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Chemically Activated 3-Methyl-1-butene and 2-Methyl-1-butene from Photolysis of Diazomethane–Isobutene–Neopentane–Oxygen Mixtures*

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Abstract

An experimental study of the decomposition kinetics of chemically activated 2-methyl-1-butene and 3-methyl-1-butene produced from photolysis of diazomethane–isobutene–neopentane–oxygen mixtures is reported. The experimental rate constants for 3-methyl-1-butene decomposition were $1.74 \pm 0.44 \times 10^8$ sec^{-1} and $1.01 \pm 0.25 \times 10^8$ sec^{-1} at 3660 and 4358 Å, respectively. 2-Methyl-1-butene experimental decomposition rate constants were found to be $5.94 \pm 0.59 \times 10^7$ sec^{-1} at 3660 Å and $3.42 \pm 0.34 \times 10^7$ sec^{-1} at 4358 Å. Activated complex structures giving Arrhenius A-factors calculated from absolute rate theory of $10^{16.6 \pm 0.5}$ sec^{-1} for 3-methyl-1-butene and $10^{16.2 \pm 0.4}$ sec^{-1} for 2-methyl-1-butene, both calculated at 1000°K, were required to fit RRKM theory calculated rate constants to the experimental rate constants at reasonable E_0 and E^* values. Corrected calculations (adjusted E_0 values) on previous results for 2-pentene decomposition gave an Arrhenius A-factor of $10^{16.45 \pm 0.35}$ sec^{-1} at 1000°K. The predicted A-factors for these three alkene decompositions giving resonance-stabilized methylallyl radicals are in good internal agreement. The fact that these A-factors are only slightly less than those for related alkane decompositions indicates that methylallylic resonance in the decomposition products leads to only a small amount of tightening in the corresponding activated complexes. This tightening is a significantly smaller factor than the large reduction in the critical energy due to resonance stabilization.

1. Introduction

Quantitative kinetic information on the primary unimolecular decomposition reactions for olefins giving allylic or methylallylic resonance-stabilized radical fragments have been limited to a few chemical activation [1–3] and thermal studies [4,5] of a relatively few olefins. The extent to which the resonance stabilization in the products appears in the activated complex structures is a particularly interesting aspect of these decompositions.

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Chemical activation results combined with RRKM theory [1] calculations can give valuable information on activated structures for unimolecular reactions, provided reliable critical energies and excitation energies are available.

A study of the decomposition kinetics of chemically activated 2-methyl-1-butene and 3-methyl-1-butene produced from the photolysis of diazomethane–isobutene–neopentane–oxygen mixtures is reported here. Comparisons of these results with related previous work are discussed and some generalizations are attempted.

2. Experimental

The materials, apparatus, and analytical procedure employed in this study have been described previously [7].

3. Experimental Results

The following reactions, the first ten of which are identical to those in ref. [7] lead to chemically activated 2-methyl-1-butene (2MB1*) and 3-methyl-1-butene (3MB1*) formation and decomposition in this work.

$$\begin{array}{lrl}
(1) & \mathrm{CH_2N_2} & \xrightarrow{h\nu} {}^1\mathrm{CH_2} + \mathrm{N_2} \\
(2) & {}^1\mathrm{CH_2} + \mathrm{IB} & \longrightarrow \mathrm{2MB2^*} \xrightarrow{W} \mathrm{2MB2} \\
(3) & & \longrightarrow \mathrm{2MB1^*} \\
(4) & & \longrightarrow \mathrm{DMC^*} \\
(5) & \mathrm{DMC^*} & \xrightarrow{W} \mathrm{DMC} \\
(6) & & \longrightarrow \mathrm{2MB2^*} \xrightarrow{W} \mathrm{2MB2} \\
(7) & & \longrightarrow \mathrm{3MB1^*} \\
(8) & \mathrm{3MB1^*} & \longrightarrow \cdot\mathrm{CH_3} + \mathrm{CH_3\dot{C}HCHCH_2} \\
(9) & & \xrightarrow{W} \mathrm{3MB1} \\
(10) & {}^1\mathrm{CH_2} + \mathrm{NP} & \longrightarrow \mathrm{NH^*} \xrightarrow{W} \mathrm{NH} \\
(11) & \mathrm{2MB1^*} & \longrightarrow \cdot\mathrm{CH_3} + \mathrm{CH_2(CH_3)\dot{C}H_2} \\
(12) & & \xrightarrow{W} \mathrm{2MB1}
\end{array}$$

where IB = isobutene, 2MB2 = 2-methyl-2-butene, 2MB1 = 2-methyl-1-butene, 3MB1 = 3-methyl-1-butene, DMC = 1,1-dimethylcyclopropane, NP = neopentane, NH = neohexane, (*) represents excess internal vibrational-rotational energy, and W is the collisional stabilization rate constant which is taken to be the gas kinetic theory collision frequency.

A. *Determination of* k_8

The steady-state treatment of the reaction scheme yields eq. 13 (see ref. [7]) and the 4358 Å and 3660 Å data were plotted according to eq. (13) in Figure 4 of ref. [7]:

$$\frac{\mathrm{DMC}}{\mathrm{3MB1}} = \frac{W}{k_7} + \frac{k_8}{k_7} \tag{13}$$

The intercept is uncertain by ~20% for the reasons discussed in ref. [7]. The values of k_8 deduced from the slopes and intercept (1.79) of Figure 4 of ref. [7] are given in Table I.

TABLE I. Decomposition rates of chemically activated 3-methyl-1-butene and 2-methyl-1-butene.

Experimental rate constant, sec^{-1}		
3660 Å	4358 Å	Equation
k_8		
1.83×10^8	1.02×10^8	(13)
1.64×10^8	1.00×10^8	(14)
1.74×10^8	1.01×10^8	average
k_{11}		
5.94×10^7	3.42×10^7	(15)

Equation (14) (see ref. [7])

$$\left(\frac{\mathrm{NH}}{\mathrm{3MB1}} \times \frac{\mathrm{IB}}{\mathrm{NP}}\right)\frac{k_4}{k_{10}}\left(\frac{W}{W + k_5}\right) = \frac{W}{k_7} + \frac{k_8}{k_7} \tag{14}$$

was also derived from the steady-state treatment of the reaction scheme. The 4358 Å and 3660 Å data were plotted according to eq. (14) in Figure 5 of ref. [7], and again the intercept (1.69) is uncertain by about 20% as discussed in ref. [7]. The values of k_8 deduced from the slopes and intercept of Figure 5 of ref. [7] are given in Table I.

B. *Determination of* k_{11}

Equation (15) was derived from the steady-state treatment of the reaction scheme:

$$\frac{\mathrm{NH}}{\mathrm{2MB1}} \times \frac{\mathrm{IB}}{\mathrm{NP}} = \frac{k_{11}}{W}\left(\frac{k_{10}}{k_3}\right) + \frac{k_{10}}{k_3} \tag{15}$$

The 4358 Å and 3660 Å photolysis data are plotted according to eq. (15) in Figure 1. The high-pressure data indicated that k_{10}/k_3 is the same at both wavelengths, as would be expected, and consequently the least-squares lines were forced to a common intercept (2.36) in Figure 1. The slopes of these lines are 1.40×10^8 sec^{-1} and 0.81×10^8 sec^{-1} at 3660 Å and 4358 Å, respectively. The corresponding k_{11} values for 2MB1* decomposition are given in Table I.

4. Theoretical Rate Calculations

The RRKM theory expression for the specific rate constant of the unimolecular decomposition of a species containing internal vibrational-rotational energy, E^*, which is greater than E^+ by the critical energy E_0 is given by eq. (16):

$$(16) \qquad k_E = (1/h)(Q^+/Q^*) \frac{\sum_{E^+_{VR}=0}^{E^+} P(E^+_{VR})}{N(E^*_{VR})}$$

The definitions of terms in eq. (16) have been given elsewhere [1]. The evaluations of the sum and density terms in eq. (16) were carried out on an IBM 360 computer utilizing the accurate approximation of Whitten and Rabinovitch [8,9] for harmonic oscillators.

A. *E^* for 3MB1**

The average internal excitation energy, E^*, of the chemically activated molecules in this study can be evaluated from eq. (17),

$$(17) \quad E^* = \Delta H^0_{f_0}(\mathrm{IB}) - \Delta H^0_{f_0}(\mathrm{A}) + [\Delta H^0_{f_0}(^1\mathrm{CH}_2) + E^*(^1\mathrm{CH}_2)] + E_{\mathrm{th}}$$

where A = 3MB1 or 2MB1 and other terms are as described previously [2,7,10]. The 0°K enthalpies of formation of isobutene and 3-methyl-1-butene are 1.0 and −0.7 kcal/mole, respectively. The value of E_{th} is 4.4 kcal/mole as evaluated in ref. [7]. The values of $[\Delta H^0_{f_0}(^1\mathrm{CH}_2) + E^*(^1\mathrm{CH}_2)]$ can be taken as 112.6 and 116.1 kcal/mole for 4358 Å and 3660 Å diazomethane photolyses, respectively, as determined from previous studies of diazomethane-*cis*-2-butene photolyses [10]. The resulting values of E^* are 118.7 and 122.2 kcal/mole at 4358 Å and 3660 Å, respectively.

B. *E^* for 2MB1**

The difference in the E^* values between 3MB1* and 2MB1* is due to their different enthapies of formation. The 0°K enthalpy of formation for 2-methyl-1-butene is −2.3 kcal/mole, which leads via eq. (17) to E^* values for 2MB1* of 120.3 and 123.8 kcal/mole at 4358 Å and 3660 Å, respectively.

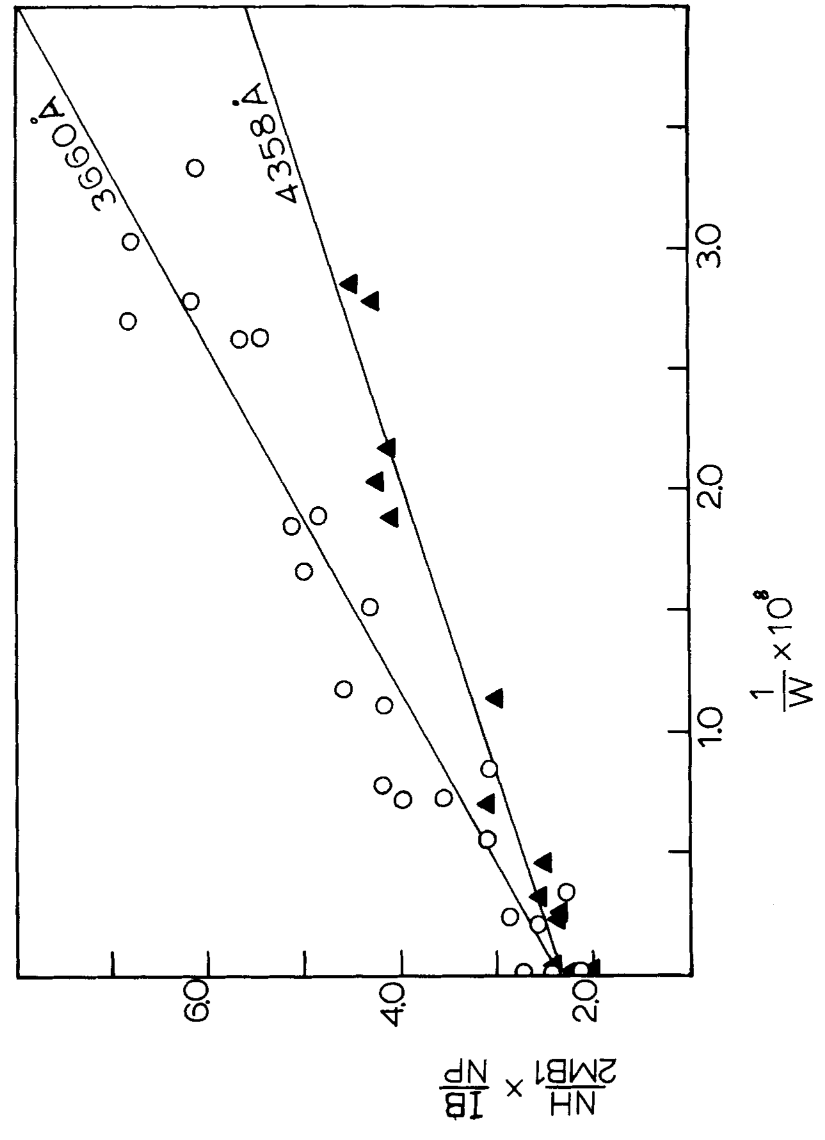

3660 Å
4358 Å
2.0
4.0
6.0
1.0
2.0
3.0
$\frac{1}{W} \times 10^8$
$\frac{NH}{2MB1} \times \frac{1B}{NP}$

Figure 1.

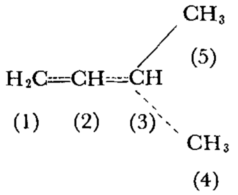
C. *Critical energies*, E_0

The critical energies for 2MB1* and 3MB1* decomposition were determined by subtracting the methylallylic resonance energy (13 kcal/mole [4,11][1]) from the appropriate 0°K C—C bond dissociation energy for the corresponding alkane [11,12][2] and adding on 2 kcal/mole as the critical energy for recombination of (methyl + methylallyl) radicals. Thus, for 3MB1*, $E_0 = 81 - 13 + 2 = 70 \pm 2$ kcal/mole and for 2MB1*, $E_0 = 83 - 13 + 2 = 72 \pm 2$ kcal/mole. A critical energy of 2 kcal/mole for (methyl + methylallyl) recombination was taken as a reasonable choice between $\sim 8 \pm 2$ kcal/mole for (methyl + olefin) [13] and $\sim 0 \pm 2$ kcal/mole for alkyl radical recombination [14]. A recent measurement of (allyl + allyl) recombination suggests that a critical energy close to ~0 is correct [15]. The 2 kcal/mole uncertainty in E_0 represents a conservative estimate of the uncertainties in the measured alkane C—C bond dissociation energies, the methylallylic resonance energy, and the critical energy of recombination.

D. *Molecular frequencies and activated complex models*

The sets of vibrational frequencies deduced for 3MB1 and 2MB1 are given in Tables II and III, respectively. The frequencies for 3MB1 were deduced from those for propane and ethylene [16]. The frequencies for 2MB1 were deduced from those for ethane and propylene [16]. In both cases the C═C torsion frequencies were derived from those for substituted ethylenes by allowing for the appropriate mass changes [16]. Skeletal bending frequencies were estimated from skeletal motions in the analogous alkanes [18]. The three internal rotations about C–C single bonds in the molecules were treated as free rotations.

The activated complex for 3MB1* decomposition is pictured as



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[1] In our previous paper [1] on 2-pentene decomposition, we used a value of 12 kcal/mole for the methylallylic resonance energy. This value was based primarily on several determinations of the allylic resonance energy. The above reference indicates that 13 kcal/mole is probably a better value for the methylallylic resonance energy. This alters the E_0 values in reference [1] (see Appendix). One referee points out that he has received a private communication of preliminary evidence indicating that the β-methylallyl radical may have a somewhat lower resonance energy than the α-radical. It does not seem justified to change the value chosen here at this point.

[2] The value (83 kcal/mole) used in reference [1] for the 298°K bond dissociation energy of a CH_3—CH_2 bond in *n*-pentane is low and corresponds to the 0°K value. This result, combined with that in ref. [8] leads to E_0 values for 2-pentene decomposition that are 2 kcal/mole higher than those used in ref. [1].

The frequencies of three complex models for 3MB1 decomposition are given in Table II. The molecular frequencies adjusted in forming the activated complex structure were those reasonably believed to be involved in the translation along the reaction coordinate. The C(3)—C(4) stretching vibration was taken as the translation along the reaction coordinate, and the C(3)—C(4) bond was taken to be extended by a factor of 2 in the activated complexes. The C(1)═C(2) torsion was lowered in the complexes, and the C(2)—C(3) internal rotation was converted to a low-frequency vibration; the magnitude of which was adjusted to fit theoretical calculations to experiment (complex II) and to fit our estimates of the combined uncertainties in the experimental rates (25%) and the E_0 (±2 kcal/mole) value. Other frequency adjustments in the complexes, the CH_3 rocks and C—C—C bends, were consistent with the extension and weakening of the C(3)—C(4) bond and some allylic tightening in the C(1)—C(2)—C(3) fragment. It is noted that a reaction path degeneracy of 2 applies here for 3MB1.

TABLE II. Molecule and complex frequencies for 3-methyl-1-butene.

Motion	Molecule[a]	Activated complex model[a] I	II	III
C—H stretch	2903(2), 2946, 2968(3) 2885, 2992, 3012, 3090			
C═C stretch	$\underline{1650}$	$\underline{1230}$	$\underline{1230}$	$\underline{1230}$
C—C stretch	$\underline{790}$, $\underline{904}$, 955	$\underline{1230}$, $\underline{\text{r.c.}}$[b]	$\underline{1230}$, $\underline{\text{r.c.}}$[b]	$\underline{1230}$, $\underline{\text{r.c.}}$[b]
CH_3 deformation	1373(2), 1451(2), 1468(2)			
CH_3 rock	748, $\underline{1000}$, 1152, 1278	$\underline{150}$, $\underline{250}$ (300)	$\underline{150}$, $\underline{250}$ (300)	$\underline{150}$, $\underline{250}$ (300)
CH bend	418, 575, 1295, 1314			
CH_2 deformation	1420			
CH_2 wag	1165			
CH_2 rock	913			
C═C torsion	$\underline{850}$	$\underline{100}$	$\underline{100}$	$\underline{100}$
C—C—C bend	375(2), $\underline{418}$, $\underline{250}$	$\underline{550}$, 50 (275)	$\underline{550}$, 5$\underline{0}$ (275)	$\underline{550}$, 5$\underline{0}$ (275)
C—$C(CH_3)_2$ torsion	I.R.[c] 1.72×10^{-39}	17	48	146
CH_3—C torsion	I.R.[c](2) 5.07×10^{-40}	4.98×10^{-40}[c]	4.98×10^{-40}[c]	4.98×10^{-40}[c]
$I_xI_yI_z$[d]	5.58×10^{-114}	1.59×10^{-113}	1.59×10^{-113}	1.59×10^{-113}
log A[e]		17.07	16.62	16.18

[a] Frequencies are in cm^{-1}; underlined frequencies are those which change between the molecule and complex. The frequencies in parentheses represent alternate values for the vibrations above them. These alternates give equivalent models which are more consistent with the other two systems of this study.

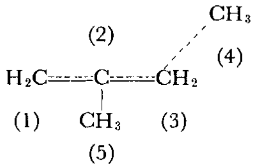
[b] Reaction coordinate.

[c] These reduced moments of inertia for internal rotation were calculated by the method of Pitzer [17]. The units are $g\text{-}cm^2$.

[d] The product of the principal moments of intertia in units of $g^3\text{-}cm^6$.

[e] The Arrhenius A-factor calculated at 1000°K in units of sec^{-1}.

The activated complex for 2MB1 decomposition is pictured as



The frequencies of three complex models derived for 2MB1* decomposition are given in Table III. These complex models were derived from the molecular frequencies of 2MB1 in much the same way as in the 3MB1 case. The C(3)—C(4) stretching vibration was taken as the translation along the reaction coordinate, and the C(3)—C(4) bond was extended by a factor of 2 in the complexes. The C(1)=C(2) torsion frequency was lowered, and the C(2)—C(3) internal rotation was taken as an adjustable vibrational frequency, so as to fit theory and experiment (complex II) and to fit the upper (complex I) and lower (complex III) limits of the combined uncertainties in E_0 (72 ± 2 kcal/mole) and the experimental rates (±10%).

5. Comparison of Theory and Experiment

The theoretically calculated specific rate constants of 3MB1* decomposition at 4358 Å and 3660 Å are presented in Table IV for three reasonable E_0 values and three activated complex models. The experimental rate constants for 3MB1* decomposition and the Arrhenius A-factors (calculated at 1000°K) also are given in Table IV. Complex II was designed so that the theoretical rate constants at $E_0 = 70$ kcal/mole were in satisfactory agreement with both the 4358 Å and 3660 Å experimental rate constants at the corresponding E^* values. Complex I was designed so that the theoretical rate constants at $E_0 = 72$ kcal/mole were in satisfactory agreement with the upper limits of both the 4358 Å and 3660 Å experimental rate constants. Complex III was designed so that the theoretical rate constants at $E_0 = 68$ kcal/mole were in satisfactory agreement with the lower limits of both the 4358 Å and 3660 Å experimental rate constants. It is seen that the calculated Arrhenius A-factor for 3MB1* decomposition is $10^{16.6\pm0.5}\text{sec}^{-1}$.

The theoretically calculated specific rate constants for 2MB1* decomposition at 4358 Å and 3660 Å are presented in Table V for three resaonable E_0 values and the corresponding three activated complex models. The experimental rates of 2MB1* decomposition and the Arrhenius A-factors (calculated at 1000°K) also are given in Table V. The basis for the three complex models for 2MB1* decomposition is the same as those discussed in the previous paragraph for 3MB1*, except that the E_0 values are 2 kcal/mole higher. The calculated Arrhenius A-factor for 2MB1* decomposition is $10^{16.2\pm0.4}\text{sec}^{-1}$.

TABLE III. Molecule and complex frequencies for 2-methyl-1-butene.

Motion	Molecule[a]	Activated complex models[a] I	II	III
C—H stretch	2955(3), 2920, 3090, 2992, 2980, 2967, 2898, 2975			
C=C stretch	$\underline{1650}$	$\underline{1230}$	$\underline{1230}$	$\underline{1230}$
C—C stretch	$\underline{920}$, $\underline{920}$, 850	$\underline{1230}$, $\underline{\text{r.c.}}$[b]	$\underline{1230}$, $\underline{\text{r.c.}}$[b]	$\underline{1230}$, $\underline{\text{r.c.}}$[b]
CH_3 deformation	1380, 1470, 1460, 1370 1451, 1468			
CH_3 rock	1215, 960, $\underline{1045}$, $\underline{875}$	$\underline{200}$, $\underline{100}$ (200)	$\underline{200}$, $\underline{100}$ (200)	$\underline{200}$, $\underline{100}$ (200)
CH_2 deformation	1468, 1420			
CH_2 twist	1280			
CH_2 wag	1152, 1165			
CH_2 rock	1179, 913			
C=C torsion	$\underline{900}$	$\underline{100}$	$\underline{100}$	$\underline{100}$
C—C—C bend	375, 250, $\underline{250}$, $\underline{420}$	$\underline{50}$, 520 (260)	$\underline{50}$, $\underline{520}$ (260)	$\underline{50}$, $\underline{520}$ (260)
C—CH_2CH_3 torsion	I.R.[c], 2.71×10^{-39}	34	79	196
CH_2—CH_3 torsion	I.R.[c], 5.40×10^{-40}	5.32×10^{-40}	5.32×10^{-40}	5.32×10^{-40}
=C—CH_3 torsion	I.R.[c], 5.07×10^{-40}	4.98×10^{-40}	4.98×10^{-40}	4.98×10^{-40}
$I_xI_yI_z$[d]	5.58×10^{-114}	1.59×10^{-113}	1.59×10^{-113}	1.59×10^{-113}
log A[e]		16.60	16.24	15.83

[a] These frequencies (cm^{-1}) were estimated from the normal mode vibrations of propylene and ethane.

[b] Reaction coordinate. Underlined frequencies are those which change between the molecule and complex. The frequencies in parentheses represent alternate values for the vibrations above them. These alternates give equivalent models which are more consistent with the other two systems of this study.

[c] These reduced moments of inertia for internal rotation were calculated by the method of Pitzer [17]. The units are g-cm^2.

[d] The product of the principal moments of inertia in units of g^3-cm^6.

[e] The Arrhenius A-factor calculated at 1000°K in units of sec^{-1}.

Dorer and Rabinovitch [3] have determined experimental decomposition rates for chemically activated 2MB1* and 3MB1* to be 1×10^7 and $>5\times10^7$ sec^{-1}, respectively, from the photolyses of diazomethane-butene-1 mixtures in the *absence* of oxygen. These values are compared to the present calculations in which complex II in each case predicts theoretical rates of 3.0×10^7 sec^{-1} at $E^* = 124.3$ kcal/mole and $E_0 = 72$ kcal/mole for 2MB1* decomposition and 1.95×10^8 sec^{-1} at $E^* = 122.7$ kcal/mole and $E_0 = 70$ kcal/mole for 3MB1* decomposition.

TABLE IV. Theoretical k_E(sec^{-1}) values for 3-methyl-1-butene decompostion at various E_0 values.

	Complex model		
	I	II	III
log A(sec^{-1})[a]	17.07	16.62	16.18
E_0, kcal/mole		$E^* = 118.7$ kcal/mole	
68	5.77×10^8	2.05×10^8	7.78×10^7
70	2.62×10^8	1.00×10^8	3.79×10^7
72	1.23×10^8	4.80×10^7	1.80×10^7
Experimental (4358 Å)		$(1.00\pm0.25)\times10^8$	
		$E^* = 122.2$ kcal/mole	
68	1.02×10^9	3.55×10^8	1.26×10^8
70	4.50×10^8	1.75×11^8	6.55×10^7
72	2.20×10^8	8.64×10^7	3.22×10^7
Experimental (3660 Å)		$(1.74\pm0.44)\times10^8$	

[a] Arrhenius A-factors calculated at 1000°K.

TABLE V. Theoretical k_E(sec^{-1}) values for 2-methyl-1-butene decomposition at various E_0 values.

	Complex model		
	I	II	III
log A(sec^{-1})[a]	16.60	16.24	15.83
E_0, kcal/mole		$E^* = 120.3$ kcal/mole	
70	1.52×10^8	6.93×10^7	3.13×10^7
72	7.60×10^7	3.42×10^7	1.54×10^7
74	3.68×10^7	1.63×10^7	7.35×10^6
Experimental (4358 Å)		$(3.42\pm0.34)\times10^7$	
		$E^* = 123.8$ kcal/mole	
70	2.61×10^8	1.18×10^8	5.25×10^7
72	1.32×10^8	5.94×10^7	2.66×10^7
74	6.62×10^7	2.95×10^7	1.32×10^7
Experimental (3660 Å)		$(5.94\pm0.59)\times10^7$	

[a] Arrhenius A-factors at 1000°K.

The E^* values were determined from eq. (17) utilizing the appropriate 0°K enthalpies of formation. The agreement between these calculations and Dorer and Rabinovitch's experimental results is not particularly good. However, in the absence of a radical scavenger, lower rate constants may be a result of reactions of unscavenged triplet methylene radicals and recombination of methyl and methylallyl radicals.

Corrected and extended calculations for chemically activated 2-pentene (P2) decomposition are presented in the Appendix, where it is seen that an Arrhenius *A*-factor of $10^{16.45\pm0.35}$ sec^{-1} is calculated.

The Arrhenius *A*-factors for 3MB1*, 2MB1*, and P2* decomposition determined in this work are in reasonable agreement with each other. If the 3MB1* *A*-factor is adjusted to a unit reaction path degeneracy, then *A*-factors of $10^{16.3\pm0.5}$, $10^{16.2\pm0.4}$, and $10^{16.45\pm0.35}$ sec^{-1} are obtained for 3MB1*, 2MB1*, and P2* decomposition, respectively. These *A*-factors are somewhat higher than those ($10^{15.8\pm0.3}$ sec^{-1}) determined in the shock tube work [5a,c,d] for similar reaction coordinates. This discrepancy is within the stated uncertainty limits of the two studies, and it has been observed that shock tube studies often give slightly lower unimoleular *A*-factors than conventional thermal studies [19] or chemical activation studies [20]. A recent conventional thermal study of 3MB1 decomposition yielded an *A*-factor of $10^{15.9\pm0.3}$ sec^{-1} [4].

The results of this work compared with the results on alkane decompositions [20] indicate that olefin decompositions leading to allylic resonance-stabilized radicals proceed via activated complex structures which are only slightly tighter (relative to the reactant) than those involved in alkane decompositions. This effect is small compared to the rather large allylic resonance energy effect.

Appendix

This Appendix presents corrected and extended theoretical calculations for 2-pentene* decomposition reported earlier [1]. Table A-I presents the molecular and complex frequencies deduced above in the same way as for 3MB1* and 2MB1*. Complex II was designed to fit theory and experiment at $E_0 = 83 - 13 + 2 = 72$ kcal/mole [10,11]. Complexes I and III were designed to fit the upper and lower limits, respectively, of the combined uncertainties in E_0 (72 ± 2 kcal/mole) and the experimental rates (±10%).

Table A-II presents the calculated rate constants for the three complex structures at the three new E_0 values. Experimental rates and Arrhenius *A*-factors (calculated from the complexes) are also presented in Table A-II. The basis for these three complexes is the same as that discussed above for 3MB1* decomposition, except that the E_0 values are 2 kcal/mole higher.

TABLE A-I. Molecule and complex frequencies for 2-pentene.

		Activated complex models[a]		
Motion	Molecule[a]	I	II	III
C—H stretch	2954(2), 3013(2), 2870 2933, 2967, 2980, 2995, 2956			
C=C stretch	1652	1200	1200	1200
C—C stretch	920, 900, 969	1200, r.c.[b]	1200, r.c.[b]	1200, r.c.[b]
CH_3 deformation	1379(2), 1477(2), 1443, 1465			
CH_3 rock	1173(2), 1045, 821	500, 400 (250), (200)	500, 400 (250,), (200)	500, 400 (250), (200)
CH_2 deformation	1486			
CH_2 twist	1179			
CH_2 wag	1152			
CH_2 rock	720			
C—H bend	1419(2), 991(2)			
C=C torsion	500	100	100	100
C—C—C bend	400, 400, 250	50, 50 (200)	50, 50 (200)	50, 50 (200)
$C—CH_2CH_3$ torsion	I.R.[c], 3.02×10^{-39}	29	63	145
$CH_2—CH_3$ torsion	I.R.[c], 4.98×10^{-40}	4.89×10^{-40}	4.89×10^{-40}	4.89×10^{-40}
$=CH—CH_3$ torsion	I.R.[c], 5.34×10^{-40}	5.31×10^{-40}	5.31×10^{-40}	5.31×10^{-40}
$I_xI_yI_z$[d]	5.58×10^{-114}	1.59×10^{-113}	1.59×10^{-113}	1.59×10^{-113}
log A		16.80	16.45	16.10

[a] Frequencies are in cm^{-1}; underlined frequencies are those which change between the molecule and complex. The frequencies in parentheses represent alternate values for the vibrations above them. These alternates give equivalent models which are more consistent with the other two systems of this study.

[b] Reaction coordinate.

[c] These reduced moments of inertia for internal rotation were calculated by the method of Pitzer [17]. The units are $g\text{-}cm^2$.

[d] The product of the principal moments of inertia in units of $g^3\text{-}cm^6$.

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Table A-II. Theoretical k_E(sec^{-1}) values for 2-pentene decomposition at various E_0 values.

	Complex model		
	I	II	III
log A(sec^{-1})[a]	16.80	16.45	16.10
E_0, kcal/mole		$E^* = 120.7$ kcal/mole	
70	1.56×10^8	7.26×10^7	3.43×10^7
72	7.71×10^7	3.60×10^7	1.70×10^7
74	3.76×10^7	1.76×10^7	8.33×10^6
Experimental (4358 Å)		$(4.1 \pm .4) \times 10^7$ sec^{-1}	
		$E^* = 124.2$ kcal/mole	
70	2.61×10^8	1.22×10^8	5.73×10^7
72	1.33×10^8	6.21×10^7	2.93×10^7
74	6.67×10^7	3.12×10^7	1.47×10^7
Experimental (3660 Å)		$(5.5 \pm .6) \times 10^7$ sec^{-1}	

[a] Arrhenius A-factors calculated at 1000°K.

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