

## GAS PHASE PHOTOLYSIS OF 1-PENTENE AT 147 nm (8.4 eV)

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### Summary

The photolysis of gaseous 1-pentene was carried out in a static system using the xenon resonance line at 147 nm (8.4 eV) at pressures in the range 0.5 - 400 Torr (0.7 - 533 hPa). Only decomposition processes were studied and no attempt was made to establish the pattern of free radical reactions. The major dissociation products observed were ethylene, allene, propylene, 1,3-butadiene, acetylene and propyne. The minor products included methane, ethane, propane, some C<sub>5</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>6</sub> hydrocarbons, and 1-butene. The radical species were identified using scavengers such as oxygen, H<sub>2</sub>S and HI. The pressure dependence of the yields of the major radicals (C<sub>3</sub>H<sub>5</sub>, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>3</sub> and C<sub>3</sub>H<sub>7</sub>) was established. The C<sub>2</sub>H, C<sub>4</sub>H<sub>5</sub>, C<sub>4</sub>H<sub>7</sub>, CH<sub>2</sub> and C<sub>3</sub>H<sub>3</sub> radicals were found to be unimportant.

The primary decomposition channels are established. The main processes are the cleavage of a C—H bond with a yield  $\phi$  of 0.45 - 0.48 and the cleavage of a C—C bond with a yield  $\phi$  of 0.47. The allylic C—C bond appears to be the only C—C bond which undergoes primary rupture. All four primary intermediates, *i.e.* C<sub>5</sub>H<sub>9</sub>, C<sub>3</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>5</sub> and H, are energized. The radicals either decompose (isomerization prior to decomposition is possible in some cases) or undergo collisional stabilization; some hydrogen atoms add to the double bond prior to thermalization. Some details of the secondary processes are established but the overall mechanism is too complex to be fully interpreted.

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### 1. Introduction

The vacuum UV photolysis of 1-pentene has been studied extensively by Collin and coworkers [1 - 3]. However, at a photon energy of 8.4 eV the results were obtained only at low pressures. We have previously reported [4, 5] investigations of 1-butene irradiated with 8.4 and 10 eV photons at pressures in the range 15 - 500 Torr (20 - 667 hPa) in the presence of scavengers. Primary decompositions of the photoexcited molecule were, as expected, unaffected by pressure; the secondary processes could be quenched by collisions. This work is an extension of these studies to the 1-pentene molecule. The range of pressures employed is 0.5 - 400 Torr (0.7 - 533 hPa).

## 2. Experimental

1-Pentene was rigorously purified. All more volatile impurities were removed by prolonged distillation in a stream of argon. Water and CO<sub>2</sub> were removed by distillation under vacuum. The purified material contained about 50 ppm of *cis*- and *trans*-2-pentene as the only detectable impurity. H<sub>2</sub>S and HI were synthesized and used after being distilled and degassed in a mercury-free vacuum line.

The vacuum UV photolyses were carried out at room temperature in a standard static system using a microwave-powered xenon resonance lamp equipped with a titanium getter assembly. The intensity of the lamp ranged from  $5 \times 10^{13}$  to  $10^{14}$  photons s<sup>-1</sup>. The duration of the runs (4 - 45 min depending on pressure) was such that the conversion was always kept below 2% at the lowest pressures (below 1 Torr); at greater pressures the conversion was well below 1%.

Analysis of hydrocarbon products was performed by gas chromatography using a 9 m squalane column operated at 50 °C either alone or coupled with a 5 m Fractonitrile column operated at room temperature. Molecular hydrogen, if formed, was not measured. In pentene photolysis experiments the yield of acetylene was found to depend on pressure (Fig. 1) but was found not to be affected by the presence of oxygen or H<sub>2</sub>S and HI. All quantum yields were calculated with respect to  $\phi(\text{C}_2\text{H}_2)$  at the corresponding pressure.  $\phi(\text{C}_2\text{H}_2)$  was obtained using  $\phi(\text{C}_2\text{H}_2) = 0.75$  in the 147 nm photolysis of C<sub>2</sub>H<sub>4</sub>. The actinometry was performed very carefully; every run of pentene irradiation was preceded and followed by the irradiation of ethylene, so that the acetylene was determined under exactly the same conditions. The accuracy of the quantum yield determinations of the stable molecules is

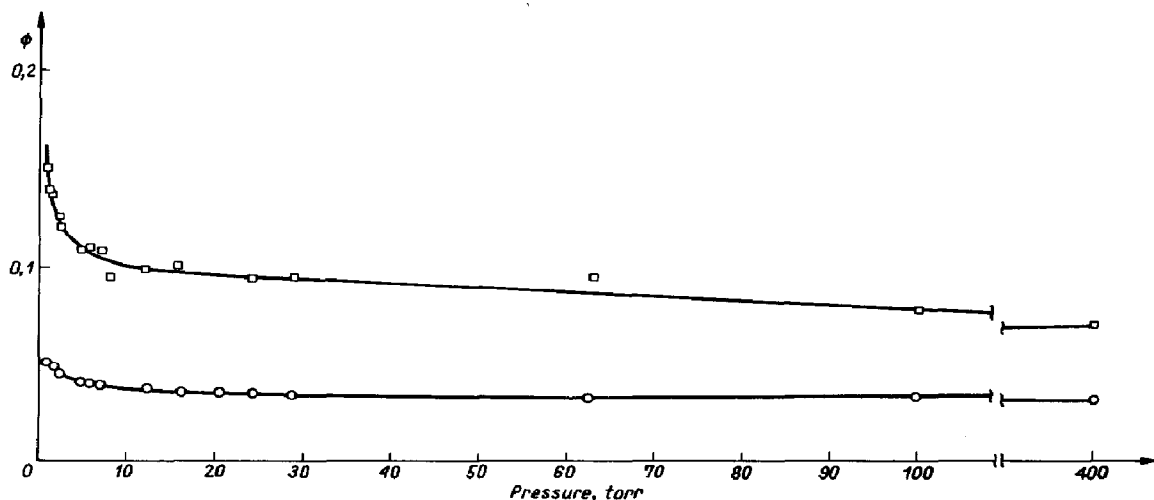


Fig. 1. The dependence of the quantum yields of acetylene ( $\circ$ ) and 1,3-butadiene ( $\square$ ) on pressure (1-pentene irradiated in the presence of 8% O<sub>2</sub>).

believed to be of the order of a few per cent. The results for the radicals were less accurate but still very good ( $\pm 10\%$  on average).

### 3. Results

The quantum yields of the products are summarized in Table 1; only three exemplary pressures (1, 5.5 and 28.6 Torr) are shown. The details of the pressure dependence for some major products are given in Figs. 1 and 2.

Some products not included in Table 1 were formed in the presence of oxygen:  $C_5H_8$  hydrocarbons (1-pentyne,  $\phi \approx 0.01 - 0.015$ ; 1,2-pentadiene,  $\phi \approx 0.003$ ; *cis*- and *trans*-1,3-pentadiene,  $\phi = 0.02$ ; 1,4-pentadiene,  $\phi = 0.01$ ),  $C_4H_6$  hydrocarbons (1-butyne, 1,2-butadiene), 2-butene, vinylacetylene, cyclopropane and propylcyclopropane. The yields of the last four products were all below 0.002. Because the ratio of the yields of propyne and allene was constant in all runs, *i.e.*  $0.1 \pm 0.02$ , these products were considered together. The quantum yields of the radicals were calculated as a difference between the yields of pertinent stable products determined in the presence of  $H_2S$  (or HI) and in the presence of oxygen.

A separate series of experiments was performed to study the effects of conversion. In the conversion range 0.15 - 3% no changes in the quantum yields could be found (at a 1-pentene pressure of 5 Torr). In some preliminary runs the conversion was as high as 15%; the results for some products were affected and these data were discarded.

### 4. Discussion

#### 4.1. Introduction

A polyatomic 1-pentene molecule under irradiation by 8.4 eV photons will dissociate in such a short time that collisional deactivation is generally assumed to be insignificant (at least under moderate pressures).

When the excited pentene molecule undergoes fragmentation either a C—C or a C—H bond must be broken. If the hydrogen atoms are neglected, four basic processes can contribute to the overall dissociation involving the rupture of the C—C bond:



Here  $C_5$  is any excited species with five carbon atoms, *i.e.* a parent primary photoexcited molecule  $C_5H_{10}$ , the pentenyl radicals  $C_5H_9$  originating from fragmentation of the excited pentene molecule, the pentyl radicals  $C_5H_{11}$

TABLE 1  
 Photolysis of 1-pentene at 8.4 eV: effect of pressure and the presence of scavengers on the formation of products

Total pressure	1 Torr (1.33 hPa)	5.5 Torr (7.33 hPa)	28.6 Torr (38.1 hPa)
O <sub>2</sub> (%)	8	8	8
H <sub>2</sub> S (%)	16	15	15
HI (%)	10	10	10
Methane	0.008 <sup>a</sup>	0.26	0.18
Acetylene	0.05	0.05	0.04
Ethylene	0.39	0.51	0.35
Ethane	0.01	0.40	0.31
C <sub>3</sub> H <sub>4</sub> <sup>b</sup>	0.17	0.18	0.13
Propylene	0.20	0.21	0.46
Propane	0.01	0.07	0.06
1,3-Butadiene	0.13	n.d. <sup>c</sup>	0.12
1-Butene	0.003	0.007	n.d.
$\Sigma\phi_{C_2} + 2\Sigma\phi_{C_3}$	1.00	0.97	0.96
$\Sigma\phi_{C_3} + 2\Sigma\phi_{C_4}$			
		0.007	0.008
		0.002	0.004
		0.11	0.09
		0.008	0.01
		0.08	0.08
		0.12	0.09
		0.08	0.04
		0.07	0.05
		0.07	0.05
		0.08	0.04
		0.32	0.27
		0.34	0.29
		0.04	0.035
		0.04	0.035
		0.18	0.13
		0.007	0.006

<sup>a</sup> All values are in quantum yield units.

<sup>b</sup> The total of allene and propyne.

<sup>c</sup> Not determined.

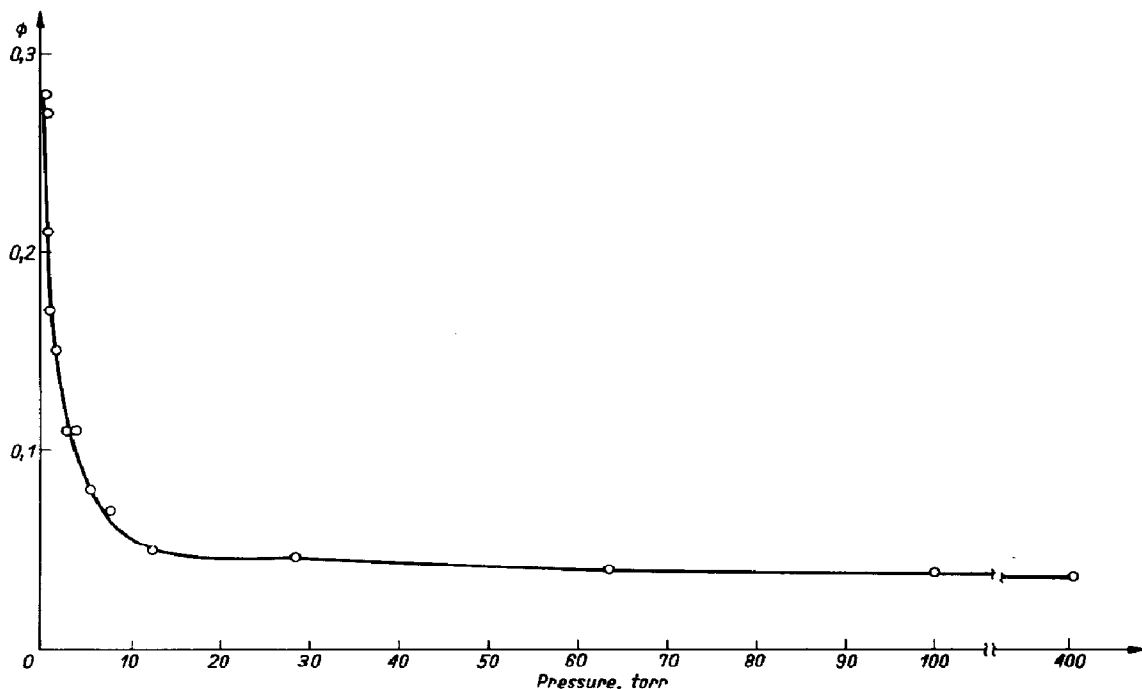


Fig. 2. The dependence of the quantum yield of propylene on 1-pentene pressure.

formed by the addition of hydrogen atoms to pentene, molecules such as  $C_5H_8$  etc.  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  are species possessing one, two, three and four carbon atoms respectively. We are not concerned now with the chemical structure of these species; both stable molecules and free radicals are involved. Simple transformations yield

$$\phi_4 = \frac{1}{5}(2\sum\phi_{C_1} + \sum\phi_{C_3} - \sum\phi_{C_2} - 2\sum\phi_{C_4}) \quad (5)$$

where  $\phi_4$  is the quantum yield for process (4) and  $\phi_{C_n}$  is the yield of the product (either a stable molecule or a free radical) with  $n$  carbon atoms. The calculated value for  $\phi_4$  is zero within the limits of experimental error. Thus eqn. (5) can be simplified to

$$\frac{\sum\phi_{C_2} + 2\sum\phi_{C_4}}{\sum\phi_{C_3} + 2\sum\phi_{C_1}} = 1 \quad (6)$$

It can be seen from Table 1 that the experimental data obey eqn. (6) satisfactorily. This self-consistence indicates that all the fragmentation products are determined and that the analyses are correct.

A mechanism represented by reactions (1) - (3) can be used to calculate the yields for the fragmentation processes of the excited pentene molecule, provided that propylene is assumed to originate exclusively from the addition of hydrogen atoms to pentene followed by the dissociation of the excited pentyl radicals (the arguments in favour of this assumption will be presented later).

The quantum yields calculated for the different reaction channels are summarized in Table 2.

TABLE 2

Fragmentation of the photoexcited 1-pentene molecule at 8.4 eV and different total pressures

	1 Torr (1.33 hPa)	5.5 Torr (7.33 hPa)	28.6 Torr (38.1 hPa)	100 Torr (133 hPa)
I 1,3-C <sub>4</sub> H <sub>6</sub> + CH <sub>3</sub> + H	0.14	0.11	0.09	0.08
II C <sub>2</sub> H <sub>2</sub> + C <sub>3</sub> H <sub>7</sub> + H	0.17	0.09	0.065	0.05
C <sub>2</sub> H <sub>3</sub> + CH <sub>3</sub> + C <sub>2</sub> H <sub>4</sub>				
III C <sub>3</sub> H <sub>5</sub> + C <sub>2</sub> H <sub>4</sub> + H	0.28	0.24	0.23	0.21
IV C <sub>3</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>5</sub> + H	0.18	0.12	0.08	0.065
V C <sub>3</sub> H <sub>5</sub> + C <sub>2</sub> H <sub>5</sub>	0.01	0.11	0.15	0.24
Total	0.78	0.67	0.615	0.64

#### 4.2. C—H cleavage

A species with four carbon atoms and a species with one carbon atom are formed in reaction (3). Of the C<sub>4</sub> products only 1,3-butadiene is important. The yields of other C<sub>4</sub>H<sub>6</sub> hydrocarbons, butenes, butenyl radicals and butynyl radicals are much smaller. Therefore the only reaction which can account for process (3) is



The quantum yield for reaction (7), which is equal to that of 1,3-butadiene, decreases with increasing pressure indicating the occurrence of a two-step process:

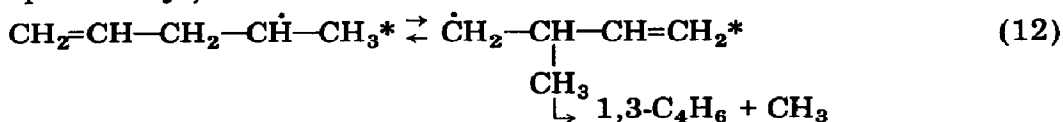


The alternative mechanism, which involves the primary rupture of a C—C bond to give butenyl and methyl radicals followed by either dissociation or collisional stabilization of excited C<sub>4</sub>H<sub>7</sub> radicals, can be rejected. Stabilization of the butenyl radicals in the presence of H<sub>2</sub>S or HI should ultimately lead to the formation of 1-butene. Enhancement of the 1-butene yield with increasing pressure is not observed.

It is uncertain which of the five C—H bonds is broken in reaction (8). From the structures of the fragmentation products formed in the dissociation, the following two radical structures can be suggested as precursors: 1-penten-3-yl,



and 1-penten-4-yl,



The occurrence of reaction (12) has been reported by Carter and Tardy [6].

The formation of 1-penten-3-yl radicals in reaction (8) seems to be more likely since the corresponding C—H bond is the weakest C—H bond in the pentene molecule. However, the isomeric structures can rearrange from one to another; isomerization can be fast enough to compete with dissociation.

The quantum yield  $\phi_7$  for reaction (7) extrapolated to zero pressure is 0.16 (it is equivalent to process I in Table 2). Since process II (see Table 2) yielding acetylene, vinyl radicals and propyl radicals is more difficult to analyse, these products are dealt with jointly; the corresponding fragments are chosen so that the process balances. Because the yield for process II decreases with increasing pressure, the products are probably formed predominantly by fragmentation of the excited pentenyl radicals. If the mechanism were to involve the primary cleavage of a C—C bond followed by dissociation, an increase in the yields of the stabilization processes with increasing pressure would be observed. This is clearly not the case. Attempts have been made [1 - 5] to assign precise values of the quantum yields to the detailed pathways of dissociation based on more or less ingenious balancing of the yields of the stable products. Such a task could be accomplished on the basis of the results presented in this work. For example, in the case of acetylene we could advance a detailed mechanism assessing the yield for the dissociation of excited pentenyl radicals (their structure and the identity of the accompanying fragments could also be postulated) and we could try to estimate the contribution, however small, of the primary rupture of a C—C bond. Although we were tempted to propose such a mechanism we were convinced that it would not be of much value for two reasons. (1) Excited  $\text{C}_5\text{H}_9$  radicals can isomerize prior to decomposition (as mentioned earlier for 1,3-butadiene) which makes the determination of the structure of the primary radical impossible. (2) The possible pathways are too numerous. The  $\phi(\text{C}_2\text{H}_2)$  dependence on pressure could be caused by collisional stabilization of  $\text{C}_5\text{H}_9$  radicals (having a 1-penten-1-yl structure), by collisional stabilization of excited vinyl radicals or by collisional stabilization of excited ethylene molecules. The  $\phi(\text{C}_2\text{H}_3)$  dependence on pressure could be caused by collisional stabilization of excited vinyl radicals, by dissociation and stabilization of  $\text{C}_5\text{H}_9$  radicals or by primary dissociation of the photochemically activated 1-pentene molecules.

The total yield for process II (Table 2) extrapolated to zero pressure is about 0.27. From the pressure dependence it can be estimated that at least approximately 0.24 of this yield results from the primary cleavage of a C—H bond (the estimate is somewhat arbitrary and represents the lowest limit). Unfortunately  $\text{C}_5\text{H}_9$  radicals could not be directly determined using the experimental techniques employed in this work.

$C_5H_8$  hydrocarbons are also formed as a result of the C—H cleavage. Their total yield is about 0.05. Thus the total yield  $\phi_{C-H}$  for the primary rupture of a C—H bond is 0.45 - 0.48.

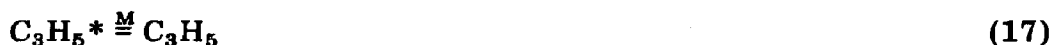
#### 4.3. C—C cleavage

The total yield for processes III - V (see Table 2) is not dependent on pressure. The contribution of process V, however, increases at the expense of processes III and IV with increasing pressure. Apparently the splitting of the photoexcited 1-pentene molecule into allyl and ethyl radicals is a primary process. ( $C_3H_5$  radicals have an allylic structure as evidenced by the absence of an increase of the  $C_3H_6$  quantum yield in the presence of  $H_2S$  compared with the experiments in the presence of oxygen. Reaction of stabilized allyl radicals with  $H_2S$  yielding propylene is endothermic [5].)



$$E_{1-C_3H_5-C_2H_5} = 69 \text{ kcal mol}^{-1} [7]$$

The remaining excitation energy of about  $125 \text{ kcal mol}^{-1}$  is distributed between both fragments; they can either undergo subsequent decomposition



or be collisionally deactivated.

As expected, a Stern-Volmer plot, *i.e.*  $1/\phi(C_3H_4) = f[M]$  (see Fig. 3), is distinctly non-linear, assuming that the excess energy is distributed more or less statistically among the various vibrational and rotational degrees of freedom of both fragments. The extrapolation to zero pressure of the yields of the individual processes III - V is not indisputable. It can be established, however, that both fragments may be capable of dissociation to some extent, *i.e.* according to the overall reaction



It appears that reaction (13) is almost the only primary reaction involving the rupture of a C—C bond. A splitting of 4-penten-1-yl radicals into propenyl radicals and ethylene is unimportant. The deactivation of such radicals would decrease the total yield of processes III - V with increasing pressure; this was not observed.

Another primary process involving the cleavage of a C—C bond is the formation of methylene by





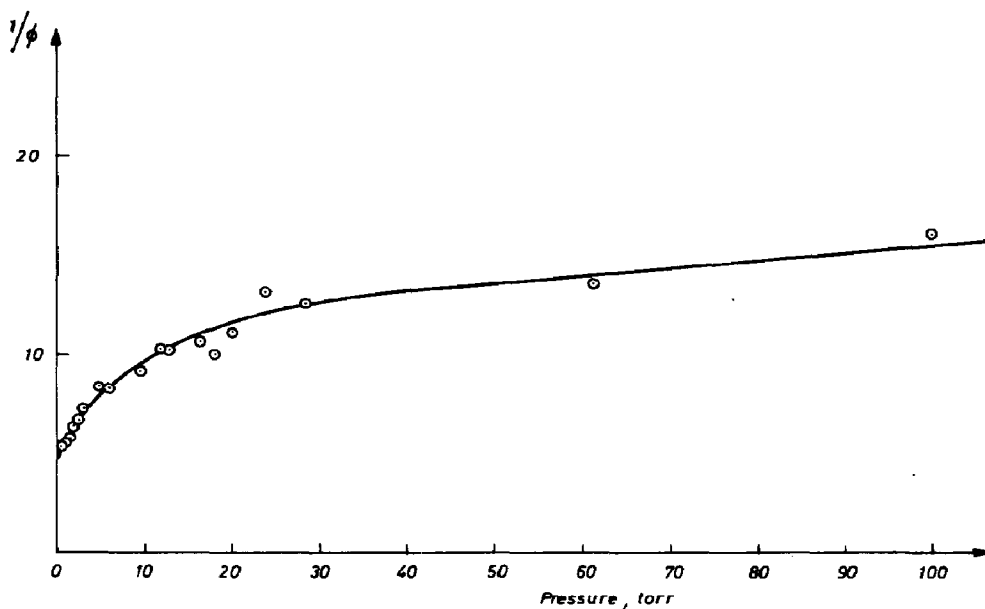


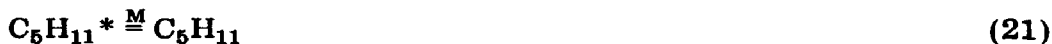
Fig. 3. A Stern-Volmer plot for the total yield of allene and propyne.

The occurrence of such a reaction is evidenced by the presence of propylcyclopropane among the photolysis products. The quantum yield is very small, however, not exceeding approximately 0.003.

Therefore the only C—C bond undergoing rupture in a primary dissociation is that twice removed from the double bond of an olefin, *i.e.* that in the  $\beta$  position.  $\phi_{C-C} \approx \phi_{13} = 0.47$ .

#### 4.4. Dissociation of pentyl radicals

The observed dependence of the quantum yield of propylene on pressure (Fig. 2) can be explained assuming the occurrence of the following reactions:



The reactions of thermal hydrogen atoms with olefins have been studied extensively by Rabinovitch and coworkers [8, 9].

Collin and Bukka [2] have considered another process which could lead to the formation of propylene:



$$\phi_{22} = 0.04$$

We believe that reaction (22) does not occur. Such a reaction should be a two-step process, involving either the primary cleavage of a C—H bond in the 4 position of the parent molecule, *i.e.*



followed by the splitting of the  $\text{C}_5\text{H}_9$  radical into the vinyl radical and propylene, or the primary cleavage of a C—C bond, *i.e.*



followed by reaction (25)



According to Carter and Tardy [6] excited 1-penten-4-yl radicals rearrange to the 3-methyl-1-buten-4-yl structure. The latter isomer splits into 1,3-butadiene and methyl radicals — reactions (11) and (12). In contrast, dissociation of the excited *n*-propyl radicals involves the cleavage of a C—C bond, *i.e.*



rather than reaction (25).

The estimation of the rate constant for the dissociation of  $\text{C}_5\text{H}_{11}$  radicals [9], although tempting, would be of dubious value, since the increase in pressure would not only augment the probability of stabilization of these radicals but also lead to a simultaneous decrease in their yield because of the decrease in the yield of atomic hydrogen. Nevertheless, some conclusions can be drawn concerning the presence of hot hydrogen atoms in the irradiated system. According to Rabinovitch and Setser [8] the apparent rate constant for the decomposition of *sec*- $\text{C}_5\text{H}_{11}$  radicals, formed as a result of the addition of thermal hydrogen atoms to the double bond, is approximately  $10^7 \text{ s}^{-1}$ . If only thermal hydrogen atoms were formed in the experiments carried out in this work, the yield of propylene should have been negligible at pressures exceeding 30 Torr (40 hPa).

In fact the decomposition into propylene is not quenched even at a pressure as high as 400 Torr (533 hPa) ( $\phi(\text{C}_3\text{H}_6) \approx 0.03$ ). This can be taken as evidence that hot hydrogen atoms are present. Experiments [10] using hydrogen atoms having an energy of about 0.8 eV have indicated that about 50% of these atoms undergo thermalization prior to the addition to the double bond. The remainder contribute their additional kinetic energy, as a whole or in part, to the total energy of the generated radicals; this results in the increase in the rate of decomposition.

## 5. Conclusions

The primary cleavage of the C—C and C—H bonds of the photoexcited 1-pentene molecule is believed to have been established. At a photon energy

of 8.4 eV the probability of both these splits is nearly the same. The C—C bond in the  $\beta$  position is almost the only C—C bond to undergo rupture.

The detailed comparison of our results with those obtained previously in Collin's laboratory is not straightforward. Collin and coworkers [1 - 3] have attempted to ascribe the quantum yields to many decomposition channels (ten primary processes were reported at photon energies of 7.1 and 7.6 eV, and eight at an energy of 8.4 eV); we resisted the temptation to do this. However, our mechanism can be used to calculate the results of Collin [2, 3] in order to obtain the yields for the breakage of the allylic C—C bond (by summing the yields for the reactions corresponding to processes III - V in this work). A comparison of the yields for process I giving 1,3-butadiene is also possible. These data are summarized in Table 3. Although incomplete, they indicate that an increase in photon energy is accompanied by an increase in the primary splitting of a C—H bond at the expense of a C—C bond.

TABLE 3

Comparison of some fragmentation patterns of the 1-pentene molecule at different energies<sup>a</sup>

	7.1 eV [3]	7.6 eV [3]	8.4 eV [2]	8.4 eV This work
$C_2H_5^* + C_3H_5^*$	0.64	0.74	0.48	0.47
$C_4H_6 + CH_3 + H$	0.08	0.09	0.15	0.16

<sup>a</sup>The data of Collin and coworkers [2, 3] were calculated based on the mechanism employed in this work.

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### References

- 1 P. M. Perrin and G. J. Collin, *Can. J. Chem.*, **51** (1973) 724.
- 2 G. J. Collin and K. Bukka, *J. Photochem.*, **6** (1977) 381.
- 3 A. Wieckowski and G. J. Collin, *Can. J. Chem.*, **56** (1978) 1435.
- 4 J. Niedzielski, W. Makulski and J. Gawłowski, *J. Photochem.*, **9** (1978) 519.
- 5 J. Niedzielski, P. Geblewicz and J. Gawłowski, *J. Photochem.*, **10** (1979) 287.
- 6 W. P. L. Carter and D. C. Tardy, *J. Phys. Chem.*, **78** (1974) 1245.
- 7 S. W. Benson, *J. Chem., Educ.*, **42** (1965) 502.
- 8 B. S. Rabinovitch and D. W. Setser, in W. A. Noyes, G. S. Hammond and J. N. Pitts, Jr., (eds.), *Advances in Photochemistry*, Vol. 3, Interscience, New York, 1964.
- 9 M. J. Pearson and B. S. Rabinovitch, *J. Chem. Phys.*, **42** (1964) 1624.
- 10 J. Gawłowski and J. Niedzielski, unpublished results, 1979.