PHOTOLYSIS OF n-BUTENE AND ISOBUTENE AT 174.3 - 174.5 nm (7.10 eV)

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(Received June 13, 1977; in revised form August 3, 1977)

Summary

The photolysis of n-butene and isobutene was carried out in a static system using nitrogen resonance lines at 174.3 - 174.5 nm (7.11 - 7.10 eV). The main fragmentation process of the photoexcited n-butene molecule is the C—C split in the β position to the double bond. The primary quantum yield Φ is 0.66. The Φ value for the α C—C split of isobutene is equal to 0.78. The stabilization and decomposition processes of $(C_3H_5)^*$ radicals formed in both systems are discussed. From the Stern–Volmer plots it is concluded that these radicals are formed in two distinct energy states. Contrary to our earlier report on *cis*-2-butene photolysis at the same wavelength, stabilization of the primary photoexcited butene molecules was observed. Certain results obtained at different photon energies are compared.

Introduction

There have been several photochemical studies of n-butene and isobutene in different UV regions. For n-butene at 185 nm, Borrell *et al.* [1, 2] have reported a prevalence of bond breakage in a β position to the double bond both for C—C and C—H bonds (in the ratio 6:1). In particular, the quantum yield of the process

$$\text{n-}C_4H_8^{**} \rightarrow CH_3 + CH_2\text{—}CH=CH_2$$
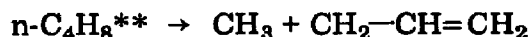
has been found to be equal to 0.71. At 147 - 105 nm we have indicated the decrease in the importance of C—C splitting with the increase in photon energy, *e.g.* at 147 nm, allene and 1,3-butadiene are formed in approximately equal amounts [3].

For the photolysis of isobutene at 185 nm, the cleavages of the C—C and of the β C—H bonds have been found to be the major processes [4]. At 147 -

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105 nm, as reported by Herman *et al.* [5], 80% of the photoexcited iso-C_4H_8 molecules dissociate as follows:

$$iso\text{-}C_4H_8** \;\rightarrow\; C_3H_4 + CH_3 + H$$

In the low energy region (185 nm), quenching of the primary photo-excited intermediates of both butenes has been observed and the similarity in quenching efficiency between different collisional quenchers has been indicated [1, 2, 4]. At 147 - 105 nm, contrary to the latter observation, no pressure dependence of the quantum yields of major primary products both for n-butene and isobutene has been reported [3, 5].

As we have reported recently [6] the region between 185 and 147 nm is very promising, especially when the kinetic characteristics of the decomposition of photoexcited butenes is taken into account. A nitrogen lamp (174 nm) was chosen and constructed as a source of energy [6].

Experimental

Experimental details were essentially the same as those reported in previous studies from this laboratory [6, 7]. Philips Research Grade n-butene and isobutene were used throughout this study. The only detectable impurities in n-butene were propane (0.0055%) and 1,3-butadiene (0.056%). In the isobutene 0.0051% of propane and 0.078% of isobutane were detected. The results described below were corrected for the presence of these impurities. The compounds nitric oxide (C.P., Matheson of Canada, 99.0%), hydrogen sulfide (C. P., Matheson of Canada, 99.5%) and hydrogen iodide (Anhydrous, Can. liquid Air, 99.8%) were used as received after being degassed in a mercury-free vacuum line.

The construction details of the nitrogen lamp are given in ref. 6. The good performance and stability of this lamp should be noted. The output, checked by ethylene actinometry [6, 8], was equal to $(5.42 \pm 0.02) \times 10^{13}$ photons s^{-1}.

Results

The quantum yields of the hydrocarbon products formed in the n-butene and the isobutene photolyses at 133 N m^{-2} (1.0 Torr) are summarized in Tables 1 - 3. The results obtained with NO, HI and H_2S are also presented in these tables. The reactions with accumulated products can be ignored since no deviations from the linearity of quantum yields of the photolytic products *versus* irradiation time were observed. There was no indication of polymer formation on the lamp window.

As seen in Tables 1 and 3, the yield of methyl radicals determined in experiments with H_2S is lower than that in HI experiments. This yield increased with the increase in the concentration of H_2S. In contrast, the yield

TABLE 1

Photolysis of n-butene at 174.3 - 174.5 nm: formation of products at 133 N m^{-2} (1.0 Torr)

Products	Pure n-butene	+ 5% NO	+ 10% HI	+ 10% H$_2$S
Methane	0.025[a]	0.01	0.90	0.66
Acetylene	0.035	0.033	0.03	0.03
Ethylene	0.091	0.090	0.13	0.13
Ethane	0.29	0.009	0.061	0.06
Propylene	0.20	0.19	0.68	0.20
Propane	0.02	–[d]	–	–
Allene	0.17	0.16	0.16	0.16
Propyne	0.014	0.013	0.01	0.01
1,3-Butadiene	n.m.[c]	0.06	n.m.	n.m.
1,2-Butadiene	0.007	0.005	n.m.	n.m.
n-Butane	0.002	–	0.05	0.10
trans-2-Butene[b]	0.01	0.01	0.02	0.01
cis-2-Butene[b]	0.01	0.01	0.02	0.01

[a]Quantum yield error limits greater than or equal to 0.005 or ± 10%
[b]Independent of pressure in the limits 15 - 133 N m^{-2}.
[c]n.m. indicates not measured.
[d]– indicates undetected.

TABLE 2

Photolysis of n-butene at 174.3 - 174.5 nm: quantum yields of products at 133 N m^{-2} (1.0 Torr)

Products[a]	Φ
2-Methyl-1-butene	0.018[b]
Isopentane	0.06
n-Pentene	0.025[b]
trans-2-Pentene	0.037[b]
cis-2-Pentene	0.005[b]
2-Methyl-2-butene	0.006[b]

[a]Products undetected in experiments with NO, HI or H$_2$S scavengers.
[b]Pressure independent values.

of C$_3$H$_5$ radicals did not depend on the HI and H$_2$S concentration above 10% and 20% respectively of the scavengers added.

In the case of n-butene an increase in pressure resulted in an increase in methane quantum yield as shown in Fig. 1. The virtual pressure independence of unsaturated C$_5$ compounds is indicated in Table 2. The decrease in Φ(C$_2$H$_6$) versus pressure is also shown in Fig. 1. The data on the effects of pressure of some products of the photolysis of isobutene are shown in Fig. 2. Except for some cases mentioned above, the yields of all the remaining products were decreased by the increase in reactant pressure as well as by the pressure of helium. The results are presented using Stern−Volmer plots (Figs. 3 - 8).

TABLE 3

Photolysis of isobutene at 174.3 - 174.5 nm: formation of products at 133 N m^{-2} (1.0 Torr)

Products	Pure isobutene	+ 5% NO	+ 10% HI	+ 10% H$_2$S
Methane	0.18[a]	0.014	0.80	0.61[e]
Acetylene	0.015	0.015	0.015	0.016
Ethylene	0.015	0.016	0.016	0.016
Ethane	0.22	–[d]	–	–
Propylene	0.053	0.019	0.33	0.32
Propyne	0.16	0.15	0.16	0.16
Allene	0.30	0.29	0.30	0.30
Isobutane	0.20	–	0.49	0.63
Neopentane	0.16[b]	–	–	–
2-Methyl-1-butene	0.17[c]	–	–	–
2-Methyl-2-butene	0.03[c]	–	–	–

[a] $\Phi(CH_4)$ = 0.16 at 26 000 N m^{-2}.
[b] Small decrease with pressure.
[c] Pressure independent value.
[d] Undetected.
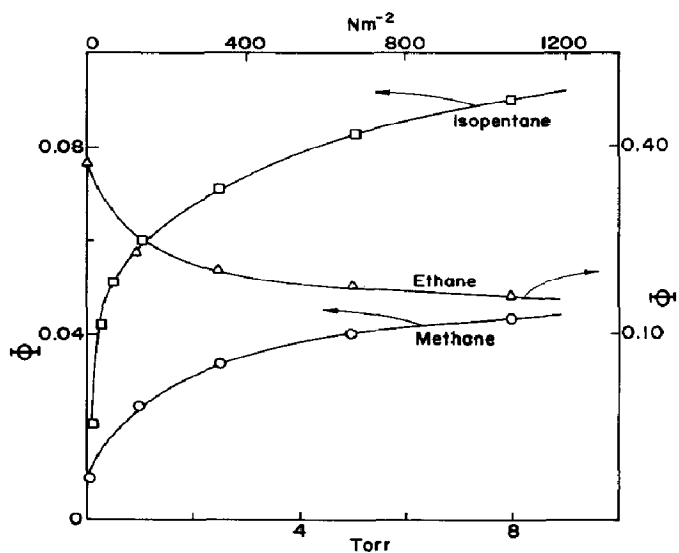[e] This value increases with an increase in the H$_2$S concentration.

Fig. 1. Photolysis of n-butene at 174 nm. The yields of methane, ethane and isopentane are plotted against n-butene pressure.

Discussion

The observed products result from the primary decomposition of the photoexcited molecules, from the decomposition of the resulting primary
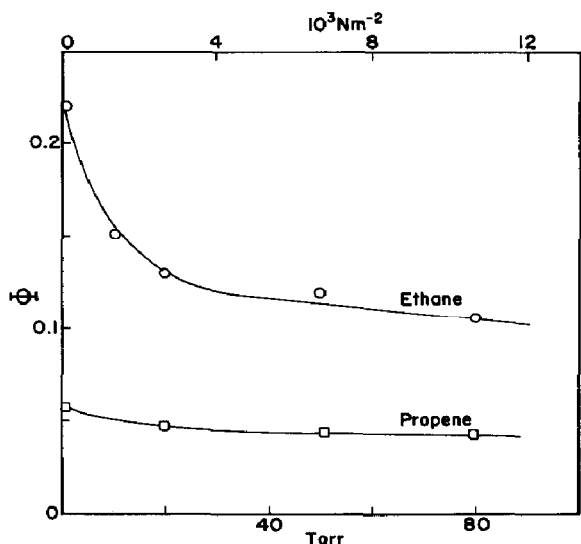
Fig. 2. Photolysis of isobutene at 174 nm. The yields of ethane and propene are plotted against the pressure of isobutene.
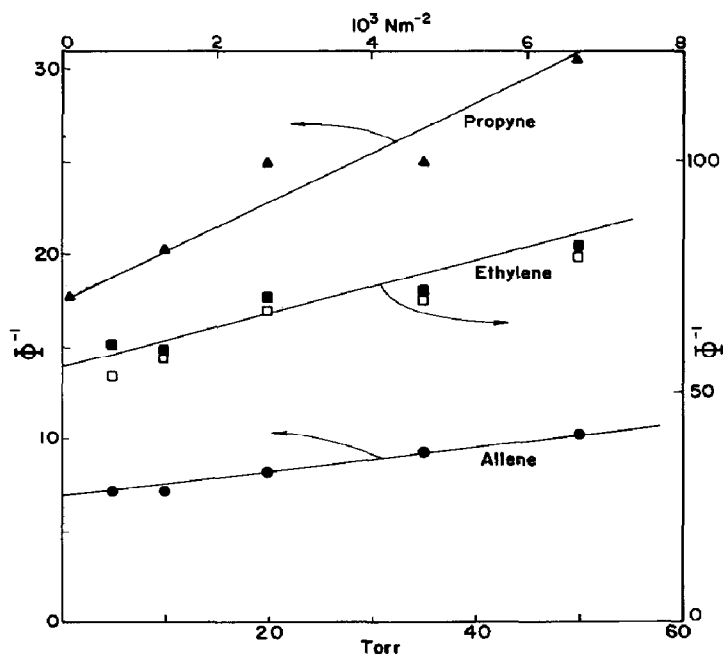

Fig. 3. Photolysis of n-butene at 174 nm. The reciprocal of the quantum yields of several products as a function of n-butene pressure (□) and helium pressure (▲●).

fragments and from radical reactions. The use of NO as a radical scavenger eliminates the latter reactions except for those involving hot radicals and the addition of a hydrogen atom to the double bond.

Contrary to our previous observation on the cis-2-butene system [6] at the same photon energy, both for n-butene and isobutene, stabilization of the
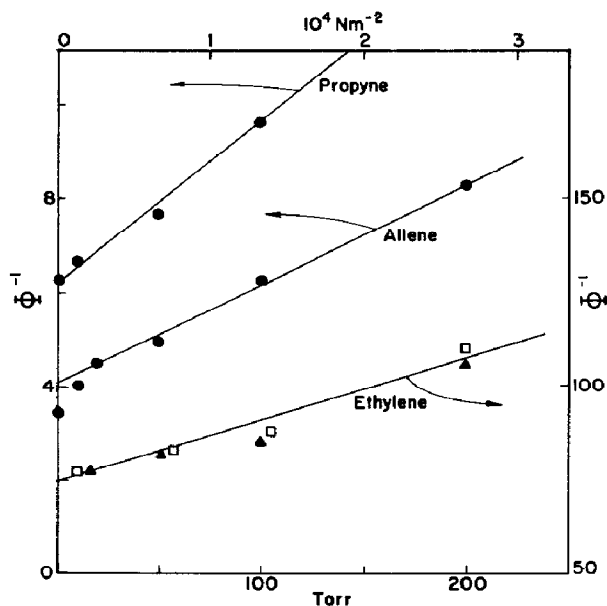
Fig. 4. Photolysis of isobutene at 174 nm. The reciprocal of the quantum yields of several products as a function of isobutene pressure (□) and helium pressure (▲●).
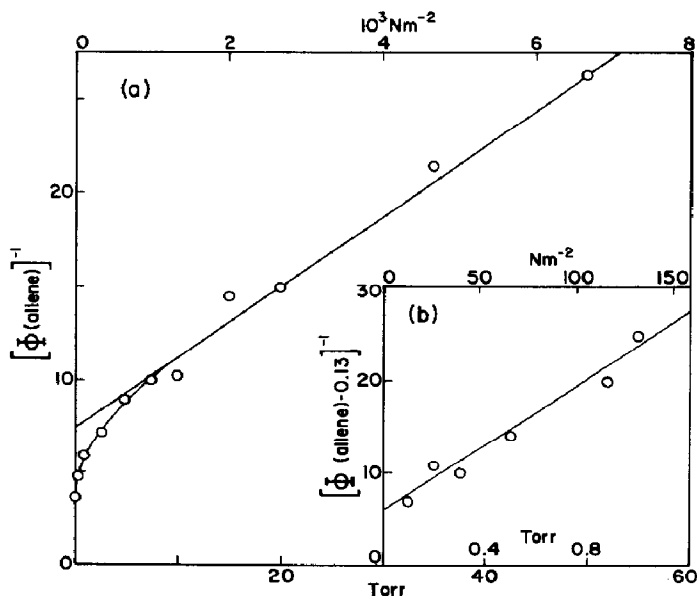

Fig. 5. Photolysis of n-butene at 174 nm. (a) The reciprocal of the quantum yields of allene against n-butene pressure. (b) The reciprocal of Φ(allene) — 0.13 against the pressure of n-butene (see text).

primary photoexcited intermediates was found. This is demonstrated in Figs. 3 and 4, respectively, where Stern–Volmer plots for ethylene yields are shown. Similar behavior was also observed for the acetylene quantum yield. In the
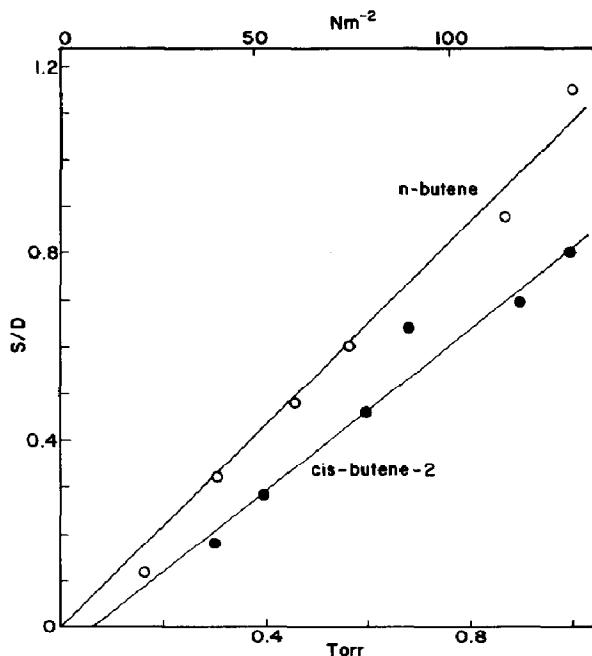
Fig. 6. The S/D ratio as a function of pressure: ○ pure n-butene system; ● pure *cis*-2-butene system (ref. 6). Photon wavelength, 174 nm.
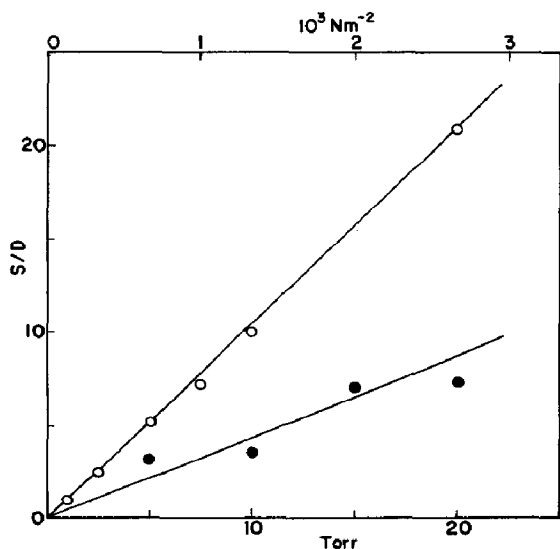

Fig. 7. The S/D ratio as a function of pressure: ○ n-butene pressure; ● helium pressure. Photon wavelength, 174 nm.

plots of $1/\Phi$(ethylene) *versus* butene and helium pressure the data points are scattered around the common line indicating, in agreement with Borrell's earlier observation [1, 2, 4], the similarity in quenching efficiency between collisional quenchers as different as butenes and helium. The difference in
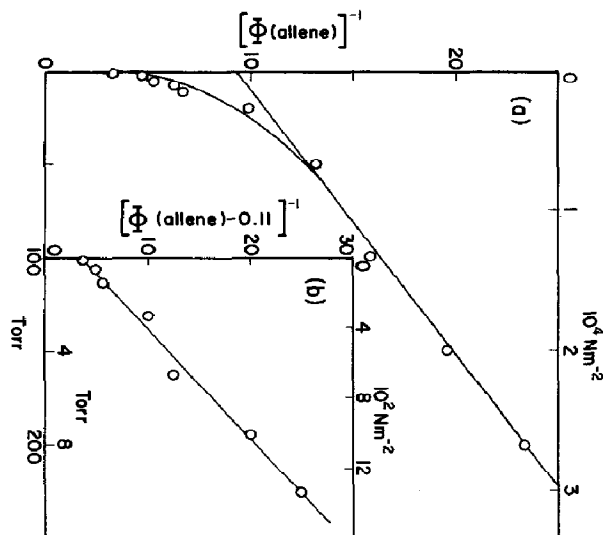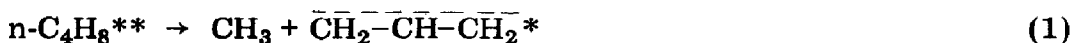
Fig. 8. Photolysis of isobutene at 174 nm. (a) The reciprocal of the quantum yield of allene against isobutene pressure. (b) The reciprocal of Φ(allene) — 0.11 against the pressure of isobutene (see text).

quenching efficiency between both deactivators is, however, clearly demonstrated for the products of radical decomposition (Figs 3, 6, 7 and 8) and this will be discussed further.
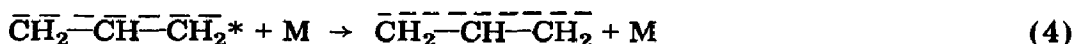
n-Butene

Radicals and their decomposition processes

There are two major radicals, C_3H_5 and s-C_4H_9, which decompose further:

$$n\text{-}C_4H_8^{**} \rightarrow CH_3 + \overline{CH_2\text{-}CH\text{-}CH_2}^* \tag{1}$$

$$n\text{-}C_4H_8 + H \rightarrow s\text{-}C_4H_9^* \; 6 \qquad \Delta H = -1.78 \text{ eV} \tag{2}$$

The yield of the C_3H_5 radicals at 133 N m^{-2} determined in HI and H_2S experiments is equal to 0.48 ± 0.07 and 0.01 ± 0.04 respectively (Table 1). Since only the vinylic form of C_3H_5 radicals reacts with H_2S [6, 8], these results indicate that isomerization of the C_3H_5 radicals originally formed in allylic form (process (1)) is an inefficient process. Indeed, the yield of propyne, which may be formed from the C_3H_5 allylic radical following the isomerization to a vinylic structure, represents no more than 8% of allene yield (Table 1). However, contrary to our recent report on *cis*-2-butene [6] the propyne yield was pressure dependent and this is demonstrated in Fig. 3.

Allylic C_3H_5 radicals decompose or they are stabilized by collisions:

$$\overline{CH_2\text{-}CH\text{-}CH_2}^* \rightarrow H + CH_2{=}C{=}CH_2 \tag{3}$$

$$\overline{CH_2\text{-}CH\text{-}CH_2}^* + M \rightarrow \overline{CH_2\text{-}CH\text{-}CH_2} + M \tag{4}$$

Stern–Volmer plots are given in Figs. 3 and 5. The similarity in the plots of $1/\Phi$ versus pressure for allene in experiments with cis-butene-2 [6] and n-butene may be noted.

(1) Two pressure regions should be distinguished.

(2) The curvature of the plot of $1/\Phi$ versus pressure in the low pressure region (from 0 to about 700 N m^{-2}, Fig. 5(a)) is followed by good linearity in the high pressure region. This yields a Φ' value (the yield of high pressure active species extrapolated to zero pressure) equal to 0.13.
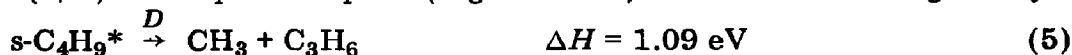
(3) The linearity of the Stern–Volmer plot in the low pressure region is obtained when the plot is drawn in coordinates of $1/(\Phi - \Phi')$ versus pressure (Fig. 4(b)). This yields a Φ'' value (low pressure limiting quantum yield) equal to 0.16.

The $\Phi' + \Phi''$ value is equal to 0.39 and may be compared with the value of Φ for C_3H_5 radicals initially formed in the photodecomposition process. The latter value is equal to 0.66 (the value $(0.68)_{HI} - (0.19)_{NO}$ (Table 1) increased by a factor of 0.16, which is equal to the Φ(allene) value at 133 N m^{-2})†. Then, 44% of C_3H_5 radicals have enough excess energy to decompose and 56% of them may react only with other radicals or may add to the double bonds of n-butene molecules.

If the fact that satisfactory linearity is observed in both pressure regions is not overestimated (Fig. 5), it may be concluded that C_3H_5 radicals are formed in two distinct energy states [6]. Each of these two groups of radicals is probably formed in its own spread of internal energy [9]. However, the sensitivity of the Stern–Volmer plot and/or the precision of experiments is not high enough to respond to these energetic differences.

On the basis of the data given in Fig. 3 one may compare the values of k_{stab}/k_{decomp} [6] for the allene and the propyne formation processes (experiments with helium) and they are equal to 1.67×10^2 and 2.90×10^2 l mol^{-1} respectively. This clearly indicates that the C_3H_4 isomers are formed from different $C_3H_5^*$ precursors. Assuming the same quenching efficiency of $C_3H_5^*$ radicals by helium, the lifetimes of the species leading to allene and propyne formation may be compared. Thus, the propyne–$C_3H_5^*$ lifetime is approximately twice as long as the allene–$C_3H_5^*$ one, indicating the lesser energy excess on the $C_3H_5^*$ in the former case. Apparently, part of the internal energy was consumed in the isomerization process of the C_3H_5 radicals from the allylic to the vinylic form.

It is a matter of tradition [6, 10, 11] that kinetic results on decomposition of s-$C_4H_9^*$ radicals are presented by the use of stabilization –decomposition (S/D) versus pressure plots (Figs. 6 and 7). The mechanism is given by

$$\text{s-}C_4H_9^* \overset{D}{\rightarrow} CH_3 + C_3H_6 \qquad \Delta H = 1.09 \text{ eV} \qquad (5)$$

$$\text{s-}C_4H_9^* + M \overset{S}{\rightarrow} \text{s-}C_4H_9 + M \qquad (6)$$

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† A small correction should be introduced here to take into account the interception of the H atom by HI (see refs. 6 and 7). The correction is considered to be within the experimental error.

It should be noted that the formation of n-C_4H_9 radicals in process (2) may be ignored as discussed previously [3, 12]. The formation of isopentane (Table 2) and the increase in its quantum yield (Fig. 1) with the increase in the n-butene pressure is consistent with the stabilization–decomposition mechanism. In Fig. 6 the plots of S/D versus pressure for n-butene and cis-2-butene [6] are compared and it is seen that within the experimental error the rates of the decomposition processes are similar. It has been recently concluded in the case of cis-2-butene that the energy distribution of H atoms is higher than normal [6]. Taking into account the difference in the free energy of the s-C_4H_9 radical formation from cis-2-butene molecules

$$cis\text{-}C_4H_8\text{-}2 + H \rightarrow s\text{-}C_4H_9^* \qquad \Delta H = -1.65 \text{ eV} \qquad (7)$$
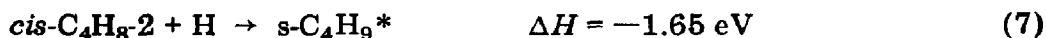
and from n-butene (process (2)), we may conclude that the average energy of hydrogen atoms is lower in n-butene than in the cis-2-butene photolytic system. The high pressure region of the plots of S/D versus pressure are shown in Fig. 7 for n-butene and helium quenchers. It is seen that in the case of the stabilization of s-$C_4H_9^*$ as well as other radicals (Figs. 3 and 5(a), see also ref. 6), the nature of the collisional quencher plays an important role. Thus the only stabilization process which turns out to be unaffected by the nature of a collisional quencher is the one involving primary photoexcited species.

Methyl radicals are formed mainly in processes (1) and (5). Their yield, found in experiments with an HI scavenger at 133 N m^{-2} (Table 1) to be equal to 0.90 ± 0.08, is comparable with the sum of $\Phi(C_3H_5)_{HI} + \Phi(C_3H_4)$ which is equal to 0.85 ± 0.10. Additional routes for CH_3 radicals are given in Table 4. The radicals may combine with the other radicals present in the system studied, the most efficient process being the formation of ethane. The yield of CH_3 radicals decreases with the increase in pressure owing to stabilization of the s-$C_4H_9^*$ radicals (process (6)) and this may partly explain the decrease in the $\Phi(C_2H_6)$ value with an increase in pressure (Fig. 1). Moreover, the increase in n-butene pressure brings about an increase in the yield of stabilized C_3H_5 and C_4H_9 radicals. These radicals may compete in the CH_3 radical capture contributing to the observed decrease in $\Phi(C_2H_6)$. The increase in $\Phi(CH_4)$ values with n-butene pressure may be explained by the disproportionation process involving CH_3 and s-C_4H_9 radicals. Another route of methane formation

$$CH_3^* + n\text{-}C_4H_8 \rightarrow CH_4 + C_4H_7 \qquad (8)$$

is an inefficient process since 5% of NO reduces the $\Phi(CH_4)$ to a low value: $\Phi(CH_4)_{NO} \approx 0.01$.

The last radicals determined directly are C_2H_5 and C_2H_3 radicals which may be formed in the process

$$n\text{-}C_4H_8^{**} \rightarrow C_2H_5 + C_2H_3 \qquad (9)$$

The yield of this process is approximately equal to 0.04 ± 0.02 (Table 1). The presence of C_2H_5 may account for the formation of propane in the unscavenged system ($C_2H_5 + CH_3 \rightarrow C_3H_8$).

TABLE 4

Fragmentation reaction of the photoexcited n-butene molecules at 174 nm[a]

Reaction no.	n-C_4H_8** fragmentation reaction	Φ	
1	CH_2—CH=CH_2 + CH_3	0.66	± 0.06
10	C_4H_7 + H	0.16	± 0.06
11	C_4H_6 + 2H(H_2)	0.06	± 0.01
12	C_2H_4 + C_2H_4	0.05	± 0.01
9	C_2H_5 + C_2H_3	0.04	± 0.02
13	C_2H_2 + 2CH_3	0.035	± 0.01
	Total	1.00	± 0.14

[a]Extrapolated to zero pressure.

The yield of C_4H_7 radicals formed in the process

$$n\text{-}C_4H_8** \rightarrow C_4H_7 + H \qquad (10)$$

may be estimated in the same way as in ref. 6; this gives a value

$$\Phi(C_4H_7) = 0.26 \pm 0.06$$

Molecular products and primary fragmentation

The final results on the primary fragmentation of photoexcited n-C_4H_8** molecules are summarized in Table 4. In accordance with the results of Borrell *et al.* [1, 2], the main fragmentation process is C—C bond splitting in the β position to the double bond (process (1)). The remaining processes explain the formation of C_2H_4, C_2H_2 and 1,3-butadiene. The isomerization of n-butene to other butenes is a minor process (see Table 1).

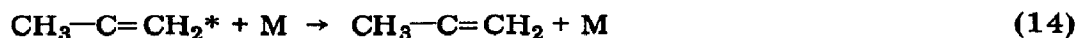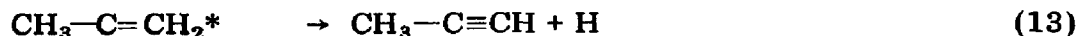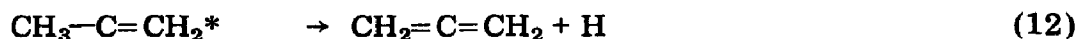*Isobutene*

Radicals and their decomposition processes

The C_3H_5 radicals are formed in the fragmentation of photoexcited isobutene molecules

$$\text{iso-}C_4H_8** \rightarrow CH_3\text{—}C\text{=}CH_2* + CH_3 \qquad (11)$$
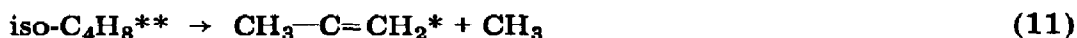
and these radicals may be both allene and propyne precursors [5] (processes (12) and (13) or may be collisionally stabilized (process (14))

$$CH_3\text{—}C\text{=}CH_2* \rightarrow CH_2\text{=}C\text{=}CH_2 + H \qquad (12)$$

$$CH_3\text{—}C\text{=}CH_2* \rightarrow CH_3\text{—}C\equiv CH + H \qquad (13)$$

$$CH_3\text{—}C\text{=}CH_2* + M \rightarrow CH_3\text{—}C\text{=}CH_2 + M \qquad (14)$$

The isomerization of the CH_3—C=CH_2 form to the allylic structure is an inefficient process as indicated by experiments with HI and H_2S radical scavengers (Table 3). The values of k_{stab}/k_{decomp} for allene and propyne formation processes (experiments with helium) determined from data presented in Fig. 4 are equal to 0.97×10^2 and 1.04×10^2 l mol^{-1} respectively and as such are considered equal within the experimental error. Moreover, the quantum yield values of allene and propyne at zero pressure, equal to 0.25 and 0.16 respectively, are approximatively in the ratio 3:2. Thus we conclude that actually both allene and propyne are formed from the same precursor and that the relative probabilities of the occurence of processes (12) and (13) are in accord with the number of hydrogen atoms on each of the two terminal carbon atoms [5].

The same behavior of the dependence of Φ(allene) on the isobutene pressure as in the cases of cis-2-butene [6] and n-butene (Fig. 5) was observed (see Fig. 8), indicating the similarity in the energy partitioning between C_3H_5 and CH_3 radicals in the photodecomposition process of the three butenes. The quantum yield values obtained at zero pressure are equal to 0.11 and 0.28 in the high and low pressure regions respectively. The comparison of the sum of the quantum yields (0.39) with the value of $\Phi(C_3H_5)$ initially formed in the photodecomposition of iso-C_4H_8**, which is equal to 0.78 ($\Phi(C_3H_5)_{HI,H_2S}$ + Φ(allene) + Φ(propyne) at 133 N m^{-2} (Table 3)) indicates that only 50% of C_3H_5 radicals have enough energy excess to decompose, yielding allene.

A substantial effect of the nature of the collisional deactivator in quenching $C_3H_5^*$ radicals may be shown when we compare the slope of the "allene" line in Fig. 4 (helium) with that in Fig. 8(a) (allene, isobutene). Thus the same conclusion as for n-butene may be drawn, i.e. only the quenching process of the primary photoexcited species is unaffected by the nature of the collisional deactivator*

The t-butyl radicals formed in the process

$$H + iso\text{-}C_4H_8 \rightarrow t\text{-}C_4H_9^* \qquad \Delta H = -1.81 \text{ eV} \qquad (15)$$
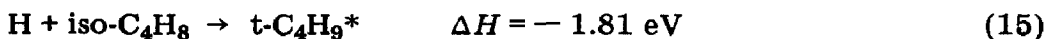
do not apparently decompose. The yield of propylene was only slightly dependent on the pressure of isobutene (Fig. 2). This is in agreement with the data of other authors [4, 5]. Radical—radical disproportionation reactions involving C_3H_5 radicals are probably responsible for the formation of propylene which is scavenged by NO; the remaining $\Phi(C_3H_5)_{NO}$ may be formed through the decomposition of t-$C_4H_9^*$ radicals formed in process (15) involving hot hydrogen atoms

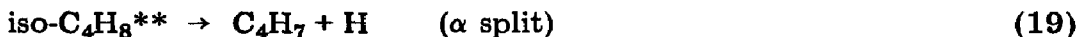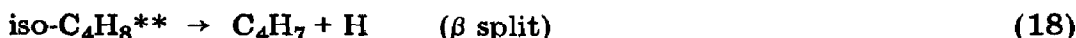$$t\text{-}C_4H_9^* \rightarrow C_3H_6 + CH_3 \qquad (16)$$

or through methylene elimination from the photoexcited molecules

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*The C_3H_5 radical formed from isobutene at 185 nm [4] does not decompose and allene is formed from the decomposition of photoexcited iso-C_4H_8 molecules. Thus, the decrease in Φ(allene) with pressure is not dependent on the nature of the added gases (see Fig. 2 in ref. 4).

$$iso\text{-}C_4H_8^{**} \rightarrow C_3H_6 + CH_2 \tag{17}$$

CH_3 radicals are formed mainly in process (11) and their yield at 133 N m^{-2}, estimated from the sum of the quantum yield values $\Phi(C_3H_5)_{HI,H_2S}$ + $\Phi(C_3H_4)$ which is equal to 0.78 ± 0.08, corresponds closely to the $\Phi(CH_3)$ determined in HI experiments (0.80 ±0.09). Neopentane and unsaturated C_5 compounds (Table 3) are formed by the combination of radicals. The virtual independence of $\Phi(C_5H_{10})$ on pressure shows that the yield of C_4H_7 radicals is not pressure dependent. Thus C_4H_7 radicals cannot be C_3H_4 isomer precursors.

The quantum yields of C_4H_7 formed in the processes

$$iso\text{-}C_4H_8^{**} \rightarrow C_4H_7 + H \qquad (\beta \text{ split}) \tag{18}$$

$$iso\text{-}C_4H_8^{**} \rightarrow C_4H_7 + H \qquad (\alpha \text{ split}) \tag{19}$$

may be determined in the same way as in ref. 6. This gives the value of 0.25 ± 0.10 for process (18) and the value of 0.05 ± 0.02 for process (19).

Molecular products and primary fragmentation

The results of the primary fragmentation of photoexcited isobutene molecules are given in Table 5. As seen, the major processes are C—C bond splitting (approximately 80%) and C—H bond rupture in the β position (approximately 20%). Processes (17), (20) and (21) are added in order to account for the formation of other minor products.

TABLE 5

Fragmentation reactions of the photoexcited isobutene molecules at 174 nm[a]

Reactions	Iso-$C_4H_8^{**}$ fragmentation reaction	Φ	
11	$CH_3\text{—}C{=}CH_2 + CH_3$	0.78	± 0.06
18	$C_4H_7(\beta \text{ splitting}) + H$	0.25	± 0.10
19	$C_4H_7(\alpha \text{ splitting}) + H$	0.05	± 0.02
20	$C_2H_2 + 2CH_3$	0.015	± 0.005
17	$C_3H_6 + CH_2$	< 0.02	± 0.01
21	$2C_2H_4$	0.01	± 0.005
	Total	1.12	± 0.20

[a]Extrapolated to zero pressure.

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Conclusions

The comparison of quantum yield values of the major primary decomposition processes of both butenes for different photon energies is done in Table 6.

TABLE 6

Quantum yield values of the major primary processes of the fragmentation of n-butene and isobutene photoexcited at various wavelengths

Wavelength (nm)	185	174	147	123.6
Energy (eV)	6.4	7.1	8.4	10.0
n-Butene reference	1,2	This work	3	3
β C—C cleavage	0.71	0.66	0.38	0.23
C—H cleavage	0.12	0.22	≈ 0.35	≈ 0.40
Isobutene reference	1,4	This work	5	5
C—C cleavage	> 0.33[a]	0.78	0.8	0.8
β C—H cleavage	> 0.23	0.25	n.m.	n.m.
α C—H cleavage	n.m.[b]	0.05	n.m.	n.m.

[a] Value probably underestimated.
[b] n.m. indicates not measured.

In the case of n-butene the β C—C bond rupture becomes less important with the increase in photon energy, and at the same time the C—H cleavage becomes more important. In the photolysis of isobutene, the situation is more confused since several values are missing. However, it seems that the C—C cleavage is much less dependent on photon energy than in the case of n-butene.

References

1 P. Borrell, P. Cashmore, A. Cervenka and F. - C. James, J. Chim. Phys., 97C (1970) 229.
2 P. Borrell and P. Cashmore, Ber. Bunsenges Phys. Chem., 72 (1968) 182.
3 G. J. Collin, Can. J. Chem., 51 (1973) 2853.
4 P. Borrell and P. Cashmore, Trans. Faraday Soc., 65 (1969) 1595.
5 J. Herman, K. Herman and P. Ausloos, J. Chem. Phys., 52 (1970) 28.
6 A. Wieckowski and G. J. Collin, J. Phys. Chem., December, 1977.
7 G. J. Collin and P. Perrin, Can.J. Chem., 50 (1972) 2823.
   G. J. Collin and K. Bukka, J. Photochem., 6 (1977) 381.
8 P. Ausloos, R. E. Rebbert and S. G. Lias, J. Photochem., 2 (1973/74) 267.
9 W. Forst, in Theory of Unimolecular Reactions, Academic Press, New York, 1973.
10 B. S. Rabinovitch and R. W. Diesen, J. Chem. Phys., 30 (1959) 735.
11 P. M. Perrin and G. J. Collin, Can. J. Chem., 51 (1973) 724.
12 W. E. Falconer and W. A. Sunder, Int. J. Chem. Kinetics, 3 (1971) 395.