

PROPYLENE PHOTOLYSIS AT 6.7 eV: CALCULATION OF THE QUANTUM YIELDS FOR THE SECONDARY PROCESSES

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Summary

The yields for the products of secondary isomerizations and decompositions of the radicals formed in the photolysis of propylene at 6.7 eV have been calculated by using data for the primary dissociation obtained by means of the variational method. The isomerization of allylic radicals into 1- and 2-propenyl structures was found to be important. While the yield for propyne agrees satisfactorily with experiment that for allene is underestimated at higher pressures. The use of a weak-collision model reveals that the lower the value of $\langle \Delta E \rangle$ the better the agreement. The yield for acetylene is overestimated in the whole range of pressures employed.

1. Introduction

Secondary processes in the photolysis of gaseous propylene have been rarely studied and many mechanistic details still remain to be unravelled. The difficulty stems from the complexity of the rearrangements undergone by the excited C_3H_5 radical [1, 2], one of the main intermediates in the photolysis.

Experimental studies of the photolysis of propylene have been extensive [3 - 6]. The mechanism was found to depend on the photon energy [6]. On increasing the energy the contribution of the processes involving molecular elimination increases at the expense of the simple cleavage of the C—C and C—H bonds. The former processes seem to involve the electronically excited states of propylene which, by analogy with ethylene [7], may isomerize especially readily by undergoing 1,2-hydrogen shifts. Such processes are little understood. However, at an energy of 6.7 eV the electronically excited states are of no importance, and the scission of the C—C and C—H bonds occurs from the ground electronic state and obeys the statistical predictions based on the Rice—Ramsperger—Kassel—Marcus (RRKM) theory.

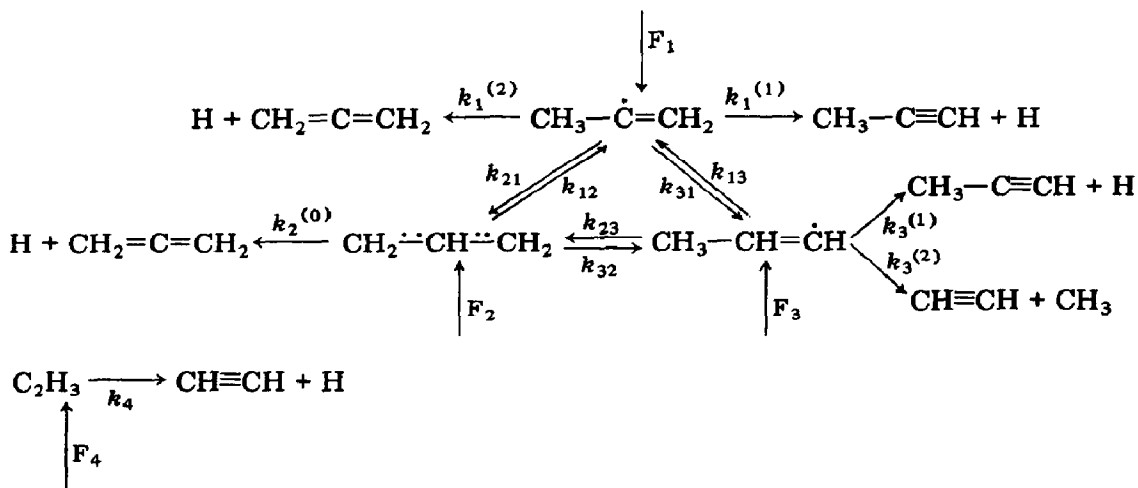
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The semiempirical calculations presented in this work focus on the reactions of allylic ($\text{CH}_2\text{---}\dot{\text{C}}\text{H---}\dot{\text{C}}\text{H}_2$), 1-propenyl ($\text{CH}_3\text{---CH}=\dot{\text{C}}\text{H}$) and 2-propenyl ($\text{CH}_3\text{---}\dot{\text{C}}=\text{CH}_2$) radicals in the 6.7 eV photolysis of propylene. The final aim is to establish the quantum yield for allene, propyne and acetylene originating from individual dissociation channels of the excited C_3H_5 radical. The calculations are handicapped by the lack of *ab initio* data concerning dissociation of propylene and C_3H_5 radicals. Thus, the transition state properties and the characteristics of the key regions of the reactive potential energy surface are not known. However, extensive *ab initio* studies on the vinyl radical, C_2H_3 , have been performed [8 - 10]; these studies were undertaken in the hope of removing the major differences noticed between the measured experimental rate constant for the $\text{H} + \text{C}_2\text{H}_2$ addition reaction and the standard chemical activation treatment of the vinyl dissociation [11, 12]. Such a goal was not fulfilled since the accurate *ab initio* calculations of Harding *et al.* [10] gave results essentially similar to those obtained by using semiempirical methods, and both results show a large overestimation of the rate constant (by as much as an order of magnitude at higher pressures). Similar difficulties were encountered in studies on the $\text{H} + \text{C}_2\text{H}_4$ reaction [13] but were overcome by Hase and Schlegel [14] who applied the latest *ab initio* calculations to determine the geometry and vibrational frequencies of both the ethyl radical and the activated complex. Harding *et al.* [10] attribute their failure in reproducing the experimental $\text{H} + \text{C}_2\text{H}_2$ rate constant to approximations made for the dynamics of the system rather than to the errors in the calculated features of the potential energy surface. The semiempirical result may be valid since the unimolecular rate constant calculated by using standard RRKM methods does not depend on the individual vibrational frequencies of the activated complex provided the entropy of activation predicted by the absolute rate theory (ART) is reproduced. Thus, the arbitrariness in choosing the structure of the activated complex should not adversely affect the results and further sophistication in the calculations, such as anharmonicity corrections and transmission coefficient tunnelling corrections, is not necessary.

The C_3H_5 radical, whose reactions are the main topic of this paper, is a primary product of propylene photolysis. The calculations of the primary processes using the variational criterion of the RRKM theory are to be published elsewhere [15]. The unimolecular reactions of radicals are characterized by a potential surface exhibiting a distinct extremum. Therefore the variational criterion for calculating rate constants is redundant and knowledge of the detailed properties of the reaction path is unnecessary [16]. The following calculations of the secondary dissociations and rearrangements of C_3H_5 are based on conventional ART and RRKM methods.

2. Reactions of allylic, propenyl and vinyl radicals

A comprehensive scheme of the dissociations and isomerizations of the radicals important in the photolysis of propylene is shown below.



Scheme (I).

Interconversions of allene and propyne are not included in this scheme. According to Hopf *et al.* [17] the reversible thermal isomerization of propyne and allene involves cyclopropene as an intermediate. Hence, the activation energy for the allene-to-propyne thermal rearrangement should be the sum $43.5 \text{ kcal mol}^{-1}$ (E_{act} of cyclopropene to allene) and $20.3 \text{ kcal mol}^{-1}$ (the difference in enthalpy of formation of allene and cyclopropene) [18]. Experimental evidence supports this estimate giving a lower limit value of $E_{\text{act}}(\text{allene to propyne}) = 62.2 \text{ kcal mol}^{-1}$ [19, 20]. The high threshold energy makes it impossible for this rearrangement to be of importance in propylene photolysis.

The standard procedure involving the weak collision model [21] was applied to calculate quantum yields for the individual dissociation channels. The concentration of reagent molecules at energy E_i is given by

$$N = \{K - \omega(I - P)\}^{-1}F \quad (1)$$

where N is the steady-state population distribution vector, K is the diagonal matrix of the unimolecular rate constants, P is the transition probability matrix and ω is the collisional efficiency. The vector F is the Boltzmann energy distribution of the reactants raised by the net energy of the photoactivation process. The quantum yield for channel d is expressed as

$$\phi_d = \sum_i (KN)_i \quad (2)$$

In order to determine the input fluxes of the radicals a statistical distribution of the excitation energy between dissociation fragments was assumed according to the expression given by Forst [22].

$$f_A(E_{\text{exc}}, E) = CN_A(E)W_B(E_{\text{exc}} - E) \quad (3)$$

where C is a constant, $N_A(E)$ is the density of states for fragment A at energy E , $W_B(E_{\text{exc}} - E)$ is the sum of states for fragment B, and E_{exc} is the energy available for distribution into fragments A and B.

$$E_{\text{exc}} = E + E_{\text{int}} - \text{BDE} \quad (4)$$

where E_{int} is the thermal energy of a molecule and BDE denotes the bond dissociation energy (BDE).

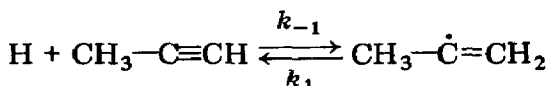
The input flux for the corresponding radical was calculated according to

$$F(E_j) = \sum_i f_A(E_{\text{exc}} - E_i, E_j) \Delta E \phi_d(E_{\text{exc}} + \text{BDE} - E_i) \quad (5)$$

where ϕ_d represents a quantum yield from the i th energy level for the channel d .

The unimolecular rate constants for the primary dissociation of propylene calculated by using the variational version of ART and RRKM [15] are assembled in Table 1. Details of the calculations as well as a discussion of the adopted thermochemical values are given elsewhere [15]. By the use of Scheme (I), $\phi_{\text{vinyl}} = 0.86$ and $\phi_{\text{allyl}} = 0.115$ have been calculated at an excitation energy of 6.7 eV. The quantum yields of 0.013 for 1-propenyl and of 0.008 for 2-propenyl are more than ten times smaller than ϕ_{allyl} . All the yields are practically unaffected by changing the pressure within the range 1 - 100 Torr. The magnitude $\langle \Delta E \rangle$ of the mean energy transferred in collision is also of negligible importance. The input fluxes of the radicals are shown in Fig. 1.

Once the yields for the primary radicals are established, the secondary processes indicated in Scheme (I) may be examined. Owing to the lack of accurate *ab initio* data the procedure for choosing the structure of the activated complex must of necessity be arbitrary. In the case of the secondary decompositions of the radicals we were guided by the reverse addition reactions which are more widely known [23 - 26]. For instance, Wagner and Zellner [23] determined the rate constant $k_1 = (6.5 \pm 1.2) \times 10^9 \exp(-2 \pm 0.2/RT) \text{ l mol}^{-1} \text{ s}^{-1}$ for the reaction



Taking $E_0^{-1} = 2.1 \text{ kcal mol}^{-1}$, the pre-exponential factor A_1 for the forward

TABLE 1

Arrhenius parameters of the thermal rate constants for propylene dissociation at $T = 298 \text{ K}$ [15]

	$\log A_\infty$	E_∞ (kcal mol ⁻¹)	E_0 (kcal mol ⁻¹)
$\text{C}_2\text{H}_3 + \text{CH}_3$	17.18	92.10	89.88
$\text{CH}_2\text{-}\dot{\text{C}}\text{H}\text{-}\dot{\text{C}}\text{H}_2 + \text{H}$	14.66	88.09	86.65
$\text{CH}_3\text{-}\dot{\text{C}}=\text{CH}_2 + \text{H}$	15.16	98.06	96.70
$\text{CH}_3\text{-CH}=\dot{\text{C}}\text{H} + \text{H}$	14.88	101.28	99.90

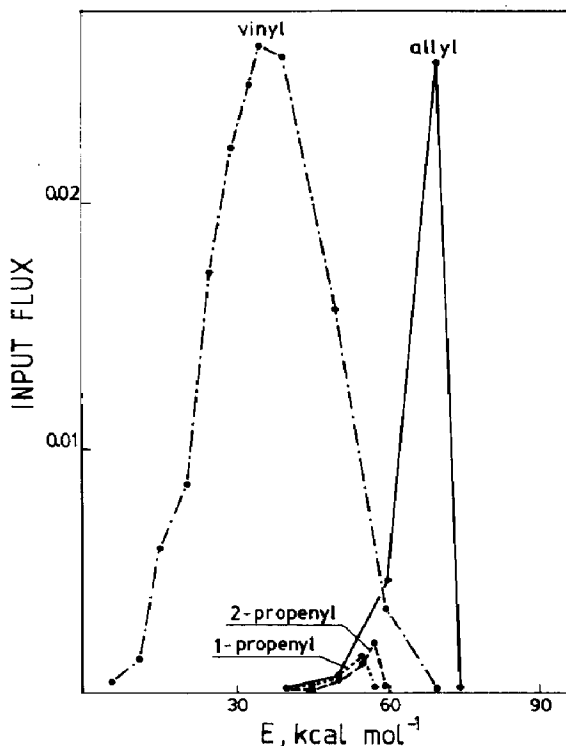


Fig. 1. Plot of the input flux for the vinyl, allyl and propenyl radicals vs. internal energy of the radical.

reaction can be found from the well-known expression

$$\log A_1 = \log A_{-1} + \frac{\Delta S_1}{4.575} \quad (6)$$

where ΔS_1 refers to 1 mol l^{-1} .

The configuration of the activated complex assumed in this work yields $\log A_1 = 12.98$. By using $S^\circ(298 \text{ K, propyne}) = 59.27 \text{ e.u.}$, $S^\circ(298 \text{ K, H}) = 27.36 \text{ e.u.}$ and $S^\circ(298 \text{ K, CH}_3\text{-}\dot{\text{C}}=\text{CH}_2) = 64.86 \text{ e.u.}$, $\Delta S_1 = 13.43 \text{ e.u.}$ since $\Delta S^\circ(1 \text{ mol l}^{-1}) = \Delta S^\circ(1 \text{ atm}) - \Delta nR \{1 + \log(0.0821T)\}$. Hence $\log A_{-1} = 10.05$. Although this value is higher than that reported by Wagner and Zellner, k_{-1} falls within the stated uncertainty limits. Further lowering of A_1 was not feasible since the structure of the activated complex became unacceptable.

A similar procedure was adopted to assess $\log A_\infty$ for other radical decompositions. All the activated complexes were chosen to be rigid and to resemble the products, *i.e.* allene and propyne. The values for the Arrhenius parameters of the radical dissociations are shown in Table 2. The values for the A factors of reactions (1) - (3) (see Scheme (I)) are lower than those reported previously [27], but exhibit better agreement with the reverse addition reactions. The dissociation of the vinyl radical (reaction (4)) is still an unsolved problem despite many efforts. Since the *ab initio* prediction of a loose complex developed by Harding *et al.* [10] contradicts the

TABLE 2

Arrhenius parameters for the radical decompositions

Reaction	From ref. 27		This work		
	log A (s ⁻¹)	E ₀ (kcal mol ⁻¹)	log A (s ⁻¹)	E ₀ (kcal mol ⁻¹)	E ₀ ⁻¹ a (kcal mol ⁻¹)
k ₁ ⁽²⁾	13.42	44.70	13.12	47.69	2.0 [23, 24]
k ₁ ⁽¹⁾	13.74	46.00	12.98	46.11	2.1 [23, 24]
k ₂ ⁽⁰⁾	13.74	60.50	13.42	59.79	2.0 [25, 26]
k ₃ ⁽¹⁾	13.70	44.00	13.35	43.51	3.0 [23, 24]
k ₃ ⁽²⁾	13.95	40.84	12.99	43.14	10.0 [23, 26]
k ₄	14.00 ^b		13.11	45.95	3.0 [10 - 13]

^aActivation energy for the reverse radical combination; the literature value refers to the radical combination.

^bFrom ref. 6.

experimental data we applied as rigid a structure as possible but even under such extreme conditions the calculated and experimental rate constants for the reverse addition reaction $H + C_2H_2$ differed by nearly an order of magnitude.

The isomerizations included in Scheme (I) have already been a subject of study [27 - 29]. The formation of activated complexes in these reactions has been determined from the elimination of the C—H stretching vibration of the initial radical and the transformation of the pertinent C—H bending vibrations to ring deformations [22, 30]. In the present work the threshold isomerization energy E_0 was assumed to be the total of the strain energy E_s of the intermediate ring and the activation energy of hydrogen atom

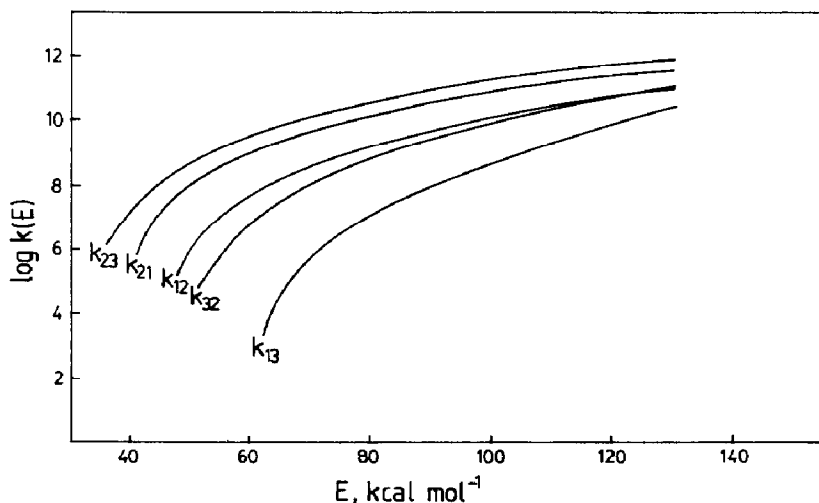


Fig. 2. Plot of the isomerization rate constant vs. internal energy of the radical. The subscripts are identified in Scheme (I).

abstraction by the radical [2, 28]. In the case of k_{31} , $E_s = 53.70 \text{ kcal mol}^{-1}$. Thus, the negligible contribution from this isomerization was not included. The Arrhenius parameters for the other isomerizations are assembled in Table 3. Compared with previous work from this laboratory [27] the differences are small. Since the complexes were formed using similar rules, the values for the pre-exponential factors are also similar. In the case of k_{21} the value of E_0 was raised by 5 kcal mol^{-1} compared with the former work [27], following the recommendation of Ibuki *et al.* [28]. The plot of the five determined isomerization rate constants against internal energy is shown in Fig. 2. The internal-energy dependence of the dissociation rate constants is shown in Fig. 3.

TABLE 3
Arrhenius parameters for the radical isomerizations

Reaction	log A (s ⁻¹)		E ₀ (kcal mol ⁻¹)
	From ref. 27	This work	
$k_2^{(1)}$	12.86	12.80	40.0 [28]
$k_1^{(2)}$	13.30	13.38	47.1 [27]
$k_1^{(3)}$	13.20	13.17	61.7 [27]
$k_3^{(2)}$	13.50	13.25	50.7 [27]
$k_2^{(3)}$	12.90	12.64	35.1 [27]

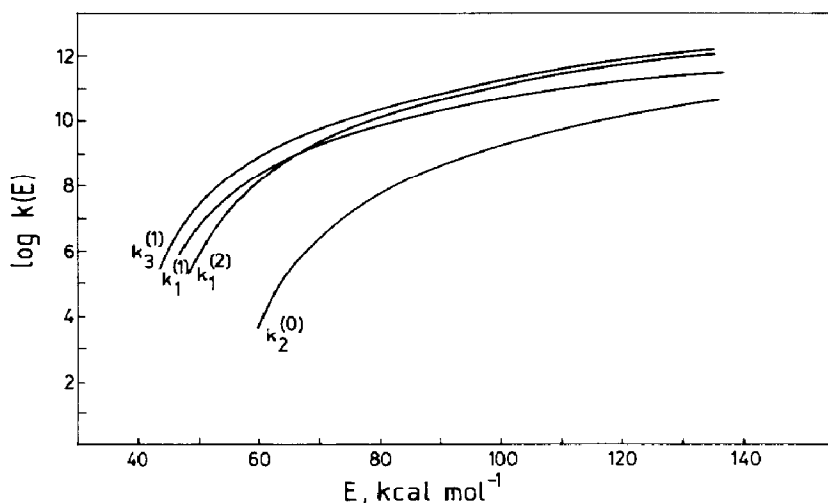


Fig. 3. The plot of the dissociation rate constant vs. internal energy of the radical. The subscripts are identified in Scheme (I).

3. RRKM calculations and quantum yields for the final products

The analysis of the complex reaction system shown in Scheme (I) follows a general method developed by Carter and Tardy [31]. To estimate

radical concentrations at successive energy levels E_i , the weak-collision concept was used. Applying the steady-state approximation, the solution is given by

$$\begin{bmatrix} N_1 \\ N_2 \\ N_3 \end{bmatrix} = \begin{bmatrix} J_{11} & -K_{12} & -K_{13} \\ -K_{21} & J_{22} & -K_{23} \\ -K_{31} & -K_{32} & J_{33} \end{bmatrix}^{-1} \begin{bmatrix} F_1 \\ F_2 \\ F_3 \end{bmatrix} \quad (7)$$

where K denotes the diagonal matrix containing the rate constants for the pertinent reactions at successive energy levels E_i , N and F are the vectors for the concentration and input flux respectively, while J is given by

$$J_{11} = K_{21} + K_{31} + K_1^{(1)} + K_1^{(2)} + \omega(I - P_1) \quad (8)$$

$$J_{22} = K_{12} + K_{32} + K_2^{(0)} + \omega(I - P_2) \quad (9)$$

$$J_{33} = K_{13} + K_{23} + K_3^{(1)} + K_3^{(2)} + \omega(I - P_3) \quad (10)$$

where ω is the collisional frequency at a given pressure p and collision number Z [32]. P is the transition probability matrix constructed according to the rules established by Tardy and Rabinovitch [33]. Only active transitions between the states exceeding the minimum threshold energy are accounted for (P_4 matrix according to the nomenclature used by Robinson and Holbrook [21]). Either normal, exponential or step-ladder models were employed to determine the distribution of the energy exchanged in collisions. The derivation and numerical solution of matrix eqn. (7) is given by Carter and Tardy [31].

The conventional RRKM formula was used to establish the energy dependence of the unimolecular rate constant [21]

$$k(E) = L^\ddagger \frac{W^\ddagger(E - E_0)}{hN(E)} \quad (11)$$

where L^\ddagger is the reaction path degeneracy and W^\ddagger and $N(E)$ represent the sums and densities of states respectively. The exact Beyer-Swinehart algorithm [34] was used as modified by Stein and Rabinovitch [35], and corrections for hindered internal rotations were applied [36].

The quantum yield for propyne is the total of the decomposition yields of 2-propenyl:

$$\phi_1(\text{propyne}) = \sum_i n_1(E_i) k_1^{(1)}(E_i) \quad (12)$$

and 1-propenyl:

$$\phi_2(\text{propyne}) = \sum_i n_3(E_i) k_3^{(1)}(E_i) \quad (13)$$

The pressure dependence of the propyne yield in the 6.7 eV photolysis is shown in Fig. 4. The experimental points have recently been obtained in Collin's laboratory [37]. Agreement with experiment is satisfactory at lower

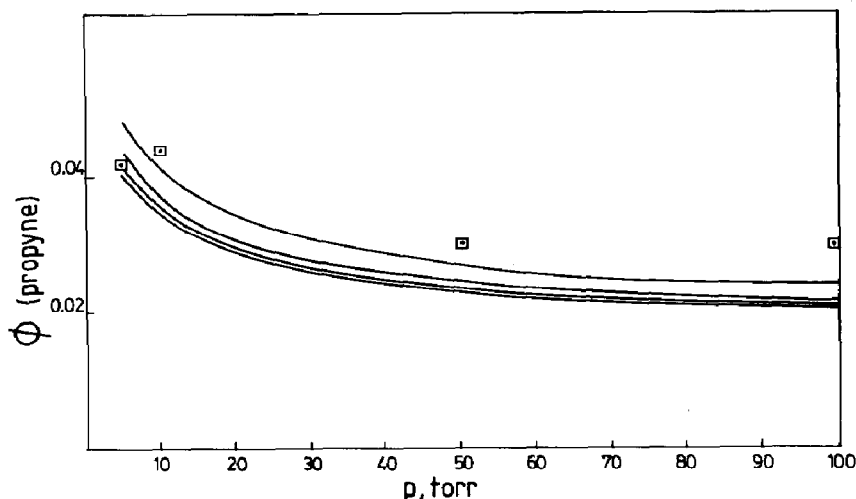


Fig. 4. Pressure dependence of the overall quantum yield for propyne. A normal distribution for the probability of energy exchange in collisions is assumed. $\langle \Delta E \rangle = 3, 6, 9$ and 12 kcal mol $^{-1}$ from top to bottom respectively. \square , Collin's experimental points.

pressures. The effect of $\langle \Delta E \rangle$ on the results is not large but is significant. Lowering of $\langle \Delta E \rangle$ below 3 kcal mol $^{-1}$ results in better agreement but such small values for $\langle \Delta E \rangle$ are unlikely. A step-ladder model for energy exchange gives results practically identical with those shown in Fig. 4 for the normal distribution. An exponential model also yields very similar results. The insignificant differences between these distributions are not shown in the figures.

It is of interest to examine the contribution of two different dissociation channels to the total yield of propyne. The data are shown in Fig. 5. The second channel prevails, *i.e.* the dissociation of 1-propenyl. 2-Propenyl

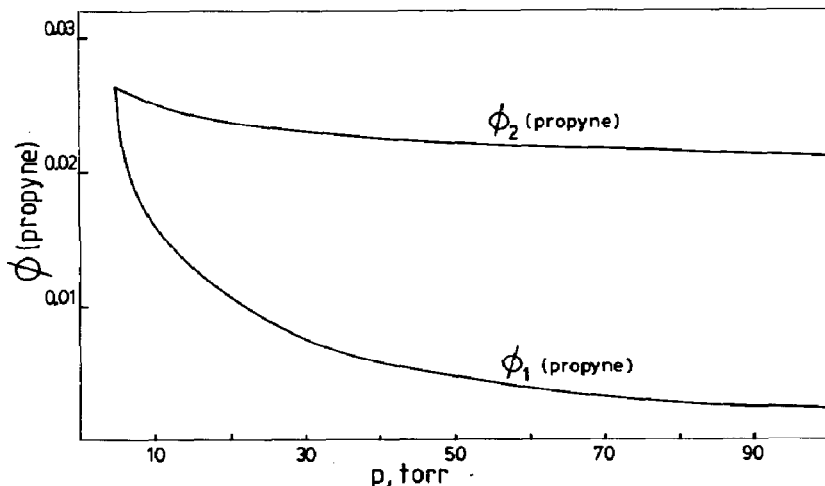


Fig. 5. Quantum yields for propyne originating from two different dissociation channels. A normal distribution of energy exchange at $\langle \Delta E \rangle = 3$ kcal mol $^{-1}$ is assumed.

dissociation is quenched to a large extent at higher pressures as a result of the much lower value for $k_1^{(1)}$. Our value for $k_1^{(1)}$ may be too low. If this value is enhanced by suitably adjusting the thermochemical input data within their uncertainty limits the discrepancies with experiment can be removed altogether.

The quantum yield for allene is the total

$$\phi(\text{allene}) = \sum_i n_2(E_i)k_2^{(0)}(E_i) + \sum_i n_1(E_i)k_1^{(2)}(E_i) \quad (14)$$

The second component is the predominant contributor. Similarly, the quantum yield for acetylene is given by

$$\phi(\text{acetylene}) = \sum_i n_3(E_i)k_3^{(2)}(E_i) + \sum_i n_4(E_i)k_4(E_i) \quad (15)$$

where $n_4(E_i)$ denotes the concentration of C_2H_3 resulting from the rupture of the C—C bond. Since the latter process predominates over the breakage of the C—H bond (Fig. 1) the second component in eqn. (15) is the major contributor. The yields for both allene and acetylene are shown in Fig. 6. The yield for allene agrees with experiment at lower pressure but is underestimated at higher pressures. Lowering $\langle\Delta E\rangle$ below 3 kcal mol^{-1} diminishes the discrepancy but to remove the error altogether, unacceptably small values for $\langle\Delta E\rangle$ would have to be adopted. The value for $\phi(\text{H}_2)$ is uncertain, but small, in the 6.7 eV photolysis of propylene; $\phi(\text{H}_2) = 0.02$ was estimated by Borrell *et al.* [3]. It is reasonable to assume that the formation of molecular hydrogen, presumably involving the electronically excited state, is accompanied by the formation of allene, and this additional pathway would reconcile the difference between experiment and our calculations. However,

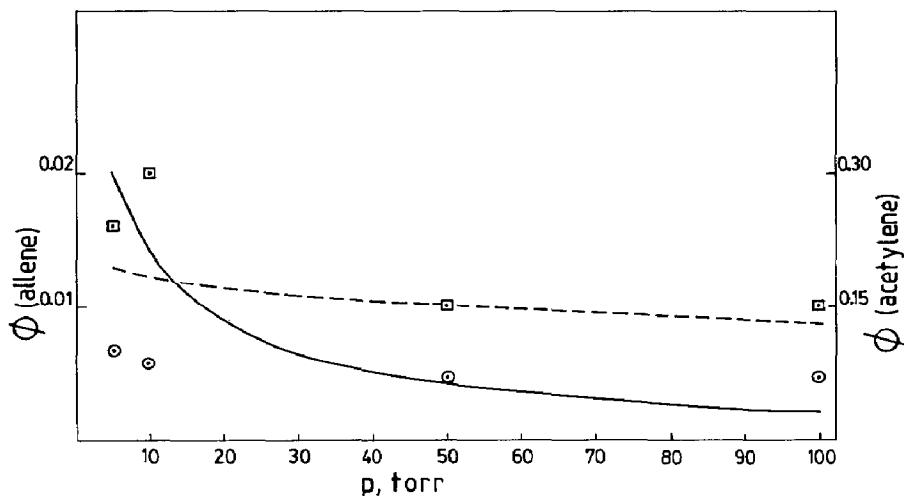


Fig. 6. Pressure dependence of the quantum yields for allene and acetylene. A normal distribution of energy exchange at $\langle\Delta E\rangle = 3 \text{ kcal mol}^{-1}$ is assumed. —, $\phi(\text{allene})$ (calculated); \square , experimental points for $\phi(\text{allene})$; ---, $\phi(\text{acetylene})$ (calculated); \circ , experimental points for $\phi(\text{acetylene})$.

the discrepancy in the case of acetylene, *i.e.* the overestimation of the yields throughout the whole pressure range, cannot be remedied by any mechanistic speculation. Another process is known to contribute significantly to the total yield of acetylene: direct molecular elimination of methane and acetylene possibly from the electronically excited state of a propylene molecule. This process becomes more important with increasing photon energy but even at 6.7 eV the estimate of its yield is $\phi = 0.04$ [3] or $\phi = 0.05$ [37]. The occurrence of this process makes the discrepancy between our calculated yield for $\phi(\text{acetylene})$ and experiment even worse.

4. Conclusions

An attempt to predict theoretically the yields for the final major decomposition products in the low energy photolysis of propylene has met with partial success. The calculated yield for propyne is in agreement with experiment while that for allene is underestimated at higher pressures; this may be ascribed to the involvement of an electronically excited primary propylene species yielding additional allene upon dissociation. The calculated yield for acetylene is more than twice as large as that determined experimentally. This is a successive failure of RRKM calculations to predict correctly the decomposition of the vinyl radical, and adds another argument to the conjecture that unimolecular dissociation involving the vinyl radical exhibits deviations from statistically randomized behaviour, this radical absorbing less than its statistical share of the available energy.

Some refinements of the RRKM calculations used in this work only slightly affect the results. Normal, step-ladder and exponential models for the energy transfer give almost identical results. The use of a weak-collision concept suggests that the average energy exchanged per collision is as low as 3 kcal mol⁻¹ or even less.

The present work emphasizes the need to take into account as accurately as possible the interconversions of C₃H₅ radicals. Of the three such radicals only the allyl is formed to a significant extent as a result of the primary cleavage of the C-H bond in propylene. The other two radicals, 1- and 2-propenyl, originate mainly from the secondary isomerizations of the allyl radical. If their interconversions are ignored, their respective contributions to the primary processes are wrongly assessed.

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