

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

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Summary

The photolysis of 1-butene was carried out in a static system using the xenon resonance line at 147 nm (8.4 eV) at pressures in the range 15 - 500 Torr (2 - 66.5 kPa). The major products observed were acetylene, ethane, ethylene, allene, propyne, 1,3-butadiene and isopentane. The radical species were identified by using scavengers such as oxygen and H₂S. Evidence is presented for the occurrence of ten primary processes to which quantum yields have been ascribed. The main process is a β cleavage of the C—C bond which occurs with a yield of $\phi = 0.51$. A hydrogen atom mechanism involving the occurrence of hot hydrogen atoms (about 30% of them have an excess energy of about 0.26 eV) was proposed to account for the pressure dependence of propylene. Dissociation of excited radicals contributes to the formation of allene and propyne.

1. Introduction

Vacuum UV photolysis of 1-butene has been studied extensively using different photon energies. A process predominating at 185 nm [1] and at 174 nm [2] is the detachment of a methyl radical (the quantum yields of β splitting for mercury and nitrogen lamps are 0.71 and 0.66 respectively). This yield was found to decrease down to 0.38 in low pressure experiments at 147 nm [3]. The aim of the present work is to examine the photolysis of 1-butene at 147 nm under high pressures in the hope of revealing that secondary fragmentation processes can be quenched by collision. The occurrence of such processes can be helpful in establishing the decomposition channels of the photochemically excited butene molecules.

2. Experimental

2.1. Materials

1-Butene was purified by gas chromatography using a 4.5 m column of AgNO₃ in triethylene glycol on Chromosorb maintained at room temperature.

Further purification included the removal of water and CO₂ by vacuum distillation. The purified material contained about 50 ppm *cis*-2-butene as the only detectable impurity. H₂S (Matheson, research grade) was used as received after being degassed in a mercury-free vacuum line.

2.2. Irradiation and analysis

The vacuum UV photolysis of 1-butene was carried out at room temperature in a standard static system using a microwave-powered xenon resonance lamp provided with a titanium getter assembly [4]. Analysis of hydrocarbon products was performed by gas chromatography using a 9 m squalane column and an 8 m Fractonitrile column coupled with a 3 m dinonyl phthalate column. Molecular hydrogen, if formed, was not measured. The quantum yields were determined using $\phi(\text{H}_2) = 0.38$ in the 147 nm photolysis of C₂H₄ [5]. In butene photolysis experiments the quantum yield of acetylene, $\phi(\text{C}_2\text{H}_2) = 0.12 \pm 0.005$, was found to depend neither on the pressure nor on the presence of oxygen and H₂S. Thus all the quantum yields reported herein were calculated using this value.

3. Results and discussion

We have used a standard scavenger technique similar to that of Collin [3], namely the irradiation of butene in the presence of free-radical scavengers such as oxygen and H₂S. The interception of radicals by oxygen makes determination of the yields of molecular products possible. In the presence of H₂S abstraction of a hydrogen atom by the free radical occurs:



which yields stable products [6, 7]. The difference between the quantum yields obtained in experiments with H₂S and oxygen gives the yields of the free radicals.

The quantum yields of the hydrocarbon products in the photolyses at 60 and 500 Torr (8 and 66.5 kPa) are summarized in Table 1 (both scavenged and unscavenged experiments are included). The accuracy of the results was good (within the limits of a few per cent). The plot of quantum yield *versus* irradiation time was linear which shows that reactions with accumulated products are of no importance. The isomerization reaction, which yields other butenes, was found to be negligible in agreement with the results of other investigators of butene photolysis [3] and this was not pursued further.

The effectiveness of H₂S in intercepting the radicals was checked under our experimental conditions by conducting a series of runs using H₂S concentrations in the range 5 - 15% at 60 Torr (8 kPa) (see Table 1). The results indicate that a 15% concentration of H₂S scavenges totally the CH₃, C₂H₃ and C₂H₅ radicals. The quantum yield of n-butane increases initially upon addition of H₂S; the increase is followed by a decrease at greater H₂S concentrations. Clearly H₂S competes with butene for H atoms:

TABLE 1

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

Total pressure	60 Torr (8 kPa)					500 Torr (66.5 kPa)		
H ₂ S (%)	—	5	10	15	—	—	15	—
O ₂ (%)	—	—	—	—	3	—	—	3
Methane	0.03 ^a	0.48	0.46	0.53	0.01	0.059	0.51	0.01
Acetylene	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
Ethylene	0.09	0.14	0.14	0.15	0.09	0.096	0.14	0.09
Ethane	0.12	0.15	0.17	0.17	0.02	0.12	0.17	0.03
C ₃ H ₄ ^b	0.17	0.17	0.17	0.18	0.18	0.13	0.12	0.15
Propylene	0.035	0.039	0.044	0.049	0.04	0.02	0.03	0.02
Propane	0.03	—	—	—	—	0.03	—	—
1,3-Butadiene	0.09	—	—	0.01	0.10	0.086	—	0.08
1,2-Butadiene	0.01	0.008	0.009	0.008	0.012	0.01	0.006	0.016
1-Butyne	0.03	0.02	0.02	0.03	0.03	0.04	0.03	0.045
n-Butane	0.05	0.55	0.50	0.46	—	0.062	0.39	—
1-Pentene	0.008	—	—	—	—	0.017	—	—
i-Pentane	0.09	—	—	—	—	0.08	—	—
n-Pentane	0.02	—	—	—	—	0.03	—	—
3-Methyl-1-butene	0.006	—	—	—	—	0.013	—	—

^aAll values are in quantum yield units with an accuracy to $\pm 10\%$ or better.

^bThe total of allene and propyne.



From the kinetic assessment of the data in Table 1 (applying the steady state approximation to the above mechanism) 15% H₂S can be estimated to intercept about 25% of the hydrogen atoms; hence $\phi(\text{n-C}_4\text{H}_{10}) \approx 0.75 \phi(\text{C}_4\text{H}_9)$.

The increase in propylene yield with the increase in H₂S concentration deserves some comment. According to reaction (1) the interception of C₃H₅ radicals might be expected:



A simple cleavage of the C—C bond in 1-butene should lead to the formation of radicals that have a CH₂=CH—CH₂ allylic structure. However, the reaction of allylic radicals with H₂S is endothermic with $\Delta H = 18.8 \text{ kJ mol}^{-1}$ [8]. Therefore the observed increase in propylene yield can be ascribed either to the formation of C₃H₅ radicals that have vinylic structure or, more likely, to the formation of hot C₃H₅ radicals. Some arguments in favour of this possibility will be presented later on.

3.1. Ethyl radicals

The quantum yield of ethyl radicals, computed as a difference between the quantum yields in the presence of 15% H₂S and 3% oxygen ranges from

0.14 to 0.15 and is independent of pressure. Two pathways involving breaking of the central C—C bond may be assumed. The first one involves reactions (6) and (7):



The quantum yield $\phi(C_2H_5)$ of reaction (6) can be assessed as 0.05 on the basis of $\phi(C_2H_3)$ determined from the increase in $\phi(C_2H_4)$ in the presence of H_2S . Thus the yield of reaction (7) is 0.09. The mechanism of this reaction is not established; the excited vinyl radicals may be formed in a primary split, subsequently undergoing dissociation to give acetylene. Even though $\phi(C_2H_3)$ and $\phi(C_2H_2)$ do not depend on pressure, the lifetime of the excited radical is likely to be shorter than the collision interval at the pressures used. The second possible pathway involves a fast fragmentation of excited butenyl radicals:



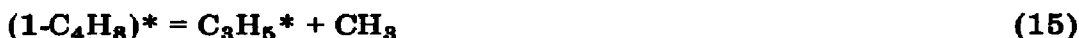
3.2. Allene and propyne

The quantum yields of allene and propyne are shown in Fig. 1 to depend strongly on the pressure of butene; however, the ratio of their yields is constant over the whole range of the pressures used and is given by $\phi(\text{propyne})/\phi(\text{allene}) = 0.14$. In the xenon photolysis at 8.4 eV Collin [3] did not observe a decrease in $\phi(C_3H_4)$ with an increase in the helium pressure. Apparently helium is not an effective collisional deactivator. It should be noted that a pronounced dependence of $\phi(C_3H_4)$ on pressure was reported by Collin and Więckowski [2] at 7.1 eV.

A mechanism suggested by Collin which involves the dissociation of the excited butene molecule



cannot explain the data reported in Fig. 1. Reaction (11) is likely to proceed in two steps — two pathways can be proposed:



The occurrence of collisional deactivation of excited $C_4H_7^*$ and $C_3H_5^*$ radicals agrees well with our data. Unfortunately, our results cannot unequivocally establish which of these two radicals (or perhaps both) is responsible for the formation of C_3H_4 hydrocarbons. The use of H_2S to identify C_4H_7 and C_3H_5 and to determine their yields is of no avail. The reaction with C_4H_7 will yield 1-butene, while C_3H_5 does not react with H_2S at all unless incompletely thermalized. Indeed, a slight increase in $\phi(C_3H_6)$ observed with increasing H_2S concentration may be due to the reactions of energized propenyl radicals.

The occurrence of the reaction sequence (15) - (17) seems to be more likely. Such a scheme would require that the quantum yield of atomic hydrogen be dependent on the pressure whereas $\phi(CH_3)$ should be constant, which is indeed the case. In the presence of H_2S $\phi(CH_4)$ is independent of pressure but $\phi(n-C_4H_{10})$ decreases (atomic hydrogen is a precursor of n-butane in such experiments). This conclusion is open to some doubt, since both methyl radicals and hydrogen atoms originate from other reactions, their yields are high and the observed changes are scarcely beyond the limit of experimental error.

A kinetic assessment of competitive reactions of dissociation and collisional stabilization of excited C_3H_5 radicals can be performed using classical Stern-Volmer plots as shown in Fig. 2. A typical assumption is made involving the distinguishing of pressure dependent and pressure independent regions. A linear Stern-Volmer plot is obtained when $\phi^\infty(C_3H_4)$ is assumed

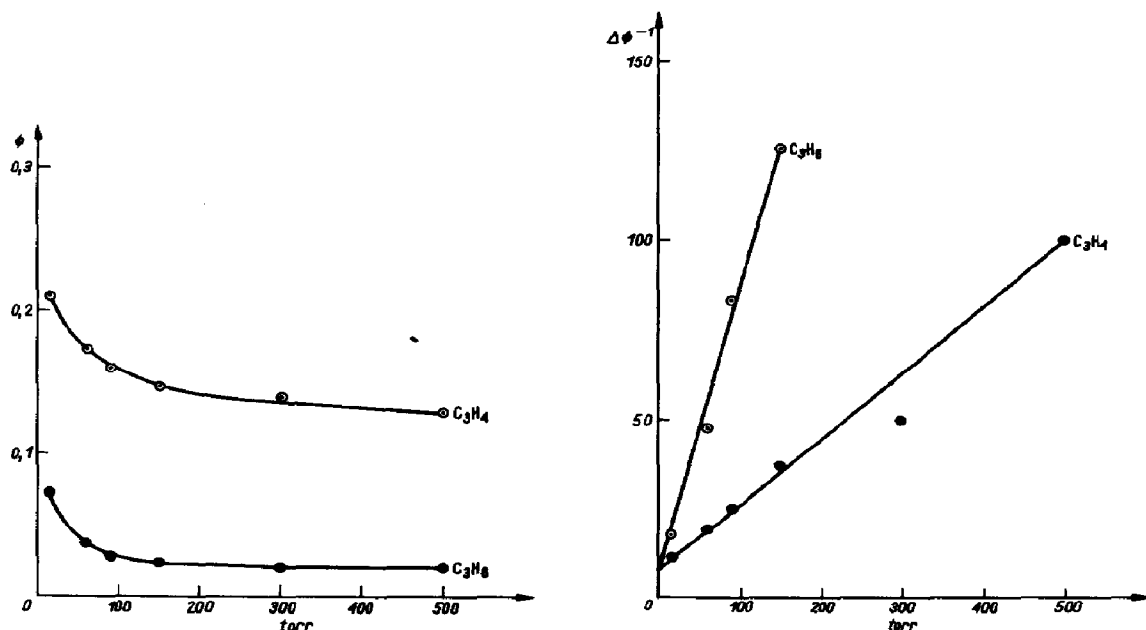


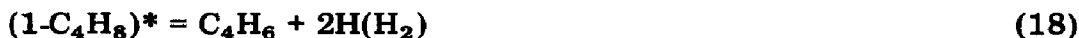
Fig. 1. Dependence of the quantum yields of propylene and C_3H_4 hydrocarbons on pressure; the experimental points represent the average values of two to four runs.

Fig. 2. Dependence of $1/\Delta\phi(C_3H_4)$ and $1/\Delta\phi(C_3H_6)$ on pressure.

to be 0.12 and independent of pressure. This leads to $k_{17}/k_{16} = 7.44 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$. The rate constant for the deactivation reaction (17) is calculated assuming a strong collision model [9] and using $\sigma(\text{C}_3\text{H}_5) = 0.467 \text{ nm}$ and $\sigma(1\text{-C}_4\text{H}_8) = 0.65 \text{ nm}$ [10, 11], and is found to be $k_{17} = 6.8 \times 10^8 \text{ s}^{-1}$. The yield of C_3H_4 hydrocarbons extrapolated to zero pressure is $\phi^0(\text{C}_3\text{H}_4) = 0.13$. In a recent investigation Collin and Wieçkowski have also established the decrease in the yields of allene and propyne with increasing 1-butene pressure at 147 nm [12]. Their value of $8.8 \times 10^8 \text{ s}^{-1}$ for the rate constant of C_3H_5^* dissociation agrees very well with our estimate. It is worth mentioning that propenyl radicals stabilized in collisions (reaction (17)) may well possess a slight excess energy, which makes possible the occurrence of an endothermic reaction with H_2S yielding propylene, as suggested earlier.

3.3. C_4H_6 hydrocarbons

The yields of 1,3- C_4H_6 , 1,2- C_4H_6 and 1-butyne are shown in Table 1. 2-Butyne was sought in vain. The total yield $\phi(\Sigma\text{C}_4\text{H}_6)$ of these hydrocarbons has a constant value of 0.14 over the range of pressures used and is independent of the presence of additives, except for 1,3-butadiene. This hydrocarbon is not observed in the presence of H_2S owing to the well-known reaction with HS radicals [13]. This suggests that the mechanism of formation involves a primary molecular process, probably the elimination of either a hydrogen molecule or two hydrogen atoms:



Collin [3] has reported much larger quantum yield $\phi_{18} = 0.32$ for this reaction. The reason for such a discrepancy is difficult to explain, particularly since he did not determine 1-butyne.

The dependence of the yields of all the individual C_4H_6 hydrocarbons on the pressure of 1-butene presents some interesting features (Fig. 3). The decrease in 1,3-butadiene with increasing pressure which is accompanied by a simultaneous increase in 1- C_4H_6 is probably due to the isomerization of the excited 1-butyne molecule formed in reaction (18):



3.4. Ethylene

The value of 0.09 for the quantum yield $\phi(\text{C}_2\text{H}_4)$ for ethylene formation is lower than the value of 0.15 reported by Collin [3]. He observed a decrease in this yield in the presence of helium added as moderator at pressures of up to 274 Torr (36.4 kPa). Under our experimental conditions $\phi(\text{C}_2\text{H}_4)$ is independent of pressure. Collin's mechanism which involves two reactions



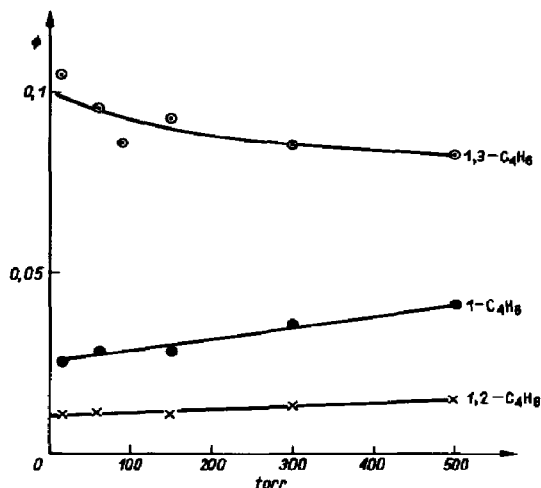


Fig. 3. Dependence of the quantum yields of C₄H₆ hydrocarbons on pressure; the experimental points represent the average values of two to four runs.

does not seem to fit our data. We suggest that reaction (20) is the sole channel. In reaction (21) vinyl radicals should have been formed; the yield for these radicals was low and could be explained satisfactorily by the occurrence of reaction (6), which has been commented on previously.

3.5. Ethane, methane and acetylene

The yields of ethane and methane in the presence of oxygen are low ($\phi(\text{C}_2\text{H}_6) = 0.03$ and $\phi(\text{CH}_4) = 0.01$, see Table 1), thus confirming Collin's earlier observations [3]. The mechanism of formation involves reactions (10) and (22):



$\phi(\text{C}_2\text{H}_2) = 0.12$ agrees well with the total yield for reactions (7) and (22).

3.6. Methyl radicals

The quantum yield for CH₃ formation has a value of 0.51 at 500 Torr. Two sources of its formation have already been discussed, namely reactions (11) and (15) which give $\phi_{11} + \phi_{15} = 0.24$, so a channel is required to provide a deficit of $\phi(\text{CH}_3) - 0.24 = 0.27$. The assignment is open to question; no products could be observed that can accompany the radical in a primary dissociation of the excited parent molecule. The only possibility remaining is a direct split into propenyl and methyl radicals:



Scavenging experiments are of little avail here since H₂S is known to fail to intercept the allyl radicals.

3.7. Atomic hydrogen

In the presence of H₂S atomic hydrogen is a precursor of n-butane in reactions (2) and (3), and $\phi(\text{n-C}_4\text{H}_{10}) = 0.39$ at 500 Torr (66.5 kPa). Using the previously derived relation $\phi(\text{n-C}_4\text{H}_{10}) \approx 0.75 \phi(\text{C}_4\text{H}_9)$ we obtain $\phi(\text{H}) = 0.52$. Reactions (7) and (11) contribute $\phi_7 + \phi_{11} = 0.21$ to the total yield of $\phi(\text{H})$. Only an upper limit ($\phi \leq 0.28$) can be ascribed to the hydrogen atoms formed in reaction (18) in which molecular hydrogen can also be formed. Finally, reaction (24) should not be forgotten:



The formation of 1-pentene and 3-methyl-1-butene in the photolysis of pure butene may be taken as evidence for the occurrence of this reaction since these products are formed by the recombination of butenyl and methyl radicals. Summing to unity will give a value of 0.12 for ϕ_{24} .

3.8. Propylene

$\phi(\text{C}_3\text{H}_6)$ decreases with increasing pressure (see Fig. 1) as a result of the occurrence of two competitive processes: dissociation of an excited butyl radical and its collisional deactivation



The kinetic treatment applied here is analogous to that used in the case of allene and propyne formation. The values $\sigma(\text{C}_4\text{H}_9) = 0.65 \text{ nm}$ and $\sigma(\text{C}_4\text{H}_8) = 0.65 \text{ nm}$ were used [11]. Linearity of the Stern-Volmer plot is achieved (see Fig. 2) provided that $\phi^\infty(\text{C}_3\text{H}_6) = 0.016$ is assumed as the yield of the pressure independent process. This value can be explained in terms of a primary dissociation



A value for the rate constant k_{26} of butyl radical dissociation of $1.55 \times 10^8 \text{ s}^{-1}$ can be obtained, which is a much higher value than that of $2.4 \times 10^7 \text{ s}^{-1}$ obtained by Rabinovitch and Setser [9] for butyl radicals originating from chemical activation experiments (the addition of a thermalized hydrogen atom to the double bond of an olefin). We are tempted to assume that hot hydrogen atoms are formed in our photolytic experiments, which provide an excess energy over that due to the exothermicity of reaction (25). A plot of the rate constant for dissociation *versus* excess energy, reported by Rabinovitch and Setser [9], can be used to assess the energy of these hot atoms. A value of 0.26 eV (25 kJ mol^{-1}) seems to be reasonable. Such an excess energy is expected to depend on the energy of the photons used. Indeed, in our hitherto unreported experiments on 1-butene photolysis using krypton resonance lines ($\lambda = 123.6 \text{ nm}$) the exactly similar kinetic treatment gives $k_{\text{diss}} = 10^9 \text{ s}^{-1}$ which corresponds to a far greater excess energy of about 0.6 eV (58 kJ mol^{-1}).

The extrapolation of the propylene yield to zero pressure gives a value of $\Delta\phi(\text{C}_3\text{H}_6) = 0.17$ which is much lower than the yield of atomic hydrogen obtained from the yield of n-butane in H_2S -scavenged experiments. Thus it should be concluded that only some hydrogen atoms formed have an initial excess energy. The dissociation of the excited butyl radicals originating from the addition of thermal hydrogen atoms to butene will be totally quenched under our experimental conditions. A pressure of 15 Torr (8 kPa) (our lowest value) is sufficient to deactivate about 95% of C_4H_9^* in collisions.

3.9 Photolysis of pure 1-butene

In the unscavenged experiments the transient radical species undergo recombination and disproportionation reactions which yield some stable products that can be observed. Thus the recombination of methyl radicals gives ethane:



Isopentane and n-pentane originate from the reactions of methyl and butyl radicals:



The presence of propane indicates the occurrence of ethyl radicals. To explain the presence of 1-pentene and 3-methyl-1-butene the reactions of butenyl radicals which differ in structure should be invoked. The yields for the recombination products are low in comparison with the yields of radicals determined in the scavenged experiments. Obviously the radicals add sufficiently fast to the double bond of 1-butene; the higher molecular products of such radical polymerizations were not determined in our experiments.

4. Conclusions

An assembly of different primary pathways for the dissociation of an excited butene molecule, originating from the absorption of an 8.4 eV photon, together with the quantum yields assigned to every reaction channel are given in Table 2. Previous results from Collin's laboratory [2, 3] are included for comparison. Our results for the main process, a rupture of the C—C bond in the β position to the double bond ($\phi = 0.51$), are far greater than those obtained by Collin but are not high enough to contradict the observation that this yield decreases with increasing photon energy (0.71 at 185 nm [1]; 0.66 at 174 nm [2]; 0.51 at 147 nm (this work)). Owing to the higher pressures used in this study the occurrence of secondary processes, dissociation of excited propenyl and butyl radicals and isomerization of C_4H_6 hydrocarbons, could be established. A kinetic treatment of the dissociation of butyl radicals results in the assessment of the rate constant for dissociation.

About 30% of hydrogen atoms appear to have an excess energy as high as 0.26 eV.

TABLE 2

Fragmentation of the photoexcited 1-butene molecule at 8.4 eV

					8.4 eV	8.4 eV	7.1 eV
					This work	[3]	[2]
C ₃ H ₄	+	CH ₃	+	H (CH ₄)	0.12	0.38	0.66
	C ₃ H ₅ *	+	CH ₃	H	0.18		
	→ C ₃ H ₄	+	CH ₃		0.26		
C ₂ H ₅	+	C ₂ H ₂	+	H	0.09	0.16	—
		2C ₂ H ₄			0.04	0.04	0.05
		+	2H (H ₂)		0.14	0.38	0.06
		+	C ₂ H ₂		0.03	0.03	—
		+	C ₂ H ₃		0.05	—	0.04
		+	2CH ₃		—	0.04	0.035
		+	CH ₂		0.02	0.03	—
		+	H		0.12	0.05	0.16
					1.00		

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