Preprint
UCRL-JC-143290

Detailed Chemical Kinetic Reaction Mechanisms for Combustion of Isomers of Heptane

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This article was submitted to
2nd Joint Meeting, US Sections of the Combustion Institute,
Oakland, CA, March 26-28, 2001

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

March 26, 2001

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This work was performed under the auspices of the United States Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

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Paper 233

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Abstract

Detailed chemical kinetic reaction mechanisms are developed for all nine chemical isomers of heptane (C_7H_{16}), following techniques and models developed previously for other smaller alkane hydrocarbon species. These reaction mechanisms are tested at high temperatures by computing shock tube ignition delay times and at lower temperatures by simulating ignition in a rapid compression machine. Although the corresponding experiments have not been reported in the literature for most of these isomers of heptane, intercomparisons between the computed results for these isomers and comparisons with available experimental results for other alkane fuels are used to validate the reaction mechanisms as much as possible. Differences in the overall reaction rates of these fuels are discussed in terms of differences in their molecular structure and the resulting variations in rates of important elementary reactions. Reaction mechanisms in this study are works in progress and the results reported here are subject to change, based on model improvements and corrections of errors not yet discovered.

INTRODUCTION

Kinetic modeling has steadily grown as a valuable technique for analysis of many types of combustion systems. This includes many well characterized laboratory experiments such as shock tubes, laminar premixed and diffusion flames, and various classes of static and flow reactors, including the rapid compression machine (RCM). Kinetic modeling is also used to study important types of practical combustion systems, including spark-ignition, diesel and homogeneous charge, compression ignition (HCCI) internal combustion engines, industrial burners, turbines, and many others. In addition to providing predictions and analysis of observable quantities in combustion systems, kinetic modeling can provide further details and insights that would be completely impossible to extract directly from the experimental results, and modeling can be used to extrapolate observed results into parameter regimes where experiments have not been carried out. Such “numerical experiments” can often be very valuable as a guide for future experiments.

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The central feature of a chemical kinetic model is the detailed chemical kinetic reaction mechanism, which describes the rates and reaction pathways of all of the elementary chemical reactions which are to be considered by the model. The mechanism includes the thermochemical data for the chemical species included in the model, including quantities such as specific heat, heat of formation, and equilibrium constants of formation.

We have been developing such reaction mechanisms for some time [1-6] and most recently for isomers of pentane [7] and hexane [8,9]. In addition, a thorough reaction mechanism was developed for n-heptane [10] which was significant because that fuel is a primary reference fuel (PRF) for measuring knocking tendency in spark-ignition engines [11] and is a convenient representative diesel fuel for studies of ignition in diesel engines [12-13].

Of particular interest is the role that the molecular size and structure of the hydrocarbon plays in determining its rate of combustion. We have shown how these variables influence the octane rating of different hydrocarbons [8,9,11] and the rate of ignition in the rapid compression machine [7,14]. In the present work, we further extend the range of structures and sizes of alkane fuels suitable for detailed kinetic studies by developing detailed kinetic mechanisms for the remaining 8 isomers of heptane. These isomers are shown schematically in Figure 1, together with the Research Octane Numbers (RON) for each isomer. The range in RON from 0 for n-heptane to 112 for 2,2,3-trimethyl butane is an important motivation for developing these mechanisms so that they can be used in further studies of knocking behavior in spark-ignited engines. Although not shown in Figure 1, the corresponding range in cetane numbers from 4 for 2,2,3-trimethyl butane to 56 for n-heptane suggests that these mechanisms could be useful in modeling studies of fuel-rich, premixed ignition in diesel engines [12,15]. These fuels can also be used in computational studies involving broad ranges of mixtures or blends of multicomponent fuels, leading to definition of realistic mixtures as computational surrogates for practical hydrocarbon fuels such as gasoline, diesel fuels, and aviation fuels.

Some interesting properties of these isomers, and the naming conventions to be used in text and figures below, in the same order as in Fig. 1, include:

Chemical Name	Short name	RON	MON	Cetane #
n-heptane	nC7	0	0	56
2-methyl hexane	2C7	42	46	38
3-methyl hexane	3C7	52	56	33
2,2-dimethyl pentane	22C7	93	96	13
3,3-dimethyl pentane	33C7	81	87	19
2,4-dimethyl pentane	24C7	83	84	18
2,3-dimethyl pentane	23C7	91	89	14
3-ethyl pentane	3ethC7	65	69	27
2,2,3-trimethyl butane	223C7	112	112	4

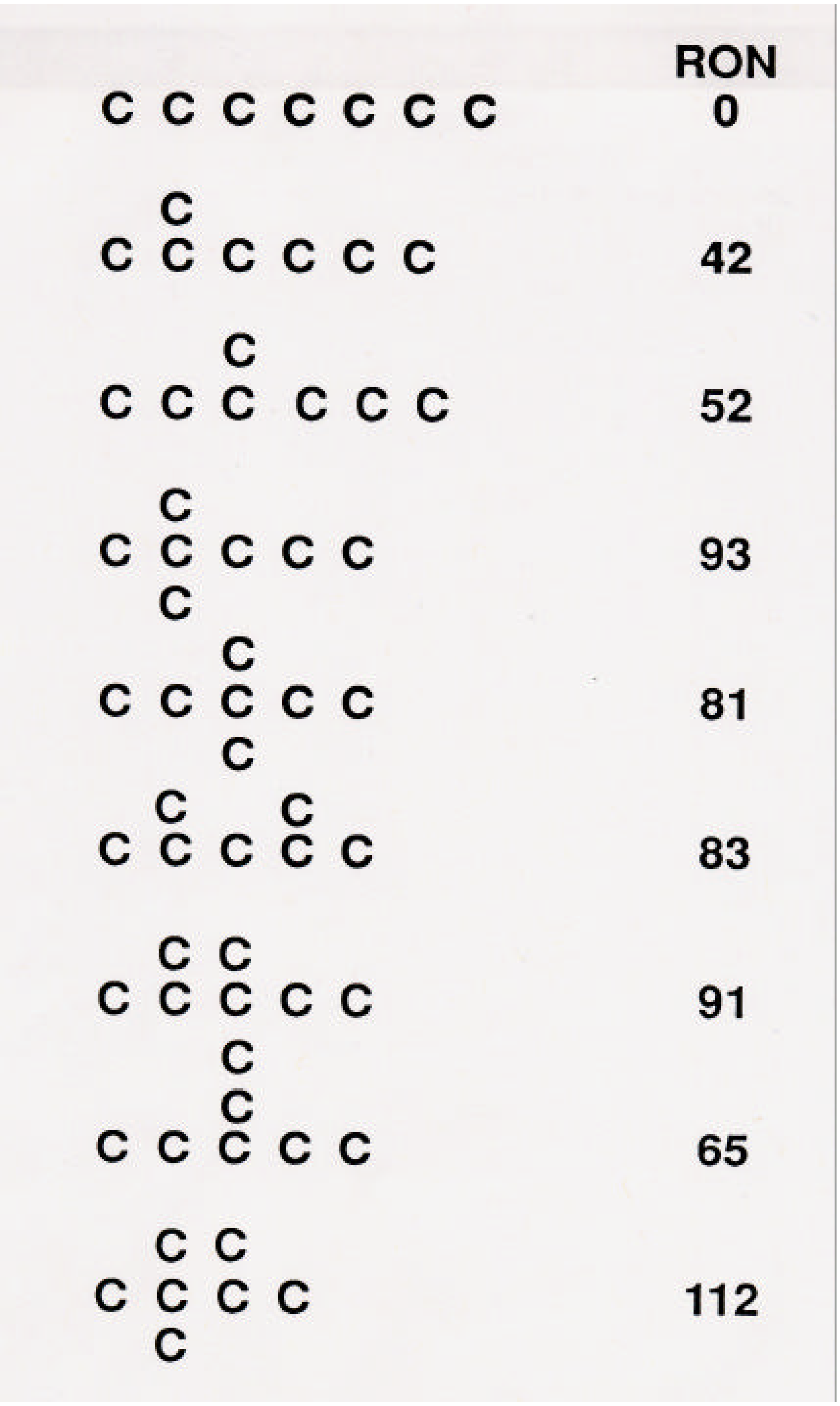


Figure 1. Schematic diagrams of isomeric heptanes

A relatively recent field of study in kinetic modeling has been that of automatic generation of detailed kinetic reaction mechanisms. Such techniques are particularly valuable when the hydrocarbon fuel is a relatively large molecule and the development of the mechanism by conventional means would represent a considerable investment in time and effort. These heptane isomer mechanisms should provide a valuable set of data that could be used to test the accuracy, strengths and weaknesses of techniques for automatic mechanism generation.

Another related field of considerable importance in combustion is that of automatic mechanism reduction. Since detailed kinetic reaction mechanisms can require enormous amounts of computer resources and very long computer running times, especially for large fuel molecules, detailed mechanisms can generally be included only in zero- and one-dimensional CFD models except for the very smallest fuel molecules such as hydrogen or methane. For use in multidimensional CFD models, it is essential that the chemistry submodel be simplified. However, it is also important that the reduction process preserve as much chemical detail as possible, especially if the usefulness of the overall model depends on reproducing those combustion features in which fuel molecule size and structure play important roles. The present family of heptane reaction mechanisms should therefore be valuable as a unique test bed for mechanism reduction studies.

MECHANISM CONSTRUCTION

Reaction mechanisms were derived for each isomer of heptane, following rules developed over the past several years. One principal group of reactions are H atom abstraction from the fuel, and the rates depend on the type of C-H bond being broken and the number of equivalent H atoms in the fuel. The rates for some of these reactions are summarized in the following table, showing values for H atom abstraction from primary, secondary and tertiary sites, per CH_3, CH_2 or CH group.

Radical	Primary			Secondary			Tertiary		
	log A	n	Ea	log A	n	Ea	log A	n	Ea
H	4.97	2.75	6280	6.11	2.40	4471	5.78	2.40	2583
OH	9.72	0.97	1590	7.67	1.61	-35	10.76	0.51	63
O	6.02	2.42	4766	5.77	2.44	2846	5.60	2.40	1150
CH_3	-0.34	3.65	7154	4.92	2.13	7574	-9.22	6.36	893
HO_2	12.92	0.00	20440	12.75	0.00	17690	12.45	0.00	16010

Other important groups of reactions involve isomerization of alkylperoxy and hydroperoxy-alkylperoxy radicals. Some elementary reactions are modeled in terms of other smaller reactions for which experimental data are available. Most of the rules for determining reaction pathways and rates are adopted from the work in reference [10], modified for each heptane isomer to account for the differences in molecular structure.

MECHANISM TESTING AND VALIDATION

These reaction mechanisms must be tested and improved through comparisons between computed results and experimental data. While careful, laboratory-scale experiments have not been carried out for most of these isomers, it is possible to relate computed results to computed and experimental results for fuels in cases for which experiments have in fact been done. In the present study, simulated shock tube ignition delays were chosen to test the mechanisms in the high temperature regime, and simulated rapid compression machine problems were chosen to study the low and intermediate temperature regimes.

Shock tube results

The experimental shock tube study of Burcat et al. [16] was selected for comparisons with computed results for heptane isomers. In the experimental study, stoichiometric mixtures of the n-alkanes methane, ethane, propane, n-butane and n-pentane in oxygen and argon were ignited over a broad range of initial temperatures above 1200K behind reflected shock waves. In contrast with most other shock tube studies, the amount of argon diluent mixed with the fuel and oxygen in the unreacted initial mixtures was chosen to approximate fuel/air amounts of total heat release, rather than being extremely diluted. Subsequent kinetic modeling analysis [17] of the same fuels demonstrated excellent agreement with the experimental results, showing that methane exhibited the slowest ignition among these fuels and ethane the most rapid. The other C_3 – C_5 n-alkanes ignited at very nearly the same rates over the entire temperature range studied. These experimental results are summarized in Figure 2, together with lines representing model calculations for the same fuels, with isobutane included as well.

These trends were interpreted in terms of two elementary reactions. Reaction (1) provides chain branching in the high temperature regime [18], consuming one H atom radical and producing two new radicals, O and OH

$$H + O_2 = O + OH \qquad (1)$$

while Reaction (2) consumes two methyl radicals and produces the stable ethane molecule, thus removing radicals from the reacting mixture and slowing the overall rate of reaction.

$$CH_3 + CH_3 = C_2H_6 \qquad (2)$$

H atom abstraction from alkane fuels produces alkyl radicals. Methane ignites slowly because the only possible alkyl radical, methyl, leads directly to Reaction (2) and chain termination. Ethane ignites most rapidly because the only alkyl

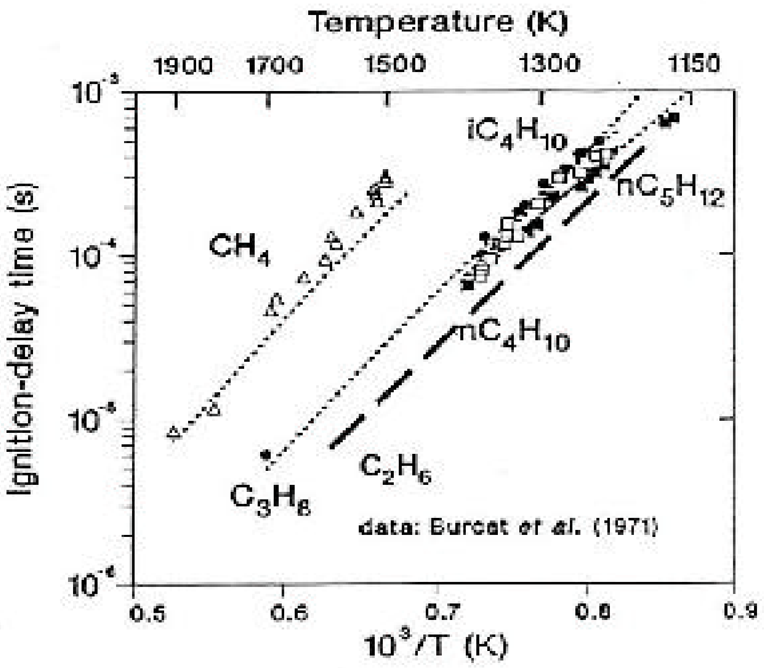


Figure 2. Shock tube ignition delay measurements for n-alkanes

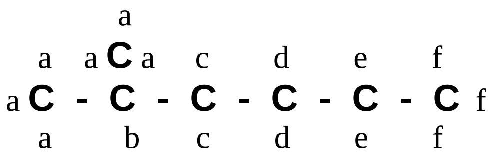
radical possible, ethyl, decomposes via Reaction (3)

$$C_2H_5 + M = C_2H_4 + H \qquad (3)$$

and the resulting H atoms provide chain branching through Reaction (1).

The fact that the larger n-alkanes ignite at approximately the same rate, intermediate between methane and ethane, can be attributed to the observation that for all of these larger fuels, more than one alkyl radical is produced from the fuel, and some of the possible alkyl radicals subsequently decompose to produce H atoms and kinetic chain branching from Reaction (1), while other possible alkyl radicals decompose to produce methyl radicals and chain termination from Reaction (2). The relative mixtures of these different alkyl radicals vary from one fuel to another, but the fact that they have mixed production of H atoms and methyl radicals is responsible for the very similar rates of ignition at high temperatures.

Each of the 9 heptane isomers produces mixtures of heptyl radicals, some of which produce H-atoms and some producing methyl radicals, and it would be expected that the high temperature ignition of these isomers would be rather similar to that of the $C_3 – C_5$ n-alkane fuels. To illustrate this point, 2-methyl hexane ($2C_7H_{16}$) can be written schematically, with lower case letters representing the 16 H atoms in this molecule. Structurally equivalent H atoms are noted by giving them the same lower case letters:



$$\begin{array}{ccccccccccccc} & & & a & & & & & & & & & \\ & a & & aCa & & c & & d & & e & & f & \\ a & C & - & C & - & C & - & C & - & C & - & C & f \\ & a & & b & & c & & d & & e & & f & \end{array}$$

If one of the ‘a’ H atoms is abstracted via a reaction

$$2C_7H_{16} + X = aC_7H_{15} + HX \qquad (4)$$

where X is the attacking radical species, and ‘aC_7H_{15}’ denotes the heptyl radical from this fuel with one of the ‘a’ H atoms removed, then the radical will decompose quite rapidly via ?-scission to produce small olefins and one H atom.

$$aC_7H_{15} \Rightarrow C_3H_6 + C_2H_4 + C_2H_4 + H \qquad (5)$$

In contrast, decomposition of the eC_7H_{15} radical under the same circumstances will lead to a similar set of small olefins but this time a methyl radical.

$$eC_7H_{15} \Rightarrow C_3H_6 + C_3H_6 + CH_3 \qquad (6)$$

In this sense, abstraction of the ‘a’ H atom will accelerate ignition at high temperature since it eventually produces H atoms to fuel Reaction (1), while abstraction of an ‘e’ H atom slows the rate of ignition because of Reaction (2). For $2C_7H_{16}$ a total of 11 of the H atom abstractions (sites ‘a’, ‘c’ and ‘f’) lead to H atom products while 5 abstractions (‘b’, ‘d’ and ‘e’) lead to methyl radicals. As a result, $2C_7H_{16}$ ignites quite rapidly in comparison to some of the other isomers which have smaller rates of H atom production from these channels.

To test this hypothesis, and to test the reaction mechanisms at high temperatures, each isomer was mixed with a stoichiometric amount of oxygen and diluted with enough argon to simulate the same “air-like” type of mixture as in the experiments of Burcat et al. Reflected shock wave simulations were carried out for initial post-shock temperatures between 1200K and 1400K. The results of these kinetic modeling calculations are summarized in Figure 3, together with fits to the comparable experimental results of Burcat et al. In Fig. 3, a single heavy line has been drawn that summarizes approximately the average of the propane, n-butane and n-pentane experimental results. From Fig. 3, it is nearly impossible to distinguish the computed results for most of the heptane isomers from the previous results for propane, n-butane and n-pentane. It is clear that the heptane isomers ignite at about the same rate as the $C_3 – C_5$ n-alkanes, consistent with the reasoning above in terms of Reactions (1) and (2).

There is a slight difference in overall activation energy for the n-alkanes as compared to the heptanes that needs further explanation, but the absolute values for ignition delay times are very similar. Within the group of heptane isomers, there is additional structure as seen in Figure 4 that further reinforces the analysis above in terms of production of H atoms and methyl radicals. The two slowest heptane isomers to ignite are 2,2-dimethyl pentane and 2,4-dimethyl pentane (22C7 and 24C7 in Figs. 3-4). Of the 16 H atoms in each of these 2 isomers, the alkyl radicals corresponding to abstraction of 14 of these 16 H atoms lead to CH_3 radicals and chain termination; none of the other 7 heptane isomers has more than 10 of its 16 alkyl radical decomposition paths that lead to chain termination. The unusually large fraction of heptyl radicals that produce methyl radicals results in the slow ignition of these two slowest fuels. However, the same analysis does not apply uniformly to the other isomers, and it is clear that this simplified analysis provides only approximate trends.

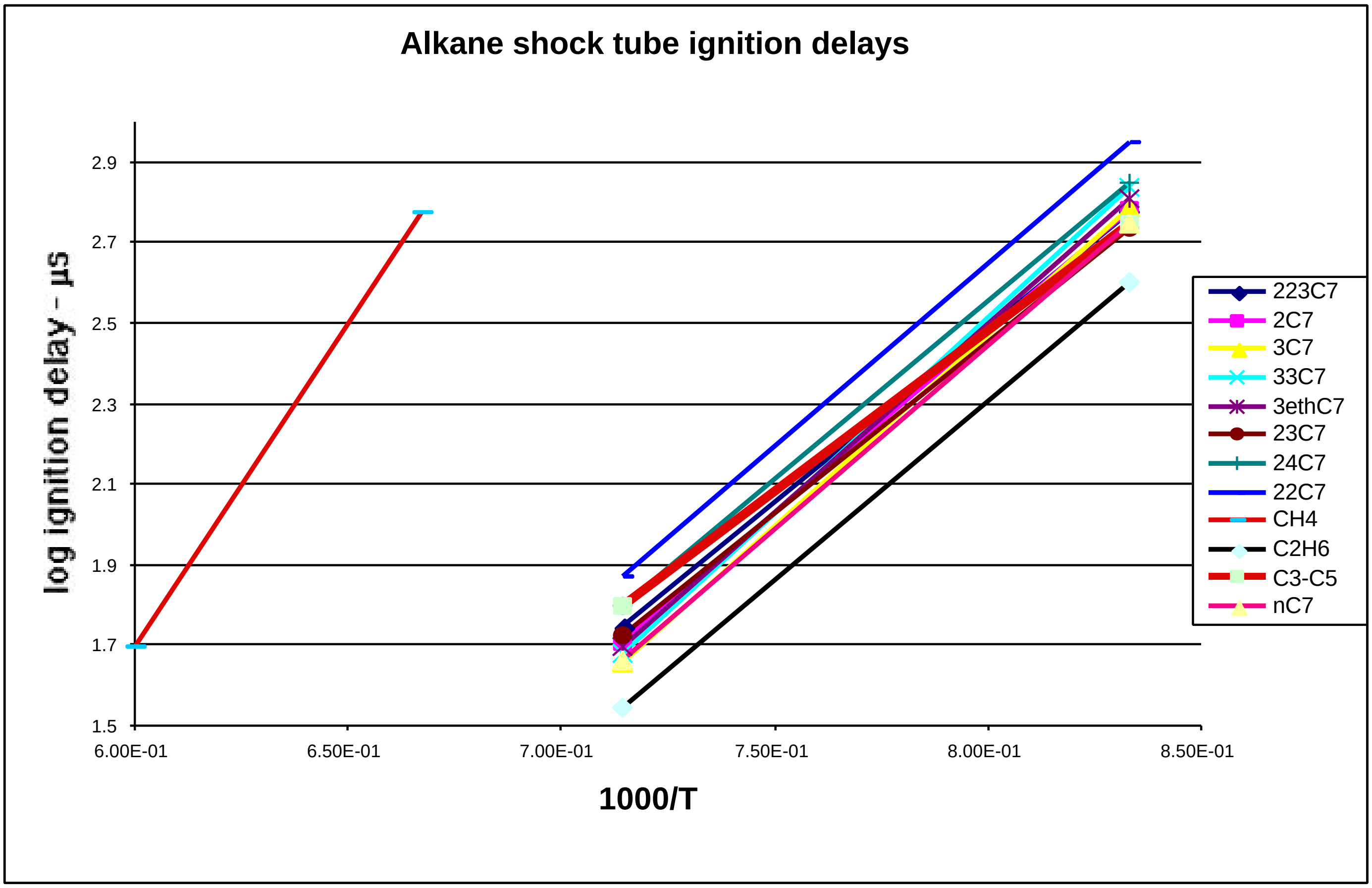


Figure 3. Computed shock tube ignition delay times for heptane isomers, in addition to values for methane, ethane and an average of propane, n-butane and n-pentane. Methane ignition is much slower than all the other fuels, and ethane is fastest to ignite.

For example, the isomer 2,2,3-trimethyl butane (223C7 in Figs. 3 and 4) has all but one of its 16 alkyl radicals lead to H atoms and chain branching, but it is not the fastest isomer to ignite. The isomers with the most rapid ignition at 1200K are 2,3-dimethyl pentane (23C7), while the fastest at 1400K is 3-methyl hexane (3C7), and n-heptane and 2-methyl hexane (2C7) ignite almost as rapidly, and all of these isomers have mixtures of alkyl radicals that produce approximately equal mixtures of H atoms and methyl radicals. The explanation for these computed results is not yet clear, but it is probably related to the relative reactivities of specific intermediate species which are produced prior to actual ignition, or there may still be some numerical errors in the reaction mechanisms that have not yet been found or corrected.

To summarize for the high temperature regime, the influence of molecular size and structure on ignition is relatively minor, and it is communicated primarily through the variations in production of high temperature chain branching H atoms.

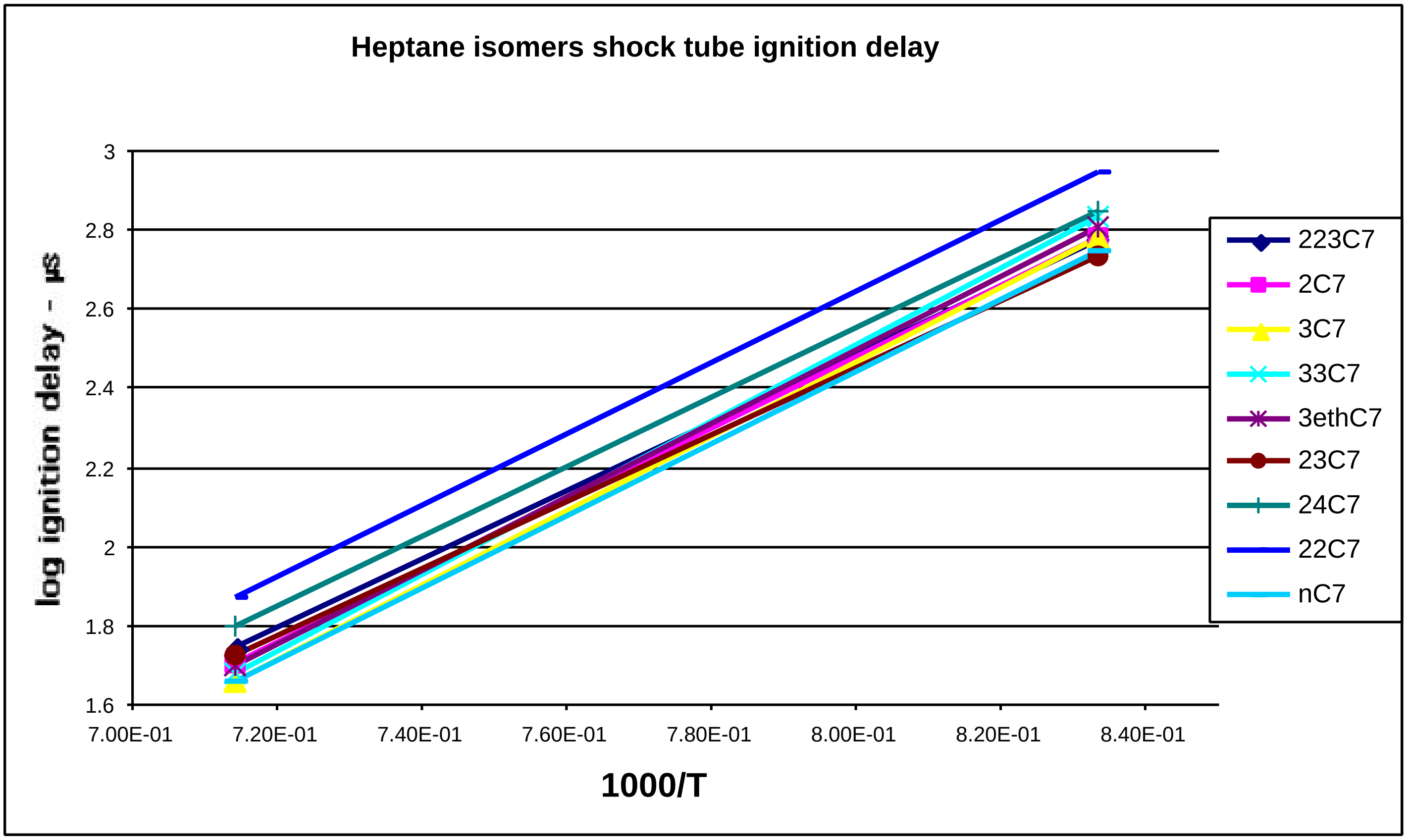


Figure 4. Computed shock tube ignition delay times for heptane isomers

Rapid compression machine results

Experiments of hydrocarbon ignition in rapid compression machines have been carried out for many years, and in recent years these experiments have been extremely useful in providing demanding tests of chemical kinetic reaction mechanisms [7,14]. Under the some conditions, the temperatures and pressures encountered at the end of the single compression stroke can result in complex, two stage ignition events. These temperatures are lower than those found in most shock tube experiments, and a completely different series of chemical reactions are responsible for this multistage ignition [18]. The overall reaction sequence, involving especially an alkylperoxy radical isomerization mechanism [19], is initiated by addition of molecular oxygen to alkyl radicals, reactions which depend sensitively on the gas temperature and to a lesser degree, on the type of radical site in the alkyl radical. Subsequent reactions of considerable importance include further addition of molecular oxygen to hydroperoxyalkyl radicals, further isomerizations, and decomposition reactions of ketohydroperoxide species. Numerical treatments of these reaction mechanisms, developed in recent years [6-10,20], have been able to describe many key features of these reactions.

The rapid compression machine, which produces ignition by heating a premixed fuel/oxidizer charge during a single compression stroke, is a convenient environment in which to study both engine knock in spark-ignition engines [11] as well as ignition in diesel engines [12]. The same experiments have also provided valuable insights into the fundamental features of a new process of homogeneous charge, compression ignition (HCCI) combustion [18,21-24]. In most of these systems in which ignition is approached from lower temperatures, ignition occurs at about 950 – 1000K, when H_2O_2 begins to decompose thermally at an appreciable rate [18]. The importance of the first stage ignition is that the amount of heat release that occurs during the first stage affects the time at which the system arrives at the H_2O_2 decomposition temperature. The present modeling project is intended to further refine the computational ability to predict the progress of the first stage ignition and thus describe subsequent full ignition in systems with practical hydrocarbon fuels.

The familiar two stage ignition sequence is shown in Figure 5, in which a stoichiometric mixture of 2,3-dimethyl pentane, diluted by a mixture of nitrogen and argon in order to achieve a temperature of 757K at the end of the compression stroke, is simulated. These are exactly the same post-compression conditions treated by Ribaucour et al. [7] for the three isomers of pentane in their rapid compression machine. The time scale is shown in seconds after the end of the compression stroke. The first stage reaction is predicted to occur at about 6 ms after the end of the stroke, with the final ignition predicted for slightly after 12 ms after the end of the stroke. The first stage ends at a temperature of approximately 900K; the amount of heat release during the first stage was found to depend on the type of $R + O_2$ addition reaction which is most important for a specific heptane isomer. For this fuel, 2,3-dimethyl pentane, the most significant RO_2 equilibrium is that of the two tertiary alkyl sites, which determines the value of 900K at which the RO_2 begins to decompose thermally. Results summarized below show that primary and secondary sites equilibrate at somewhat higher temperatures, so the amount of overall heat release varies with changes in molecular structure of the fuel.

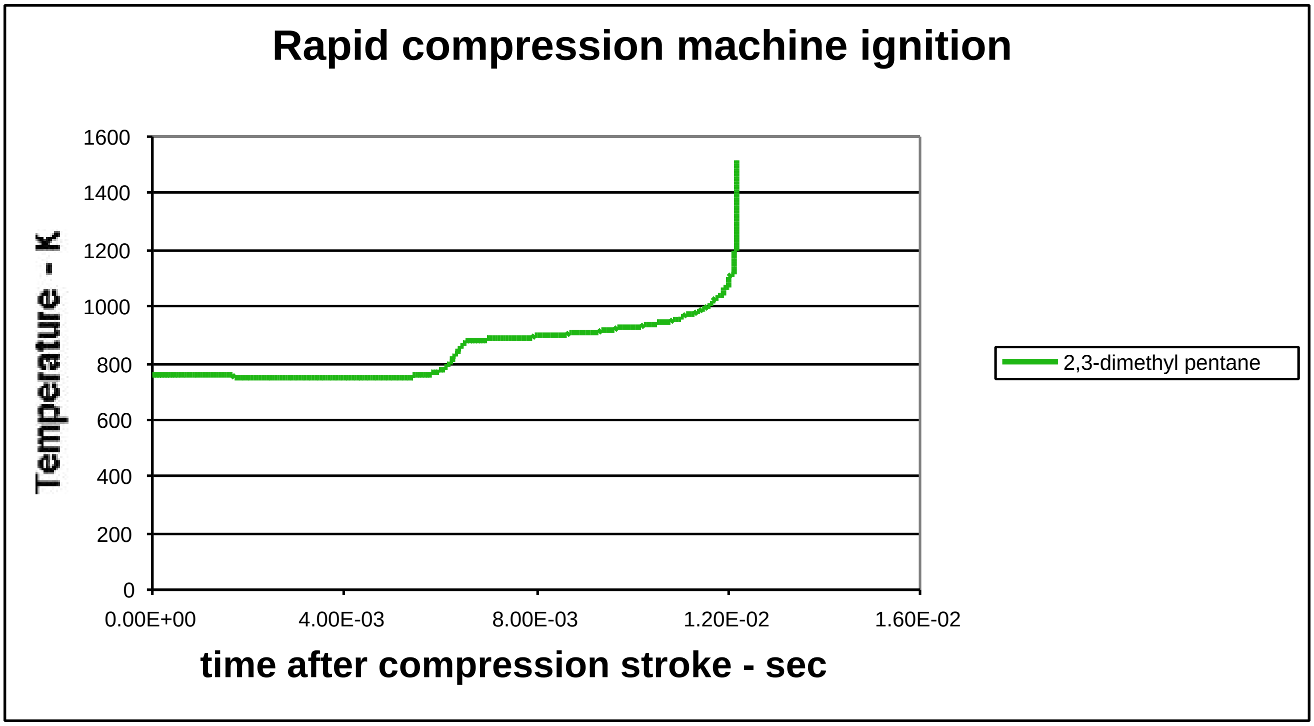


Figure 5. Computed ignition in a rapid compression machine

Ignition of the other isomers of heptane was then computed for exactly the same post-compression temperature and pressure as used above for Fig. 5 and for the pentane studies of Ribaucour et al. [7], with the computed results summarized in Figure 6.

There is a general trend in these results that the fuels with longer ignition delay times correspond roughly with higher octane numbers. The four longest ignition delays are for heptanes with RON values of 81, 112, 91 and 93. In addition, the earliest fuel to ignite in n-heptane, which has the smallest octane number of 0. However, the ignition delay variation in not monotonic with RON for all the isomers, and there is no obvious trend among the lower octane fuels. There are also apparent trends in the amount of heat release during the first stage of ignition, as already noted; however, the computed end of the first stage for 3,3-dimethyl pentane at about 825K appears anomalous and will be examined further.

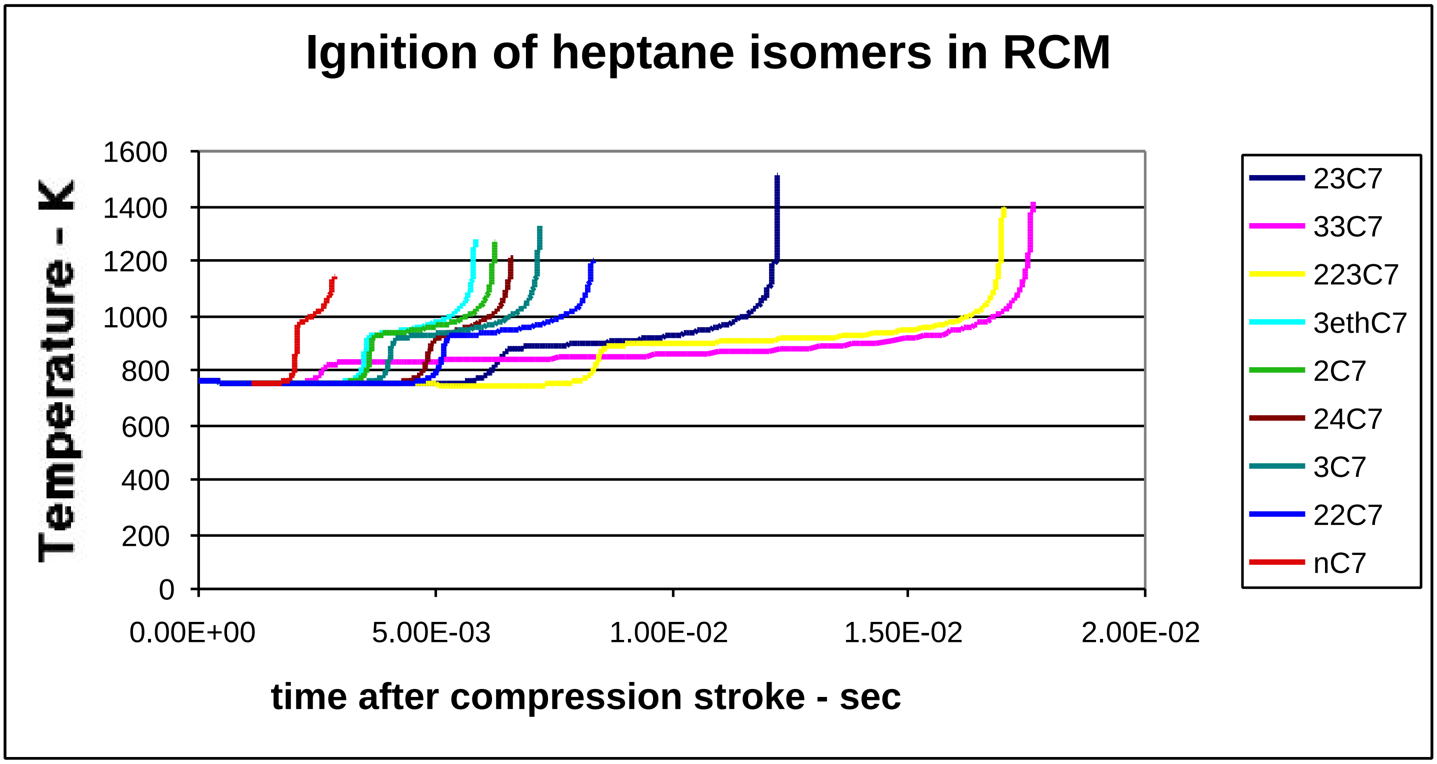


Figure 6. Ignition of heptane isomers in a simulated rapid compression machine

For the most part, those mixtures which exhibit the greatest amount of heat release during the first stage also reach the final ignition temperature earlier.
There is no particular reason to expect the ignition delay time observed in the rapid compression machine to correlate well with octane number, which is measured in a real engine under conditions with flame propagation and considerably higher heat transfer to the combustion chamber walls. However, with the present family of fuels, such a correlation might be expected to be approximately correct, and it is a challenge for this modeling effort to explain why the computed results behave in this way. As already noted above, these model results are quite preliminary and corrections of simple errors may improve the correlations. Those differences that remain may provide valuable insights into the kinetic differences in two different experimental configurations.

The influence of fuel molecular size and structure on ignition in this temperature range is quite complex, unlike the situation at higher temperatures. Previous work [8-11,19,20} has shown that structural factors affect the rates of oxygen addition to alkyl and hydroperoxyalkyl radicals as noted above, as well as alkylperoxy isomerization, and many other related steps, due to the influence of differing C-H bond energies, ring strain energies, and other factors. These factors play exactly the same roles in the present case of the heptane isomers, except that as the size of the fuel molecule increases to heptane, the variety and complexity of the possible reaction paths and structures continue to increase. The results summarized in Fig. 6 show that the more highly branched isomers are the slowest to ignite; this is consistent with the fact that these species contain a higher fraction of strong primary C - H bonds and that alkylperoxy and hydroperoxyalkylperoxy radical isomerization reaction pathways involve smaller ring-like transition states with higher activation energy barriers than the less branched isomers. These trends relating the relative ignition rates and knocking tendencies of long chain and highly branched fuels were recognized a long time ago [25] but the explanations in terms of elementary reaction pathways has been developed only recently. Future tests through careful experiments of these classes of problems will assess whether or not all of the important phenomena have been accurately and completely included in the present reaction mechanisms.

Further mechanism validations planned

The tests of these heptane isomer reaction mechanisms with shock tube and rapid compression machine ignition are not yet completed and work on them will continue until we are content that any simple, correctable errors in the mechanisms are eliminated. Current plans call for additional families of mechanism tests using laminar flame models and perhaps stirred reactor simulations for inclusion. In addition, we will compute critical compression ratio values to compare with other fuels in previous studies [8,9,11]. Computed results from these computations have been found to provide the best available correlations between computed results and octane numbers in spark-ignition gasoline engines. The range of octane numbers included in the isomeric heptanes will provide a particularly thorough test of the kinetic mechanisms and their variations with fuel molecular structure. Other experimental regimes and any actual experimental data available will be included as necessary to further test the reaction mechanisms and the underlying understanding of hydrocarbon oxidation kinetics.

CONCLUSIONS

The present paper is a first effort to extend current kinetic modeling capabilities to the level of heptane and its 9 isomers. This is done to focus greater attention on the ways that fuel molecular structure influence combustion properties in general and ignition particularly. The model provides estimates of ignition rates under shock tube and rapid compression machines, and there are further such tests in progress and which will be included as they are completed. There are a number of errors and inconsistencies that still remain in these detailed reaction mechanisms, and work is in progress to correct them. The most important trends expected for these fuels are already correctly reproduced by the reaction mechanisms, and it is expected that further mechanism refinement will improve that accuracy. Once completed, the present set of reaction mechanisms will provide a very useful computational tool for analysis of hydrocarbon oxidation and ignition in practical systems.

Very few of these isomers of heptane have received careful experimental attention in any of the types of experiments that provide results that depend on chemical kinetic factors. The exceptions are n-heptane, which has been studied in many relevant regimes, due in large measure to its importance as a reference fuel in automotive engines. The only type of experiment that has been carried out with suitable precision is the automotive octane rating test, and the results of such tests are readily available. Those tests are difficult to interpret and simulate, and the critical compression ratio tests noted above are convenient approximations to those octane tests. The availability of the present reaction mechanisms may prompt experiments in kinetic problems that can be used to further test and refine these reaction mechanisms.

ACKNOWLEDGMENTS

This work has been carried out under the auspices of the US Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48. This work was supported by the US Department of Energy, Office of Transportation Technologies, Steve Chalk and Gurpreet Singh, program managers, and by the Office of Basic Energy Sciences, Division of Chemical Sciences, William Kirchhoff, program manager.

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