A Compilation of Kinetic Parameters for the Thermal Degradation of *n*-Alkane Molecules

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A list of several hundred free-radical reactions which occur during the low temperature (700–850 K) pyrolysis of small *n*-alkane molecules has been assembled and a set of reliable, self-consistent Arrhenius rate parameters has been assigned on the basis of experiment, theory, thermochemical estimates and structural analogy. Rate parameters have been recommended for the following types of reactions, with the number of each type in parentheses: initiation (32), recombination (135), disproportionation (108), H-transfer (112), decomposition (41), addition (58), and isomerization (11), giving a total of 505 reactions. This compilation is intended for use in assembling reaction matrices in computational modeling studies of the thermal reactions of hydrocarbon molecules.

Key words: Addition; chemical kinetics; decomposition; disproportionation; H-transfer; initiation; isomerization; *n*-alkane pyrolysis; rate constants; recombination.

Contents

1. Introduction

1.1. Objectives

The objectives of this report are to compile a reasonably complete list of the reactions which occur during the low temperature (700–850 K) pyrolysis of small *n*-alkane molecules and to assign a set of reliable and self-consistent rate parameters. These data are intended for use in assembling reaction matrices in computational modeling studies of thermal reactions of small alkane molecules.

1.2. Scope and Limitations

The total number of reactions which can occur during the pyrolysis of an alkane molecule number in the thousands. The present compilation is restricted to several hundred of the most significant reactions. Rate parameters have been recommended for the following types of reactions, with the number of each type in parentheses: initiation (32), recombination (135), disproportionation (108), H-transfer (112), decomposition (41), addition (58), and isomerization (11), giving a total of 505 reactions. Many of these may or may not participate significantly in a given pyrolysis depending upon the concentrations of initial species present and the extents of conversion, but at low conversions (several percent) and temperatures (700–850 K) this compilation is a reasonably complete representation of the pyrolysis reaction set of *n*-alkanes up to C_5H_{12}. Other reactions may be added to this set as needed and in many cases the rate parameters may be estimated by analogy with similar reactions in the present set.

Reactions of vibrationally excited radicals and surface reactions have not been considered. The reactions are thus restricted to conditions of high pressures (in general, several hundred torr) and inert reactor walls.

The parameters are evaluated, wherever possible, at 700 K, the low temperature side of the pyrolysis region. This lends more confidence to the application of many of the experimental data on free radical reactions which have been traditionally measured at tem-

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peratures within 100–200 K of ambient. In a few cases (H-abstraction reactions) where high and low temperature parameters appear to differ dramatically, suggested high temperature parameters have also been included to extend the set to temperatures >900 K.

Finally, although the literature through 1977 has been searched, this compilation is not intended to be a thorough review nor a comprehensive critical evaluation of experimental methods or data. Rather, it is intended to be a selected set of parameters chosen on a reasonably self-consistent basis. For example, wherever possible, parameters for corresponding forward and back reactions have been chosen to be consistent with thermochemical parameters. In other cases, such as addition and abstraction reactions, the assignments have been made to be consistent with thermochemistry and addition/abstraction ratios. Many types of rate data in the literature have been reported relative to radical recombination rates and an effort has been made to apply the preferred recombination rates in this report to recalculate literature data based on different recombination rates.

1.3. Methods of Assignment

1.3.a. Experimental Values

Many of the experimental data on pyrolysis reactions can be found in recent reviews on alkane pyrolysis [1, 2],[1] several general rate compilations [3–6] and recent reports of critically evaluated data for addition reactions [7] and unimolecular reactions [9]. Wherever possible, experimental data taken close to 700 K were used. An effort was made to select experimental data which were obtained under conditions free from wall effects, interfering side reactions and vibrationally excited species. In cases where rate parameters were determined relative to radical recombination rates the data were recalculated on the basis of the recombination assignments in this compilation. In most cases, data totally inconsistent with an independent, consistent set of experimentally and theoretically based values, were rejected.

In the tables, the following notations are used for experimental data: E, experimental; EP, pyrolysis experiments; EN, nonpyrolysis experiments; and EP* (or E*), high temperature pyrolysis data inapplicable to lower temperatures. Values taken from critical reviews of other authors are designated by R.

1.3.b. Calculated Values

Calculated and estimated values were based on theoretical models (designated T in the tables), reverse reaction kinetics and thermochemistry (B, in the tables) or structural analogy (S, in the tables). Theoretical calculations based on models which successfully describe independent experiments (such as chemically activated decomposition) were preferred. When assignments were made by structural analogy, cases were chosen, where possible, for which structural differences would not appreciably alter the thermochemical changes in the reacting parts of the molecules. Where appropriate, corrections have been made for changes in $\Delta S\ddagger$ due to changes in product and transition state rotational and/or optical symmetry. For some reactions, generalized rate parameter values have been estimated for primary and secondary radicals, designated in the tables as 1–R and 2–R, respectively.

The methods for calculating rate parameters from reverse reactions and thermochemical data are given below. Details may be found in several sources [8, 9]. The Arrhenius expression $k=Ae^{-E/RT}$ is used and the parameters are always expressed in units of moles, liters and seconds. The standard thermochemical quantities $\Delta H°$, $\Delta S°$ and $\Delta C_p°$ refer to a standard state of 1 atm (101325 Pa) of gas and are expressed in units of kcal/mol for $\Delta H°$ and cal/(mol K) for the others. The constant R in the equations is 1.99 cal/(mol K) and R' is 0.0821 L atm/(mol K). SI units are used throughout except for 1 cal=4.184 J. Benson's [9] abbreviation, $\theta=2.303\times10^{-3}\,RT$ kcal/mol, is also used.

1. $A\underset{-1}{\overset{1}{\rightleftharpoons}}B+C$, radical decomposition-addition.

$$\Delta H°=E(1)-E(-1)+RT$$

$$A(1)/A(-1)=e^{\Delta S°/R}/(eR'T).$$

2. $A\underset{-1}{\overset{1}{\rightleftharpoons}}B+C$, initiation-radical recombination from the realationship between absolute rate theory and Arrhenius parameters:

$$E(-1)=RT+\Delta E_0^{\ddagger}(-1)+T<\Delta C_v^{\ddagger}>(-1),$$

where $\Delta E_0^{\ddagger}$ is the energy of activation at 0 K for the reverse reaction and $T\,\langle\Delta Cv^{\ddagger}\rangle(-1)$ is the corresponding thermal energy at temperature T. Using the assumption of Benson and O'Neal [8] that $\Delta E_0^{\ddagger}$ and $\Delta Cv^{\ddagger}$ are zero for radical recombination reactions:

$$E(1)=\Delta H°$$

$$A(1)=\frac{k(-1)}{R'T}\,e^{\Delta S°/R.}$$

3. $A+B\underset{-1}{\overset{1}{\rightleftharpoons}}C+D$, H-abstraction

$$\Delta H°=(1)-E(-1),$$

$$A(1)/A(-1)=e^{\Delta S°/R.}$$

4. $A\underset{-1}{\overset{1}{\rightleftharpoons}}B$, isomerization

$$\Delta H°=E(1)-E(-1),$$

$$A(1)/A(-1)=e^{\Delta S°/R.}$$

Values of the standard thermochemical parameters for alkanes and alkenes were taken from the tables of Stull, Westrum and Sinke [10] or calculated from

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[1] Figures in brackets indicate literature references

group additivity [11]. Values for the thermochemistry of free radical species were assembled from several sources and have been presented in a table in section 2 for convenience.

For many of the additions reactions a value of the "lower limit" of the A-factor was calculated (designated L in the table). The value of the lower limit is calculated from the relationship between the A-factor and $\Delta S^{\ddagger}$,

$$A(-1)=\frac{ekT}{h}e^{\Delta(S\ddagger(-1)/R.}$$

for the case where $\Delta S^{\ddagger}(-1)=-\Delta S^{\circ}$ and the parameters all refer to the equilibrium:

$$A\underset{-1}{\overset{1}{\rightleftharpoons}}B+C.$$

This value represents a situation where the activated complex has the same degree of freedom as the product radical and traditionally is thus held to be a lower limit for the addition A-factor. Unfortunately most of the experimental data for addition decomposition reaction sets do not seem to obey this limit (e.g., see reference 7).

1.3.c. Recommended Values

Where multiple entries (from different sources) appear in a table, a single set of recommended parameters, designated Rec, is also given. In selecting recommended values, each reaction was considered separately. The following conditions were considered: temperature, pressure, method of extracting the data from the experiment (for example, the complexities of the assumed mechanism necessary to derive rate parameters for specific contributing reactions), and the reliability of the assumed models and related parameters on which theoretical calculations were based. Results calculated from thermochemistry and Arrhenius parameters for back reactions were judged on the basis of the reliability of the input data. The recommended values were based on averages weighted by considerations based on the above criteria.

References

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2. Radical Thermochemistry

The radical thermochemistry used to calculate Arrhenius parameters from reverse reaction kinetics is summarized in table 1. The data are expected to be accurate to ±1 kcal/mol or ±1 cal/(mol K). However, it must be pointed out that this is a particularly active area of research and the heats of formation of the methyl, ethyl, 2-propyl, and 2-methyl-2-propyl radicals are under current investigation.

Table 1. Radical Thermochemistry

The units of ΔH_f^o are kcal/mol.
The units of S^o and C_p^o are cal/(mol K).

The term "source" refers to the notes following the table.

Radical	$\Delta H^o{}_f(300)$	Source	$S^o(300)$	Source	$C^o{}_p(300)$	Source	$C_p(700)$	Source
H	52.1	1	27.4	1	5.0	1	5.0	1
$CH_3\cdot$	34.3	1	46.4	1	8.8	1	12.3	2
$C_2H_5\cdot$	26.5	1	58.0	1	11.1	1	20.2	2
$1\text{-}C_3H_7\cdot$	21.0	1	68.5	1	17.1	1	30.9	2
$2\text{-}C_3H_7\cdot$	17.6	1	66.7	1	17.0	1	30.4	2
$C_3H_5\cdot$	40.6	10	62.1	1	14.1	1	26.6	3
$1\text{-}C_4H_9\cdot$	16.0	4	77.9	4	22.6	4	41.2	4
$2\text{-}C_4H_9\cdot$	12.6	6	67.5	6	22.5	6	40.7	6
2-methyl-1-propyl	13.7	1	75.2	1	22.6	1	41.8	2
2-methyl-2-propyl	8.4	1	72.1	1	22.6	1	41.8	3
$C_4H_7\cdot$	30.4	7	70.8	5	20.0	5	36.8	3
$1\text{-}C_5H_{11}\cdot$	11.0	4	87.3	4	28.1	4	51.5	4
$2\text{-}C_5H_{11}\cdot$	7.6	6	86.9	6	28.0	6	51.0	6
$3\text{-}C_5H_{11}\cdot$	7.6	6	85.5	6	28.0	6	51.0	6
2-methyl-1-butyl	8.7	8	84.6	8	28.1	8	52.1	8
3-methyl-1-butyl	8.7	8	84.6	8	28.1	8	52.1	8
$2\text{-}C_6H_{13}\cdot$	2.6	6	96.3	6	33.5	6	61.3	6
4-methyl-2-hexyl	-5.0	9	105.2	9	39.3	9	72.2	9

Notes for Radical Thermochemistry

1. Values recommended by Benson [1].
2. Linear interpolation of values [1] at 500 K and 800 K.
3. Linear interpolation of values [2] at 600 K and 800 K.
4. Estimated from 1-C_3H_7 by group additivity [1].
5. Values recommended by O'Neal and Benson [2].
6. Estimated from 2-C_3H_7 by group additivity [1].
7. Value recommended by Golden and Benson [3].
8. Estimated from 2-methyl-1-propyl by group additivity [1].
9. Estimated from group values [1].
10. Taken from reference 1. This value agrees within experimental error with the experimental value of Golden, Gac and Benson [4].

References to Notes for Radical Thermochemistry

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3. Radical Recombination

Rate constants for radical recombination at 700 K are listed in table 2 and are given in the dimensionless logarithmic form $\log[k/(\mathrm{L\ mol^{-1}s^{-1}})]$. Unless otherwise noted values in the table were calculated using the geometric mean formula $k_{12}=2(k_{11}k_{22})^{1/2}$, where k_{12} is the cross constant and k_{11} and k_{22} are the self-constants for species 1 and 2.

Rate constants for alkyl radical recombination are among the most accurately known rate constants for gas-phase free radical reactions. All of the rate constants in the table are probably accurate to within half a power of ten. In the case of the recombination of methyl radicals, the rate constant is probably accurate to within 0.1 or 0.2 of a power of ten. The experimentally measured values were obtained by a variety of independent methods all of which are regarded as reliable. Most of the values in the table were obtained using the widely accepted geometric mean rule (see above). Well-established results for recombinations are needed because rate constants of other types of reaction such as H-abstraction are usually measured relative to recombination. There has been a great deal of recent activity in the field. The results for small alkyl radicals such as ethyl fall into two groups, one of high values around 10^{10} L $\mathrm{mol^{-1}s^{-1}}$, and the other of low values around $10^{8.5}$ L $\mathrm{mol^{-1}s^{-1}}$. We believe the high values to be the more accurate (see note 5), and have weighted our recommended values in favor of the high group. If our assessment turns out to be accurate, in time the best values for these rate constants will increase as the lower rate constants become discounted. We have neglected any temperature coefficients, that is we have assumed zero activation energy for recombination. However, we believe that this assumption is far from proved (see for example, reference [13]) and expect to see continued research in this area. When considering the reactions of small radicals such as $H+CH_3$, care must be taken to ensure that the pressure is sufficiently high (of the order of 10^3 Torr).

Table 2. Rate constants at 700 K for radical recombination. The form of the rate constant is log $[k/(L\ mol^{-1}s^{-1})]$.

The numbers in parentheses indicate the notes (source) following the table.

	$CH_3^\bullet$	$C_2H_5^\bullet$	$1\text{-}C_3H_7^\bullet$	$2\text{-}C_3H_7^\bullet$	$C_3H_5^\bullet$	$1\text{-}C_4H_9^\bullet$	$2\text{-}C_4H_9^\bullet$	$i\text{-}C_4H_9^\bullet$	$C_4H_7^\bullet$	$1\text{-}C_5H_{11}^\bullet$	$2\text{-}C_5H_{11}^\bullet$	$3\text{-}C_5H_{11}^\bullet$	2-methyl-1-butyl	$1\text{-}R^\bullet$ (Prin.)	$2\text{-}R^\bullet$ (sec.)
H	11.3(1)	10.6(2)	~11(3)	~11(3)	~11(3)	~11(3)	~11(3)	~11(3)	~11(3)	~11(3)	~11(3)	~11(3)	~11(3)	~11(3)	~11(3)
$CH_3^\bullet$	10.4(4)	10.3	10.3	10.2	10.3(11)	10.3	10.2	10.3	10.4	10.3	10.2	10.2	10.3	10.3	10.2
$C_2H_5^\bullet$		9.6(5)	9.9	9.9	10.0	9.9	9.8	9.9	10.0	9.9	9.8	9.8	9.9	9.9	9.8
$1\text{-}C_3H_7^\bullet$			9.6(7)	9.9	10.0	9.9	9.8	9.9	10.0	9.9	9.8	9.8	9.9	9.9	9.8
$2\text{-}C_3H_7^\bullet$				9.5(6)	10.0	9.8	9.8	9.8	10.0	9.8	9.8	9.8	9.8	9.8	9.8
$C_3H_5^\bullet$					9.8(8)	10.0	10.0	10.0	10.1	10.0	10.0	10.0	10.0	10.0	10.0
$1\text{-}C_4H_9^\bullet$						9.6(7)	9.8	9.9	10.0	9.9	9.8	9.8	9.9	9.9	9.8
$2\text{-}C_4H_9^\bullet$							9.5(9)	9.8	10.0	9.8	9.8	9.8	9.8	9.8	9.8
$i\text{-}C_4H_9^\bullet$								9.6(7)	10.0	9.9	9.8	9.8	9.9	9.9	9.8
$C_4H_7^\bullet$									9.8(10)	10.0	10.0	10.0	10.0	10.0	10.0
$1\text{-}C_5H_{11}^\bullet$										9.6(7)	9.8	9.8	9.9	9.9	9.8
$2\text{-}C_5H_{11}^\bullet$											9.5(9)	9.8	9.8	9.8	9.8
$3\text{-}C_5H_{11}^\bullet$												9.5(9)	9.8	9.8	9.8
2-methyl-1-butyl													9.6(7)	9.9	9.8
$1\text{-}R^\bullet$ (Prim.)														9.6(7)	9.8
$2\text{-}R^\bullet$ (sec.)															9.5(9)

Notes for Radical Recombination

1. High pressure limit value calculated by Cheng and Yeh [1] from pressure dependent rate data at 308 K. The reaction is pressure dependent up to $\sim 10^3$ Torr and values for lower pressure experiments are available in their paper. Their high pressure value agrees with the earlier prediction of Benson and O'Neal [2]. Rate constants have also been reported by Halsted et al. [3] and Teng and Jones [4] but these values are considerably lower (average value of $\sim 10^{9.2}$) and probably are well into the fall-off region.

2. Data of Kurylo, Peterson, and Braun [5] at 298 K and of Pratt and Veltman [6] at 700 K. At low pressures the ethane may be vibrationally excited and the overall reaction will yield CH_3 radicals.

3. An average of the values for $CH_3\cdot + H$ and for $C_2H_5\cdot + H$.

4. Glanzer, Quack, and Troe [7] list ten values of the rate constant for methyl radical recombination measured at 293 to 450 K. Seven of the values lie between 10.4 and 10.5, with an average of 10.4. Two of the other values are lower limits (measured in the falloff region). Parkes, Paul, and Quinn [8] conclude that the rate constant is independent of temperature up to 900 K. Glanzer, Quack, and Troe [7] believe that the rate constant is "approximately constant" with possibly "a small decrease of the high pressure recombination coefficient with temperature". A rigorous correction based on simple collision theory [9] gives a factor of 1.3 between 300 and 900 K.

5. Parkes and Quinn [10] measured a value of 9.9 at 300 K for the recombination of ethyl radicals by direct measurement of the radical concentration using molecular modulation spectrometry. They were unable to confirm the spectrum of the ethyl radical. Nevertheless, their value is in excellent agreement with the value of 10.0 at 860 K obtained by Golden, Choo, Perona, and Piszkiewicz, [11] using very low pressure pyrolysis. Their value is also in good agreement with the earlier rotating sector measurement [12] of 10.4 obtained by Shepp and Kutschke at 373 K. All three techniques directly measured the radical concentration. Other less direct methods have given the values 8.6 at 384 K (radical buffer plus thermochemistry) [13], 8.4 at 693 to 803 K (pyrolysis and theory) [14], and 8.6 at 895 to 981 K (pyrolysis and thermochemistry) [15]. An average value, weighted two to one in favor of the more direct methods, is 9.6 at 700 K.

6. Value of Parkes and Quinn [10], neglecting any temperature coefficient.

7. Assumed to have the same value as $k(C_2H5\cdot + C_2H_5\cdot)$.

8. Average of three reported values: 9.9 at 913 K by Golden, Gac, and Benson [16]; 9.9 at 300 K by Van den Bergh and Callear [17]; and 9.6 at 300 K by Throssell [18].

9. Assumed to have the same value as $k(2\text{-}C_3H_7\cdot + 2\text{-}C_3H_7\cdot)$.

10. Assumed to be the same as $k(C_3H_5\cdot + C_3H_5\cdot)$.

11. Average of the geometric mean value of 10.4 and the value of 10.2 calculated by Throssell [18] (from unspecified thermochemistry) and the corresponding 1-butene decomposition parameters of Trenwith [19].

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4. Radical Disproportionation

Values of the rate constants at 700 K for disproportionation have been calculated from absolute rates of radical recombination (see recombination section) and disproportionation/combination ratios. The latter have been taken from literature data and estimated on the basis of general structural similarities between reacting radical pairs. In most cases where several measurements are reported preference has been given to those at the highest temperature. The absolute rates are in table 3 along with the disproportionation/combination rate ratio, Δ, given in parentheses. The quantity $\Delta(a\cdot, b\cdot)$ is defined as the disproportionation/combination ratio where $a\cdot$ is the radical abstracting the hydrogen atom and $b\cdot$ correspondingly forms the olefin. All disproportionations were assumed to have no activation energy.

Disproportionations are measured relative to recombinations. It follows therefore that the accuracy for disproportionations can not exceed that for recombinations. In general the accuracy of disproportionation to recombination ratios is of the order of two, so that the absolute accuracy of disproportionations ranges from about $10^{0.3}$ to $10^{0.8}$ L mol^{-1}s^{-1}. Little recent work has been done in the field. In general, disproportionations are of minor importance in controlling kinetic features of pyrolysis reactions so relatively large uncertainties in the rate parameters can be tolerated.

TABLE 3. Rate constants at 700 K for radical disproportionation. The form of the rate constant is log k/(L mol $^{-1}$s^{-1}). The disproportionation/combination ratios are in parentheses; the numbers of the source notes to the tables are listed in the columns headed by "S" (for source)

R -> Olefin

R->RH	C_2H_5•	S	$1-C_3H_7$•	S	$2-C_3H_7$•	S	$1-C_4H_9$•	S	$2-C_4H_9$•	S	2-methyl -1-propyl•	S	C_4H_7•	S	$1-C_5H_{11}$•, & 1-R•	S	$2-C_5H_{11}$•, $3-C_5H_{11}$•, & 2-R•	S
H	(0.05) 9.3	39	(0.1) 10.0	40	(0.5) 10.7	41	(0.1) 10.0	40	(0.5) 10.7	42	(0.1) 10.0	40	(0.3) 10.5	43	(0.1) 10.0	40	(0.5) 10.7	42
CH_3•	(0.04) 8.9	1	(0.06) 9.1	2	(0.16) 9.4	2	(0.1) 9.3	3	(0.07) 9.0	3	(0.06) 9.1	3	(0.3) 9.9	4	(0.1) 9.3	5	(0.07) 9.0	6
C_2H_5•	(0.13) 8.7	7	(0.065) 8.7	2	(0.18) 9.2	2	(0.06) 8.7	8a	(0.23) 9.2	8b	(0.04) 8.5	9	(0.4) 9.6	10	(0.06) 8.7	11	(0.23) 9.2	12
$1-C_3H_7$•	(0.057) 8.7	2	(0.15) 8.8	13a	(0.25) 9.3	15c	(0.1) 8.9	3	(0.1) 8.8	3	(0.1) 8.9	3	(0.4) 9.6	14	(0.056) 8.7	15a	(0.11) 8.8	15a
$2-C_3H_7$•	(0.16) 9.1	15b	(0.16) 9.1	15c	(0.65) 9.3	16	(0.17) 9.0	3	(0.2) 9.1	3	(0.7) 9.6	3	(0.5) 9.7	17	(0.17) 9.0	18	(0.2) 9.1	19
C_3H_5•	(0.13) 9.1	20	(0.1) 9.0	21	(0.1) 9.0	21	(0.1) 9.0	21	(0.1) 9.0	21	(0.1) 9.0	21	(0.5) 9.8	22	(0.1) 9.0	21	(0.1) 9.0	21
$1-C_4H_9$•	(0.066) 8.7	8a	(0.1) 8.9	3	(0.2) 9.1	3	(0.12) 8.7	23a	(0.32) 9.3	23b	(0.11) 8.9	3	(0.4) 9.6	14	(0.12) 9.0	24	(0.32) 9.3	25
$2-C_4H_9$•	(0.12) 8.9	3	(0.5) 9.0	3	(0.4) 9.4	26	(0.3) 8.9	23b	(0.69) 9.3	13b	(0.2) 9.1	3	(0.5) 9.7	17	(0.13) 8.9	27	(0.69) 9.6	28
2-methyl-1-propyl•	(0.04) 8.5	9	(0.08) 8.8	3	(0.3) 9.3	3	(0.1) 8.9	3	(0.1) 8.8	3	(0.075) 8.5	29	(0.4) 9.6	14	(0.1) 8.9	30	(0.1) 8.8	31

TABLE 3. Rate constants at 700 K for radical disproportionation. The form of the rate constant is log k/(L mol $^{-1}$s^{-1}). The disproportionation/combination ratios are in parentheses; the numbers of the source notes to the tables are listed in the columns headed by "S" (for source)... Continued

R -> Olefin

R->RH	C_2H_5•	S	1-C_3H_7•	S	2-C_3H_7•	S	1-C_4H_9•	S	2-C_4H_9•	S	2-nethyl -1-propyl•	S	C_4H_7•	S	1-$C_5H_{11}^•$, & 1-R•	S	2-$C_5H_{11}^•$, 3-$C_5H_{11}^•$, & 2-R•	S
C_4H_7 •	(0.1) 9.0	21	(0.1) 9.0	21	(0.1) 9.0	21	(0.1) 9.1	21	(0.1) 9.0	21	(0.1) 9.0	21	(0.5) 9.5	22	(0.1) 9.0	21	(0.1) 9.0	21
1-$C_5H_{11}^•$ and 1-R•	(0.1) 8.9	32	(0.1) 8.9	33	(0.2) 9.1	34	(0.1) 8.9	24	(0.32) 9.3	25	(0.1) 8.9	35a	(0.4) 9.6	14	(0.15) 8.8	15a	(0.32) 9.3	25
2-$C_5H_{11}^•$, 3-$C_5H_{11}^•$ and 2-R•	(0.1) 8.8	40	(0.15) 9.0	37	(0.4) 9.4	38	(0.13) 8.9	27	(0.69) 9.6	28	(0.2) 9.1	35b	(0.5) 9.7	17	(0.13) 8.9	27	(0.69) 9.3	28

Notes for Radical Disproportionation

1. Experimental data (298 K) of Borrell and Platt [1] and evaluated data of Konar [2].

2. Data of Terry and Futrell [3] (~300 K).

3. Calculated from the equation [3] $\log \Delta = 0.111(S_d^\circ - S_c^\circ) - 4.88$, where S_d° and S_c° are the molar entropies in cal/(mol K) for the disproportionation and combination product molecules, respectively. Since the relation was derived for small alkyl radicals [3] the present estimates of Δ were restricted to these types of radicals and thus do not include allyl and methylallyl radicals nor hydrogen atoms. For convenience, only the most stable isomers of olefins were used in calculating the value of S_d°.

4. Assumed to have the same value as $\Delta(CH_3\cdot$, cyclohexadienyl $\cdot)$ [4]. Pratt and Veltman [6b] found log rate constant$=10.8-(0.2/\theta)=10.7$ at 700 K.

5. Assumed to be same as $\Delta(CH_3\cdot, 1\text{-}C_4H_9\cdot)$.

6. Assumed to be the same as $\Delta(CH_3\cdot, 2\text{-}C_4H_9\cdot)$.

7. Data of LaLonde and Price [5a] (673 K) and Hooper, Simon, and Back [5b] (298 to 173 K).

8a. Data of Watkins and O'Deen [6a]; recalculated by Inel [7a].

8b. Data of Holroyd and Klein [7b], quoted by Stein and Rabinovitch [7c].

9. Data of Terry and Futrell [8] (~300 K).

10. Assumed to be the same as $\Delta(C_2H_5\cdot$, cyclohexadienyl $\cdot)$ [4].

11. Assumed to be the same as $\Delta(C_2H_5\cdot, 1\text{-}C_4H_9\cdot)$.

12. Assumed to be the same as $\Delta(C_2H_5\cdot, 2\text{-}C_4H_9\cdot)$; Watkins and Ostreko [9] have determined a value of ~0.25 for $\Delta(C_2H_5\cdot, 2\text{-}C_6H_{13}\cdot)$ at 325–388 K.

13a. Data of Falconer and Sunder [10] (298 K).

13b. Average of data by Falconer and Sunder [10] (0.77 at 298 K) and Oref, Schuetzle, and Rabinovitch [16b] (0.60 at 296 K).

14. Assumed to be the same as $k(C_2H_5\cdot, C_4H_7\cdot)$.

15a. Data of Watkins and Lawson [11a] (330–370 K).

15b. Average of data by Terry and Futrell [3] and Thynne [11b].

15c. Recalculated from reference 3. The value of 0.41 was taken to be the sum of $\Delta(1\text{-}C_3H_7\cdot, 2\text{-}C_3H_7\cdot)$ and $\Delta(2\text{-}C_3H_7\cdot, 1\text{-}C_3H_7\cdot)$ and the individual Δ's calculated on the statistical number of hydrogens available for the appropriate olefin formation (3/5 and $2/5\times\Delta$, respectively). The overall value of 0.41 agrees with data of Falconer and Sunder [10].

16. Excellent agreement between the results of Parkes and Quinn [12a] (0.65 at 300 to 800 K), Cadman, Inel, and Trotman-Dickenson [12b] (0.61 at 299 to 480 K), and Falconer and Sunder [10] (0.69 at 298 K).

17. Assumed to be the same as $\Delta(2\text{-}C_3H_7\cdot$, cyclohexadienyl$\cdot)$, determined by Suart [13].

18. Assumed to be the same as $\Delta(2\text{-}C_3H_7\cdot, 1\text{-}C_4H_9\cdot)$.

19. Assumed to be the same as $\Delta(2\text{-}C_3H_7\cdot, 2\text{-}C_4H_9\cdot)$.

20. Data of James and Troughton [14] (407–448 K).

21. Assumed to be approximately the same as $\Delta(C_3H_5\cdot, C_2H_5\cdot)$.

22. Assumed to be approximately the same as Δ(cyclohexadienyl·, cyclohexadienyl·) determined by James and Suart [15] (336–374 K).

23a. See note 8a; value consistent with data of Falconer and Sunder (note 13a).

23b. Falconer and Sunder [10] obtained a value of 0.45 for what was essentially the sum of $\Delta(2\text{-}C_4H_9\cdot, 1\text{-}C_4H_9\cdot)$ and $\Delta(1\text{-}C_4H_9\cdot, 2\text{-}C_4H_9\cdot)$. Based on the number of atoms to be disproportionated, the following values are estimated: $\Delta(2\text{-}C_4H_9\cdot, 1\text{-}C_4H_9\cdot)=0.11$ and $\Delta(1\text{-}C_4H_9\cdot, 2\text{-}C_4H_9\cdot)=0.32$.

24. $\Delta(1\text{-}C_4H_9\cdot, 1\text{-}C_4H_9\cdot)$.

25. $\Delta(1\text{-}C_4H_9\cdot, 2\text{-}C_4H_9\cdot)$.

26. Data of Boddy and Robb [16a] (~300 K).

27. $\Delta(2\text{-}C_4H_9\cdot, 1\text{-}C_4H_9\cdot)$.

28. $\Delta(2\text{-}C_4H_9\cdot, 2\text{-}C_4H_9\cdot)$.

29. Data of Slater, Collier and Calvert [17] (298–441 K); consistent with data of Terry and Futrell [8].

30. Δ(2-methyl-1-propyl·, $1\text{-}C_4H_9\cdot$).

31. Δ(2-methyl-1-propyl·, $2\text{-}C_4H_9\cdot$).

32. Data of Watkins and Ostreko [9] for $\Delta(1\text{-}C_6H_{13}\cdot, C_2H_5\cdot)$, (350–388 K).

33. $\Delta(1\text{-}C_4H_9\cdot, 1\text{-}C_3H_7\cdot)$.

34. $\Delta(1\text{-}C_4H_9\cdot, 2\text{-}C_3H_7\cdot)$.

35a. $\Delta(1\text{-}C_4H_9\cdot$, 2-methyl-1-propyl).

35b. $\Delta(2\text{-}C_4H_9\cdot$, 2-methyl-1-propyl).

36. Data of Watkins and Ostreko [9] for $\Delta(2\text{-}C_6H_{13}\cdot, C_2H_5\cdot)$ (350–388 K).

37. $\Delta(2\text{-}C_4H_9\cdot, 1\text{-}C_3H_7\cdot)$.

38. $\Delta(2\text{-}C_4H_9\cdot, 2\text{-}C_3H_7\cdot)$.

39. Data of Heller and Gordon [18] (297–476 K).

40. Average value for pentyl [19] and hexyl [20] radicals (298 K).

41. Average of three experimental values [21, 22] (300 K).

42. $\Delta(H\cdot, 2\text{-}C_3H_7\cdot)$.

43. $\Delta(CH_3\cdot, C_4H_7\cdot)$.

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5. Initiation

Arrhenius parameters and rate constants at 700 K for initiation are listed in table 4.

The accuracy of the Arrhenius A factors is probably of the order of half a power of ten. The activation energies are perhaps accurate to within 2 kcal/mol. Thus the accuracy of the rate constants at 700 K is of the order of one power of ten. Much of the available data has been measured at temperatures too high for reliable extrapolation to 700 K. Such data, marked E*, are not used in the evaluation and are included for comparison only. This leaves very few reliable values. However good relative data for higher alkanes have been obtained from shock tube experiments on competitive systems. Many of the values in the table are based on back reactions and thermochemistry. These values will be subject to significant change if the thermochemical values change because the reaction produces two free radicals and the changes due to thermochemistry will therefore be additive. Arrhenius parameters based on theoretical calculations suffer from lack of knowledge on the exact structure of the transition states. When small alkanes are under consideration, care must be taken to ensure that the pressure is sufficiently high for the reaction to be in the first order region. The best experiments are usually done at the highest pressures, unless unusual care is taken to correct the results.

Table 4. Arrhenius parameters and rate constants at 700 K for initiation

Reactant	Products		log [A/s^{-1}]	Source	E, kcal/mol	Source	log [k/s^{-1}] at 700 K	$\Delta S^{o}(700)$ cal/(mol K)	Source	$\Delta H^{o}(700)$ kcal/mol	Source	$\langle \Delta C_p \rangle \,{}^{(700)}_{(300)}$ cal/(mol K)	Source
C_2H_6	$CH_3^{\bullet}$	$CH_3^{\bullet}$	16.3	EP, 1a	87.5	EP, 1a	-11.0	40.4	1c	90.1	1c	3.0	1c
			17.4	B	90.1	B	-10.8						
			16.3	EN, 1b	89.0	EN, 1b	-11.5						
			16.8	R, 1d	89.5	R, 1d	-11.2						
			16.7	Rec, 1e	89.0	Rec, 1e	-11.1						
C_3H_8	$CH_3^{\bullet}$	$C_2H_5^{\bullet}$	17.2	B	85.7	B	-9.6	40.0		85.7		0.25	
			16.6	EN, 2	84.5	EN, 2	-9.8						
			16.9	Rec, 1e	85.1	Rec, 1e	-9.7						
C_3H_6	H	$C_3H_5^{\bullet}$	14.4	B, 3a	89.2	B, 3a	-13.5	28.6		89.2		3.5	
			13.4	EP, 3b	78	EP, 3b	-11.0						
			15.3	R, 1d	89.2	R, 1d	-12.6						
			14.8	Rec, 3c	89.2	Rec, 3c	-13.1						
n-C_4H_{10}	$CH_3^{\bullet}$	1-$C_3H_7^{\bullet}$	17.5	B	85.7	B	-9.3	41.1		85.7		0.6	
			16.9	T, 4	87.4	T, 4	-10.4						
			17.6	R, 1d	85.9	R, 1d	-9.2						
			17.5	Rec, 5a	85.7	Rec, 5a	-9.3						
n-C_4H_{10}	$C_2H_5^{\bullet}$	$C_2H_5^{\bullet}$	16.4	B, 5a	82.1	B, 5a	-9.2	39.4		82.1		-2.7	
			16.4	T, 4	82.4	T, 4	-9.4						
			16.4	EN, 5b	82.1	EN, 5b	-9.2						
			17.3	R, 1d	81.8	R, 1d	-8.3						
			16.4	Rec, 5a	82.1	Rec, 5a	-9.2						
2-methylpropane	$CH_3^{\bullet}$	2-$C_3H_7^{\bullet}$	17.7	B	84.2	B	-8.6	42.7		84.2		0.2	
			17.2	T, 6a	85.0	T, 6a	-9.4						
			16.6	EN, 1b	82.6	EN, 1b	-9.2						
			17.8	EP, 6b	82.0	EP, 6b	-7.8						
			17.3	Rec, 1e	83.4	Rec, 1e	-8.8						
1-C_4H_8	$CH_3^{\bullet}$	$C_3H_5^{\bullet}$	16.4	B	75.5	B	-7.2	36.4		75.5		1.3	
			16.3	EP, 7a	71.3	EP, 7a	-6.0						
			15.7	EN, 1b	73.5	EN, 1b	7.3						
			16.0	R, 1d	73.3	R, 1d	-6.9						
			16.1	Rec, 1e	73.4	Rec, 1e	-6.8						
n-C_5H_{12}	$CH_3^{\bullet}$	1-$C_4H_9^{\bullet}$	17.5	B	85.5	B	-9.2	41.2		85.5		0.6	
			16.1	T, 8	85.4	T, 8	-10.6						
			16.8	Rec, 1e	85.4	Rec, 1e	-9.9						
n-C_5H_{12}	$C_2H_5^{\bullet}$	1-$C_3H_7^{\bullet}$	17.1	B	81.6	B	-8.4	41.0		81.6		-2.2	
			16.7	S, 9	82.1	S, 9	-9.0						

Table 4. Arrhenius parameters and rate constants at 700 K for initiation...Continued

Reactant	Products		log [A/s^{-1}]	Source	E, kcal/mol	Source	log [k/s^{-1}] at 700 K	ΔS°(700) cal/(mol K)	Source	ΔH°(700) kcal/mol	Source	$\langle\Delta C_p\rangle^{(700)}_{(300)}$ cal/(mol K)	Source
			16.7	T, 8	81.9	T, 8	-8.9						
			16.8	Rec, 1e	81.9	Rec, 1e	-8.8						
2-Methylbutane	$CH_3^{\bullet}$	$2\text{-}C_4H_9^{\bullet}$	17.5	B	84.0	B	-8.8	41.8		84.0		0.3	
			16.8	S, 10	82.6	S, 10	-9.0						
			16.9	T, 8	82.1	T, 8	-8.8						
			17.1	Rec, 1e	82.9	Rec, 1e	-8.8						
"	$C_2H_5^{\bullet}$	$2\text{-}C_3H_7^{\bullet}$	16.9	B	80.1	B	-8.1	40.3		80.1		-2.5	
			16.2	EN, 5b	78.8	EN, 5b	-8.4						
			16.8	T, 8	78.7	T, 8	-7.8						
			16.6	Rec, 1e	79.2	Rec, 1e	-8.2						
"	$CH_3^{\bullet}$	2-methyl-1 - propyl	17.4	B	85.4	B	-9.3	40.1		85.4		0.9	
			16.3	S, 11	84.5	S, 11	-10.1						
			16.5	T, 8	85.0	T, 8	-10.1						
			16.7	Rec, 1e	85.0	Rec, 1e	-9.9						
$1\text{-}C_5H_{10}$	$C_2H_5^{\bullet}$	$C_3H_5^{\bullet}$	16.0	B	71.4	B	-6.3	35.8		71.4		-1.7	
$2\text{-}C_5H_{10}$	$CH_3^{\bullet}$	$C_4H_7^{\bullet}$	16.7	B	73.0	B	-6.1	37.2	12	72.9	12	1.7	12
$n\text{-}C_6H_{14}$	$CH_3^{\bullet}$	$1\text{-}C_5H_{11}^{\bullet}$	16.8	S, 13	85.4	S, 13	-9.9						
"	$C_2H_5^{\bullet}$	$1\text{-}C_4H_9^{\bullet}$	16.8	S, 14	81.9	S, 14	-8.8						
"	$1\text{-}C_3H_7^{\bullet}$	$1\text{-}C_3H_7^{\bullet}$	16.5	S, 15	81.9	S, 15	-9.1						
2-Methylpentane	$CH_3^{\bullet}$	$2\text{-}C_5H_{11}^{\bullet}$	17.1	S, 16	82.9	S, 16	-8.8						
"	$1\text{-}C_3H_7^{\bullet}$	$2\text{-}C_3H_7^{\bullet}$	16.6	S, 16	79.2	S, 16	-8.2						
"	2-Methyl-1-propyl	$C_2H_5^{\bullet}$	16.8	B	81.0	B	-8.5	40.0		81.0		-2.3	
"	3-Methyl-1-butyl	$CH_3^{\bullet}$	16.7	S, 16	85.0	S, 16	-9.9						
$1\text{-}C_6H_{12}$	$1\text{-}C_3H_7^{\bullet}$	$C_3H_5^{\bullet}$	16.4	B	71.1	B	-5.8	37.5		71.1		-1.2	
$2\text{-}C_6H_{12}$	$C_2H_5^{\bullet}$	$C_4H_7^{\bullet}$	16.2	B	69.3	B	-5.5	36.5	12	69.3	12	-1.3	12
$3\text{-}C_6H_{12}$	$CH_3^{\bullet}$	2-penten-1-yl	17.0	S, 17	73.0	S, 17	-5.8						

Table 4. Arrhenius parameters and rate constants at 700 K for initiation...continued

Reactant	Products		log [A/s^{-1}]	Source	E, kcal/mol	Source	log [k/s^{-1}] at 700 K	ΔS^{o}(700) cal/(mol K)	Source	ΔH^{o}(700) kcal/mol	Source	$\langle\Delta C_p\rangle_{(300)}^{(700)}$ cal/(mol K)	Source
$(C_3H_5)_2$	$C_3H_5^{\cdot}$	$C_3H_5^{\cdot}$	15.5 13.4 14.4	B EP, 18b Rec, 1e	62.8 56.0 59.4	B EP, 18b Rec, 1e	-4.1 -4.1 -4.2	34.8	18a	0	18a		
2-C_7H_{14}	1-$C_3H_7^{\cdot}$	$C_4H_7^{\cdot}$	16.2	S, 19	69.3	S, 19	-5.4						
1,5-heptadiene	$C_3H_5^{\cdot}$	$C_4H_7^{\cdot}$	15.7	B	58.7	B	-2.6	33.8	20	58.7	20	0.2	20
2-C_8H_{16}	1-$C_4H_9^{\cdot}$	$C_4H_7^{\cdot}$	16.2	S, 19	69.3	S, 19	-5.4						
$(C_4H_7)_2$	$C_4H_7^{\cdot}$	$C_4H_7^{\cdot}$	15.8	B	56.6	B	-1.9	35.8	21	56.6	21	0.8	21
2-C_9H_{18}	1-$C_5H_{11}^{\cdot}$	$C_4H_7^{\cdot}$	16.2	S, 19	69.3	S, 19	-5.4						
5-methyl-2-octene	2-$C_5H_{11}^{\cdot}$	$C_4H_7^{\cdot}$	17.0	B	67.7	B	-4.2	40.2	22	67.7	22	-0.5	22
5-ethyl-2-heptene	3-$C_5H_{11}^{\cdot}$	$C_4H_7^{\cdot}$	17.0	S, 23	67.7	S, 23	-4.2						

Notes for Initiation

1a. Average of reasonably consistent experimental values (800–1000 K) reported by Lin and Back [1], Trenwith [2] and Pacey and Purnell [3]. Other values have been measured but these appear to be the most reliable. For a discussion of discrepancies between experimental values and calculated values see Waage and Rabinovitch [4].

1b. Values calculated by Tsang [5a] from shock tube data at 1100 K using $\Delta H_f^\circ(CH_3\cdot)=34$ kcal/mol.

1c. Unless otherwise noted, thermochemical properties of the reactants at 300 K were obtained from Stull, Westum, and Sinke [5b], and were corrected to those at 700 K by techniques given by Benson [5c].

1d. Preferred value of Benson and O'Neal [6].

2. See note 1b.

3a. Calculated using $\log k \sim 10.3$ from the estimate that $k \sim pZ$ with $Z \sim 10^{12}$L mol^{-1}s^{-1} and $p \sim 0.02$. Simons, Rabinovitch and Dorer [7] have calculated $p \geq 0.015$ (assuming $E \sim 0$) at 298 K. Benson and O'Neal [6] estimate that at 1000 K, $p \sim 0.05$ and $Z \sim 10^{12}$ The correction for collision frequency with temperature is negligible and with an averaged value of p between 298 and 1000 K the above estimate of k follows.

3b. Obtained by toluene carrier method [8b] considered unreliable by Benson and O'Neal [6].

3c. Average (omitting toulene carrier data).

4. Theoretical values calculated for 800 K (for butane only) by Hase, Johnson and Simons [9] using a transition state model with torsion modes treated as free rotors. Calculations with this model in conjunction with hindered rotation, radical models lead both to excellent agreement with observed rates of activated decomposition of the alkane [9] but to some disagreement with our preferred rates of radical recombination (see recombination section); using the tight radical models the following calculated recombination rates (log) are reported [9] for 400 K: $CH_3\cdot+1\text{-}C_3H_7\cdot$, 9.8; $C_2H_5\cdot+C_2H_5\cdot$, 8.6; $C_2H_5\cdot+C_3H_7\cdot$, 9.3; $CH_3\cdot+1\text{-}C_4H_9\cdot$, 8.9; $CH_3\cdot+2\text{-}C_4H_9\cdot$, 9.6; $C_2H_5\cdot+2\text{-}C_3H_7\cdot$, 9.8 and $CH_3\cdot+$2-methyl-1-propyl., 9.6.

5a. These recommended parameters give a value of the overall decomposition rate constant of $1.4\times10^{-4}+2.0\times10^{-4}=3.4\times10^{-4}$s^{-1} at 886 K. This value compares closely with the experimental value of 2.0×10^{-4}s^{-1} measured at this temperature [10].

5b. Values determined by Tsang [5a] from shock tube experiments at 1100 K.

6a. Theoretical values calculated for 800 K by Hase and Simons [11] on the basis of a free-rotor activated complex structure, tight radical structures and high critical energies. This model leads to good agreement with activated isobutane decomposition [11] and gives a value of $\log k=9.8$ for the methyl-isopropyl recombination, compared with the preferred value of 10.3 (see recombination section).

6b. Experimental values reported by Konar and coworkers [12].

7. Experimentally determined values by Trenwith [13]. However, Dorer and Rabinovitch [14] in a study of chemically activated olefin decomposition have calculated that a low A-factor, $\sim10^{14}$, is expected. In addition, results of Halstead and Quinn [15] indicate a lower limit of the A-factor is $10^{13.9}$s^{-1}.

8. A-factor values calculated for 1000 K. See note 4.

9. Estimated to be the same as Tsang's shock tube value for $n\text{-}C_4H_{10}\rightarrow 2C_2H_5\cdot$ with a correction for $\Delta S\ddagger$ for the loss of the two-fold rotational symmetry in the transition state of pentane (see note 5b). Tsang [5a] has suggested that similarly structured types of C–C bonds break with the same A-factors regardless of the size of the alkane.

10. Tsang's shock tube value for $i\text{-}C_4H_{10}\rightarrow CH_3\cdot+1\text{-}C_3H_7\cdot$ (see footnote 1b) with the correction $\Delta S\ddagger\ (i\text{-}C_5H_{10})=\Delta S\ddagger\ (i\text{-}C_4H_{10})-R\ln 3+R\ln 2$ for different rotational ground state symmetries and optical asymmetries of transition states.

11. Tsang's shock tube values for C_3H_8 decomposition [5a] with a correction for the loss of two-fold rotational symmetry in the ground state (see note 1b) for the A factor.

12. Thermochemistry calculated for trans isomers of olefinic species.

13. Values chosen to be the same as the recommended value for $n\text{-}C_5H_{12}\rightarrow CH_3\cdot+1\text{-}C_4H_9\cdot$.

14. Values chosen to be the same as the recommended values for $n\text{-}C_5H_{12}\rightarrow C_2H_5\cdot+1\text{-}C_3H_7\cdot$.

15. See note 14; A-factor corrected for change of two-fold rotational symmetry in transition states.

16. Values chosen to be the same as the recommended values for the corresponding reaction of 2-methylbutane.

17. Assumed to be the same as $2\text{-}C_5H_{10}\rightarrow CH_3\cdot+C_4H_7\cdot$ with a correction for two-fold rotational symmetry in $2\text{-}C_5H_{10}$ molecules.

18a. Measured values at 913 K of Golden, Gac and Benson [8a] were used. The average heat capacity between 700 and 1000 K is nearly zero so no correction was made for temperature.

18b. Recalculated data of Throssell [16].

19. Assumed same values as for $2\text{-}C_6H_{12}$; used kinetic-thermochemical based value.

20. The thermochemical parameters for the diene were calculated using group additivity [17].

21. Calculated for trans, trans isomer of 2,6-octadiene.

22. Thermochemistry of the olefin calculated from group additivity [17]. All olefinic bonds assigned trans configuration.

23. Assumed to be the same as the 5-methyl-2-octene decomposition.

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6. H-Transfer

Arrhenius parameters and rate constants at 700 K for H–transfer are listed in table 5. The accuracy of the Arrhenius *A* factors is of the order of half a power of ten. That of the activation energies is about 2 kcal/mol. The accuracy of the rate constants at 700 K is therefore of the order of one power of ten. There is surprisingly little good experimental data other than for H and CH_3. Much of the table is based on a few key values for reactions such as 2-propyl+ethane and ethyl+*n*-butane. Wherever possible Arrhenius parameters were selected so that sensible reactivities prevailed. For example, for the same radical and alkane, abstraction from the secondary position may be expected to be faster than from the primary position.

The notation and method of evaluation was the same as in the previous section with the additional notation that E^* denotes experimental results at temperatures that are too high for extrapolation back to 700 K. Abstraction from methane was excluded in view of methane's stability.

Table 5. Arrhenius Parameters and rate constants at 700 K for H-Transfer

Reactants		Products		log [A/L mol^{-1}s^{-1}]	Source	E, kcal/mol	Source	log [k/L mol^{-1}s^{-1}] at 700 K	ΔS^o(700) cal/(mol K)	ΔH^o(700) kcal/mol	$<\Delta C_p>$ (700) (300) cal/(mol K)
H_2	$CH_3^{\cdot}$	H	CH_4	9.6	B, 1a	11.3	B, 1a	6.1	-6.7	-0.6	-1.2
				9.5	E, 1b	12.2	E, 1b	5.7			
				8.7	E, 1c	10.3	E, 1c	5.5			
				9.0	T, 1d	11.2	T, 1d	5.5			
				8.6	T, 1e	8.6	T, 1e	5.9			
				8.9	R, 1f	10.9	R, 1f	5.5			
				9.2	Rec, 1g	11.3	Rec, 1g	5.7			
H_2	$C_2H_5^{\cdot}$	H	C_2H_6	9.7	B, 2a	15.2	B, 2a	5.0	-6.4	5.5	0.6
				9.8	E, 2b	14.1	E, 2b	5.4			
				8.8	E, 2c	11.8	E, 2c	5.1			
				9.6	E, 2d	13.7	E, 2d	5.3			
				9.1	T, 2e	12.8	T, 2e	5.1			
				9.6	Rec, 2f	14.0	Rec, 2f	5.2			
H_2	$1\text{-}C_3H_7^{\cdot}$	H	C_3H_8	9.4	B, 3a	16.0	B, 3a	4.4	-7.7	6.3	-0.0
				9.0	E, 3b	14.8	E, 3b	4.4			
				9.2	Rec, 3c	15.4	Rec, 3c	4.4			
H_2	$2\text{-}C_3H_7^{\cdot}$	H	C_3H_8	9.6	B, 4a	17.5	B, 4a	4.1	-5.6	9.8	-0.3
				9.5	E, 4b	15.9	E, 4b	4.5			
				9.6	Rec, 3c	16.7	Rec, 3c	4.4			
H_2	$C_3H_5^{\cdot}$	H	C_3H_6	10.5	B, 5	19.7	B, 5	4.3	-2.4	16.2	-0.4
H_2	$1\text{-}C_4H_9^{\cdot}$	H	$n\text{-}C_4H_{10}$	9.5	B, 6	15.7	B, 6	4.6	-7.3	6.0	-0.2
H_2	$2\text{-}C_4H_9^{\cdot}$	H	$n\text{-}C_4H_{10}$	9.7	B, 7	17.2	B, 7	4.3	-6.6	9.5	0.4
H_2	2-methyl-1-propyl	H	2-methyl-propane	9.5	S, 8	15.7	S, 8	4.6			
H_2	$C_4H_7^{\cdot}$	H	$1\text{-}C_4H_8$	10.6	B, 9	25.2	B, 9	2.7	-2.0	21.3	-0.7
H_2	$C_4H_7^{\cdot}$	H	$2\text{-}C_4H_8$	10.5	B, 10	22.3	B, 10	3.5	-3.8	18.8	-0.6
H_2	$1\text{-}R^{\cdot}$	H	RH	9.5	S, 8	15.7	S, 8	4.6			
H_2	$2\text{-}R^{\cdot}$	H	RH	9.7	S, 11	17.2	S, 11	4.3			
C_2H_6	H	$C_2H_5^{\cdot}$	H_2	11.1	E, 12	9.7	E, 12	8.1			

ble 5. Arrhenius Parameters and rate constants at 700 K for H-Transfer ...Continued

Reactants		Products		log [A/L mol^{-1}s^{-1}]	Source	E, kcal/mol	Source	log [k/L mol^{-1}s^{-1}] at 700 K	ΔS^o(700) cal/(mol K)	ΔH^o(700) kcal/mol	$\langle \Delta C_p \rangle_{(300)}^{(700)}$ cal/(mol K)
C_2H_6	$CH_3^{\bullet}$	$C_2H_5^{\bullet}$	CH_4	9.2	E, 13	11.7	E, 13	5.5			
				11.7	E*, 14a	21.5	E*, 14	5.0			
				8.8	E, 1f	11.6	E, 1f	5.2			
				9.2	E, 13	11.7	E, 13	5.5			
				10.5	E*, 14b	17.9	E*, 14b	4.9			
				8.8	Rec, 1f	11.6	Rec, 1f	5.2			
C_2H_6	1-$C_3H_7^{\bullet}$	$C_2H_5^{\bullet}$	C_3H_8	8.5	S, 15	12.3	S, 15	4.6			
C_2H_6	2-$C_3H_7^{\bullet}$	$C_2H_5^{\bullet}$	C_3H_8	8.0	E, 16	12.9	E, 16	4.0			
C_2H_6	$C_3H_5^{\bullet}$	$C_2H_5^{\bullet}$	C_3H_6	8.9	B, 17	20.5	B, 17	2.5	4.0	10.7	-1.0
C_2H_6	1-$C_4H_9^{\bullet}$	$C_2H_5^{\bullet}$	n-C_4H_{10}	8.5	S, 15	12.3	S, 15	4.6			
				8.4	E*, 18a	15	E*, 18a	3.7			
				8.5	Rec, 15	12.3	Rec, 15	4.6			
C_2H_6	2-$C_4H_9^{\bullet}$	$C_2H_5^{\bullet}$	n-C_4H_{10}	8.0	S, 18b	12.9	S, 18b	4.0			
C_2H_6	2-methyl-1-propyl	$C_2H_5^{\bullet}$	2-methyl-propane	8.5	S, 15	12.3	S, 15	4.6			
C_2H_6	$C_4H_7^{\bullet}$	$C_2H_5^{\bullet}$	1-C_4H_8	9.0	B, 19	24.1	B, 19	1.4	4.4	15.8	-1.2
C_2H_6	$C_4H_7^{\bullet}$	$C_2H_5^{\bullet}$	2-C_4H_8	8.8	B, 20	23.0	B, 20	1.6	2.3	13.2	-1.2
C_2H_6	1-$R^{\bullet}$	$C_2H_5^{\bullet}$	RH	8.5	S, 15	12.3	S, 15	4.6			
C_2H_6	2-$R^{\bullet}$	$C_2H_5^{\bullet}$	RH	8.0	S, 18b	12.9	S, 18b	4.0			
C_3H_8	H	1-$C_3H_7^{\bullet}$	H_2	11.1	S, 21a	9.7	S, 21a	8.1			
C_3H_8	H	2-$C_3H_7^{\bullet}$	H_2	10.7	B, 21b	7.1	B, 21b	8.5			
				11.0	E, 21c	8.3	E, 21c	8.4			
				10.8	Rec, 21d	7.7	Rec, 21d	8.4			
C_3H_8	$CH_3^{\bullet}$	1-$C_3H_7^{\bullet}$	CH_4	9.0	E, 22	11.5	E, 22	5.4			
C_3H_8	$CH_3^{\bullet}$	2-$C_3H_7^{\bullet}$	CH_4	8.8	E, 23a	10.1	E, 23a	5.6			
				9.3	E, 23b	11.3	E, 23b	5.8			
				10.4	E, 23c	15.1	E, 23c	5.7			
				8.3	R, 1f	9.6	R, 1f	5.3			
				8.8	Rec, 23d	10.5	Rec, 23d	5.5			

Table 5. Arrhenius Parameters and rate constants at 700 K for H-Transfer...Continued

Reactants		Products		log [A/L $mol^{-1}s^{-1}$]	Source	E, kcal/mol	Source	log [k/L $mol^{-1}s^{-1}$] at 700 K	ΔS^o(700) cal/(mol K)	ΔH^o(700) kcal/mol	$\langle \Delta C_p \rangle_{(300)}^{(700)}$ cal/(mol K)
C_3H_8	$C_2H_5^•$	1-$C_3H_7^•$	C_2H_6	8.5	S, 15	12.3	S, 15	4.6			
C_3H_8	$C_2H_5^•$	2-$C_3H_7^•$	C_2H_6	7.7	S, 24	10.4	S, 24	4.4			
C_3H_8	2-$C_3H_7^•$	1-$C_3H_7^•$	C_3H_8	8.0	S, 18b	12.9	S, 18b	4.0			
C_3H_8	1-$C_3H_7^•$	2-$C_3H_7^•$	C_3H_8	7.7	S, 25	10.4	S, 25	4.4			
C_3H_8	$C_3H_5^•$	1-$C_3H_7^•$	C_3H_6	8.9	S, 26	20.5	S, 26	2.5			
C_3H_8	$C_3H_5^•$	2-$C_3H_7^•$	C_3H_6	8.3	B, 27	16.1	B, 27	3.3	3.3	6.4	-0.7
C_3H_8	1-$C_4H_9^•$	1-$C_3H_7^•$	n-C_4H_{10}	8.5	S, 15	12.3	S, 15	4.6			
C_3H_8	1-$C_4H_9^•$	2-$C_3H_7^•$	n-C_4H_{10}	7.7	S, 24	10.4	S, 24	4.4			
C_3H_8	2-$C_4H_9^•$	1-$C_3H_7^•$	n-C_4H_{10}	8.0	S, 18b	12.9	S, 18b	4.0			
C_3H_8	2-$C_4H_9^•$	2-$C_3H_7^•$	n-C_4H_{10}	7.9	S, 28	12.3	S, 28	4.1			
C_3H_8	2-methyl-1-propyl	1-$C_3H_7^•$	2-methylpropane	8.5	S, 15	12.3	S, 15	4.6			
C_3H_8	2-methyl-1-propyl	2-$C_3H_7^•$	2-methylpropane	7.7	S, 24	10.4	S, 24	4.4			
C_3H_8	$C_4H_7^•$	1-$C_3H_7^•$	1-C_4H_8	9.0	S, 29	24.1	S, 29	1.4			
C_3H_8	$C_4H_7^•$	2-$C_3H_7^•$	1-C_4H_8	7.8	S, 30	18.6	S, 30	2.0			
C_3H_8	$C_4H_7^•$	1-C_3H_7	2-C_4H_8	8.8	S, 31	23.0	S, 31	1.6			
C_3H_8	$C_4H_7^•$	2-$C_3H_7^•$	2-C_4H_8	7.8	S, 32	19.0	S, 32	1.9			
C_3H_8	1-$R^•$	1-$C_3H_7^•$	RH	8.5	S, 15	12.3	S, 15	4.6			
C_3H_8	1-$R^•$	2-$C_3H_7^•$	RH	7.7	S, 24	10.4	S, 24	4.4			
C_3H_8	2-$R^•$	1-$C_3H_7^•$	RH	8.0	S, 18b	12.9	S, 18b	4.0			
C_3H_8	2-$R^•$	2-$C_3H_7^•$	RH	7.9	S, 28	12.3	S, 28	4.1			
n-C_4H_{10}	H	1-$C_4H_9^•$	H_2	11.1	S, 21a	9.7	S, 21a	8.1			
n-C_4H_{10}	H	2-$C_4H_9^•$	H_2	11.1	S, 21e	7.7	S, 21e	8.7			

Table 5. Arrhenius Parameters and rate constants at 700 K for H-Transfer...Continued

Reactants		Products		log [A/L $mol^{-1}s^{-1}$]	Source	E, kcal/mol	Source	log [k/L $mol^{-1}s^{-1}$] at 700K	ΔS^o (700) cal/(mol K)	ΔH^o (700) kcal/mol	$<\Delta C_p>^{(700)}_{(300)}$ cal/(mol K)
n-C_4H_{10}	$CH_3\cdot$	1-$C_4H_9\cdot$	CH_4	8.6	R, 33	11.4	R, 33	5.0			
n-C_4H_{10}	$CH_3\cdot$	2-$C_4H_9\cdot$	CH_4	8.9 11.4 8.6 8.6	E, 34a E*, 34b R, 1f Rec, 1f	9.5 18.2 9.6 9.6	E, 34a E*, 34b R, 1f Rec, 1f	5.9 5.7 5.6 5.6			
n-C_4H_{10}	$C_2H_5\cdot$	1-$C_4H_9\cdot$	C_2H_6	8.5	S, 35	12.3	S, 35	4.6			
n-C_4H_{10}	$C_2H_5\cdot$	2-$C_4H_9\cdot$	C_2H_6	8.0 10.5 8.0	E, 36a E*, 36b Rec, 36a	10.4 20.1 10.4	E, 36a E*, 36b Rec, 36a	4.8 4.2 4.8			
n-C_4H_{10}	1-$C_3H_7\cdot$	1-$C_4H_9\cdot$	C_3H_8	8.5	S, 15	12.3	S, 15	4.6			
n-C_4H_{10}	1-$C_3H_7\cdot$	2-$C_4H_9\cdot$	C_3H_8	8.0	S, 37	10.4	S, 37	4.8			
n-C_4H_{10}	2-$C_3H_7\cdot$	1-$C_4H_9\cdot$	C_3H_8	8.0	S, 38	12.9	S, 38	4.0			
n-C_4H_{10}	2-$C_3H_7\cdot$	2-$C_4H_9\cdot$	C_3H_8	8.0	S, 39	12.3	S, 39	4.2			
n-C_4H_{10}	$C_3H_5\cdot$	1-$C_4H_9\cdot$	C_3H_6	8.9	S, 26	20.5	S, 26	2.5			
n-C_4H_{10}	$C_3H_5\cdot$	2-$C_4H_9\cdot$	C_3H_6	8.5	B, 40	16.4	B, 40	3.4	4.2	6.7	-0.9
n-C_4H_{10}	2-$C_4H_9\cdot$	1-$C_4H_9\cdot$	n-C_4H_{10}	8.0	S, 38	12.9	S, 38	4.0			
n-C_4H_{10}	1-$C_4H_9\cdot$	2-$C_4H_9\cdot$	n-C_4H_{10}	8.0	S, 37	10.4	S, 37	4.8			
n-C_4H_{10}	2-methyl-1-propyl	1-$C_4H_9\cdot$	2-methyl-propane	8.5	S, 15	12.3	S, 15	4.6			
n-C_4H_{10}	2-methyl-1-propyl	2-$C_4H_9\cdot$	2-methyl-propane	8.0	S, 37	10.4	S, 37	4.8			
n-C_4H_{10}	$C_4H_7\cdot$	1-$C_4H_9\cdot$	1-C_4H_8	9.0	B, 41	20.1	B, 41	2.7	4.6	11.8	-1.2
n-C_4H_{10}	$C_4H_7\cdot$	2-$C_4H_9\cdot$	1-C_4H_8	8.2	B, 42a	19.0	B, 42	2.3	2.5	9.3	-1.0
n-C_4H_{10}	$C_4H_7\cdot$	1-$C_4H_9\cdot$	2-C_4H_8	8.8	S, 31	23.0	S, 31	1.6			
n-C_4H_{10}	$C_4H_7\cdot$	2-$C_4H_9\cdot$	2-C_4H_8	8.4	B, 42b	19.0	B, 42	2.5	2.5	9.3	-1.0
n-C_4H_{10}	1-R$\cdot$	1-$C_4H_9\cdot$	RH	8.5	S, 15	12.3	S, 15	4.6			

Table 5. Arrhenius Parameters and rate constants at 700 K for H-Transfer...Continued

Reactants		Products		log [A/L $mol^{-1}s^{-1}$]	Source	E, kcal/mol	Source	log [k/L $mol^{-1}s^{-1}$] at 700K	ΔS °(700) cal/(mol K)	ΔH°(700) kcal/mol	$<\Delta C_p>^{(700)}_{(300)}$ cal/(mol K)
n-C_4H_{10}	1-$R^•$	2-$C_4H_9^•$	RH	8.0	S, 37	10.4	S, 37	4.8			
n-C_4H_{10}	2-$R^•$	1-$C_4H_9^•$	RH	8.0	S, 38	12.9	S, 38	4.0			
n-C_4H_{10}	2-$R^•$	2-$C_4H_9^•$	RH	8.0	S, 39	12.3	S, 39	4.2			
C_3H_6	H	$C_3H_5^•$	H_2	10.7	E, 43	5.0	E, 43	9.1			
				11.0	E, 44	3.5	E, 44	9.9			
				11.0	Rec, 44	3.5	Rec, 44	9.9			
C_3H_6	$CH_3^•$	$C_3H_5^•$	CH_4	7.3	E, 45	7.2	E, 45	5.0			
				8.1	E, 46	8.2	E, 46	5.5			
				8.2	R, 1f	8.8	R, 1f	5.4			
				8.2	Rec, 1f	8.8	Rec, 1f	5.4			
C_3H_6	$C_2H_5^•$	$C_3H_5^•$	C_2H_6	8.0	S, 47	9.8	S, 47	4.9			
C_3H_6	1-$C_3H_7^•$	$C_3H_5^•$	C_3H_8	8.0	S, 47	9.8	S, 47	4.9			
C_3H_6	2-$C_3H_7^•$	$C_3H_5^•$	C_3H_8	8.0	S, 48a	10.8	S, 48a	4.6			
				6.7	E, 48b	7.6	E, 48b	4.3			
				7.6	Rec, 48c	9.7	Rec, 48c	4.6			
C_3H_6	1-$C_4H_9^•$	$C_3H_5^•$	n-C_4H_{10}	8.0	S, 49	9.8	S, 49	4.9			
C_3H_6	2-$C_4H_9^•$	$C_3H_5^•$	n-C_4H_{10}	7.6	S, 50	9.7	S, 50	4.6			
C_3H_6	2-methyl-1-propyl	$C_3H_5^•$	2-methyl-propane	8.0	S, 49	9.8	S, 49	4.9			
C_3H_6	$C_4H_7^•$	$C_3H_5^•$	1-C_4H_8	8.0	S, 51	17.5	S, 51	2.5			
C_3H_6	$C_4H_7^•$	$C_3H_5^•$	2-C_4H_8	8.0	S, 52	15.9	S, 52	3.0			
C_3H_6	1-$R^•$	$C_3H_5^•$	RH	8.0	S, 49	9.8	S, 49	4.9			
C_3H_6	2-$R^•$	$C_3H_5^•$	RH	7.6	S, 50	9.7	S, 50	4.6			
1-C_4H_8	H	$C_4H_7^•$	H_2	11.0	E, 53a	3.9	E, 53a	9.8			
				11.0	S, 53b	3.5	S, 53b	9.9			
				11.0	Rec, 53a	3.9	Rec, 53a	9.8			

Table 5. Arrhenius Parameters and rate constants at 700 K for H-Transfer...Continued

Reactants		Products		log [A/L $mol^{-1}s^{-1}$]	Source	E, kcal/mol	Source	log [k/L $mol^{-1}s^{-1}$] at 700K	$\Delta S^{o}(700)$ cal/(mol K)	$\Delta H^{o}(700)$ kcal/mol	$<\Delta C_p>^{(700)}_{(300)}$ cal/(mol K)
1-C_4H_8	$CH_3^•$	$C_4H_7^•$	CH_4	8.0	E, 54	7.3	E, 54	5.7			
1-C_4H_8	$C_2H_5^•$	$C_4H_7^•$	C_2H_6	8.0	S, 47	8.3	S, 47	5.4			
1-C_4H_8	1-$C_3H_7^•$	$C_4H_7^•$	C_3H_8	8.0	S, 55	8.3	S, 55	5.4			
1-C_4H_8	2-$C_3H_7^•$	$C_4H_7^•$	C_3H_8	7.6	S, 50	9.7	S, 50	4.6			
1-C_4H_8	$C_3H_5^•$	$C_4H_7^•$	C_3H_6	7.9	B, 56	12.4	B, 56	4.0	-0.4	-5.1	0.2
1-C_4H_8	1-$C_4H_9^•$	$C_4H_7^•$	n-C_4H_{10}	8.0	S, 55	8.3	S, 55	5.4			
1-C_4H_8	2-$C_4H_9^•$	$C_4H_7^•$	n-C_4H_{10}	7.6	S, 50	9.7	S, 50	4.6			
1-C_4H_8	2-methyl-1-propyl	$C_4H_7^•$	2-methyl-propane	8.0	S, 55	8.3	S, 55	5.4			
1-C_4H_8	$C_4H_7^•$	$C_4H_7^•$	2-C_4H_8	7.6	S, 57	12.4	S, 57	3.7			
1-C_4H_8	1-$R^•$	$C_4H_7^•$	RH	8.0	S, 55	8.3	S, 55	5.4			
1-C_4H_8	2-$R^•$	$C_4H_7^•$	RH	7.6	S, 50	9.7	S, 50	4.6			
2-C_4H_8	H	$C_4H_7^•$	H_2	11.3	S, 58	3.5	S, 58	10.2			
2-C_4H_8	$CH_3^•$	$C_4H_7^•$	CH_4	8.4	E, 54	8.2	E, 54	5.8			
2-C_4H_8	$C_2H_5^•$	$C_4H_7^•$	C_2H_6	8.3	S, 58	9.8	S, 58	5.2			
2-C_4H_8	1-$C_3H_7^•$	$C_4H_7^•$	C_3H_8	8.3	S, 58	9.8	S, 58	5.2			
2-C_4H_8	2-$C_3H_7^•$	$C_4H_7^•$	C_3H_8	7.9	S, 58	9.7	S, 58	4.9			
2-C_4H_8	$C_3H_5^•$	$C_4H_7^•$	C_3H_6	8.4	B, 59	13.4	B, 59	4.2	1.7	-2.5	0.2
2-C_4H_8	1-$C_4H_9^•$	$C_4H_7^•$	n-C_4H_{10}	8.3	S, 58	9.8	S, 58	5.2			
2-C_4H_8	2-$C_4H_9^•$	$C_4H_7^•$	n-C_4H_{10}	7.9	S, 58	9.7	S, 58	4.9			
2-C_4H_8	2-methyl-1-propyl	$C_4H_7^•$	2-methyl-propane	8.3	S, 58	9.8	S, 58	5.2			
2-C_4H_8	$C_4H_7^•$	$C_4H_7^•$	1-C_4H_8	8.0	B, 60	15.0	B, 60	3.3	2.1	2.6	-0.1
2-C_4H_8	1-$R^•$	$C_4H_7^•$	RH	8.3	S, 58	9.8	S, 58	5.2			
2-C_4H_8	2-$R^•$	$C_4H_7^•$	RH	7.9	S, 58	9.7	S, 58	4.9			

Notes on H-Transfer

1a. $\log k_{\mathrm{back}}=11.1-11.9/\theta$, recommended value of Walker [1].

1b. Recommended value of Walker [1] based on a critical review of experimental data (~300–1000 K).

1c. Average of six consistent sets of parameters taken from the review of Gray, Herrod and Jones [2a].

1d. Modified BEBO calculation by Arthur, Donchi, and McDonell [2b].

1e. Calculation based on molecular-orbital method by Bell and Perkins [2c].

1f. Critical review by Kerr and Parsonage [2d].

1g. Average of all values except the mo calculations which seem too low.

2a. $\log k_{\mathrm{back}}=11.1-9.7/\theta$, (this table).

2b. Data of Baldwin et al. [3b] at 713 K.

2c. Data of Boddy and Steacie [3c].

2d. Data of Reid and Le Roy [3d].

2e. Modified BEBO calculation by Arthur, Donchi and McDonell [39].

2f. Average of all values except those of Boddy and Steacie which appear to be too low.

3a. $\log k_{\mathrm{back}}= 11.1-9.7/\theta$, (this table).

3b. Data of Baldwin, Walker, and Yorke [3e], corrected for the more recent value of the rate constant for recombination of $1-C_3H_7\cdot$ given in table 2.

3c. Average value.

4a. $\log k_{\mathrm{back}}=10.8-7.7/\theta$, (this table).

4b. Data of Baldwin, Cleugh, and Walker [3f].

5. $\log k_{\mathrm{back}}=11.0-3.5/\theta$, (this table)

6. $\log k_{\mathrm{back}}=11.1-9.7/\theta$, (this table).

7. $\log k_{\mathrm{back}}=11.1-7.7/\theta$, (this table).

8. Assumed to be the same as the value for $1\text{-}C_4H_9\cdot+H_2$.

9. $\log k_{\mathrm{back}}=11.0-3.9/\theta$, (this table).

10. $\log k_{\mathrm{back}}=11.3-3.5/\theta$, (this table).

11. Assumed to have the same value as $2\text{-}C_4H_9\cdot+H_2$.

12. Data of Baldwin, Jackson, Walker and Webster [3a]. These values are quite consistent with previous values measured by other workers at lower temperatures (see refs. 5, 6, and 7).

13. Experimental data [8] in the range 533–673 K; consistent with a number of data on $-CH_3$ group attack [2].

14a. High temperature values of Pacey and Purnell [9a] in the range 920–1040 K. These authors propose curvature in the Arrhenius plot at temperatures above the range 700–800 K.

14b. High temperature data of Bradley and West [9b].

15. Assumed to have the same values as for $C_2H_5\cdot+n\text{-}C_4H_{10}\rightarrow C_2H_6+1\text{-}C_4H_9$.

16. Experimental values of Szirovicza and Marta [9c].

17. $\log k_{\mathrm{back}}=8.0-9.2/\theta$, (this table).

18a. Recalculated from the data of Lin and Bac [10a] (843–913 K) using a value of $10^{9.6}$ L mol^{-1} s^{-} for the ethyl recombination constant.

18b. Assumed to have the same values as fo $2\text{-}C_3H_7\cdot+C_2H_6$.

19. $\log k_{\mathrm{back}}=8.0-8.3/\theta$, (this table).

20. $\log k_{\mathrm{back}}=8.3-9.2/\theta$, (this table).

21a. Assumed to be the same as $H+C_2H_6$.

21b. Data of Baldwin, Cleugh, and Walker a 713 K [3f].

21c. Calculated from bond reactivities determine by Baker, Baldwin and Walker [4].

21d. Average of both values.

21e. Assigned the recommended value fo $H+C_3H_8\rightarrow H_2+2\text{-}C_3H_7$. But A was corrected fo the different number of secondary hydrogens.

22. Experimental data, 569–693 K (see ref. 8).

23a. Experimental data, 573–726 K (see ref. 8).

23b. Data of Camilleri, Marshall and Purnell (CMP) [10b], below 743 K. The Arrhenius plot is curved and values of E and A must be given for different temperature ranges.

23c. Values of CMP [10b] for the overall temperature range 676 to 813 K (see note 23b).

23d. Average of all values except 23c.

24. Assumed to be the same as for $C_2H_5\cdot+n\text{-}C_4H_{10}\rightarrow C_2H_6+2\text{-}C_4H_9\cdot$, but A corrected for the different number of secondary hydrogens.

25. Same assumption as in note 24. Experimental data is also available for this reaction as Berkeley and coworkers [11] have measured $k/k_c^{1/2}$ between 303–403 K, where k_c is the $1\text{-}C_3H_7\cdot$ recombination constant. Using $k_c=10^{9.6}$ (see recombination section) we calculate $\log k=5.9-7.9/\theta$. This value of the A-factor appears unreasonably small.

26. Assumed to be same as $C_3H_5\cdot+C_2H_6$.

27. $\log k_{\mathrm{back}}=7.6-9.7/\theta$, (this table).

28. Assumed to be the same as for $2\text{-}C_3H_7\cdot+n\text{-}C_4H_{10}\rightarrow C_3H_8+2\text{-}C_4H_9\cdot$ except A corrected for different number of secondary hydrogens.

29. Assumed to be the same as for $C_4H_7\cdot+C_2H_6\rightarrow 1\text{-}C_4H_8+C_2H_5$.

30. Assumed to be the same as for $C_4H_7\cdot+nC_4H_{10}\rightarrow 1\text{-}C_4H_8+2\text{-}C_4H_9\cdot$ with a correction for the different number of secondary hydrogens in C_3H_8.

31. Assumed to be the same as for $C_4H_7\cdot+C_2H_6\rightarrow 2\text{-}C_4H_8+C_2H_5$.

32. Assumed to be the same as for $C_4H_7\cdot+n\text{-}C_4H_{10}\rightarrow 2\text{-}C_4H_8+2\text{-}C_4H_9\cdot$ with a correction for the different number of secondary hydrogens in C_3H_8.

33. Based on experimental work [8] recalculated by Kerr and Parsonage [2d].

34a. Experimental data [8] in the range 523–723 K.

34b. Parameters determined by Pacey and Purnell at 951 K for attack at all positions [12]. These workers conclude that E is strongly temperature dependent.

35. The value of $\log A$ was chosen as 8.5 (~±0.5) on the basis of the general values obtained from

experiments with alkyl radicals and alkanes (particularly $CH_3\cdot$ abstractions). Boddy and Steacie [13] have measured a value of 11.7 for ethyl and neopentane (recalculated from their data using an ethyl recombination value of 9.6). Their value seems unreasonably high and may reflect activated radical reactions in their photochemical system. The activation energy was estimated as 12.3 kcal/mol which is an average of the corresponding $CH_3\cdot$ and $2\text{-}C_3H_7\cdot$ abstraction energies for the primary position of *n*-butane (11.6 and 12.9, respectively).

36a. Previous data of Steacie and coworkers [13, 14, 15] gives values of the abstraction parameters relative to $C_2D_5\cdot$ recombination in the range ~350–600 K. Using the ethyl recombination rate of $10^{9.6}$ L mol^{-1}s^{-1}, values of log A for attack on cyclohexane, *n*-butane, *n*-hexane and *n*-heptane average about 8.0. The average value of the measured activation energies for these reactions is 10.4 kcal/mol (±1–2) and appears reasonable.

36b. See note 34b. Values of E have been reported at temperatures between 700 K and 951 K: $\log k = 9.4-16.8/\theta$ (693–803 K) [16] and $\log k = 9.8-18.6/\theta$ (793–863 K) [17].

37. Assumed to have the same value as for $C_2H_5\cdot + n\text{-}C_4H_{10} \rightarrow C_2H_6 + 2\text{-}C_4H_9$.

38. Assumed to have the same value as $2\text{-}C_3H_7\cdot + C_2H_6 \rightarrow C_3H_8 + C_2H_5\cdot$

39. The A-factor was assumed to be the same as for $C_2H_5\cdot$ radical attack. The reaction is approximately thermoneutral and the value of $E=12.3$, used for $C_2H_5\cdot + n\text{-}C_4H_{10} \rightarrow C_2H_6 + 1\text{-}C_4H_9\cdot$, was assumed to be the value for a thermoneutral reaction.

40. $\log k_{back} = 7.6-9.7/\theta$.

41. $\log k_{back} = 8.0-8.3/\theta$, (this table).

42a. $\log k_{back} = 7.6-9.7/\theta$, (this table).

42b. $\log k_{back} = 7.9-9.7/\theta$, (this table).

43. Experimental data of Darwent and Roberts [18].

44. Woolley and Cvetanovic [19] have determined k_{abs}/k_{addn} for $H + C_3H_6$ to be 0.082 at 296 K and Darwent and Roberts [18] obtained 0.42 at 298 K for the same ratio, giving an average of 0.25 at 298 K. Evaluating k_{addn} (total) at 298 K (see addition section for the addition parameters) and combining with the above ratio gives $k_{abs} = 10^{8.4}$ L mol^{-1}s^{-1}. (The data of Darwent and Roberts (see above) gives $k_{abs} \sim 10^{7.0}$ L mol^{-1}s^{-1}). If we assign log $A_{abs} \sim 11.0$ then to be consistent with $k_{abs} = 10^{8.4}$ the value of E must be 3.5 kcal/mol.

45. Experimental data of Cvetanovic and Irwin [20] (353–453 K); relative to methyl abstraction from isobutane and methyl recombination.

46. Data of Miyoshi and Brinton [21a] (381–441 K); calculated relative to k(methyl recombination) $= 10^{10.4}$ L mol^{-1}s^{-1}.

47. The A-factor was estimated to be the rounded value of $10^{8.0}$ L mol^{-1}s^{-1}. This value is close to the value of $10^{8.2}$ L mol^{-1}s^{-1} for $CH_3\cdot + C_3H_6$ (see table). The value of E for $C_2H_5\cdot$ is assumed to be ~1 kcal/mol larger than for the corresponding $CH_3\cdot$ attack. This increment is similar to those for thermoneutral-exothermic alkane abstraction reactions.

48a. The A-factor was estimated to be $10^{8.0}$ L mol^{-1}s^{-1}, the general value for alkene abstractions (see 47). E was estimated to be ~1 kcal/mol larger than for $C_2H_5\cdot$ attack, similar to the situation for alkane abstractions.

48b. Experimental values of Szirovicza and Marta [9c] at 496–548 K.

48c. Recommended value obtained by giving a weight of 1 to the experimental values and 2 to the structural analogy. The experimental values were given less weight because the reported A factor ($10^{6.7}$) seems low compared to the general values for alkyl abstraction reactions.

49. Assumed to be the same as for $C_2H_5\cdot$ attack.

50. Assumed to be the same as for $2\text{-}C_3H_7\cdot$ attack on C_3H_6.

51. The A-factor was assumed to be the general value for alkene abstractions while the value of E was assigned as 12.3 kcal/mol (the value for another thermoneutral reaction, $C_2H_5\cdot + n\text{-}C_4H_{10} \rightarrow C_2H_6 + 1\text{-}C_4H_9$), +5.2 kcal/mol (the endothermicity of the reaction) =17.5 kcal/mol.

52. The A-factor was assumed to have the general value for alkane abstractions while the value of E was assigned as 12.3 kcal/mol (the thermoneutral value) +3.6 kcal/mol (the endothermicity of the abstraction) =15.9 kcal/mol.

53a. Using Wooley and Cvetanovic's [19] value of 0.093 for k_{abs}/k_{addn} (at 296 K) and evaluating k_{addn} (see addition reaction section) gives $k_{abs} = 10^{8.1}$ L mol^{-1}s^{-1}. Assuming log $A_{abs} \sim 11.0$ gives $E=3.9$.

53b. Assumed to be the same as for $H + C_3H_6 = H_2 + C_3H_5\cdot$.

54. Data of Cvetanovic and Irwin [20] (353–453 K).

55. Assumed to be the same as for $C_2H_5\cdot$ attack on $1\text{-}C_4H_8$.

56. $\log k_{back} = 8.0-17.5/\theta$, (this table).

57. Assumed to be the same value as for the corresponding reaction with the allyl radical with a correction for the two-fold rotational symmetry of the allyl radical.

58. Assumed to be the same as for attack on C_3H_6 except for a correction in $\Delta S^\dagger$ for two-fold rotational symmetry of $2\text{-}C_4H_8$.

59. $\log k_{back} = 8.0-15.9/\theta$, (this table).

60. $\log k_{back} = 7.6-14.4/\theta$, (this table).

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7. Addition Reactions

Arrhenius parameters and rate constants at 700 K for addition reactions are listed in table 6. The Arrhenius *A* factors are probably accurate to within half a power of ten, the activation energies to within 2 kcal/mol, and the rate constants to within a power of ten. The data fall into two groups. The one is for hydrogen atoms. Here a great deal of work has been done. Hydrogen atom concentrations can be measured to a fair degree of accuracy. The rate constants are reliable. The other group is for addition of radicals. Here the experimental problems are more severe. Much of the data is relative, that is addition to one olefin is compared with addition to another olefin. Because many of the activation energies are low, care must be taken to ensure that the additions are in the true second order region and are not into the fall-off. The notation is the same as in the previous table with the additional L for lower limit, calculated from the entropy change as described in the Introduction. An extensive critical compilation of data on the kinetics and thermochemistry of atom and radical additions to olefins has been prepared by Kerr and Parsonage [1] and is highly recommended for detailed discussions of these reactions.

Table 6. Arrhenius parameters and Rate Constants at 700 K for addition

Reactants		Products	log[A/L mol^{-1}s^{-1}]	Source	E, kcal/mol	Source	log [k/L mol^{-1}s^{-1}] at 700 K
H	C_2H_4	$C_2H_5^{\cdot}$	9.9	E, 1a	1.5	E, 1a	9.4
			10.5	E, 1b	3.2	E, 1b	9.5
			8.1	L			
			11.0	R, 1c	2.8	E, 1c	10.1
			10.6	Rec, 1d	2.6	Rec, 1d	9.8
H	C_3H_6	$2-C_3H_7^{\cdot}$	10.0	E, 2a	1.2	E, 2a	9.6
			7.6	L			
			9.8	E, 2b	1.7	E, 2b	9.3
			10.1	E, 2c	1.6	E, 2c	9.6
			9.9	R, 1c	1.2	R, 1c	9.5
			9.9	Rec, 1c	1.2	Rec, 1c	9.5
H	C_3H_6	$1-C_3H_7^{\cdot}$	10.0	E, 3	2.9	E, 3	9.1
			8.1	L			
			9.9	R, 1c	2.9	R, 1c	9.0
			9.9	Rec, 1c	2.9	Rec, 1c	9.0
H	$1-C_4H_8$	$2-C_4H_9^{\cdot}$	9.9	S, 4	1.2	S, 4	9.5
			8.0	L			
H	$1-C_4H_8$	$1-C_4H_9^{\cdot}$	9.9	S, 5	2.9	S, 5	9.0
			8.1	L			
H	$2-C_4H_8$	$2-C_4H_9^{\cdot}$	9.7	S, 6	1.2	S, 6	9.3
			8.4	L			
H	C_4H_6	$C_4H_7^{\cdot}$	10.6	E, 7	1.3	E, 7	10.2
			7.9	L			
H	$1-C_5H_{10}$	$1-C_5H_{11}^{\cdot}$	9.9	S, 8	2.9	S, 8	9.0
H	$1-C_5H_{10}$	$2-C_5H_{11}^{\cdot}$	9.9	S, 8	1.2	S, 8	9.5
H	$2-C_5H_{10}$	$2-C_5H_{11}^{\cdot}$	9.4	S, 9a	1.2	S, 9a	9.0
			8.6	E, 9b			
			9.4	Rec, 9a	1.2	Rec, 9a	9.0
H	$2-C_5H_{10}$	$3-C_5H_{11}^{\cdot}$	9.4	S, 9a	1.2	S, 9a	9.0
			8.6	E, 9b			
			9.4	Rec, 9a	1.2	Rec, 9a	9.0
$CH_3^{\cdot}$	C_2H_4	$1-C_3H_7^{\cdot}$	8.6	E, 10a	7.9	E, 10a	6.1
			6.8	L			
			8.5	R, 1c	7.7	R, 1c	6.1
			8.3	E, 10b	7.3	E, 10b	6.0
			7.5	E, 2b	7.9	E, 2b	5.0
			8.0	E, 2c	7.9	E, 2c	5.5
			8.1	Rec, 10c	7.7	Rec, 10c	5.7
$CH_3^{\cdot}$	C_3H_6	$2-C_4H_9^{\cdot}$	8.5	E, 10a	7.4	E, 10a	6.2
			6.3	L			
$CH_3^{\cdot}$	C_3H_6	2-methyl-1-propyl	8.5	E, 11	9.1	E, 11	5.6
			5.9	L			
$CH_3^{\cdot}$	$1-C_4H_8$	$3-C_5H_{11}^{\cdot}$	8.3	E, 10a	7.2	E, 10a	6.0
			6.0	L			
$CH_3^{\cdot}$	$1-C_4H_8$	2-methyl-1-butyl	8.3	S, 12	8.9	S, 12	5.5
$CH_3^{\cdot}$	$1-C_5H_{10}$	$3-C_6H_{13}^{\cdot}$	8.3	S, 13	7.2	S, 13	6.0
$CH_3^{\cdot}$	C_4H_6	1-penten-3-yl	7.9	E, 14	4.1	E, 14	6.6
$C_2H_5^{\cdot}$	C_2H_4	$1-C_4H_9^{\cdot}$	7.8	E, 15	7.6	E, 15	5.4
			6.8	L			
$C_2H_5^{\cdot}$	C_3H_6	$2-C_5H_{11}^{\cdot}$	7.6	S, 16	7.5	S, 16	5.2
			6.3	L			
$C_2H_5^{\cdot}$	C_3H_6	2-methyl-1-butyl	7.6	S, 17	9.2	S, 17	4.7
			5.9	L			
$C_2H_5^{\cdot}$	$1-C_4H_8$	$3-C_6H_{13}^{\cdot}$	7.6	S, 16	7.5	S, 16	5.2
$C_2H_5^{\cdot}$	$1-C_4H_8$	2-ethyl-1-butyl	7.6	S, 17	9.2	S, 17	4.7
$C_2H_5^{\cdot}$	C_4H_6	1-hexen-3-yl	7.8	S, 18	4.5	S, 18	6.4
$1-C_3H_7^{\cdot}$	C_2H_4	$1-C_5H_{11}^{\cdot}$	7.8	E, 19	7.4	E, 19	5.5
			6.4	L			
$1-C_3H_7^{\cdot}$	C_3H_6	$2-C_6H_{13}^{\cdot}$	~7.8	S, 20	~7.0	S, 20	5.6
			6.0	L			

Table 6. Arrhenius parameters and Rate Constants at 700 K for addition...Continued

Reactants		Products	log[A/L mol^{-1}s^{-1}]	Source	E, kcal/mol	Source	log [k/L mol^{-1}s^{-1}] at 700 K
1-$C_3H_7^\bullet$	C_3H_6	2-methyl-1-pentyl	~7.8	S, 21	~8.7	S, 21	5.1
1-$C_3H_7^\bullet$	1-C_4H_8	3-$C_7H_{15}^\bullet$	~7.8	S, 20	~7.0	S, 20	5.6
1-$C_3H_7^\bullet$	1-C_4H_8	2-ethyl-1-pentyl	~7.8	S, 21	~8.7	S, 21	5.1
1-C_3H_7	C_4H_6	1-heptene-3-yl	7.8	S, 22	4.5	S, 22	6.4
2-$C_3H_7^\bullet$	C_2H_4	3-methyl-1-butyl	7.6 6.4	E, 23 L	6.9	E, 23	5.4
2-$C_3H_7^\bullet$	C_3H_6	4-methyl-2-pentyl	~7.6	S, 24	~6.9	S, 24	5.4
2-$C_3H_7^\bullet$	1-C_4H_8	2-methyl-4-hexyl	~7.6	S, 24	~6.9	S, 24	5.4
2-$C_3H_7^\bullet$	C_4H_6	5-methyl-1-hexen-3-yl	~7.6	S, 24	4.5	S, 24	5.4
$C_3H_5^\bullet$	C_2H_4	4-penten-1-yl	~7.8	S, 25	17.4	S, 25	2.4
$C_3H_5^\bullet$	C_3H_6	5-hexen-2-yl	~7.8	S, 25	~17.0	S, 25	2.5
$C_3H_5^\bullet$	1-C_4H_8	5-hepten-3-yl	~7.8	S, 25	~17.0	S, 25	2.5
$C_3H_5^\bullet$	C_4H_6	1,6-heptadien-3-yl	~7.8	S, 25	~14.5	S, 25	3.3
1-$C_4H_9^\bullet$	C_2H_4	1-$C_6H_{13}^\bullet$	7.8 7.3 7.3	S, 26 E, 27 Rec, 27	7.4 6.7 6.7	S, 26 E, 27 Rec, 27	5.5 5.2 5.2
1-$C_4H_9^\bullet$	C_3H_6	2-$C_7H_{15}^\bullet$	~7.8	S, 26	~7.0	S, 26	5.6
1-$C_4H_9^\bullet$	1-C_4H_8	3-$C_8H_{17}^\bullet$	~7.8	S, 26	~7.0	S, 26	5.6
1-$C_4H_9^\bullet$	C_4H_6	1-octen-3-yl	7.8	S, 26	4.5	S, 26	6.4
2-$C_4H_9^\bullet$	C_2H_4	3-methyl-1-pentyl	7.6	S, 28	6.9	S, 28	5.4
2-$C_4H_9^\bullet$	C_3H_6	4-methyl-2-hexyl	~7.6 8.6 8.1	S, 28 E, 29a Rec, 29b	~6.9 9.2 8.0	S, 28 E, 29a Rec, 29b	5.4 5.7 5.6
2-$C_4H_9^\bullet$	1-C_4H_8	5-methyl-3-heptyl	~8.1	S, 30	~8.0	S, 30	5.6
2-$C_4H_9^\bullet$	C_4H_6	5-methyl-1-hepten-3-yl	~7.6	S, 28	4.5	S, 28	5.4
1-$C_5H_{11}^\bullet$	C_2H_4	1-$C_7H_{15}^\bullet$	7.3	S, 31	6.7	S, 31	5.2
1-$C_5H_{11}^\bullet$	C_3H_6	2-$C_8H_{17}^\bullet$	~7.8	S, 26	~7.0	S, 26	5.6
1-$C_5H_{11}^\bullet$	1-C_4H_8	3-$C_9H_{19}^\bullet$	~7.8	S, 26	~7.0	S, 26	5.6
1-$C_5H_{11}^\bullet$	C_4H_6	1-nonen-3-yl	7.8	S, 26	4.5	S, 26	6.4
2-$C_5H_{11}^\bullet$	C_2H_4	3-methyl-1-hexyl	7.6	S, 32	6.9	S, 32	5.4
2-$C_5H_{11}^\bullet$	C_3H_6	4-methyl-2-heptyl	~8.1	S, 32	8.0	S, 32	5.6
2-$C_5H_{11}^\bullet$	1-C_4H_8	5-methyl-3-octyl	8.1	S, 32	8.0	S, 32	5.6
2-$C_5H_{11}^\bullet$	C_4H_6	5-methyl-1-octen-3-yl	~7.6	S, 32	4.5	S, 32	5.4
3-$C_5H_{11}^\bullet$	C_2H_4	3-ethyl-1-pentyl	7.6	S, 32	6.9	S, 32	5.4
3-$C_5H_{11}^\bullet$	C_3H_6	3-ethyl-5-hexyl	8.1	S, 32	8.0	S, 32	5.6
3-$C_5H_{11}^\bullet$	1-C_4H_8	3-ethyl-5-heptyl	8.1	S, 32	8.0	S, 32	5.6
3-$C_5H_{11}^\bullet$	C_4H_6	5-ethyl-1-hepten-3-yl	~7.6	S, 32	4.5	S, 32	5.4

Notes on Addition Reactions

1a. Experimental data of Wooley and Cventaovic [2] at 298 K give $k(C_3H_6)/k(C_2H_4)=1.5$ for H addition. Assuming this difference is due only to differences in E and using the recommended value for propylene addition we calculate $\log k(C_2H_4)=9.9-1.5/\theta$.

1b. Parameters recommended by Baldwin, Simmons and Walker [4] based on experimentally obtained values.

1c. Value recommended by Kerr and Parsonage [1].

1d. Weighted average, giving a weight of 2 to 1c, and 1 each to 1a and 1b.

2a. Experimental data of Kurylo, Peterson and Braun [3a].

2b. Calculated data of Camilleri, Marshall, and Purnell [3b] (CMP) at 676 to 813 K, from back reaction, recombination rates, and thermochemistry.

2c. Recalculated from CMP's data using recombination rates and thermochemistry given earlier in this paper.

3. Falconer and Sunder [5] have observed 5.7% nonterminal addition of H atoms to C_3H_6 (at 300 K). Attributing this selectivity solely to differences in activation energy leads to a 1.7 kcal/mol higher energy for nonterminal addition with equal A-factors.

4. Parameters assumed to be the same as for $H + C_3H_6 \rightarrow 2\text{-}C_3H_7\cdot$. Wooley and Cvetanovic [2] observed $k(C_3H_6)/k(1\text{-}C_4H_8) \sim 1.0$ ($\sim$300 K), while Falconer and Sunder [5] observed equal selectivities for terminal-nonterminal addition in propylene and 1-butene thus suggesting that the activation parameters are quite similar.

5. Parameters assumed to be the same as for $H + C_3H_6 \rightarrow 1\text{-}C_3H_7\cdot$. See note 4.

6. Experimentally determined addition rate constants [1] for propylene are 1.6 and 2.0 times as large as those respectively for *trans* and *cis*-3-butene at $\sim$200 K. Assuming changes are due only to A, leads to $A(1\text{-}C_4H_8) \sim 10^{9.7}$ (for *trans* isomer).

7. Data of Yang [6] at 304 K.

8. Assumed to have the same values as for appropriate addition to $1\text{-}C_4H_8$. A number of experimentally measured rate constants ($\sim$300 K) for addition (both positions) to 1-butene and 1-pentene are nearly identical [1].

9a. Assumed to have the same values as for $H + 2\text{-}C_4H_8 \rightarrow 2\text{-}C_4H_9\cdot$ but with $\Delta S^\ddagger$ corrected for two-fold rotational symmetry in $2\text{-}C_4H_8$.

9b. Experimental value of Cvetanovic and Doyle [7] measured for *trans*-2-pentene.

10a. Experimental data of Cventanovic and Irwin [8a] at 400 K.

10b. Experimental data and review of others' results by Holt and Kerr [8b].

10c. Average value.

11. Assuming that the A-factors for terminal and nonterminal addition are equal, the observed [9] 9/1 ratio (at 380 K) for the addition selectivity can be attributed to E and thus, $E_{\text{terminal}}-E_{\text{nonterminal}}=1.7$ kcal/mol.

12. The same assumptions were made as in note 11. McNesby and Gordon [10] have observed a ratio of terminal to nonterminal addition of between 8 and 9 at 673 K for $1\text{-}C_4H_8 + CH_3$.

13. Assumed to have the same values as for $CH_3\cdot + 1\text{-}C_4H_8 \rightarrow 3\text{-}C_5H_{11}$.

14. Experimental values of Cvetanovic and Irwin [8] at $\sim$400 K.

15. Watkins and O'Deen [15] determined $\log (k_{\text{add}}/k_c^{1/2})=3.0-7.6/\theta$ ($\sim$380 K) where k_c refers to the rate of ethyl recombination. Using $\log k_c=9.6$ (see recombination section) $\log k_{\text{add}}=7.8-7.6/\theta$.

16. A rough average of reported values for addition of $C_2H_5\cdot$ to the series of olefins; ethylene [15], 1-hexene, 1-heptene [11] and 1-octene; gives a value of $\log k \sim 8.0-7.5/\theta$ calculated relative to $\log k_c^{1/2}$ ($C_2H_5\cdot$ recombination rate)$=5.2$. Using $\log k_c^{1/2}=4.8$ (see recombination section) gives $\log k \sim 7.6-7.5/\theta$.

17. The ratio of terminal to nonterminal addition was assumed to be the same as for the $CH_3\cdot$ radical (see note 11) and similarly attributed to a difference in activation energies.

18. Rate constants for $C_2H_5\cdot + 2,3$-dimethylbutadiene-1,3 have been determined relative to $k^{1/2}(C_2H_5\cdot$ recombination) at $\sim$350 K [11, 12]. Using $k(C_2H_5\cdot)=10^{9.6}$ we calculate $\log k=7.8-4.5/\theta$.

19. Watkins and Lawson [12] observed that $\log k/k_c^{1/2}$ ($C_2H_5\cdot$ recombination)$=3.0-7.4/\theta$ between 330 and 373 K. Using $10^{9.6}$ L mol^{-1}s^{-1} for ethyl recombination (see recombination section), $\log k=7.8-7.4/\theta$.

20. The A-factor was estimated to be about the same as $1\text{-}C_3H_7\cdot + C_2H_4$ whereas E is taken as an approximate average from critical energy values for the addition of $1\text{-}C_3H_7\cdot$ to $1\text{-}C_4H_8$ and $1\text{-}C_5H_{10}$ [13].

21. Assumed to be the same as $1\text{-}C_3H_7\cdot + C_3H_6 \rightarrow 2\text{-}C_6H_{13}\cdot$ with 1.7 kcal/mol higher energy for nonterminal addition in analogy with $CH_3\cdot$ addition (see note 11).

22. Assumed to be the same as $C_2H_5\cdot + C_4H_6$.

23. The value of the ratio $\log k/k_c^{1/2}$ has been determined by two sets of workers [14, 15] to be $2.8-6.9/\theta$ at $\sim$400 K, where k_c is the $2\text{-}C_3H_7\cdot$ recombination rate constant. Using $k_c=10^{9.5}$ L mol^{-1}s^{-1} we calculate $\log k=7.5-6.9/\theta$.

24. Assumed to have the same values as for $2\text{-}C_3H_7\cdot + C_2H_4$ except for the activation energy for $2\text{-}C_3H_7\cdot + C_4H_6$ which is assumed to have the same value as for $1\text{-}C_3H_7\cdot + C_4H_6$.

25. The rate parameters are assumed to be the same as for the analogous reaction with the $1\text{-}C_3H_7\cdot$ radical except the activation energy is assumed to be $\sim$10 kcal/mol higher, reflecting an assumed complete loss of the allyl resonance energy [16] in the transition state. The later assumption appears reasonable since the low A-factors observed for addition correspond to low values of $\Delta S^\ddagger$ and thus "tight" transition states, which must closely resemble the product radicals.

26. Parameters are assumed to have the same value as for the analogous addition with the 1-$C_3H_7 \cdot$ radical.

27. Watkins and O'Deen [15] have measured log $(kk_c^{1/2}/k_3)=2.2-6.7/\theta$ between 352–405 K, where k_c and k_3 are the recombination rate constants respectively for the 1-$C_4H_9 \cdot$ radical with itself and the $C_2H_5 \cdot$ radical. Using $k_c=10^{9.6}$ L mol^{-1}s^{-1} and $k_3=10^{9.9}$ L mol^{-1}s^{-1} (see recombination section) we calculate log $k=7.3-6.7/\theta$.

28. Assumed to have the same values as for the analogous reactions of the 2-$C_3H_7 \cdot$ radical.

29a. Experimental value for log $(k/k_c^{1/2})$ has been measured by Miyoshi and Brinton [9] where k_c is the recombination constant for 2-$C_4H_9 \cdot$. Using log $k_c=9.5$ we calculate log $k=8.1-9.2/\theta$.

29b. Average value.

30. Assumed to have the same values as for 2-$C_4H_9 \cdot + C_3H_6$.

31. Assumed to have the same values as for the analagous reactions of the 1-$C_4H_9 \cdot$ radical.

32. Assumed to have the same values as for the analagous reactions of the 2-$C_4H_9 \cdot$ radical.

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8. Radical Decomposition

Arrhenius parameters and rate constants at 700 K for radical decompositions are in table 7. The notation is the same as in the previous table. The Arrhenius A factors are probably accurate to within a power of ten, the activation energies to within 3 kcal/mol, and the rate constants at 700 K to within about one and a half powers of ten. As with addition reactions, care must be taken to ensure that the pressures are high enough for the decomposition of small alkyl radicals to be in their true first order region. All rates of decomposition are measured relative to radical recombination. Thus as recombination rate constants change in the future, decomposition rate constants will change in the same direction by half as much (decompositions are first order in radical concentration and recombinations are second order). Many of the values in the table are calculated from the rate constants for their reverse reaction (addition) and thermochemistry. Changes in addition rates will affect these values directly. Changes in radical thermochemistry may cancel as one radical reacts to give another. For example in the decomposition of n-propyl to give methyl and ethylene, if the heats of formation of methyl and n-propyl both increase by the same amount and the rate of the addition stays constant, then the rate of decomposition calculated from the rate of addition will remain the same.

Table 7. Arrhenius parameters and rate constants at 700 K for radical decomposition

Reactant	Products		$\log[A/s^{-1}]$	Source	E, kcal/mol	Source	$\log[k/s^{-1}]$	ΔS^o (700) cal/(mol K)	ΔH^o (700) kcal/mol	$<\Delta C_p>^{(700)}_{(300)}$ cal/(mol K)
$C_2H_5^\bullet$	H	C_2H_4	13.5	E, 1a	40	E, 1a	1.0	25.2	39.7	4.0
			13.9	B, 1b	40.9	B, 1b	1.1			
			13.5	R, 1c	40.7	R, 1c	0.8			
			13.6	Rec, 1d	40.5	rec, 1d	0.9			
$1-C_3H_7^\bullet$	$CH_3^\bullet$	C_2H_4	14.0	E, 2a	32.6	E, 2a	3.8	31.4	26.3	1.2
			12.8	B, 2b	32.6	B, 2b	2.6			
			12.6	E, 2c	32.5	E, 2c	2.4			
			13.6	R, 2d	33.1	R, 2d	3.2			
			13.1	Rec, 2e	32.5	Rec, 2e	2.9			
$1-C_3H_7^\bullet$	H	C_3H_6	13.2	B, 3	38.6	B, 3	1.1	25.2	37.1	2.8
$2-C_3H_7^\bullet$	H	C_3H_6	13.9	E, 4a	38.7	E, 4a	1.8	27.3	40.7	3.2
			13.6	B, 4b	40.5	B, 4b	0.9			
			13.9	E, 4c	40.9	E, 4c	1.1			
			14.3	R, 1c	41.3	R, 1c	1.4			
			13.9	Rec, 4d	40.4	Rec. 4d	1.3			
$1-C_4H_9^\bullet$	$C_2H_5^\bullet$	C_2H_4	13.2	E, 5a	28.7	E, 5a	4.2	31.2	22.3	-1.6
			12.4	B, 5b	28.5	B, 5b	3.5			
			13.6	R, 1c	29	R, 1c	4.5			
			13.4	Rec, 5c	28.8	Rec. 5c	4.4			
$1-C_4H_9^\bullet$	H	$1-C_4H_8$	13.1	B, 6	38.6	B, 6	1.0	24.7	37.1	22.8
$2-C_4H_9^\bullet$	$CH_3^\bullet$	C_3H_6	14.4	E, 7a	32.6	E, 7a	4.2	33.5	26.9	0.8
			13.6	B, 7b	32.9	B, 7b	3.3			
			14.2	R, 1c	33.9	R, 1c	3.6			
			14.3	Rec, 7c	33.2	Rec, 7c	3.9			
$2-C_4H_9^\bullet$	H	$1-C_4H_8$	13.3	B, 8	40.4	B, 8	0.7	25.7	40.6	3.0
$2-C_4H_9^\bullet$	H	$2-C_4H_8$	12.7	B, 9	37.9	B, 9	0.8	23.6	38.1	3.2
2-methyl-1-propyl	$CH_3^\bullet$	C_3H_6	14.0	B, 10a	33.3	B, 10a	3.6	35.3	25.6	0.2
			14.2	R, 1c	32.7	R, 1c	4.0			
			12.0	E, 10b	31.0	E, 10b	2.3			
			14.0	Rec, 10c	32.8	Rec,10c	3.8			
$C_4H_7^\bullet$	H	C_4H_6	14.1	B, 11	49.3	B, 11	1.3	26.2	49.4	3.4
$1-C_5H_{11}^\bullet$	$1-C_3H_7^\bullet$	C_2H_4	13.4	S, 12a	28.8	S, 12a	4.4	32.7	22.0	-1.2
			12.7	B, 12b	28.0	B, 12b	4.0			

Table 7. Arrhenius parameters and rate constants at 700 K for radical decomposition...continued

Reactant	Products		log[A/s^{-1}]	Source	E, kcal/mol	Source	log[k/s^{-1}]	ΔS° (700) cal/(mol K)	ΔH° (700) kcal/mol	$<\Delta C_p>^{(700)}_{(300)}$ cal/(mol K)
			14.1 13.5	T, 12c Rec, 12d	28.4	Rec, 12d	4.6			
1-$C_5H_{11}^{\bullet}$	H	1-C_5H_{10}	13.1	S, 13	38.6	S, 13	1.0			
2-$C_5H_{11}^{\bullet}$	C_2H_5	C_3H_6	12.7	B, 14	29.1	B, 14	3.6	33.3	23.0	-2.0
2-$C_5H_{11}^{\bullet}$	H	1-C_5H_{10}	13.3	S, 15	40.4	S, 15	0.7			
2-$C_5H_{11}^{\bullet}$	H	2-C_5H_{10}	12.7	S, 16	37.9	S, 16	0.8			
3-$C_5H_{11}^{\bullet}$	$CH_3^{\bullet}$	1-C_4H_8	14.6 13.7 14.2	33.2 B, 17b Rec, 12d	S, 17a 32.7 33.0	4.2 B, 17b Rec, 12d	 3.5 3.9	34.7	26.9	0.7
3-$C_5H_{11}^{\bullet}$	H	2-C_5H_{10}	13.0	S, 18	37.9	S, 18	1.2			
2-methyl-1-butyl	$CH_3^{\bullet}$	1-C_4H_8	13.7	S, 19	32.8	S, 19	3.5			
2-methyl-1-butyl	$C_2H_5^{\bullet}$	C_3H_6	13.1	B, 20	29.5	B, 20	3.9	35.1	21.7	-2.6
3-methyl-1-butyl	2-$C_3H_7^{\bullet}$	C_2H_4	12.6	B, 21	26.2	B, 21	4.4	33.1	20.7	-1.8
1-$C_6H_{13}^{\bullet}$	1-$C_4H_9^{\bullet}$	C_2H_4	13.4	S, 12A	28.8	S, 12a	4.4			
2-$C_6H_{13}^{\bullet}$	1-$C_3H_7^{\bullet}$	C_3H_6	13.2	B, 22	28.3	B, 22	4.4	34.8	22.7	-1.6
3-$C_6H_{13}^{\bullet}$	$CH_3^{\bullet}$	1-C_5H_{10}	13.9	S, 23	33.0	S, 23	3.6			
3-$C_6H_{13}^{\bullet}$	$C_2H_5^{\bullet}$	1-C_4H_8	12.7	S, 24	29.1	S, 24	3.6			
3-methyl-1-pentyl	2-$C_4H_9^{\bullet}$	C_2H_4	12.6	S, 25	26.2	S, 25	4.4			
4-methyl-2-pentyl	2-$C_3H_7^{\bullet}$	C_3H_6	13.4	S, 26	28.2	S, 26	4.6			
4-methyl-2-hexyl	2-$C_4H_9^{\bullet}$	C_3H_6	13.4	B, 27	28.2	B, 27	4.6	34.2	21.6	-2.3
1-$C_7H_{15}^{\bullet}$	1-$C_5H_{11}^{\bullet}$	C_2H_4	13.4	S, 12a	28.8	S, 12a	4.4			
2-$C_7H_{15}^{\bullet}$	1-$C_4H_9^{\bullet}$	C_3H_6	13.2	S, 28	28.3	S, 28	4.4			
3-$C_7H_{15}^{\bullet}$	$CH_3^{\bullet}$	1-C_6H_{12}	13.9	S, 23	33.0	S, 23	3.6			
3-$C_7H_{15}^{\bullet}$	1-C_3H_7	1-C_4H_8	12.7	S, 24	29.1	S, 24	3.6			

Table 7. Arrhenius parameters and rate constants at 700 K for radical decomposition...continued

Reactant	Products		$\log[A/s^{-1}]$	Source	E, kcal/mol	Source	$\log[k/s^{-1}]$	ΔS^o (700) cal/(mol K)	ΔE^o (700) kcal/mol	$<\Delta C_p>^{(700)}_{(300)}$ cal/(mol K)
3-methyl-1-hexyl	2-$C_5H_{11}^{\bullet}$	C_2H_4	12.6	S, 25	26.2	S, 25	4.4			
1-$C_8H_{17}^{\bullet}$	1-$C_6H_{13}^{\bullet}$	C_2H_4	13.4	S, 12a	28.8	S, 12a	4.4			
2-$C_8H_{17}^{\bullet}$	1-$C_5H_{11}^{\bullet}$	C_3H_6	13.2	S, 28	28.3	S, 28	4.4			
3-$C_8H_{17}^{\bullet}$	$CH_3^{\bullet}$	1-C_7H_{14}	13.9	S, 23	33.0	S, 23	3.6			
3-$C_8H_{17}^{\bullet}$	1-$C_4H_9^{\bullet}$	1-C_4H_8	12.7	S, 24	29.1	S, 24	3.6			
4-methyl-2-heptyl	2-$C_5H_{11}^{\bullet}$	C_3H_6	13.4	S, 26	28.2	S, 26	4.6			
4-ethyl-2-hexyl	3-$C_5H_{11}^{\bullet}$	C_3H_6	13.4	S, 26	28.2	S, 26	4.6			
3-$C_9H_{19}^{\bullet}$	$CH_3^{\bullet}$	1-C_8H_{16}	13.9	S, 23	33.0	S, 23	3.6			
3-$C_9H_{19}^{\bullet}$	1-$C_5H_{11}^{\bullet}$	1-C_4H_8	12.7	S, 24	29.1	S, 24	3.6			

Notes for Radical Decomposition

1a. The average of three consistent sets of experimental values reported by Purnell and Quinn [1], Lin and Back [2] and Loucks and Laidler [3a].

1b. Calculated using back reaction parameters of $E=2.6$ kcal/mol and $\log A=10.6$ (see addition section).

1c. Values preferred by Benson and O'Neal [3b].

1d. Weighted average obtained by giving a weight of 2 each to the experimental value (note 1a) and Benson and O'Neal's value (note 1c), and a weight of one to the value calculated from the back reaction.

2a. Papic and Laidler [4] have determined the rate constant relative to the $1\text{-}C_3H_7\cdot$ recombination constant between 525 and 625 K. From their data, using $10^{9.6}$ for the $1\text{-}C_3H_7\cdot$ recombination constant (see recombination sections) we calculate $\log k=14.0-32.6/\theta$.

2b. Calculated using $E_{back}=7.7$ kcal/mol and $\log A=8.1$ (see addition section).

2c. Camilleri, Marshall, and Purnell [3c] have found $\log k=12.1-32.5/\theta$ using $k_c=10^{8.6}$ L mol^{-1}s^{-1} for *n*-propyl radical recombination. From their data, using $10^{9.6}$ for the recombination (see earlier section), we obtain $\log k=12.6-32.5/\theta$.

2d. Values preferred by Benson and O'Neal [3b].

2e. Weighted average giving a weight of 2 to 2c and one to the others.

3. Calculated using $E_{back}=2.9$ kcal/mol and $\log A=9.9$ (see addition section).

4a. Papic and Laidler [4] have determined the rate constant relative to the $2\text{-}C_3H_7\cdot$ recombination constant between 757 and 625 K. Using $10^{9.6}$ for the $2\text{-}C_3H_7\cdot$ recombination constant (see recombination section) leads to $\log k=13.9-38.7/\theta$.

4b. Calculated using $E_{back}=1.2$ kcal/mol and $\log A=9.9$ (see addition section).

5a. Morganroth and Calvert [5] have determined the rate constant relative to the $1\text{-}C_4H_9\cdot$ recombination constant between 430–520 K. Using $10^{9.6}$ for the recombination constant (see recombination section) gives $\log k=13.2-28.7/\theta$.

5b. Calculated using $E_{back}=7.6$ kcal/mol and $\log A=7.8$.

5c. Average of 5a and 1c.

6. $\log k_{back}=9.9-2.9/\theta$.

7a. Value recalculated from the data of Lin and Laidler [6] changing the value of $2\text{-}C_4H_9\cdot$ recombination from Lin and Laidler's assumed value of $\log k=\log A=10.34$ L mol^{-1}s^{-1} to $\log k=9.5$ L mol^{-1}s^{-1}; see recombination section.

7b. $\log k_{back}=8.5-7.4/\theta$.

7c. Average of 7a and 1c.

8. $\log k_{back}=9.9-1.2/\theta$.

9. $\log k_{back}=9.7-1.2/\theta$.

10a. $\log k_{back}=8.5-9.1/\theta$.

10b. Slater, Collier and Calvert [7], have measured the decomposition constant relative to $k_c^{1/2}$ where k_c= the recombination constant for the 2-meth 1-propyl radical. Using $k_c=10^{9.6}$ gives a value of $k=12.0-31/\theta$ (300–600 K.) This *A*-factor appears be quite low compared to the general values of oth decomposition reactions although *E* appe reasonable.

10c. Average of 10a and 1c.

11. $\log k_{back}=10.6-1.3/\theta$.

12a. Parameters assumed to be the same as f $1\text{-}C_4H_9\cdot \rightarrow C_2H_5\cdot+C_2H_4$.

12b. $\log k_{back}=7.8-7.4/\theta$ at 330 K.

12c. Watkins and Lawson [8] have calculated l $A=14.1$ on the basis of a transition state model a sumed for activated decomposition.

12d. Average.

13. Assumed to be the same as $1\text{-}C_4H_9\cdot\rightarrow$ $+1\text{-}C_4H_8$; back reaction-thermochemical value give

14. Log $k_{back}=7.6-7.5/\theta$.

15. Assumed to have the same value as $2\text{-}C_4H_9\cdot$— $H+1\text{-}C_4H_8$.

16. Assumed to have the same value as $2\text{-}C_4H_9\cdot$— $H+2\text{-}C_4H_8$.

17a. Assume parameters are the same as for $2\text{-}C_4H_9\cdot$— $CH_3\cdot+C_3H_6$ except for two-fold rotational symmetry correction for $\Delta S\ddagger$ of the $3\text{-}C_5H_{11}\cdot$ radical; based on recalculated experimental value.

17b. $\log k_{back}=8.3-7.2/\theta$.

18. Assume parameters are the same as for $2\text{-}C_4H_9\cdot\rightarrow H+2\text{-}C_4H_8$ with a $\Delta S\ddagger$ correction for the two-fold rotational symmetry of the $3\text{-}C_5H_{11}\cdot$ radical.

19. Estimated to be the same as the values for 2-methyl-1-propyl$\cdot\rightarrow CH_3\cdot+C_3H_6$ with a correction to $\Delta S\ddagger$ for the optical assymetry of the 2-methyl-1-butyl radical; based on back reaction-thermochemical value.

20. $\log k_{back}=7.6-9.2/\theta$.

21. $\log k_{back}=7.6-6.9/\theta$; based on the experimental value of $k_{back}/k_c^{1/2}$ determined by Watkins and O'Deen [9], where k_c=rate constant for $2\text{-}C_3H_7\cdot$ recombination and is assigned our preferred value of $10^{9.5}$ (see recombination section).

22. $\log k_{back}=7.8-7.0/\theta$. Quinn [10] has estimated from experimental data that at ~800 K $\log k$ for decomposition has a value of $13.5-22.4/\theta$. This value of *E* appears to be too low relative to the back-reaction-thermochemical value.

23. Assume values are the same as for $3\text{-}C_5H_{11}\cdot\rightarrow CH_3\cdot+1\text{-}C_4H_8$ but correct $\Delta S\ddagger$ for loss of two-fold rotational symmetry in the $3\text{-}C_6H_{13}\cdot$ radical.

24. Assume values are the same as for $2\text{-}C_5H_{11}\cdot\rightarrow C_2H_5\cdot+C_3H_6$.

25. Assume values are the same as for 3-methyl-1-butyl$\cdot\rightarrow 2\text{-}C_3H_7\cdot+C_2H_4$.

26. Assumed to have the same value as for 4-methyl-2-hexyl$\cdot\rightarrow 2\text{-}C_4H_9\cdot+C_3H_6$.

27. $\log k_{back}\sim 8.1-8.0/\theta$;

28. Assume values are the same as for $2\text{-}C_6H_{13}\cdot\rightarrow C_3H_7\cdot+C_3H_6$.

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9. Isomerization

Arrhenius parameters and rate constants at 700 K for isomerization are in table 8. The notation is the same as in previous sections. The Arrhenius *A* factors for isomerization are probably accurate to within one and a half powers of ten, the activation energies to within 2 kcal/mol and the rate constants at 700 K to about two powers of ten. As the table shows, very few experiments have been made. The difficulties are considerable. The biggest problem is competing reactions. Furthermore, activated radicals almost always are involved. In short, isomerizations have the most uncertain rates of elementary reactions in pyrolyses.

Table 8. Arrhenius parameters and rate constants at 700 K for isomerization.

Reactant	Products	$\log[A/s^{-1}]$	Source	E, kcal/mol	Source	$\log[k/s^{-1}]$ at 700 K	ΔS^{o} (700) cal/(mol K)	Source	ΔH^{o} (700) kcal/mol	Source	$\langle \Delta C_p \rangle_{(300)}^{(700)}$ cal/(mol K)	Source
$1\text{-}C_5H_{11}^{\bullet}$	$2\text{-}C_5H_{11}^{\bullet}$	11.0	T, 1	20	T, 1	4.8						
$2\text{-}C_5H_{11}^{\bullet}$	$1\text{-}C_5H_{11}^{\bullet}$	11.1	B	23.4	B	3.8	0.7		3.4		0.3	
$1\text{-}C_6H_{13}^{\bullet}$	$2\text{-}C_6H_{13}^{\bullet}$	11.0 7.2 9.4 9.2	S, 2a E, 2b E, 2c Rec, 2d	13.7 8.3 11.2 11.1	S, 2a E, 2b E, 2c Rec, 2d	6.7 4.6 5.9 5.7						
$2\text{-}C_6H_{13}^{\bullet}$	$1\text{-}C_6H_{13}^{\bullet}$	9.3	B	14.5	B	4.8	0.7	3	3.4	3	0.3	3
2-methyl-1-pentyl	2-methyl-4-pentyl	11.0	S, 3	20	S, 3	4.8						
$1\text{-}C_7H_{15}^{\bullet}$	$3\text{-}C_7H_{15}^{\bullet}$	9.2	S, 4	11.1	S, 4	5.7						
2-ethyl-1-pentyl	4-methyl-2-hexyl	11.0	S, 3	20	S, 3	4.8						
3-methyl-1-hexyl	4-methyl-2-hexyl	9.2	S, 4	11.1	S, 4	5.7						
3-ethyl-1-pentyl	3-ethyl-2-pentyl	11.0	S, 3	20	S, 3	4.8						
4-penten-1-yl	cyclopentyl	11.3	T, 5	18	T, 5	5.7						
5-hexen-2-yl	2-methyl-1-cyclopentyl	~11.3	S, 6	~18	S, 6	5.7						

Notes for Isomerization

1. Recently recalculated values [1] based on chemical activation studies of Watkins [2] (433 K).

2a. The A-factor was assumed to have the same value as for 1-$C_5H_{11}\cdot$ isomerization and E also was estimated to be the same as 1-$C_5H_{11}\cdot$ isomerization except a correction of −6.3 kcal/mol was made assuming that the pentyl isomerization transition state has ring strain similar in energy to the cyclopentane ring strain [3].

2b. Watkins and Ostreko [4a] have measured the temperature dependence of the hexyl isomerization relative to ethyl recombination and ethyl/n-hexyl recombination. Using values of $10^{9.6}$ and $10^{9.9}$ L $mol^{-1}s^{-1}$ for these latter constants, respectively, one calculates $\log k_{isom}=7.2-8.3/\theta$ (352–405 K). This A-factor appears unreasonably low for a unimolecular reaction and the activation energy is slightly lower than that for a similar bimolecular abstraction (10.4 kcal/mol, preferred value of this compilation).

2c. Experimental values of Watkins [4b].

3. Assumed to be the same as 1-$C_5H_{11}\cdot$ isomerization.

4. Assumed to be the same as 1-$C_6H_{13}\cdot$ isomerization.

5. Values calculated by Watkins and Olsen [5] on the basis of a model which gives agreement with reactions of chemically activated 4-pentene-1-yl radicals. However, a lower value of $E\sim14$ kcal/mol has been estimated by Walsh [6].

6. Estimated to be the same as the isomerization of the 4-pentene-1-yl· radical.

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Glossary of Compounds

1-$C_3H_7\cdot$	$CH_2CH_2CH_3$
2-$C_3H_7\cdot$	CH_3CHCH_3
$C_3H_5\cdot$	CH_2CHCH_2
1-$C_4H_9\cdot$	$CH_2CH_2CH_2CH_3$
2-$C_4H_9\cdot$	$CH_3CHCH_2CH_3$
2-methyl-1-propyl (i-$C_4H_9\cdot$)	$CH_2CH(CH_3)_2$
2-methyl-2-propyl	$(CH_3)_3C$
$C_4H_7\cdot$	$CH_3CHCHCH_2$
1-$C_5H_{11}\cdot$	$CH_2(CH_2)_3CH_3$
2-$C_5H_{11}\cdot$	$CH_3CH(CH_2)_2CH_3$
3-$C_5H_{11}\cdot$	$CH_3CH_2CHCH_2CH_3$
2-methyl-1-butyl	$CH_2CH(CH_3)CH_2CH_3$
3-methyl-1-butyl	$CH_2CH_2CH(CH_3)_2$
2-$C_6H_{13}\cdot$	$CH_2CH(CH_2)_3CH_3$
4-methyl-2-hexyl	$CH_3CHCH_2CH(CH_3)CH_2CH_3$
2-penten-1-yl	$CH_2CHCHCH_2CH_3$

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