



The decomposition of 2-pentyl and 3-pentyl radicals

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Abstract

The isomerization and decomposition reactions of 2-pentyl and 3-pentyl radicals have been studied in a single-pulse shock tube over a temperature range of 973–1121 K and pressures of 120–800 kPa. The results represent the first direct study of the alkene product branching ratio resulting from the kinetics of the competition between isomerization and beta C–C bond scission for a secondary straight-chain alkyl radical at high temperatures. Such species are representative of intermediates important in the combustion of typical hydrocarbon fuels. In the present work, a small quantity of precursor ($\sim 45 \mu\text{L/L}$) is used to thermally generate H atoms in the presence of excess (*E*)-2-pentene, leading to the radicals of interest via addition of H to the double bond. Decomposition of the chemically activated pentyl radicals results in the stable olefin products ethene, propene, and 1-butene, which are detected in postshock gas chromatographic analyses utilizing flame-ionization and mass-spectrometric detection. It is shown that the olefin product ratios can be related to the isomerization and decomposition reactions of the 2-pentyl and 3-pentyl radicals and the results are consistent with the existence of distinct non-overlapping cracking patterns for the two radicals. The data are compared with predictions made on the basis of a model developed from experiments on the decomposition of thermal (i.e. not chemically activated) 1-pentyl radicals. Good agreement is observed. In conjunction with an RRKM/Master Equation analysis, the results for 2-pentyl and 3-pentyl radicals are projected over a wide range of temperatures. In addition, the rate constants for addition of H atoms to the alternate double bond positions of (*E*)-2-pentene are derived relative to a standard reaction and absolute rate constants for these processes are reported.

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Keywords: 2-Pentyl; 3-Pentyl; Kinetics; H-atoms; (*E*)-2-pentene

1. Introduction

Alkyl radicals are prominent species formed during the combustion of hydrocarbon fuels and their unimolecular decomposition reactions compete with bimolecular oxidation steps. Under many conditions the unimolecular processes are

the main initial reactions. The pyrolysis steps involve isomerization reactions and the formation of olefins and smaller alkyl radicals via beta bond scission reactions. The cracking pattern of the parent radical is a primary determinant of the subsequent behavior of the system: it influences both the course of oxidation and the formation of unwanted byproducts such as soot. Reliable kinetic data and an understanding of the decomposition mechanisms is required to develop accurate simulation based engineering models used in combustion energy science [1–3].

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In previous work we have examined the decomposition of a number of 1-alkyl radicals [4–6] and have carried out Rice Ramsberger Kassel Marcus/Master Equation (RRKM/ME) analyses to fit the data and project the results over the pressure and temperature conditions of interest to combustion energy scientists. The RRKM/ME analyses require the construction of potential energy surfaces (PES) for the decomposition reactions, and these typically involve a number of competing channels with similar barriers. The quality of the model, and hence the accuracy of the kinetic extrapolations, can be improved if one is able to enter the system from multiple positions on the PES.

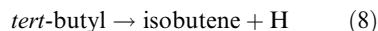
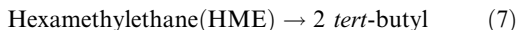
We have recently investigated the decomposition and isomerization reactions of the 1-pentyl radical at temperatures near 1000 K and pressures between 80 and 5000 kPa [7,8]. The present work represents an effort to confirm the results by entering the C_5H_{11} system from the side of the secondary alkyl radicals. There appear to be no previous experimental studies that directly probe the decomposition pattern of non-cyclic secondary alkyl radicals at high temperatures.

2. Experimental procedures [9]

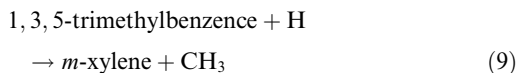
A heated single pulse shock tube has been used to carry out the experiments. Earlier publications [6,10] describe the instrument and general analytical procedures in detail. Experimental temperatures ranged from 973 to 1121 K and shock pressures were 120–800 kPa. Heating times, as derived from recorded pressure traces, were $500 \pm 50 \mu s$.

To generate the pentyl radicals of interest, we place a small amount (typically $45 \mu L/L$) of a hydrogen atom precursor in the presence of a large excess ($5000 \mu L/L$) of (E)-2-pentene. Hydrogen atoms add rapidly to the double bond, forming either the 2-pentyl or the 3-pentyl radical, depending on the site of addition. Reactions (1)–(6) in Scheme 1 summarize the postulated chemistry, and lead to ethene, propene and 1-butene as stable olefin products. Products that may be uniquely identified with specific precursor radicals are enclosed in boxes. A key point is that the product spectrums from 2-pentyl and 3-pentyl radicals are distinct and do not overlap. This will be justified later, but is a consequence of the slowness of the isomerization of 3-pentyl radical, so that this species undergoes only beta scission of the CH_3 group under our conditions. Also note that the radical intermediates decompose on the time scale of a few microseconds or less, even at the lowest temperatures of our studies. The concentrations of the main products can thus not be significantly affected by the small fraction of radicals that survive until the postshock quenching period.

We form the necessary hydrogen atoms by the thermal decomposition of hexamethylethane (HME), reactions 7 and 8, a technique used in this laboratory for many years [11]:



Chain processes are controlled by the addition of about $5000 \mu L/L$ of the free radical scavenger 1,3,5-trimethylbenzene (135TMB). Some H atoms are lost by reaction with 135TMB, either via abstraction of H to give the unreactive 3,5-dimethylbenzyl radical (DMB), or displacement of methyl from the ring to produce m-xylene:



Methyl radicals produced above can similarly abstract H from 135TMB. H atoms and methyl radicals can also abstract H from 2-pentene. These reactions and the recombination processes of stabilized radicals lead to some secondary products that will be discussed subsequently, but this chemistry will be shown to have no impact on the C2–C4 olefins of primary interest.

Product analysis employs an Agilent Technologies 6890N gas chromatograph (GC) equipped with a J & W Scientific DB-1 $30 \text{ m} \times 0.53 \text{ mm}$ internal diameter (i.d.) fused silica capillary column for the larger species and a Restek $30 \text{ m} \times 0.53 \text{ mm}$ i.d. Rt–Alumina (aluminum oxide porous layer) capillary column for the lighter components. The GC is equipped with both flame ionization detection (FID) and an Agilent Technologies 5973 Inert mass selective detector. The sample eluting from the DB-1 column was split for simultaneous identification and quantification of the mixture components by mass spectrometry and FID analysis. The GC oven temperature was programmed from $-60 \text{ }^\circ\text{C}$ to $180 \text{ }^\circ\text{C}$.

Shock temperatures are determined by following the progression of a standard reaction with a known rate constant. At temperatures above 1020 K we utilized the decomposition of HME as our temperature standard, using the known [12,13] rate expression $k(\text{HME} \rightarrow 2\text{-t-butyl}) = 10^{15.4} \exp(-31100/T) \text{ s}^{-1}$. At temperatures lower than 1020 K we employed the decomposition of chlorocyclopentane. This standard is more accurate than HME at lower temperatures where conversion of HME is very low. It additionally provides a direct comparison with results from our study of 1-pentyl radical, where it was also used. The rate expression $k(\text{chlorocyclopentane} \rightarrow \text{cyclopentene} + \text{HCl}) = 10^{15.4} \exp(-31100/T) \text{ s}^{-1}$ is from our recent comprehensive study [14] and critical evaluation of several temperature standards. Around 1020 K, where both standards should be

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