

GAS PHASE PHOTOLYSIS OF 1-PENTENE AT 123.7 nm (10.0 eV)

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Summary

The photolysis of gaseous 1-pentene was carried out in a static system using the krypton resonance line at 123.7 nm (10.0 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, propyne and 1-pentyne. The minor products included methane, ethane, propane, some C_5H_8 and C_4H_6 hydrocarbons, and 1-butene. The radical species were identified using scavengers such as oxygen, H_2S and HI. The pressure dependence of the yields of the major radicals (C_3H_5 , CH_3 , C_2H_5 , C_2H_3 , C_3H_7 and C_4H_7) was established. The C_2H , C_4H_5 , CH_2 and C_3H_3 radicals were found to be unimportant.

The primary decomposition channels are established. The cleavage of a C-H bond occurs with a yield of $\phi = 0.34 \pm 0.06$ and the cleavage of a C-C bond occurs with nearly the same yield of $\phi = 0.39 \pm 0.06$. The C-C bond breaks mainly in the position which is β to the double bond; some contribution ($\phi = 0.06$) is due to a rupture in the γ position which yields stable C_4H_7 radicals. All four primary intermediates, *i.e.* C_5H_9 , C_3H_5 , C_2H_5 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. The contribution of ionic processes to the formation of low molecular weight products is slight. Some details of the secondary processes are established but the overall mechanism is too complex to be fully unravelled.

1. Introduction

The vacuum UV photolysis of 1-pentene has been studied extensively [1 - 4]. In recent work from this laboratory [4] we have reported investigations of 1-pentene irradiated with 8.4 eV photons over a wide range of pressures in the presence of scavengers. The occurrence of a competition between dissociation and collisional stabilization has made it possible to distinguish be-

tween primary and secondary decompositions. In the present work these studies were extended to the higher energy of 10.0 eV, *i.e.* slightly above the ionization potential (9.50 eV [5]) of 1-pentene, in order to obtain data on the dissociation of superexcited molecules and to gain some information on ionic processes.

2. Experimental

The experimental techniques were the same as those previously described [4]. As in the 8.4 eV photolysis the actinometry was based on $\phi(\text{C}_2\text{H}_2)$ 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 123.7 nm photolysis of ethylene. It was found that for conversion greater than approximately 5% the results were appreciably affected; therefore the conversion was always kept below 2%, being well below 1% at greater pressures.

3. Results

The quantum yields of the products are given in Table 1; to conserve space only three exemplary pressures (1, 4.8 and 28.6 Torr) are shown. The details of the pressure dependence for some major products can be seen in Figs. 1 and 2.

Propyne and allene were considered together since the ratio of their yields was constant in all runs, *i.e.* 0.13 ± 0.02 . Some products not included in Table 1 persisted in the presence of oxygen: C_4H_6 hydrocarbons, 2-butenes, vinylacetylene, cyclopropane, propylcyclopropane and 2-pentenenes. All were formed with very small yields not exceeding $\phi = 0.004$. 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.

In a separate series of experiments ammonia added in the presence of oxygen was found to lower the yields for ethane, propane and *n*-pentane. The results are shown in Table 2.

4. Discussion

4.1. Introduction

Following closely the reasoning applied previously [4] it can be deduced that of the four basic processes contributing to the overall dissociation involving the rupture of the C-C bond, *i.e.*



TABLE 1
 Photolysis of 1-pentene at 10.0 eV: effect of pressure and the presence of scavengers on the formation of products

Total pressure	1 Torr (1.33 hPa)		4.76 Torr (6.33 hPa)		28.6 Torr (38.1 hPa)	
	8	15	8	15	8	15
O ₂ (%)	—	—	—	—	—	—
H ₂ S (%)	—	15	—	15	—	15
HI (%)	—	—	—	—	—	—
		10		10		10
Methane	0.02 ^a	0.32	0.01	0.26	0.02	0.24
Acetylene	0.08	0.08	0.065	0.065	0.06	0.06
Ethylene	0.32	0.36	0.28	0.32	0.23	0.27
Ethane	0.03	0.46	0.035	0.28	0.02	0.19
C ₃ H ₄ ^b	0.19	0.18	0.15	0.15	0.12	0.13
Propylene	0.32	0.33	0.14	0.18	0.07	0.20
Propane	0.02	0.10	0.08	0.09	0.03	0.08
1,3-Butadiene	0.13	n.d. ^c	0.12	n.d.	0.11	0.11
1-Butene	0.006	0.06	0.01	0.08	0.008	0.07
1-Pentyne	0.08	0.07	0.07	0.06	0.08	0.08
C ₅ H ₈ ^d	0.06	0.02	0.04	0.01	0.04	0.06
n-Pentane	0.02	0.70	0.03	0.75	0.04	0.015
$\Sigma\phi_{C_2} + 2\Sigma\phi_{C_3}$	0.98		0.95		1.03	
$\Sigma\phi_{C_3} + 2\Sigma\phi_{C_4}$						

^aAll values are in quantum yield units.

^bThe total of allene and propyne.

^cn.d., not determined.

^dThe total of 1,2-1,3- and 1,4-pentadienes.

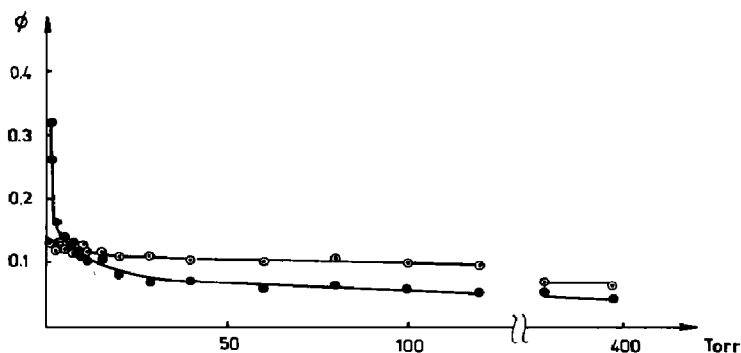


Fig. 1. The dependence of the quantum yields for 1,3-butadiene (○) and propylene (●) on pressure (1-pentene irradiated in the presence of 8% O₂).

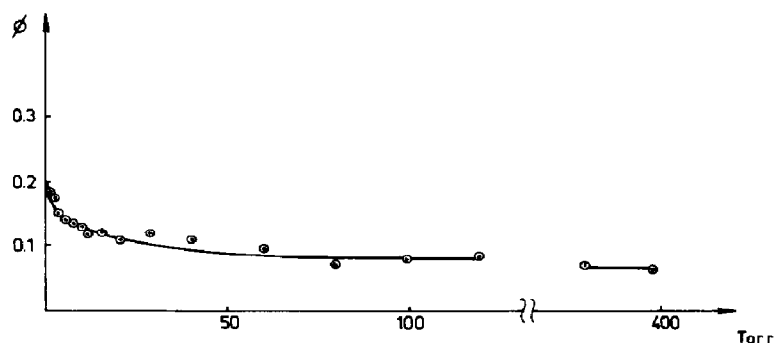


Fig. 2. The dependence of the total quantum yield for allene and propyne on pressure (1-pentene irradiated in the presence of 8% O₂).

TABLE 2

The effect of ammonia on the quantum yields of some products in the presence of 8% O₂ at a 1-pentene pressure of 8.6 Torr

	—	10% NH ₃	30% NH ₃
$\phi_{C_2H_6}$	0.022	0.010	0.006
$\phi_{C_3H_8}$	0.029	0.012	0.005
$\phi_{n-C_5H_{12}}$	0.035	0.010	0.005

$$C_5 = C_4 + C_1 \quad (3)$$

$$C_5 = C_3 + 2C_1 \quad (4)$$

(where C₅ is any excited species with five carbon atoms), process (4) is of no importance (within the limits of experimental error). Therefore the simplified equation eqn. (5) should be obeyed:

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

(ϕ_{C_n} denotes the yield for the product — either a stable molecule or a free radical — that has n carbon atoms). This is indeed the case as can be seen in Table 1. Apparently all the fragmentation products are determined and the analyses are fairly accurate.

A procedure analogous to that used previously [4] enables the assessment of the quantum yield for every dissociation channel of the decomposing superexcited molecule. The pressure dependence of such data is shown in Table 3.

TABLE 3

Fragmentation of the photoexcited 1-pentene molecule at 10.0 eV and different total pressures

		1 Torr (1.33 hPa)	4.76 Torr (6.33 hPa)	28.6 Torr (38.1 hPa)	100 Torr (133 hPa)
I	1,3-C ₄ H ₆ + CH ₃ + H	0.13	0.12	0.11	0.10
II	C ₂ H ₂ + C ₃ H ₇ + H C ₂ H ₃ + CH ₃ + C ₂ H ₄	0.13	0.12	0.09	0.08
III	C ₃ H ₅ + C ₂ H ₄ + H	0.07	0.10	0.12	0.14
IV	C ₃ H ₄ + C ₂ H ₅ + H	0.10	0.10	0.10	0.08
V	C ₃ H ₅ + C ₂ H ₅	—	—	—	0.05
VI	C ₃ H ₄ + C ₂ H ₄ + 2H	0.09	0.05	0.02	—
VII	1-C ₅ H ₈ + 2H(H ₂)	0.08	0.08	0.07	0.08
	C ₅ H ₈ ^a + 2H(H ₂)	0.05	0.04	0.05	0.06
VIII	C ₄ H ₇ + CH ₃	0.06	0.06	0.07	0.06
Total		0.71	0.68	0.63	0.65

^a The total for the yields of 1,2- 1,3- and 1,4-pentadienes.

To avoid repeating the arguments already advanced [4], in what follows the discussion will be limited only to more detailed considerations of the differences between the 8.4 and 10.0 eV photolyses.

4.2. C-H cleavage

At a photon energy of 8.4 eV the primary cleavage of a C-H bond is responsible for the formation of 1,3-butadiene — process I in Table 3.



The same holds true at 10.0 eV, even though the stable C₄H₇ radical is also formed. However, $\phi_{C_4H_7} = 0.06$ was found to be independent of pressure; therefore the alternative mechanism, which involves the primary rup-

ture of a C–C bond between the fourth and the fifth carbon atoms followed by the dissociation of the excited C_4H_7 radical into atomic hydrogen and butadiene, should be rejected. The decrease in $\phi_{C_4H_6}$ with increasing pressure (see Fig. 1) is less pronounced at 10.0 eV than at 8.4 eV; this is not surprising since pentenyl radicals formed in reaction (6) should possess a greater excess of internal energy. $\phi_{1,3-C_4H_6}$ extrapolated to zero pressure is 0.14, and is assumed to be equal to the yield for process I ($\phi_I = 0.14$).

As in the treatment of the xenon photolysis, products such as acetylene, ethylene, vinyl and propyl radicals (together with corresponding fragments necessary to obtain a stoichiometric balance — see process II in Table 3) are dealt with jointly. We believe that a mechanism suggested for the 8.4 eV photolysis, *i.e.* primary C–H bond splitting followed by the dissociation of the excited C_5H_9 radicals, may be used to explain the results obtained at 10.0 eV, although we admit that the mechanism is more open to criticism for the 10.0 eV photolysis. At higher energy the pressure dependence of process II is, as is only to be expected, less marked and some contribution to the formation of these products through the primary breakage of a C–C bond cannot be ruled out.

As previously stressed the detailed balancing of all the reactions leading to the corresponding products, although feasible, seems to be of no value. We assume arbitrarily that about half of the products originating in process II are formed as a result of the primary C–C bond splitting; the other half are ascribed to the primary cleavage of a C–H bond. The error due to this assumption in the estimation of the respective contributions of the two primary processes is not large, since the yield for process II extrapolated to zero pressure is 0.14.

A new reaction, practically unobserved at 8.4 eV ($\phi \approx 0.01$ [4]), is the formation of 1-pentyne with a yield of approximately 0.08:



Also the yields for the other C_5H_8 hydrocarbons are slightly higher than those at 8.4 eV. Pressure does not affect (within the limits of experimental error) the yields for these C_5H_8 hydrocarbons which indicates the occurrence of a single-step process, *i.e.* the elimination of either a hydrogen molecule or two hydrogen atoms.

Although it is possible in principle to achieve a material balance of atomic hydrogen, in practice such a task would be very difficult. The following products that have atomic hydrogen as a precursor should be determined in the presence of HI: (a) molecular hydrogen formed in the reaction of hydrogen atoms with HI and 1-pentene (the presence of hot hydrogen atoms makes such an estimate especially difficult); (b) *n*-pentane, formed by the addition of hydrogen atoms to 1-pentene followed by the stabilization of pentyl radicals reacting subsequently with hydrogen iodide; (c) products of the decomposition of excited pentyl radicals, *i.e.* propylene and ethyl radicals, and ethylene and *n*-propyl radicals.

Not only the yields for all these products should be accounted for but also appropriate assumptions should be made concerning the ratios of the

rate constants for the reactions of hydrogen atoms with HI and 1-pentene (which are dependent on the energy of the hydrogen atoms). The substantial errors occurring in such estimations would have made them useless.

The use of H₂S instead of HI would be of no avail. The yield for *n*-pentane is much greater in the presence of H₂S than in the presence of HI due to the occurrence of ionic reactions which transform alkenes into the corresponding alkanes [6]. Since reaction (9) does not occur at 8.4 eV its occurrence at 10.0 eV involves a superexcited molecule of 1-pentene. Ultimately these considerations lead to the assessment of the yield for C-H bond rupture at 10.0 eV as being equal to 0.34 ± 0.06 .

4.3. C-C cleavage

C-C bond rupture occurs mainly in the position which is β to the double bond, similar to that in the xenon photolysis:



Both fragments are excited and are capable of further decomposition yielding allene, propyne and ethylene (processes III - V in Table 3; the pressure dependence of $\phi_{\Sigma\text{C}_3\text{H}_4}$ is shown in Fig. 2). Although the detailed balancing of the individual processes at different pressures would not be accurate, it could be established that the yields for stabilized C₃H₅ and C₂H₅ radicals increase at the expense of C₃H₄ and C₂H₄ with increasing pressure. The total yield for reaction (10) is $\phi_{(10)} = 0.26$ and is independent of pressure.

The increase in $\phi_{\text{propyne}}/\phi_{\text{allene}}$ from 0.1 at 8.4 eV to 0.13 at 10.0 eV is worth noting. A similar observation has been made in the photolyses and radiolysis of 1-butene, and has been ascribed to the greater excess energy of the C₃H₅ radicals [6, 7].

A new product, practically absent in the xenon photolysis, is a stable C₄H₇ radical; it is formed with a yield which is independent of pressure, indicating the occurrence of a primary reaction:



Więckowski and Collin [3] have reported $\phi_{\text{C}_4\text{H}_7} = 0.02$ at a photon energy in the range 7.1 - 7.6 eV but they have not established the pressure dependence of this yield.

The enthalpy for reaction (11) is about 85 kcal mol⁻¹. At a photon energy of 231 kcal mol⁻¹ (10.0 eV) the excess energy of both fragments should amount to about 146 kcal mol⁻¹. Using a very rough approximation, *i.e.* taking into account only the number of degrees of freedom of both fragments, it could be assessed that, under the free flow of energy hypothesis, the mean excess energy for C₄H₇ radicals would have reached a level of about 110 kcal mol⁻¹, *i.e.* far in excess of that required for splitting C₄H₇ into C₄H₆ and atomic hydrogen. (The threshold energy is about 35 kcal mol⁻¹; this value was estimated on the basis of the enthalpy and the activation energy reported for the reverse reaction [8].) The radical might be expected to decompose which is not the case. Although very approximate,

these considerations indicate departure from statistical behaviour. Apparently the methyl group in the 1-pentene molecule absorbs the energy, and dissociation follows the conversion of electronic excitation into oscillation excitation so rapidly that complete randomization prior to decomposition is not attained.

Looking for other primary processes involving the cleavage of a C-C bond we should account for the formation of methylene in the following reaction:



Such a reaction occurs, as is evidenced by the presence of propylcyclopropane among the photolysis products, but its yield as well as the yield for 1-butene in the presence of oxygen are so small that the contribution of this process is unimportant.

Therefore the yield for the primary rupture of a C-C bond can be finally assessed as being equal to 0.39 ± 0.06 .

The total quantum yield for the dissociation of a 1-pentene molecule extrapolated to $p = 0$ is 0.72. Since the ionization quantum yield is $\phi = 0.17$ [9], $\Sigma\phi \approx 0.9$ can be obtained. The deviation from unity is small (within the limits of experimental error of pentene photolyses and actinometry).

It is interesting to consider the dependence of the yield for the primary rupture of C-C and C-H bonds on the energy of the photons, based on the present data and those obtained in Collin's laboratory. Taking into account only main and unequivocally established processes of the primary dissociation of C-C (reaction (10)) and C-H (reactions (6), (7) and (9)) bonds, it can be observed that the yield for the rupture of the weakest bond in the molecule (C-C in the position β to the double bond) decreases with increasing photon energy (from $\phi = 0.64$ at a photon energy of 7.1 eV to $\phi = 0.26$ at 10.0 eV; see Table 4). These data can be compared with those obtained in the photolysis of 1-butene (see Table 5).

The yields for the rupture of the allylic C-C bond are nearly the same for both hydrocarbons. Apparently the role of the double bond is crucial; the excitation of π electrons seems to be most likely. With increasing photon energy the contribution of absorption by σ electrons of the C-H bonds increases; further processes of energy transformation result in an increase in C-H bond rupture, as is evidenced by the increase in the yields of the respective products in the photolyses of both 1-pentene and 1-butene. It would be of great importance to estimate the yields for the cleavage of individual C-C and C-H bonds. Unfortunately the experimental data hitherto available are of little help. The destruction of the molecule is so complete that for many dissociation products two or more alternative reaction pathways can be proposed; we have already mentioned this problem in Section 4.2. We think that the commonly used conventional methods of photolytic investigations, which are based on the analysis of stable products combined with the use of scavengers, isotopic labelling and so on, are not adequate for establishing with reasonable certainty the precise mechanism of primary processes. There

TABLE 4

Comparison of some fragmentation patterns of the 1-pentene molecule at different energies

		7.1 eV [3]	7.6 eV [3]	8.4 eV [2]	8.4 eV [4]	10.0 eV This work
I	$C_4H_6 + CH_3 + H$	0.08	0.09	0.15	0.16	0.14
V	$C_3H_5 + C_2H_5$	0.64	0.74	0.48	0.47	0.26
VII	$C_5H_8 + 2H(H_2)$	n.d. ^a	n.d.	0.06	0.05	0.13
ϕ_I/ϕ_V		0.125	0.122	0.312	0.34	0.54

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

The quantum yields are extrapolated to zero pressure.

^a n.d., not determined.

TABLE 5

Comparison of some dissociation pathways of the excited 1-butene molecule at different photon energies

Process	Bond undergoing rupture	7.1 eV [10]	8.4 eV [11]	10.0 eV [6]
$C_3H_5 + CH_3$	C-C	0.66	0.51	0.29
$C_4H_6 + 2H(H_2)$	C-H	0.06	0.14	0.23
$C_4H_7 + H$	C-H	0.16	0.12	?

The literature data were calculated using a mechanism similar to that proposed for 1-pentene [4].

is a great need for independent data on the kinetics of reactions of highly excited C_4H_7 and C_5H_9 radicals having different structures.

4.4. Dissociation of pentyl radicals

The pressure dependence of $\phi_{C_3H_6}$ (see Fig. 1) can be explained by the occurrence of hydrogen atom addition to 1-pentene followed by the dissociation of an excited pentyl radical:



A comparison of the results obtained at 8.4 and 10.0 eV reveals that the pressure dependence on $\phi_{C_3H_6}$ is smaller at 10.0 eV; hence, the apparent rate constant for the *sec*- C_5H_{11} decomposition is greater. The result is explained by assuming that at greater photon energy the hydrogen atoms would have more kinetic energy. A similar phenomenon has been observed in the photolysis of 1-butene [6, 11].

4.5. Ionic processes

Since the energy of the photons exceeds that required for ionization, the formation of ionic products should be examined. Ammonia, which is expected to scavenge positive ions, was found to decrease the yield of ethane, propane and *n*-pentane when used in the presence of oxygen (see Table 2).

Similar processes have been observed in the krypton photolysis of 1-butene; there the yields for ethane and *n*-butane were affected by the presence of ammonia.

The mechanism of these ionic reactions is not understood. *n*-Pentane probably originates from the well-known hydrogen transfer from a higher order ion to 1-pentene. There is no evidence that the ions contribute to the formation of other low molecular weight products. In pure 1-pentene the primary $C_5H_{10}^+$ ions will probably undergo ionic polymerization. We did not attempt to examine this process.

5. Conclusions

The increase in photon energy from 8.4 to 10.0 eV resulted in a decrease in the yield for the rupture of an allylic C–C bond, confirming the trend observed in the photolysis of 1-pentene over the range of energies 7.1 - 8.4 eV as well as in the photolysis of 1-butene. Two new channels of the primary dissociation of the superexcited pentene molecule were observed: the formation of 1-pentyne and the formation of stable C_4H_7 radicals. The stable C_4H_7 radical originates from the cleavage of a C–C bond in the position γ to the double bond; the occurrence of this reaction involves deviations from statistical behaviour.

The ionic processes are of little importance in the formation of low molecular weight products.

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