

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

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Summary

The photolysis of 1-butene was carried out in a static system using the krypton resonance line at 123.7 nm (10.0 eV) at pressures in the range 15 - 500 Torr (2 - 66.5 kPa). The major products observed were ethylene, acetylene, 1,3-butadiene, allene, n-butane and propylene. Identification of the radical species was made by the use of scavengers such as oxygen and H₂S. Evidence is presented for the occurrence of nine primary processes to which quantum yields have been ascribed. The main processes are fragmentation giving C₃H₅ radicals with a yield ϕ of 0.29 and the formation of C₄H₆ hydrocarbons with a yield ϕ of 0.23. A hydrogen atom mechanism, involving the occurrence of hot hydrogen atoms that have an excess energy as high as 0.6 eV, was proposed to account for the pressure dependence of propylene. Dissociation of excited radicals contributes to the formation of ethylene.

1. Introduction

The vacuum photolysis of 1-butene has previously been investigated at relatively low pressures using different photon energies [1 - 3].

In a recent paper we have reported the photolysis of 1-butene at 147 nm over the pressure range 15 - 500 Torr (2 - 66.5 kPa) [4]. At these pressures some secondary dissociation processes were observed to undergo collisional stabilization. The present work is an extension of these studies to a greater photon energy of 10.0 eV (123.7 nm).

2. Experimental

Since the experimental techniques have been described previously [4], only some supplementary details will be given.

TABLE 1

Photolysis of 1-butene at 10.0 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)		
	—	15	—	—	15	—
H ₂ S (%)	—	—	—	—	—	—
O ₂ (%)	—	—	3	—	—	3
Methane	0.052 ^a	0.40	0.03	0.056	0.33	0.03
Acetylene	0.17	0.17	0.17	0.17	0.17	0.17
Ethylene	0.185	0.28	0.18	0.175	0.25	0.14
Ethane	0.093	0.16	0.050	0.047	0.16	0.031
Allene + propyne	0.18	0.175	0.165	0.17	0.16	0.17
Propylene	0.10	0.16	0.090	0.043	0.11	0.035
Propane	0.040	0.011	0.010	0.015	0.005	—
1,3-Butadiene	0.16	?	0.17	0.16	?	0.16
1,2-Butadiene	0.031	?	0.033	0.030	?	0.029
1-Butyne	0.041	?	0.040	0.042	?	0.040
n-Butane	0.13	1.1	0.035	0.06	1.5	0.041
i-Pentane	0.12	—	—	0.019	—	—
n-Pentane	0.022	—	—	0.009	—	—
1-Pentene	0.023	—	—	0.010	—	—
3-Methyl-1-butene	0.010	—	—	0.011	—	—

^aAll values are in quantum yield units to an accuracy of $\pm 5\%$ or better.

A standard titanium gettered krypton resonance lamp of intensity 6×10^{12} photons s^{-1} was used in a static system working at ambient temperature. Quantum yields were determined using an ethylene actinometer based on $\phi(C_2H_2) = 1$ [5]. Since the quantum yield $\phi(C_2H_2) = 0.17 \pm 0.05$ of acetylene formed in butene photolysis was found to be independent of the pressure and of the presence of scavengers all the quantum yields reported herein were calculated using this value.

3. Results and discussion

A standard scavenger technique was used, namely the irradiation of butene in the presence of oxygen and H₂S. The oxygen unscavenged products were assumed to be formed by a molecular mechanism. H₂S was used as a test for the presence of free radicals. The abstraction of a hydrogen atom by the free radical



yields stable products [6, 7]. The difference in quantum yields between H₂S and oxygen experiments gives the free radical yields.

The quantum yields of the hydrocarbon products in the photolyses at 60 and 500 Torr are shown in Table 1 (both scavenged and unscavenged

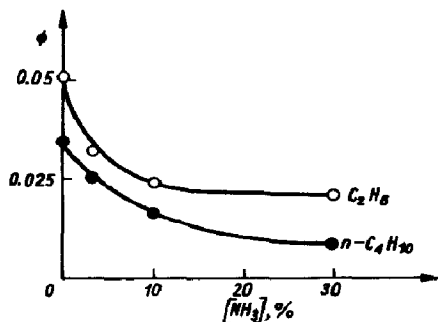


Fig. 1. Dependence of the quantum yields of ethane and n-butane on the concentration of ammonia.

experiments are included). The accuracy of the reported quantum yields is estimated to be better than 5%. The yields were independent of the irradiation time (over the range 0.5 - 4 h); thus the reactions with accumulated products could be ignored. The routine period of irradiation was 1 h.

The isomerization reaction yielding other butenes was found to be of no importance, as reported previously in other investigations of 1-butene photolysis [3, 4].

The absorption of a 123.7 nm photon (10.0 eV) by 1-butene, which has an ionization energy of 9.58 eV, results in the formation of an electronically superexcited neutral molecule. Since the efficiency of preionization is reported to be about 0.20 [8], the $C_4H_8^+$ butene ions formed in such a process are expected to initiate a sequence of ion-molecule reactions leading to higher molecular products. We have not attempted to determine these products and hence this work gives no data related to the ionic polymerization. In order to ascertain whether the ionic reactions interfere with the formation of lower hydrocarbons (up to C_5) a series of experiments using ammonia as a positive ion scavenger was performed. Only the yields of ethane and n-butane were affected which indicates the contribution of ionic processes to their formation (see Fig. 1). The mechanism of these processes is unknown.

It has previously been established [4] that a 15% addition of H_2S appears to be sufficient to intercept the radical species present. Hence this concentration of H_2S was used throughout. The effect of H_2S on the quantum yield of n-butane is unexpectedly large. $\phi(n-C_4H_{10})$ is much higher than that reported in xenon photolysis ($\phi(n-C_4H_{10}) \approx 0.4$) [4] and markedly increases with the increase in pressure (up to 1.4 at 500 Torr). The occurrence of the reaction



is unlikely to account for these results. There seems to be a substantial contribution from some unknown ionic processes similar to those reported in the radiolyses of 1-butene [9] and ethylene [10]. The use of either HI or

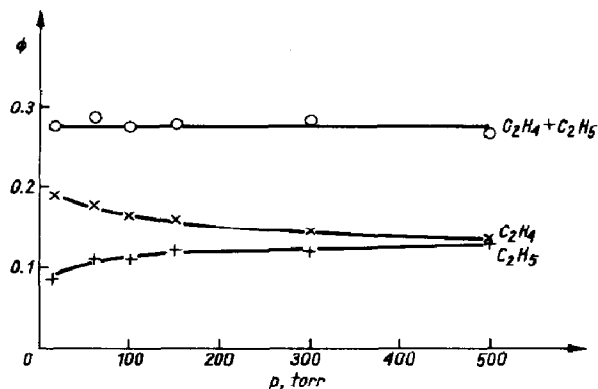


Fig. 2. Pressure dependence of the quantum yields of ethyl radicals and ethylene.

CH_3I would be of little use since when the photon energy is high enough to ionize the molecules both intercept electrons.

Thus the yields of n-butyl radicals and their precursor hydrogen atoms could not be established.

3.1. C_2 products

The quantum yield of molecular ethylene decreases with increasing pressure in the presence of O_2 . The decrease is accompanied by an increase in the yield of ethyl radicals (Fig. 2). The total yield remains constant over the whole pressure range. Apparently an excited ethyl radical formed in a primary fragmentation of the butene molecule undergoes a further split into ethylene and atomic hydrogen:



The lifetime of this excited radical is comparable with the collision interval at the pressures used, so the contribution of collisional stabilization



increases with increasing pressure.

A kinetic treatment of the data shown in Fig. 2 gives a quantum yield $\phi(C_2H_5)$ of 0.08 for the excited ethyl radicals, a quantum yield $\phi^0(C_2H_5)$ of 0.07 for the stable ethyl radicals, i.e. extrapolated to zero pressure, and $\phi(C_2H_4) = 0.12$ at $p \rightarrow \infty$ when reaction (3) is entirely quenched.

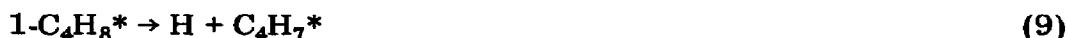
These results are in sharp contrast to those reported for the xenon photolysis where the yield for both the ethylene and the ethyl radical is independent of pressure [4]. Obviously the increase in excitation energy of the ethyl radical due to the increase in the photon energy will favour further fragmentation.

No pressure effect is observed for the remaining C_2 hydrocarbons and radicals: $\phi(C_2H_2) = 0.17$ and $\phi(C_2H_3) = 0.10$.

From these results the quantum yields can be attributed to the following different pathways which give the observed products:



Reactions (5) - (7) may involve the direct split of a central C—C bond followed by very fast dissociation of one of the fragments to yield atomic hydrogen, acetylene or ethylene. An alternative mechanism involves the primary split of a C—H bond



followed by a fast dissociation of excited butenyl radicals



Our results do not enable us to distinguish between these two routes. Perhaps both mechanisms are involved.

In the presence of oxygen ethane is formed with a quantum yield $\phi(\text{C}_2\text{H}_6)$ of 0.05 at 60 Torr. The decrease of this yield in the presence of ammonia indicates an ionic mechanism, which is rather surprisingly since the known chemistry of butene ions gives no clue to the form of this mechanism. Such a process is not observed in the radiolysis of 1-butene [9]. Thus it could be due to wall effects. The reactions of methyl radicals at the window surface may not be affected by the presence of oxygen. Polar molecules of ammonia will be adsorbed more strongly than those of CH_3 , and a decrease in the yield of ethane will follow as a result of oxygen scavenging in the bulk of the gas.

The yields for other processes giving C_2 products do not exceed 0.02.

3.2. C_3 products

The main C_3 hydrocarbon products are allene and propyne. Their quantum yields are independent of pressure and the presence of scavengers: $\phi(\text{C}_3\text{H}_4) = 0.17$ while $\phi(\text{propyne})/\phi(\text{allene}) = 0.18$.

In the xenon photolysis at 8.4 eV competition is observed between the dissociation of excited C_3H_5 radicals and their collisional stabilization [4]:



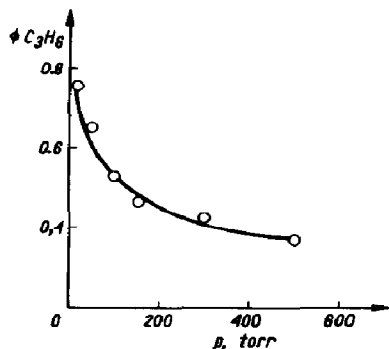


Fig. 3. Pressure dependence of the quantum yield of propylene.



$$k_{13} \approx 7 \times 10^8 \text{ s}^{-1} \quad \text{at 8.4 eV [4]}$$

In the krypton photolysis reactions (12) and (13) are also likely to occur, but the excess energy of the C_3H_5 radicals becomes so large that reaction (13) cannot be collisionally quenched at the pressures used. Therefore the yield ϕ_{15} for the reaction



can be assumed to be 0.17.

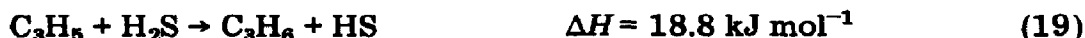
The quantum yield for propylene in the presence of oxygen is strongly pressure dependent (Fig. 3). As in the case of the xenon photolysis the occurrence of two competitive processes, dissociation of an excited butyl radical and its collisional deactivation, can be assumed:



A kinetic treatment, analogous to that previously applied [4], gives $k_{17} = 1 \times 10^9 \text{ s}^{-1}$. This value is higher than $k = 2.4 \times 10^7 \text{ s}^{-1}$ obtained by Rabino-vitch and Setser [11] for chemically activated butyl radicals (addition of thermal hydrogen atoms to the double bond of a butene molecule) and higher than our estimate $k = 1.6 \times 10^8 \text{ s}^{-1}$ obtained for xenon photolysis. This confirms the possibility that the hydrogen atoms formed when a butene molecule absorbs a quantum of light may be hot. Using a plot of the rate constant for dissociation *versus* excess energy reported by Rabino-vitch and Setser [11] the energy of these hot atoms can be estimated to be about 0.6 eV (58 kJ mol^{-1}).

The yield of propylene in the presence of H_2S is greater than that in the presence of oxygen: $\Delta\phi(\text{C}_3\text{H}_6) = 0.07$, compared with a value of 0.01 reported at 8.4 eV.

The thermalized C_3H_5 radicals that have an allylic structure cannot be involved in the endothermic reaction[†]



Therefore either excited allylic radicals or vinylic radicals are involved. The contribution of reaction (19) significantly increases with increasing photon energy as expected. The total yield of non-dissociating C_3H_5 radicals is probably higher than that estimated on the basis of $\Delta\phi(C_3H_6) \approx 0.7$ because some allylic radicals, if they are correctly recognized as precursors of excess propylene formed in the presence of H_2S , are likely to lose some excitation energy prior to their reaction with H_2S . The quantum yield for methyl radicals offers a means of establishing the yield of C_3H_5 . $\phi(CH_3)$ is 0.37 and 0.29 at pressures of 60 and 500 Torr (8 and 66.5 kPa) respectively. Reaction (15) contributes 0.15 and reaction (17) contributes 0.07 and 0.015 at pressures of 60 and 500 Torr respectively to the total yield of CH_3 . The difference $\Delta\phi(CH_3)$ of 0.13 and 0.11 at pressures of 60 and 500 Torr respectively can be assigned as the yield of reaction (20):



3.3. C_4 products

The total yield of C_4H_6 hydrocarbons is about 0.23 (see Table 1). Their only source seems to be the reaction



ϕ_{21} is much higher than the analogous value obtained at 8.4 eV. The ratio of quantum yields of individual hydrocarbons is constant and independent of pressure:

$$\phi(1.3-C_4H_6) : \phi(1.2-C_4H_6) : \phi(1-C_4H_6) = 1:0.18:0.13$$

The data obtained at 8.4 eV are shown below for comparison:

$$\begin{array}{ll} 1 : 0.11 : 0.33 & \text{at 60 Torr} \\ 1 : 0.20 : 0.50 & \text{at 500 Torr} \end{array}$$

Isomerization competing with collisional deactivation, which is observed in the xenon photolytic experiments, does not occur at higher photon energies. Either the direct formation of 1,3- C_4H_6 is favoured or isomerization at greater energies is too fast to be affected by the changes in pressure used in this study.

A relatively high yield of n-butane persists in the presence of oxygen (Table 1). The arguments in favour of an ionic mechanism have already been mentioned. Ion-molecule reactions of an H_2^- transfer type could be held

[†] ΔH for reaction (19) was calculated from data reported in ref. 12.

TABLE 2

Fragmentation of the photoexcited 1-butene molecule at 10.0 eV

	10.0 eV (this work)	10.0 eV [2]	8.4 eV [4]
$C_3H_4 + CH_3 + H$	0.17		0.12
$C_3H_5^* \rightarrow C_3H_4 + H$	—	0.23	0.13
$C_3H_5 + CH_3$	0.12	—	0.26
$C_2H_5 + C_2H_2 + H$	0.07		0.09
$C_2H_5^* + C_2H_2 + H$	0.08	0.12	—
$C_2H_3 + H + C_2H_4$	0.10	0.09	—
$C_2H_2 + C_2H_4 + 2H(H_2)$	0.02	—	—
$2C_2H_4$	—	0.05	0.04
$C_4H_6 + 2H(H_2)$	0.23	0.36	0.14
$C_2H_2 + 2CH_3$	0.02	0.05	—
$C_3H_6 + CH_2$	0.02	0.045	0.02
$C_4H_7 + H$?	0.05	0.12
$C_2H_5 + C_2H_3$	—	—	0.05
$C_4H_8^+ + e^-$	0.20 ^a	?	—
Total	1.01		

^aSee ref. 8.

responsible for the effect but the evidence is too meagre to justify further speculation.

3.4. Photolysis of pure 1-butene

In the unscavenged experiments the radicals undergo recombination and disproportionation reactions, yielding some stable products that can be analysed. Thus the presence of ethane indicates the occurrence of the recombination of methyl radicals; isopentane and n-pentane originate from the reactions of methyl, sec-butyl and n-butyl radicals respectively; propane must have ethyl radical as its precursor; 1-pentene and 3-methyl-1-butene are likely to be formed in reactions of butenyl radicals that differ in structure. In the scheme presented in Table 2 the mode of formation of butenyl radicals is not accounted for. However, they are likely to originate from the secondary process: hot hydrogen atoms present in the system along with addition to a double bond may abstract the hydrogen from a parent butene molecule



The yields for all these radical products are low owing to the competition of the parent butene for the radicals in the system. We have not attempted to determine the higher molecular products of such radical polymerization.

4. Conclusions

Quantum yields of the major modes of decomposition of 1-butene at 123.7 nm can be assigned. The results are summarized in Table 2. The total is 1.01; such excellent agreement is of course fortuitous, but is nevertheless reassuring. The data obtained in Collin's laboratory [2] and our results at 147 nm [4] are included for comparison. The discrepancies between our results and those of Collin may be due to the differences in experimental conditions.

With an increase in photon energy from 8.4 to 10.0 eV the contribution of the split of a C—C bond in the β position to the double bond decreases from $\phi = 0.51$ at 8.4 eV to $\phi = 0.29$ at 10.0 eV. However, both the contribution of the rupture of a C—H bond yielding butadiene and the fragmentation giving C_2 products are found to increase.

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