. For 1-pentene, more C3H3 is produced through the breakage of the C2–C3 bond, and the C3H6 generated from R540 would participate in reaction R549 (C3H6 + OH ⇔ C3H5A + H2O) and R555 (C3H5 + H ⇔ C3H4A + H2), regenerating the allyl radical. In the sensitivity analysis part, these three reactions have an inhibiting effect on the ignition. For n-pentane, the reaction R1 (H + O2 ⇔ O + OH), which is an important chain branching reaction promoting the overall reactivity, dominates the H consumption since more oxygen exists in the n-pentane–oxygen-argon mixtures.

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Appendix A. Supplementary material

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References
