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The development of a detailed chemical kinetic mechanism for diisobutylene and comparison to shock tube ignition times [☆]

Wayne K. Metcalfe ^{a,*}, William J. Pitz ^b, Henry J. Curran ^a,
John M. Simmie ^a, Charles K. Westbrook ^b

^a National University of Ireland, Galway, Ireland

^b Lawrence Livermore National Laboratory, Livermore, CA 94551, USA

Abstract

Shock tube experiments and chemical kinetic modeling were carried out on 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene, the two isomers of diisobutylene, a compound intended for use as an alkene component in a surrogate diesel. Ignition delay times were obtained behind reflected shock waves at 1 and 4 atm, and between temperatures of 1200 and 1550 K. Equivalence ratios ranging from 1.0 to 0.25 were examined for the 1-pentene isomer. A comparative study was carried out on the 2-pentene isomer and on the blend of the two isomers. It was found that the 2-pentene isomer ignited significantly faster under shock tube conditions than the 1-pentene isomer and that the ignition delay times for the blend were directly dependant on the proportions of each isomer. These characteristics were successfully predicted using a detailed chemical kinetic mechanism. It was found that reactions involving isobutene were important in the decomposition of the 1-pentene isomer. The 2-pentene isomer reacted through a different pathway involving resonantly stabilized radicals, highlighting the effect on the chemistry of a slight change in molecular structure.

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1. Introduction

There is much demand for chemical kinetic models to represent practical fuels such as gasoline, diesel and aviation fuel. These blended fuels may contain hundreds of components whose identity

and amounts are often unknown. A chemical kinetic mechanism that would represent the oxidation of all these species with accompanying chemical reactions is intractable with current computational capabilities, chemical knowledge and manpower resources [1]. The use of surrogate fuels is an approach to make the development of chemical kinetic mechanisms for practical fuels tractable. A surrogate fuel consists of a small number of components that can be used to represent the practical fuel and still predict characteristics of the real fuel. These desirable characteristics may include ignition behavior, burning velocity, viscosity, vaporization,

[☆] Supplementary data for this article can be accessed online. See Appendix A.

* Corresponding author.

E-mail address: wayne.metcalfe@nuigalway.ie (W.K. Metcalfe).

and emissions such as carbon monoxide, hydrocarbons, soot and nitrogen oxides.

Gasoline consists of many different classes of hydrocarbons including straight and branched alkanes, cycloalkanes, alkenes, cycloalkenes, and aromatics. One approach to surrogate fuels is to include one or more components from each class of hydrocarbon in gasoline so that the unique molecular structure of each class is represented. This approach may lead to reliable predictions of many of the combustion properties of the practical fuel. In order to obtain a fuel surrogate mechanism, detailed chemical kinetic mechanisms must be developed for each component in the mix compound.

In this study, a detailed chemical kinetic mechanism is developed for diisobutylene, which is intended to represent the hydrocarbon class of alkenes in practical fuels. Diisobutylene is not a pure compound but is a mixture of two conjugate olefins of iso-octane: 2,4,4-trimethyl-1- (and -2-) pentene. Diisobutylene has a similar molecular structure to iso-octane, so that its kinetics offers an insight into the effect of including a double bond in the carbon skeletal structure of iso-octane.

There are few previous studies on diisobutylene. Kaiser et al. [2] examined the exhaust emissions from a production spark ignition engine with neat diisobutylene and a mixture of it with gasoline. They found that the exhaust emissions of diisobutylene are similar to that of iso-octane. However a significant increase in the amount of 2-methyl-1,3-butadiene was observed in the engine exhaust relative to iso-octane. They also found appreciable amounts of propene in the exhaust, but could not explain the source of this product in terms of C–C bond β scission of alkyl radicals. More recently Risberg et al. [3] studied a number of fuel blends to evaluate their autoignition quality for use in a homogeneous charge compression ignition engine, using diisobutylene to represent olefins in one of their test fuels.

In this study, experiments on the shock tube ignition of both isomers of diisobutylene will be described. Then, the development of a detailed chemical kinetic mechanism for the two isomers of diisobutylene will be discussed. Finally, the mechanism will be applied to the shock tube ignition of diisobutylene.

2. Experimental

All shock tube measurements presented in this paper were obtained in a helium-driven shock tube built and characterized at the National University of Ireland, Galway [4,5]. The experimental apparatus consists of a shock tube, gas handling facility, and light emission diagnostic.

The stainless steel shock tube consists of a 53 cm long, 52 cm outer diameter driver section, terminated at one end with a 10 cm long,

10.24 cm internal diameter tube, which is separated from the 6 m long, 10.24 cm internal diameter test section by a diaphragm. Shock waves were generated not by allowing the polycarbonate diaphragm (Makrofol DE, Coloprint GmbH) to burst under pressure alone, but with the aid of a cross-shaped cutter to ensure uniform petalling of the diaphragm. A series of four pressure transducers (PCB 113A21) mounted flush with the internal wall, and located at precise distances from the end-wall were used to measure the incident shock velocity using three universal time counters (Fluke/Phillips PM6666). In order to allow for shock attenuation, the shock velocity at the end-wall was calculated by linearly extrapolating the incident shock velocity to the end-wall.

The emission of CH^* behind the reflected shock wave was monitored using an end-on detection diagnostic [6], consisting of a photodiode array detector (Thorlabs Inc., model PDA55), located directly behind a 431 nm narrow band-pass filter with a spectral bandwidth of 10 nm. Both the filter and the PDA are aligned behind a 6 mm outer diameter fused silica window embedded in the end-wall. Reflected shock conditions were calculated from shock velocities using the one-dimensional shock relations via the application GASEQ [7].

Test mixtures were prepared in a 35 L stainless steel tank using standard manometric methods. Gases were obtained from BOC Ireland Ltd.: Argon Zero Grade 99.998%, and Oxygen Research Grade 99.985%. All gases were used without further purification. The two isomers of diisobutylene (99% pure) were obtained from Aldrich Chemical Co. Ltd. To minimize the presence of atmospheric air in the sample each isomer was subjected to several freeze–pump–thaw degassing cycles before being used. The liquid isomer was incorporated into the mixing vessel by vaporization of the fuel into the evacuated mixing tank. Both fuel and oxygen partial pressures were measured using a 100 Torr Baratron gauge to an accuracy of 0.01 Torr. For reactant gas pressures above 100 Torr, a Wallace and Tiernan 800 Torr absolute pressure gauge was used. Test gas mixtures were normally made up to a final pressure of 800 Torr. To ensure homogeneity, the mixtures were allowed to stand for 24 h or mixed for 2 h using a magnetic stirring bar—both methods gave identical results, indicating that the mixing procedure was adequate. From the resulting mix, initial pressures of 20–100 Torr were used.

Prior to an experiment both the driver and driven sections of the shock tube were evacuated independently. The driver section was evacuated to 10^{-3} Torr using a rotary oil pump, while the driven section was firstly pumped to 10^{-2} Torr using a rotary oil pump, and the final pressure of 10^{-6} Torr was achieved using a diffusion pump. The range of experimental data generated for 2,4,4-trimethyl-1-pentene is provided in Table 1.

Table 1

Mole fractions of reactants, reflected shock pressures and equivalence ratios for 2,4,4-trimethyl-1-pentene experiments (balance is argon)

Fuel (%)	O ₂ (%)	P ₅ (atm)	ϕ
0.75	9.0	1.0	1.0
0.375	9.0	1.0	0.5
0.75	9.0	4.0	1.0
0.75	18.0	4.0	0.5
0.375	18.0	4.0	0.25

All ignition delay times, τ , for the current study were measured behind the reflected shock, with τ defined as the time interval from shock arrival at the end-wall, as indicated by an in-situ pressure transducer (Kistler 601H), to the maximum in the rate of change of emission of light from CH* at 431 nm with respect to time. This definition is taken from that of Gutman et al. [8] where a similar end-wall diagnostic was used to measure the emission of light from the reaction $\text{CO} + \text{O} \rightarrow \text{CO}_2 + h\nu$. All the measurements were taken at a constant reflected shock pressure with at most a 10% variation about a mean value.

3. Chemical kinetic model

The chemical kinetic model for diisobutylene was based on the original iso-octane mechanism of Curran et al. [9] together with later enhancements [10]. Due to the importance of the isobutene submechanism to the chemistry of the 1-pentene isomer (discussed below), the C₄ portion of the mechanism has been amended taking the work of Curran [11] on isobutene into account.

Species and reactions were added to the iso-octane mechanism to treat the oxidation of both isomers of diisobutylene, abbreviated to DIB. The thermodynamic parameters for the new species were computed using THERM [12] with updates from (J.W. Bozzelli, Private communication, 2005.) and are given in the [Supplementary data](#). There are several different types of reactions that were added. Examples of these

types of reactions and the source of their rate constants are discussed below. [Table 2](#) includes a listing of some of the added reactions and their associated rate constants. A full list of the added species and their structures can be found in the [Supplementary data](#). The final version of the mechanism, DIB1v2, and the associated thermodynamic data is available in electronic format [13] and in the [Supplementary data](#).

Molecular elimination reactions (or retroene reaction [14]) for DIB were added using the rate constants of Tsang [15]. A retroene reaction is only possible from the 1-pentene isomer (JC₈H₁₆) and not from the 2-pentene isomer (IC₈H₁₆). The retroene reaction was not found to play a role in the shock tube ignition of DIB.

Both C–C and C–H bond breaking reactions were included for the parent fuel. The high-pressure rate constants were specified by their reverse rate constants with the forward decomposition rate constants being computed from microscopic reversibility. The C–H bond breaking reaction rates are slow, but were included because they were important in the reverse direction under shock tube conditions. The pressure and temperature dependence of the fuel decomposition reaction rate constants were computed using Quantum RRK analysis to obtain $k(E)$ and master equation analysis to evaluate pressure fall-off [16]. For the master equation analysis, an exponential-down energy-transfer model was used, with a collisional step-size down (ΔE_{down}) of 350 cm^{−1} for an Ar collider. The addition of these factors decreased the ignition delays for the 1-pentene isomer slightly. Reaction of DIB with O₂ was also included, but it is not important under our conditions. Under shock tube conditions, the decomposition of the 1-pentene isomer was much faster than the 2-pentene isomer of C₈H₁₆. The same rate constant for C–C bond breakage was assumed in the reverse direction for both isomers by analogy with the allyl + methyl radical combination reaction. However, in the forward decomposition direction, the pre-exponential factor computed from microscopic reversibility for the 1-pentene-isomer decomposition was much faster than the 2-pentene isomer. Shock tube igni-

Table 2

Important reactions of diisobutylene (cm^{−3}–mol–s–cal units)

Reaction	A	n	E _a
JC8H16 = TC4H9 + IC4H7	1.13E + 92	−21.99	109,815
JC8H16 = IC4H8 + IC4H8	3.96E + 27	−5.02	53,633
JC8H16 = XC7H13-Y2 + CH3	2.13E + 108	−26.53	135,011
JC8H16 + H = JC8H15-A + H2	7.34E + 05	2.77	8147
IC8H16 = YC7H13-Y2 + CH3	7.05E + 66	−14.79	100,101
IC8H16 + H = IC8H15-A + H2	7.34E + 05	2.77	8147
DMPD13 + CH3 = IC8H15-A	2.92E + 03	2.36	8360
DMPD13 + H = YC7H13-Y2	1.06E + 12	0.51	1230
DMPD13 + H = DMPD13-E + H2	3.79E + 05	2.5	2390
DMPD13 + H = DMPD13-B + H2	1.89E + 05	2.5	2390

See [Supplementary data](#) for glossary.

tion delay times are usually dependent on initiation reactions, but for the 1-pentene isomer the decomposition to $\text{TC}_4\text{H}_9 + \text{IC}_4\text{H}_7$ (see Fig. 6) is not the rate determining step, with the ignition delay instead being sensitive to the decomposition of isobutene.

Abstraction of H atoms from both alkylic and allylic C–H bonds in DIB was included in the mechanism. The abstraction from vinylic C–H bonds was neglected because the rate constants are much lower than that of allylic or alkyl C–H [17]. Abstraction by OH, H, CH_3 , HO_2 , CH_3O_2 , CH_3O , C_2H_5 , and C_2H_3 radicals were considered. For abstraction by OH, H, and CH_3 radicals the rate constant parameters for the abstraction of alkyl hydrogen atoms were taken from Curran et al. [9], while those for the abstraction of primary and secondary allylic hydrogen atoms were taken from Heyberger et al. [17]. For H atom abstraction by HO_2 radicals rate constants were taken from Scott and Walker [18]. Rate constants for abstraction by CH_3O_2 radicals were assumed to be identical to those for HO_2 . Rate constants for abstraction of allylic H atoms by CH_3O and C_2H_3 radicals are not available in the literature and were estimated.

The rate constants for the decomposition of DIB radicals were specified in the reverse exothermic direction, that is, the addition of a radical to a double bond based on the recent publication by Curran [19].

Some reactions of the excited state of methyne, CH^* , were included in the mechanism based on the work of Hall et al. [20]. Their results showed that the reaction of $\text{C}_2\text{H} + \text{O}_2 \rightarrow \text{CO}_2 + \text{CH}^*$ is the most important reaction in the formation of CH^* . However, as experimental delays are defined by the time of maximum rate of change of CH^* emission, we have found that the predicted time of maximum product of $[\text{C}_2\text{H}] \times [\text{O}]$ coincides well with the simulated time of maximum rate of change of CH^* concentration using Hall's CH^* mechanism and thus we have used this simple criterion in simulations of our ignition delay times.

The simulations were carried out with CHEMKIN 3 [21], using the Aurora code assuming constant pressure. Constant volume conditions were also considered, with these calculations consistently predicting ignition delay times 10% shorter than the constant pressure calculations. Since some pressure increase is experimentally observed during the ignition event, the experimental result can be expected to lie in between the constant pressure and constant volume assumptions.

4. Results and discussion

We will first consider the results for 2,4,4-trimethyl-1-pentene. The experimental and computational results show how the ignition delay times are influenced by fuel concentration, oxygen

concentration, pressure and isomeric composition. The influence of fuel concentration is seen in Fig. 1 where the ignition delay times increase with increasing fuel concentration. The reason for this behavior is that the fuel reacts with H atoms that would otherwise react with oxygen and provide chain branching through $\text{H} + \text{O}_2 = \text{OH} + \text{O}$. The effect of fuel concentration on ignition delay diminishes as the temperature is lowered (Fig. 1) until the effect is reversed for most hydrocarbon fuels at low temperatures [22]. Qualitatively, the trends with fuel concentration are similar in both the experimental and modeling results. The mechanism predicts ignition delay times that are in good agreement with those measured experimentally. As the fuel concentration is decreased by a factor of 2, from 0.75% fuel (squares) to 0.375% fuel (circles) so the ignition delay time also decreases in tandem. This behavior is similar to other hydrocarbon fuels, which normally show a slightly positive dependence of ignition delay time on fuel concentration.

Measured ignition delay times greater than 1300 μs are probably unreliable because of the complex shockwave contact surface/rarefaction wave interactions which result in unpredictable effects.

The influence of oxygen concentration is seen in Fig. 2. The ignition delay time decreases as the oxygen concentration increases from 9% (squares) to 18% (circles). This behavior is commonly seen for hydrocarbons where ignition delay time has a negative exponent for its dependence on oxygen concentration [23]. Figure 2 shows that the effect of a factor of two change in oxygen concentration has a much more pronounced effect on ignition delay times than a factor of two change in fuel concentration. The model shows approximately correct dependence on oxygen concentra-

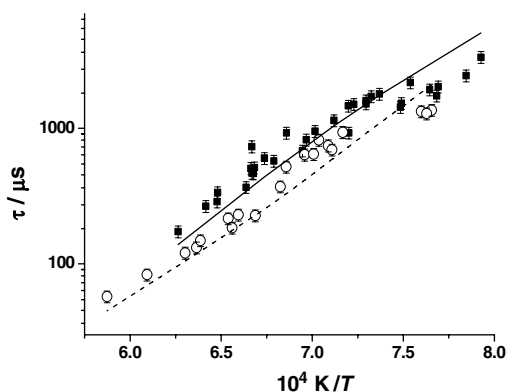


Fig. 1. Experimental (points) and model-predicted (lines) ignition delay times for 2,4,4-trimethyl-1-pentene oxidation behind reflected shock waves at 1.0 atm in Ar, (■) 0.75% fuel, $\phi = 1.0$, (○) 0.375% fuel, $\phi = 0.5$. Dashed line corresponds to open symbols. 10% error bars on experimental data.

tion but predicts about a factor of two greater dependence on the fuel concentration than observed in this set of experiments.

The influence of pressure is seen in Fig. 3 where increasing pressure decreases the ignition delay time. The relative shift toward decreased ignition delay times with increasing pressure is well reproduced by the model. The predicted ignition delay times are in good agreement for the 1 atm data and are about 25% too fast for the 4 atm case.

Finally, the effect of fuel composition is considered, examining both isomers and their mixtures (Fig. 4). The experiments show that 2,4,4-trimethyl-2-pentene (triangles) is considerably faster to ignite than 2,4,4-trimethyl-1-pentene (squares). In addition, the mixture that contains three parts 2,4,4-trimethyl-1-pentene to one part 2,4,4-trimethyl-2-pentene is intermediate to the pure components. Ignition delay times appear to be directly proportional to the quantity of each isomer present.

The comparative trends in the model results as the fuel is changed from 2,4,4-trimethyl-1-pentene to 2,4,4-trimethyl-2-pentene and to the mixture are quite similar to the experiment results (Fig. 4). The predicted delays for 2,4,4-trimethyl-2-pentene are approximately 25% too slow overall with the discrepancy increasing at lower temperatures, but the prediction for the mixture is in good agreement with experiment.

4.1. Sensitivity analysis

A detailed analysis was carried out to investigate the sensitivity of the principal reactions involved in the oxidation of both isomers of diisobutylene. This was achieved by multiplying the rate constants of a particular reaction or reaction class by a factor of two (both forward and reverse

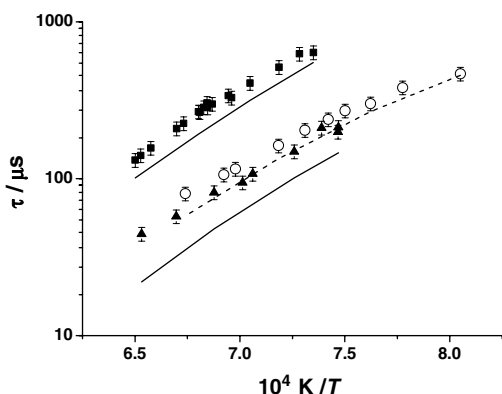


Fig. 2. Experimental (points) and model-predicted (lines) ignition delay times for 2,4,4-trimethyl-1-pentene oxidation behind reflected shock waves at 4.0 atm in Ar, (■) 0.75% fuel, 9.0% oxygen, $\phi = 1.0$, (○) 0.75% fuel, 18.0% oxygen, $\phi = 0.5$, (▲) 0.375% fuel, 18.0% oxygen, $\phi = 0.25$. Dashed line corresponds to open symbols. 10% error bars on experimental data.

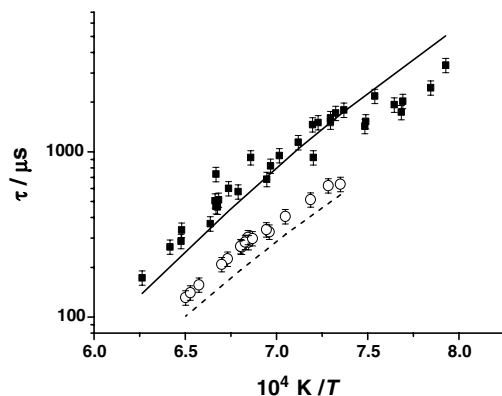


Fig. 3. Experimental (points) and model-predicted (lines) ignition delay times for 2,4,4-trimethyl-1-pentene oxidation behind reflected shock waves at 0.75% fuel, $\phi = 1.0$ in Ar, (■) 1.0 atm, (○) 4.0 atm. Dashed line corresponds to open symbols. 10% error bars on experimental data.

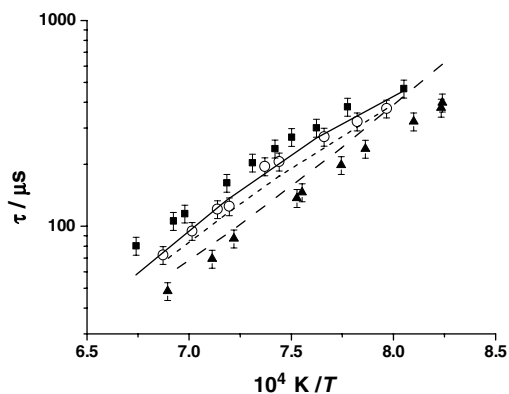


Fig. 4. Experimental (points) and model predicted (lines) ignition delay times for 0.75% fuel oxidation behind reflected shock waves at $\phi = 0.5$, 4.0 atm in Ar, (■) 2,4,4-trimethyl-1-pentene, (○) 2,4,4-trimethyl-1-pentene:2,4,4-trimethyl-2-pentene (3:1), (▲) 2,4,4-trimethyl-2-pentene. 10% error bars on experimental data.

rates) and seeing the effect on the calculated ignition delay time (Figs. 5 and 7). A sensitivity coefficient, σ , was defined as: $\sigma = (\tau' - \tau)/\tau$, where τ is the original delay and τ' is the delay time calculated using the adjusted rate constant. Therefore, a positive sensitivity coefficient represents a longer ignition delay and an overall reduction in reactivity, and a negative coefficient indicates a shorter ignition delay and an increase in reactivity.

Figure 5 shows the dependence of isobutene (IC_4H_8) chemistry on measured ignition delay times for 2,4,4-trimethyl-1-pentene (JC_8H_{16}). The main (unimolecular) decomposition pathway of this isomer leads to the formation of TC_4H_9

+ IC₄H₇, with TC₄H₉ in turn producing isobutene (Fig. 6). Ignition delay is far more sensitive to the decomposition and reactions of isobutene than to the decomposition of the fuel itself. The reaction of $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$ is obviously important in the oxidation of both isomers as it is an example of chain branching, producing reactive oxygen atoms and hydroxyl radicals. The oxidation of the 1-pentene isomer has a large positive coefficient to the reaction of $\text{IC}_4\text{H}_8 \rightarrow \text{IC}_4\text{H}_7 + \text{H}$. This reaction primarily proceeds in the reverse direction, consuming reactive hydrogen atoms to produce stable isobutene. This explains why increasing the rate of this reaction shows an overall reduction in reactivity.

The primary decomposition pathway for 2,4,4-trimethyl-2-pentene (IC₈H₁₆) is shown in Fig. 8. Comparing Figs. 6 and 8 it is immediately clear how a slight change in structure has a large effect on the chemistry of the isomers. The 2-pentene isomer decomposes to a resonantly stabilized radical

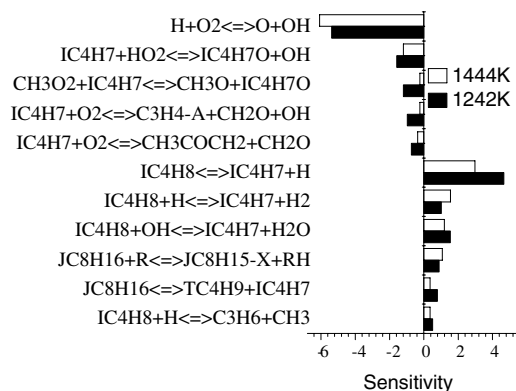


Fig. 5. Sensitivity analysis showing effect of increasing rate constants by a factor of 2 on ignition delay time for 2,4,4-trimethyl-1-pentene. 4.0 atm, $\phi = 0.5$ and 1242 and 1444 K.

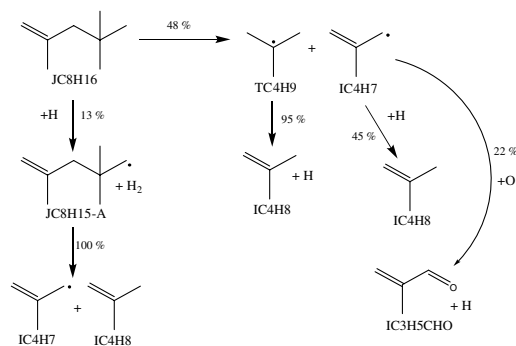


Fig. 6. Decomposition of 2,4,4-trimethyl-1-pentene at 4.0 atm, $\phi = 0.5$ and 1200 K. 10% fuel consumed. Percentages indicate percent of parent species going to daughter species.

(YC₇H₁₃-Y2) and a methyl radical, $\text{IC}_8\text{H}_{16} \rightarrow \text{YC}_7\text{H}_{13}\text{-Y2} + \text{CH}_3$. Figure 7 shows how increasing the rate of this reaction increases the reactivity of the system. The abstraction reactions producing the radicals IC₈H₁₅-A and JC₈H₁₅-B (Fig. 9), show positive sensitivity coefficients. These both decompose to produce a methyl radical and 2,4-dimethyl-1,3-pentadiene (DMPD13), which is the stable intermediate in the decomposition shown in Fig. 8. Reactions involving the 2,4-dimethyl-1,3-pentadiene radical, (DMPD13-E) also show significant sensitivity:

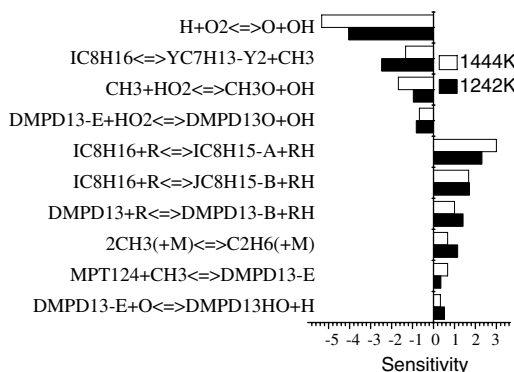


Fig. 7. Sensitivity analysis showing effect of increasing rate constants by a factor of 2 on ignition delay time for 2,4,4-trimethyl-2-pentene; 4.0 atm, $\phi = 0.5$ and 1242 and 1444 K.

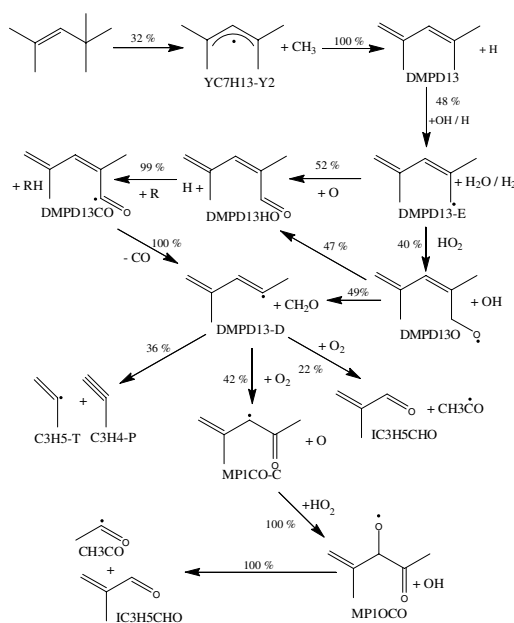


Fig. 8. Decomposition of 2,4,4-trimethyl-2-pentene at 4.0 atm, $\phi = 0.5$ and 1200 K. 10% fuel consumed. Percentages indicate percent of parent species going to daughter species.

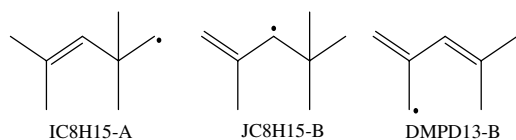
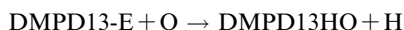
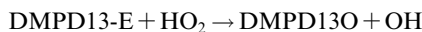


Fig. 9. Structures of three radicals involved in 2,4,4-trimethyl-2-pentene decomposition.



Close attention to the chemistry of this radical was important to obtain reasonable predictions for the ignition delay of the 2-pentene isomer.

5. Conclusions

Ignition delay times for 2,4,4-trimethyl-1-pentene have been measured behind reflected shock waves at 4 atm and at equivalence ratios of 0.25, 0.5, and 1.0. Experiments performed at 1.0 and 4.0 atm with an equivalence ratio of 1.0 show the influence of pressure. In addition, the reactivity of pure 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, and a 0.75 2,4,4-trimethyl-1-pentene/0.25 2,4,4-trimethyl-2-pentene mixture was examined. It was found that of the two isomers, 2,4,4-trimethyl-2-pentene is significantly faster to ignite throughout the temperature range (1200–1550 K) of this study. The chemical kinetic mechanism developed to interpret these experiments reproduces these effects.

Despite being slower to ignite, the 1-pentene isomer is consumed much faster than the 2-pentene isomer. For example, under the identical conditions described in Figs. 6 and 8, 10% of the 1-pentene isomer is consumed after just 3 μs , producing principally isobutene. Whereas, it takes 31 μs for the same amount of 2,4,4-trimethyl-2-pentene to be consumed. This further highlights the dependence of the combustion of 2,4,4-trimethyl-1-pentene on the reactions of isobutene and the effect of a slight structural change on the chemistry of the system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.proci.2006.07.207.

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Comments

C.T. Bowman, Stanford University, USA. You have sufficient data to cast your ignition delay data in canonical form as function of reactant concentrations and temperature. This would be very useful to report.

Reply. Multiple regression analysis of our 2,4,4-trimethyl-1-pentene data yields:

$$\tau = 4.67 \times 10^{-3} [\text{F}]^{0.555} [\text{O}_2]^{-1.481} [\text{Ar}]^{0.356} \exp\left(\frac{+17,798}{T}\right)$$

where the ignition delay (τ) is in μs and the concentrations in mol m^{-3} . The above equation is a typical result for a hydrocarbon fuel in that there is a positive dependence on the fuel and a larger negative dependence on oxygen. It was found to be a good predictor of the measured data, with the square of the multiple correlation coefficient, $R^2 = 0.96$.

William H. Green, MIT, USA. 1. It appears that you looked at each species and then guessed a few reactions which might be important then you estimated those rates, often by analogy to other similar reactions in the literature. This approach risks missing an important reaction—why did not you use automated reaction mechanism construction techniques to be more confident you considered all the important reactions?

2. Did you compute the T -dependence of all the reactions? If so, how did you compute the required $k(E)$'s?

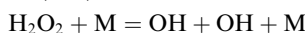
Reply. 1. Automatic mechanism generators for olefins were not freely available at the time when the di-isobutylene (DIB) mechanism was developed. Over the last 20 years, we have become intimately familiar with the types of reactions that occur for olefins and have developed reaction rate rules for each type. When we came across new reaction types in the case of DIB, we had to develop new reaction rate rules based on rate constants from the literature or from our own estimates. By performing computer simulations with the detailed mechanism, we were able to identify reaction paths that had been left out in the initial formation of the mechanism. In the future, as automatic mechanism generators become more available and improve, we expect to take advantage of their capability to identify reaction paths for newly considered fuel components.

2. No, we do not do this for all reactions. However, pressure-dependent rate constants for unimolecular decomposition reactions of the fuel are known to be important in accurately predicting ignition delay times. Thus, we have included a QRRK/Master equation analysis for this class/type of reaction as stated in the main text of our paper. In addition, fall-off is included in other important reactions of the sub-mechanism such as $\text{CH}_3 + \text{CH}_3 + \text{M} = \text{C}_2\text{H}_6 + \text{M}$, $\text{H}_2\text{O}_2 + \text{M} = \text{OH} + \text{OH} + \text{M}$, etc.

Magnus Sjoberg, Sandia National Laboratories, USA. Why is the ignition delay longer for $\Phi = 1$, compared to $\Phi = 0.5$? Is this the case also for temperatures relevant for HCCI engines (800–1100 K)?

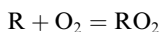
Reply. The experiments described in this paper were carried out in reflected shock waves, where the reaction temperatures were above 1200 K. In this high temperature range, the major chain branching reaction responsible for autoignition is the reaction of atomic H with molecular O_2 , and the radical pool available for fuel consumption is relatively insensitive to the equivalence ratio. This approximately constant radical pool takes a longer time to consume the larger amounts of fuel that are present as the equivalence ratio increases, leading to longer ignition times as equivalence ratio increases. This is a very familiar situation and has been observed in virtually all high temperature ignition studies.

At lower temperatures from about 800 to 900 K, the chain branching reactions involve species including alkyl radicals derived from the fuel itself, producing hydrogen peroxide, which leads to branching when the H_2O_2 decomposes, according roughly to the following sequence:



which converts one HO_2 radical into two OH radicals – a chain branching process. Under these conditions, the fuel molecule participates directly in the chain branching process, and therefore rich mixtures ignite more rapidly than lean mixtures.

At temperatures below about 800 K, the chain branching reactions involve the addition of alkyl radicals to molecular oxygen,



and subsequent RO_2 isomerization paths that lead to chain branching as discussed in the paper. As the fuel concentration is increased, more RO_2 results and more chain branching from the subsequent RO_2 isomerization paths. The combined chain branching paths occurring from about 650 to 900 K contribute to the experimentally observed behavior that the ignition delay time is reduced as the fuel/air equivalence ratio is increased. A more comprehensive description can be found in [1].

From your question, it is clear that your intuition is based on lower temperature autoignition phenomena where rich mixtures ignite fastest, while our high temperature study is characterized by a different chain branching mechanism where lean mixtures ignite fastest. The lower temperature range chain branching described here is predominant in HCCI ignitions, explaining why stoichiometric fuel/air mixtures generally ignite more rapidly than lean mixtures under HCCI conditions.

Reference

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