Unimolecular Decomposition of Chemically Activated Propylene

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It was found that the cross combination of methyl and vinyl radicals produces chemically activated propylene which decomposes unimolecularly into H and allyl radical. The rate constant for the decomposition was found to be $(5.04\pm0.11)\times10^7$ sec^{-1} at 15°C. By using the RRKM and ART (absolute rate theory) theories, the propylene decomposition is characterized by a loose vibrational complex model.

KEY WORDS: RRKM calculations / Reaction kinetics /

INTRODUCTION

Numerous studies on the pyrolysis of propylene have been carried out for about half a century[1~12] as an instance of the thermal decomposition of simple olefins. The primary steps of the "hot" propylene molecules are the following C–C and C–H bond fissions[9]:

$$CH_3CH=CH_2* \longrightarrow
\begin{cases}
CH_3+CH=CH_2 \\
CH_2CH=CH_2+H \\
CH_3C=CH_2+H
\end{cases}$$
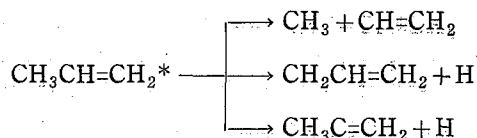
The first C–C bond fission is thought to be a main primary step and its reaction mechanism has been investigated kinetically in detail.[11, 13~15] The second C–H bond cleavage remains uncertain: recent studies[12, 16] show the activation energy to be within the range 87–90 kcal mol^{-1}, but the Arrhenius A factor shows large discrepancies as shown in Table I. The last C–H bond dissociation contains a vinylic C–H bond cleavage, the activation energy of which must be high ($\sim$110 kcal mol^{-1})[17, 18], and hence the possibility of the fission is negligible.[9]

It has been found that α-olefins decompose unimolecularly into alkyl and allyl radicals.[19] Simons, Rabinovitch, and Dorer (referred to as SRD hereafter)[20] studied the unimolecular decomposition of chemically activated propylene into H+allyl radical. Their procedure to produce active propylene was the addition of methylene radical to acetylene, but unfortunately the obtained rate constants showed the variation with total pressures because of the inaccuracy in the products analysis and seem to be semiquantitative. In the present work a different procedure is used to produce

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Table I.   Arrhenius parameters for the unimolecular decomposition of $C_3H_6 \rightarrow H + CH_2CH=CH_2$

	$\log A$ (sec^{-1})	E_a (kcal mol^{-1})	Temp. (mean °K)	Ref.	Note
Szwarc (1949)	13.04	72.0	1048	7	
Amano and Uchiyama (1963)	15	99.2–Q^a	1073	8	b
Marshall, Purnell, and Shurlock (1966)	15.7	100–Q^a	873	9	b
Benson and O'Neal (1970)	15.3	89.2	1048	16	b
Benson and O'Neal (1970)	16.6	89.9	1048	16	c
Berces, Seres, and Marta (1972)	14.8	88.4	800	12	b
Simons, Rabinovitch, and Dorer (1966)		81–84^d		20	e

   a Q denotes allylic resonance energy.
   b   Calculated value.
   c   Estimated k_{max} value.
   d   Critical energy.
   e   RRKM calculations.

propylene molecule: the cross combination of vinyl and methyl radicals forms chemically activated propylene and its unimolecular decomposition into H+allyl is studied kinetically.

EXPERIMENTAL

The apparatus and experimental technique is similar to that described in detail previously.[21]   The $Hg6(^3P_1)$ photosensitization of methane produces methyl radical and H atom.   The produced H atom adds to the coexisting acetylene to form vinyl radical.   Methane (99.5%) and acetylene (99.6%) were purchased from Takachiho Company.   The methane contained a very small amount of ethane as a hydrocarbon impurity, but it did not affect the experiments and was used without further purification.   The acetylene was purified by a gas chromatograph provided with a 1.75-m active charcoal column at 200°C.   The purified gas showed no impurity.   The reaction temperature was kept at 15°C.

The reactant-product mixture was collected by a Töpler pump to be analyzed by a gas chromatograph using a 2.25-m Porapak N column.   The reaction products were identified by the retention time of the authentic substances and also by means of Simadzu Model LKB–9000 gas chromatograph-mass spectrometer.

Acetylene is a hard compound to be decomposed by the Hg-sensitization,[22] while the collision cross section of methane with $Hg6(^3P_1)$ atom is small.[23]   Therefore the ratio of reactants, [acetylene]/[methane], was kept less than 0.05 in order to suppress the Hg-sensitized reaction of acetylene.

RESULTS

Reaction Mechanism

The interaction between methane and $Hg6(^3P_1)$ atom has not been always

explained clearly, but it is sure that methyl radical and H atom are produced consequentially[24, 25]:

$$Hg6(^1S_0) + h\nu(253.7\,nm) \longrightarrow Hg6(^3P_1) \tag{a}$$

$$CH_4 + Hg6(^3P_1) \longrightarrow CH_3 + H + Hg6(^1S_0) \tag{1}$$

$$H + CH_4 \longrightarrow H_2 + CH_3 \tag{2}$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \tag{3}$$

$$H + H + M \longrightarrow H_2 + M \tag{4}$$
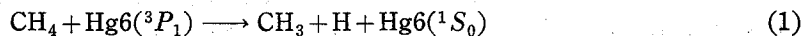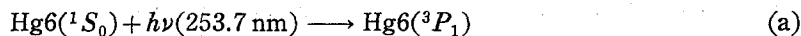
Table II. Experimental results at 15°C

No.	Reactants (%)		Total Pressure (Torr)	Temp. (°C)	t^a (sec)	Rate[b]	
	C_2H_2	CH_4				C_2H_4	C_2H_6
24	3.9	96.1	26.7	15.2	120	22.82	17.53
21	4.5	95.5	34.7	15.2	150	22.92	18.92
25	2.7	97.3	40.6	15.5	150	19.84	23.72
23	4.4	95.6	50.1	15.2	180	19.92	22.96
22	4.4	95.6	70.2	15.2	210	18.13	27.21
12	3.3	96.7	77.9	15.0	180	20.20	27.34
14	7.5	92.5	90.2	15.0	180	21.26	27.79
27	3.6	96.4	91.9	15.0	240	13.26	31.31
28	3.5	96.5	133.8	15.0	240	6.28	44.60
26	2.0	98.0	239.6	15.0	240	5.17	85.85
13[c]	6.8	89.4	60.2	15.0	180	0	trace[d]

(Table II. Continued)

No.	Rate					
	C_3H_6	C_3H_4[e]	$1-C_4H_8$	$1, 3-C_4H_6$	C_4H_4[f]	C_6H_6
24	4.030	0.1652	0.9211	1.664	4.761	7.071
21	3.744	0.0899	0.6264	2.236	4.610	8.150
25	4.938	0.1045	0.6449	1.976	4.473	3.497
23	3.616	0.0433	0.4343	2.628	4.472	5.733
22	3.822	0.0316	0.3354	2.800	4.340	7.696
12	6.456	n.d.[g]	0.5024	2.721	4.994	8.725
14	4.483	n.d.	0.3391	4.013	5.926	8.439
27	3.781	0.0328	0.2512	2.546	3.707	8.187
28	2.015	0.0144	0.0979	2.134	2.458	9.548
26	2.845	~0	0.0890	1.961	2.183	7.854
13	0	0	0	0	0	0

a Photolysis time.
b Products are expressed in terms of their rates of formation in mol $cc^{-1}sec^{-1} \times 10^{13}$.
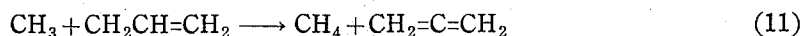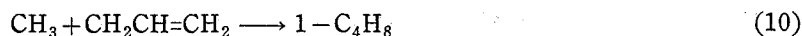c 2.3 Torr NO was added.
d Impurity contained in methane.
e Allene.
f Vinylacetylene.
g not determined.
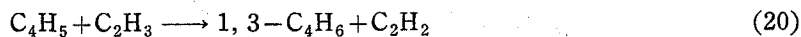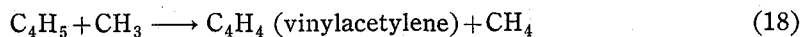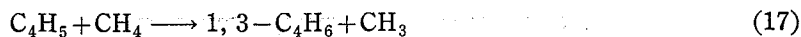
Table II shows the product distribution found in the CH_4-C_2H_2 mercury photosensitized reaction: ethylene and ethane were formed mainly, and propylene, 1, 3-butadiene, vinylacetylene, benzene, 1-butene, and allene were also found. In addition to these products four peaks which seemed to be C_5 or C_6 hydrocarbon were found in the gas chromatogram. However, their amounts were too small to be measured quantitatively.

The products were suppressed completely by the addition of a small amount of a radical scavenger NO (Run 13 in Table II). This implies that all the products were formed by radical reactions. The rate constant for the addition of H atom to acetylene is $\sim 10^{10}$ cc mol^{-1} $sec,^{-1}$ [26] while that for methyl radical addition has been found to be expressed as $10^{11.79}$ exp $(-7700/RT)$ cc mol^{-1} sec^{-1} [27] giving the value $\sim 10^5$ cc mol^{-1} sec^{-1} at 15°C. Therefore the addition of methyl radicals could be neglected. Since it has been found that the rate constant for the addition of H atom to acetylene shows the pressure dependence when total pressures are lower than 10 Torr,[28,29] total pressures in the present work were kept higher than 25 Torr in methane to prevent the reverse reaction of vinyl radical formation (i.e., $C_2H_3 \rightarrow C_2H_2+H$).

Propylene formed by the cross combination of methyl and vinyl radicals carries the excess energies of 102 kcal mol^{-1} on the average as shown in the following RRKM calculations. Thus the unimolecular decomposition of the vibrationally excited propylene into H+allyl is thermochemically possible if the activation energy for the decomposition is approximately 90 kcal mol^{-1} as shown in Table I. When the unimolecular decomposition occurs, 1-butene should be formed by the cross combination of the produced allyl and methyl radicals. We can see from Table II that the ratio, R (1-butene)/R (propylene), increases proportionally with the decrease of total pressures. This pressure effect and the products distribution shown in Table II can be explained by the following scheme:

$$H+C_2H_2 \longrightarrow C_2H_3 \qquad (5)$$

$$CH_3+C_2H_3 \longrightarrow C_3H_6^* \qquad (6)$$

$$CH_3+C_2H_3 \longrightarrow CH_4+C_2H_2 \qquad (7)$$

$$C_3H_6^*+M \xrightarrow{\omega} C_3H_6+M \qquad (8)$$

$$C_3H_6^* \xrightarrow{k_d} CH_2CH{=}CH_2+H \qquad (9)$$

$$CH_3+CH_2CH{=}CH_2 \longrightarrow 1-C_4H_8 \qquad (10)$$

$$CH_3+CH_2CH{=}CH_2 \longrightarrow CH_4+CH_2{=}C{=}CH_2 \qquad (11)$$

$$C_2H_3+CH_4 \longrightarrow C_2H_4+CH_3 \qquad (12)$$

$$C_2H_3+C_2H_3 \longrightarrow 1, 3-C_4H_6 \qquad (13)$$

$$C_2H_3+C_2H_3 \longrightarrow C_2H_4+C_2H_4 \qquad (14)$$

$$C_2H_3+C_2H_2 \longrightarrow C_4H_5^* \qquad (15)$$

$$C_4H_5^*+M \longrightarrow C_4H_5+M \qquad (16)$$

$$C_4H_5 + CH_4 \longrightarrow 1, 3 - C_4H_6 + CH_3 \tag{17}$$

$$C_4H_5 + CH_3 \longrightarrow C_4H_4 \text{ (vinylacetylene)} + CH_4 \tag{18}$$

$$C_4H_5 + C_2H_3 \longrightarrow C_4H_4 + C_2H_4 \tag{19}$$

$$C_4H_5 + C_2H_3 \longrightarrow 1, 3 - C_4H_6 + C_2H_2 \tag{20}$$

$$C_4H_5 + C_2H_2 \longrightarrow C_6H_7^* \tag{21}$$

$$C_6H_7^* \longrightarrow C_6H_6 + H \tag{22}$$

$$C_6H_7^* + M \longrightarrow C_6H_7 + M \tag{23}$$

$$C_6H_7 + nC_2H_2 \longrightarrow \text{Polymer} \tag{24}$$

where the asterisk signifies vibrational excitation and M denotes the third body. Although the formation of 1, 5-hexadiene, 1, 3-pentadiene, and 1, 3, 5-hexatriene which are the cross combination products of allyl or vinylic radicals was searched carefully, their formation could not be confirmed. In the vacuum ultra-violet photolysis of acetylene too, it has been reported that vinylacetylene has been formed by the disproportionation of C_4H_5 and C_2H_3 radicals, but the formation of 1, 3, 5-hexatriene has not been observed.[30, 31]

Kinetic Treatments

The average rate constant for a unimolecular reaction is given by $k_a = \omega(D/S)$ where D is the total rate of formation of the decomposed products and S is the total rate of formation of the stabilized products and they are given as follows in the present study:

$$S = R \text{ (propylene)}$$
$$D = R \text{ (allyl products)}$$

where allyl products are 1-butene and allene formed by reactions (10) and (11), respectively. From the data in Table II one can get

$$R(\text{allene})/R(\text{1-butene}) = k_{11}/k_{10} = 0.018 \pm 0.003$$

which is in agreement with the predicted value 0.023 by Holroyed and Klein[32] and considered to be reasonable. Thus the allyl products are expressed as
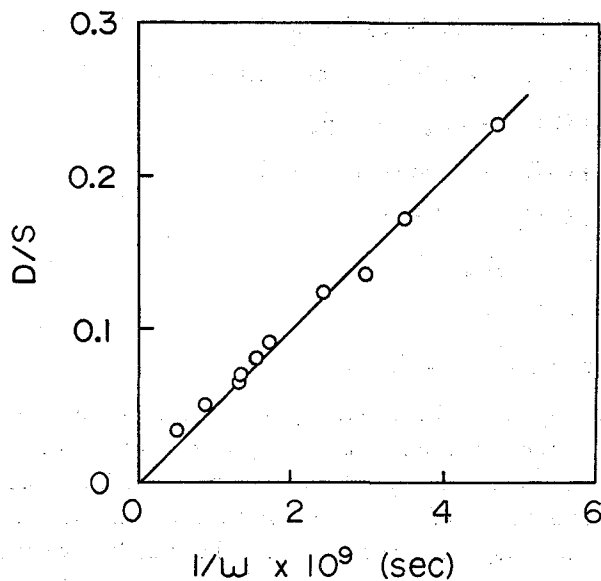
$$D = 1.02R \text{ (1-butene)}$$

A plot of D/S *vs* $1/\omega$ from the data in Table II is shown in Fig. 1 and the slope gives the value $k_a = (5.04 \pm 0.11) \times 10^7 \text{ sec}^{-1}$ at 15°C. The collision rates were calculated by the method of Chan *et al.*[33]

DISCUSSION

RRKM Calculations

The RRKM calculational procedures were described in detail previously[21] and

Fig. 1. Plots of D/S vs $1/\omega$.

Table III. Frequency assignments for propylene decomposition by CH rupture[a]

CH₃CH=CH₂ molecule			C–H rupture complex					CH₃··CH=CH₂ complex
			A	B	C	D	E	
CH	str	3090 cm⁻¹						
		2954(2)						
		3013						
		2992						
		2933	...	...	...	...	...	
CH₃	def	1474⎱ 1443⎰	300(2)	150(2)	75(2)	allyl rot 150	allyl rot(2)	1230(2)
		1378						661
CH₃	rock	1045	925	925	925	925	925	261
		912						228
CH₂	def	1419						
CH₂	wag	1172						
CH₂	twist	991	700	700	700	700	700	949
CH₂	rock	963	900	900	900	900	900	
=CH	bend	1298						324
		578	375	375	375	375	375	
C=C	str	1652	1400	1400	1400	1400	1400	828
CC	str	920	1300	1300	1300	1300	1300	...
CC=C	bend	428	375	375	375	375	375	214
CH₃	tors	225	500	500	500	500	500	112
I_r (for model D and E)		1.058×10^{-38} (g cm²)						

a Frequencies except model D are given by Simons *et al.* From Ref. 20.

will not be reproduced here. The frequency assignments for propylene are shown in Table III.[20]

For the reverse of the excited propylene formation (*i.e.*, $CH_3CH=CH_2^* \rightarrow CH_3 + CH=CH_2$), it has been found that the rate constant is expressed by the equation $\log k$ (sec^{-1}) = $(16.07 \pm 0.40) - (85840 \pm 237)/2.30 RT$ in the temperature range of 1100–1650°K in a shock tube.[11] This large Arrhenius A factor implies that the $CH_3 \cdots CH=CH$ complex is "looser" than propylene molecule[34] and then the vibrational frequencies for the activated complex should be assigned so that the frequencies give the positive entropy change in the reaction:

$$A_\infty = (\sigma ek T/h) \exp(\Delta S\ddagger/R)$$

where σ is the reaction path degeneracy and $\Delta S\ddagger$ is the entropy of activation. The frequencies were assumed to be made up by using the frequencies for methyl[36~40] and vinyl radicals as shown in Table III. The vibrational frequencies for vinyl radical were directly taken from ethylene.[41] The calculated A_∞ value is found to be $\log A_\infty$ (sec^{-1}, 1300°K) = 16.1, which agrees well with the experimental one.[11]

Table III shows also several complex models for the C–H rupture of propylene. These models except model D have been proposed by SRD[20] for the analysis of the $CH_2 + C_2H_4 \rightarrow \triangledown^* \rightarrow C_3H_6^* \rightarrow H + allyl$ system. The models were used to the theoretical calculations for the present $CH_3 + CH=CH_2 \rightarrow C_3H_6^* \rightarrow H + allyl$ system. The Whitten-Rabinovitch-Tardy equations were used for the RRKM calculations.[42~45] The calculated energy distribution of propylene is shown in Fig. 2. The average excess energy was found to be $\bar{E} = 102.4$ Kcal mol^{-1} at 15°C. The heats of formation and bond dissociation energy used in this work are given in Table IV. It can be seen from the figure that more than 90% of the excited molecules are concentrated in the energy range of $\bar{E} \pm 3$ kcal $mol.^{-1}$ That is, the thermal distribution of energies for the chemically activated propylene in the present study is narrow enough so that an essentially monoenergetic species is formed. Thus, $k_{\bar{E}}$ at the average energy was compared with the experimental value.

The allylic resonance energy has been found to be ~ 12[19,46,47] or 9.6–10 kcal $mol.^{-1}$[48] Therefore the activation energies shown in Table I lie in the range 88.5 ± 1.5 kcal mol^{-1}, which is very close to the C–H bond dissociation energy of propylene $D°_{298}$ (allyl-H) = 88.6 ± 1.1 kcal $mol.^{-1}$[17] The high pressure Arrhenius activation energy in RRKM theory is given by the following expression[35]:

$$E_\infty = E_0 + RT + \bar{E}^\dagger - \bar{E}$$

where $\bar{E}^\dagger$ and $\bar{E}$ are the average internal energies for activated complex and reactant molecule, respectively. Thus the rate constants $k_{\bar{E}}$ were calculated by using the critical energies E_0 determined when the E_∞ values were taken equal to 87.5, 88.5, and 89.5 kcal $mol.^{-1}$ The calculational results are shown in Table V. Comparison of the calculated $k_{\bar{E}}$ with the experimental result shows that model C seems to be a good representation of the C–H rupture of propylene. Model B appears a little too tight and model A considerably too tight. Models D and E, both containing the free internal rotation(s), are undoubtedly too loose.
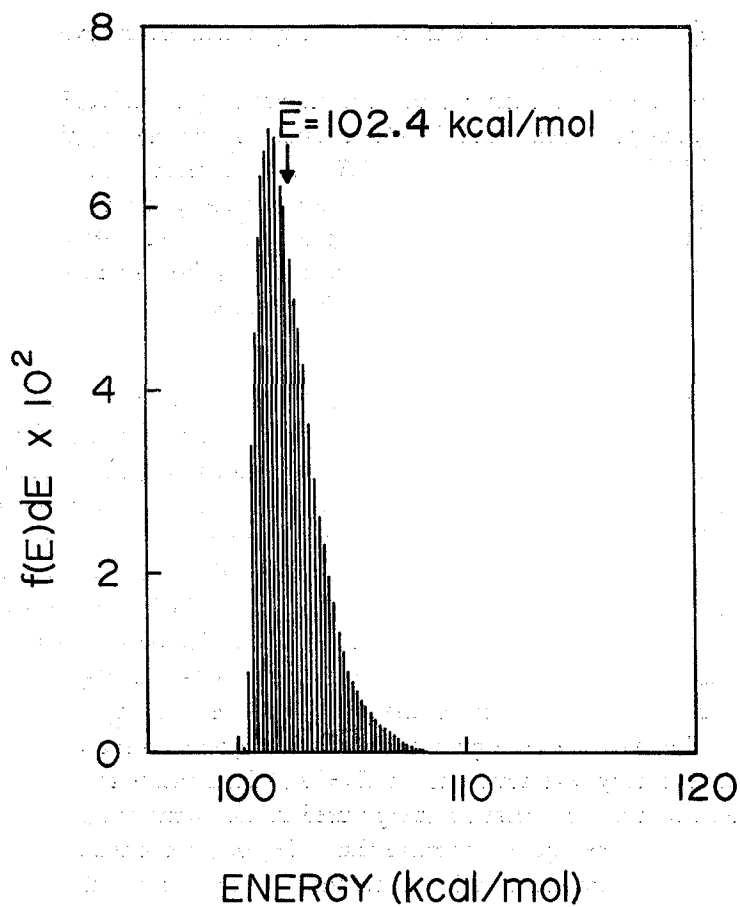
Fig. 2. Energy distribution function at 15°C.

Table IV. Gaseous heats of formation and bond dissociation energies at 0°K (kcal mol^{-1})

$\Delta H_f{}^\circ(CH_3)$	34.4[a]	$\Delta H_f{}^\circ(CH{=}CH_2)$	73.1
$\Delta H_f{}^\circ(C_2H_4)$	14.5[a]	$\Delta H_f{}^\circ(allyl)$	44.0[b]
$\Delta H_f{}^\circ(H)$	51.6[a]	$D^\circ(H{-}CH_2CH{=}CH_2)$	87.1[b]
$\Delta H_f{}^\circ(C_3H_6)$	8.5[a]	$D^\circ(H{-}CH{=}CH_2)$	110.2[c]

a From Ref. 45.
b From Ref. 17.
c From Ref. 18.

The ART (absolute rate theory) Calculations

The ART expression for the second order rate constant is given by

$$k = \kappa(kT/h)(Q^\dagger/Q_1Q_2)\exp(-E_0/RT)$$

where κ is the transmission coefficient and Q denotes the appropriate partition function.

Table V. Calculational results for $k_{\bar{E}}$ (sec^{-1}) for various complexes and values of E_0

Model	E_0 (kcal/mol)	$k_{\bar{E}} \times 10^{-7}$ (sec^{-1})	E_∞^a (kcal/mol)	$\log A_\infty^a$ (sec^{-1})
	83.5	0.41	87.5	
A	84.5	0.26	88.5	15.29
	85.5	0.16	89.5	
	83.2	1.77	87.5	
B	84.2	1.08	88.5	15.89
	85.2	0.70	89.5	
	83.0	7.87	87.5	
C	84.0	4.99	88.5	16.49
	85.0	3.21	89.5	
	83.8	25.4	87.5	
D	84.8	16.1	88.5	17.13
	85.8	10.1	89.5	
	84.6	109	87.5	
E	85.6	69.7	88.5	17.70
	86.6	43.7	89.5	
k_d(obs)		5.04 ± 0.11		
Ref. data[b]			88.5 ± 1.5	≥ 16.6

a Calculated at 1048°K.
b See Table I.

Recombination rate constants for H+allyl radical using the activated complex models in Table III are given in Table VI. The frequencies for allyl radical used to calculate Q were taken from the most loosened model E in Table III under the condition that

Table VI. ART calculations of recombination rate constants for H + allyl[a]

Model	$k \times 10^{-13}$ (cc mol^{-1}sec^{-1})	E_∞ (kcal mol^{-1})
A	0.51	0.370
B	1.22	0.653
C	3.50	0.832
D	35.1	0.650
E	287	0.547
Ref. data[b]	~5	

a Calculated at 298.16°K.
b From Ref. 16.

Table VII. Frequency assignments for allyl radical[a] (cm^{-1})

CH	str	3090
		3013
		2954(2)
		2992
CH$_2$	def	1419
		900
CH$_2$	wag	1172(2)
C=C	tors	500(2)
CH$_2$	rock	240(2)
=CH	bend	1298
=CH & CCC	bend	375(2)
C=C		1300(2)

$S° = 62.15$ e.u.
$I_A I_B I_C = 1.49 \times 10^{-116}$ (g cm^2)^3

a Assuming a 120° angle for symmetrical allyl radical.

the calculated entropy of the allyl radical is equal to the thermochemically recommended value $S°$ (allyl) $=62.1$ e.u.[16] and are shown in Table VII. The cross combination rate constant for H+allyl has not been measured experimentally. Its magnitude has been estimated to be $k \simeq 5 \times 10^{13}$ cc mol^{-1} sec.$^{-1}$ [16] Thus in the ART calculations too, model C gives the recombination rate constant in best agreement with estimated one. Model D and E having free rotator are not good representation for the C–H bond cleavage of propylene.

In the present work both the RRKM and the ART calculations show that model C is a good representation for the unimolecular decomposition of propylene into H+ allyl radical. This model is looser than those supported by SRD.[20] In their paper they noted that impurities in the ketene and, sepecially, diazomethane which are precursors for methylene radical caused an overestimate of the experimental rate constants, particularly at high pressures. The most reliable measure of the experimental rates was obtained at limitingly low pressures. By the extrapolation to zero-pressure they estimated the value $k_d \simeq 3 \times 10^8$ sec^{-1} both in the photolyses of the diazomethane-ethylene and ketene-ethylene systems, and recommended moedl A for the former system and model B for the latter.

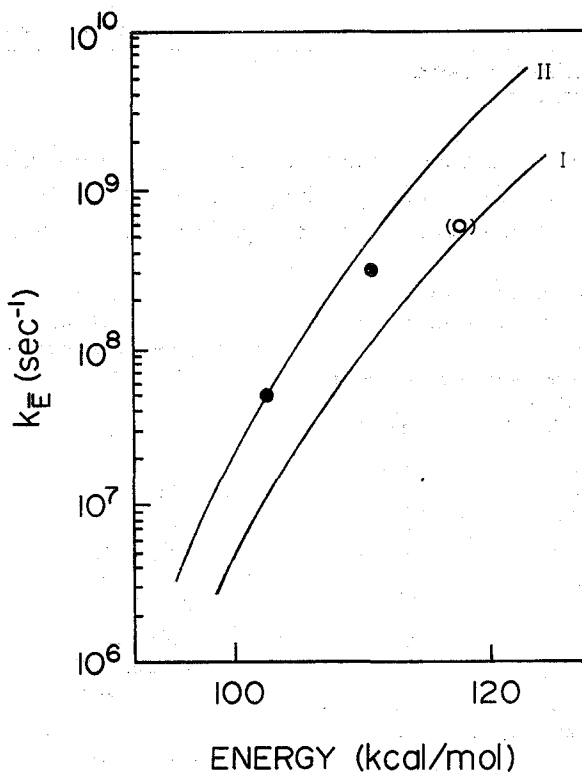Our reextrapolation of the SRD's data gives the value $k_d \simeq 5 \times 10^8$ and 3×10^8

Fig. 3. Plots of k_d vs $\bar{E}$ and calculated RRKM rate constants:
Curve I ; model B, $E_0 = 84.2$ kcal mol^{-1}.
Curve II; model C, $E_0 = 84.0$ kcal mol^{-1}.

sec^{-1} in the diazomethane-ethylene ($\bar{E}$ of the formed propylene has been estimated to be 118 kcal mol^{-1})[20] and ketene-ethylene system ($\bar{E} \simeq 111$ kcal mol^{-1}), respectively. However the former value is only semiquantitative in nature as they have noted.

Figure 3 shows the plot of k_d(obs) vs $\bar{E}$ of the vibrationally excited propylene. From this figure it seems safe to conclude that the unimolecular decomposition of propylene into H+allyl is not characterized by a free rotator model but by a loose vibrational model such as model C in Table III.

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