A kinetic modeling study on the oxidation of five hexane isomers

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Abstract

Chemical kinetic models have been developed for the five hexane isomers (*n*-hexane, 2-methyl pentane, 3-methyl pentane, 2,2-dimethyl butane and 2,3-dimethyl butane). The low-temperature reaction pathways have been refined by the addition of alternative isomerization reactions for hydroperoxyl-alkyl-peroxyl ($\dot{O}2QOOH$) radicals. New reaction rate rules, mostly from recently reported high-level calculations, have been applied. The thermodynamic parameters were estimated using the group additivity method. To validate these models, experimental ignition delay times for the oxidation of stoichiometric fuel/air mixtures of the five hexane isomers were obtained in a rapid compression machine and in a high-pressure shock tube. The reactivity of *n*-hexane, 2-methyl pentane, 3-methyl pentane and 2,2-dimethyl butane are well predicted by the models. Further work is needed for the 2,3-dimethyl butane sub mechanism.

Introduction

The oxidation of hexanes are less studied [1–5] in comparison to heptanes, especially *n*-heptane, which is a primary reference fuel [6–12]. Moreover, studies focusing on the low temperature oxidation of hexanes are even more scarce [3, 5]. In 1996, Burcat *et al.* [1] studied the ignition delay time of *n*-hexane-oxygen-argon mixtures in a shock tube over a temperature range of 1020–1725 K, at pressures of 1–7 atm. A mechanism with 386 elementary reactions was validated against the experimental results. Later in 2004, Zhukov *et al.* [4] studied the ignition delay time for *n*-hexane at much higher pressures of 13–220 atm over the temperature range of 822–1380 K. The kinetic model for *n*-heptane published by Curran *et al.* [7] was used to simulate the ignition delay times with satisfactory agreement. However, these studies focused on the high temperature conditions under which the more complex low-temperature chemistry of *n*-hexane had no obvious effect.

In 2014, Mevel *et al.* [3] performed an experimental study of *n*-hexane oxidation in a flow reactor at low temperatures. Therein, *n*-hexane was used as a single component surrogate for kerosene. The temperature range studied was 450–1000 K and the pressure was 100 kPa. The gas phase mixture composition was measured by both laser-based diagnostics and gas chromatography at the reactor outlet. However, the species measured were mainly reactants, C_2–C_5 olefins and major products such as H_2O, CO and CO_2. Although the model from Ramirez *et al.* [13] which was used to simulate *n*-decane and biofuel chemistry reproduced most of the trends in the experimental observations, more detailed information about the speciation, especially about the important intermediates such as alkyl peroxides and cyclic ethers are needed to provide more insight into the low-temperature chemistry. However, detecting and quantifying these intermediates that are less stable is difficult.

Wang and coworkers [5] performed an experimental study of the low-temperature oxidation of the five hexane isomers in a JSR reactor over a temperature range of 550–1000 K at 1 atm. Both gas chromatography and synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) were used to measure the concentrations of the species, with good agreement observed between the two methods. Cyclic ethers, which are important intermediates in the negative temperature coefficient (NTC) temperature regime, have been identified and quantified for all five isomers, providing valuable data for the validation of kinetic models over the NTC region.

This work reports a modeling study of the oxidation of the five hexane isomers. Measurements of ignition delay times for stoichiometric fuel/air mixtures have been carried out in a rapid compression machine and in a high-pressure shock tube over a temperature range of approximately 626–1010 K at a pressure of 15 atm. These data, in addition to the aforementioned speciation data from Wang *et al.* is used to validate an updated hexane isomers oxidation mechanism. This mechanism is based on our previous work [14] as a part of our continuous effort in building the oxidation mechanisms for alkanes in a hierarchical way (normal, branched and highly branched alkanes). New reaction pathways for the low-temperature region have been adopted to provide alternative isomerization reactions for hydroperoxyl-alkyl-peroxyl radicals, leading to di-hydroperoxyl-alkyl radicals, which have multiple product channels analogous to those of the hydroperoxyl-alkyl radicals.

Experiment

Rapid compression machine

The rapid compression machine at NUIG, which has a twin opposed piston configuration, has been described in detail by Brett *et al.* [15] and Affleck *et al.* [16]. A description of the heating system can also be found in a previous work [17]. A pressure transducer (Kistler 601A) was used to measure the pressure profiles. The signal passes through a charge amplifier and is recorded using a digital oscilloscope. Typical compression times in experiments are approximately 16 ms. The ignition delay time is defined as the time from the end of compression to the maximum rate of pressure rise due to fuel ignition. The compressed gas temperature T_c can be calculated using the adiabatic compression/expansion routine in Gaseq [18] from the initial temperature T_i, initial pressure p_i, mixture composition, and the compressed gas pressure p_c, which is the first local maximum of the pressure profile. The ignition delay times for the hexane isomers in 'air' at stoichiometric conditions have been measured in the low-temperature region, and show characteristic NTC behaviour. Ignition delay times of *n*-hexane are too short in the NTC region for accurate measurement using the RCM and these data were obtained using the high pressure shock tube.

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Shock tube

The shock tube at NUIG has been described by Nakamura *et al.* [19]. Six PCB 113A and one Kistler 603B pressure transducers have been equipped at the sidewall and endwall of the tube, respectively. The inner diameter of the tube is 6.35 cm. The driver section is 3 m in length and separated from the driven section (5.73 m) by the 3-cm diaphragm section. The diaphragm section contains two pre-scored aluminum diaphragms.

Further details of the experiment can be found in another paper "An experimental investigation of the effect of alkane fuel structure on reactivity demonstrated through the hexane isomers" (C. Banyon, K. Zhang, H.J. Curran) presented at ECM 2015.

Kinetic model

The C_6 mechanism uses AramcoMech1.3 mechanism as its sub-set. This mechanism has been validated against a variety of experimental results across a wide range of conditions [14]. Very recently, the sub-mechanism for the three pentane isomers has been updated.

It is on these sub-mechanisms that the hexane isomers mechanisms have been built following the hierarchical structure of alkane oxidation, including all reaction classes that were included in previous mechanisms [7], [20] with the addition of several new reaction pathways. Figure 1 shows a reaction path diagram for the oxidation of alkanes. The grey arrows are previously included reaction classes [20] and and the red arrows indicate newly added reaction classes. While many rate constants for C_4 and C_5 alkanes have been calculated at a high level of quantum chemical theory or derived from experiments [21–25], fewer are available for C_6, C_7 or larger alkanes [26], which adds to the significance of the analogies and rate rules used.

High temperature mechanism

The high-temperature mechanism is based on the *n*-hexane part of the *n*-heptane mechanism proposed by Curran *et al.* [7]. The high temperature oxidation regime is relatively simple, with fewer reaction classes compared to the low-temperature regime, as shown in the lower part of Fig. 1. The rate constants for the uni-molecular decomposition of fuel, hydrogen-atom abstraction by OH radicals and the beta-scission of fuel-derived alkyl radicals have been updated.

The pressure dependent rate constants for the uni-molecular decomposition of *n*-hexane have been calculated using Quantum-Rice-Ramsperger-Kassel/Modified Strong Collision (QRRK/MSC) theory based on the high-pressure limit rate constants used previously, since good agreement has been obtained between this method and the more precise Rice-Ramsperger-Kassel-Marcus/Master Equation (RRKM/ME) approach for alkane decomposition. The Lennard-Jones parameters for *n*-hexane have been reported by Jasper and Miller [27], which were $\sigma = 4.37$ Å and $\varepsilon = 201$ cm^{-1} in a bath gas of N_2.

The branching ratio of hydrogen abstraction from

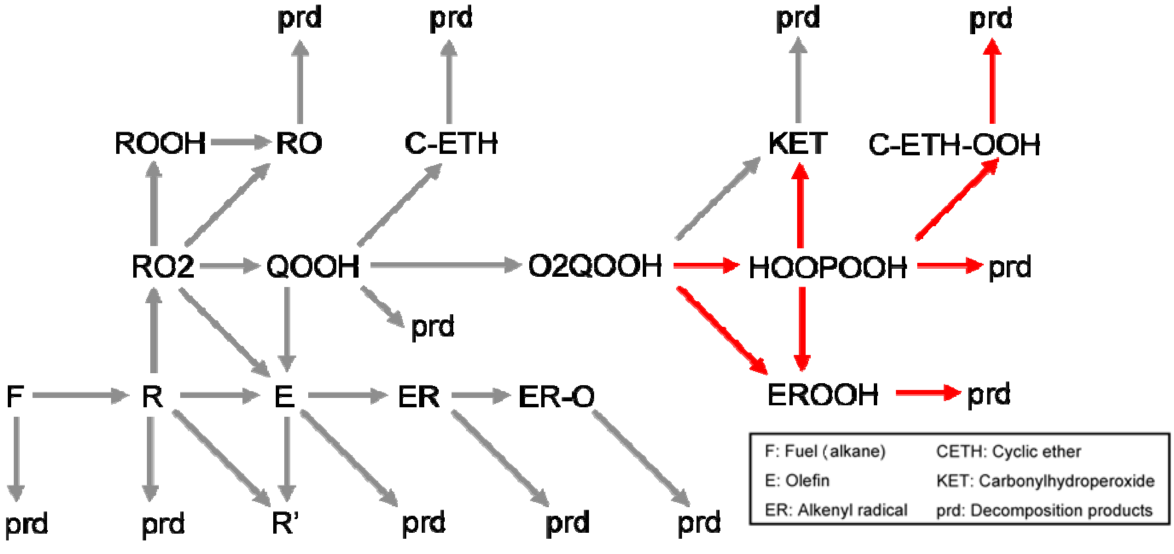


Fig. 1. Reaction pathways considered in kinetic model development in this work

the fuel by the radical pool has a significant effect at both low- and high-temperature regimes because this step determines the ratios between different fuel-derived radicals, and therefore influences the subsequent beta-scission reactions of alkyl radicals and their product distributions at high temperatures, or alkyl radical addition to molecular oxygen at low temperatures. Hydrogen-atom abstraction by OH radicals is the most important H-atom abstraction reaction for hydrocarbon oxidation. Recently, Sivaramakrishnan and Michael proposed rate rules for hydrogen abstraction by OH from saturated alkanes [26], including abstraction of various types of primary, secondary, and tertiary H-atoms, which have been adopted in our mechanism.

Tsang *et al.* derived the high-pressure limit rate constants for the decomposition of *n*-hexyl radicals from experiments perfromed in a single pulse shock tube over a temperature range of 890–1020 K and at pressures of 1.5–5.0 bar [28]. The rate constants of the isomerization reactions of *n*-hexyl radicals were also obtained by combining the experimental results with literature values of the beta bond scission reactions of hexyl radicals. Also, Tsang *et al.* suggested that the pressure effect may become insignificant as the size of the molecule increased, while the isomerization process would be enhanced due to the increase in chain length. The high-pressure limit rate constants for the decomposition and isomerization of *n*-hexyl radicals are used directly in the mechanism without further consideration of pressure effects, due to the expected negligibility of fall-off from the high-pressure limit for a fuel of this size at the conditions investigated.

Low temperature mechanism

The reaction pathways for the low-temperature oxidation of alkanes are shown in the upper part of Fig. 1. Having been produced by H-atom abstraction from alkanes, at low temperatures the alkyl radicals (R) add to molecular oxygen to form alkyl-peroxyl radicals (RO_2), which can isomerize into hydroperoxyl-alkyl radicals (QOOH), which can further add to oxygen (second O_2 addition) to produce hydroperoxyl-alkyl-peroxyl radicals (O_2QOOH). This is a chain propagating process. It was assumed previously [7], [20] that the only consumption channel for O_2QOOH is the reaction involving internal transfer of hydrogen and subsequent decomposition into ketohydroperoxides in one step. The formation and decomposition of ketohydroperoxides are chain branching due to the production of one OH radical in each step. However, this assumption is based on the fact that the C–H bonds on the carbon atom neighbouring the hydroperoxyl group are much weaker than analogous C–H bonds on a regular alkyl chain. This may not be accurate and detailed enough to describe the complexity of low-temperature oxidation chemistry.

In this work, new reaction pathways for O_2QOOH radicals have been considered, which allow O_2QOOH radicals to undergo internal H-atom transfer from carbons other than the carbon atom that neighbours the hydroperoxy group, forming a di-hydroperoxyl-alkyl radical ($P(OOH)_2$). This kind of intermediate has two hydroperoxyl groups attached to two different carbon atoms and one radical site on a third carbon atom, and therefore is similar to a hydroperoxyl-alkyl radical (QOOH). This alternative isomerization pathway could be very important for branched alkanes due to the existence of tertiary carbons bearing hydroperoxyl groups which have no hydrogen to be abstracted. However, even an influence on *n*-alkanes, such as *n*-hexane cannot be ignored, as will be presented in the discussion part of the paper.

At intermediate temperatures, the concerted elimination of HO_2 radicals from RO_2 radicals becomes competitive with the isomerization of RO_2 radicals to produce QOOH radicals, as does its dissociation reaction back to R + O_2. The concerted elimination of HO_2 from RO_2 has also been considered for O_2QOOH by analogy with that of RO_2, in addition to isomerization reactions to produce $P(OOH)_2$ radicals, which are analogous to $RO_2 \rightleftharpoons QOOH$. Depending on whether the radical site is alpha, beta or gamma to the hydroperoxyl group, $P(OOH)_2$ radicals tend to decompose through different channels, producing unsaturated hydroperoxides or small molecules and radicals. Another pathway considered is the formation of hydroperoxyl cyclic ethers, which decompose easily because of the weakness of the O–O bond in the hydroperoxyl moiety. However, since $P(OOH)_2$ is the product of a series of subsequent chain propagation reactions, its significance is limited to the low-temperature region. This is essential because it is the competition between chain branching and chain propagation reactions that leads to NTC behaviour. Thus these reactions have to be assigned with proper rate constants for better predictions of the reactivity.

A series of quantum chemistry calculations have been reported on the low temperature oxidation reactions of alkanes [21–25]. However, these cacluations are only for species only up to pentanes, so either the rate rules proposed in these works or analogies to similar reactions have been used here for the hexane isomers, with certain modification within the unceraincy range to achieve better agreement with the experimental observations.

For the addition of alkyl radicals to O_2, the rate rules from Miyoshi are used which were based on calculations using variational transition state theory (VTST) and Rice-Ramsperger-Kassel-Marcus theory (RRKM)/master equation calculations. While the rate constants for the second O_2 addition to QOOH has been calculated for the propyl + O_2 system by Goldsmith *et al.* [25], using these as a direct analogy for the hexyl + O_2 system may probably not be accurate. Therefore, for the second addition to O_2 we use rate constants for the first addition to O_2 proposed by Miyoshi [29] with a reduction by approximately a factor of two, which is in general the same trend as with the propyl + O_2 system reported by Goldsmith *et al.* [25].

For the formation of cyclic ethers and the beta-scission reactions of hydroperoxyl-alkyl radical, we have adopted the rate rules developed by Villano *et al.* [23], which connects the activation energies with the heats of reaction in a linear relationship. Villano *et al.* reported that the uncertainty in the A-factors is a factor of two, while the uncertainty in the activation energy is ±1 kcal mol^{-1}. Therefore, to obtain better agreement with the experimental observations, especially with the measured ratios between different cyclic ethers, certain modifications within the uncertainty range of the rate rules have been adopted. Alternatively, direct analogous rate constants can be used for this reaction class.

The concerted elimination of an olefin HO_2 radicals from RO_2 radicals has been calculated by Villano *et al.* from both the forward and reverse direction [21,22]. However, at lower temperatures the forward rate constants derived through microscopic reversibility from [21] utilizing the CHEMRev software package [30] are much higher than the previous results [22], leading to under-prediction of the reactivity over the low-temperature region. Therefore, the results from [22] have been adopted. Although rate rules have been included in [22], we chose to use the rate constants by analogy to the calculated results for *n*-pentane, with modifications within the uncertainty range to match the experimental results. The rate rules for the beta-scission of the C–O bond in beta-hydroperoxyl-alkyl radicals producing an olefin + HO_2 has been adopted from another work by Villano *et al.* [23]. Meanwhile, the hydroperoxyl-alkyl radicals have other channels of decomposition, the rate rules of which have been adopted from Villano *et al.* [23] in order to be consistent.

Sharma *et al.* [24] calculated the isomerization reactions $RO_2 \rightleftharpoons QOOH$ for a series of alkyl-peroxyl radicals using the CBS-QB3 quantum chemical method, as well as the isomerization and sequent decomposition of O_2QOOH radicals into a ketohydroperoxide species and an OH radical. These rate constants are adopted in this mechanism.

Due to the similarity between QOOH and $P(OOH)_2$, the analogy and rate rules have been applied to $P(OOH)_2$ according to analogous reactions of QOOH, including the formation of cyclic ethers (formation of hydroperoxyl cyclic ethers), concerted HO_2 elimination and C–O bond beta-scission (producing olefinic hydroperoxides), as well as decomposition into smaller molecules. The modifications to the rate rules for hydroperoxyl-alkyl radicals have also been applied to $P(OOH)_2$.

Thermodynamic database

Thermodynamic data reflects the thermodynamic properties of species from which the equilibrium constants and reverse reaction rates are determined and is therefore has critical importance. The thermodynamic data for the C_6 species has been determined using the software THERM [31] based on the group additivity method proposed by Benson [32], which largely depends on the group values used. In this work, updated THERM group values from multiple sources such as high level quantum chemistry calculations, experiments and online databases have been employed [33].

Results and discussion

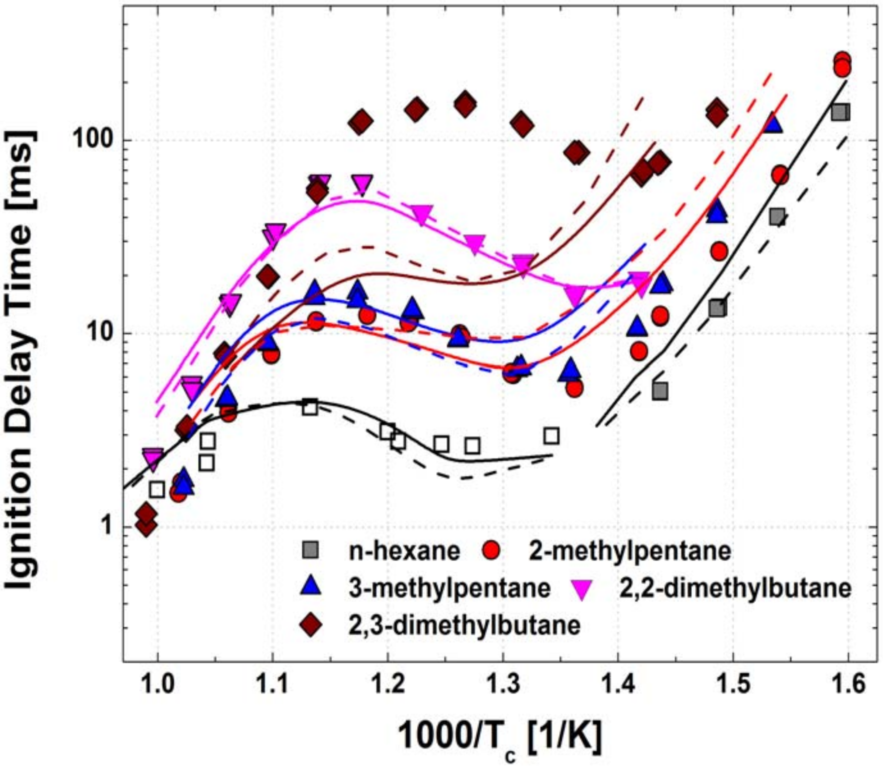
Low and intermediate temperature regions

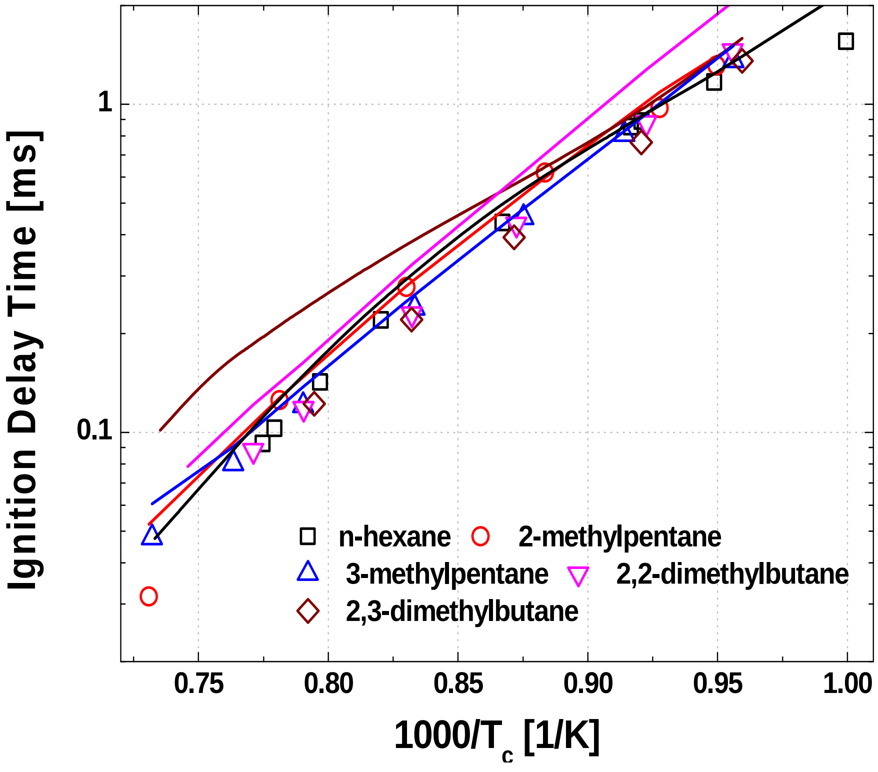
Fig. 2 shows the measured ignition delay times for hexane/air mixtures over the temperature range of 625–1010 K measured with RCM (solid symbols). The equivalence ratio is 1.0 (hexane/O_2/N_2=2.21/21/79) and at a pressure of 15 atm. Compared with the other isomers in which the number of secondary hydrogen atoms are equal or less than the primary ones, the *n*-hexane molecule contains 8 secondary hydrogen atoms, which are readily abstracted by the radical pool. In addition, the internal hydrogen transfer producing hydroperoxyl alkyl radical by abstracting a secondary hydrogen atom via a six member ring is available for all the C_6 peroxides derived from *n*-hexane. Therefore the reactivity of *n*-hexane is obviously higher than the other isomers. 2-methyl pentane is slightly more reactive than 3-methyl pentane but they both have overall similar reactivity. 2,2-dimethyl butane has a lower reactivity still, with 2,3-dimethyl butane having the lowest reactivity of the five isomers.

At pressures of around 15 atm and in the low-temperature range, the ignition delay time of the stoichiometric *n*-hexane/air mixture decreases sharply with increasing temperature, until the scale becomes comparable to that of the compression time during which the mixture may have already started to react. Therefore experimental ignition delay times that are shorter than 5 ms are not reliable due to possible reactions during compression and are not presented here.

Good agreement has been obtained between the experimental and simulated ignition delay times for *n*-hexane and 2,2-dimethyl butane especially in the NTC region, while the predictions for 2-methyl pentane and 3-methyl pentane are reasonably satisfactory, as shown with the solid lines in corresponding color to the symbols. However, there is a large over-prediction of ignition delay times for 2,3-dimethyl butane, indicating that more work is needed to improve this sub-mechanism. There are only two types of C–C bond in 2,3-dimethyl butane, that is, primary-tertiary and tertiary-tertiary. This may indicate that reactions and rate rules related to these structures may need to be refined. The predictions for 2-methyl butane and 3-methyl butane are not as good as those for *n*-hexane and 2,2-dimethyl butane. Since they both contain a primary-tertiary C–C bond in their molecules, this might be another clue that the reactions and rate rules related to primary-tertiary C–C bond needs to be re-considered.

The dashed lines show the predictions of the model when alternative isomerization reactions for hydroperoxyalkylperoxy radicals are not considered. It can be seen that the absence of this pathway leads to different influences upon the ignition delay times, depending on the structure of the fuel. In general, the adoption of the alternative isomerization reactions shows a positive effect for the predictions. It is interesting that the prediction for 2,3-dimethyl butane improves when the alternative isomerization is not


Ignition Delay Time [ms]
1000/T_c [1/K]
1
10
100
1.0
1.1
1.2
1.3
1.4
1.5
1.6
n-hexane
2-methylpentane
3-methylpentane
2,2-dimethylbutane
2,3-dimethylbutane


Ignition Delay Time [ms]
1000/T_c [1/K]
0.1
1
0.75
0.80
0.85
0.90
0.95
1.00
n-hexane
2-methylpentane
3-methylpentane
2,2-dimethylbutane
2,3-dimethylbutane

the trend of which has been well captured by the numerical simulation.

High temperature region

The ignition delay times for the hexane isomers measured in the high-pressure shock tube at temperatures above 1000 K are depicted in Fig. 3. At the high temperature region, all the hexane isomers have considered, which suggests that reaction rate rules may not apply for certain special fuel structures. As has been stated above, due to the high reactivity of *n*-hexane, its ignition delay times over the NTC region were measured using the high pressure shock tube instead of the RCM. These data are presented in Fig. 2 as open symbols in black, similar reactivity as observed in the experiments. This trend has been well reproduced for all hexane isomers except for 2,3-dimethyl butane, as shown by the solid lines. Therefore the high-temperature chemistry of 2,3-dimethyl butane may need more accurate estimation or better analogy since most reactions are not available from high level quantum chemical calculations or from experiments.

Conclusion and future work

In this work, the sub-mechanisms for the oxidation of the five hexane isomers have been developed. Based on the previous work for alkane oxidation, these mechanisms have adopted alternative isomerization reactions for hydroperoxyalkylperoxy radicals and new reaction rate rules that have been reported recently. Experimental results from both a rapid compression machine and a high pressure shock tube have been obtained in the temperature range of 626–1010 K. The models have successfully reproduced the ignition delay times satisfactorily for four hexane isomers, being *n*-hexane, 2-methyl pentane, 3-methyl pentane and 2,2 dimethyl butane. However, the ignition delay times for 2,3-dimethyl butane are obviously under predicted, indicating that refinement is needed for this sub-mechanism and relevant reaction rate rules, which is part of the future work. These models will also be validated against the experimental speciation data, such as the experimental results from jet-stirred reactor recently published by Wang *et al* [5]. Moreover, the influence of using different rate rules/analogies upon the predictions will be compared and discussed.

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