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Multichannel decomposition and isomerization of octyl radicals

Wing Tsang*, W. Sean McGivern, Jeffrey A. Manion

National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

Abstract

The thermal cracking patterns from the decomposition and isomerization of octyl-1 radicals have been determined from the pyrolysis of *n*-octyl iodide in single pulse shock tube experiments at temperatures in the 850–1000 K range and pressures near 2 bar. Rate constants for the six beta bond scission and five of the six isomerization processes have been derived over all combustion conditions [0.1–100 bar, 700–1900 K]. Comparisons are made with previous studies on the decomposition of other primary radicals. Results are consistent with similar types of reactions having equal rate constants. The larger size of the octyl radicals makes contributions from secondary to secondary radical isomerization increasingly important. The results confirm that the 1–3 H-transfer process (involving a seven member cyclic transition state) have rate constants that are within a factor of 2 of those for the 1–4 process (six member cyclic transition state) It appears that rate constants for 1–2 H-transfer isomerization, involving an eight member cyclic transition state is unimportant in comparison to contributions from other isomerization processes. The strain energy does not appear to play an important role for these larger transition states. The implications of these results to larger fuel radicals will be discussed.

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Keywords: Octyl; Unimolecular; Decomposition; Isomerization; Pyrolysis

1. Introduction

The improving capability of computational fluid dynamics codes has made possible computer simulation of the combustion of real fuels in real devices [1,2]. This paper is part of a project aimed at developing the chemical kinetic databases necessary to support this effort. The elements of this database are the rate constants of single step reactions that describe the transformation of fuel molecules across the whole range of stoichiometries. Focus of the present work is on the reactions in-

involved in pyrolytic processes. These reactions represent an integral part of any *complete* combustion kinetics database. They can be competitive with oxidation processes and hence extend the range of current combustion models to richer mixtures. They lead to the formation of small unsaturated compounds that are the precursors to PAH (polynuclear aromatic hydrocarbon)/soot and are necessary for relating particle formation to fuel composition.

Normal alkanes are important components of real fuel mixtures [3]. The abstraction of a hydrogen atom from these molecules leads to the formation of primary and secondary alkyl radicals. The aim of this work is to discover the general rules that govern the quantitative details of their

* Corresponding author. Fax: +1 301 975 3670.
E-mail address: Wing.tsang@nist.gov (W. Tsang).

unimolecular decomposition and isomerization processes in combustion environments. Previous studies have covered normal pentyl [4], hexyl [5] and heptyl [6] radicals. Cracking patterns and thermal rate constants have been derived. The current work is concerned with the corresponding reactions of the next compound in this series, octyl radicals. It represents an extension of unimolecular rate theory to larger molecules with low reaction thresholds and is absolutely *vital for the quantitative understanding of the combustion of realistic fuels*.

Real fuels are complex mixtures of hydrocarbons. Without specification of the chemical nature of the fuel, it is not possible to carry out the type of molecule based simulations that are important elements in modern combustion research. In order to simplify the experimental problem and provide a basis for comparisons, there has been much progress in selecting a small number of fuel compounds that can serve as surrogates [7] for real fuel mixtures. The necessity of using mixtures of varying compositions, depending on the application, means that a fundamental approach is desirable. Most of the earlier databases [8–10] have focused on single molecule fuels and require adjustments of the rate constants to fit experimental targets. A kinetics database for fuel mixtures cannot be constructed by simply agglomerating all the rate constants derived from combustion studies involving single fuel molecules. A more fundamental approach has the advantage that the mixing rules in terms of the rate expressions for fundamental single step thermal reactions are transparent and may be the most efficient procedure.

2. Background

During the pyrolytic breakdown of any large fuel radical smaller fragments are formed. Thus for any normal alkyl radical, the reactions

Alkyl Radical (n carbon atoms)

= 1-olefin + smaller alkyl-1 radical

× (at most $n-2$ carbon atoms)

lead to the necessity of specifying the rate constants for the pyrolytic breakdown of the smaller radicals. Note the special role of 1-olefins and alkyl-1 radicals. For a homologous class of molecules an examination of the literature shows that rate parameters for many reactions are related [11]. This is largely due to the localized nature of the transition states for many types of reactions. The aim of this work is to discover these relationships for the reactions of interest. This will lead to the possibility of accurate predictions of the rate constants for larger and more realistic fuel molecules. There are a number of unique features in

the reactivity of the radicals being considered. Their relatively large size means that there are a multiplicity of reaction channels, including both isomerizations and beta bond scissions. All of these processes have low reaction thresholds. These situations are rarely considered in standard texts. These unique problems have now been satisfactorily solved and are discussed in previous reports [4–6].

The earlier studies [4–6] are based on the combination of experimental work in a single pulse shock tube and available literature results. These have demonstrated the consistency of the experimental results with the assumption that after methyl high pressure rate expressions for beta bond scissions is independent of the size of the linear alkyl radical being ejected. This is expected since C–H bond strengths are known to be invariant with substitution in the beta position [11,13]. The increase in the size of the fuel radical leads to the possibility of contributions from isomerization channels that are not possible in smaller fuel molecules. For the five to seven carbon radicals it appears that the H-transfer isomerization processes involving five and six cyclic carbon structures have rate constants that are specific for a particular process and independent of adjacent alkyl groupings. The difference in rate constants suggests the importance of strain energy and the role of the ring size for the transition state on A-factors. In the heptyl case results have also been obtained for H-transfer isomerization involving a seven member transition state. (1–6 hydrogen transfer) From measured yields of the associated marker olefin for this process (propene), the contribution from hydrogen transfer appear to be surprisingly large. One might have expected that in the seven member transition state the ring strain (similar to that for the 1–4 process) and loss of entropy associated with the larger ring would make such processes much less important than hydrogen transfer involving six member transition states. However, the increasing length of the fuel molecules leads to the possibility of hydrogen migration from secondary sites. Thus the concentration of a particular olefin can be due to the contribution from two or more isomerization processes. Although our estimates are based on reasonable assumptions, this adds a degree of uncertainty to the results. Results from this study should clarify this issue. Previous data involving H-transfer isomerizations through 5 and 6 centered transition states via primary to secondary radicals have been summarized in an earlier paper [5]. Dobe et al. [12] have studied secondary to secondary radical isomerization involving 2-octyl radicals.

An important problem in the older literature data on H-transfer isomerization has been the extremely low A-factors and activation energies from the low reaction temperature studies [12].

Such parameters make it impossible to derive reasonable traditional transition state structures. We have attributed this to tunneling [5] and used in the present work for the construction of the transition states. They lead to highly curved Arrhenius plots.

Larger alkyl iodides have been used as radical precursors. Advantage is taken of the low strength of the C–I bond. Their cleavage releases the relevant radicals into the shock heated system. By setting concentrations so that the radical can only undergo unimolecular decomposition and isomerization, it is possible to obtain a thermal cracking pattern. This thermal cracking pattern together with existing data is used to deduce the high pressure rate expressions for all the possible unimolecular processes. Although the thermal cracking results do not show a pressure dependence, solution of the master equation taking into account literature values of the step size down parameter demonstrate that the experiments are in the region where $k/k_\infty = 0.3\text{--}0.5$. The lack of pressure dependence in the thermal cracking patterns is because all the reactions are in the fall-off region. The actual values are somewhat different (see Table 2) but they are not sufficient to permit the deduction of pressure effects. The high pressure rate expressions can then be used again through master equation modeling to deduce rate constants under all relevant combustion conditions. This is in the 0.1–100 bar pressure and 600–1900 K temperature range. The departures from high pressure behavior can be more than a factor of 10 at sufficiently high temperatures. It is expected that these pressure effects will decrease with molecular size. It will then be possible to describe the reactions in the traditional Arrhenius form. This will represent a great simplification and is helpful for treatment of truly large fuel molecules. Up to heptyl this decrease appears to be very slow. The present work will extend results to cover the larger octyl radicals.

There is very little experience in the determination of rate constants or expressions for multi-channel reactions through thermal cracking patterns. The values of the experimental olefin cracking patterns (ratio of one olefin to all the olefins) are extremely accurate. It is estimated that the uncertainties in the relative concentrations will not exceed 5%. *Such results cannot be obtained by any estimation or calculational approaches. The rate expressions presented here represent the best possible fit of the data.* They are however actually relative values and to a large extent depend on the values for beta bond scission.

The rate expressions are the direct inputs for simulations. However, for high temperature only, the short lifetimes of the alkyl radical means that the relative concentration of the olefins can be directly used and radical concentrations can be ignored. Rate expressions are useful for lower

temperature simulations and as a basis for estimation in related molecules. An accurate branching ratio from the shock tube experiments facilitates correct extrapolations even if there are considerable uncertainties in the actual rate expressions.

Another rationale for treating the pyrolytic decompositions in a rigorous fashion is to set the base for studying oxidation processes. These reactions are responsible for ignition behavior. It is obvious that mechanistically the C, H system is much simpler than the C, H, O system. Thus a thorough understanding of the behavior of the former is a prerequisite for the proper description of the latter. There is almost no experimentally clean determination of rate constants for the various stages of the oxidation process. This will be the subject for subsequent work.

3. Experimental

Pyrolytic studies using a single pulse shock tube is a well established technique [13]. Details have been described in earlier publications and various review articles. Normal octyl iodide is the source for the alkyl radical in this study. The thermal decomposition of alkyl iodides can also involve a direct 1,2 elimination of hydrogen iodide. This produces a 1-olefin with the same number of carbons as the radical itself. This 1-olefin is not formed by any of the decomposition reactions of interest and can be ignored for present purposes.

The mixture used in the present study is 180 ppm ($\mu\text{l/l}$) 1-iodooctane, 100 ppm chlorocyclopentane and 1% 1,3,5-trimethylbenzene (mesitylene) in argon. The concentrations are such that the octyl radicals released into the system can only undergo unimolecular isomerization and decomposition. This is due to a combination of short residence time (500 μs) and the instability of the radicals (lifetimes of the order of μs or less). Any active radical such as methyl or H atom will preferentially react with the mesitylene forming a benzyl type radical. Benzyl radicals, with a resonance stabilized structure cannot attack any of the species in the several hundred ppm range in the time scale of these experiments. Indeed, the only process they can undergo is combination with other radical species in the system and thus adding to the inhibitory power of mesitylene. The prevention of radical chain process in these experiments means that it is possible to study simultaneously several unimolecular reactions in the same shock tube experiment. This is the basis of the comparative rate technique. A reaction, preferably one that leads to stable products and whose rate expression is well established, is carried out simultaneously with the target process. It must experience the same temperature as the other

process and serves as an internal temperature standard. The reaction selected as the standard is the dehydrochlorination reaction of cyclopentyl chloride [14]. The rate expression is

$$k(c - C_5H_9Cl = c - C_5H_8 + HCl) = 3 \times 10^{13} \exp(-24220/T) s^{-1}.$$

This can then be converted to the reaction temperature through the relation

$$1/T = [\ln(\ln(1 - \text{fractional conversion})/3 \times 10^{13} \times t)] / -24220,$$

where the fractional conversion is derived from the conversion to cyclopentene from cyclopentyl chloride, t is the residence time and has been found to be 500 μ s for the present geometry. Cyclopentene is not a decomposition product of the n -alkyl radicals. There is no possibility of interferences. Actually, the cracking patterns have only very small dependence on temperature. An exact value of the reaction temperature is not absolutely necessary.

Analysis was by gas chromatography with flame ionization detection. A 30 m \times 0.53 mm Rtx-524 column (from Restek)[15] for the heavy compounds (greater than C5), and a 1 m HayesSep S in series with a 1 m HayesSep Q micropacked columns (1/16" diam). Temperature program was 40–225 $^{\circ}$ C (no cryo). The n -octyl iodide, cyclopentyl chloride and mesitylene were from Aldrich and used without further purification. The argon was from Matheson and has stated purity of 99.9999%. Gas chromatographic analysis did not reveal the presence of any interfering impurities.

4. Results

The mechanism for the unimolecular reactions of octyl radicals under shock tube conditions is summarized in Fig. 1. The multichannel nature of the reaction makes this a complicated process. There are four isomeric octyl radicals that can undergo six beta bond fission reactions and six reversible H-transfer isomerization processes. A summary of the specific reactions can be found in Table 1. All the normal C₁ to C₆ alkyl radicals are formed. The mechanism of decomposition for 1-propyl and 1-butyl is straightforward (beta bond scission and no isomerization). Analysis of the data begins with the rate expressions derived in earlier studies on the three smaller fuel radicals. Within the experimental uncertainties, the rate constants are virtually identical for the same type of process.

For beta bond scissions octyl-1 and octyl-2 have only one reaction channel. Octyl-3 and octyl-4 can lose alkyl radicals from both sides of the radical site. For isomerization, four of the processes involve exothermic transfer of H-atoms

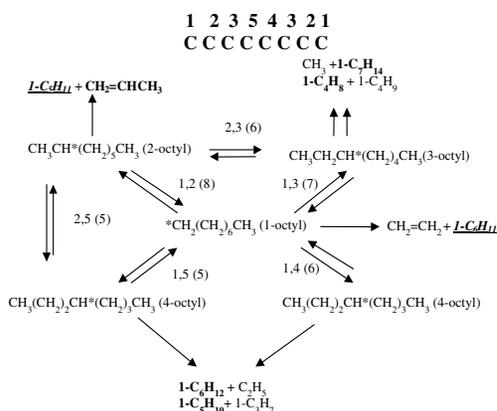


Fig. 1. Mechanism for octyl radical decomposition and isomerization. The arrows pointing in opposite directions refer to isomerization processes. The numbers are the type of H-transfer processes. The arrows in one direction are for beta bond scission processes. The two parallel arrows are for the two channel processes. The numbers in the parenthesis refer to the size of the cyclic transition state. The numbers at the top of the figure and the carbons represent the standard convention used in the paper. The bold letters refer to the olefins that are detected. The italicized underlined radicals indicate compounds whose olefinic decomposition products are deduced from earlier studies.

from the 1 to 5(5), 4(6), 3(7) and 2(8) positions. The numbers in the parenthesis refer to the size of the cyclic transition states and the labeling of positions is defined in Fig. 1. The other two processes are thermally neutral conversions of secondary radicals and involve five and six member ring transition states. Serial isomerizations are added complications. When they make contributions, results on some of these processes can only be obtained from information on isomerizations involving H-transfers from secondary to secondary radicals.

The experimental branching ratio for olefin yields are summarized in Fig. 2. All the expected 1-olefins are found. This is a demonstration of the importance of isomerization in the decomposition of these large radicals. If isomerization were unimportant, the only product would be ethylene from successive beta bond scissions. Ethylene is the main product. It is formed from many of the possible reaction channels and does not yield unique mechanistic information. The larger 1-olefins can be uniquely matched with particular radical precursors. 1-Heptene and methyl can only originate from octyl-3. From the other side of the radical site, beta bond scission will lead to the formation of 1-butene and butyl-1. Beta scissions from octyl-4 leads to the production of 1-hexene and ethyl and 1-pentene and n -propyl. 1-Hexene and 1-pentene are present in equal amount. This is consistent with a mechanism where the rate of C–C bond scission increases when changing from a methyl to an ethyl group,

Table 1
Fundamental kinetic [A] and thermodynamic [B] properties of octyl radicals

	A: Reaction	Log A	<i>n</i>	<i>E/R</i>	Log (<i>k</i> [1000])
1	1-octyl = ethene + 1-hexyl	11.96	.31	13708	6.93
2	2-octyl = propene + 1-pentyl	10.78	.84	14001	7.24
3	3-octyl = 1-butene + 1-butyl	13.31	.04	14340	7.21
4	3-octyl = 1-heptene + methyl	9.98	1.08	14790	6.78
5	4-octyl = 1-pentene + 1-propyl	11.74	.55	14134	7.26
6	4-octyl = 1-hexene + ethyl	9.83	1.11	13600	7.25
7	1-octyl = 4-octyl (1-4-H trans)	.71	3.23	8479	6.72
8	1-octyl = 4-octyl (1-5-Htrans)	1.36	2.82	5413	7.46
9	1-octyl = 3-octyl	.47	3.08	5544	7.29
10	4-octyl = 1 octyl 1-4-H trans	−.38	3.57	9532	6.20
11	4-octyl = 1-octyl 1-5-H trans	.27	3.16	6466	6.94
12	3-octyl = 1-octyl	.52	3.11	6579	6.99
13	2-octyl = 3-octyl	.27	3.27	6642	7.20
14	2-octyl = 4-octyl	.15	3.32	8125	6.60
15	3-octyl = 2-octyl	1.33	2.96	6625	7.34
16	4-octyl = 2-octyl	.071	3.32	8128	6.52

Compound B	Equilibrium constant of formation log [<i>k_p</i>]
Octyl-1	$-38.931 - 1.031 \times 10^3/T + 4.904 \times 10^6/T^2 - 2.601 \times 10^9/T^3 + 4.473 \times 10^{11}/T^4$
Octyl-2	$-39.196 - 1.941 \times 10^2/T + 4.736 \times 10^6/T^2 - 2.554 \times 10^9/T^3 + 4.403 \times 10^{11}/T^4$
Octyl-3	$-39.098 - 5.633 \times 10^2/T + 4.912 \times 10^6/T^2 - 2.608 \times 10^9/T^3 + 4.485 \times 10^{11}/T^4$
Octyl-4	$-39.109 - 2.265 \times 10^2/T + 4.780 \times 10^6/T^2 - 2.577 \times 10^9/T^3 + 4.468 \times 10^{11}/T^4$

The rate parameters (limiting high pressure values) are derived so that they give the fit to the data in Fig. 2. The number of places of the values are not significant. The two reactions involving 1-7 H-transfer are not listed since as mentioned in the text the experiments are not sensitive to their contributions.

but the change from ethyl to propyl has negligible effect. 1-Butene is formed not only from the decomposition of octyl-3 but also from the decomposition of hexyl-1 formed through beta bond scission of octyl-1. This accounts for the ratio of 1-butene to 1-heptene of four in comparison to a factor of 3.4 for similar reactions with 3-hexyl and 3-heptyl.

5. Discussion

From the data in Fig. 2, rate constants for the processes listed on Table 1 will be assigned. To

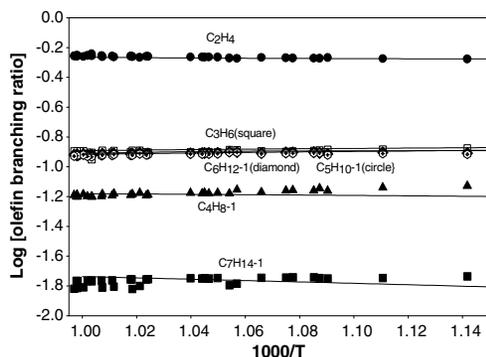


Fig. 2. Branching ratios for olefin production from single pulse shock tube experiments. The lines represent the fit of the results based on rate constants in Table 1.

this end we carry out a master equation – RRKM analysis. It is necessary to assign values for the molecular properties of the four alkyl radicals and the transition states. This treatment attempts to be consistent with the values for stable compounds in the API Tables [16]. We follow the observation of Pitzer [17] on the additional vibrational frequencies needed upon insertion of a methylene group into a linear hydrocarbon molecule. We then adjust the low frequency modes so that the thermodynamic properties are the same as those given in the standard tables [16]. Radical properties are derived on the basis of the prescription of Benson [18]. Vibrational frequencies associated with the hydrogen motion (at the radical site) are eliminated and the hindered rotors adjacent to the radical site are converted into free rotors. The resulting properties of the four octyl isomers can be found in the Supplementary material. Table 2 contains a tabulation of their equilibrium constants of formation in polynomial form. The transition states were defined so that the desired rate expressions were reproduced.

There are two internal isomerization processes. They involve 2,5 (5) and 2,3(6) H-atom transfers or the reverse. As before it was assumed that the rate constants for these thermally neutral processes roughly intermediate between those for the exothermic 1–4 (5) and 1–5(6) and reverse endothermic processes. The former is particularly important since they couple the radical that is formed by 1–4 (6) transfer, the most favored isom-

Table 2
Departure from high pressure behavior for unimolecular processes from the pyrolysis of 1-octyl radical

Temp	pressure bar	Reactions (log [k_∞/k])															
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
600	0.1	0.14	0.07	0.08	0.10	0.09	0.09	0.09	0.05	0.04	0.01	0.03	0.02	-0.01	0.01	0.01	0.03
	1.0	0.03	0.01	0.02	0.01	0.01	0.02	0.03	0.03	0.02	0.00	0.01	0.01	-0.02	0.00	0.00	0.01
	10.0	0.01	0.00	0.01	0.00	0.00	0.01	0.02	0.03	0.01	0.00	0.00	0.01	-0.02	0.00	0.00	0.00
	100.0	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.03	0.01	0.00	0.00	0.01	-0.02	0.00	0.00	0.00
700	0.1	0.43	0.22	0.24	0.30	0.28	0.28	0.28	0.15	0.17	0.07	0.13	0.07	0.08	0.08	0.07	0.10
	1.0	0.13	0.05	0.06	0.07	0.07	0.08	0.09	0.05	0.06	0.02	0.03	0.02	0.03	0.02	0.02	0.01
	10.0	0.02	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.03	0.00	0.00	0.01	0.02	0.00	0.00	-0.01
	100.0	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.00	0.00	0.01	0.02	0.00	0.00	-0.01
800	0.1	0.76	0.46	0.50	0.60	0.56	0.55	0.56	0.34	0.35	0.21	0.31	0.20	0.19	0.23	0.19	0.26
	1.0	0.32	0.15	0.16	0.20	0.20	0.20	0.25	0.16	0.15	0.07	0.10	0.06	0.06	0.07	0.06	0.07
	10.0	0.08	0.03	0.03	0.04	0.04	0.05	0.08	0.06	0.05	0.01	0.02	0.01	0.03	0.01	0.01	-0.01
	100.0	0.01	0.00	0.01	0.00	0.00	0.01	0.04	0.04	0.03	0.00	0.00	0.01	0.02	0.00	0.00	-0.03
900	0.1	0.99	0.74	0.77	0.91	0.84	0.84	0.77	0.49	0.50	0.38	0.54	0.36	0.35	0.43	0.36	0.48
	1.0	0.52	0.30	0.33	0.40	0.38	0.38	0.42	0.26	0.27	0.16	0.22	0.15	0.14	0.17	0.14	0.20
	10.0	0.17	0.07	0.08	0.10	0.11	0.11	0.15	0.10	0.10	0.04	0.05	0.04	0.04	0.04	0.03	0.03
	100.0	0.03	0.01	0.01	0.01	0.02	0.02	0.05	0.04	0.03	0.01	0.01	0.01	0.02	0.00	0.01	-0.02
1000	0.1	1.09	0.98	0.98	1.14	1.07	1.07	0.89	0.59	0.61	0.55	0.76	0.53	0.52	0.63	0.52	0.69
	1.0	0.67	0.49	0.51	0.60	0.57	0.58	0.55	0.36	0.37	0.28	0.38	0.26	0.25	0.30	0.26	0.35
	10.0	0.28	0.16	0.17	0.21	0.21	0.21	0.24	0.16	0.16	0.10	0.12	0.09	0.08	0.09	0.08	0.11
	100.0	0.06	0.03	0.03	0.04	0.04	0.05	0.07	0.05	0.05	0.02	0.02	0.02	0.03	0.01	0.02	0.00
1200	0.1	1.05	1.25	1.19	1.35	1.31	1.33	0.89	0.62	0.67	0.81	1.02	0.76	0.79	0.92	0.75	1.00
	1.0	0.79	0.79	0.78	0.90	0.86	0.88	0.65	0.43	0.48	0.51	0.63	0.49	0.48	0.57	0.48	0.65
	10.0	0.46	0.37	0.38	0.45	0.44	0.45	0.37	0.24	0.27	0.26	0.30	0.23	0.22	0.26	0.23	0.33
	100.0	0.16	0.10	0.11	0.14	0.14	0.15	0.12	0.07	0.10	0.08	0.08	0.07	0.07	0.07	0.07	0.11
1400	0.1	0.89	1.29	1.19	1.32	1.32	1.34	0.80	0.59	0.63	0.91	1.03	0.86	0.91	1.04	0.84	1.09
	1.0	0.75	0.93	0.88	1.00	0.98	1.00	0.66	0.47	0.51	0.66	0.74	0.62	0.64	0.73	0.61	0.79
	10.0	0.53	0.54	0.54	0.63	0.61	0.62	0.46	0.32	0.35	0.40	0.45	0.37	0.37	0.42	0.36	0.49
	100.0	0.27	0.21	0.23	0.27	0.27	0.28	0.22	0.15	0.17	0.17	0.18	0.15	0.14	0.16	0.15	0.21
1600	0.1	0.73	1.17	1.06	1.17	1.19	1.20	0.68	0.52	0.55	0.89	0.89	0.83	0.90	1.00	0.81	1.03
	1.0	0.66	0.92	0.87	0.97	0.96	0.97	0.61	0.46	0.49	0.70	0.72	0.66	0.69	0.77	0.65	0.81
	10.0	0.53	0.63	0.61	0.70	0.68	0.69	0.49	0.36	0.38	0.48	0.51	0.46	0.46	0.51	0.45	0.57
	100.0	0.33	0.31	0.33	0.38	0.37	0.38	0.30	0.22	0.24	0.26	0.27	0.24	0.23	0.25	0.23	0.31
1900	0.1	0.52	0.86	0.79	0.87	0.87	0.89	0.49	0.38	0.40	0.71	0.63	0.66	0.71	0.76	0.65	0.78
	1.0	0.50	0.75	0.72	0.79	0.78	0.80	0.47	0.36	0.38	0.62	0.57	0.59	0.61	0.67	0.58	0.69
	10.0	0.45	0.60	0.59	0.66	0.64	0.65	0.43	0.32	0.34	0.50	0.48	0.48	0.48	0.52	0.47	0.55
	100.0	0.35	0.39	0.39	0.45	0.43	0.44	0.32	0.24	0.25	0.33	0.33	0.32	0.30	0.33	0.31	0.37

The numbers for reactions are those in Table 1.

erization process with the radicals formed as a consequence of 1–6 (7) and 1–7 (8) H-transfer. It can serve as means of forming octyl-2 and 3. This involves a five member transition state and has rate constants that are much smaller than those involving six member transition states. When this rate constant is made larger in order to match the yields from octyl-3, the yield of propene from octyl-2 increases to such an extent that it becomes impossible to reproduce the experimental results. It is clear that rate constant for H-transfer isomerization involving seven member transition states must be larger than would be predicted on the basis of the trends observed in going from the five to six center transition state processes. The rate constant from the heptyl radical system involving the seven member transition state is completely compatible with this results. Another consequence is that propene formation is dominated by hexyl-1 radical decomposition and isomerization from octyl-3. As a result it is not possible to include a rate constant or expression for the 1–7 (8) process. Hence no rate expression for the two processes are listed in Table 1.

The values for the rate parameters in Table 1 are not as accurate in an absolute sense as the number of places suggest. They are the values at the reaction temperatures that give the fit of the data in Fig. 2. On an absolute basis we estimate uncertainties in the rate constants of a factor of 1.5, a factor of 2.5 in the A-factor and and 5 kJ/mol in the activation energy. To some extent, the experimental measurements are really a determination of relative rates. Simply using the uncertainty estimates given here in a random manner will not reproduce the measured branching ratio. The first priority should be to fit the experimental observations. When this is accomplished extrapolations using the given rate expressions can withstand considerable errors.

The experimental study of Dobe et al. [12] near room temperature on octyl radical is consistent with this for the six-center transition state situation but leads to rate constants that are much too large for the five center transition state. It is difficult to believe that the thermally neutral process could have rate constants that are substantially larger than those for the exothermic reaction.

The data in Table 1 lead to high pressure rate constants that favor isomerization processes at low temperatures and beta bond fission at high temperatures. The shock tube experiments are in the temperature range where both processes contribute. Having derived high pressure rate expressions from the experimental measurements, it is possible to reverse the process and derive rate constants for all combustion conditions. The range covered is from 0.1–100 bar and 500–1900 K. The departures from high pressure values are expressed as $\log [k_{\infty}/k]$ and for the 1-octyl radical

are summarized in Table 2. The step size down values in wave numbers $0.3 \times T$ [19] where T the temperature, is the same as that used in the previous studies[5,6]. Similar tables for the other three octyl radicals can be found in the [supplementary material](#). In the fall-off region the departures from high pressure values are different for each isomer since the distribution functions for each of the isomers are different. We present results in tabular form since the usual formats are not applicable for the present application.

A comparison of the results for the rate constants of decomposition for 1-alkyl radicals containing 4–8 carbon atoms can be found in Fig. 3. They show the expected decrease in pressure dependence with molecular size. However this decrease is slow and for 1-octyl the maximum decrease of rate constants with pressure is about a factor of five and presumably cannot be ignored. The slowness of the decrease in pressure dependence is due to the opening of more reaction channels with increasing molecular size. It is not clear when a fuel radical will be of sufficient size such that pressure effects can be ignored. From the data summarized in Table 2, the shape of the fall-off curve can vary depending on the nature of the process. Generally, the isomerization processes have a smaller pressure dependence. This is consistent with the smaller A-factors for such processes. Attention is also called to the shape of the curves in Fig. 3. As a function of temperature, the values reach a maximum and then begin a slow decline. This is a direct consequence of the low threshold and large size of the molecule. From the data in Table 2 it can be seen that at 100 bar the departure from high pressure values is less than a factor of 2 for beta bond scission.

6. Summary and conclusions

Thermal cracking patterns from the decomposition of 1-octyl radicals have been determined.

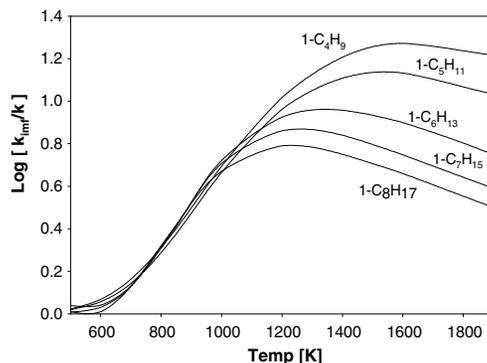


Fig. 3. Deviation from high pressure behavior for the decomposition of 1-alkyl radicals to form ethylene and corresponding radical.

Rate constants required to fit the results are virtually identical with earlier values for pentyl [4], hexyl [5] and heptyl [6] radicals. The results confirm the earlier observation for heptyl radicals that H-transfer isomerization involving a seven member transition state have rate constants within a factor of two of those involving the six member transition state. Contributions from processes involving an eight member transition state are obscured by competitive isomerization processes. It may be possible to ignore larger ring H-transfer transition states for larger hydrocarbons. The experimental results do not provide any information on the rates of such processes. These results provide a basis for predicting the cracking patterns of larger linear alkanes. The decrease in energy transfer effects with molecular size is small and therefore cannot be neglected for larger fuel molecules in the 1–10 bar region.

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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.2008.05.048](https://doi.org/10.1016/j.proci.2008.05.048).

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