PRIMARY PROCESSES IN THE PHOTOLYSIS OF n-BUTANE WITH 8.4 AND 10.0 eV PHOTONS*

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Summary

The photolysis of $n\text{-}C_4D_{10}$ has been investigated with 8.4 eV and 10.0 eV photons, using HI to scavenge free radicals through the reaction: R_D + HI → R_DH + I (where R_D is a fully deuterated alkyl or alkenyl radical). From the results of such experiments, the quantum yields of the molecular and radical products are obtained over a pressure range from 3 to 47 Torr at both energies. In addition, the photolysis of $CD_3CH_2CH_2CD_3$ and $CD_3CD_2CH_2CH_3$ have been investigated in the presence of radical scavengers over a range of pressures at both energies. The results are discussed with particular emphasis on deriving the quantum yields of all the primary processes, and following changes in the quantum yields as a function of energy. Major conclusions are: (a) the quantum yield of the process (C_4D_{10} → C_4D_8 + D_2) diminishes from 0.70 to 0.37 when the photon energy is increased from 8.4 to 10.0 eV; (b) the relative overall importance of direct C–C bond cleavage processes, alkane elimination processes, and D-atom elimination processes do not change significantly as a function of energy; (c) processes involving breakage of the 2, 3 C–C bond strongly predominate over processes involving the 1, 2 C–C bond at both energies, although there is a lower probability for localization of the energy in the center bond when the energy is increased.

Introduction

The photolysis of n-butane, using 8.4, 10.0, and 11.6 - 11.8 eV photons, has been investigated on several occasions [1], and the major primary processes have been identified. In addition, the dissociation of n-butane excited by electron impact in a glow discharge has been studied [2], and it has been suggested that the same primary processes may occur as in the vacuum ultraviolet photolysis. Although relative yields of fragments formed in the photolysis of n-butane [1d] and the isotopic distributions of products formed in

$CD_3CH_2CH_2CD_3$ [1d] and $CH_3CD_2CD_2CH_3$ [1b], have been reported, no quantum yield determinations have ever been made. Also no detailed analysis of the dissociation processes leading to the formation of the products has been undertaken since a complete product distribution became available.

This study of the photolysis of n-butane was instigated by the results of a recent investigation of the photolysis of propane [3], in which HI was used as a radical scavenger in fully deuterated propane:

$$R_D + HI \rightarrow R_DH + I \tag{1}$$

It was shown in that study [3] that HI is a more effective scavenger of radicals and H atoms than H_2S; previous determinations of radicals formed in n-butane [1d] were made using H_2S. A detailed analysis of the quantitative results obtained in that study [3], as well as of results obtained with the partly deuterated propane $CD_3CH_2CD_3$, indicated that the relative quantum yields of the various primary processes involving C–C cleavage did not change significantly as a function of energy in the energy range 8.4 to 11.8 eV. On this basis, it was suggested that these processes resulted from excitation of a C–C bond.

In view of these results, it was considered of interest to re-examine the photolysis of n-butane in more detail in order to establish whether the conclusions of the propane study have a general validity for alkanes photolyzed at these energies. Therefore, n-C_4D_{10}/HI mixtures, as well as $CD_3CH_2CH_2CD_3$ and $CD_3CD_2CH_2CH_3$ have been photolyzed with 8.4 and 10.0 eV photons, and the quantum yields of the dissociation products have been determined.

Experimental

The vacuum ultra-violet photolysis experiments described here were carried out using as light sources the xenon and krypton resonance lamps described in an earlier report [4]. After irradiation, an aliquot of the sample was expanded into the evacuated gas inlet system of a calibrated gas chromatograph equipped with a squalane column and a flame ionization detector in order to quantitatively determine the yields of the photolytic products. In experiments in which it was necessary to determine the relative yields of two or more isotopic analogues of a given compound, the entire sample was subsequently injected onto a squalane column and the various products of interest were frozen out from the helium stream in individual traps maintained at liquid nitrogen temperature. The helium was then pumped from the separated isotopically labelled products, which were subsequently analyzed using a commercial analytical mass spectrometer. Hydrogen and methane products were determined in a few experiments by gas distillation procedures carried out on a vacuum line.

Chemical actinometry was based on the photolysis of ethylene, for which it was assumed that the quantum yield for acetylene formation is unity at both 8.4 eV and 10.0 eV. Every third or fourth experiment was follow-

ed by an ethylene photolysis experiment, carried out under the same conditions as the butane photolysis experiments.
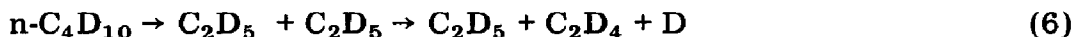
Results and Discussion

The possible primary processes which can occur in n-butane (exemplified here by $n\text{-}C_4D_{10}$, since this compound was used for most of our experiments) include processes in which the end C–C bond is broken with the simultaneous transfer of an H(D) atom to form an alkane molecular product:
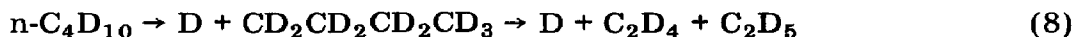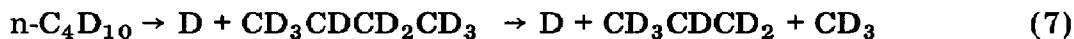
$$n\text{-}C_4D_{10} \rightarrow CD_4 \quad + C_3D_6 \tag{2}$$

$$n\text{-}C_4D_{10} \rightarrow C_3D_8 \quad + CD_2 \tag{3}$$

a similar alkane elimination process involving breakage of the center C–C bond:

$$n\text{-}C_4D_{10} \rightarrow C_2D_6 \quad + C_2D_4 \tag{4}$$

as well as processes initiated by a direct C–C bond cleavage:

$$n\text{-}C_4D_{10} \rightarrow CD_3 \quad + C_3D_7 \rightarrow CD_3 + CD_3 + C_2D_4 \tag{5}$$

$$n\text{-}C_4D_{10} \rightarrow C_2D_5 \quad + C_2D_5 \rightarrow C_2D_5 + C_2D_4 + D \tag{6}$$

or, C–D bond cleavage:

$$n\text{-}C_4D_{10} \rightarrow D + CD_3CDCD_2CD_3 \quad \rightarrow D + CD_3CDCD_2 + CD_3 \tag{7}$$

$$n\text{-}C_4D_{10} \rightarrow D + CD_2CD_2CD_2CD_3 \rightarrow D + C_2D_4 + C_2D_5 \tag{8}$$

Processes (5) to (8) may, or may not, be followed by the secondary decomposition processes listed here, depending on the energy of the photon, the pressure, and the exact mechanism of the primary process. It should be pointed out that the final decomposition products of process (8) cannot be distinguished from those of process (6).

Finally, it has been demonstrated [1] that excited n-butane eliminates a molecule of hydrogen:

$$n\text{-}C_4D_{10} \rightarrow D_2 + C_4D_8 \tag{9}$$

The quantum yields of the molecular products as well as the radicals formed by dissociation of $n\text{-}C_4D_{10}$ excited by 8.4 eV and 10.0 eV photons are shown in Tables 1 and 2, respectively. The quantum yields of the various partly deuterated products formed at these energies in $CD_3CH_2CH_2CD_3$ in the presence of NO added as a radical scavenger are shown in Table 3. These results will be discussed in terms of the primary processes (2) to (9).

$n\text{-}C_4D_{10} \rightarrow CD_4 + C_3D_6$
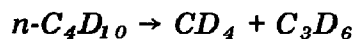
The occurrence of the primary process (2) was demonstrated by Okabe and Becker [1b] who showed that the methane formed in the photolysis of $n\text{-}C_4H_{10}/n\text{-}C_4D_{10}$ (1:1) in the presence of a radical scavenger consisted of about 90% CD_4 and CH_4. The results given in Tables 1 and 2 show that the

154

TABLE 1

Quantum yields of fragments formed in the photolysis of $n\text{-}C_4D_{10}$ with 8.4 eV photons

	3 Torr	6 Torr	15 Torr	46 Torr
CD_3	0.29	0.22	0.20	0.19
CD_4	0.0058	0.0064	0.0062 (0.0065)	0.0053
C_2D_2	0.042	0.044	0.038 (0.034)	0.029
C_2D_3	0.016	0.0215	0.017	0.021
C_2D_4	0.27	0.28	0.25 (0.28)	0.28
C_2D_5	0.14	0.14	0.14	0.16
C_2D_6	0.11	0.11	0.11	0.13
C_3D_5	n.d.	0.032	n.d.	0.023
C_3D_6	n.d.	0.042	0.043 (0.044)	0.038
C_3D_7	0.0031	0.0042	0.0060	0.0078
C_3D_8	(0.0036)	(0.0036)	(0.0036)	(0.0036)
$1\text{-}C_4D_8$	0.0638	0.066	0.071	0.101
D	0.39			
D_2	0.70			

Yields determined in the photolysis of $n\text{-}C_4D_{10}/HI$ (1:0.04) mixtures; radical yields listed correspond to the yields of R_DH products. Quantum yields in parentheses are those determined for molecular products in $n\text{-}C_4D_{10}/O_2$ (1:0.05) mixtures.

TABLE 2

Quantum yields of fragments formed in the photolysis of $n\text{-}C_4D_{10}$ with 10.0 eV photons

|	5 Torr	16 Torr	47 Torr
CD_3	0.42	0.40	0.36
CD_4	0.039	0.040 (0.040)	0.040 (0.038)
C_2D_2	0.129	0.122 (0.117)	0.103 (0.0951)
C_2D_3	0.068	0.074	0.052
C_2D_4	0.463	0.475 (0.512)	0.464 (0.474)
C_2D_5	0.217	0.240	0.212
C_2D_6	0.200	0.200 (0.204)	0.200 (0.200)
C_3D_5	0.068	0.065	0.050
C_3D_6	n.d.	0.090	0.096 (0.0930)
C_3D_7	0.0049	n.d.	0.0101
C_3D_8	(0.0183)	0.0183 (0.0183)	(0.0198)
C_4D_7		0.0102	0.0070
$1\text{-}C_4D_8$	n.d.	(0.043)	(0.052)
D	0.63	0.65	0.60
D_2	0.44	0.44	0.37

Yields determined in the photolysis of $n\text{-}C_4D_{10}/HI$ (1:0.04) mixtures; radical yields listed correspond to the yields of R_DH products. Quantum yields in parentheses are those determined for molecular products in $n\text{-}C_4D_{10}/O_2$ (1:0.05) mixtures.

quantum yield of methane formed in n-C_4D_{10} at 8.4 and 10.0 eV is 0.006 and 0.040, respectively, and is invariant with increasing pressure, within experimental error. Making the reasonable assumption, then, that the methane produced in process (2) does not undergo further dissociation, we tentatively assign these quantum yields as the quantum yields of process (2).

The results obtained in the earlier study [1b] indicated that in the photolysis of $CH_3CD_2CD_2CH_3$, the methane consisted mainly of CH_3D and CH_4; the presence of CH_4 indicated that some of the methane originated from a process in which a hydrogen atom from one methyl group was transferred to the other methyl group in the methane elimination process. The results obtained in this study do not give any evidence for the occurrence of such a 1,4-elimination process. In the photolysis of $CD_3CH_2CH_2CD_3$, the methane consists entirely of CD_3H within the limits of detection (1%). This methane can only originate in a process in which a methyl group departs with a H atom from one of the center carbon atoms. In the photolysis of $CD_3CD_2CH_2CH_3$ in the presence of NO at 10.0 eV, CD_4 and CD_3H are formed in a ratio of approximately 1:0.4, indicating that there are two mechanisms for methane elimination:

$$CD_3CD_2CH_2CH_3 \rightarrow CD_4 \quad + CDCH_2CH_3 \tag{10}$$

$$CD_3CD_2CH_2CH_3 \rightarrow CD_3H + CD_2CHCH_3 \tag{11}$$
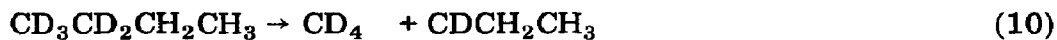
(Unfortunately, an accurate analysis of the CH_4 and CH_3D formed in this experiment was not possible). As some of the results which will be discussed below will show, there are isotope effects favoring processes in which a C–H bond is broken over similar processes in which a C–D bond is broken. Therefore, it is probable that in $CD_3CD_2CH_2CH_3$, the 1,3-elimination to form CD_3H (reaction 11) is more important than the analogous 1,3-elimination in $CD_3CH_2CH_2CD_3$, C_4H_{10}, or C_4D_{10}. We can say that at least 70% of the methane formed in n-butane originates from a 1,2-elimination process.

n-$C_4D_{10} \rightarrow C_3D_8 + CD_2$
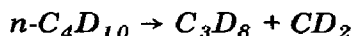
The results given in Tables 1 and 2 show that C_3D_8 is formed in the photolysis of n-C_4D_{10}/NO mixtures with a quantum yield of 0.0036 at 8.4 eV and 0.018 at 10.0 eV. At the higher energy, there may be a slight increase in the yield of propane with increasing pressure, indicating some further dissociation of the propane product, but this increase is so slight that it is impossible to tell if it is real. The quantum yields observed for C_3D_8 can thus be equated to the quantum yield of process (3). The fate of the CD_2 species formed in these experiments was not investigated. Singlet methylene formed in process (3) would insert into n-butane to give pentane products which should be stabilized in the pressure range covered in this study.

n-$C_4D_{10} \rightarrow C_2D_6 + C_2D_4$
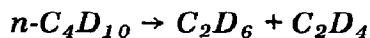
In an earlier study [1b] in which an equimolar C_4D_{10}–C_4H_{10}–NO mixture was photolyzed with 8.4 eV photons, it was shown that 90% of the

TABLE 3

Quantum yields of products formed in the photolysis of $CD_3CH_2CH_2CD_3$/NO (1:0.05)

	8.4 eV			10.0 eV	
	15 Torr	46 Torr	94 Torr	15 Torr	47 Torr
Methane:					
CD_3H	n.d.	0.006 (0.18)	n.d.	0.040 (0.44)	0.040 (0.36)
CDH_3	n.d.	(0.021)	n.d.	(0.041)	(0.044)
Acetylene	n.d.	0.023	0.0059	0.12	0.12
Ethylenes:					
C_2D_3H	0.11	0.10 (0.00)	0.11	0.16 (0.036)	0.16
$C_2D_2H_2$	0.15	0.13 (0.00)	0.13	0.23 (0.069)	0.25
C_2H_4	0.031	0.021 (0.00)	0.041	0.055	0.055
Ethanes:					
$C_2D_4H_2$	0.010	0.013 (0.005)	0.016	0.010 (0.003)	0.010
$C_2D_3H_3$	0.094	0.089 (0.13)	0.097	0.19 (0.23)	0.19
Propylenes:					
$C_3D_3H_3$	0.053	0.053	0.052	0.085	n.d.
$C_3D_2H_4$			0.011	0.048	n.d.
1-Butene	n.d.	n.d.	n.d.	n.d.	0.16
Hydrogens:					
D_2		0.023		0.069 (0.0)	0.071
HD		0.061		0.13 (0.22)	0.13
H_2		0.69		0.22 (0.41)	0.24

$\Phi(C_2D_4) \sim 0.001$ at 8.4 eV, ~ 0.008 at 10.0 eV; $\Phi(C_2DH_3) \sim 0.005$ at 8.4 eV, 0.016 at 10.0 eV. Figures in parentheses represent *increases* in the yield of a particular analogue when HI is used as a radical scavenger; *i.e.* figures in parentheses are yields of the radical corresponding to the particular analogue minus one H atom.

ethane consisted of C_2H_6 or C_2D_6, demonstrating that ethane is eliminated as a molecule from excited butane. The results given in Tables 1 and 2 show that the quantum yield of C_2D_6 formed in n-C_4D_{10} at 8.4 and 10.0 eV is 0.11 and 0.20, respectively. The experiments carried out with $CD_3CH_2CH_2CD_3$ (Table 3) show that at both energies, most of the ethane is formed in an elimination process in which a hydrogen is transferred from a center carbon atom across the bond being broken to form ethane and C_2HD_3:

$$CD_3CH_2CH_2CD_3 \rightarrow CD_3CH_3 + C_2HD_3 \tag{12}$$

The C_2HD_3 formed in primary process (12) shows up as $CHDCD_2$; the yield of this ethylene analogue is approximately equal to the yield of the corresponding ethane, CD_3CH_3, at both energies (Table 3). There is also evidence that at both energies some ethane is formed in a process involving transfer of a D atom from the methyl group:

$$CD_3CH_2CH_2CD_3 \rightarrow CD_3CH_2D + CD_2CH_2 \tag{13}$$

At 8.4 eV, 13%, and at 10.0 eV, 5% of the ethane formed in $CD_3CH_2CH_2CD_3$ is CD_3CH_2D. (As will be seen below, ethylene CD_2CH_2 is also formed in another process; therefore its yield is much larger than that of CD_3CH_2D). Since process (12) may proceed through formation of an ethylidene diradical, process (13) may be a lower energy process than process (12); therefore, the ethane formed in process (13) may carry away more excess energy than that produced in process (12), and further dissociation could be more likely. Actually, there is some evidence that a fraction of the ethane, CD_3CH_2D, may undergo fragmentation to give two methyl radicals; CH_2D radicals are formed in the photolysis of $CD_3CH_2CH_2CD_3$ (Table 3). When HI is added as a radical scavenger to $CD_3CH_2CH_2CD_3$, CH_3D appears as a product:

$$CH_2D + HI \rightarrow CH_3D + I \tag{14}$$

The CH_2D radicals most likely originate in the decomposition of CD_3CH_2D. Corroborative evidence for this conclusion is found in the fact that the yield of CD_3CH_2D (process 13) increases with increasing pressure in the 8.4 eV experiments. The yield of CH_2D radicals (i.e. the yield of $CD_3CH_2D^*$ which dissociates at these energies and at pressures in the range 5 - 100 Torr) is about 0.02 at 8.4 eV and 0.04 at 10.0 eV. This, taken together with the observed yields of CD_3CH_3 and CD_3CH_2D (Table 3) leads to an estimate that the ratio of the relative importance of process (13) and process (12) is about 0.3:1 at both 8.4 and 10.0 eV. The results given in Tables 1 and 2 indicate, however, that the total yield of the molecular ethane product shows no apparent increase with an increase in pressure in this pressure range. This is not surprising, however, if we consider that in this pressure range a large fraction of the CD_3CH_2D apparently dissociates; changes in the relatively small yield of stabilized CD_3CH_2D could not easily be discerned.

$n\text{-}C_4D_{10} \rightarrow CD_3 + C_3D_7 \rightarrow CD_3 + C_2D_4 + CD_3$
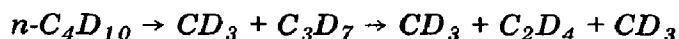
Stable propyl radicals are intercepted by HI in the photolysis of $n\text{-}C_4D_{10}$, as the results given in Tables 1 and 2 indicate. It is also seen that the yields of C_3D_7 increase as a function of increasing pressure, indicating that a fragmentation process is being collisionally quenched. The propyl and methyl radicals formed in process (5) will share 4.69 or 6.29 eV of excess energy in these experiments with 8.4 or 10.0 eV photons, respectively. The most probable mode of dissociation of a propyl radical at energies in this range would be:

$$C_3D_7^* \rightarrow CD_3 + CD_2CD_2 \tag{15}$$

In the photolysis of $CD_3CH_2CH_2CD_3$, the fragmentation process analogous to (15) will lead to the formation of ethylene, C_2H_4:

$$CD_3CH_2CH_2^* \rightarrow CD_3 + CH_2CH_2 \tag{16}$$

Making the reasonable assumption that all the C_2H_4 formed in $CD_3CH_2CH_2CD_3$ originates in process (16), we can obtain an estimate of the quantum yield of the primary process (5) by adding the observed quantum yield of

C_2H_4 formed in $CD_3CH_2CH_2CD_3$. This leads to an estimate that Φ (process 5) is about 0.03 in the 8.4 eV experiments, and about 0.07 in the 10.0 eV experiments.

n-$C_4D_{10} \rightarrow C_2D_5 + C_2D_4 + D$

Process (6), a direct C–C bond cleavage leading to the formation of two ethyl radicals, and process (8), a C–H bond cleavage leading to the formation of an n-butyl radical, may both, through further dissociation lead finally to the formation of C_2D_5, C_2D_4 and D as products. In the recent study of the photolysis of propane, evidence was presented which indicated that the importance of direct C–H bond cleavage processes analogous to (7) and (8) was minor compared to the importance of C–C bond cleavage processes. By analogy we will therefore assume that the importance of process (8) is minor compared to that of process (6), although no quantitative information about their relative importance can be derived from the data presented here.

The yield of stable ethyl radicals intercepted by HI in the 8.4 eV and 10.0 eV experiments is 0.14 and about 0.22 - 0.24, respectively. When HI is added to $CD_3CH_2CH_2CD_3$, the quantum yield of CD_3CH_3 increases by 0.13 and 0.23 respectively, indicating that most of the ethyl radicals are indeed formed in a process involving a direct C–C bond cleavage, rather than some process involving a rearrangement.
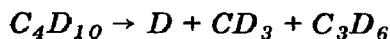
$$CD_3CH_2CH_2CD_3 \rightarrow CD_3CH_2 + CD_2CH_2 + D \quad (17)$$

$$CD_3CH_2 + HI \rightarrow CD_3CH_3 + I \quad (18)$$
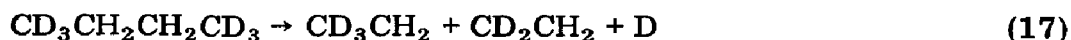
The yield of the corresponding ethylene in these experiments, CD_2CH_2, is about 0.13 at 8.4 eV and 0.24 at 10.0 eV. A fraction of this ethylene, however, is formed in process (13); the quantum yields which we have estimated for process (13) are approximately 0.03 at 8.4 eV and 0.05 at 10.0 eV, leaving yields of about 0.10 and 0.19 of CD_2CH_2 which can be described to process (17).

Some ethyl radicals may originate in a process such as:

$$n\text{-}C_4D_{10} \rightarrow CD_3CD_2CD_2CD + D_2 \rightarrow CD_3CD_2 + C_2D_3 + D_2 \quad (19)$$
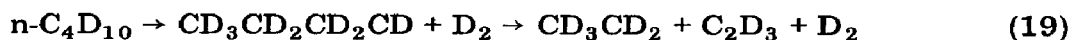
The maximum possible contribution of process (19) to the ethyl radical yield is given either by the yield of intercepted vinyl radicals (Tables 1 and 2), or the yield of molecular D_2 formed in the photolysis of $CD_3CH_2CH_2CD_3$ (Table 3). Both of these estimates lead to values of about 0.02 at 8.4 eV, or 0.07 at 10.0 eV. On this basis, the estimated yield of processes (6) + (8) in these experiments is 0.12 and $\sim$ 0.16 at 8.4 and 10.0 eV, respectively.

*$C_4D_{10} \rightarrow D + CD_3 + C_3D_6$*

Since the processes listed above do not account for the yields of propylene observed in these experiments, it can be assumed that a primary process such as (7) occurs. The experiments carried out with $CD_3CH_2CH_2CD_3$ confirm that most of the propylene is $C_3D_3H_3$, which indicates that the mecha-

nism for this process may involve the initial loss of a secondary hydrogen, followed by the dissociation of the resulting s-butyl radical to give propylene and a methyl radical. Small amounts of $C_3D_2H_4$ are also observed in these experiments. The formation of this product is not easily explained in view of the fact that no CD_4 is seen in these experiments.

It should be noted that there is an isotope effect on the yield of propylene, since the total yield of this product is much larger in experiments with $CD_3CH_2CH_2CD_3$ (Φ = 0.053 at 8.4 eV) than with n-C_4D_{10} (Φ = 0.042 at 8.4 eV). The quantum yield of propylene in the 8.4 eV photolysis of n-C_4H_{10} is still larger ($\sim$ 0.085). The existence of this isotope effect tends to corroborate our assumption that the propylene originates mainly in a process involving the initial cleavage of one of the C–H bonds. Such a process might be expected to show an isotope effect favoring C–H cleavage over C–D cleavage.

The overall yields which can be estimated for process (7) in n-C_4D_{10} from the results given in Tables 1 and 2 are about 0.03 and 0.05 at 8.4 and 10.0 eV, respectively, after correction for process (2).

$C_4D_{10} \rightarrow D_2 + C_4D_8$
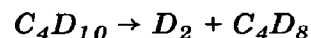
Process (9), the molecular elimination of hydrogen, is the single most important primary process occurring in the photolysis of n-butane at 8.4 eV, as was demonstrated in two earlier studies [1a, 1b]. In one of the previous studies [1b], it was also demonstrated that when $CH_3CD_2CD_2CH_3$ is photolyzed in the presence of a radical scavenger, at 8.4 eV, 60% of the hydrogen product consists of D_2, i.e. the hydrogen molecule is eliminated from one or both of the center carbon atoms with a high probability. This is corroborated by the results of the experiments reported here on $CD_3CH_2CH_2CD_3$ (Table 3) where it is seen that about 90% and 53%, respectively of the hydrogen is H_2 at 8.4 and 10.0 eV. The quantum yield of D_2 in these experiments is about 0.02 at 8.4 eV and 0.07 at 10.0 eV, demonstrating that hydrogen elimination from a methyl group also occurs, but is a minor process; we have already cited process (19) as a possible source of ethyl and vinyl radicals.

The major hydrogen elimination process, involving loss of hydrogen from the center carbon atoms, would be expected to lead to the formation of 2-butene and 1-butene as the corresponding products. Unfortunately, the yields of 2-butene could not be determined in these experiments. The yields of 1-butene were seen to be strongly dependent on pressure (Table 1), suggesting that further dissociation of the butene products is important. In addition to process (19), one would expect the dissociation:

$$C_4D_8 \rightarrow C_3D_5 + CD_3 \tag{20}$$
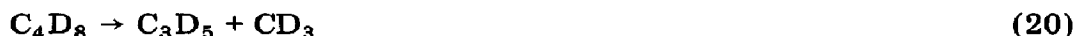
Indeed, the results given in Tables 1 and 2 show that the yield of C_3D_5 is strongly reduced as the pressure is increased, corroborating that this species is formed in a secondary decomposition such as (20).

TABLE 4

Approximate quantum yields of primary processes in the photolysis of n-butane

Reaction	Products	Φ	
		8.4 eV	10.0 eV
(2)	$\rightarrow CD_4 + C_3D_6$	0.006	0.040
(3)	$\rightarrow C_3D_8 + CD_2$	0.0036	0.018
(4)	$\rightarrow C_2D_6 + C_2D_4$ (total)	0.14	0.24
(4a)	C_2D_6 (stable) $+ C_2D_4$	(0.12)	(0.20)
(4b)	$C_2D_6^* \rightarrow 2CD_3$	(0.021)	(0.040)
(5)	$\rightarrow CD_3 + C_3D_7$ (total)	0.029	0.068
(5a)	$CD_3 + C_3D_7$ (stable)	(0.0078)	(0.013)
(5b)	$C_3D_7^* \rightarrow C_2D_4 + CD_3$	(0.021)	(0.055)
(6) + (8)	$\rightarrow C_2D_5 + C_2D_5$ (or $n\text{-}C_4D_9 + D$)	0.10	0.14
(7)	$\rightarrow D + C_4D_9 \rightarrow D + C_3D_6 + CD_3$	0.038	0.092
(9)	$\rightarrow D_2 + C_4D_8$	0.70	0.37
(9a)	$C_4D_8^* \rightarrow C_3D_5 + CD_3$	(0.023)	(0.050)
(9b)	$C_4D_8^* \rightarrow C_2D_3 + C_2D_5$	(0.021)	(0.052)
	Total:	1.02	0.97

Yields from experiments at 46 - 47 Torr have been used.

Summary and Conclusions

A summary of the approximate quantum yields which we have ascribed to the various primary processes occurring in n-butane at 8.4 eV and 10.0 eV is given in Table 4. It should be emphasized that these values are only approximations, since it is not possible to adequately account for every minor process and every secondary decomposition which occurs in these systems. Also, the existence of isotope effects causes differences in the importance of various processes between $n\text{-}C_4D_{10}$ and $CD_3CH_2CH_2CD_3$ or $CD_3CD_2CH_2CH_3$, as we have seen, and such differences have been ignored in deriving the overall quantum yields of the various primary processes listed in Table 4.

In spite of these limitations, however, it is encouraging that the total quantum yields of all the primary processes add up within experimental error, to unity. In addition, if one attempts to predict the yields of small fragment species such as CD_3 or C_2D_4 using the derived quantum yields for the various primary and secondary processes, fairly good agreement with measured yields is obtained. For instance, the total measured CD_3 yield at 8.4 and 10.0 eV, respectively is 0.19 and 0.36 (Tables 1 and 2). The yields of CD_3 at these energies predicted by adding up the contributions from processes (4b), (5a), (5b), (7), and (9a) are 0.15 and 0.36, respectively. Similarly, if we accept that the acetylene is formed by decomposition of the ethylene product [1e],

TABLE 5

Relative importance of types of primary processes as a function of energy

	%	
	8.4 eV	10.0 eV
1. Primary processes exclusive of hydrogen elimination:		
Direct C–C cleavage [processes (5) + (6)]	41	35
C–D cleavage (process 7)	12	15
Alkane elimination [processes (2) + (3) + (4)]	47	50
2. Importance of processes involving initial breakage of the 1, 2 or 2, 3 C–C bond:		
1, 2 [processes (2) + (3) + (5)]	23	33
2, 3 [processes (4) + (6)]	77	67
3. Importance of primary processes involving cleavage of the 2, 3 C–C bond:		
Process (4) ($\rightarrow C_2D_6 + C_2D_4$)	59	63
Process (6) ($\rightarrow C_2D_5 + C_2D_5$)	41	37

the total measured (ethylene + acetylene) yield is 0.31 and 0.57 at 8.4 and 10.0 eV. The yields of ethylene product predicted from the summary in Table 4 are 0.26 and 0.49 at the two energies.

Because of the approximate nature of the conclusions presented in Table 4, it is difficult to draw firm conclusions about the effects of energy on the relative importance of all the primary processes occurring in n-butane. It is clear, however, that the importance of the hydrogen elimination processes (reaction 9) diminishes with increasing energy. This is in agreement with the conclusions reached earlier by Okabe and Becker [1b]. Similar diminutions in the quantum yields of hydrogen elimination processes with increasing energy have been documented in the photolysis of ethane [5] and propane [3].

The diminution in the importance of hydrogen elimination as a function of energy is compensated by increases in the yields of all other primary processes. Table 5 summarizes some observations about the variations in the relative importance of the various primary processes as a function of energy. Section 1 of this Table demonstrates that the overall relative importance of the primary processes other than D_2 elimination (direct C–C cleavage, C–H cleavage, or alkane elimination) do not show any important variations when the energy is raised from 8.4 to 10.0 eV.

Section 2 of Table 5 shows that at both energies, processes involving cleavage of the center 2, 3 C–C bond [processes (4) and (6)] strongly predominate over the processes involving the 1, 2 C–C bond [processes (2), (3) and (5)]. There is no pronounced effect of energy on the relative importance of primary processes at these two sites, but the 1, 2 C–C bond breakage pro-

cesses do show a slightly increased importance at the higher energy. Apparently, there is a lower probability for the localization of the excitation energy in the center bond, as the energy is increased and the lifetime of the excited molecule shortened.

In Section 3 of Table 5 the relative importance of processes (4) and (6), which involve breaking the 2, 3 C–C bond, are compared, and it is seen that there is essentially no change with increasing energy. This is in agreement with the observation [3] that in the photolysis of propane the relative importance of such processes did not change as a function of energy. If one focuses attention on the relative importances of the three 1, 2 C–C bond cleavage processes, however, it seems that process (5) decreases while processes (2) and (3) increase in importance. Considering the very minor importance of the latter two processes at both energies, however, it is probable that no quantitative significance should be attached to such observed trends.

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