J. Phys. Chem. A **2006,** *110,* 8501−8509

Mechanism and Rate Constants for the Decomposition of 1-Pentenyl Radicals[†]

Wing Tsang

National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received: April 13, 2005; In Final Form: July 19, 2005

This paper is concerned with the mechanisms and rate constants for the decomposition of 1-penten-3-yl, 1-penten-4-yl, and 1-penten-5-yl radicals. They are formed from radical attack on 1-pentene, which is an important decomposition product of normal alkyl radicals with more than 6 carbon atoms in combustion systems. This work is based on related data in the literature. These involve rate constants for the reverse radical addition process under high-pressure conditions, chemical activation experiments, and more recent direct studies. The high-pressure rate constants are based on detailed balance. The energy transfer effects and the pressure dependences of the rate constants are determined through the solution of the master equation and are projected to cover combustion conditions. The low barriers to these reactions make it necessary to treat these thermal reactions as open systems, as in chemical activation studies. The multiple reaction channels make the nature of the pressure effects different from those usually described in standard texts. The order of stability is 1-penten-3-yl ≈ 1-penten-4-yl > 1-penten-5-yl and straddles those for the *n*-alkyl radicals. A key feature in these reactions is the effects traceable to allylic resonance. However, the 50 kJ/mol allylic resonance energy is not fully manifested. The important unsaturated products are 1,3-butadiene, the pentadienes, allyl radicals, and vinyl radicals. The results are compared with the recommendations in the literature, and significant differences are noted. Extensions to larger radicals with similar structures are discussed.

Introduction

This study is part of a program to develop chemical kinetic databases that can be used for the description of the behavior of real liquid transportation fuels. We are particularly interested in developing an understanding of the scale and nature of such efforts. The aim is to enable the increased capability of the new computational fluid dynamics (CFD) tools for handling detailed chemistry. This can lead to exciting possibilities for simulating real systems and developing new design tools.

Hydrocarbon fuels contain large quantities of normal alkanes.[1] Their pyrolytic reactions compete with oxidation and lead to the formation of precursors of soot/polycyclic aromatic hydrocarbons (PAHs). The mechanism for pyrolytic breakdown involves successive degradation of large radical structures via isomerization and beta bond cleavage to smaller unsaturated fragments. These can serve as part of the boundary conditions for soot/PAH models. This work concerns the breakdown of the 1-pentenyl radicals formed as a consequence of the abstraction of hydrogen atoms from 1-pentene. The latter is formed via the following sequence of reactions: normal alkanes (beginning with hexane) => alkyl radicals with the electron in the 4 position => 1-pentene + alkyl radical. Relevant structures and mechanisms can be found in Figure 1. Energy level diagrams for the three processes are in Figure 2. Broadly speaking, they cover the full range of radical decomposition processes likely to be encountered. The first, for 1-penten-3-yl, is a straightforward single-step β-bond scission. The second involves a rapid isomerization. In the third process, the isomerization is an integral part of the decomposition process.

There has been considerable recent work in simulating the combustion of larger and more realistic liquid fuels.[2−5] Most of the focus has been on reproducing behavior traceable to oxidative processes. Although the databases used in the simulations contain a sampling of the pyrolytic reactions of the larger radicals, the selection of mechanisms and assignment of rate constants for these processes have not been critical to the success of these studies. Since there are few direct kinetic studies, it is difficult to build the database by simply abstracting results directly from the literature. In most of the earlier studies, the isomeric nature of the 1-olefinyl radicals was ignored. Thus, the extension of such databases for soot/PAH applications is problematic. Curran et al.[2] developed probably the most complete and traceable chemical kinetic database for the combustion of heptane. They assumed that the main decomposition channel for the 1-olefinyl radicals is the formation of the

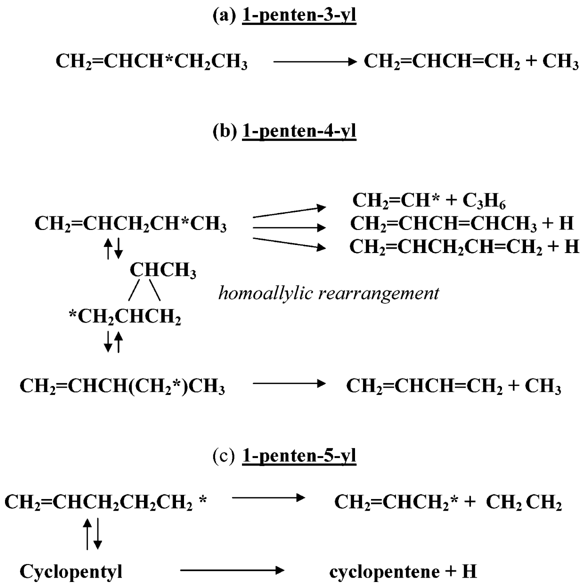

Figure 1. Structures of the radicals under consideration and their mechanisms for decomposition and isomerization.

[†] Part of the Chava Lifshitz Memorial Issue.

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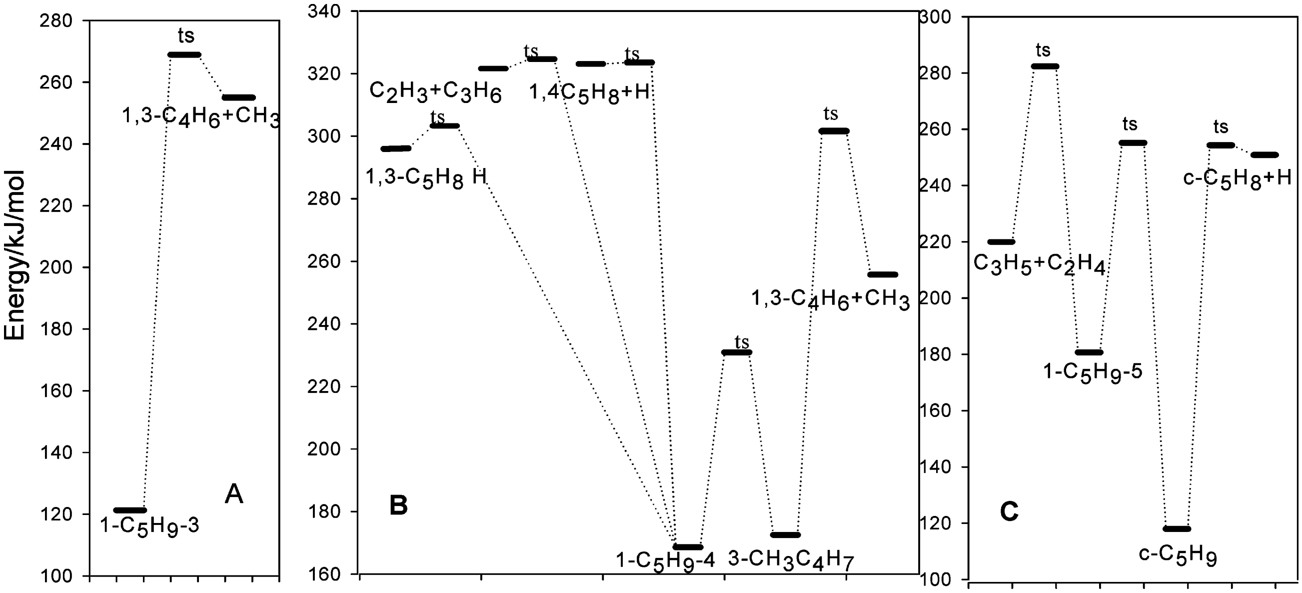

Figure 2. Energy level diagram for the decomposition of 1-penten-3-yl, 1-penten-4-yl, and 1-penten-5-yl radicals. Energies are based on the discussion given in the text.

allyl radical and the appropriate alkene. In the present case, this would be ethylene. The rate expression is estimated to be $2.5 \times 10^{13} \exp(-22700/T)$ s^{-1}. This implies that radical attack on 1-pentene will lead to the formation of the 1-pentenyl-5 radical.

The rate constants related to the unimolecular breakdown or isomerization of many organic radicals, and the 1-pentenyl radicals in particular, under combustion conditions will be affected by energy transfer effects. The processes are characterized by low barriers for reactions. By low barriers we mean the situation in which the peak of the molecular energy distribution function is near or above the reaction threshold. With these low barriers, at sufficiently high temperatures, it becomes impossible to establish a steady-state distribution of reactant energies using the standard "closed" system approach (i.e., a system in which the reactant molecule is present at time = 0, and the rate of reaction is determined by following its concentration decay). To describe any system in terms of rate constants, it is necessary that a steady-state energy distribution function be achieved before significant reaction occurs. This is the standard approach for the treatment of thermal unimolecular reactions described in standard texts and, as will be shown in this study, is actually only appropriate for reactions with high reaction thresholds. Instead, we have found that an "open" system, as in chemical activation (in which reactive molecules are continuously created), is the only means to accurately derive rate constants, since the influx of reactive species guarantees the achievement of a steady-state distribution. This reflects the actual physical situation for the decomposition of the 1-pentenyl radicals, since the unstable radicals are created in the course of the reaction process.

An important issue is the internal energy of the radical. For this study, we assume that they are formed by the abstraction of a hydrogen atom from 1-pentene. Since the 1-pentene must have equilibrated with the bath, we make the additional assumption that removing a hydrogen will not have significant effects on the internal energy of the radical. If the 1-pentenyl radicals were formed by a different mechanism (i.e., by an addition reaction), then rate constants could be different. Indeed, the initial rate constant will be that of a chemical activation process. This is an added complication. Together with the increased number of molecules and reaction pathways, they represent problems that must be faced as one attempts to build databases for more realistic fuels. For current CFD codes, the systematic reduction of the mechanism will be absolutely necessary. The entire process can only be initiated with a database that is as complete as possible. The neglect of a reaction is equivalent to assigning it a rate constant of zero.

We have developed a procedure for carrying out calculations[6,7] to take account of energy transfer effects. We solve the master equation for the molecular distribution function of the reacting molecule, and, when this is combined with the specific rates from Rice−Ramsperger−Kassel−Marcus (RRKM) calculations, rate constants as a function of time are obtained. The inputs for these calculations are the same as those required for the computation of the JANNAF tables,[8] except that the properties of the transition state are also required, and parameters for specifying energy transfer, the step-size down, must be defined. This leads to the determination of the complete temporal history of the rate constants, beginning with the incubation or induction period (the time required for all the rate constants of the system to become time independent) and ending with the rate constant appropriate for the steady-state energy distribution.

The organization of the paper is as follows: We begin with a brief discussion of the scope of the problem. We will summarize the basic information (thermodynamics and experimental) used to derive the mechanisms and rate constants on the decomposition of these radicals. High-pressure rate expressions for the isomerization and β C−C bond cleavage reactions will then be extracted. These will be projected to cover temperatures and pressures relevant to combustion applications. The paper will conclude with a discussion of the significance of these results and possible extensions to larger fuel fragments.

Problem Definition

The 1-pentenyl radicals under consideration are characterized by unpaired electrons in the 3, 4, and 5 positions. Radicals at the 1 and 2 positions can only be formed from the much slower abstraction of vinylic H atoms and are expected to be much less important. They are not considered here. The specific reactions are given in Figure 1. Figure 2 contains an energy level diagram of the processes of interest. The energy scale is derived on the basis of the subsequent discussion.

The decomposition of 1-penten-3-yl is a single-step reaction. This is a resonance-stabilized radical, and rate constants can be

TABLE 1: Equilibrium Constants of Formation for the Five Radicals of Interest

radicals	$\log_{10}$ (equilibrium constant of formation, 1 bar std state)
1-C_5H_9-3	$-17.502 - 5279/T + 6.69 \times 10^5/T^2 - 3.96 \times 10^8/T^3 + 5.35 \times 10^{10}/T^4$
1-C_5H_9-4	$-16.322 - 7125/T + 2.88 \times 10^5/T^2 - 2.90 \times 10^8/T^3 + 4.22 \times 10^{10}/T^4$
3-CH_3-1-C_4H_7-4	$-16.725 - 8081/T + 4.00 \times 10^5/T^2 - 3.00 \times 10^8/T^3 + 4.22 \times 10^{10}/T^4$
1-C_5H_9-5	$-16.960 - 8069/T + 3.86 \times 10^5/T^2 - 3.03 \times 10^8/T^3 + 4.29 \times 10^{10}/T^4$
c-C_5H_9	$-18.812 - 6175/T + 14.34 \times 10^5/T^2 - 6.32 \times 10^8/T^3 + 7.98 \times 10^{10}/T^4$

expected to be smaller than those found when it is absent. 1-Penten-4-yl and 1-penten-5-yl decompositions also involve isomerizations. Note the presence of the homoallylic rearrangement for the 1-penten-4-yl radical. An interesting aspect of the decomposition of the 1-penten-5-yl radical is the possibility of cyclization to form cyclopentyl. Since this can ultimately lead to cyclopentadiene, an important issue is the contribution of these reactions to PAH/soot formation mechanisms. These isomerization reactions are brought about by the presence of the double bond. For *n*-alkyl radicals, 1,4 and higher hydrogen atom migrations are the only modes for isomerization. For 1-olefinyl radicals larger than the 1-pentenyl radicals considered here, hydrogen atom migration processes will also contribute to isomerization. Another important aspect of the 1-olefinyl radicals is their formation from the decomposition of cycloalkyl radicals. Their precursors, the cycloalkanes, are important components of common liquid fuels.

Basis for Estimates

Since there are very few direct experimental data that deal with the processes of interest, estimates will be largely based on measurements that can be related to the reactions through detailed balance. A great deal of the work will depend on estimates of the properties of the radicals. In the following, we summarize data on molecular properties and experimental results that can be related to the rate constants. This will lead to recommendations for the decomposition and isomerization rate constants.

A. Thermodynamic Properties. Thermodynamic properties are very important for the present application since rate constants are derived from the equilibrium constant. For this purpose, the logarithms of the equilibrium constants of formation for pertinent radicals have been calculated with standard statistical mechanical formulas and are listed in Table 1. This approach is used instead of using group properties since the molecular frequency and structure information are needed in the subsequent calculations. It is the more rigorous approach and naturally takes into account problems dealing with internal rotors. The frequencies of these radicals are based on the suggestion of Benson.[9] We remove from the parent molecule the three frequencies associated with hydrogen motion. In addition, we change the hindered rotors adjacent to the radical site to free rotors. In the case of the allylic hydrogens, their removal lead to the formation of stiffened allylic groupings. The weakly hindered rotors are now changed into torsions. This general technique was used earlier to successfully determine the heat of formation of the smaller alkyl radicals (up to four carbons).[10] These are, in fact, within the stated uncertainties of values used today. The same procedure should therefore be capable of determining the thermodynamic properties of five-carbon radicals. A particularly useful advantage of this approach is that there should be a cancellation of any errors in the molecular frequency and structures. Thus, the relative entropies of the radicals should be determined to high accuracy.

Modern computational methods can also be used to determine thermodynamic properties. We are, however, uncertain about their accuracy. The stated uncertainties of 4−7 kJ/mol in the heat of formation and the uncertainties on how to scale the low frequencies can lead to unacceptably large errors in the equilibrium constants of formation and the rate constants derived from them. We are particularly concerned that the relative values of the thermodynamic properties be self-consistent and obey group additivity. This is because we are interested in building up kinetic databases for large groups of hydrocarbons for use in the simulation of the behavior of real fuels. Obviously they cannot vary in a random manner. Our preference for basing selections on experimental measurement arises from the fact that these techniques are well understood and are, in essence, validated from data on related systems. There is a real need for a systematic evaluation of the accuracy of ab initio calculations, both in an absolute and in a relative sense. Of course, in the absence of experimental results, theory must be used. For the cyclopentyl radical, we used the results from Matheu et al.[11] This is based on a theoretical calculation.

Our results are based on the following bond dissociation energies: 421 ± 2 kJ/mol, primary C−H bond; 410 ± 2 kJ/mol, secondary C−H bond; and 413.3 ± 5 kJ/mol for the C−H bond strength in cyclopentane. There does not appear to be any issues regarding these values. The value chosen for the allylic resonance energy was 50 ± 4 kJ/mol.[12] Senosian et al.[13] recently suggested 60 ± 5 kJ/mol for this important quantity. They apparently misread the value reported in ref 14 that summarized the experimental results and cited it as support for their value. Indeed, the experimental number in the reference they quote would have led to a resonance energy of 52 kJ/mol. Note that their calculated number is 64 kJ/mol. Deviations in this amount between calculations and experiments are not unreasonable. The exponential dependence of rate constants on the activation energy means that these differences can have serious consequences.

An interesting issue is how allylic resonance will be manifested in the transition state. The three cases are

(1) an allylic type radical is directly formed, for example, from the decomposition of 1-penten-5-yl to form allyl and ethylene;

(2) an allylic bond is broken, leading to the formation of a 1,3 diene, for example, from the decomposition of 1-penten-4-yl to form a H atom and 1,3 pentadiene;

(3) an allylic type radical decomposes to form a 1,3-diene, for example, from the decomposition of 1-penten-3-yl to form 1,3 butadiene and methyl.

The various reactions can be found in Figure 1. The consequences will involve increases or decreases in the stability of the radicals. One of the aims of this work is to obtain some idea of the magnitude of these effects.

B. Rate Expressions and Energy Transfer. High-pressure rate expressions are particularly important. The activation energy defines the magnitude of the energy barrier, and the A-factor is related to the entropy of activation. These values are the basis for the RRKM calculations[15] that determine the specific rates. Competition with collisional deactivation processes defines the distribution function. Although these calculations require molecular frequencies and rotational constants, it is known that if the desired rate expression is reproduced, results are insensitive to the exact nature of the molecular properties. In line with most transition state calculations for large polyatomics, tunneling is ignored. Such effects are lumped into the rate expression. We expressed the energy removed per collision as (step-size down) = 3600 + 2.4*x*(temp) in units of J/mol, in which the 2.4 is in units of J/mol cm^{-1} with nitrogen as the collision partner. This is in the range of values determined from studies on decompositions over extended temperature ranges.[16,17] The results from this work can therefore be directly used in combustion models.

C. Related Experimental Results. The following sections represent the experimental basis for our estimates.

C1. 1-Penten-3-yl. Kerr and Parsonage[18] analyzed the experimental literature for the terminal addition of methyl to butadiene to form 1-penten-3-yl. They recommended, over the temperature range of 353−453 K, the rate expression k(1,3-butadiene + methyl = 1-penten-3-yl) = $1.34 \times 10^{-13} \exp(-2063/T)$ cm^3 $molecule^{-1}$ s^{-1}. At the low temperatures at which these studies were carried out, the rate constants are at the high-pressure limit. The high-pressure rate expression for the reverse decomposition process is determined through detailed balance.

C2. 1-Penten-4-yl. The chemically activated decomposition of the 1-penten-4-yl radical was studied by Carter and Tardy[19] from experiments on the addition of hydrogen atoms to 1,4-pentadiene. The most interesting observation is the occurrence of a very fast isomerization process, the homoallylic rearrangement, at room temperature. The mechanism can be found in Figure 1. An estimated maximum rate expression is k(1-C_5H_9-4-yl => 3-CH_3-1-C_4H_6-4-yl) = $8 \times 10^{12} \exp(-7850/T)$ s^{-1}. They also found that the barrier for methyl addition to the nonterminal bond in butadiene is 13−17 kJ/mol higher than that for terminal addition to an olefin, and attributed this to the conjugation stabilization of 1,3-butadiene. We have used this to estimate the high-pressure rate expression for the ejection of the nonterminal methyl and hydrogen from 3-methyl-1-butenyl-4-yl and 1-penten-4-yl, respectively. The rate expressions for breaking the vinylic C−C bond is based on the rate constant for the addition of vinyl to ethylene and used for the decomposition of 1-butene-4-yl.[20] For the ejection of the terminal hydrogen, the rate expression is based on hydrogen addition to butadiene.[18]

C3. 1-Penten-5-yl. Tsang and Walker[21] generated 1-penten-5-yl from the decomposition of 1,7-octadiene in single-pulse shock tube experiments and found the expression for the ratio of cyclopentene and ethylene to be (cyclopentene)/(ethylene) = $6.9 \times 10^{-3} \exp(2118/T)$ over the temperature range of 1050−1150 K and at a pressure of 3 bar argon. Since these products are formed rapidly under the reaction conditions, they are a direct measure of the branching ratio for 1-penten-5-yl decomposition. Handford-Styring and Walker[22] determined the rate expression for ethylene formation during the decomposition of cyclopentyl radicals in a slowly reacting hydrogen/oxygen mixture to be $1.4 \times 10^{13} \exp(-17260/T)$ s^{-1}. Their analysis also included the earlier experimental work of Gordon.[23] This is the rate-determining step if the ring-opening reaction is not reversed. This has been confirmed in the course of the present work. Experimental rate constants for hydrogen addition to cyclohexene and *cis*-butene-2 were found by Parsonage and Kerr[18] to be near 8×10^{-13} cm^3 $molecule^{-1}$ s^{-1} with an activation energy of 17 kJ/mol. This is used to derive a rate expression of $6.6 \times 10^{-10} \exp(-2000/T)$ cm^3 $molecule^{-1}$ s^{-1} for H addition to cyclopentene. Detailed balance leads to a high-pressure rate expression for the ejection of a hydrogen atom from a cyclopentyl radical. We then adjusted the barriers to the decylization of cyclopentyl radicals and the decomposition of 1-penten-5-yl to match the experimental observations. It appears that the experimental determinations are within a factor of 2−3 of the high-pressure limit.

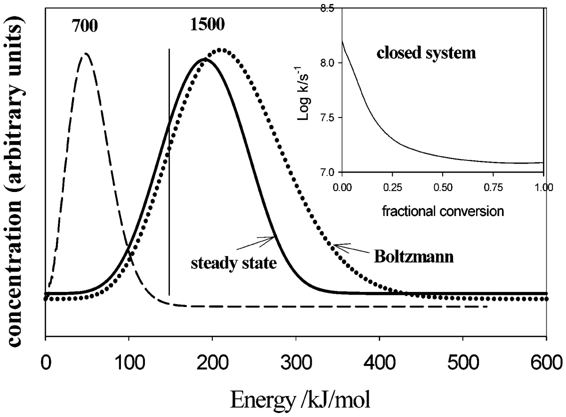

Figure 3. Distribution functions for 1-penten-3-yl at 700 and 1500 K. The initial (Boltzmann) and final steady-state values are indistinguishable at 700 K. At 1500 K, the initial (Boltzmann) distributions are the dotted lines. The final steady-state distribution is the solid line. The results are for closed and open systems at 700 K and for an open system at 1500 K. The inset contains calculated results at 1500 K for a closed system and shows the extent of decomposition while rate constants are varying. The pressure is 1 bar. The vertical line is the reaction threshold. The scale for the *y*-axis is arbitrary for each distribution and has been displaced for clarity.

Derived Rate Constants

Before describing the specific rate constants and expressions, it is of interest to consider the nature of the distribution functions and the general behavior of the systems. Figure 3 contains a plot of the initial and final distribution functions for 1-penten-3-yl at 700 and 1500 K. Other 1-pentenyl radicals will have similar distribution functions. At the lower temperature, the peak of the Boltzmann distribution function is well below the reaction threshold. A steady-state distribution is rapidly achieved, and this distribution function differs from the original one only in that the high-energy end is depleted by the rapidity of the reaction. It is indistinguishable in this plot from the Boltzmann distribution. The physical picture is that which is usually treated in standard texts.[15] At 1500 K, however, the peak of the distribution function is now at energies higher than the reaction threshold. Reactions move the entire distribution function toward lower energies. If this is treated in the standard manner, the results can be seen in the inset. Decomposition is occurring before the establishment of a steady state. Hence, rate constants are changing with time, and it will be impossible to use such data in standard simulation programs. A solution to this problem is to treat such systems in the same manner as that used for chemical activation experiments. The essential difference is that, in traditional studies of thermal reactions, the physical picture is that of a molecule in a closed vessel that is reacting in a unimolecular sense. Traditional chemical activation experiments are carried out with a constant flux of active radicals being formed. This is, in fact, the situation for radical decomposition. It is convenient to describe these two equivalent ways of treating unimolecular reactions as involving “closed” or “open” systems. In the present case, the latter is the preferred methodology since it leads to an invariant molecular energy distribution function that can be used to obtain rate constants.

The situation for rate constants determined on the basis of the open system can be seen in Figure 4. Within the incubation

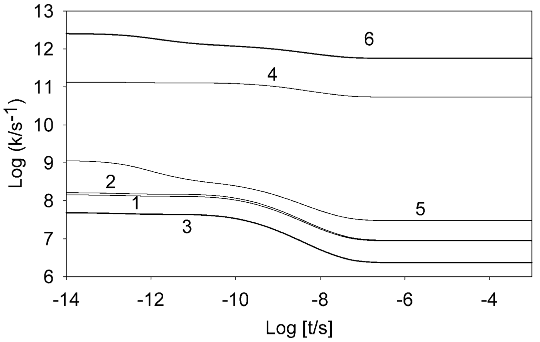

Figure 4. Rate constants as a function of time for the reactions involved in 1-penten-4-yl decomposition. Specific reactions are (1) 1-C_5H_9-4 = 1,3-C_5H_8 + H; (2) 1-C_5H_9-4 = C_3H_6 + C_2H_3; (3)1-C_5H_9–4 = 1,4-C_5H_8 + H; (4) C_5H_9-4 = 3-$CH_2C_4H_7$; (5) 3-CH_3-1-C_4H_6-4 = 1,3-C_4H_6 + CH_3; and (6) 3-CH_3-1-C_4H_6-4 = C_5H_9-4. The temperature is 1600 K, and the pressure is 1 bar. The logarithm of time is used to cover the entire range of behavior.

or induction period, steady-state rate constants are not applicable. The initial rate constants for the isomerization products are larger than the high-pressure number. Unlike the situation for the reactant, which initially has a Boltzmann distribution, the higher energy levels of the isomerization products are the first to be populated. These are therefore more likely to react. The initial rate constant of the starting reactant is the high-pressure value. The incubation or induction time sets a limit on the time scales of applicability for the present analysis.

Table 2 contains the recommended rate constants. We have chosen to express the results in terms of a high-pressure rate expression and the deviations from these values. Also included in the first column, together with the reaction thresholds (in both directions), are rate constants at 1100 K at 1 bar. This gives the reader a sense of the magnitudes. At every temperature, a broadening factor that will fit the pressure dependence can be found. It is not possible, however, to describe these reactions in the generalized Troe form that is required to fit data over extended temperature ranges, even on a purely empirical basis. Figure 5 contains a plot of the rate constant for the decomposition of 1-penten-3-yl to form butadiene and methyl as a function of temperature. Note the indication of the rate constants returning to high-pressure values as the temperature is increased. This is contrary to the standard case in which, at constant pressure, the rate constants show continual departures from the high-pressure value with increasing temperature. A look-up table may be the most appropriate way to report data for simulation purposes. An analogous approach is to report results in an isobaric form. For errors less than a factor of 1.1, we have found it necessary to use four parameters in the form

$$(k_\infty/k) = a + b(1/T) + c(1/T)^2 + d[\log 10(1/T)]$$

as the basis of an empirical fit. This is particularly appropriate for combustion applications in the lower temperature range, since the deviations from high-pressure behavior are not large.

TABLE 2: Summary of Recommended Rate Expression for 1-Pentenyl Decompositions

reactions (reaction thresholds, kJ/mol, forward and backward at 0 K) log k (1100 K, 1 bar)	high-pressure rate expressions s^{-1}			log($k\infty/k$)[a] at various pressures				
	log A	N	E (kJ/mol)	P (bar)	A	B	C	D
1-C_5H_9-3 = 1,3-C_4H_6 + CH_3	13.76	0.10	150.2	0.1	87.76	−26386	7.01e6	22.6
(148.3; 22.2)				1	39.52	−14340	4.25e6	9.73
5.98				10	10.32	−669.3	7.4e5	−3.44
1-C_5H_9-4 = 1,3-C_5H_8 + H	9.06	1.30	144.8	0.1	83.57	−26209	7.06e6	21.2
(140.4; 19.3)				1	38.61	−14990	4.53e6	9.28
5.68				10	−12.2	−1116	9.99e5	−4.14
1-C_5H_9-4 = C_3H_6 + C_2H_3	11.87	0.56	155.7	0.1	91.39	−27920	7.42e6	23.4
(152.3; 4.4)				1.0	44.99	−16539	4.89e6	11
5.66				10	−7.86	−2241	1.29e6	−2.97
1-C_5H_9-4 = 1,4-C_5H_8 + H	9.76	1.04	155.0	0.1	96.98	−29405	7.77e6	24.9
(156.6; 9.3)				1.0	48.60	−17612	5.17e6	11.9
5.05				10	−7.23	−2586	1.40e6	−2.85
1-C_5H_9-4 = 3-CH_3-1-C_4H_6-4	8.70	1.43	61.0	0.1	2.16	−3782	1.47e6	−8.97
(60, 50.6)				1.0	11.22	245	3.92e5	−3.54
10.08				10	22.29	3866	6.49e5	6.36
3-CH_3-1-C_4H_6-4 = 1,3-C_4H_6 + CH_3	11.63	0.42	128.1	0.1	71.44	−22519	6.10e6	18.2
(126.8; 55.3)				1.0	33.46	−12947	3.92e6	8.06
6.43				10	−9.19	−1217	9.20e5	−3.91
3-CH_3-1-C_4H_6-4 = 1-C_5H_9-4	10.22	1.135	49.0	0.1	5.44	−4051	1.46e6	.90
(50.6; 60)				1.0	−6.4	−547.6	5.33e5	−2.17
11.24				10	−16.68	2730	3.97e5	−4.8
1-C_5H_9-5 = C_3H_5 + C_2H_4	11.96	0.39	102.9	0.1	102.2	−24182	5.11e6	27.3
(103.4; 66.9)				1.0	89.11	−23061	5.44e6	23.6
7.62				10	58.63	−16819	4.39e6	15.3
c-C_5H_9 = 1-C_5H_9-5	12.81	0.156	142.5	0.1	74.6	−22525	5.99e6	19.2
(137.8; 78.8)				1.0	33.30	−12080	3.57e6	8.19
6.00				10	−9.20	−423.9	5.86e5	−3.04
c-C_5H_9 = c−C_5H_8 + H	11.80	0.46	138.6	0.1	73.3	−22313	5.97e6	18.8
(137.5; 8.9)				1.0	32.22	−11860	3.53e6	7.89
6.11				10	−9.85	−282.0	5.57e5	−3.21
1-C_5H_9-5 = c-C_5H_9	6.22	1.39	71.76	0.1	83.44	−21421	4.96e6	22.1
(78.8; 137.8)				1.0	65.87	−18068	4.50e6	17.3
6.61				10	38.38	−11737	3.21e6	9.88

[a] Log($k\infty/k$) = $a + b(1/T) + c(1/T)^2 + d[\log 10(1/T)]$.

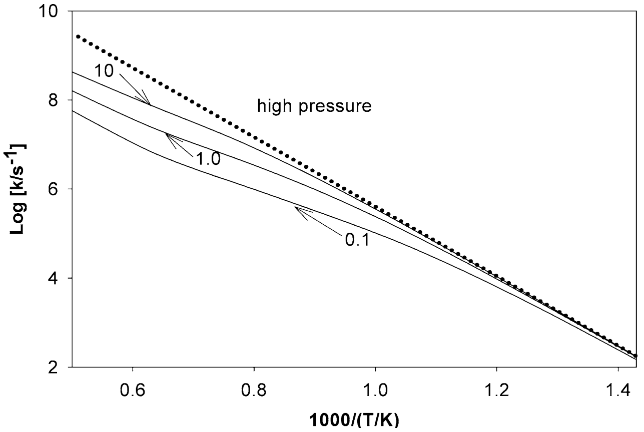

Figure 5. Rate constants as a function of temperature for the reaction 1-C_5H_9-3 = 1,3-C_4H_6 + CH_3. The dotted line is at the high-pressure limit. The solid lines refer to reactions at the numbered pressures (in bar).

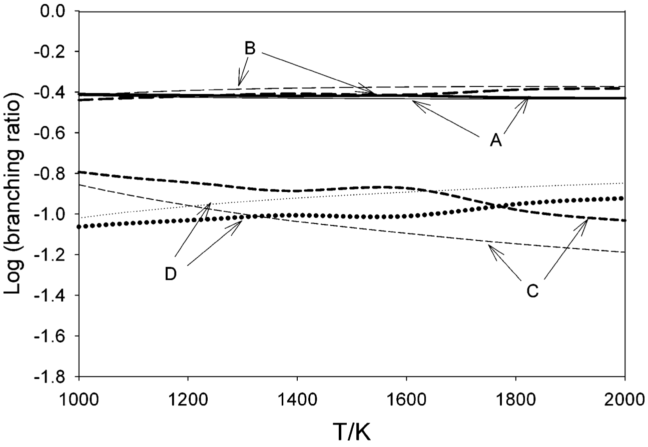

Figure 6. Branching ratios for specific reactions and the sum of all the decomposition processes as a function of temperature at 1 bar (dark lines) and near the high-pressure limit (light lines) for reactions (A)1-C_5H_9-4 = 1,3-C_5H_8 + H; (B) 1-C_5H_9-4 = C_3H_6 + C_2H_3; (C) 1-C_5H_9-4 = 1,4-C_5H_8 + H; and (D) 3-CH_3-1-C_4H_6-4 = 1,3-C_4H_6 + CH_3.

Deviation from the high-pressure results may be larger at the higher temperatures. However, under such conditions, rate constants become very large, and the key factors are the branching ratios for product formation, since no other reactions can make contributions. Some typical results can be found in Figure 6. This involves the decomposition of 1-penten-4-yl. The branching ratios at 1 bar are very near the value at the high-pressure limit. The greatest deviations are those for the minor channels. Even here, the departures of the 1 bar values are no more than a factor of 2 from the high-pressure numbers.

The very fast homoallylic rearrangement can produce large quantities of 3-methyl-1-buten-4-yl from the parent 1-penten-4-yl. However, the greater stability of the latter makes it the major reactant. Equilibrium is rapidly achieved. Thus, the results are not particularly sensitive to the rate expression used. As a result, the 1,4-pentadiene- and vinyl-producing processes account for a substantial part of the decomposition products.

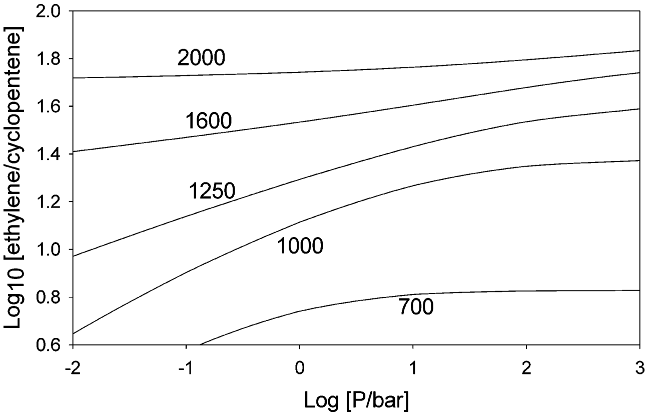

Figure 7. Calculated branching ratio for ethylene-to-cyclopentene formation from 1-penten-5-yl decomposition at various temperatures and pressures.

There is a wealth of experimental data on the unimolecular reactions involving 1-penten-5-yl. Our conclusions, therefore, have a high degree of validity. It should provide an excellent test for the state of the theory. This is, however, beyond the scope of this work. The main reactive channel involves the breaking of the allylic C−C bond to form allyl and ethylene. The cyclopentene formation channel makes only a minor contribution, even at the lowest temperatures considered here. It is interesting that the barrier for bond breaking is higher than that for cyclopentyl formation. The low A-factor for isomerization to cyclopentyl more than makes up for this deficiency. A summary of predicted ethylene-to-cyclopentene ratios at various temperatures and over a pressure range of 0.01−1000 bar is given in Figure 7. Even at 1000 K, the variation of this ratio is only about a factor of 2 under the combustion conditions of 1−1000 bar. These general trends are in line with the earlier situation for 1-penten-4-yl.

A particularly interesting result is the similarity in rate expressions for the C−C and C−H bond cleavage for cyclopentyl radical decomposition (see Table 2). This is in striking contrast to the situation for normal alkyl radicals in which there are differences of the order of 25 kJ/mol in favor of C−C bond cleavage. Thus, for cyclopentyl radical decomposition, both bond cleavage channels must be taken into account. The difference in activation energies between the normal alkyl radicals and cyclopentyl is strikingly similar to those for alkanes and cyclopentane, even though there is a tremendous difference in the reaction thresholds (on the order of 210 kJ/mol). It appears that, in the transition state, aside from the lengthening of the C−C bond, there are factors, for example, twisting of the methylene group in the cyclic compound, that must take place before bond breaking can occur.

From the rate constants for the decomposition of 1-penten-5-yl to form ethylene and allyl, it is possible to derive from detailed balance the rate expression for allyl radical addition to ethylene. The expression that we obtained is 8.5×10^{-13} exp($-8700/T$) cm^3 $molecule^{-1}$ s^{-1}. This can be compared with the recommendation of Kerr and Parsonage[18] and confirmed by Knyazev and Slagle[24] for the addition of ethyl to ethylene of 2.6×10^{-14} exp($-3674/T$) cm^3 $molecule^{-1}$ s^{-1}. Thus, the resonance energy is manifested almost completely in the rate expression for addition and not in that for the reverse process.

Stein and Rabinovitch[25] and Carter and Tardy[26] studied the chemically activated decomposition of cyclopentyl radicals generated from the addition of hydrogen atoms to cyclopentene at room temperature. Their results in terms of the stabilization-to-decomposition ratio in a bath of hydrogen as a function of pressure can be found in Figure 8. These results were obtained using the same procedure as that outlined earlier for the thermal reaction, that is, through the solution of the master equation. We solve for the distribution function (chemically activated) and extract rate constants by convoluting with the RRKM specific rates. We are able to reproduce their results if it is assumed that 720 J/mol (60 cm^{-1}) of energy is removed by each collision of cyclopentyl with the hydrogen bath gas. This

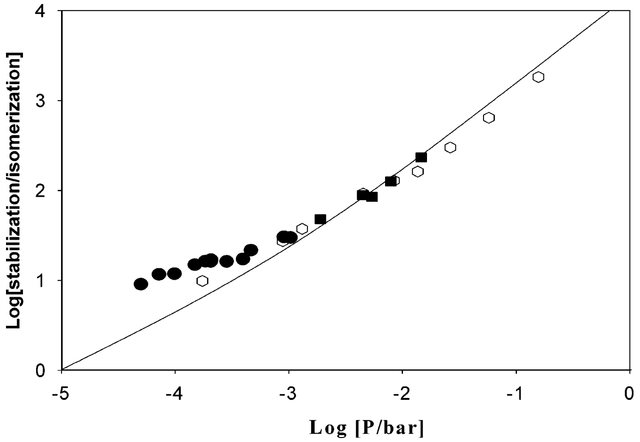

Figure 8. Stabilization-to-decomposition ratio as a function of pressure at room temperature for the chemically activated decomposition of the cyclopentyl radical formed from H-atom addition to cyclopentene. The open polygons are values from the work of Stein and Rabinovitch. The filled symbols are values from the work of Carter and Tardy; the filled circles are from experiments using ethylene (ethyl getter), and the filled squares are from experiments using *cis*-butene-2 (methyl getter).

number is consistent with the decreased efficiency of hydrogen as a collider for other systems at these temperatures.[16,17] It is lower than the published values used in the earlier studies to fit results. This is a consequence of the differences between the rate expressions used for cyclopentyl decomposition to form the 1-penten-5-yl radical in this and the earlier work. The rate expressions used here and given in Table 2 are compatible with all the existing results bearing on the transformations involved in the cyclopentyl−1-penten-5-yl system. The effect of the high-pressure rate expression on the step-sized down parameter chosen to fit the results was discussed by Knyazev and Tsang.[17]

Discussion

A very interesting general result from this study is the demonstration that the standard closed-system approach to the treatment of thermal unimolecular reactions is increasingly questionable for low reaction barriers under high-temperature conditions. The open-system approach has been found to be fully satisfactory. It is, however, difficult to fit the data in the standard analytical format. The results are indicative of the scale of effort necessary to describe the chemistry of realistic liquid fuels.

The results, summarized in Table 2, demonstrate the errors introduced by treating the three 1-pentenyl radicals as one species or undergoing one reaction. This can be seen in Figure 9, in which the high-pressure rate constants for the bond cleavage reactions are plotted as a function of temperature. Due to the similarities in reaction thresholds and molecular structure, the falloff effects are not that much different for these reactions. At 1 bar, rate constants are lowered by factors of 6−10. Thus, the differences in Figure 9 will be quite similar under all conditions. Also included are the recommendations of Curran et al.[2] for the treatment of 1-olefinyl radicals in general and the rate expression for the breaking of a C−C bond in the decomposition of a secondary heptyl radical. It is clear that it is not proper to express all the possible decomposition channels of the 1-olefinyl radicals in terms of one rate expression. There is no question that, in going to larger molecules, there is a need for lumping. However, these should only be based on reliable results for all the elements in a lumped process. Most striking is the underestimate of Curran et al.[2] for all the rate constants for the decomposition of the 1-pentenyl radicals. One can conclude that, with such values in a database, soot/PAH precursors will be under predicted, since a smaller rate constant means that there will be more time for the radical to be destroyed by the oxygen. The differences in the rate constants are largely due to differences in activation energies. 1-Penten-5-yl radical decomposition, leading to the formation of the allyl radical, has a threshold of 103.4 kJ/mol and is thus less stable than the comparable alkyl radical. The stability of 1-penten-3-yl is enhanced by its allylic resonance energy. However, is the full value of the resonance energy is manifested in neither case. Instead, the data seems to be consistent with an intermediate value.

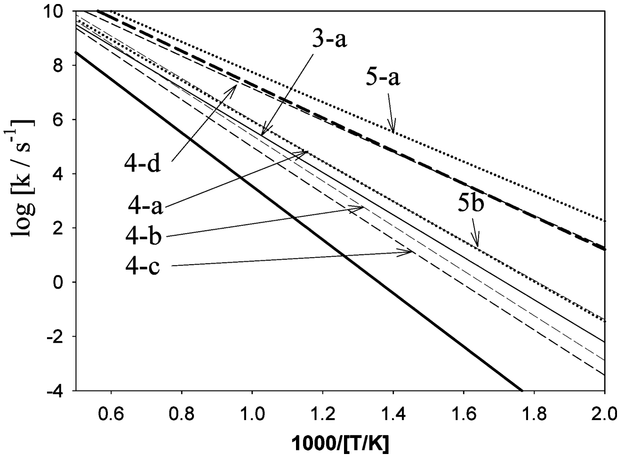

Figure 9. High-pressure rate constants as a function of temperature for the decomposition of 1-olefinyl radicals as recommended by Curran et al. (dark line); secondary heptyl radical (dark dashed line); 1-penten-3-yl (1-C_5H_9-3 = 1,3-C_4H_6 + CH_3; line 3-a); 1-penten-4-yl (1-C_5H_9-4 = 1,3-C_5H_8 + H; line 4-a); 1-C_5H_9-4 = C_3H_6 + C_2H_3 (line 4-b); 1-C_5H_9-4 = 1,4-C_5H_8 + H (line 4-c); (3-$CH_3C_4H_6$ = 1,3-C_4H_6 + CH_3 (line 4-d); 1-penten-5-yl (1-C_5H_9-5 = C_3H_5 + C_2H_4; line 5-a); and *c*-C_5H_9 = *c*-C_5H_8 + H (line 5-b).

It is difficult to make an exact error estimate for the data presented in Table 2. The following are our estimates: The uncertainties in the rate constants for 1-penten-3-yl and 1-penten-5-yl decomposition and isomerization should be on the order of factors of 1.5 and 2. For 1-penten-4-yl, the errors may be larger and may be in the range of factors of 2 and 3.

From the data in Table 1 and Figure 9, the stability ranking is 1-penten-3-yl $\approx$ 1-penten-4-yl $\gg$ 1-penten-5-yl. It is clear that allyl radicals will be rapidly released into the system. The greater stability of the other radicals means that there is a greater probability for their being attacked by oxygen molecules. Note that, under stoichiometric conditions, at temperatures where the decomposition rate is below 10^6 s^{-1}, oxidation is controlling (assuming a rate constant of 1.6×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for oxygen addition to the radical).

The relative importance of the various reaction channels is related to the amount of radicals produced as a result of abstraction reactions. It is known that allylic resonance energy is not fully manifested for abstraction processes.[27] The consequence is that, although abstraction rate constants are enhanced by the resonance energy, the overall effect is no more than a factor of 2 or 3 in comparison to the system in which it is absent. Thus, although the predominating radical will, in fact, be 1-penten-3-yl, a significant amount of other radicals will also be present.

Finally, is important to note that, although the focus of this work is on the decomposition of the 1-pentenyl radicals, the necessity of considering all the channels means that rate

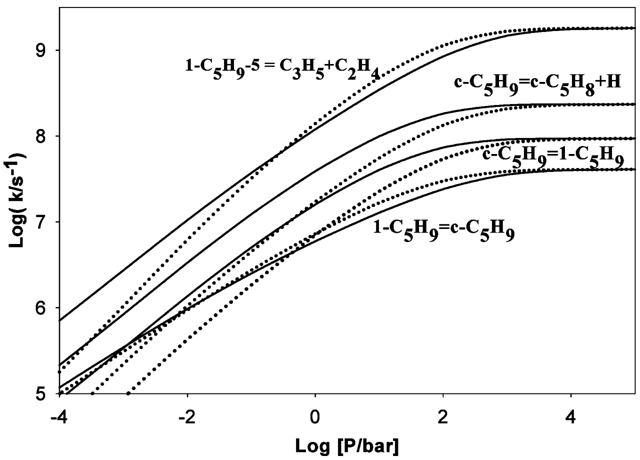

Figure 10. Rate constant as a function of pressure at 1400 K for the decomposition of reactions in this system beginning with 1-penten-5-yl (solid line) and cyclopentyl (dotted line).

constants for many other reactions can be derived from the same set of input parameters. These include the thermal decomposition of cyclopentyl and 3-methylbuten-1-yl radicals. In addition, it will also be possible to derive rate constants for the chemically activated decomposition of 1-penten-5-yl from allyl + methyl and cyclopentyl from H + cyclopentene.

A particularly serious consequence of the isomerization processes being important is that, in the falloff region, the rate constants of the individual isomers are dependent on how they are formed. Falloff curves at 1400 K for the four reaction channels for the decomposition of 1-penten-5-yl and cyclopentyl radicals, with each of the compounds as the starting reactant, can be found in Figure 10. The high-pressure rate constants are, of course, the same. However, as the pressure is lowered, there is increasing divergence in the values for three of the four cases. There are also changes in the shape of the falloff curve. Obviously, these differences are a reflection of the changed distribution functions. Note that, for the two isomerization reactions, detailed balance does not hold in the pressure-dependent region. All of these results are a striking demonstration of the simplification brought about at the high-pressure limit where all molecules follow a Boltzmann distribution. For combustion applications in which all experiments are at 1 bar or above, it can be seen that the largest spread of results is no more than a factor of 2 at the lowest pressures. An important issue will be the maximum tolerable range of errors.

Another consequence of energy transfer effects can be deduced from Figure 3. It can be seen that the new distribution function at high temperatures is that of a much cooler molecule. If this molecule were to undergo reactions other than that of decomposition, rate constants are likely to be smaller than those for the bath temperature. Thus, for example, the chemically activated decomposition of a molecule formed from the combination of 1-penten-3-yl and another radical at 1500 K will have rate constants consonant with a 20 kJ/mol smaller internal energy.

Since direct measurements are unavailable, most of the earlier databases for complex organic fuels are based, at best, on thermochemical kinetics considerations. Although at some stage this must be used for larger systems, the present study shows that through detailed balance and the use of chemical activation data, one can rigorously enlarge the database. This can then serve as a basis for further extensions. It is known that the rate constants of many reactions are unaffected by methylene substitution in distant positions. The high-pressure rate constants obtained here are equally applicable to larger normal hydrocarbons. New problems arise from the possibility of isomerization involving hydrogen transfer across four or more carbon atoms. One suspects that the rate expressions for such isomerizations involving alkyl and olefinyl radicals will be similar. Another problem is the formation of cyclic radicals. Chemical activation results from the chemically activated decomposition of the cyclohexyl radical show the preference for the formation of five-membered rings in comparison to six-membered structures.[24] On this basis, very few cyclohexyl radicals will be formed from the decomposition of the 1-hexen-5-yl radical. Obviously, high-reliability experimental results in addition to theory can resolve much of the uncertainties and thus fine-tune the recommendations. Finally, the results on the pressure dependence of the decomposition of these radicals suggests that using high-pressure rate expressions may be sufficient to describe the behavior of these systems under certain ranges of combustion conditions.

Summary

We have derived rate expressions for the decomposition of the three isomeric 1-pentenyl radicals over extended temperature and pressure ranges that encompass combustion conditions. They lead to the formation of a variety of unsaturated compounds that are the boundary conditions to soot/PAH formation models. Energy transfer effects have been determined, and thus, formally, the recommended rate constants take into account all possible physical situations. The recommendations are based on existing data that cover various aspects of these reactions over limited temperature and pressure ranges. The procedures used to derive the data are described. Extensions to cover the larger fragments that are the products of the combustion of larger and more realistic fuels are indicated. Some of the problems that arise from taking into account energy exchange effects are discussed.

Acknowledgment. This research was supported by the US Department of Defense through the Strategic Environmental and Development Program (SERDP #1198), Charles Pellerin, Scientific Officer. The author is also grateful for the support from the Department of Energy, Office of Basic Energy Sciences on the fundamental aspects of this work dealing with the treatment of low-threshold unimolecular reactions.

Supporting Information Available: Estimated molecular properties used in the calculations and the transition-state properties. This material is available free of charge via the Internet at http://pubs.acs.org.

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