

## THE VACUUM UV PHOTOLYSIS OF 1-HEXENE AND 1-HEXYNE

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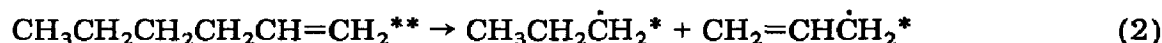
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**Summary**

A comparative study was made of the photolysis of 1-hexene and 1-hexyne at 184.9 and 147 nm. Three primary processes were observed in each system. They are, in decreasing order of importance, the rupture of the  $\beta(\text{C}-\text{C})$  bond, the rupture of the  $\gamma(\text{C}-\text{C})$  bond and the retro-ene process. Thus the behaviour of both photoexcited molecules is similar to a first approximation. However, there are meaningful differences. In particular, the rupture of the  $\gamma(\text{C}-\text{C})$  bond is relatively more important in the 1-hexyne case and leads to the formation of vinylacetylene at 147 nm. This observation suggests that the  $\gamma(\text{C}-\text{C})$  rupture may be the result of isomerization of the photoexcited molecule (a 1,3 hydrogen shift) which is followed by the rupture of the  $\beta(\text{C}-\text{C})$  bond.

**1. Introduction**

We have recently studied the vacuum UV photolysis of gaseous 1-hexene at 147, 163 and 174 nm. In each case the main fragmentation process for the photoexcited molecules is the rupture of the  $\beta(\text{C}-\text{C})$  bond to produce *n*-propyl and allyl radicals [1]. At low pressures this primary process is followed by secondary fragmentation of the propyl radical:



$$\Delta H = 71.2 \text{ kcal mol}^{-1} [2]$$



The Stern-Volmer plot of  $[\Phi(\text{C}_2\text{H}_4)]^{-1}$  versus pressure gives an indication of the energy content of the propyl radicals. The intercept of this plot with the pressure axis gives the  $k_d/k_s$  ratio in pressure units. By using the stabilization

process as an internal clock, or by assuming a strong collisional process, we can estimate the rate constant of the fragmentation process. Then the energy content of the decomposing species can be estimated using a Rice-Ramsperger-Kassel-Marcus calculation which is available in the literature [1, 4].

This paper has two purposes. First, we want to provide a better view of the photolysis of 1-hexene by extending the previous study from 123.6 to 185 nm. Secondly, it is of interest to determine whether photoexcited alkyne molecules behave similarly to alkene molecules by comparing the fate of photoexcited 1-hexene and 1-hexyne molecules.

## 2. Experimental details

All the experimental details have been described previously [1]. The krypton [5] and mercury [6] lamps have also been described in the literature. All the emission spectra were recorded between 105 and 250 nm using a 0.5 m McPherson monochromator (GCA 225). Although we did not measure the absorption coefficient at each wavelength, we checked that more than 99% of the incident beam was absorbed at a pressure of less than 1 Torr ( $133 \text{ N m}^{-2}$ ) in each reaction chamber.

The actinometry has already been described [1, 6]. Ethylene ( $\Phi(\text{C}_2\text{H}_2) = 0.50$  [7, 8]) was used to determine the quantum yield of the products particularly at 184.9 nm. However, in order to avoid contamination of the analytical system by ethylene, *cis*-2-butene was photolysed first and the measured quantum yields of its products were used.

## 3. Results

All the results are expressed as quantum yields and are given in tabular and graphical form in Section 4. The following observations were also made.

The formation of the 1-hexene isomers was difficult to measure owing to the relative retention times of these molecules. However, the photolysis of the 10.0 Torr:1.0 Torr: $x$  Torr 1-hexene:oxygen:sulphur hexafluoride system ( $0 \leq x \leq 300$ ) at 185 nm indicates a very low isomerization quantum yield ( $\Phi(2\text{-hexene}) \approx 0.004 \pm 15\%$  independent of the sulphur hexafluoride pressure) and the formation of 3-hexene was not observed ( $\Phi \leq 0.002$ ). Similar results were observed when the sulphur hexafluoride was replaced by propane at a pressure of 200 - 300 Torr ( $\Phi(2\text{-hexene}) \approx 0.01$ ).

No decrease in the transmission of the window was observed at 184.9 nm. However, a drastic decrease was observed in the photolysis of 1-hexyne at 147 nm.

The photolysis of the 100:10 1-hexyne:oxygen mixture at 184.9 nm shows only the formation of ethylene, propene and propadiene.

## 4. Discussion

### 4.1. Photolysis of 1-hexene between 123.6 and 184.9 nm

Table 1 adds quantitative data to ref. 1, Table 1. The main product observed at all wavelengths was ethylene and its quantum yields measured at low pressure decreased from 1.0 at 123.6 nm to about 0.5 at 185 nm (Table 2). Similar behaviour was observed for the propylene and 1,3-butadiene quantum yields (Figs. 1 - 3). These are the only noticeable products mea-

TABLE 1

Vacuum UV photolysis of pure 1-hexene and of 1-hexene in the presence of additives<sup>a</sup>

Product	Quantum yields				
	$\lambda = 123.6 \text{ nm}$		$\lambda = 184.9 \text{ nm}$		
	Pure	10% O <sub>2</sub>	Pure	10% O <sub>2</sub> <sup>b</sup>	10% DI
Methane	0.13	0.05	0.01	0.00 <sub>4</sub>	0.40
Acetylene	0.02	0.02	0.00	0.00	0.00
Ethylene	0.91	0.81	0.47	0.43	0.40
Ethane	0.13	0.01	0.06	0.00	0.12
Propadiene	0.15	0.16	0.00	0.00	0.00
Propene	0.26	0.24 <sub>5</sub>	0.10	0.06 <sub>5</sub>	0.55
Propane	0.09	0.02	0.03	0.00	0.34
1,3-butadiene	0.22	0.22 <sub>5</sub>	0.01	0.00 <sub>5</sub>	0.02
1-butene	0.17	0.01	0.18	0.00	0.04
<i>n</i> -butane	0.07	0.00	0.07	0.00	0.01 <sub>5</sub>
1,5-hexadiene	0.04	0.00	0.05	0.00	0.00
<i>n</i> -hexane	0.15	0.00	0.02	0.00	0.11

<sup>a</sup>Monomer pressure, 10 Torr (1330 N m<sup>-2</sup>).

<sup>b</sup>Similar values were obtained in the presence of 10% NO.

TABLE 2

Vacuum UV photolysis of 1-hexene: quantum yields at low pressure<sup>a</sup>

	Quantum yields at the following wavelengths				
	$\lambda =$	$\lambda =$	$\lambda =$	$\lambda =$	$\lambda =$
	123.6 nm	147 nm <sup>b</sup>	163 nm <sup>b</sup>	174 nm <sup>b</sup>	184.9 nm <sup>b</sup>
$\Phi(\text{C}_2\text{H}_4)$	~ 1.0	0.86	0.59	0.44	0.56
$\Phi(\text{C}_3\text{H}_6)$	0.30	0.135	0.07 <sub>9</sub>	0.05 <sub>8</sub>	0.07 <sub>8</sub>
$\Phi(1,3\text{-C}_4\text{H}_6)$	0.27	0.11	0.03 <sub>8</sub>	0.02 <sub>8</sub>	0.02
$\Phi(\text{C}_3\text{H}_6)/\Phi(\text{C}_2\text{H}_4)$	0.287 <sup>c</sup>	0.157	0.134	0.132	0.126

<sup>a</sup>10% O<sub>2</sub> was added in all experiments ( $P \approx 1.0$  Torr).

<sup>b</sup>These values were obtained from the intercept of the linear regression of the Stern-Volmer plots (Figs. 1 - 3).

<sup>c</sup>This value is constant between pressures of 1 and 65 Torr (133 - 8650 N m<sup>-2</sup>).

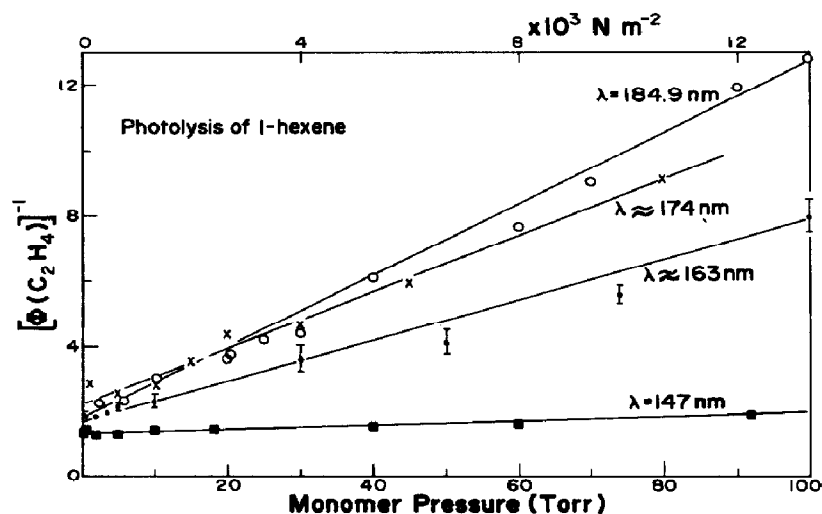


Fig. 1. Photolysis of gaseous 1-hexene: Stern-Volmer plots of the ethylene quantum yield measured in the presence of oxygen or nitric oxide (5% - 10%).

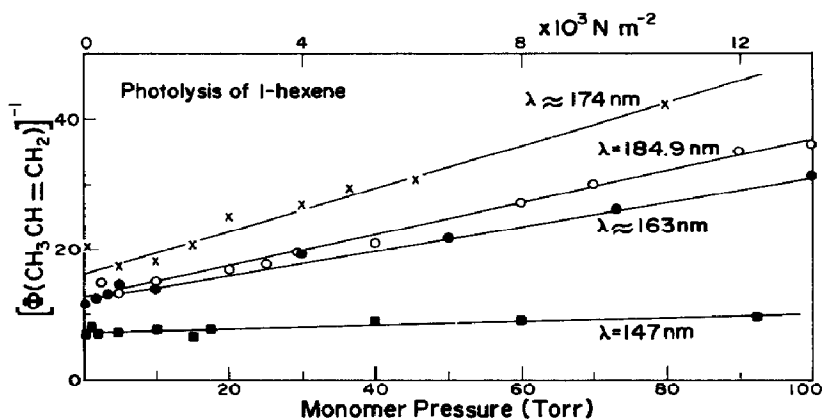


Fig. 2. Photolysis of gaseous 1-hexene: Stern-Volmer plots of the propylene quantum yield measured in the presence of oxygen or nitric oxide (5% - 10%).

sured at 184.9 nm in the presence of oxygen or nitric oxide. Allene is a product at 147 and 123.6 nm, and in both cases its formation can be related to the energy content of the allyl fragments formed in process (2). Since the maximum available energy increases as the incident wavelength decreases, the allyl radicals may decompose at low pressures [9]:



In addition to the primary rupture of the  $\beta(C-C)$  bond, two other minor primary processes have been proposed. The first corresponds to the formation of 1,3-butadiene via the rupture of the  $\gamma(C-C)$  bond [1]. The

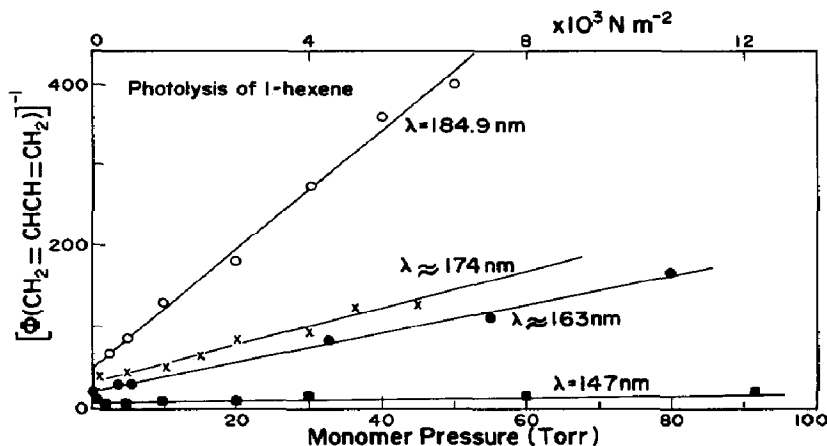
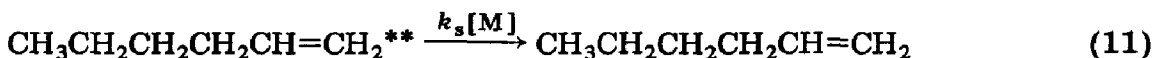


Fig. 3. Photolysis of gaseous 1-hexene: Stern-Volmer plots of the 1,3-butadiene quantum yield measured in the presence of oxygen or nitric oxide (5% - 10%).

second contributes small amounts of vinyl and the *n*-butyl radical via the rupture of the  $\alpha(\text{C}-\text{C})$  bond. No explanation has been proposed for the formation of propylene. At least two alternative routes can be investigated. Since process (2) leads to the formation of energized normal propyl radicals, isomerization to the iso structure may result in the formation of propylene. Alternatively, a retro-ene process similar to that observed in shock tube or low pressure pyrolysis experiments may also lead to the same product [10, 11] (Table 2):



Both mechanisms obey the Stern-Volmer equation (Fig. 2 and Table 3). The combination of iso-propyl and methyl radicals results in the formation of isobutane and this product was not observed. The limits of detection are such that a low probability for sequence (7) - (9) can be inferred. Process (10) is more efficient than process (2) at low temperatures in the pyrolysis experiments [11]. The propylene precursor should also have a lifetime long enough to be stabilized by collision. Thus the rate constant of process (10) is of the same magnitude as the collisional rate constant in the 1 - 100 Torr pressure region. It should also be noted that the total quantum yield  $\Phi_{\text{DI}}(\text{C}_3\text{H}_8) + \Phi_{\text{DI}}(\text{C}_2\text{H}_4) = A$  decreases with increasing pressure at 147 nm [1]. The same behaviour was observed at 184.9 nm. Since the above relationship gives a good value for process (2), the Stern-Volmer plot for  $A$  (Fig. 4)

TABLE 3

Vacuum UV photolysis of 1-hexene: stabilization pressure of the intermediates

	$k_s/k_d^a$ (Torr) at the following wavelengths			
	$\lambda = 147 \text{ nm}$	$\lambda \approx 163 \text{ nm}$	$\lambda \approx 174 \text{ nm}$	$\lambda = 184.9 \text{ nm}$
Ethylene	$\approx 160$	33	32	14
Propylene	$\approx 260$	76	52	50
1,3-butadiene	$\approx 60$	12	13	7

<sup>a</sup>  $k_s/k_d$  is the intercept of the linear regression of the Stern–Volmer plot with the pressure axis (see Figs. 1 - 3). The error is  $\pm 10\%$ .

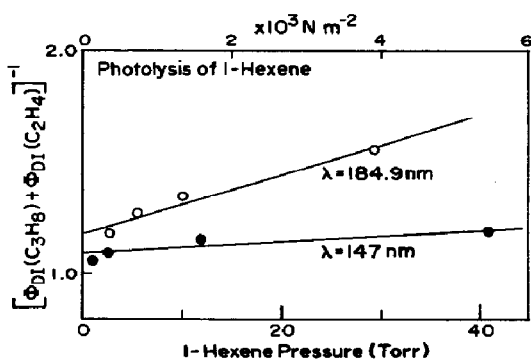
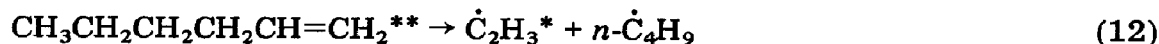


Fig. 4. Photolysis of gaseous 1-hexene: Stern–Volmer plots of  $\Phi_{DI}(C_3H_8) + \Phi_{DI}(C_2H_4)$  at 147 and 184.9 nm.

indicates that the photoexcited molecule has lifetimes of  $(1.3 \pm 0.3) \times 10^9 \text{ s}^{-1}$  and  $(2 \pm 0.5) \times 10^9 \text{ s}^{-1}$  at 147.0 nm and 184.9 nm respectively (the collision diameter of the 1-hexene molecule is 0.62 nm [11]). These values are not unexpected since similar behaviour at 184.9 nm was observed in the photolysis of tetramethylethylene [6]. Thus both mechanisms (processes (7) - (9) or processes (10) and (11)) may play a role in the formation of propylene.

Ethylene is formed in process (3) and, in the presence of deuterium iodide, it is also a product of the rupture of the  $\alpha(C-C)$  bond:



Thus  $A$  is a measure of the sum  $\phi(2) + \phi(12)$ .  $\Phi_{O_2}(C_3H_6)$  gives a maximum value which is twice that of the retro-ene process, and  $\Phi_{DI}(C_2H_6)$  gives a maximum value for the primary rupture of the  $\gamma(C-C)$  bond:

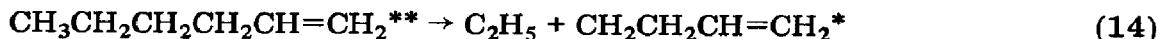


TABLE 4

Photolysis of gaseous 1-hexene: quantum yields<sup>a</sup> at low pressure<sup>b</sup>

Process	Quantum yields at the following wavelengths		
	$\lambda = 147 \text{ nm}$	$\lambda \approx 163 \text{ nm}$	$\lambda = 184.9 \text{ nm}$
$\text{C}_6^{**} \rightarrow n\text{-C}_3\text{H}_7^* + \text{C}_3\text{H}_5$ $\quad \quad \quad \downarrow$ $\rightarrow \text{C}_2\text{H}_4 + \text{CH}_3$	0.80	0.65	0.75
	0.76	0.59	0.56
$\text{C}_6^{**} \rightarrow \text{C}_2\text{H}_3 + \text{C}_4\text{H}_9$	0.05	0.10	0.08
$\text{C}_6^{**} \rightarrow 2\text{C}_3\text{H}_6$	0.06	0.04	0.035
$\text{C}_6^{**} \rightarrow \text{C}_2\text{H}_5 + \text{C}_4\text{H}_7$	0.15	0.10	0.13
Total	1.06	0.89	0.995

<sup>a</sup> $\Delta\Phi/\Phi < 0.15$ .<sup>b</sup>At 1 Torr ( $133 \text{ N m}^{-2}$ ) or less.

Table 4 gives the quantum yields of each of the primary processes calculated in this way.

#### 4.2. Photolysis of 1-hexyne at 184.9 and 147.0 nm

Here again the main product is ethylene (Table 5 and Figs. 5 and 6) and its quantum yield shows Stern–Volmer behaviour. Two more products, propylene and propadiene (see Section 3), are observed at 184.9 nm with lower quantum yields. The propylene quantum yield also shows Stern–

TABLE 5

Photolysis of 1-hexyne at 184.9 nm: quantum yields<sup>a</sup>

	Quantum yields for the following pressures (Torr) of 1-hexyne					
	3 (0.35 <sup>b</sup> )	10 (1 <sup>b</sup> )	30 (3 <sup>b</sup> )	1	10	30
Methane	0.37	0.30	0.17	0.07	0.08	0.07
Acetylene	0.01	0.01	0.05	0.01	0.02	0.02
Ethylene	0.36	0.32	0.25	0.44	0.43	0.31
Ethane	0.22	0.21	0.17	0.06	0.06	0.04
Propene	N.M. <sup>c</sup>	N.M. <sup>c</sup>	N.M. <sup>c</sup>	0.14	0.12	0.09
Propane	0.07	0.10	0.18	0.05	0.05	0.05
Propadiene	0.18	0.17	0.08	0.01 <sub>5</sub>	0.02	0.02 <sub>5</sub>
Propyne	0.08 <sub>5</sub>	0.08	0.06 <sub>5</sub>	0.03	0.03	0.03
1-butyne	0.06	0.07	0.09	0.12	0.10	0.07
1,3-butadiene	0.14	0.14	0.17			
Vinylacetylene	0.02	0.01	Trace	0.03	0.02	0.00 <sub>6</sub>
<i>n</i> -butane	0.00	0.0	0.03	0.02	0.03	0.04
1,2-pentadiene	0.02	Trace	Trace	Trace	0.04	N.M. <sup>c</sup>
$\text{C}_6(?)$	—	—	—	—	0.12	0.11

<sup>a</sup> $\Delta\Phi/\Phi < 0.10$ .<sup>b</sup>Pressure (Torr) of added deuterium iodide.<sup>c</sup>N.M., not measured.

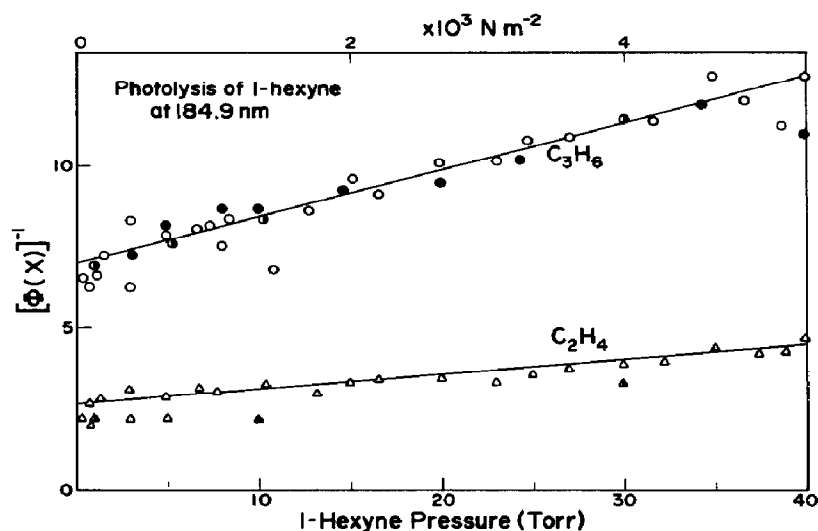


Fig. 5. Photolysis of gaseous 1-hexyne at 184.9 nm: Stern-Volmer plots of ethylene and propylene quantum yields ( $\circ$ ,  $\Delta$ , in the presence of oxygen;  $\bullet$ , in the presence of nitric oxide;  $\Delta$ ,  $\circ$ , in the pure system).

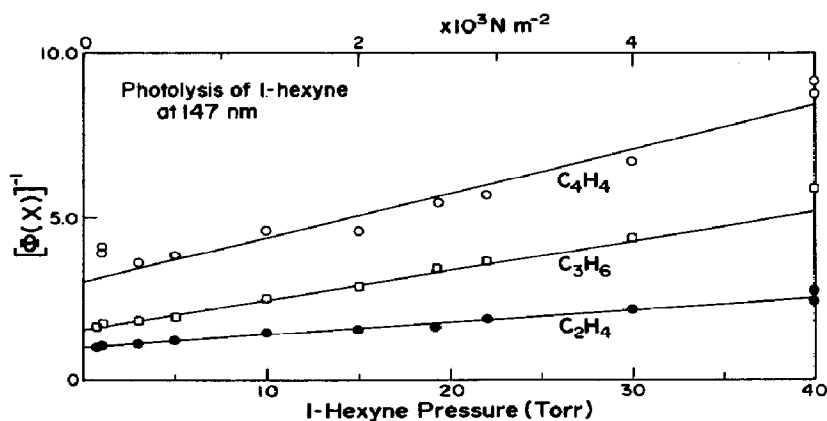
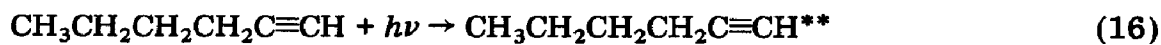


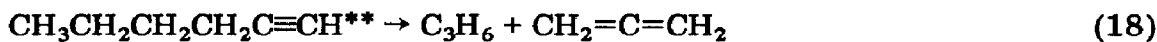
Fig. 6. Photolysis of gaseous 1-hexyne at 147 nm: Stern-Volmer plots of the quantum yields of various products in the presence of 10%  $O_2$ .

Volmer behaviour (Fig. 5) whereas  $\Phi$ (propadiene) has a constant value of about 0.035 between 0.5 and 40 Torr. In the absence of a radical scavenger, or in the presence of deuterium iodide a number of additional products are formed (Table 5). A similar mechanism to the one proposed for 1-hexene photolysis can be assumed for 1-hexyne, *i.e.* the primary rupture of the  $\beta$ (C-C) bond and the retro-ene process:



$$E_A = 70.7 \text{ kcal mol}^{-1} [12]$$





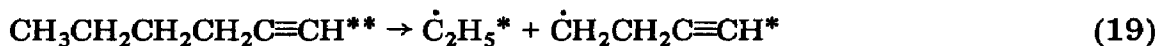
$$E_A = 56.4 \text{ kcal mol}^{-1} [12]$$

The propargyl structure of the  $\dot{\text{C}}\text{H}_2\text{C}\equiv\text{CH}$  radical is in electronic resonance with the allenyl structure  $\text{CH}_2=\text{C}=\dot{\text{C}}\text{H}$ . Both process (17) and process (18) were observed in low pressure pyrolysis experiments [12]. Since the  $\Phi(\text{CH}_2=\text{C}=\text{CH}_2)$  value is constant over the pressure range investigated, it can be assumed that process (18) has a constant quantum yield:  $\phi(18) = 0.035$ . However, it must be remembered that if hot hydrogen atoms are formed their addition to the triple bond of 1-hexyne leads to vibrationally excited  $\text{RCH}_2\text{C}=\text{CH}_2^{\ddagger}$  which decomposes into  $\text{R} + \text{CH}_2=\text{C}=\text{CH}_2$  [13] although a pressure effect should be observed. Thus the above assumption may overestimate the importance of the retro-ene process.

When the propadiene quantum yield measured in the presence of molecular oxygen is subtracted from the quantum yield measured in the presence of deuterium iodide a value of  $3.3 \pm 0.6$  is obtained for the ratio  $\Phi_{\text{DI}}(\text{propyne}) / \{\Phi_{\text{DI}}(\text{propadiene}) - \Phi_{\text{O}_2}(\text{propadiene})\}$ . This value is in reasonable agreement with the equilibrium ratio  $[\text{CH}_2\text{C}\equiv\text{CH}] / [\text{CH}_2=\text{C}=\dot{\text{C}}\text{H}]$  which was observed to be 3 [14]. The sum  $\Phi_{\text{DI}}(\text{propene}) + \Phi_{\text{DI}}(\text{propadiene})$ , however, is smaller than the sum  $\Phi_{\text{O}_2}(\text{ethylene}) + \Phi_{\text{DI}}(\text{propane})$  particularly at high pressures (Table 5). The efficiency of deuterium iodide in the scavenging of very unsaturated radicals is not necessarily quantitative [15]. Some of these radicals may react with the monomer and contribute to its polymerization.

A second source of propylene must be proposed to take account of the higher yield of this compound, particularly at 147 nm where no satisfactory explanation can be given. Processes (7) - (9) are still available.

The use of deuterium iodide adds at least one other process since this additive increases the ethane yield (process (15)). The ethane formation results either from a primary rupture of the  $\gamma(\text{C}-\text{C})$  bond or from a primary rupture of the  $\alpha(\text{C}-\text{C})$  bond followed by fragmentation of the *n*-butyl radical:



$$\Delta H \approx 85 \text{ kcal mol}^{-1}$$

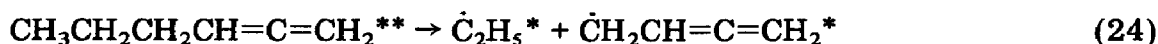


$$\Delta H = 113 \text{ kcal mol}^{-1} [16]$$



It is not easy to choose between these two possibilities: the use of deuterium iodide does not give a straightforward answer. In its presence only a small amount of *n*-butane is formed and there is no increase in the acetylene quantum yield. However, methane, ethane and propane are formed

with rather high quantum yields. Thus we can assume that ethyl radicals are formed in process (19) rather than in processes (20) and (21). The formation of 1-butyne in the experiments in which deuterium iodide was added is also a good indication of the occurrence of process (19), but again  $\Phi_{DI}(1\text{-butyne})$  is much smaller than  $\Phi_{DI}(\text{ethane})$ . The formation of 1,3-butadiene is intriguing. It may be an indication of the isomerization of the photoexcited molecule before its fragmentation:

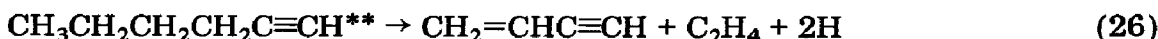


In this case process (24) corresponds to a rupture of the  $\beta(\text{C}-\text{C})$  bond and the 1,2-butadien-4-yl radical is in electronic resonance with the 1,3-butadien-2-yl structure  $\text{CH}_2=\text{CH}\dot{\text{C}}=\text{CH}_2^*$ .

The energy of the incident photon at 147 nm is 194 kcal einstein<sup>-1</sup>. If the above mechanism is still valid, secondary fragmentation will be more favoured than it would be at 184.9 nm. For example, the large quantity of vinylacetylene may be the result of the fragmentation of the excited  $\text{C}_4\text{H}_5^*$  species formed in processes (19) and/or (24) (Table 6):



This assertion is also true for the ethyl radical, so that the following overall process may be quantitative at low pressures:



$$\Delta H = 163.5 \text{ kcal mol}^{-1}$$

TABLE 6

Photolysis of 1-hexyne at 147 nm: quantum yields<sup>a</sup>

	<i>Quantum yields for the following pressures (Torr) of 1-hexyne</i>						
	10	30	3 (10% O <sub>2</sub> )	10 (10% O <sub>2</sub> )	30 (10% O <sub>2</sub> )	3 (10% DI)	10 (10% DI)
Methane	0.05	0.03	0.02	0.02 <sub>5</sub>	0.01 <sub>2</sub>	0.27	0.33
Acetylene	0.05 <sub>5</sub>	0.06 <sub>5</sub>	0.05	0.04	0.04	0.05	0.05
Ethylene	0.70	0.45	0.90	0.65	0.47	0.81	0.70
Ethane	0.05	0.03 <sub>5</sub>	0.00	0.00	0.00	0.38	0.40
Propene	0.37	0.20	0.54	0.35	0.23	0.50	0.42
Propadiene	0.02	0.02	0.03	0.02 <sub>5</sub>	0.02	0.03 <sub>5</sub>	0.08
Propyne	0.02	0.02 <sub>5</sub>	0.02	0.02	0.03	0.04	0.18
Propane	0.05	0.03 <sub>5</sub>	0.00	0.00	0.00	0.05	0.07
Vinylacetylene	0.26	0.15	0.27 <sub>6</sub>	0.22	0.15	0.29	0.25
1,3-butadiene	0.08	0.04	0.12 <sub>5</sub>	0.05	0.05	0.12	0.11
1-butyne	0.07	0.05	0.0	0.0	0.0	0.11	0.14
1,2-butadiene	0.02	0.01 <sub>2</sub>	0.0	0.0	0.0	0.00	0.01
n-butane	0.03	0.02 <sub>4</sub>	0.00	0.00	0.00	0.03	0.03

<sup>a</sup> $\Delta\Phi/\Phi \approx 0.10$ .

TABLE 7

Photolysis of 1-hexyne at 184.9 nm: primary processes

Process	$\Phi$
$C_6^{**} \rightarrow n\text{-}C_3H_7^* + C_3H_3$ $\quad \quad \quad \downarrow$ $\quad \quad \quad C_2H_4 + CH_3$	0.53 (0.38)
$C_6^{**} \rightarrow C_3H_4 + C_3H_6$	0.03 <sub>5</sub>
$C_6^{**} \rightarrow C_2H_5 + C_4H_5$	0.23
$C_6^{**} \rightarrow \text{fluorescence}$	0.01
<b>Total</b>	<b>0.80<sub>5</sub></b>

Table 7 summarizes the fate of the photoexcited 1-hexyne molecules. Again at least three primary photochemical processes are identified: the  $\beta(C-C)$  bond rupture, the retro-ene process and the  $\gamma(C-C)$  bond rupture. However, the relative importance of each of these processes is different from that in the 1-hexene case. In both cases the  $\beta(C-C)$  bond rupture is the major contributor, but the  $\gamma(C-C)$  bond rupture in 1-hexyne is twice that in 1-hexene. The  $\gamma$  bond rupture is exemplified by the high vinylacetylene quantum yield measured at 147.0 nm. Moreover if this  $\gamma(C-C)$  bond rupture is actually a  $\beta(C-C)$  bond rupture following a 1,3 hydrogen shift, we require to know whether this 1,3 hydrogen shift occurs more easily in the photoexcited 1-hexyne molecule than in the photoexcited 1-hexene molecule. A photophysical process, *i.e.* fluorescence, has been observed in each compound. The fluorescence quantum yields of 1-hexene and 1-hexyne at 184.9 nm are  $2 \times 10^{-6}$  [18] and 0.01 [19] respectively. Again, the difference is important and may be partially due to the longer lifetime of the photoexcited 1-hexyne molecule. Unfortunately the complexity of the fragmentation pattern of this molecule precludes a study of its lifetime similar to that performed for 1-hexene (Fig. 4).

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