Decomposition and Isomerization of 5-Methylhex-1-yl Radical

Iftikhar A. Awan, W. Sean McGivern, Wing Tsang, and Jeffrey A. Manion*

National Institute of Standards and Technology, Chemical and Biochemical Reference Data, Gaithersburg, Maryland 20899-8320

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The decomposition and isomerization reactions of the 5-methylhex-1-yl radical (1-5MeH) have been studied at temperatures of 889-1064 K and pressures of 1.6-2.2 bar using the single pulse shock tube technique. The radical of interest was generated by shock heating dilute mixtures of 5-methylhexyl iodide to break the weak C-I bond, and the kinetics and reaction mechanism deduced on the basis of the olefin cracking pattern observed by gas chromatographic analysis of the products. In order of decreasing molar yields, alkene products from 1-5MeH decomposition are ethene, isobutene, propene, 3-methylbut-1-ene, but-1-ene, *E*/*Z*-hex-2-ene, 4-methylpent-1-ene, and hex-1-ene. The first three products account for almost 90% of the carbon balance. The mechanism involves reversible intramolecular H-transfer reactions that lead to the formation of the radicals 5-methylhex-5-yl (5-5MeH), 5-methylhex-2-yl (2-5MeH), 5-methylhex-4-yl (4-5MeH), 5-methylhex-6-yl (6-5MeH), and 5-methylhex-3-yl (3-5MeH). Competitive with isomerization reactions are decompositions by β C–C bond scission. The main product forming radical is 5-5MeH, which is formed by intramolecular abstraction of the lone tertiary H in the radical. This reaction is deduced to be a factor of 4.0 ± 0.7 faster on a per hydrogen basis than the analogous abstraction of a secondary hydrogen in 1-hexyl radical. The estimated uncertainty corresponds to 1 standard deviation. The following relative rates have been deduced under our reaction conditions: $k(4-5MeH \rightarrow$ $C_2H_5 + 3$ -methylbut-1-ene)/k(4-5MeH \rightarrow CH₃ + Z-hex-2-ene) = $10^{(0.39\pm0.12)} \exp[(675\pm270)K/T]; k(4-5MeH)^{-1}$ $5MeH \rightarrow C_2H_5 + 3$ -methylbut-1-ene)/k(4-5MeH $\rightarrow CH_3 + E$ -hex-2-ene) = $10^{(-0.10\pm0.09)} \exp[(1125 \pm 10^{-0.10\pm0.09})]$ 210) K/T]; $k(3-5 \text{MeH} \rightarrow iso-C_3 H_7 + \text{but-1-ene})/k(3-5 \text{MeH} \rightarrow \text{CH}_3 + 4-\text{methylpent-1-ene}) = 10^{(0.26\pm0.55)}$ $\exp[(1720 \pm 1300)K/T]$. Observed olefin distributions depend on the relative rate constants and the interplay of chemical activation and falloff behavior as the energy distributions of the various radicals relax to steady-state values. A kinetic model using an RRKM/master equation analysis has been developed, and absolute rate expressions have been deduced. The model was used to extrapolate the data to temperatures between 500 and 1900 K and pressures of 0.1-1000 bar, and results for 12 isomerization reactions and 10 β C–C bond scission reactions are reported.

Introduction

Alkyl radicals are the initial products formed during the combustion of hydrocarbon fuels. Their subsequent reactions involve a competition between oxidative and pyrolytic chemistry. Under high-temperature conditions, they are extremely unstable and decompose via unimolecular processes to a smaller radical and a corresponding olefin. The latter species in particular can be a precursor to polyaromatic hydrocarbons (PAH) and soot.^{1–3} Under many combustion conditions the radical lifetimes are so short that bimolecular oxidation reactions cannot compete. Under these circumstances the exact decomposition rates are unimportant. However, for larger radicals, as produced in many fuels, decomposition can occur by multiple reaction channels. The relative contribution from each of these channels may be important for the subsequent course of reaction.

The reactions described above involve short-lived intermediates and complex potential energy surfaces containing many energetically similar pathways; these qualities make it difficult to isolate the individual channels in kinetic studies. To probe these reactions, our strategy has been to utilize the shock tube to thermally generate the radical of interest under conditions where only the unimolecular decomposition and isomerization reactions can make contributions to the cracking pattern. We observe the product olefins, which are stable on the time scale of our experiments, and use their distributions to obtain information on the relative rates of specific processes. By then placing any one of the reactions on an absolute scale, generally on the basis of independent literature data, we are able to derive absolute values useful in combustion models. A complicating factor is that the reaction thresholds for decomposition are so low relative to the internal energy distribution of the radicals that the rates are not correctly described by standard thermal rate constants. To generalize our experimental results, we therefore develop a detailed chemical kinetic model of each system and carry out a Rice-Ramsberger-Kassel-Marcus/ Master Equation (RRKM/ME) analysis; this allows us to extrapolate the primary data to a variety of conditions of interest to combustion scientists.

We have previously reported on the behavior of a number of linear alkyl radicals, including pentyl,⁴ hexyl,⁵ heptyl,⁶ and octyl⁷ radicals. Our observations show that product distributions are dominated by the rates of intramolecular hydrogen abstractions relative to rates of β C–C bond fissions. To identify generic intramolecular hydrogen transfer reactions, we shall describe them as m-n processes, where

^{*} To whom correspondence should be addressed, jeffrey.manion@nist.gov.



Figure 1. Schematic of the apparatus.

the initial radical site is on the carbon in position "m" and a hydrogen is transferred from the carbon in the *n*th position. Our experimental studies⁴⁻⁸ and recent theoretical work⁹ have shown that 1-2 and 1-3 H transfer reactions are much slower than 1-4, 1-5, and 1-6 processes. The observed rate patterns can be rationalized in terms of the conformational energies associated with the cyclic transition states. We have additionally shown that, for the studied normal alkyl radicals, rates of 1-n transfers are similar for equal values of *n*. While this result might be anticipated on the basis of thermochemical kinetic arguments, it is a very important finding that allows transferal of the data to unexamined systems.

Our studies of the linear radicals have systematically built up an experimental database of information on the rates of intramolecular hydrogen abstraction from -CH₂- groups by carbon-centered radicals. Branched hydrocarbons are an important component of many fuels, and an understanding of their behavior requires information on rates of intramolecular H transfer from -CH(R)- moieties. Of particular note are methyl-substituted species, which are prevalent in Fischer-Tropsch fuels. We have recently studied and reported on the decomposition and isomerization pathways for 4-methylpentyl radicals;8 that work allowed us to probe the effect of methyl substitution on the rate of 1-4 hydrogen transfers (having a cyclic five-center transition state). We now report on extension of this work to cover 5-methylhexyl radicals with the aim of determining the effect of methyl substitution on 1-5 hydrogen transfers, which proceed via a six-center transition state.

2. Experimental Methods¹⁰

Chemicals. 5-Methylhexyl iodide (Inno Chemie GmbH, Germany, 99% pure by gas chromatographic (GC) analysis), chlorocyclopentane (99%, Aldrich), chlorocyclohexane (99% Aldrich), 1,3,5-trimethylbenzene (135TMB, 99%, Aldrich), and argon (Matheson, high purity grade, 99.999%) were the primary chemicals used. All chemicals were used without further purification other than degassing during preparation of the mixtures.

Apparatus and Gas Chromatographic/Mass Spectral (GC/ MS) Analysis. Experiments are conducted in a single pulse shock tube of conventional design. A simplified schematic is shown in Figure 1. The shock tube is constructed from 3.2 cm square aluminum tubing, with a 125 cm driver section and 171 cm driven section. Other components are of stainless steel. The volume of the dump tank is approximately 19 L. The shock tube, the sample preparation system, and the product sampling system are all heated to typically 100 °C to maintain components in the gas phase. Species concentrations in the starting mixtures are established by vapor pressures measured with calibrated MKS Instruments (Andover MA) capacitance manometers with 1.33 kPa (10 Torr), 13.3 kPa (100 Torr), or 666 kPa (5000 Torr) pressure heads (accuracy 0.12% of full scale) or, in less demanding applications, by volumetric injection of liquids using calibrated syringes. Concentrations are checked by GC analyses of the unshocked mixtures. Prior to use, prepared mixtures are stored in 15 L stainless steel bulbs whose inner surfaces have been passivated with Restek (Bellefonte, PA) Silcosteel, a silicon surface deposition treatment. Shock waves are produced by rupture of a cellophane diaphragm and the shock pressure profiles monitored with high-frequency pressure sensors (PCB Piezotronics, Inc., Buffalo NY, model 113A26). As determined from the pressure profiles, the shock-heated gas remains at temperature for about (500 \pm 50) μ s prior to rapid quenching through interaction with the expansion fan. Immediately following each experiment a port 5 cm from the end of the shock tube is opened to extract a sample of the shocked gas into an evacuated valve and loop sampling system that is integrated with the GC. Undiluted sample gas admitted into two valve and loop samplers (Valco Instruments Co., Inc., TX) is compressed to a known pressure (typically 1 bar), and the separate loop volumes (1 mL each) are injected onto two GC columns for analysis. Pressures are monitored with a calibrated model 2500 (0 to 140 kPa) gauge (Mensor Corp. San Marcos TX), accuracy 0.01% of full scale.

Analyses utilize an Agilent Technologies (Santa Clara, CA) 6890N GC equipped with twin flame ionization detectors (FIDs) and an Agilent Technologies 5973 inert mass selective detector. Mass spectral analyses are performed after separating the components on a J & W Scientific (Folsom, CA) $30 \text{ m} \times 0.53$ mm i.d. DB-1 (100% dimethypolysiloxane) fused silica column with the GC oven temperature programmed from -60 to 180 °C and the carrier gas controls set to the constant flow mode. The sample eluting from the DB-1 column is split with quantitative accuracy using an Agilent Technologies Dean's Switch to allow simultaneous FID and mass spectral analyses. While most components are well-separated on the DB-1 column, a better separation of the lighter gases is achieved in a simultaneous analysis using a Restek 30 m \times 0.53 mm i.d. Rt-Alumina (aluminum oxide porous layer) capillary column. In particular this column gives excellent separation of 1-butene and isobutene, components which are usually difficult to isolate. This configuration uses a back-flushable precolumn to trap heavy species and prevent contamination of the alumina column with slowly eluting components. FID peak areas are determined using the Agilent Technologies ChemStation software and converted to molar quantities using responses determined from standard samples. The use of two columns results in duplicate analyses for many components smaller than C5; concentrations from the two analyses generally agreed to within a few percent. Representative chromatograms are given in the Supporting Information.

Reaction Conditions. Compositions of the gas mixtures used in the present studies are given in Table 1. We utilize very low concentrations of the radical precursor and temperature standard, typically 70–140 μ L/L, in the presence of a much larger concentration of the inhibitor, typically 8000 μ L/L. The bath gas is argon. The compositions are specifically chosen to prevent secondary chemistry from impacting the results, while providing product concentrations large enough to quantify even minor products of the reaction. To aid in identification of the minor

TABLE 1: Gas Mixtures Used in the Present Experiments^a

	components in mixtures (μ L/L)							
mixture no.	5MeHI ^b	CCP^{c}	CCH^d	135TMB ^e				
А	70	100		7200				
В	140		100	8000				
\mathbf{C}^{f}	830		100	8200				

^{*a*} The remaining balance is argon. ^{*b*} 5MeHI = 5-methylhexyl iodide. ^{*c*} CCP = chlorocyclopentane (temperature standard). ^{*d*} CCH = chlorocyclohexane (temperature standard). ^{*e*} 135TMB = 1,3,5-trimethylbenzene (inhibitor). ^{*f*} Experiments with this mixture were utilized primarily for product identification studies.

species via mass spectrometry, or deduce aspects of the mechanism, some experiments have been carried out at iodide concentrations near 800 μ L/L. Shock temperatures are determined by a comparative rate technique in which the unimolecular decomposition of a standard, chlorocyclopentane or chlorocyclohexane, is monitored and used to deduce the reaction temperature. Thus $k_{\text{std}} = \tau^{-1} \ln([\text{std}]_i/[\text{std}]_f)]$, where τ is the residence time of about 500 µs and the subscripts i and f refer to the initial and final concentrations, respectively. The temperature has been derived using our recently measured¹¹ rate expressions k(chlorocyclopentane \rightarrow cyclopentene + HCl)/s⁻¹ = $4.47 \times 10^{13} \exp(-24570 K/T)$ and k(chlorocyclohexane \rightarrow cyclohexene + HCl)/s⁻¹ = $2.15 \times 10^{14} \exp(-25950/T) \text{ s}^{-1}$, whose rates have been determined relative to each other and several other reactions and are linked to our rate expression for the decomposition of cyclohexene, k(cyclohexene \rightarrow butadiene + ethene)/ $s^{-1} = 4.47 \times 10^{13} \exp(-24570 K/T)$. Cyclopentene and cyclohexene are not products of the decomposition of the radicals under study or any of the other compounds in our mixtures. Initial experiments were conducted with chlorocyclopentane as the standard. However, we later identified a minor product, 4-methylpent-1-ene, that was not well separated from cyclopentene in the GC analysis. This difficulty did not impact our temperature determinations as 4-methylpent-1-ene is formed in trace quantities only, but to obtain data for 4-methylpent-1ene we subsequently carried out a second set of experiments using chlorocyclohexane as the temperature standard. The cyclohexene product of this standard can undergo secondary decyclization to give ethene and butadiene, but this process is negligible at even the highest temperatures of our study and perturbs simple first-order kinetics by less than 0.2%. Shock pressures have been calculated from the temperature and mixture composition via the ideal shock equations;¹² these values are not significantly different from those derivable from the pressure traces but should provide more consistent relative values, which is important for the RRKM analysis. Temperatures in the reflected shock ranged from 889 to 1064 K with shock pressures of 1.6-2.2 bar.

3. Results

3.1. Products and the Reaction Mechanism. The 5-methylhex-1-yl radical was generated by the thermal decomposition of 5-methylhexyl iodide. The iodide was found to yield ethene, 2-methylpropene (isobutene), propene, and 5-methylhex-1-ene as the major stable olefin products; also found were much smaller amounts of several other product alkenes, including 3-methylbut-1-ene, but-1-ene, *E*-hex-2-ene, *Z*-hex-2-ene hex-1-ene, 4-methylpent-1-ene, 2-methylhex-1-ene, and 2-methylhex-2-ene. A detailed quantitative breakdown of the conditions and products of each experiment is provided in the Supporting Information. Thermolysis of 5-methylhexyl iodide is expected to proceed via two parallel channels: fission of the weak C–I bond to produce the 5-methylhex-1-yl radical of interest and 1,2 elimination of hydrogen iodide to give 5-methylhex-1-ene:

5-methylhexyl iodide
$$\rightarrow$$
 Products (a)

5-methylhexyl iodide
$$\rightarrow$$
 5-methylhex-1-yl + I (b)

5-methylhexyl iodide
$$\rightarrow$$
 5-methyl-1-hexene + HI (c)

The alkene product of HI elimination, 5-methyl-1-hexene, accounts for about 30% of the reacted substrate. Olefins other than 5-methylhex-1-ene are attributed to decomposition of the 5-methylhex-1-yl radical. On a mass basis, almost 90% of the material from this species is accounted for by isobutene, ethene, and propene. While the remaining compounds are of relatively minor importance in terms of the reaction outcome, they serve to constrain the rate constants and provide crucial validation data for the kinetics and mechanism.

When released into the system, 5-methylhex-1-yl radicals can isomerize or decompose via β bond fission reactions. Scheme 1 shows the reactions postulated to be of principal importance in the mechanism. Therein, and throughout the remainder of this paper, we identify radical isomers as x-5MeH, where x is the position of the radical site if the carbon numbering is unchanged from the initial radical, which is designated as *I*-5MeH. This system labels the backbone of the structure as "5MeH" and considers the methyl to be substituted at the "5" position in all C7 radicals in the mechanism. Reaction numbering and the nomenclature and abbreviations used to identify other species are shown in Scheme 1.

At our reaction temperatures radicals typically decompose via unimolecular bond fission processes on the time scale of microseconds; under the dilute conditions of our experiments the decompositions are much faster than competing bimolecular reactions and are irreversible. The olefin products are stable and serve as marker species for the corresponding reactions and precursor radicals. Isomerizations occur via intramolecular H transfer reactions and are both reversible and competitive with decompositions; if an isomerization occurs, the resulting radical can undergo its own set of isomerization and bond fission processes. Each C-C bond fission produces a stable alkene and another alkyl radical whose subsequent reactions must be considered. Note that β scission of a C-H bond has a much higher activation energy than C-C bond scission and the former reaction may be largely neglected if both channels are present.

A detailed breakdown of the alkene products from the decomposition of 5-methylhexyl-1 radical, plotted as the molar ratio of each alkene to the total alkene yield, is given in Figure 2. Table 2 gives fitted analytical expressions that describe the data. The C7 part of the system involves 6 reversible isomerizations and 10 β -bond fission channels. As shown in Scheme 1, 1-4, 1-5, 1-6, 5-2, and 6-3 hydrogen transfers produce 4-5MeH, 5-5MeH, 6-5MeH, 2-5MeH, and 3-5MeH radicals, respectively. The alkene products enclosed in boxes are unique markers for specific channels, and their occurrence in the product spectrum is unequivocal evidence for the presence of the precursor radicals. Specifically, isobutene can only arise from the 5-5MeH radical isomer, which is formed via a 1-5 hydrogen transfer (having a six-

SCHEME 1: Reactions of Principal Importance in the Decomposition of 5-Methylhex-1-yl Radicals^a



^{*a*} The starting radical is indicated by the dashed oval. The seven alkenes enclosed in boxes are marker species that are formed from the indicated precursor radicals. Two other alkenes, ethene and propene, are derived from multiple sources.



Figure 2. Alkene yields from the decomposition of 5-methylhexyl radicals. See Scheme 1 for species nomenclature. Symbols are experimental data; lines represent fits from the RRKM/Master equation model described in the text. The values for $1-C_6H_{12}$ have been divided by 2 for clarity.

center transition state). 3-Methyl-1-butene, *E*-hex-2-ene, and *Z*-hex-2-ene serve as unique markers for the 4-5MeH radical produced via a 1-4 H transfer (five-center transition state). Hex-1-ene is formed only from the 6-5MeH radical derived via a 1-6 transfer (seven-center transition state). But-1-ene and 4-methylpent-1-ene are the products of 3-5MeH. As noted in the Experimental Section, because of separation difficulties in the GC analysis, data on 4-methylpent-1-ene are available only from experiments in which chlorocyclohexane was the temperature standard.

As shown in Scheme 1, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, and isobutyl radicals are formed in association with the olefin products used as marker compounds. These species have no facile isomerization channels and will decompose variously to yield hydrogen atoms, methyl radicals, ethene, and propene

 TABLE 2: Analytical Fits Describing the Olefin Product

 Branching Ratios^a

alkene	$\log(x_i)$
ethene	$-(0.038 \pm 0.013) - (300 \pm 13)$ K/T
isobutene	$-(1.15 \pm 0.035) + (625 \pm 34)K/T$
propene	$-(0.46 \pm 0.043) - (288 \pm 42)K/T$
3-methylbut-1-ene	$-(1.36 \pm 0.054) - (297 \pm 52)K/T$
but-1-ene	$-(2.58 \pm 0.020) + (701 \pm 19)K/T$
E-hex-2-ene	$-(1.26 \pm 0.077) - (785 \pm 74)K/T$
Z-hex-2-ene	$-(1.75 \pm 0.11) - (590 \pm 105)$ K/T
hex-1-ene	$-(1.44 \pm 0.061) - (897 \pm 59)$ K/T
4-methylpent-1-ene	$-(2.92 \pm 0.54) + (30 \pm 550)$ K/T

^{*a*} x_i is the mol fraction of the *i*th alkene in the olefin product spectrum of *1*-5MeH, given by $x_i = m_i / \sum_{i=1}^{n} m$, where *m* is the molar yield of a given alkene.

$$C_{2}H_{5} \rightarrow C_{2}H_{4} + H$$

$$n - C_{3}H_{7} \rightarrow C_{2}H_{4} + CH_{3}$$

$$i - C_{3}H_{7} \rightarrow C_{3}H_{6} + H$$

$$n - C_{4}H_{9} \rightarrow C_{2}H_{4} + C_{2}H_{5}$$

$$i - C_{4}H_{9} \rightarrow C_{3}H_{6} + CH_{3}$$

Methyl radicals and H atoms are primarily scavenged by the excess 135TMB inhibitor, and the stable olefins are detected in our analyses. While propene and ethene cannot be assigned to unique channels, our model must be consistent with the aggregate quantity of each species. At the lowest temperatures of our study we had concerns that ethyl radicals may not be fully decomposed on the time scale of our experiments. The quantity of ethyl radical surviving the heating period was modeled using the same procedure described previously⁸ and

SCHEME 2: Decomposition Mechanism of 3-Methylbut-1-yl Radicals^a

^a The starting radical is indicated by the dashed oval.

found to have a negligible effect (<0.2%) on ethene yields, in part because only a small fraction of the ethene is formed from ethyl radicals in the present system.

In addition to the simple radicals discussed above, the 3-methylbut-1-yl radical is also formed and it may have more complex behavior: its decomposition chemistry is shown in Scheme 2. Isomerization to 2-methylbut-1-yl can occur via a 1-4 H transfer in competition with β C–C bond scission. The C-C bond scission that gives ethene and isopropyl radical is expected to be promoted by the secondary nature of the radical product, but we are unaware of any direct experimental information on the branching ratio. The 2-methylbut-1-yl radicals can undergo β C-C bond scissions to give either propene + ethyl or 1-butene + methyl. Ethyl scission is expected to be favored by about 3:1 on the basis of our previous work. To better estimate the behavior of 3-methylbut-1-yl, we modeled this system using rate constants estimated from our work on the 4-methylpentyl⁸ and 3,3-dimethylbutyl¹³ systems. On this basis, the 1-butene + methyl channel is estimated to account for 4% of the reaction, independent of temperature between 890 and 1065 K, with the remainder leading to propene + ethene + H.

The relative molar yields of the alkene products at 969 K, the midpoint of our 1/T range, are ethene:isobutene:propene: 3-methylbut-1-ene:1-butene:hex-2-ene (E+Z):1-hexene:4-me*thylpent-1-ene* = 1000:695:390:48:31:29:10:2.9. If isomerization did not occur, the only products of the decomposition of 1-5MeH would be ethene and propene in a 2:1 molar ratio. The large amount of isobutene in the product spectrum shows that isomerization is the dominant process, since this product can only be formed following conversion to 5-5MeH (see Scheme 1). Because this channel leads to equimolar amounts of ethene and isobutene, we conclude from the relative yields that 695 of the observed 1000 units of ethene stem from decomposition of the 5-5MeH radical. Of the remaining 305 units, 48 are formed in the same channel that leads to 3-methyl-1-butene, so the unaccounted for portion is only 255 units. These must stem from decomposition of 1-5MeH and 6-5MeH radicals. Both of these channels lead to a 2:1 molar ratio of ethene to propene, or equivalently, to 127 units of propene. The only other sources of propene are 2-5MeH and 3-5MeH radicals, and the amount from latter channel is equal to the molar amount of 1-butene. This means that (390 - 127 - 31 = 232)of the total 390 units of propene must come from 2-5MeH. The above analysis shows that the primary product forming radicals in this system are 5-5MeH and 2-5MeH.

Secondary Chemistry. While we have carefully selected our conditions so as to limit interfering chemistry, the high sensitivity of GC/MS analysis makes it possible to identify minor secondary products. Identified compounds include methane, ethane, propane, *n*-butane, isobutane, iodomethane, iodo-ethane, iodopropane, isobutyl iodide, *m*-xylene, and 3,5-

dimethylethylbenzene (see chromatograms in the Supporting Information). These are accounted for by expected reactions with the 135TMB scavenger, radical recombination processes, or reaction with HI

$$CH_3 + 135TMB \rightarrow CH_4 + 3,5$$
-dimethylbenzyl

 $CH_3 + 3,5$ -dimethylbenzyl $\rightarrow 3,5$ -dimethylbenzene

$$2CH_3 \rightarrow C_2H_6$$

$$CH_3 + C_2H_5 \rightarrow C_3H_8$$

$$CH_3 + i \cdot C_3H_7 \rightarrow isobutane$$

$$C_2H_5 + C_2H_5 \rightarrow n \cdot butane$$

$$H + 135TMB \rightarrow m \cdot xylene + CH_3$$

$$CH_3 + I \rightarrow CH_3I$$

$$C_2H_5 + I \rightarrow C_2H_5I$$

$$C_2H_4 + HI \rightarrow C_2H_5I$$

$$C_3H_7 + I \rightarrow C_3H_7I$$

$$C_3H_6 + HI \rightarrow C_3H_7I$$

Iodomethane must be formed from methyl + I recombination, while the other alkyl iodides can be formed either via R + Ireactions or addition of HI to the corresponding olefin. These reactions may occur partly in the postshock quenching period. A fourth iodide, the product of 3,5-dimethylbenzyl + I, is undoubtedly formed but is believed not to elute from the GC column during our analysis (the stability requirements of the alumina column limited the maximum oven temperature to 180 °C). The formation of alkyl iodides could potentially perturb our measurements of the olefins. However, in the studies used for quantitative work (Table 1, mixtures A and B) the ratios of the ethyl and propyl iodides to the corresponding alkenes were 0.03 or smaller; the ratio of isobutyl iodide to isobutene was about an order of magnitude smaller. Although observable, trace products from R + R alkyl radical recombinations perturb the measured olefin ratios even less than formation of iodides.

Any C7 radicals undergoing C-H bond fissions would lead to C7 alkenes. Excluding the product of HI elimination, reaction c, the only C7 alkenes identified were traces of 2-methylhex-1-ene and 2-methylhex-2-ene, which were identified on the basis of their retention times and MS analyses in comparison with commercial samples. The latter of these two compounds coeluted with propyl iodide in the GC analysis. The amount of this product was therefore obtained from the mass spectral analyses, comparing the integrated peak areas of the parent ions for 2-methylhex-1-ene and 2-methylhex-2-ene, and making the assumption that the relative response factors for the two isomers

Figure 3. Yields of the trace methylhexene products corresponding to loss of H atom from the 5-methylhex-5-yl radical (5-5MeH). The dependence of the result on the starting iodide concentration indicates a significant contribution from secondary chemistry. Solid and dashed lines show the modeled contributions to 2-methylhex-1-ene and 2-methylhex-2-ene, respectively, from unimolecular decomposition of 5-5MeH.

were identical. These two alkenes are consistent with those that would be expected on the basis of a small amount of C-H bond fission from 5-5MeH, which is the major product forming radical in the system.

$$5-5MeH \rightarrow 2$$
-methylhex-1-ene + H (17)

$$5-5MeH \rightarrow 2$$
-methylhex-2-ene + H (18)

Unlike the other alkene products, however, the relative amounts of the methylhexenes were found to increase by a factor of 2 as the starting concentration of the iodide was raised from 70 to 830 ppm. These data are shown in Figure 3. Evidently at least a portion of these compounds are formed via a more complex mechanism than C-H bond fission. Two possibilities are radical disproportionation reactions or recombination of 5-5MeH with iodine atoms followed by thermal or chemically activated loss of HI: $(5-5MeH + I \rightarrow 5\text{-}iodo\text{-}5\text{-}methylhexane*)$ \rightarrow 2-methylhexenes + HI). Although the data thus do not provide a precise determination of the relative rate of C-H to C-C bond fission from 5 to 5MeH, we are able to derive (k_{17}) $(k_{18})/k_8 \leq 0.015$. This value is close to our modeled result (Figure 3) and is reasonably consistent with expectations and theoretical predictions on related systems.¹⁴ The disparity in the modeled temperature dependence may suggest, however, that secondary processes are important even at the lowest concentration of the starting iodide.

As indicated above, none of the secondary chemistry has a significant impact on the concentrations of the olefins of primary interest, which is the quantitative information needed to deduce the decomposition behavior of the radical.

Kinetics of the Initial Reactions. 5-Methylhexyl iodide decomposes via parallel reactions b and c. Because the product spectra do not overlap, we are able to derive rate parameters for these two processes. Channel c is easily monitored by formation of 5-methylhex-1-ene. For reaction b we have summed the total carbon units present in the alkene products expected on the basis of Scheme 1, together with small stoichiometric corrections for additional carbons lost as methyl radicals. Mass balances ranged from (91 to 102)% and were typically >97%, with a gradual decrease at the highest levels

Figure 4. Arrhenius plots for the decomposition of 5-methylhexyl iodide.

of conversion. On this basis we are able to derive rate constants for the total reaction a and the individual channels b and c. Considering only the data where the degree of conversion was less than 65%, the following rate expressions have been derived for 889-1001 K, 1.6-2.0 bar

k(5-methylhexyl iodide
$$\rightarrow$$
 Products)/s⁻¹ =
10^(13.90±0.24) exp[-(24360 ± 530)K/T]

k(5-methylhexyl iodide → 5-methylhex-1-yl + I)/s⁻¹ =
$$10^{(13.89\pm0.24)} \exp[-(24650 \pm 530)K/T]$$

$$k$$
(5-methylhexyl iodide \rightarrow 5-methylhex-1-ene +
HI)/s⁻¹ = 10^(12.97\pm0.25) exp[-(23585 ± 540)K/T]

Arrhenius plots are shown in Figure 4. Errors are given as the standard uncertainties (1σ) derived from the statistical fits. The above rate expressions are about what one would expect on the basis of the kinetics literature.^{4,5,8,15,16} Although reported for completeness, the precise values are of little consequence in terms of our study of the reactions of 5-methylhexyl radical and will not be considered further.

Directly Measured Relative Rates. In cases where a specific intermediate radical is the sole source of multiple alkenes the relative yields of the olefins directly correspond to the relative rate constants for the competing channels. Thus 4-5MeH is the only source of E-hex-2-ene, Z-hex-2-ene, and 3-methylbut-1-ene, while the precursor of but-1-ene and 4-methylpent-1-ene is 3-5MeH. In the case of but-1-ene, a very small amount of this product could arise from secondary chemistry associated with the decomposition of the 3-methylbutyl radical (Scheme 2). Our model suggests that the contribution to but-1-ene from this source is less than 10%, but we have made no corrections in the absence of more information. The data are plotted in Figure 5. The data for 3-5MeH required a large correction to 4-methylpent-1-ene for a background impurity peak at low temperatures and we have used only the higher temperature results where this correction was small in estimating the relative rate parameters. The following rate relations have been for 889-1064 K, 1.2-2.2 bar:

$$k_1/k_2 = 10^{(0.39\pm0.12)} \exp[(675\pm270)K/T]$$

Figure 5. Relative rate plots for β C–C fission reactions of 3-5MeH and 4-5MeH. Reactions are as given in the legend (see also Scheme 1). The data on k_9/k_{10} required a large correction for a background peak at low temperatures and only the more reliable data (unfilled squares) were used for the least-squares analysis.

$$k_1/k_3 = 10^{(-0.10\pm0.09)} \exp[(1125\pm210)K/T]$$

 $k_3/k_2 = 10^{(0.49\pm0.08)} \exp[-(450\pm180)K/T]$

For the ratio k_9/k_{10} we find, for 990–1049 K, 2.0–2.2 bar,

$$k_9/k_{10} = 10^{(0.26 \pm 0.55)} \exp[(1720 \pm 1300)K/T]$$

Errors are given as the standard uncertainties (1σ) derived from the statistical fits. Note that under our conditions interconversion of the *E*- and *Z*-isomers of hex-2-ene is expected to be slow and, on the basis of extensive studies of the isomerization of *Z*-but-2-ene,^{15–19} one can estimate $(t_{1/2}(1000 \text{ K}) \approx$ 0.5 s), which is much longer that the 500 μ s time scale of the experiment. The consequence is that the observed product ratios can be directly associated with the relative rate constants. Although the above expressions pertain to our conditions and do not directly correspond to thermal rate expressions, our RRKM/ME model suggests that deviations from the thermal values are small.

3.2. Kinetic Model and RRKM/Master Equation Parameters. The isomerization reactions considered in this work are reversible, and their rates are pressure dependent. The experimental results can thus not be extrapolated to other conditions without the use of a reaction model. We have consequently modeled the reactions in the system and carried out a RRKM/ ME analysis to fit the data and allow extrapolation over a range of pressure and temperature conditions were carried out with the ChemRate software package.^{20–22} The calculations were performed with a series of energy grain sizes and variations in the maximum system energy to ensure that results had converged.

Our experimental product branching ratios are quite sensitive to the relative rate constants but do not directly yield absolute values. Fortunately we have a number of experimental and theoretical results from the literature that provide a set of anchor points and constrain the kinetics. Fits were achieved via an iterative procedure in which we began with a baseline model and then modified the kinetic parameters within their estimated uncertainties until the product data were matched. To help with the fitting procedure and better understand the system, the kinetic model was subjected to a sensitivity analysis using the CHEMKIN PRO²³ software package. This analysis utilized rate parameters specific to the pressure and temperature conditions of the experiments as given by the RRKM/ME calculations. Our model development procedure is described below; a detailed listing of the molecular properties and other parameters used in the final RRKM/ME analysis is available in the Supporting Information.

Radical Thermodynamics. Thermodynamic properties were calculated using the standard rigid rotor harmonic oscillator approach with inclusion of hindered internal rotations where appropriate. Molecular properties of the radicals were based on the computations of Burgess²⁴ at the B3LYP/6-31G(d) level of theory and are listed in the model summary given in the Supporting Information. Frequencies from the calculations have been scaled by 0.96, and those corresponding to internal rotational modes have been removed and approximated with symmetric *n*-fold potentials using the methodology of Pitzer.²⁵ Rotational barriers adjacent to radical centers were assumed to be zero. Generic values for other alkyl groups were taken as follows (where R represents an arbitrary alkyl group): $V(\text{RCH}_2-\text{CH}_3) = 14.9 \text{ kJ mol}^{-1}, V(\text{RCH}_2-\text{CH}_2\text{R}] = 22.5 \text{ kJ}$ mol^{-1} , V[(CH₃)₂CH-CH₂R] = 20.5 kJ mol⁻¹. For closed shell hydrocarbons these values have been found²⁴ to provide a good match to known hydrocarbon entropies and thermofunctions, and this was assumed to hold also for the radicals. Heats of formation of the radicals were taken from the calculated atomization energies and are given in Table 3 together with the equilibrium constants of formation. These data result in relative bond energies for primary, secondary, and tertiary C-H bonds of: BDE(Primary) – BDE(Secondary) $\approx 10 \text{ kJ mol}^{-1}$, BDE(Primary) – BDE(Tertiary) $\approx 16 \text{ kJ mol}^{-1}$. These values are close to standard evaluations.²⁶

Transition-State Structures. The initial transition state structures for β bond fission reactions were derived from the parent radical by removing the frequency corresponding to the C-C stretch that becomes the reaction coordinate. Barriers for internal rotors in the transition state were not changed except for those corresponding to the incipient double bond and the breaking bond, which were frozen and allowed to become free, respectively. Slight adjustments to the low-frequency vibrations were subsequently made as necessary to reproduce the desired A-factors in the rate expressions. An analogous procedure was adopted for the intramolecular H-transfer reactions, which have cyclic transition states. Again beginning with the parent radical, the C-H stretch corresponding to the reaction coordinate was removed, as were the hindered rotors that become part of the cyclic transition state. These latter frequencies were initially replaced with 450 cm⁻¹ vibrations, a somewhat arbitrary choice, but a reasonable estimate for C-C-C "wag" modes. As with the β bond fission reactions, we subsequently adjusted the lowfrequency vibrations to match the kinetics required by the experimental data; hence the exact choices for the wag modes have only a minor effect on our final results. Note that the number of frozen hindered rotors increases with the ring size of the transition state and this results in a natural decrease in the reaction entropy and pre-exponential factor for larger rings.

Reaction Energetics. As discussed more fully below, we have elected to normalize our relative rate constants by fixing the absolute rate parameters for selected reactions based on our previous results for *n*-hexyl radical. For the nonfixed decomposition reactions, the enthalpies of formation of the transition states were initially estimated so as to be compatible with the results of Saeys et al.,²⁷ who used the CBS-QB3 methodology to systematically examine structural effects on the activation

TABLE 3: Standard State Thermodynamic Properties and Equilibrium Constants of Formation (K_p) of the Reactant Radical Isomers^{*a*}

species	$\Delta_{\mathrm{f}} H^{\circ}{}_{298}$	S°_{298}	$\log_{10}(K_{\rm p})$
1-5MeH	12.03	441.8	$-60.714 + 3.275 \ln T - (3.291 \times 10^{-4})T + 7686.5T^{-1} - (2.06 \times 10^{-4})T + 7686.5T^{-1} + 7686.5$
2-5MeH	0.79	445.0	$\frac{10^{6}}{T^{-2}} + (2.35 \times 10^{8})T^{-3} - (1.02 \times 10^{10})T^{-4} - 61.737 + 3.3521 \ln T - (3.379 \times 10^{-4})T + 8411.8T^{-1} - (2.09 \times 10^{6})T^{-2} + (2.37 \times 10^{8})T^{-3} - (1.02 \times 10^{10})T^{-4}$
3-5MeH	-0.36	447.3	$-61.323 + 3.3011 \ln T - (3.310 \times 10^{-4})T + 8761.7T^{-1} - (2.19 \times 10^{-4})T + 8761.7T^{-1}$
4-5MeH	2.24	447.8	$\frac{10^{6}}{T^{-2}} + (2.49 \times 10^{8})T^{-3} - (1.08 \times 10^{10})T^{-4} \\ -61.104 + 3.2791 \ln T - (3.29 \times 10^{-4})T + 8601.5T^{-1} - (2.18 \times 10^{6})T^{-2} + (2.49 \times 10^{8})T^{-3} - (1.08 \times 10^{10})T^{-4}$
5-5MeH	-4.42	449.2	$-61.842 + 3.335 \ln T - (3.35 \times 10^{-4})T + 9073.9T^{-1} - (2.21 \times 10^{-4})T + 9073.9T^{-1} + 9073.9T^{-1}$
6-5MeH	11.91	447.4	$ \begin{array}{l} 10^{6})T^{-2} + (2.53 \times 10^{8})T^{-3} - (1.09 \times 10^{10})T^{-4} \\ -60.703 + 3.277 \ln T - (3.29 \times 10^{-4})T + 7705.6T^{-1} - (2.07 \times 10^{6})T^{-2} + (2.36 \times 10^{8})T^{-3} - (1.02 \times 10^{10})T^{-4} \end{array} $

 ${}^{a}\Delta_{f}H^{o}{}_{298}$ in kJ mol⁻¹, $S^{o}{}_{298}$ in J mol⁻¹ K⁻¹, *T* is the temperature in kelvin; significant figures are given in order to specify the model and do not imply accuracy. See Scheme 1 for nomenclature.

energies for hydrocarbon radical addition and β -scission reactions. We assumed the error bounds of the calculations to be $\pm 10 \text{ kJ mol}^{-1}$ and adjusted the initial estimates within these values so as to fit our experimental data. More directly, as shown in Figure 5, our data define the relationships between k_1 , k_2 , and k_3 , and the ratio k_9/k_{10} ; in these cases we have used our measured values as our starting basis. For isomerization reactions, our starting estimates of the reaction energetics are based on the calculations of Hayes and Burgess,⁹ who have derived barriers for a series of intramolecular H-transfers at the B3LYP/ δ -31G(d) level of theory. They have estimated these values to be accurate to within $\pm 6 \text{ kJ mol}^{-1}$ and in our fits we attempted to maintain the required parameters within these limits.

Collisional Energy Transfer and Tunneling. Collisional energy transfer with the argon bath gas has been treated with a standard exponential-down model^{28–31} with $\alpha = 0.293T$ cm⁻¹, where α is the usual parameter that relates to the average energy transferred in deactivating collisions and *T* is the temperature in kelvin. In our analysis of the decomposition of *n*-hexyl radicals,⁵ we found it necessary to consider tunneling in order to fit both our shock tube results and data on the isomerization reaction from studies at lower temperatures. In the *n*-hexyl case we found that a good fit could be obtained using a symmetric Eckart barrier³² with a width of 1.15 Å. There are no data from low temperatures for the present radical system. For purposes of extrapolating our results over the range of combustion conditions of interest, we have taken the tunneling properties to be the same as those derived for the *n*-hexyl system.

Energy Distributions. The radical decompositions considered here have low reaction thresholds and differ from typical thermal reactions in that the radicals are formed with average energies that are already above these values. The general picture has been discussed in detail in previous publications,^{8,20} and only the most salient features are described here. They are best treated as chemical activation systems. In our treatment, the iodide precursor is assumed to produce a constant incoming flux of *1*-5MeH radicals having a Boltzmann energy distribution corresponding to the reaction temperature. The initial Boltzmann distribution then tends toward a new steady state distribution at a rate that depends on the temperature, pressure, and decomposition rate constants. Energy distributions of the other radicals in the system depend on that of the precursor radical and the reaction energetics.

The time-dependent energy distributions for the methylhexyl radicals are shown in Figure 6. The initial Boltzmann distribution of *1*-5MeH evolves toward a final steady-state distribution

that peaks at an energy lower than that of the initial distribution. At the illustrated temperature of 969 K most but not all of the molecules are above the reaction thresholds; at higher temperatures the distribution is moved to higher energies until essentially all molecules are above the barriers to reaction. The other radicals exhibit qualitatively similar behavior, but the initial distributions are shifted to higher energies by the requirement that the incoming molecules pass over the respective reaction barriers. The highest initial energy distributions are observed for 2-5MeH and 3-5MeH, cases in which two consecutive isomerizations are required to form the radical.

The time to reach the steady-state distribution is the induction period. If the time scale of interest is shorter than the induction period, or the molecules react fast enough so that a significant fraction have reacted prior to reaching the final energy distribution, the traditional steady-state RRKM solution is not valid and the rate constants are time-dependent. Such situations lead to reduced falloff behavior and ultimately, if a large enough fraction of the molecules react while the energies lie above the Boltzmann distribution, as rate constants that are larger than the high pressure limit. Fortunately there are relatively few conditions of practical interest where such complications arise. At the temperatures and pressures of our experiments steadystate energy distributions are achieved and time-independent rate constants can be defined in the usual manner.

3.3. Fitting the Kinetic Model to the Data. *Sensitivity Analysis.* To help guide our fits and to determine the reactions and rate constants to which our experimental data are most sensitive, a reaction model based on the mechanism given in Scheme 1 was constructed in CHEMKIN PRO²³ using the plug flow reactor module. To estimate how changes in the reaction rate coefficients affect the concentration of alkene products, a linear sensitivity analysis was performed with this software and normalized sensitivity coefficients (NSC) were derived. These are defined as

$$NSC = d[x_i]/[x_i]/d[k_i]/[k_i]$$

where x_i is the concentration of the *i*th alkene product and k_j is the *j*th rate constant. Results were qualitatively very similar over the range of temperatures and pressures of our experiments and showed no significant variation with the time of reaction. Here we present the values obtained using our final fit at 500 μ s (the shock heating time) with the reaction temperature and pressure fixed at 969 K and 2 bar. Figure 7 shows the sensitivities of the alkene concentrations to the radical isomerization and β bond fission reactions.

Figure 6. Normalized energy distributions as a function of time for methylhexyl radical isomers derived from the reaction of 5-methylhex-1-yl radical at 969 K and 2.0 bar pressure. Dashed vertical lines represent thresholds for the various reactions of the isomer.

Figure 7. Sensitivity of the alkene product distributions at 969 K to β -bond fission reactions (left graph) and H-transfer reactions (right), expressed as normalized sensitivity coefficients (NSC), NSC = $d[x_i]/[x_i]/dk_j/k_j$, where x_i is the concentration of the *i*th alkene product and k_j is the *j*th rate constant.

TABLE 4: High-Pressure Limiting Rate Expressions, $k/s^{-1} = A(T/298)^n \exp(-E/T)$, from 500 to 1900 K, Derived for Reactions in the Thermal Decomposition of 5-Methylhex-1-yl radical (1-5MeH)^{*a*}

	reaction	log A	n	E/R	$\log(k/s^{-1})$ 1000 K
k_1	$4\text{-5MeH} \rightarrow C_2H_5 + 3\text{-MeC}_4H_7$	13.57	0.033	14591	7.25
k_2	$4\text{-}5\text{MeH} \rightarrow \text{CH}_3 + E\text{-}\text{C}_6\text{H}_{12}$	13.52	0.11	15371	6.90
k_3	$4\text{-}5\text{MeH} \rightarrow \text{CH}_3 + Z\text{-}\text{C}_6\text{H}_{12}$	12.97	0.14	14866	6.59
k_4	$1-5MeH \rightarrow C_2H_4 + 3-MeC_4H_8$	14.06	-0.55	15670	6.96
k_5	$6\text{-5MeH} \rightarrow \text{CH}_3 + 1\text{-}\text{C}_6\text{H}_{12}$	13.52	-0.59	15396	6.52
k_6	$6\text{-5MeH} \rightarrow \text{C}_3\text{H}_6 + n\text{-}\text{C}_4\text{H}_9$	14.18	-0.56	15782	7.03
k_7	$2\text{-5MeH} \rightarrow C_3H_6 + I\text{-}C_4H_9$	13.20	0.07	13651	7.31
k_8	$5-5 \text{MeH} \rightarrow i-\text{C}_4\text{H}_8 + n-\text{C}_3\text{H}_7$	13.00	0.31	13392	7.34
k_9	$3-5MeH \rightarrow i-C_3H_7 + 1-C_4H_8$	13.24	0.16	12563	7.87
k_{10}	$3-5MeH \rightarrow 4-MeC_5H_9 + CH_3$	13.05	0.16	14326	6.91
k_{11}	$1\text{-}5\text{MeH} \rightarrow 4\text{-}5\text{MeH}$	9.19	2.13	7937	6.86
k_{-11}	$4\text{-5MeH} \rightarrow 1\text{-5MeH}$	8.64	2.84	8985	6.23
k_{12}	$1\text{-}5\text{MeH} \rightarrow 6\text{-}5\text{MeH}$	8.79	2.36	6969	7.01
k_{-12}	$6\text{-5MeH} \rightarrow 1\text{-5MeH}$	8.54	2.31	7020	6.71
k ₁₃	$1\text{-}5\text{MeH} \rightarrow 5\text{-}5\text{MeH}$	8.67	1.71	4041	7.81
k_{-13}	$5-5MeH \rightarrow 1-5MeH$	8.17	2.62	6044	6.92
k_{14}	$6\text{-5MeH} \rightarrow 2\text{-5MeH}$	8.69	1.69	4748	7.52
k_{-14}	$2\text{-5MeH} \rightarrow 6\text{-5MeH}$	8.65	2.28	6005	7.24
k_{15}	$2\text{-5MeH} \rightarrow 5\text{-5MeH}$	8.91	2.70	8081	6.82
k_{-15}	5-5MeH → 2-5MeH	8.70	3.07	8776	6.51
k_{16}	$6\text{-5MeH} \rightarrow 3\text{-5MeH}$	9.28	2.01	8103	6.82
k_{-16}	$3\text{-}5\text{MeH} \rightarrow 6\text{-}5\text{MeH}$	8.99	2.79	9403	6.38
k_{17}	$5-5MeH \rightarrow 2-CH_3-hex-1-ene + H$	13.17^{b}	0.71^{b}	17787^{b}	5.82^{b}
k_{18}	$5-5MeH \rightarrow 2-CH_3$ -hex-2-ene + H	12.76^{b}	0.69^{b}	17287^{b}	5.61^{b}

^{*a*} See Scheme 1 for the description of the mechanism. Significant figures are given in order to specify the model and do not imply accuracy (see text for discussion). ^{*b*} The experiments provide only approximate maximum values for these reactions; the above parameters are estimated via thermochemical kinetics. See also Figure 3 and discussion of secondary chemistry in the text.

Kinetic Constraints. While the model can be made to fit the experimental data with a variety of ad hoc rate constants, the selected values should be consistent with data from other systems. Chief among the kinetic constraints are our previous results on the linear alkyl radicals. Of particular importance are the pentyl⁴ and hexyl⁵ systems, which provide benchmark experimental information on the rates H-transfer processes relative to β C–C bond fission for less complicated systems. Both theory and a general knowledge of thermochemical kinetics³³ suggest that analogous processes in the present system should proceed with similar rates. To derive reliable absolute rate parameters, we have required at the midpoint of our 1/Trange, 969 K, that the value of the β bond fission reaction $k_4(1-$ 5MeH \rightarrow ethene +3-methylbut-1-yl) equal that of k(hexyl \rightarrow ethene + but-1-yl), and have taken the latter from our previous work.⁵ The ratio k_4/k_{11} , is likewise expected to be similar to that for the analogous ratio in the hexyl system. We have not fixed this value per se but in our final fit we obtain $k_4/k_{11}(969)$ K) = 1.08, which may be compared with the value of 1.24 in the hexyl system. On the basis of the observed values for methyl versus ethyl bond fission in radicals,^{5,6} we have used k_6/k_5 (969 K) = 3.2 ± 0.4 , where the indicated uncertainty is our estimate at the 1σ level of confidence. Trial fits within the estimated uncertainty bounds did not show reasons to favor a particular value. The reactions 6-5MeH \rightarrow 3-5MeH and 6-5MeH \rightarrow 2-5MeH involve 1-4 and 1-5 H shift reactions, respectively. One would expect the ratios k_4/k_{16} and k_4/k_{14} to have some similarity to the relative rate for the analogous reactions determined in the hexyl system, although a degree of perturbation is likely because of the added methyl group in the present system. We therefore initially allowed these ratios to deviate from the hexyl case. Testing showed the system to be only slightly sensitive to k_{14} , and the final fit utilized k_4/k_{14} (969 K) = 0.21. Finally, in addition to the rate constant constraints discussed above we have attempted to maintain the reaction barriers within the bounds of the values computed for β C–C bond fissions²⁷ and intramolecular H-transfers.⁹

The fitting procedure adopted was to alter the initial rate constant estimates so as to match the data at the midpoint of our 1/T range, 969 K. Relative reaction rates and activation energies of the sensitive reactions were then adjusted to fit the slopes of our experimental data for alkene formation. These procedures are complicated by the fact that the kinetic behavior represents a complex interplay of chemical activation and energy transfer effects. This necessitates an iterative approach. Table 4 lists the high pressure rate parameters for 12 H-transfer reactions and 10 β C–C bond fissions that have been derived from our final fit.

4. Discussion

The present results demonstrate that isomerization of the *1*-5MeH radical occurs in concert with its decomposition via β C-C bond fission under the conditions of our study. Isomerization is the dominant channel and the most important product forming species is the tertiary radical, 5-5MeH, which can be formed directly from the starting radical via a 1-5 intramolecular H abstraction with a six-center transition state. Decomposition of the 5-5MeH radical leads to isobutene and ethene, the two primary product alkenes. Propene is the next most important product and arises mainly from the decomposition of 2-5MeH, formed via a secondary isomerization 5-5MeH ₹ 2-5MeH. A more complete accounting of the observed products requires one to consider the kinetics of a system consisting of 6 reversible intramolecular H-transfer reactions and 10 C-C bond fissions reactions. The results provide detailed information on the relative rate constants. Although it is possible to fit the experimental data with a variety of parametrizations, the range of reasonable values is highly constrained by thermochemical kinetic considerations and a significant body of knowledge from both experimental and theory.

Formation of Ethene, Isobutene, and Propene. As indicated by the sensitivity analysis, and confirmed by empirical testing, the main three products, ethene, isobutene, and propene, are sensitive primarily to the relative rates of the isomerization reactions 1-5MeH \rightleftharpoons 5-5MeH (k_{13} and k_{-13}), 5-5MeH \rightleftharpoons 2-5MeH (k_{15} and k_{-15}), and the product forming β -scission reactions 1-5MeH \rightarrow Products (k_4), 5-5MeH \rightarrow Products (k_8), and 2-5MeH \rightarrow Products (k_7). The temperature dependence of the olefin product ratios is likewise sensitive to the parameters for these reactions. Propene formation additionally depends on the isomerizations *1*-5MeH \rightleftharpoons 6-5MeH (k_{12} and k_{-12}) and 6-5MeH \rightleftharpoons 2-5MeH (k_{14} and k_{-14}). The sensitivity of the system to both the forward and reverse rates of several of the isomerization reactions emphasizes the necessity of matching the radical thermofunctions with the kinetic parameters when modeling the system. Testing showed that moderate changes in the radical properties can be compensated for by changes in the kinetic parameters; likewise, use of an unmatched set will introduce errors.

The six minor olefin products can be divided into two sets of three products that are sensitive to the kinetics in similar ways. These are discussed below.

Formation of But-1-ene, 4-Methylpent-1-ene, and 1-Hexene. Production rates of these three products are affected equally by five of the six H-transfer reactions, the lone exception being the 6-5MeH \rightarrow 3-5MeH isomerization that primarily impacts formation of but-1-ene and 4-methylpent-1-ene, a consequence of this reaction producing the direct precursor of these two products. Of the other H-transfer reactions, (12), (13), and (14) are the most important and the products are sensitive to both the forward and reverse rates, particularly for (14), which indicates that equilibrium constants impact the modeling of these species. As would be expected, each product is also highly sensitive to the specific β C–C bond scission reaction that leads to its formation. Less intuitive is that all of these species are strongly influenced by k_8 and k_7 , the rate constants for the β C-C bond sessions leading to isobutene and propene, respectively. In the case of but-1-ene and 4-methylpent-1-ene, which are formed competitively in the decomposition of 3-5MeH, the ratio of k_{10}/k_9 is given by our experiments (Figure 5). Note that k_{-16} is relatively unimportant, signifying that 3-5MeH goes predominantly to products without further isomerization. In our final fits, k_8 and k_7 have values that are very close to those found for related reactions in the hexyl and octyl systems. The five and six center H transfer reactions 6-5MeH \rightleftharpoons 2-5MeH (k_{14}) and 6-5MeH \rightleftharpoons 3-5MeH (k_{16}) likewise have values that are very similar to those deduced for the hexyl system. We could not, however, reproduce the observed low formation levels of 1-hexene and 1-butene unless the seven center primary to primary H-transfer reaction 1-5MeH $\rightleftharpoons 6-5$ MeH is relatively slow. It is deduced to be approximately a factor of 6 slower than the analogous six center reaction in 4-methylpentyl radical at 1000 K (k_{15} in McGivern et al.⁸) This is somewhat at odds with the octyl radical system, where the six and seven center primary to secondary H transfer reactions were deduced have rates equal within a factor of 2. The calculations of Hayes and Burgess⁹ suggest that, for seven center H-transfers, the primary to primary reaction has a barrier about 10 kJ mol⁻¹ higher than the primary to secondary reaction. This translates to a factor of 3.3 in rate at 1000 K on a per-H basis. Comparing with k_9 in Tsang et al.,⁷ the value of k_{12} is about 60% of that "expected" on this basis. It is not clear how to completely reconcile the slower rate deduced in the present system in comparison with the data from the 4-methylpentyl and octyl systems. Increasing k_{12} could be compensated by large increases in k_4 and k_{11} and k_{13} . One could also lower k_5 , k_6 , and k_{16} . Such fits would result in other inconsistencies. Uncertainties in the radical thermo-functions may also play a role. Our suspicion is that the actual rate constants for the seven center H-transfers should show a degree of correspondence similar to that observed for the five and six-center reactions. To date none of the studied systems have product pathways that may be uniquely identified with a seven center H-transfer and the apparent differences probably result from combined uncertainties in the various fits. More data or fitting all systems together could perhaps clarify the situation.

Formation of 3-Methylbut-1-ene, E-Hex-2-ene, and Z-Hex-**2-ene.** From Figure 7 it is seen that the products $E-C_6H_{12}$, $Z-C_6H_{12}$, and $3-MeC_4H_7$ are very sensitive to isomerization rate constants k_{11} and k_{13} , together with the rate constants for β bond fission k_1 , k_2 , and k_3 . The relative rates of the latter three rate constants are defined by our data (Figure 5) and, on the basis of thermochemical kinetic arguments, the absolute values cannot be too different from that of k_4 and analogous reactions of the hexyl radical. Note that the system is not very sensitive to k_{-11} . A primary interest in the present study is the rate of k_{13} since this reaction provides benchmark data on the rate of intramolecular abstraction of a tertiary H via a six-center transition state. The sensitivity analysis shows the interesting result that the allowable rate of this reaction is restricted by the data on the production of the above minor alkene products. This is largely because the 4-5MeH radical does not have a facile isomerization reaction available other than the reverse 4-5MeH \rightarrow 1-5MeH process, which is endothermic and slow compared with the three β C-C bond fissions, all of which are marked with specific products. With the ratio k_4/k_{11} expected to be similar to the analogous reactions observed in the hexyl radical system, the range of acceptable values of k_{13} is limited. Thus, although a relatively small amount of product is formed via 4-5MeH, this species is important in defining k_{13} , the rate constant of particular interest.

To better gauge the range of possible solutions, we have conducted a number of systematic explorations of the model predictions to key rate parameters and thermodynamic properties. As an illustration of the effect of the radical thermofunctions, Figure 8 shows the effect of raising or lowering by $R \ln 2$ the entropy of the two primary product forming radicals in the system while keeping the decomposition rate constants unchanged. It is seen that the fits are altered substantially although the temperature dependences are largely unaffected. The match to the experimental data can be recovered if corresponding changes are made to appropriate rate parameters.

Comparison of k_{13} , our rate constant for isomerization of *I*-5MeH \rightarrow 5-5MeH, with that found earlier⁵ for 1-hexyl \rightarrow 2-hexyl (a similar six-center isomerization reaction without a methyl substituent at carbon 5) shows that

$$k(1-5MeH \rightarrow 5-5MeH)/k(1-hexyl \rightarrow 2-hexyl) =$$

2.0 ± 0.35

On a per H basis, abstraction of a prototypical tertiary hydrogen by a primary carbon-centered radical via a six-center process is thus estimated to be 4.0 ± 0.7 times faster than the analogous abstraction of a secondary H. This increase in rate can be attributed to the effect of the methyl substituent. The uncertainties listed in the above values correspond to 1 standard deviation and have been estimated on the basis of empirical testing of the effect of rate constant changes during the fitting procedure.

Figure 8. Effect of the thermodynamic properties of 5-5MeH and 2-5MeH on the model results for the main three olefin products. The solid lines show our final fit. The dotted and dashed lines show the results if the entropy of the indicated radical is raised or lowered, respectively, by a factor of *R* ln 2 while keeping decomposition rate constants and other parts of the model unchanged.³⁴

Modeling the present system also requires rate parameters for reaction 15, 2-5MeH ₹ 5-5MeH, which involves the interconversion of a secondary and tertiary radical through a five-center transition state. Our value for this rate constant may be compared with that derived in our previous work for a fivecenter secondary to secondary transfer such as 2-octyl ≠ 4-octyl $(k_{14} \text{ in Tsang et al.}^7)$. Comparing our value of k_{15} with the octyl radical data indicates that, on a per-H basis, the presence of the methyl group increases the rate constant by a factor of 3.3. This is similar to the methyl effect on the six-center H transfer derived above and close to the value of about 2.8 predicted on the basis of the relative barriers calculated by Hayes and Burgess.9 The present system, however, is more sensitive to equilibrium constant K_{15} than the absolute rate of k_{15} ; thus although the given value appears consistent with expectations, the uncertainty is estimated as a factor of 2, somewhat higher than that for k_{13} .

It should be noted that the rate constants of Table 4 are given to a precision that allows accurate reproduction of the model results. This is not meant to imply absolute accuracy. We estimate the standard uncertainties in the absolute values are in the range of 1.5-2. This estimate does not include the uncertainties in the thermodynamic quantities. Much better defined are the product branching ratios, which have standard uncertainties (1 σ) of typically $\pm 6\%$ and translate through the model to relative rate constants. Priority in any model of the system should be given to matching the experimental branching ratios; it is thus not appropriate to arbitrarily vary individual rate constants within their estimated uncertainties with no regard to the effect on the global fit. Matching the experimental branching ratios necessarily requires a degree of cancellation of errors in the rate constants, significantly improving the fidelity of the model for purposes of extrapolation.

Relative Rates of β C–C Bond Fission. As shown in Figure 5, our results provide direct information on the relative rates of several C–C bond fission reactions. At 969 K loss of ethyl from 4-5MeH is found to be factors of 2.54 ± 0.13 and 4.93 ± 0.34 faster than fission of methyl to give *E*-hex-2-ene and *Z*-hex-2-ene, respectively, where the uncertainties are reported as the standard errors (1 σ) in the relative rates from the regression analyses of the data of Figure 5. Ejection of methyl from 4-5MeH occurs so as to preferentially give the *E* isomer of hex-2-ene, which is the thermodynamically more stable species. In the similar decompositions of 3-hexyl and 3-heptyl radicals, where the competitions are between ejection of methyl and ethyl or *n*-propyl, respectively, we previously found that rates for the larger alkyl group were higher at 1000 K by factors of 3.2 and 3.1, respectively. The averaged per-group relative rate for ethyl

vs. methyl ejection from the present data is $[2k_1/(k_2 + k_3)]$, which has a value of 3.0 at 1000 K.

From the relative amounts of but-1-ene and 4-methylpent-1-ene we find that fission of isopropyl from 3-5MeH is a factor of (10.7, \pm 0.8/ \pm 1.9) faster than fission of the methyl group. Our error limits are asymmetrical in this case to account for a small potential contribution to but-1-ene from the decomposition of 3-methylbutyl radicals as discussed previously. To our knowledge this is the first experimental measurement of the relative rate for ejection of methyl and a secondary alkyl group from an alkyl radical. It is interesting that the rate differences in C–C bond fissions in the radicals considered here are very close to the rate differences observed in closed shell hydrocarbons, despite the 200 kJ mol⁻¹ difference in the bond energies.

The mechanism contains five C–C bond fissions in addition to those considered above. The relevant rate constants are k_4 , k_5 , k_6 , k_7 , and k_8 . Our experiments provide information on the rates of these processes insofar as our model of the system is correct. We have fixed k_4 on the basis of our hexyl radical data. As seen from the sensitivity analysis, many parts of the system depend on the value of k_8 , including the minor products but-1-ene, 4-methylpentene, and hex-1-ene. The fact that these products arise from radicals that are two or three H-transfer reactions removed from reaction 8 gives some indication of the connectedness of the system. Fairly wide ranges of rate constants were found to yield reasonable fits to the data at the midpoint of our temperature range. The allowed values are narrowed considerably by the temperature dependences of the branching ratios.

The slight deviations of the model from experiment can arise from a number of factors. As noted earlier, the required kinetics are linked to the thermodynamic properties of the radicals and these have a degree of uncertainty. There are likewise uncertainties in the parameters and assumptions used in the RRKM/ME analysis. Increasing, for example, the energy transfer parameter to 500 cm⁻¹ slightly changes the derived rate constants but has no significant impact on the quality of the fits. Finally the possibility of small, undetected systematic errors in the experiments could impact the derived branching ratios, particularly the slopes of the data. In this regard it would be desirable to have more extensive data covering a broader temperature range. The most remarkable feature of the present results, however, is how well the data can be fit using rate parameters that are very similar to those derived earlier for analogous systems. This suggests that the present benchmark data can be generalized for use in modeling the chemistry of related branched hydrocarbons, such as those found in Fischer-Tropsch fuels.

TABLE 5: Deviation of the Rate Constants for β C–C Bond Fission from Their High-Pressure Limits at Selected Temperatures and Pressures, Given as Values of $k(T,P)/k_{\infty}^{a}$

-					-							
rate constant	pressure/bar	500 K	600 K	700 K	800 K	900 K	1000 K	1100 K	1300 K	1500 K	1700 K	1900 K
k_1	0.1	0.937	0.760	0.498	0.279	0.160	0.103	0.078	0.064	0.073	0.099	0.135
	1	0.991	0.945	0.818	0.617	0.424	0.286	0.207	0.138	0.125	0.138	0.165
10 100	0.999	0.992	0.966	0.896	0.775	0.624	0.487	0.312	0.239	0.224	0.229	
	1.000	0.999	0.996	0.985	0.959	0.908	0.830	0.638	0.485	0.411	0.371	
	1000	1.000	1.000	1.000	0.998	0.995	0.988	0.975	0.917	0.819	0.723	0.634
k_2	0.1	0.909	0.701	0.432	0.229	0.127	0.082	0.063	0.054	0.064	0.088	0.123
	1	0.986	0.926	0.779	0.565	0.374	0.247	0.177	0.119	0.109	0.124	0.150
	10	0.998	0.99	0.957	0.876	0.743	0.585	0.448	0.28	0.214	0.202	0.210
	100	1.000	0.999	0.995	0.982	0.952	0.894	0.810	0.608	0.455	0.383	0.346
	1000	1.000	1.000	1.000	0.998	0.994	0.986	0.971	0.907	0.802	0.703	0.611
k_3	0.1	0.927	0.738	0.47	0.257	0.145	0.093	0.071	0.059	0.069	0.093	0.129
	1	0.989	0.939	0.802	0.594	0.402	0.268	0.193	0.129	0.117	0.131	0.157
	10	0.999	0.992	0.962	0.887	0.761	0.606	0.469	0.297	0.227	0.213	0.220
	100	1.000	1.000	0.995	0.984	0.956	0.902	0.821	0.625	0.471	0.397	0.359
	1000	1.000	1.000	1.000	0.998	0.995	0.987	0.973	0.913	0.811	0.713	0.623
k_4	0.1	0.743	0.398	0.157	0.075	0.059	0.062	0.073	0.099	0.136	0.178	0.226
	1	0.962	0.803	0.512	0.284	0.183	0.146	0.138	0.140	0.162	0.196	0.237
	10	0.997	0.972	0.878	0.707	0.531	0.403	0.324	0.248	0.230	0.245	0.272
	100	1.000	0.997	0.985	0.953	0.891	0.803	0.702	0.518	0.409	0.376	0.367
	1000	1.000	1.000	0.998	0.995	0.987	0.972	0.948	0.854	0.728	0.641	0.574
k_5	0.1	0.836	0.589	0.331	0.170	0.097	0.071	0.061	0.063	0.077	0.096	0.124
	1	0.979	0.915	0.763	0.551	0.362	0.247	0.181	0.130	0.121	0.127	0.148
	10	0.998	0.991	0.967	0.904	0.776	0.623	0.478	0.301	0.228	0.204	0.208
	100	1.000	0.999	0.997	0.991	0.970	0.926	0.844	0.643	0.482	0.392	0.352
	1000	1.000	1.000	0.999	0.999	0.997	0.993	0.980	0.927	0.830	0.721	0.631
k_6	0.1	0.812	0.555	0.302	0.151	0.086	0.064	0.055	0.058	0.072	0.09	0.118
	1	0.976	0.904	0.742	0.525	0.340	0.230	0.168	0.120	0.113	0.120	0.141
	10	0.998	0.99	0.964	0.895	0.761	0.604	0.459	0.286	0.215	0.194	0.198
	100	1.000	0.999	0.996	0.989	0.967	0.919	0.835	0.629	0.467	0.379	0.339
	1000	1.000	1.000	0.999	0.999	0.997	0.992	0.979	0.922	0.822	0.711	0.620
k_7	0.1	0.950	0.795	0.543	0.317	0.183	0.115	0.08	0.055	0.051	0.057	0.071
	1	0.994	0.961	0.859	0.680	0.486	0.335	0.233	0.139	0.106	0.098	0.105
	10	0.999	0.995	0.977	0.926	0.827	0.694	0.553	0.350	0.245	0.201	0.186
	100	1.000	1.000	0.997	0.990	0.972	0.936	0.875	0.706	0.541	0.435	0.371
	1000	1.000	1.000	1.000	0.999	0.997	0.993	0.984	0.945	0.873	0.783	0.691
k_8	0.1	0.943	0.755	0.475	0.261	0.152	0.098	0.073	0.056	0.059	0.072	0.093
	1	0.992	0.946	0.813	0.605	0.415	0.282	0.202	0.132	0.110	0.111	0.124
	10	0.999	0.993	0.967	0.896	0.777	0.628	0.491	0.318	0.232	0.201	0.194
	100	1.000	0.999	0.996	0.986	0.959	0.909	0.830	0.648	0.489	0.397	0.347
	1000	1.000	1.000	1.000	0.998	0.995	0.988	0.973	0.916	0.816	0.709	0.617
k_9	0.1	0.91	0.772	0.573	0.378	0.24	0.165	0.124	0.098	0.101	0.114	0.140
	1	0.984	0.942	0.859	0.728	0.568	0.431	0.326	0.219	0.179	0.169	0.183
	10	0.998	0.991	0.972	0.938	0.873	0.779	0.659	0.459	0.341	0.288	0.274
	100	1.000	0.999	0.996	0.991	0.981	0.964	0.928	0.797	0.640	0.527	0.464
	1000	1.000	1.000	1.000	0.999	0.998	0.997	0.994	0.979	0.932	0.851	0.767
k_{10}	0.1	0.821	0.648	0.440	0.265	0.158	0.106	0.080	0.068	0.074	0.087	0.113
	1	0.964	0.898	0.790	0.638	0.469	0.339	0.248	0.164	0.136	0.132	0.148
	10	0.995	0.983	0.955	0.909	0.828	0.717	0.586	0.386	0.28	0.235	0.228
	100	1.000	0.998	0.994	0.987	0.973	0.951	0.906	0.752	0.583	0.468	0.409
	1000	1.000	1.000	0.999	0.999	0.997	0.995	0.992	0.974	0.915	0.821	0.729

^{*a*} To account for numerical round-off errors, ratios have been normalized (an adjustment of typically a few percent or less) so that the high-pressure limiting values of $k(T,P)/k_{\infty}$ are exactly 1.

Extrapolated Results for Chemical Modeling. We have used our model to project our results to temperatures ranging from 500 to 1900 K and pressures of 0.1–1000 bar. These data are presented in Tables 5 and 6 and are given as fractional deviations of the rate constants from their high-pressure limits (Table 4). These data represent limiting values after the induction period is over and steady-state energy distributions have been established. Data are given in tabular form because of the difficulty in providing accurate analytical expressions covering the full range of conditions considered. In Table S2 of the Supporting Information we provide analytical expressions that approximate the rate constants in a modified Arrhenius format compatible with the PLOG function in CHEMKIN PRO. This function allows a facile, though not fully accurate, description

of the pressure dependence through interpolation between values at specified pressures. Differences between the analytical values and the RRKM/ME results at selected pressures and temperatures are given in Tables S3 and S4 (Supporting Information) and are found to be up to about 60%. If greater accuracy is required, it will be necessary to interpolate between the values in Tables 5 and 6 or parametrize the data over a narrower range of conditions.

5. Conclusions

The branching ratios of the products formed in the decomposition and isomerization of 5-methylhex-1-yl radicals have been precisely measured. The data show that isomerization of _

TABLE 6: Deviation of the Rate Constants for Isomerization from Their High-Pressure Limits at Selected Temperatures and Pressures, Given as Values of $k(T,P)/k_{\infty}^{a}$

rate constant	P/bar	500 K	600 K	700 K	800 K	900 K	1000 K	1100 K	1300 K	1500 K	1700 K	1900 K
k_{11}	0.1	0.971	0.783	0.479	0.284	0.203	0.172	0.172	0.189	0.225	0.263	0.306
	1	0.996	0.946	0.771	0.551	0.403	0.323	0.289	0.26	0.266	0.287	0.32
10 100	10	1.000	0.993	0.954	0.857	0.726	0.604	0.517	0.404	0.357	0.350	0.363
	100	1.000	0.999	0.995	0.979	0.946	0.890	0.819	0.662	0.546	0.493	0.467
	1000	1.000	1.000	0.999	0.998	0.994	0.985	0.971	0.908	0.81	0.729	0.661
k_{-11}	0.1	0.993	0.931	0.748	0.502	0.315	0.204	0.147	0.103	0.102	0.122	0.156
	1	0.999	0.988	0.927	0.781	0.592	0.426	0.314	0.201	0.167	0.169	0.189
	10	1.000	0.999	0.988	0.95	0.863	0.732	0.596	0.394	0.296	0.264	0.259
	100	1.000	1.000	0.999	0.993	0.977	0.941	0.878	0.701	0.543	0.455	0.404
	1000	1.000	1.000	1.000	0.999	0.997	0.993	0.982	0.935	0.846	0.751	0.658
k_{12}	0.1	0.978	0.817	0.528	0.33	0.241	0.204	0.197	0.209	0.241	0.277	0.317
	1	0.997	0.955	0.8	0.593	0.447	0.364	0.321	0.285	0.284	0.302	0.332
	10	1.000	0.994	0.961	0.875	0.755	0.64	0.548	0.431	0.377	0.367	0.375
	100	1.000	0.999	0.996	0.982	0.952	0.902	0.835	0.682	0.563	0.508	0.477
	1000	1.000	1.000	1.000	0.998	0.995	0.987	0.973	0.914	0.818	0.739	0.668
k_{-12}	0.1	0.992	0.937	0.775	0.556	0.382	0.276	0.216	0.171	0.168	0.176	0.198
	1	1.000	0.992	0.952	0.843	0.682	0.532	0.419	0.293	0.243	0.226	0.232
	10	1.000	1.000	0.995	0.977	0.921	0.824	0.703	0.502	0.385	0.329	0.309
	100	1.000	1.000	1.000	0.998	0.991	0.972	0.929	0.784	0.632	0.526	0.464
	1000	1.000	1.000	1.000	1.000	0.999	0.997	0.992	0.96	0.891	0.801	0.715
k_{13}	0.1	0.993	0.917	0.729	0.560	0.459	0.403	0.381	0.376	0.402	0.430	0.462
	1	0.999	0.982	0.901	0.767	0.652	0.572	0.523	0.470	0.456	0.461	0.479
	10	1.000	0.998	0.983	0.938	0.867	0.789	0.721	0.617	0.556	0.532	0.527
	100	1.000	1.000	0.998	0.992	0.977	0.949	0.909	0.809	0.716	0.663	0.627
	1000	1.000	1.000	1.000	1.000	0.997	0.994	0.986	0.952	0.892	0.835	0.780
k_{-13}	0.1	0.998	0.964	0.831	0.624	0.446	0.32	0.242	0.169	0.146	0.147	0.164
	1	1.000	0.995	0.959	0.856	0.705	0.554	0.436	0.298	0.234	0.211	0.21
	10	1.000	0.999	0.994	0.971	0.914	0.817	0.703	0.513	0.391	0.33	0.301
	100	1.000	1.000	0.999	0.997	0.987	0.962	0.917	0.783	0.637	0.533	0.465
	1000	1.000	1.000	1.000	1.000	0.999	0.995	0.988	0.954	0.882	0.793	0.707
k_{14}	0.1	0.998	0.978	0.896	0.743	0.585	0.467	0.383	0.311	0.295	0.294	0.306
	1	1.000	0.997	0.982	0.925	0.819	0.700	0.592	0.456	0.391	0.359	0.349
	10	1.000	0.999	0.998	0.991	0.962	0.903	0.818	0.653	0.541	0.474	0.438
	100	1.000	1.000	1.000	0.999	0.996	0.986	0.961	0.865	0.75	0.657	0.590
	1000	1.000	1.000	1.000	1.000	1.000	0.999	0.996	0.977	0.933	0.868	0.799
k_{-14}	0.1	0.999	0.979	0.888	0.713	0.528	0.386	0.288	0.191	0.153	0.142	0.148
	1	1.000	0.997	0.977	0.906	0.780	0.635	0.503	0.336	0.253	0.215	0.203
	10	1.000	1.000	0.997	0.983	0.943	0.869	0.767	0.569	0.43	0.354	0.313
	100	1.000	1.000	1.000	0.998	0.992	0.977	0.945	0.835	0.697	0.587	0.508
	1000	1.000	1.000	1.000	1.000	0.999	0.998	0.993	0.972	0.925	0.857	0.779
k_{15}	0.1	0.994	0.944	0.78	0.549	0.357	0.235	0.166	0.104	0.085	0.082	0.094
	1	0.999	0.992	0.946	0.828	0.655	0.488	0.361	0.218	0.158	0.135	0.135
	10	0.999	0.999	0.992	0.965	0.900	0.793	0.666	0.448	0.317	0.252	0.227
	100	1.000	1.000	0.999	0.996	0.985	0.960	0.914	0.768	0.606	0.489	0.416
	1000	1.000	1.000	1.000	1.000	0.998	0.995	0.989	0.958	0.895	0.811	0.72
k_{-15}	0.1	0.988	0.893	0.658	0.408	0.249	0.16	0.114	0.079	0.074	0.081	0.099
	1	0.998	0.98	0.897	0.723	0.528	0.372	0.268	0.169	0.132	0.124	0.131
	10	1.000	0.998	0.984	0.935	0.836	0.698	0.558	0.364	0.261	0.218	0.203
	100	1.000	1.000	0.998	0.991	0.972	0.930	0.859	0.681	0.516	0.413	0.354
	1000	1.000	1.000	1.000	0.999	0.997	0.991	0.978	0.925	0.827	0.717	0.619
k_{16}	0.1	0.988	0.913	0.722	0.491	0.325	0.231	0.179	0.148	0.149	0.161	0.187
	1	0.999	0.988	0.936	0.809	0.635	0.485	0.374	0.263	0.220	0.209	0.220
	10	1.000	0.999	0.993	0.971	0.905	0.798	0.670	0.471	0.360	0.309	0.296
	100	1.000	1.000	0.999	0.998	0.989	0.967	0.918	0.766	0.612	0.508	0.452
	1000	1.000	1.000	1.000	1.000	0.999	0.997	0.991	0.956	0.885	0.792	0.708
k_{-16}	0.1	0.963	0.853	0.657	0.443	0.281	0.188	0.136	0.099	0.096	0.105	0.126
	1	0.994	0.966	0.893	0.766	0.601	0.453	0.338	0.218	0.17	0.156	0.164
	10	0.999	0.995	0.98	0.947	0.885	0.788	0.664	0.452	0.326	0.266	0.248
	100	1.000	1.000	0.997	0.993	0.983	0.965	0.928	0.790	0.622	0.499	0.430
	1000	1.000	1.000	1.000	0.999	0.998	0.997	0.994	0.979	0.925	0.834	0.741

^{*a*} To account for numerical round-off errors, ratios have been normalized (an adjustment of typically a few percent or less) so that the high-pressure limiting values of $k(T,P)/k_{\infty}$ are exactly 1.

the starting radical is faster than its decomposition via β C–C bond fission and that 5-methylhex-5-yl and 5-methylhex-2-yl are the primary product-forming radicals in the system. Relative rates of ejection of methyl, ethyl, and isopropyl from intermediate radicals have been measured. The observed olefin product

ratios have been fit with a kinetic model derived via a timedependent RRKM/Master Equation analysis and the highpressure rate expressions for 6 reversible isomerizations and 10 β C–C bond scission channels have been obtained. The observed high yield of isobutene indicates the importance of the 1-5 hydrogen shift in the starting radical. Compared with the value for the 1-hexyl radical, the methyl group increased the reaction rate for 1-5 hydrogen transfer by about a factor of about 4 on a per hydrogen basis. The present system also provides new information on the seven-center primary to primary H-transfer reaction and the five-center secondary to tertiary H-transfer. The results are projected over the temperature range of (500-1900) K and pressures of (0.1-1000) bar.

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Supporting Information Available: Product data and conditions of individual experiments (Table S1), representative chromatograms from the GC analyses (Figures S1 and S2), approximate analytical expressions for the rate constants at selected pressures in the PLOG format used by CHEMKIN PRO, together with tables of the deviations from the RRKM/ ME result, and molecular properties of the methylhexyl radicals and transition states used in the RRKM/ME model (Tables S5–S28). This material is available free of charge via the Internet at http://pubs.acs.org.

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