

VACUUM UV PHOTOLYSIS OF *n*-1-HEXENE AND 4-METHYL-1-PENTENE

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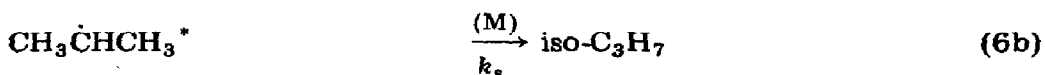
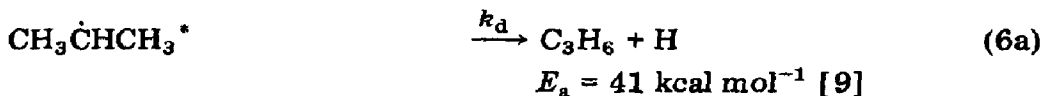
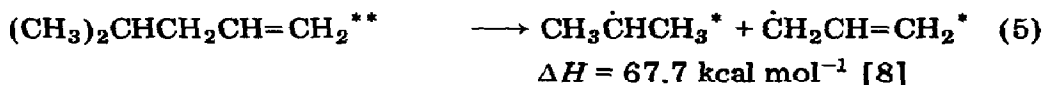
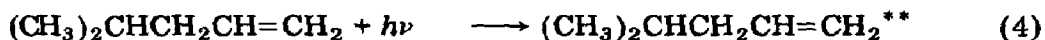
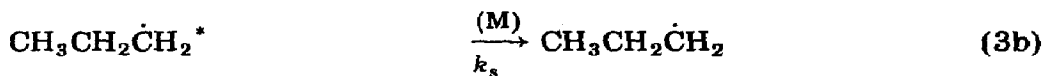
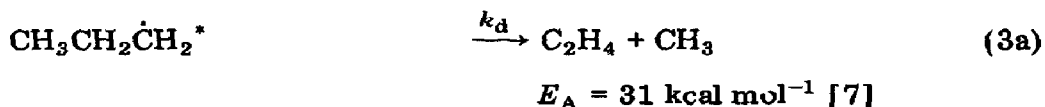
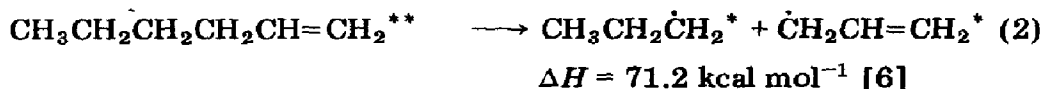
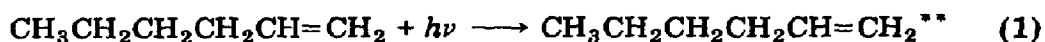
Summary

We studied the vacuum UV photolysis of *n*-1-hexene and 4-methyl-1-pentene at 147, 163 and 174 nm. In both systems the use of NO or O₂ and DI indicates that the main fragmentation process ($\Phi \approx 0.8$) of the 147 nm photoexcited molecule is the breaking of the C—C bond located at the β position. This process leads to the formation of allyl and propyl radicals. The propyl radicals decompose further at low pressure, giving rise to the formation of ethylene or propylene. By following the pressure effect on the ethylene or propylene quantum yields, and using RRKM results, it is shown that the *n*-propyl radicals formed in the *n*-1-hexene photolysis carry less energy than would be expected from a statistical distribution of the excess energy. The situation seems to be more complex for 4-methyl-1-pentene, and the isopropyl radicals have an energy content not far from the statistical distribution.

1. Introduction

Recently we have shown that, in the vacuum UV photolysis of gaseous olefins, the quantum yields of several products are pressure dependent [1, 2]. The rate constants k_d of the decomposition process of several intermediates have been calculated using the rate constant of the stabilization process (via collision) as an internal standard. By the use of simple RRKM calculations, these k_d values have been used to determine the energy content of some unsaturated radical intermediates in order to throw more light on the distribution of the excess energy of the photon between the fragments [3, 4]. Unfortunately only a fraction of these unsaturated intermediates decompose at low pressure. Therefore it has been impossible to determine the excess energy distribution accurately. In this work we photolyse *n*-1-hexene and 4-methyl-1-pentene. In both cases the expected main fragmentation process is the breaking of the β C—C bond [5]. Because the resulting

n-propyl and isopropyl radicals carry part of the excess energy, they are expected to undergo decomposition at low pressure:



where M^{**} is a photoexcited molecule and R^* is an excited radical formed in the primary decomposition process of the photoexcited molecule.

Thus this work has a double purpose. We will confirm the validity of this mechanism and we will try to obtain information on the excess energy distribution [10] from Stern-Volmer plots ($\{\Phi(x)\}^{-1}$ versus the total pressure) of the ethylene quantum yield (n-1-hexene photolysis) and of the propylene quantum yield (4-methyl-1-pentene photolysis).

2. Experimental

The experimental details have been described previously [1 - 4]. Oxygen (99.99%) was a Matheson Research Purity product. DI was obtained from Merck, Sharp and Dohme of Canada. n-1-Hexene (99.86%) and 4-methyl-1-pentene (99.82%) were API standard reference materials and were used as received after being degassed on a mercury-free vacuum line equipped with Teflon stopcocks. Xenon resonance lamps as well as bromine and nitrogen resonance lamps were used. Chemical actinometry was carried out. The area of each peak of the chromatographic analysis was compared with that of the acetylene peak obtained in the photolysis of *cis*-2-butene and this procedure was performed each day.

The gas chromatographic techniques are also well known. A squalane column or a durapak column was installed in a chromatograph equipped with a double-flame ionization detector. This system had a good reproducibility of $100 \pm 3\%$ and the estimated error, including the actinometry for each quantum value, was well below 5%.

3. Results

3.1. *n*-1-Hexene

The quantum yields of several products formed at a pressure of 1 Torr in the pure system or in the presence of additives are reported in Table 1. In each case the main product is ethylene.

At 147 nm the quantum yield of ethylene is close to 0.90, both in pure hexene and in the presence of O₂ or DI. The addition of 10% O₂ eliminates the formation of ethane, propane, 1-butene and several C₆ products, and diminishes that of propylene. In the presence of 20% DI the methane and propylene quantum yields are almost as great as that of ethylene, *i.e.* $\Phi(\text{CH}_4) \approx \Phi(\text{C}_3\text{H}_6) = 0.80$. Moreover, in the presence of DI the ethane and propane yields increase and *n*-hexane is a new product (Tables 1 and 2). For the ethylene and propylene quantum yields a strong pressure effect was observed; in Fig. 1 the variation of $\{\Phi(x)\}^{-1}$ with the total pressure (Stern-Volmer plots) is shown.

Because the results obtained at 163 and 174 nm are similar to those measured at 147 nm they will not be discussed in detail. However, some comments should be added. Contrary to the observations at 147 nm, the addition of DI at 163 nm does not completely eliminate the formation of 1,5-hexadiene, nor does it strongly increase the methane and propylene yields. Although we have no proof of it, the scavenging effect of DI on allyl radicals is probably slower than that on propyl radicals. This effect, combined with the high intensity output of the bromine lamp, prevents the scavenging of all the allyl radicals by 20% DI. In fact, in the presence of 20% DI, we did not obtain a plateau value for the propylene yield.

Finally, it should be mentioned that the measured quantum yields decrease with an increase in the photolysing wavelength. Thus (Table 1), $\Phi(\text{C}_2\text{H}_4)$ is 0.86, 0.55 and 0.34 at 147, 163 and 174 nm respectively.

3.2. 4-Methyl-1-pentene

The measured values for the quantum yields of 16 products obtained under various conditions are shown in Table 3. They are very similar to those shown in Table 1 and as such do not need to be presented in detail.

TABLE 1
 Photolysis of n-1-hexene at a pressure of 1 Torr^a in the presence of additives^b: quantum yields

Product	Wavelength = 147 nm			Wavelength = 163 nm			Wavelength = 174 nm		
	O ₂	DI	-	O ₂	DI	-	O ₂	DI	-
CH ₄	0.035	0.015	0.80	0.04	0.01	0.39	0.015	0.006	0.42
C ₂ H ₂	0.020	0.020	0.05	0.010	0.01	0.01	0.006	0.009	0.009
C ₂ H ₄	0.86	0.84	0.87	0.45	0.55	0.55	0.34	0.34	0.39
C ₂ H ₆	0.145	0.00	0.22	0.094	0.00	0.10	0.07	0.00	0.09
C ₃ H ₆	0.19	0.13	0.80	0.075	0.08	0.16	0.05	0.05	0.30
C ₃ H ₈ ^c	0.07	<0.01	0.20	0.034	0.002	0.09	0.026	0.001	0.08
C ₃ H ₄ ^c	0.030	0.030	0.026	0.005	0.003	0.01	0.002	0.001	0.006
1,3-C ₄ H ₆	0.08	0.10	0.09	0.06	0.05	0.12	0.04	0.025	<0.10
1-C ₄ H ₈	0.30	<0.02	0.05	0.14	0.05	0.12	0.11	0.02	0.02
1,5-C ₆ H ₁₀	0.13	0.00	0.00	0.072	n.d. ^f	0.10	0.045	0.00	0.00
C ₆ H ₁₄	0.07 ^d	0.00	0.28 ^e	0.03 ^d	n.d.	0.10 ^e	0.02 ^d	0.00	0.06

^a 1 Torr = 133 N m⁻².

^b O₂ (10%) or DI (20%).

^c Allene; Φ (propyne) \leq 0.01; $\Delta\Phi/\Phi \geq$ 5%.

^d 2,3-Dimethylbutane.

^e n-C₆H₁₄.

^f Not determined.

TABLE 2

Effect of DI in the photolysis of n-1-hexene at various pressures

Total pressure (Torr) ^a	$\Phi(\text{CH}_4)$	$\Phi(\text{C}_2\text{H}_4)$	$\Phi(\text{C}_2\text{H}_6)$	$\Phi(\text{C}_3\text{H}_8)$	$\Phi(\text{n-C}_4\text{H}_{10})$
0.6	0.91	0.78	0.22	0.16	0.00
2.4	0.83	0.71	0.20	0.21	0.02
12.0	0.72	0.61	0.18	0.25	0.03
41.0	0.61	0.57	0.165	0.285	0.03

^a 1 Torr = 133 N m⁻²; n-1-hexene:DI = 100:20; $\Delta\Phi/\Phi > 5\%$.

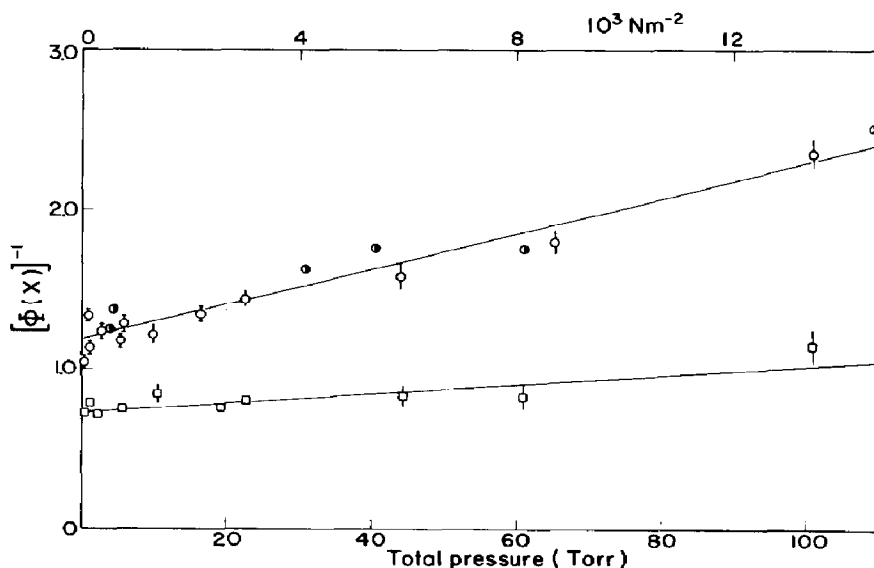


Fig. 1. Stern-Volmer plots ($\{\Phi(x)\}^{-1}$ vs. total pressure) for the formation of ethylene and propylene in the 147 nm photolysis of n-1-hexene: \bullet , \circ , ethylene; \circ , n-1-hexene:O₂ = 100:10; \bullet , n-1-hexene:DI = 100:20; \square , propylene \times 10.

4. Discussion

4.1. Fragmentation of the photoexcited species

4.1.1. n-1-Hexene

At 147 nm in the pure system, or in the presence of oxygen, ethylene is the major product with a high quantum yield; $\Phi(\text{C}_2\text{H}_4) \approx 0.88$. The addition of DI significantly increases the quantum yields of methane and propylene:

$$\Delta\{\Phi(\text{CH}_4)\} = \Phi_{\text{DI}}(\text{CH}_4) - \Phi_{\text{O}_2}(\text{CH}_4) \approx 0.78$$

and

$$\Delta\{\Phi(\text{C}_3\text{H}_8)\} = \Phi_{\text{DI}}(\text{C}_3\text{H}_8) - \Phi_{\text{O}_2}(\text{C}_3\text{H}_8) \approx 0.67$$

Assuming that DI is a good radical scavenger [11 - 13]

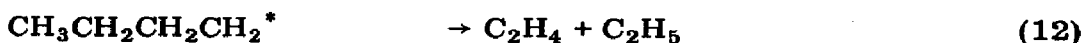
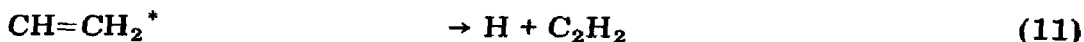
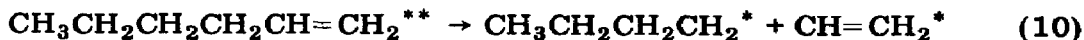


then the large increase in the yields of methane and propylene should be related to the presence of the methyl and C_3H_5 radicals. Thus, $\Phi(CH_3) = \Delta\{\Phi(CH_4)\}$ and $\Phi(C_3H_5) = \Delta\{\Phi(C_3H_6)\}$. The nature of the C_3H_5 radical can be determined from the formation of 1-butene and 1,5-hexadiene in the pure system. Both products disappear in the presence of oxygen (Table 1). Thus the radical nature of their formation is confirmed and both products originate from the reactions of allyl radicals. It follows that the main fragmentation products are ethylene, and methyl and allyl radicals. From Table 2 it can be seen that the sum $\Phi_{DI}(C_3H_8) + \Phi_{DI}(C_2H_4)$ is constant between 0.6 and 41 Torr, *i.e.* $\Phi_{DI}(C_3H_8) + \Phi_{DI}(C_2H_4) = 0.89 \pm 0.04^*$. Thus from an analysis of the pressure effect it seems that, in the presence of DI, ethylene and propyl radicals have the same precursors. All these observations are expected and are in agreement with processes (1), (2) and (3).

Other minor processes are also active in this system. For example, the quantum yield of 1,3-butadiene both in the absence and the presence of additive, together with the formation of ethane in the presence of DI, may be ascribed to the following mechanism (see also the formation of 1-butene in the presence of DI):



From the behaviour of the 1,3-butadiene quantum yield with pressure, a value for $\Phi_0(1,3\text{-butadiene})$ of 0.10 ± 0.02 can be obtained. Thus, $\Phi_0(9a) = 0.10$. The yield of process (9b) may be obtained from the yield of 1-butene in the DI system; $\Phi(9b) \approx 0.05 \pm 0.02$. These results give a maximum value for process (8) of $\Phi(8) = \Phi(9a) + \Phi(9b) = 0.15 \pm 0.04$. The formation of ethane shows a higher ethane quantum yield in the DI system; $\Phi_{DI}(C_2H_6) \approx 0.22$ at low pressure. However, because the $\Phi_{DI}(C_2H_6)$ value decreases with increasing pressure (Table 2), another source for the ethyl radical is required. The reactions



and the stabilization processes via collision of the excited intermediates $CH=CH_2^*$ and $CH_3CH_2CH_2CH_2^*$ are the most likely explanations for (1) the

*One referee states "the total $\Phi(C_3H_8) + \Phi(C_2H_4)$ does not seem to be constant (Table 2)... There is probably another route yielding the propane..." We have ignored this possibility since the minimum and maximum values for the sum are 0.855 ± 0.05 and 0.94 ± 0.05 (experimental uncertainties).

increase of $\Phi_{DI}(n-C_4H_{10})$ values with increasing pressure (Table 2), (2) the formation of tiny amounts of acetylene and (3) the ethane quantum yield measured in the presence of DI.

Process (10) is not very important and may be roughly estimated from the $\Phi_{DI}(n-C_4H_{10})$ value and the increased $\Phi_{DI}(C_2H_6)$ value measured at high pressure. Thus the $\Phi(10)$ value is probably not greater than 0.05. The same value may be calculated from the $\Delta\{\Phi(C_2H_4)\}$ value:

$$\Delta\{(C_2H_4)\} = \Phi_{DI}(C_2H_4) - \Phi_{O_2}(C_2H_4)$$

and from the acetylene quantum yield measured in the presence of oxygen.

The propylene formation process could not be easily determined in this work. One possibility is that a small fraction of the n-propyl radicals may undergo decomposition to propylene and a hydrogen atom. The decrease of its quantum yield with decreasing photon energy indicates that this process may be more important at higher energy [9].

Thus, the main fragmentation processes of the photoexcited n-1-hexene molecules are reactions (2), (8) and (10) with quantum yields of 0.81 ± 0.03 , 0.15 ± 0.04 and 0.05 ± 0.02 respectively. The quantum yield of process (1) is lower than that for the formation of ethylene at zero pressure (see Fig. 1), because ethylene is also formed in process (12).

At 163 and 174 nm the results are similar to those measured at 147 nm. However, it is evident that the secondary processes are of lesser importance. For example, the quantum yields of acetylene, ethylene, propylene, ... decrease with an increase in the incident wavelength (Table 1).

4.1.2. 4-Methyl-1-pentene

At 147 nm the results are similar to those obtained in the n-1-hexene system, except that propylene is the major product (Table 3). The addition of NO eliminates the formation of ethane, propane, isobutane, 1,5-hexadiene and 2,3-dimethylbutane. Therefore these products probably arise through radical-radical reactions. Because of their nature, they are probably formed from methyl, isopropyl and allyl radicals. The quantum yields of several radical intermediates can be calculated from the increase of the quantum yields on the addition of DI. Thus $\Delta\{\Phi(CH_4)\} = 0.28 = \Phi(CH_3)$, $\Delta\{\Phi(C_2H_4)\} = 0.02 = \Phi(C_2H_3)$, $\Delta\{\Phi(C_3H_8)\} = 0.31 = \Phi(C_3H_7)$ and $\Delta\{\Phi(C_6H_{14})\} = 0.14 = \Phi(C_6H_{13})$, and processes (4) - (6) are qualitatively confirmed. In order to explain all these results, we propose the following mechanism (plus processes (4) - (6)):

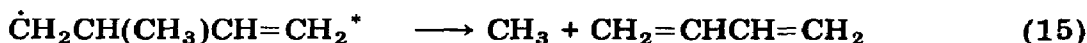
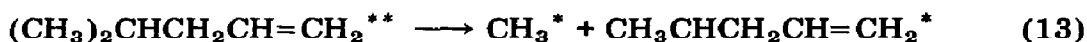


TABLE 3
 Photolysis of 4-methyl-1-pentene at a pressure of 1 Torr^a in the presence of additives^b: quantum yields

Product	Wavelength = 147 nm		Wavelength = 163 nm		Wavelength = 174 nm	
	NO	DI	O ₂	DI	O ₂	DI
CH ₄	0.03	0.16	0.015	0.14	0.018	0.14
C ₂ H ₂	0.016	0.013	0.005	0.005	0.003	0.002
C ₂ H ₄	0.040	0.060	0.028	0.03	0.018	0.023
C ₂ H ₆	0.03	0.00	0.013	0.00	0.012	0.00
C ₃ H ₆	0.70	1.10	0.50	0.53	0.355	0.56
C ₃ H ₈	0.045		0.04		0.021	0.24
C ₃ H ₄ ^c	0.01	0.32	0.01	0.27	0.00	0.01
C ₃ H ₄ ^d	0.070	0.060	0.012	0.016	0.005	0.007
iso-C ₄ H ₁₀	0.053	0.005	0.035	0.00	0.025	0.004
1,3-C ₄ H ₆	0.095		0.05		0.045	
1-C ₄ H ₆	0.055	0.055	0.035	0.05	0.03	0.06
1,3-C ₅ H ₈	0.055		0.07		0.04	
1-C ₅ H ₈	0.06	0.06	0.02	0.02	0.00	0.00
1-C ₅ H ₁₀	0.004	0.04	0.00	Tr ^e	Tr	0.00
1,5-C ₆ H ₁₀	0.11	<0.01	0.15	0.07	0.072	0.00
C ₆ H ₁₄	0.09 ^f	0.144 ^g	0.04 ^f	0.22 ^g	0.043 ^f	0.17 ^g

^a 1 Torr = 133 N m⁻².

^b 10% NO or O₂; 20% DI.

^c Propyne.

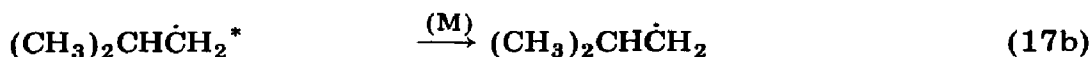
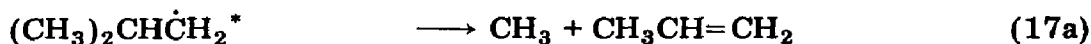
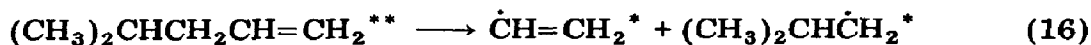
^d Allene.

^e Traces.

^f 2,3-Dimethylbutane.

^g 2-Methylpentane.

and



Process (14a) is the most likely reaction leading to the formation of 1,3-pentadiene. Carter and Tardy [14] have reported that 1-pentene-4-yl and 3-methyl-1-buten-4-yl radicals are in equilibrium even when they are thermalized at 0 °C. This isomerization process is interesting because it gives a facile explanation for the 1,3-butadiene formation [14]. Moreover, the formation of 1-pentene in the presence of DI may be related to the presence of 1-penten-4-yl radicals. Thus the quantum yield of process [13] is, at any pressure, $\Phi(\text{process (13)}) = \Phi(1,3\text{-pentadiene}) + \Phi(1,3\text{-butadiene}) + \Phi_{\text{DI}}(1\text{-pentene})$ and $\Phi(\text{process (13)}) \approx 0.20 \pm 0.05$.

Processes (16), (17) and (11) are likely explanations for the formation of acetylene, methyl and vinyl radicals and, in the presence of DI, of isobutane. The quantum yield of process (16) is equal to that for the formation of acetylene plus that of vinyl radicals. Thus $\Phi(\text{process (17)}) = 0.035$. Therefore

$$\Phi(\text{process (4)}) \leq 1.0 - \Phi(\text{process (16)}) - \Phi(\text{process (13)})$$

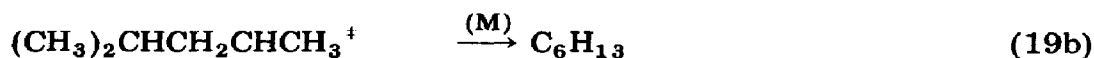
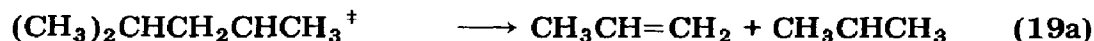
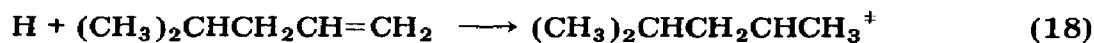
and

$$\Phi(\text{process (4)}) \leq 0.77$$

From the mechanism given earlier, the quantum yield of process (4) is, at any pressure,

$$\begin{aligned} \Phi(\text{process (4)}) &= \Phi_{\text{NO}}(\text{propylene}) + \Phi_{\text{DI}}(\text{propane}) - \Phi(\text{process (17a)}) \\ &= \Phi_{\text{NO}}(\text{propylene}) + \Phi_{\text{DI}}(\text{propane}) - \Phi(\text{process (16)}) + \\ &\quad + \Phi_{\text{DI}}(\text{isobutane}) \end{aligned}$$

and $\Phi(\text{process (4)}) = 0.97$. Because this value is greater than that mentioned previously, at least one other process must be involved. One possible process is related to the presence of hydrogen atoms, *i.e.* processes (6a), (14a) and (11).



where R^\ddagger is a chemically activated radical. The sum of the quantum yields of processes (6a), (11) and (14a) is close to 0.7 at a pressure of 1 Torr. Therefore $\Phi(\text{H})$ is of the same magnitude. The ratio k_{19a}/k_{19b} is not known, but we may assume that 10% of the chemically activated $\text{C}_6\text{H}_{13}^\ddagger$ radicals de-

compose at 1 Torr [15]. Thus a correction of -0.07 must be applied to both $\Phi_{\text{DI}}(\text{propane})$ and $\Phi_{\text{NO}}(\text{propylene})$. Hence $\Phi(\text{process (4)})$ is very probably much closer to 0.8. The use of DI does not permit an exact measurement of the C_6H_{13} quantum yield because of the partial interception of hydrogen atoms by DI [12].

4.2. The fragmentation of intermediate species

4.2.1. In the *n*-1-hexene system

In the 147 nm photolysis, the main product was shown earlier to be produced by the fragmentation of excited *n*-propyl radicals, *i.e.* process (3a). Figure 1 shows the effect of the total pressure on the reciprocal of the ethylene quantum yield under various conditions. From the slope/intercept ratio of this Stern-Volmer plot, the k_d/k_s ratio for the intermediate involved in this process can be calculated (Table 4). Using the stabilization process reaction (3b) as an internal standard, the absolute value of the first order rate constant of process (3a) can be deduced (Table 4). Using the RRKM calculations made by Rabinovitch and Setser [9], this leads to an excess internal energy of 21 kcal mol^{-1} for the *n*-propyl precursor and, taking into account the energy needed for reaction (2) [6], this leads us to attribute an internal energy of 52 kcal mol^{-1} to these *n*-propyl radicals. The photon energy is $194 \text{ kcal mol}^{-1}$ at 147 nm. Thus $123 \text{ kcal mol}^{-1}$ must be distributed among the fragments. If the *n*-propyl fragment has 52 kcal mol^{-1} , the allyl species will have the difference, *i.e.* $\langle E \rangle_{\text{C}_3\text{H}_5} \approx 71 \text{ kcal mol}^{-1}$. The RRKM calculations take into account the vibrational and rotational energies. Both fragments probably also have translational energy. Since the splitting of the photoexcited molecule results from the transformation of vibrational energy, a large amount of translational energy is not expected in the fragments. If this is true, then neglecting this translational energy, the smaller fragment C_3H_5 carries more energy (58%) than the larger fragment C_3H_7 which has 42%. The fragmentation of the photoexcited molecule probably occurs for long enough after its formation to allow an internal redistribution of the energy, but not long enough for a complete randomization of this internal energy.

TABLE 4

Fragmentation of *n*-propyl radicals in the photolysis of *n*-1-hexene

Wavelength (nm)	$\Phi_0(\text{C}_2\text{H}_4)^a$	k_d/k_s (Torr)	k_d (s^{-1})	E_{excess}^b (kcal mol^{-1})	$\langle E_{\text{int}} \rangle^c$ (kcal mol^{-1})
147	0.81 ± 0.02	105	2×10^9	21	52
163	0.58 ± 0.02	33	6.3×10^8	15	46

^aFrom an extrapolated value at zero pressure.

^bFrom RRKM calculations [9].

^c $\langle E_{\text{int}} \rangle$ is the mean energy content, *i.e.* E_{excess} plus the energy needed for the fragmentation process.

Moreover the majority, if not all, of the n-propyl radicals decompose at low pressure. Thus they support at least the energy needed for the fragmentation process, *i.e.* 31 kcal mol⁻¹. This indicates that the distribution of energy is relatively narrower than could have been expected, *i.e.* between zero and the maximum available energy of 123 kcal mol⁻¹.

In the 163 nm photolysis, it is more difficult to draw any conclusion because only a fraction of the propyl radicals decompose at low pressure (Table 4). Thus 70% of the propyl radicals support an internal energy of about 46 kcal mol⁻¹ and 30% have less energy, *i.e.* less than about 35 kcal mol⁻¹. Ignoring these last 30% of n-propyl radicals, the 70% group has an internal energy smaller than would be expected from a statistical energy distribution. Because of the 24 vibrational degrees of freedom, a statistical distribution gives exactly one half of the energy excess to the propyl radical; there are 48 vibrational degrees of freedom in the n-1-hexene molecule. Thus, the statistical distribution gives 51.5 kcal mol⁻¹ to the n-propyl radicals.

4.2.2. In the 4-methyl-1-pentene system

The situation is similar to that observed in the n-1-hexene system, except that the propyl radical has a secondary structure. Figures 2 and 3 show Stern-Volmer plots of the propylene quantum yield. The plot of Fig. 2 is far from linear. Many reasons may be invoked to explain this fact. (1) It should be recalled that the linearity of the Stern-Volmer plot is an ideal situation and the observation of curvature is more general [16]. For n-1-hexene, where highly excited intermediates are involved, curvature is probably observed in the high pressure region (Fig. 1). (2) The reproducibility and the sensitivity of the analytical system decrease at higher pressure. For example, the introduction of a large amount of starting material in the chromatograph results in a non-symmetric peak. Therefore the exact calibration of the whole system becomes less and less accurate. However, the curvature observed at 147 nm (Fig. 2) is much more pronounced than that observed at 163 nm (Fig. 3). The difference may be partly explained by the occurrence of secondary processes which are more important at 147 nm. For example, at least two secondary processes lead to the formation of propylene, *i.e.* processes (6a) and (17a). Process (19a) has also been invoked at lower pressure and may partly explain the strong curvature observed in the photolysis at 147 nm. Thus it is not an easy task to apply the previous argument to determine the rate constant of the decomposition process of the propyl intermediate. The intercept of the tentatively drawn broken line with the pressure axis occurs at -55 ± 5 Torr. It corresponds to a first order rate constant k_d for process (6a) of approximately 7.8×10^{-8} s⁻¹. An RRKM calculation yields an excess energy of 31.5 kcal mol⁻¹. Thus 80% of the secondary propyl radicals (0.65/0.80) carry 72.5 kcal mol⁻¹. These figures are, of course, tentative; some propyl radicals have less internal energy and some have more. Hence this value of 72.5 kcal mol⁻¹ is an average energy. This figure must be compared with the maximum energy at 147 nm, *i.e.* 127 kcal mol⁻¹. The energy of the photon (194 kcal mol⁻¹) is decreased by

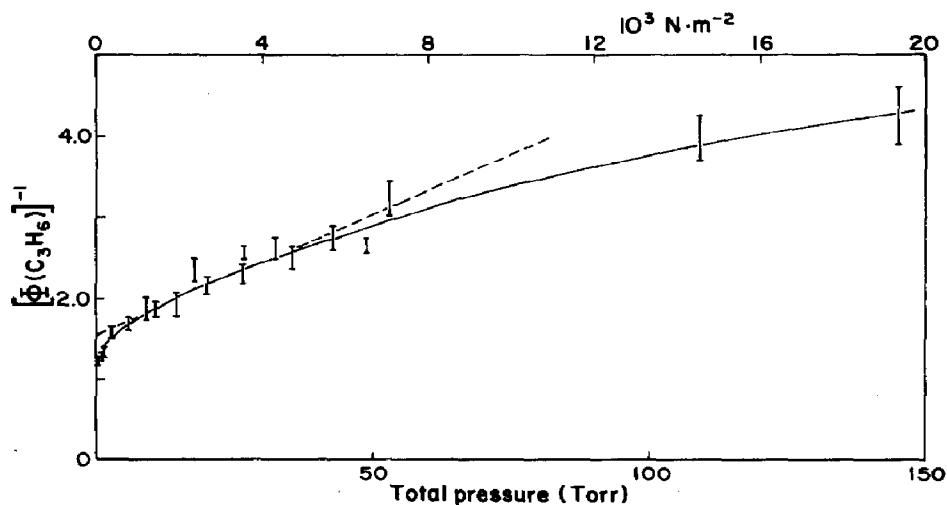


Fig. 2. A Stern-Volmer plot ($\{\Phi(\text{C}_3\text{H}_6)\}^{-1}$ vs. total pressure) for the formation of propylene in the 147 nm photolysis of 4-methyl-1-pentene: 4-methyl-1-pentene:NO = 100:10.

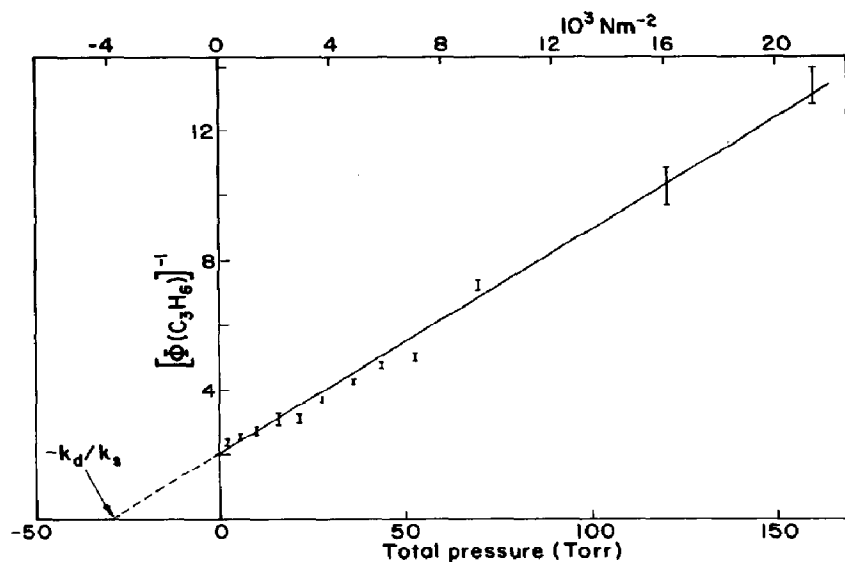
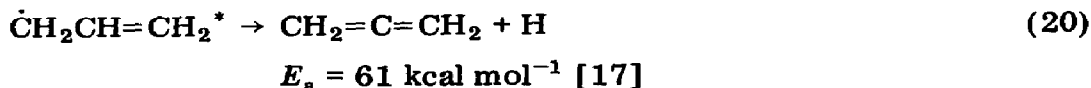


Fig. 3. A Stern-Volmer plot ($\{\Phi(\text{C}_3\text{H}_6)\}^{-1}$ vs. total pressure) for the formation of propylene in the 163 nm photolysis of 4-methyl-1-pentene: 4-methyl-1-pentene: O_2 = 100:10.

the energy for process (5). Taking into consideration the curvature of the Stern-Volmer line and the accuracy of the required parameters, the distribution of the excess energy among the fragments is not far from the statistical distribution.

Finally, it should be noted that the quantum yield of allene formation is twice as great in the 4-methyl-1-pentene system as in the n-1-hexene system. Because processes (2) and (4) have the same probability (approx-

mately 0.8), this gives support to the higher energy content of the allyl fragment formed in the 4-methyl-1-pentene system. This observation indicates that the available energy supported by the isopropyl radicals is less important than that supported by the n-propyl radicals in the n-1-hexene system. This observation is, of course, contrary to the earlier calculations of the energy content of the propyl radicals:



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