

Multichannel Decomposition of Heptyl Radicals

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Abstract

This paper is concerned with the decomposition of heptyl radicals in high temperature combustion environments. Experimental results on the decomposition of n-heptyl iodide in single pulse shock tube studies will be presented. All the products resulting from the decomposition of the 4 heptyl radical isomers are found. This is indicative of the contributions from all possible isomerization and decomposition channels. Analysis of the data show that results are in the region where energy transfer effects must be considered. High pressure rate expressions for the isomerization and decomposition processes are derived. Results are projected to all temperature and pressures. The problems in describing rate constants in the Chemkin format are described.

Introduction

Linear alkanes are important ingredients of many liquid fuels [1]. The radical induced decomposition of such compounds involves the formation of primary and secondary radicals. An important complication is that these radicals not only decompose but can also isomerize. Competitive with these processes in oxidative systems are reactions with the oxygen molecule. In rich mixtures the yields of radicals and unsaturated compounds will ultimately lead to compounds that are the precursors to soot[2,3]. Of particular concern will be the branching ratios for the formation of the various unsaturates since the tendency to soot for unsaturated compounds are different.

The present work will focus on the heptyl radical. It is formed from radical attack on heptane or in the presence of larger alkanes from beta bond fission of a larger radical. Heptane is a reference fuel for determination of a fuel's tendency to knock. It is a liquid fuel and can undergo many of the same type of reactions as larger alkanes. Heptane represents a model fuel for the alkane component of practical fuels. There are many databases that have been used successfully for simulating the behavior of the oxidation of heptane[4-6]. In practically all of these databases the description of the cracking process that is of key importance for describing soot formation from real fuels is not satisfactory. This is due to the lack of experimental data for the type of reactions to be considered here. Approximations and lumpings that may well not be justified are necessary. This is an important impetus for the present work. This paper will begin with a description of the experimental work used to determine the branching ratios for the formation of the 1-olefinic products from the decomposition of the heptyl radicals. We will then

describe the procedure used to derive high pressure rate expressions. We then use these high pressure rate expressions to project results over all relevant temperature and pressures. This will demonstrate some of the numerical problems that arise in trying to fit the present results into a format that is compatible with Chemkin[7].

There have not been any previous work on the decomposition of heptyl radicals. We have previously determined in experiments very similar to these the rate constants for the decomposition and isomerization of pentyl [8] and hexyl [9] radicals. We were not able to analyze the data in the manner carried out here. It is now clear that strictly speaking, such data is only valid in the range of conditions where the experimental data was obtained. We have now developed a program[10] that can be used to extend the range of validity over all relevant temperature and pressure ranges.

The need for a formalism to extend the range of the experimental measurement is due to the possibility of contributions from energy exchange effects [11]. This is brought about by a combination of low reaction thresholds and the size of the molecule. This leads not only to pressure effects for the individual isomerization and decomposition rate constants, but also to cases where the rate constants are varying with time.

Experimental Procedure

Experiments are carried out in a single pulse shock tube[12]. Figure 1 is a schematic of the equipment. For present purposes it is essentially a pulse reactor. The test gas is heated by the reflected shock wave to the 900-1000 K range and a pressure of 4 bar pressure. With hydrogen as the driver gas a quench wave is generated by

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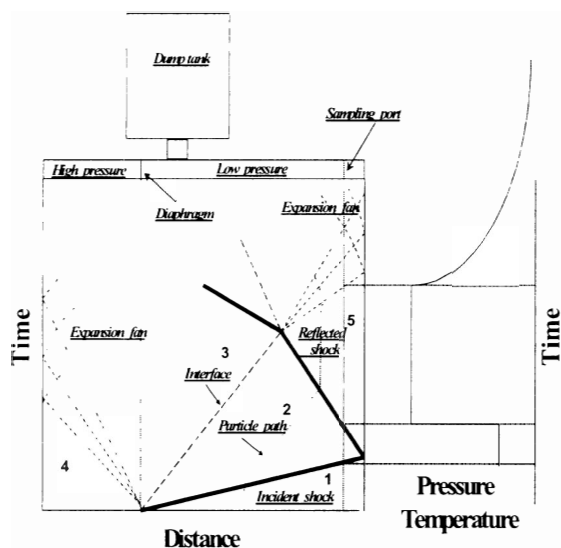


Figure 1: Single pulse shock tube, wave diagram and pressure-temperature and time history.

the interaction of the shock wave and driver-driven gas interface. With the geometry and the composition used in the present study, the consequence is a heating pulse of 500 μ sec. Subsequently the sample is extracted from the shock tube and subject to analysis using gas chromatography with flame ionization detection. With a sample size of the order of 10 cm³ this means that the lower detection limits are in the ppb range.

Of key importance is the preparation of the heptyl radicals. Since it is an unstable species, it must be prepared in situ. For this purpose n-heptyl iodide is an ideal precursor. The weakness of the C-I bond ensures that this will be the predominating bond breaking reaction. 1-Heptyl radical will be released into the system. The 1-heptyl radical can now isomerize or decompose. Isomerizations will lead to the formation of the three other heptyl radicals. The latter can also decompose. The isomerizations are reversible. The overall situation is quite complex and the key issue is how to interpret results in terms of the individual processes that are the essence of programs such as Chemkin [7]. The general mechanism is illustrated in Figure 2. It can be seen that there are four isomerization processes and five decomposition reactions. The isomerization reactions involve the shifting of hydrogen from the 1 to 2, 1 to 3, 1 to 4 and 2 to 3 positions through 7, 6 and 5 member transition states. The decomposition reactions involve beta C-C bond scission. There is also a direct 1-2 direct elimination of hydrogen iodide leading to the formation of 1-heptene. The latter cannot be formed from the decomposition of the heptyl radicals through C-C bond fission. It plays no part in the analysis of the results.

Since heptyl radicals are released into the system, it is essential that they or their products be prevented from reacting with the precursor or other radicals that are in the system. This is achieved by adding

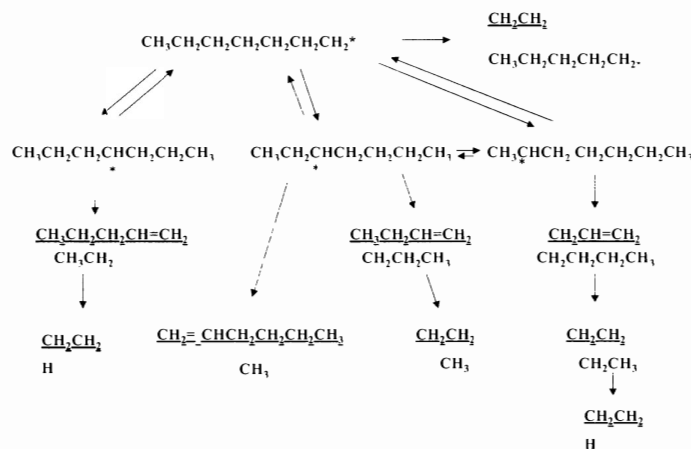


Figure 2: Mechanism for the reactions of the four possible heptyl radical isomers in single pulse shock tube experiments

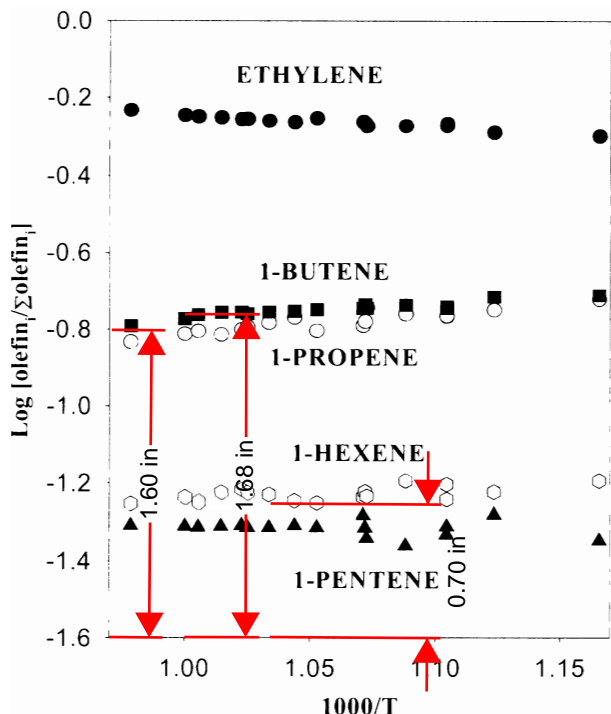


Figure 3: Product distribution from the decomposition of heptyl radicals from *n*-heptyl iodide pyrolysis

excesses of a radical scavenger[12]. In the present study mesitylene (1,3,5 trimethylbenzene) serves this role. Its reactions with active radicals lead to the creation of benzyl type radicals. The benzyl resonance energy adds an extra degree of stability to this radical. As a result, rate constants for its attack on the precursor are too small to induce reaction. When this is coupled with the extremely short lifetimes of alkyl radicals in the present environment, quantitative conversion of the heptyl radicals by unimolecular decompositions are the only possible processes. For our purposes this means that upon the release 1-heptyl radical, their isomerization and decomposition will lead to the formation of the C₂ to C₆ 1-olefins. These are the products detected during the study and the ratios of the products and can be used to deduce the branching ratios for the decomposition of 1-heptyl. However the quantitative conversion of ethyl may not be completely achieved at the lowest temperatures. This will cause problems in the interpretation of the results and discussed subsequently.

Experimental Results

Products from the decomposition of *n*-heptyl

iodides are all the expected 1-olefins. A summary of the results can be found in Figure 3. We have excluded 1-heptene from the analysis. As explained earlier, this can only be due to a direct hydrogen iodide elimination channel. Results are expressed in terms of the ratio of a particular olefin and the sum of all the olefins. These results can be compared with the postulated mechanism in Figure 3. It is clear the upon the cleavage of the C-I bond and the release of the 1-heptyl radical into the system beta bond cleavage is sufficiently slow so that isomerization to all the other radicals can occur. These can then in turn undergo beta bond cleavage producing the other olefins.

There are two channels for the decomposition of 3-heptyl. One of the channels involve the ejection of methyl while for the other, a *n*-propyl group is expelled. From Figure 3 it can be seen that the yields of 1-hexene is considerably smaller than those of 1-butene. This is a clear demonstration of the effect of alkyl substitution at the site of the bond being broken. It is very similar to the situation for the decomposition of 3-hexyl radical [9]. Indeed, the magnitude of the difference of about a factor of 3 is very similar to those for methyl substitution on alkanes. This is very interesting in view of the tremendous difference between the activation energies for bond breaking in alkanes and beta bond fission in alkyl radicals. For the present analysis this is useful in developing a set of rate parameters for beta bond cleavage for the decomposition of the heptyl radicals.

We assume that the experimental results summarized in Figure 3 are independent of pressure. This is based on results for the decomposition of pentyl and hexyl radicals. This does not mean that there are no energy transfer effects. As will be shown subsequently there are pressure dependences for the individual reactions. However by focussing on ratios there is a great deal of cancellation of such effects.

Analysis of Data

This section will be divided into three parts. The first will involve the conversion of the results in Figure 3 to branching ratios for the decomposition from the various heptyl radicals. We then use this result to derive a set of high pressure rate expressions on the basis of the mechanism specified in Figure 2. The third will be concerned with projecting results over all relevant pressure and temperature ranges.

A: Conversion of Results to Branching Ratios

The results summarized in Figure 3 can now be converted to branching ratios for the various precursors.

Table 1. High pressure rate expressions and constant ratios for the decomposition of heptyl radicals. $k=AT^n \exp(-E/T)$

Reactions:	A	N	E/T	k/k _∞ for reactions at 1 bar and various temperatures with 1-heptyl as reactant				
				700	800	900	1000	1150
k1: C7H15-1 ----> C2H4 + nC5H11	11.07	0.614	13358	-17	-.34	-.60	-.85	-.89
k2: C7H15-2 ----> C3H6 + nC4H9	11.94	0.431	13702	.21	.15	.06	-.12	-.10
k3: C7H15-3 ----> 1-C4H8 + nC3H7	11.91	0.434	13674	.16	.06	-.06	-.26	-.24
k4: C7H15-3 ----> CH3 + 1-C6H12	11.94	0.44	14748	.17	.04	-.11	-.33	-.32
k5: C7H15-4 ----> 1-C5H10 + C2H5	11.35	0.68	13397	.35	.22	.08	-.13	-.13
k6: C7H15-2 <---> C7H15-1	2.721	2.429	8599.3	.12	.13	.10	-.01	0
k7: C7H15-3 <---> C7H15-1	3.647	2.362	8862.6	.10	.07	.01	-.12	-.12
k8: C7H15-4 <---> C7H15-1	5.805	1.961	12509.7	.36	.22	.07	-.15	-.16
k9: C7H15-2 <---> C7H15-3	5.291	2.117	10854.8	.17	.15	-.35	-.07	-.07
k10: C7H15-1 <---> C7H15-2	3.473	2.205	7185.3	-.05	-.20	-.35	-.50	-.47
k11: C7H15-1 <---> C7H15-3	4.26	2.211	7504.9	-.07	-.25	-.40	-.56	-.54
k12: C7H15-1 <---> C7H15-4	6.592	1.734	11136.3	-.13	-.37	-.59	-.82	-.79
k13: C7H15-3 <---> C7H15-2	5.438	2.042	10841.2	.15	.11	.01	-.16	-.15

We have mentioned that the hexene-1 and butene-1 must have originated from the 3-heptyl radical. The pentene-1 is from 4-heptyl. Propene can be formed from either 2-heptyl or 1-heptyl. Ethylene is a special case. It can be formed from all four isomers. Furthermore more than one ethylene can be formed from a particular isomer. The precursors of ethylene are either n-propyl and ethyl radicals. Unfortunately, for the present purposes it is necessary to assume that the ethyl radical in this system is also quantitatively decomposed to form ethylene and a hydrogen atom. However the activation energy for beta C-H bond scission is about 40 kJ/mol larger than that for C-C bond cleavage. Thus lifetimes are estimated to be of the order of 100 μsecs at the lower temperature limit of these experiments. At the highest temperatures the lifetimes will be about 10 μsecs. With a 500 μsecs residence time it is probably only at the highest temperatures that complete conversions occur. In the present analysis it is necessary to successively subtract the ethylene from all the other sources in order to obtain the contribution of the channel involving three ethylene formation from 1-heptyl decomposition. At the highest temperature this is only about 15% of the total ethylene. Since three ethylenes are formed when 1-heptyl radical is decomposed by successive C-C bond cleavages it can be seen that the contribution from this channel is not large and therefore does not effect the contributions from 3 and 4 heptyls greatly. We have previously found that ratio of rate constants for the decomposition of 1-pentyl to 2 ethylene and 1-pentyl to ethylene and propene as $8.5 \exp(-2821/T)$. Then the total contribution from 1-heptyl decomposition includes a component that is larger than that from successive C-C bond cleavage. Furthermore by assignment of the propene yield from this component will also reduce the contribution of 2-heptyl radical decomposition to the propene formed. The consequence is

that the branching ratio for the 4 heptyl isomers at the highest temperatures are 175:221:495:112 for 1-heptyl: 2-heptyl: 3-heptyl: 4-heptyl. This ordering is compatible with the importance of 1-5 hydrogen shift. Furthermore 1-6 hydrogen shift appears to be more important than 1-4 hydrogen shift. Note that our results for the former is a maximum number.

B. High pressure rate expressions

The results summarized in Figure 3 represent a direct measure of the branching ratios for olefin production for 1-heptyl radical decomposition under the conditions of these experiments. There is however sufficient data to obtain information on the branching ratios for the decomposition of the other isomeric heptyls. It is also desirable to deduce information over extended and pressure ranges. For this purposes it is essential to compile a set of high pressure rate expressions compatible with the present measurements.

The estimation procedure involves the solution of the master equation to determine energy effects and requires data on the molecular and thermodynamic properties of the molecules and transitions states. Our approach was to first derive the properties of heptane. The tabulated values are all based on group additivity and is not sufficient for the present purposes. The procedure follows the prescription of Pitzer [13] on the additional vibrational frequencies needed when a methylene group is inserted into the next smaller alkane. The rotational constant for heptane was derived assuming a zigzag structure. We then make small adjustment in the vibrational frequencies of the heptane to bring the thermodynamic properties in line with the tabulated results[14]. For the radical we follow the procedure

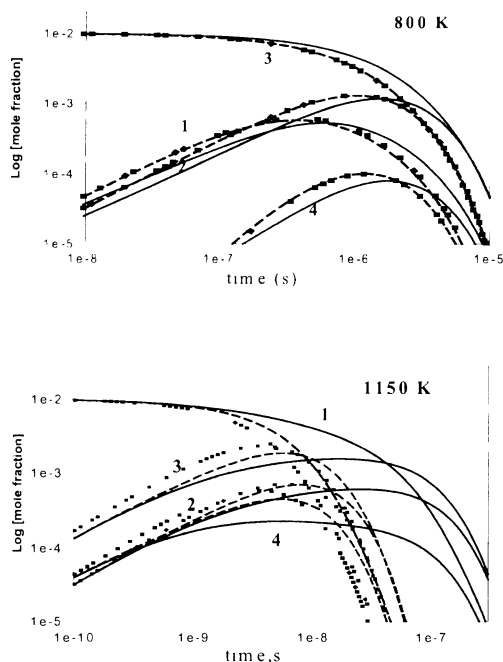


Figure 4: Temporal behavior of heptyl radicals at 800K for 3-heptyl and 1150 K for 1-heptyl. The numbers refer to the specific isomer. Solid line is for 1 bar, dashed line for 100 bar and dotted line for infinite pressure.

outlined by Benson[15]. This involves removing the vibrational modes associated with the appropriate hydrogen atom and treating the alkyl group(s) adjacent to the radical site as free rotors instead of the hindered rotors in the molecule. The heat of formation of the radicals are based on C-H bond strengths of 410 kJ/mol for a secondary C-H bond and 417 kJ/mol[16] for a primary C-H bond.

From the data in Figure 3, it is possible to derive five rate expressions for the branching ratios. This is not sufficient to determine the set of 9 high pressure rate expressions. We have therefore made assumptions regarding the beta bond scission reactions and then derived the isomerization rate constants. The present work is therefore based on a combination of published rate expressions for the decomposition of n-propyl and s-butyl radicals[17] and the observed effect of alkyl substitution on the site for beta bond cleavage. The isomerization rate expressions are then determined iteratively using as a guide the branching ratios from Figure 3 (at the highest temperatures), the differences in A-factors from PM-3 calculations [18] and from the solution of the master equation with a step size down of 500 cm^{-1} . Results can be found in Table 1. Also included

are k/k_{∞} values for the situation where 1-heptyl radical is the initial reactant. Note that for some of the isomerization products the k/k_{∞} ratio is actually greater than 1. This is because during isomerization, the higher energy levels are first populated. Our results show that in our temperature range energy transfer effects are quite important and lifetimes of the heptyl radicals are about a factor of 3 to 5 larger than the high pressure lifetimes. A serious consequence of the present work is that the k/k_{∞} ratio will vary with the starting isomer. Forward and reverse isomerization reactions are no longer related by the equilibrium constant.

C: Rate Expressions over Extended Temperature and Pressure Regimes:

With the high pressure rate expressions given in Table 3 and assuming the same 500 cm^{-1} step size down parameter for energy transfer on the basis of an exponential down model we can now project results over all temperature and pressure ranges. The basic procedure is the same as that used in converting the experimental shock tube results to high pressure rate expressions except that the iterative procedure used earlier is no longer required and the solution of the master equation immediately produce results such as found in Figure 4.

Our results show that for 1 bar pressures the system follow high pressure behavior up to temperatures of 650 K. As the temperature is increased, the reactions from the isomerization products exhibit an initial rate constant that is higher than the high pressure value and relaxes much slower than that for the initial reactant. Nevertheless the time scales is sufficiently long so that one approaches steady state behavior and it is possible to represent reactions in terms of rate constants. However as the temperature is increased to higher than 1000 K, conversions in the induction region becomes increasingly important. Although at first it is still possible to describe reactions in terms of an average rate constant, we find that as the temperature is increased it becomes increasingly difficult to represent temporal curves of the type in Figure 4 in terms of constant rate constants.

This raises the issue of how to represent rate constants of the single step process so that the temporal behavior of the system can be reproduced. It is clear that it will not be possible to represent energy transfer effects in the manner currently prescribed in Chemkin. This has been developed for single step reactions and is not applicable for this type of system. We do not believe that it will be possible to develop a similar type of elegant solution that covers rate constants over all pressure conditions. Particularly serious is the situation where rate constants are not constant. It will be necessary to develop isobaric rate expressions and to truncate the temperatures into a number of appropriate regions.

Although it becomes impossible to describe reactions in terms of single rate constants at temperatures above 1200K, the instability of the heptyl radicals makes unnecessary the exact value of the rate constants. What is required is the branching ratio for the production of the various products. As noted earlier the competitive reaction with radical decomposition is the attack of oxygen molecules on the radicals. An appropriate rate constant for such a process is $10^{12}\text{cm}^3\text{mol}^{-1}$. For a stoichiometric mixture this leads to a lifetime of 1 μsec or rate constant of 10^9s^{-1} . Thus at temperatures above 1000 K decomposition will dominate. This means that only the branching ratios will be of interest. This can be easily obtained from our calculations. We have also found that a very good approximation to the actual situation is obtained from the high pressure rate expression. The advantage of using the branching ratio is that it will no longer be necessary to include the heptyl radical in the system. Another interesting observation is that except for the 1-heptyl, isomerization processes for the other radicals are relatively unimportant.

Concluding Remarks

We have described experimental and calculational efforts at determining the fate of heptyl radicals in high temperature combustion environments. The general procedures are applicable to larger linear alkyl radicals. The determination of the quantitative details of the cracking of these compounds are of key importance for the development of databases for the simulation of the behavior of real fuels [19] in real systems. The new databases will admittedly be very large. They do however provide a proper basis for the powerful tools for mechanism reduction and the equally exciting new developments in CFD codes that can take increasingly large quantities of chemistry.

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