Photolysis of Liquid *n*-Pentane and 2,2,4-Trimethylpentane at 1470 Å[1]

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Abstract: *n*-Pentane and 2,2,4-trimethylpentane were photolyzed in the liquid phase at 1470 Å to determine the modes of decomposition of the excited molecules. The most important primary processes in the photolysis of 2,2,4-trimethylpentane are alkane elimination reactions. Also methyl, isopropyl, butyl, neopentyl, and heptyl radicals are formed from cleavage of carbon–carbon bonds. The results show that cleavage at the central carbon–carbon bond is most likely. In *n*-pentane the principal primary process is H_2 elimination, and the main radical process is the formation of hydrogen atoms and pentyl radicals. A correlation of the primary processes with the electronic absorption spectra is suggested. In many respects the 1470-Å photolysis of alkanes is similar to γ radiolysis, indicating a major role for excited molecules in radiolysis. Fragmentation of the excited alkane molecule into smaller radicals is shown to be similar in the photolysis and radiolysis. The major products are the same in both cases. The principal difference is that carbon–hydrogen bond cleavage is much more important in radiolysis than in photolysis.

Numerous studies of the vacuum ultraviolet photolysis of alkanes in the gas phase have been made which have provided insight into the modes of decomposition of excited alkane molecules.[2] However, the liquid-phase photolysis of alkanes has received comparatively little attention. It was of interest to examine the photolysis of some alkanes in the liquid phase and to compare the results to those obtained in γ radiolysis of these alkanes. Such a comparison permits an evaluation of the role of excited molecules in the radiolysis. Of particular interest to us was the formation of radical intermediates in photolysis since the identification and yields of radical intermediates in radiolysis are well documented.[3]

Gas-phase studies have shown that an important primary process in normal alkanes is the elimination of H_2. Alkane elimination reactions in which methane or ethane, for example, are formed from a higher molecular weight alkane also occur.[2,4] In addition to molecular elimination processes, there is evidence that radical formation also occurs.[2]

In the liquid-phase photolysis the primary processes are similar to those observed in the gas phase. However, secondary fragmentation of excited species formed in the primary processes is less important. For example, in the photolysis of ethane in liquid nitrogen excited ethylene molecules are formed. The decomposition of these excited molecules into acetylene, which is important in the gas phase, is inhibited by collisional deactivation in solution.[5] Similarly in the photolysis of cyclohexane, decomposition of the excited cyclohexene is much less important in the liquid[6] than in the gas phase. Secondary fragmentation has also been shown to be suppressed in the solid-phase photolysis of alkanes.[7-9] Although secondary deactivation steps are inhibited, the various primary modes of decomposition of excited alkane molecules are unquenched and quantum efficiencies remain high in the condensed phase. For example, in the photolysis of liquid cyclohexane at 1470 Å the quantum yield of hydrogen has been reported to be unity.[6]

In this study, quantum yields of the principal products and radical intermediates in the 1470-Å photolysis of liquid *n*-pentane and 2,2,4-trimethylpentane were measured. A linear alkane, *n*-pentane, was compared to a branched alkane, 2,2,4-trimethylpentane, to determine the effect of structure on the primary process. The yields of radicals were determined with the $^{14}CH_3$-radical "sampling" technique,[10] in which $^{14}CH_3$ radicals are generated during photolysis from $^{14}CH_3I$ solute. During photolysis the $^{14}CH_3$ radicals "sample" the radicals produced by the photolysis of the hydrocarbon. Carbon-14-labeled hydrocarbons are thereby produced which characterize the radical intermediates. The yields of radicals can be calculated from the yields of these labeled hydrocarbons. The use of the technique has been described in general terms elsewhere,[3,10] and it has been used to detect radicals in radiolysis studies.[10-13] In this paper it is applied for the first time to a photochemical system.

Experimental Section

The hydrocarbons were Phillips research grade and were purified by passage through a silica gel column. The $^{14}CH_3I$ (Volk Radiochemical Co.) was diluted to a specific activity of ~0.5 mCi/mmole and purified by gas chromatography.

The photolysis arc and reaction cell employed in this work have been described elsewhere.[14] The arc was a Xe resonance lamp prepared as prescribed by McNesby and Okabe[2] and operated by a microwave discharge. The sapphire exit window on the arc was bathed by the liquid during photolysis. The liquid was thermostated to 10° and stirred continuously. Approximately 90% of the light is absorbed in a liquid layer within 0.1 μ of the window. In spite of this absorption near the window, no deposit was observed to form on the window, and the lamp output was very reproducible. The extent of sample conversion was generally less than 0.5%. A

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[1] This work was supported by the Research Division of the U. S. Atomic Energy Commission.

[2] J. R. McNesby and H. Okabe, *Advan. Photochem.*, 3, 157 (1964).

[3] R. A. Holroyd in "Aspects of Hydrocarbon Radiolysis," T. Gaumann and J. Hoigne, Ed., Academic Press, London, 1968, pp 1–32.

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[5] J. A. Pirog and J. R. McNesby, *ibid.*, 42, 2490 (1965).

[6] R. A. Holroyd, J. Y. Yang, and F. M. Servedio, *ibid.*, 46, 4540 (1967); 48, 1331 (1968).

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[8] R. E. Rebbert and P. Ausloos, *ibid.*, 46, 4333 (1967).

[9] A. A. Scala and P. Ausloos, *ibid.*, 47, 5129 (1967).

[10] R. A. Holroyd and G. W. Klein, *Intern. J. Appl. Radiation Isotopes*, 15, 633 (1964).

[11] R. A. Holroyd, *J. Am. Chem. Soc.*, 88, 5381 (1966).

[12] R. A. Holroyd, *J. Phys., Chem.*, 70, 1341 (1966).

[13] R. A. Holroyd and G. W. Klein, *ibid.*, 69, 194 (1965).

[14] D. Radnoti, E. Eisel, and J. Yang, *Rev. Sci. Instr.*, 37, 910 (1966).

Table I. Quantum Yields of Products of the Photolysis of 2,2,4-Trimethylpentane at 1470 Å[a]

Solute	Concn, mM	Quantum yields							
		H_2	CH_4	C_3H_6	i-C_4H_{10}	i-C_4H_8	neo-C_5H_{12}	i-C_5H_{12}	CH_3I
None		0.11	0.18	0.058	0.48	0.45	0.081	0.011	
$^{14}CH_3I$	1.8			0.064	0.48	0.48		0.012	
I_2	1.2			0.047	0.36	0.37	0.058	0.002	0.031
C_6H_6	560		0.17	0.057	0.43	0.35	0.081		

[a] Blanks indicate product was not determined.

finger of the Xe arc was cooled to −78° during photolysis to trap out any condensable contaminants in the Xe.

For analysis of products and determination of activity yields, a radio-gas chromatograph (Nuclear Chicago, Model 4998) was employed. The yield of hydrogen from cyclohexane was used as an actinometer and $\phi(H_2)$ was taken to be unity.[6]

Results

2,2,4-Trimethylpentane. The quantum yields of the products of the photolysis of liquid 2,2,4-trimethylpentane are shown in Table I. The principal products are lower molecular weight alkanes and alkenes. The products formed in largest yields are isobutane and isobutylene. Hydrogen is a minor product (ϕ = 0.11). Photolysis in the presence of iodine, which was added to react with radicals, reduced the yields of propylene, isobutane, isobutylene, and neopentane by about 20%. Isopentane was almost eliminated in the presence of iodine, suggesting it is formed largely by the reaction of methyl with isobutyl radicals. Benzene, which quenches the photolysis of cyclohexane,[6] was found to have little effect on the photolysis of 2,2,4-trimethylpentane.

Photolysis of 2,2,4-trimethylpentane in the presence of millimolar concentrations of $^{14}CH_3I$ resulted in the formation of ^{14}C-labeled ethane, isobutane, neopentane, isopentane, 2,2-dimethylbutane, and four different nonanes. (The formation of all these labeled products, except 2,2-dimethylbutane, is illustrated in Figure 1, lower curve.) These products indicate that methyl, isopropyl, t-butyl, isobutyl, neopentyl, and octyl radicals are formed, respectively. The radical yields were calculated from the yields of the labeled products and the results are shown in Table II. A typical calculation is given in the Appendix.

The fragment radicals result from cleavage of carbon–carbon bonds, but it is not clear whether or not octyl radicals are formed by cleavage of carbon–hydrogen bonds in the primary process. They may be formed by a secondary reaction of hydrogen atoms. The yield of hydrogen atoms was therefore measured to compare it to the yield of octyl radicals. To do this, ethylene was added; this resulted in the formation of ethyl radicals, reaction 1. This reaction competes with abstraction

$$\mathrm{H} + \mathrm{C_2H_4} \longrightarrow \mathrm{C_2H_5} \tag{1}$$

$$\mathrm{H} + \mathrm{C_8H_{18}} \longrightarrow \mathrm{H_2} + \mathrm{C_8H_{17}} \tag{2}$$

from the solvent, reaction 2. At 9 mM ethylene the quantum yield of ethyl radicals (calculated from the radioactive propane yield) was 0.0065. Since k_2/k_1 is 6.3×10^{-3},[15] ethylene at this concentration is expected to scavenge 20% of the hydrogen atoms; thus $\phi(H)$ is estimated to be ~0.03. Since $\phi(H)$ is approximately equal to ϕ(octyl), the formation of octyl radicals can be accounted for by reaction 2.

Methyl iodide is a slightly more efficient scavenger of hydrogen atoms than ethylene. An estimate of the rate of reaction 3 was obtained from the yields of

$$\mathrm{H} + {}^{14}\mathrm{CH_3I} \longrightarrow {}^{14}\mathrm{CH_3} + \mathrm{HI} \text{ and } {}^{14}\mathrm{CH_4} + \mathrm{I} \tag{3}$$

$\phi(^{14}CH_3)$ at various $^{14}CH_3I$ concentrations. The observed quantum yields of $^{14}CH_3$ radicals were 0.0014, 0.0045, and 0.0069 at $^{14}CH_3I$ concentrations of 0.52, 1.3, and 1.8 mM, respectively. From these data and the fact that reaction 3 leads to methyl radicals about 50% of the time, k_2/k_3 is $5 \pm 2 \times 10^{-4}$. Since k_2 is about $5 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$,[6, 15] k_3 is $\sim 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$.

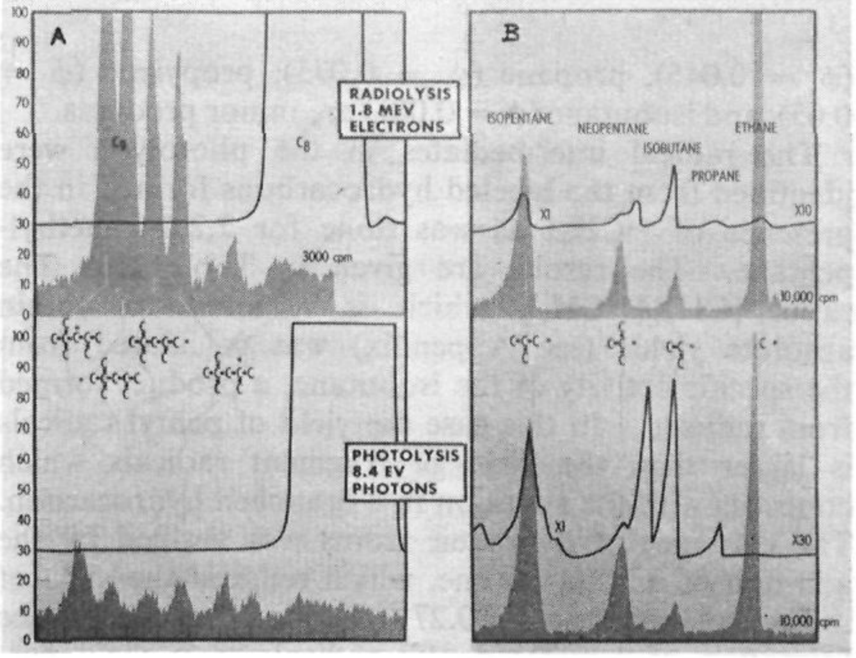

Figure 1. Radio-gas chromatograph trace of products of the radiolysis (top) and photolysis (bottom) of 2,2,4-trimethylpentane solutions containing 1 mM $^{14}CH_3I$. Solid lines are the thermal conductivity outputs which show total products. Shaded peaks show yield of radioactive products: (A) C_8–C_9 region, (B) C_1–C_5 region.

The experiments with added iodine also provided a measure of the total radical yield and $\phi(CH_3)$. The total radical yield is given by the rate of iodine consumption, and the yield of methyl radicals is given by the yield of CH_3I. At iodine concentrations between 0.7 and 1.9 mM the iodine consumption rate corresponded to $\phi(-I_2) = 0.11$. The total radical yield is twice this value or $\phi(R) = 0.22 \pm 0.2$. The yield of methyl iodide was found to be 0.032 ± 0.002. These results are in good agreement with the $^{14}CH_3$-radical sampling results which gave $\phi(R) = 0.19$ and $\phi(CH_3) = 0.037$.

***n*-Pentane.** The main product of the photolysis of n-pentane is hydrogen, $\phi(H_2) = 1.0$. The quantum yield of pentene-1 is 0.2 and that of pentene-2 is 0.7; thus the total yield of pentenes is comparable to that of H_2. Methane (ϕ = 0.014), ethane (ϕ = 0.05), ethylene

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(15) R. A. Holroyd, *J. Phys. Chem.*, **70**, 1341 (1966).

Table II. Radical Yields in 2,2,4-Trimethylpentane

	Photolysis				Radiolysis
Radical (R)	Rel yield of R-$^{14}CH_3$	D/C	Rel yield of R	ϕ(R)	Rel yield of R[e]
Methyl	0.69	0	69	0.037 ± 0.003	86
Isopropyl	0.095	0.22[a]	12	0.006 ± 0.001	16
t-Butyl	0.37	0.9[b]	70	0.038 ± 0.002	68
Isobutyl	1.0	0	100	0.054 ± 0.004	100
Neopentyl	0.14	0	14	0.007 ± 0.001	21
Heptyl	0.19	0.9[c]	36	0.019 ± 0.002	...
Octyl	0.32	0.4[d]	45	0.024 ± 0.002	280

[a] J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1609 (1960). [b] G. R. McMillan, *J. Am. Chem. Soc.*, **82**, 2422 (1960). [c] Assumed to be the same as *t*-butyl. [d] Estimated from R. A. Holroyd and G. W. Klein, *J. Phys. Chem.*, **67**, 2273 (1963). [e] Reference 11.

Table III. Radical Yields in *n*-Pentane

	Photolysis				Radiolysis
Radical (R)	Rel yield of R-$^{14}CH_3$	D/C	Rel yield of R	ϕ(R)	Rel yield of R[a]
Methyl	33	0	30	0.022	30
Ethyl	100	0.06	100	0.073	100
n-Propyl	72	0.1	74	0.054	70
Isopropyl	17	0.22	20	0.014	9
1-Methylbutyl	210	0.2	233	0.170	435
1-Ethylpropyl	122	0.2	137	0.100	215
n-Pentyl	40	0.16	41	0.030	191

[a] Reference 23.

(ϕ = 0.045), propane (ϕ = 0.073), propylene (ϕ = 0.05), and isobutane (ϕ = 0.001) are minor products.

The radical intermediates in the photolysis were identified from the labeled hydrocarbons formed in the presence of $^{14}CH_3I$ as was done for 2,2,4-trimethylpentane. The results are given in Table III. The ratio, $[CH_3]/[^{14}CH_3]$, which is required to obtain absolute yields (see Appendix) was calculated from the specific activity of the isobutane, a product formed from radicals. In this case the yield of pentyl radicals is larger than the yield of fragment radicals which contrasts with the situation in a branched hydrocarbon. The existence of hydrogen atoms was verified by the addition of 0.2% 1-hexene, which reduced the yield of *sec*-pentyl radicals from 0.27 to 0.23 and resulted in the formation of 1-methylpentyl radicals in a yield corresponding to this reduction. The total quantum yield, given by $\phi(H_2) + \phi(CH_4) + \phi(C_2H_4) + \phi(C_2H_6) + \phi(CH_3) + \phi(C_2H_5)$, is 1.2. Since the primary quantum yield cannot exceed unity, it is likely that the light intensity was underestimated slightly.

Discussion

Primary Processes in 2,2,4-Trimethylpentane. On the basis of the radicals identified in the photolysis of 2,2,4-trimethylpentane, several different radical formation processes can be identified. The most important of these is cleavage of a carbon–carbon bond to form butyl radicals, reaction 4. This process is approximately seven times more probable than the unsymmetrical cleavage into propyl and neopentyl radicals, reaction 5. The other process involving carbon–carbon bond cleavage is loss of a methyl radical, reaction 6.

2,2,4-trimethylpentane + $h\nu$

$$\xrightarrow{\phi\,=\,0.046} i\text{-}C_4H_9\ (59\%) + t\text{-}C_4H_9\ (41\%) \quad (4)$$

$$\xrightarrow{\phi\,=\,0.007} C_3H_7 + neo\text{-}C_5H_{11} \quad (5)$$

$$\xrightarrow{\phi\,=\,0.02} CH_3 + C_7H_{15} \quad (6)$$

The quantum yields (ϕ) of these processes are taken from the yields of the various radical intermediates. In the case of reaction 5, the yields of propyl and neopentyl radicals are nearly equal, and ϕ(5) is taken as equal to ϕ(neopentyl). Equal yields of isobutyl and *t*-butyl radicals might be expected from reaction 4, yet experimentally ϕ(*t*-butyl) was observed to be about 70% of ϕ(isobutyl). The following reasons for this inequality were considered: there may be some isomerization of *t*-butyl to isobutyl radicals, the gas-phase values of D/C used in calculating butyl radical yields may not be applicable, or some decomposition of *t*-butyl radicals into smaller fragments may occur.

The difference in yields of butyl radicals may be explained by the isomerization of a fraction of the *t*-butyl radicals, formed in reaction 4, into isobutyl radicals. This possibility is quite reasonable since in the photolysis of liquid 2,2-dimethylbutane, where only *t*-butyl radicals would be expected, isobutyl radicals are formed and ϕ(isobutyl) is actually one-sixth of ϕ(*t*-butyl).[16] In calculating the yield of process 4 (ϕ = 0.046), we assumed that one-sixth of the *t*-butyl radicals isomerized to isobutyl radicals.

The possibility that gas-phase values of D/C are not applicable is not likely for the following reason. Disproportionation of *t*-butyl and methyl radicals would have to be about 100% greater than assumed to make the yields of butyl radicals equal. The value of D/C used for the reaction of methyl with *t*-butyl was 0.9.[13] Assuming a much higher value of D/C for the liquid is unjustified since it has been shown that disproportionation is no more than 25% more important in the liquid for the reactions of methyl,[17] ethyl,[17] and *t*-pentyl[18] radicals.

The possibility of a secondary decomposition of *t*-butyl radicals into CH_3 and C_3H_6 or into H and C_4H_8

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(16) R. A. Holroyd, unpublished work.

(17) P. S. Dixon, A. P. Stefane, and M. Szwarc, *J. Am. Chem. Soc.*, **85**, 2551, 3344 (1963).

(18) R. Kuntz, *J. Phys. Chem.*, **69**, 2291 (1965).

cannot be entirely excluded. This mechanism could provide an explanation for the fact that $\phi(CH_3)$ exceeds $\phi(C_7H_{15})$. The liquid phase tends to suppress such secondary decompositions of vibrationally excited species. Apparently there is no further fragmentation of the products of reaction 5 since the yields of these radicals are approximately equal.

At least one more primary process in which radicals are formed must occur to account for the formation of hydrogen atoms ($\phi \cong 0.03$) and the small yield of octyl radicals ($\phi = 0.024$). There may be a process in which carbon–hydrogen bonds are broken (reaction 7a), but this would require, contrary to the facts, that $\phi(H)$ be $^1/_2\phi$(octyl), since hydrogen atoms are expected to abstract to form more octyl radicals, reaction 2. A more attractive process, which would also explain the fact that there is an excess yield (of about 0.02) of methyl radicals, is reaction 7b, which gives H atoms,

$$\text{2,2,4-trimethylpentane} + h\nu \longrightarrow H + C_8H_{17} \qquad (7a)$$

$$\xrightarrow{\phi\, =\, 0.02} H + CH_3 + C_7H_{14} \qquad (7b)$$

methyl radicals, and heptene in one step. Heptenes could not be detected on the chromatography columns employed but are probably formed since they are produced in γ radiolysis in significant yields.[19,20] Process 7b has also been postulated to occur during radiolysis.[19]

The major products of the photolysis of 2,2,4-trimethylpentane are attributed to molecular processes. The most important products are isobutane and isobutylene (see Table I), which suggests that process 8 occurs. Methane, propylene, neopentane, and hydrogen are formed in lower yields, suggesting processes 9–11. The molecular nature of these processes is

$$\text{2,2,4-trimethylpentane} + h\nu \xrightarrow{\phi\, =\, 0.36} i\text{-}C_4H_8 + i\text{-}C_4H_{10} \qquad (8)$$

$$\xrightarrow{\phi\, \approx\, 0.05} C_3H_6 + neo\text{-}C_5H_{12} \qquad (9)$$

$$\xrightarrow{\phi\, =\, 0.17} CH_4 + C_7H_{14} \qquad (10)$$

$$\xrightarrow{\phi\, =\, 0.08} H_2 + C_8H_{16} \qquad (11)$$

indicated since the products were formed even in the presence of radical scavengers. The yields of processes 8–10 are taken from the yields of products formed in the presence of radical scavengers. Molecular elimination of hydrogen is of minor importance; the yield of this process is taken to be $\phi(H_2) - \phi(H)$.

The values of ΔH for these molecular processes are small compared to the photon energy of 8.4 eV. Therefore the product molecules contain much excess vibrational energy when formed. Deactivation of the excited products must occur readily, since the yield of the alkane eliminated is equal to the yield of the olefin left behind, at least for processes 8 and 9. This is in contrast to the gas-phase photolysis, where the yield of the alkane is generally much less than that of the olefin as a result of secondary fragmentation of the alkane.

The molecular products can be formed to some extent by disproportionation of radicals in a cage in the liquid. First, it should be noted that this is a plausible mechanism since the products of the molecular processes 8–10 are those that would be expected from disproportionation of the radical pairs formed in processes 4–6. However, the importance of cage disproportionation depends on the fraction of radicals which do not escape the cage. If this fraction is 30%, then cage disproportionation accounts for less than 5% of the molecular products. A fraction much greater than this, although it would account for more of the molecular products, would be inconsistent with the high observed quantum efficiency. Cage recombination must accompany disproportionation, and this would lead to a much lower efficiency than observed. Another good reason for postulating these molecular processes is that analogous molecular elimination processes have been shown to occur in the gas-phase photolysis of the lower alkanes[2] where the cage effect is not operative.

Primary Processes in *n*-Pentane. From the radicals identified as intermediates in the photolysis of *n*-pentane (Table III), radical processes 12–14 can be identified. The yield of process 12 is assumed to be equal to one-half the total yield of C_5H_{11} radicals. The yield of process 13 is given by either $\phi(C_2H_5)$ or by the total

$$n\text{-pentane} + h\nu \xrightarrow{\phi\, =\, 0.15} H + \left\{\begin{array}{l}\text{1-methylbutyl } (57\%)\\ \text{1-ethylpropyl } (33\%)\\ n\text{-pentyl } (10\%)\end{array}\right. \qquad (12)$$

$$\xrightarrow{\phi\, =\, 0.07} C_2H_5 + \left\{\begin{array}{l}n\text{-}C_3H_7 \ (79\%)\\ i\text{-}C_3H_7 \ (21\%)\end{array}\right. \qquad (13)$$

$$\xrightarrow{\phi\, =\, 0.02} CH_3 + C_4H_9 \qquad (14)$$

yield of propyl radicals, both of which are approximately 0.07. The yield of process 14 is taken as the yield of methyl radicals ($\phi = 0.02$). Carbon–hydrogen bond cleavage is more important here than in the photolysis of branched alkanes and about as important as in cyclohexane.[6] The distribution of C_5H_{11} radicals given is the over-all yield which includes those C_5H_{11} radicals formed by hydrogen-atom abstraction. The latter leads principally to 1-methylbutyl and 1-ethylpropyl radicals.

The formation of isopropyl radicals is important. These radicals are not the result of a secondary reaction of hydrogen atoms with the small amount of propylene which is formed. Such a reaction is of minor importance since pentenes are formed at a rate approximately 16 times faster than propylene and hydrogen atoms would be preferentially scavenged by pentenes. Thus, isopropyl radicals are primary products here as are isobutyl radicals in the photolysis of 2,2-dimethylbutane.[16]

By far the most important primary process in the photolysis of *n*-pentane is reaction 15. The quantum yield of this process is taken to be $\phi(H_2)$ less $\phi(H)$. Processes 16–18 account for the formation of lower

$$n\text{-pentane} + h\nu \xrightarrow{\phi\, =\, 0.82} H_2 + C_5H_{10} \qquad (15)$$

$$\xrightarrow{\phi\, \approx\, 0.06} C_2H_4 + C_3H_8 \qquad (16)$$

$$\xrightarrow{\phi\, =\, 0.05} C_2H_6 + C_3H_6 \qquad (17)$$

$$\xrightarrow{\phi\, =\, 0.01} CH_4 + C_4H_8 \qquad (18)$$

molecular weight hydrocarbons. Identical molecular processes have been shown to occur in the photolysis of *n*-pentane in the gas phase.[3] In the liquid phase the yield of ethane is comparable to that of propylene and the yield of propane is comparable to that of ethylene,

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(19) T. Kudo and S. Shida, *J. Phys. Chem.*, **67**, 2871 (1963).

(20) T. Kudo, *ibid.*, **71**, 3681 (1967).

whereas in the gas phase the yield of olefins is greatly in excess of the yields of the corresponding alkanes because of secondary decomposition reactions.

Correlation of Molecular and Radical Processes. If the primary processes in each of the hydrocarbons studied are examined, a striking correlation of the relative yields of the molecular with the radical processes is noted. For each molecular process there is a corresponding radical process and the yields of each are related. In 2,2,4-trimethylpentane, for example, compare the molecular processes 8–10 with the radical processes 4–6. The cleavage of the central carbon–carbon bond into isobutane and isobutylene, process 8, is about seven times more probable than a split into two butyl radicals, reaction 4. For dissociation at each carbon–carbon bond, the molecular process is more important than the radical process by a factor of about 7 for this alkane. For *n*-pentane, the split into H_2 and pentene is about six times more likely than a split into H and pentyl. The complete significance of this correlation of radical and molecular processes is not clear but it helps to emphasize that for each molecule there is a preferred location at which dissociation is apt to occur. Photolysis can lead either to molecular or radical products but the former is favored.

Spectral Correlation. A theoretical interpretation of the ultraviolet absorption spectra of alkanes has recently been made,[21] and it is interesting to compare the observed primary processes with the expected electronic transitions in these alkanes. According to the theory[21] the absorption spectra of alkanes may be considered as absorptions of independent systems of C–C and C–H bonds. The total absorption spectrum represents the sum of absorptions by the two systems. At 1470 Å the absorption by 2,2,4-trimethylpentane is strong (ϵ 17,000)[21] and is shown by the theory to be primarily $\sigma^* \leftarrow \sigma$ transitions in the C–C bonds. Absorption by C–H bonds is negligible at this wavelength but becomes quite important at shorter wavelengths. All the principal primary processes in 2,2,4-trimethylpentane involve carbon–carbon bond cleavage, and these we associate with the main transition which is C–C bond excitation. Carbon–hydrogen bond cleavage is minor since ϕ(H) is only 0.03. Thus, in this case the primary processes correlate well with the electronic transitions.

Absorption by *n*-pentane at 1470 Å is not as strong (ϵ 10,000),[21] but the main transition at this wavelength is still the $\sigma^* \leftarrow \sigma$ excitation in the C–C bonds. Absorption by C–H bonds is still expected to be minor. Cleavage of carbon–hydrogen bonds is more important in *n*-pentane ($\phi = 0.15$) than in 2,2,4-trimethylpentane but is still a small fraction of the total process. The major primary process in *n*-pentane is molecular elimination of H_2. Since this process is the most important, we associate it with the C–C bond excitation which is dominate at this wavelength.

According to the theory,[21] carbon–hydrogen bond cleavage will become more important (and other processes less important) at shorter wavelengths. This derives from the fact that absorption by C–H bonds is much stronger at shorter wavelengths, around 1200 Å. Data from the gas-phase photolysis of *n*-pentane[4] support this interpretation, since H_2 elimination (process 15) is less important at 1237 than at 1470 Å.

Comparison to Radiolysis. A comparison of these photolysis results to radiolysis results is useful to determine what facets of the radiolysis of hydrocarbons can be accounted for by decomposition of photoexcited molecules. Oversimplification of the mechanism of radiolysis strictly in terms of the decomposition of excited molecules is not intended here; ionic reactions, spur effects, etc., must be considered in radiolysis. However, it is clear that excited molecules may be formed in radiolysis either directly or as a result of ion neutralization reactions.

The relative radical yields observed in both the photolysis and radiolysis of the two hydrocarbons studied are compared in Tables II and III (columns 4 and 6). Figure 1 shows a qualitative comparison of the photolysis and radiolysis of 2,2,4-trimethylpentane; the heights of the shaded peaks are a measure of the radical yields. The similarity in the distribution in yields of fragment radicals arising from carbon–carbon bond scission is striking. The relative yields of fragment radicals in photolysis are identical with those in radiolysis within experimental error.

The effect of molecular structure on radical yields, observed in radiolysis,[11,22] is operative in photolysis; that is, the probability of cleavage at a particular carbon–carbon bond increases as the number of adjacent carbon–carbon bonds increases. For example, in *n*-pentane the ethyl radical yield is three times the methyl radical yield in both photolysis and radiolysis. The C–C bond which breaks to form ethyl radicals has one more adjacent C–C bond than does the bond which breaks to form methyl radicals. In 2,2,4-trimethylpentane, cleavage into butyl radicals, where there are four C–C bonds adjacent to the one that splits, is six times more probable than cleavage into isopropyl and neopentyl, where there are three C–C bonds adjacent; a similar effect was noted in radiolysis.[11] Cleavage of the more substituted carbon–carbon bond is always preferred. These similarities show that the decomposition of excited molecules can account for the fragment radicals formed in radiolysis.

It is also interesting to note that isomerized radicals are formed in both radiolysis[11,23] and photolysis. In the photolysis of *n*-pentane, 21% of the propyl radicals isomerize to isopropyl, and in 2,2-dimethylbutane 15% of the butyl radicals isomerize to isobutyl.[16] The isomerization in each case involves the shift of a hydrogen atom without skeletal rearrangement. The yields of isomerized radicals are small, but the fact that they are observed in photolysis suggests that they may be formed in radiolysis by decomposition of excited molecules.

In contrast to the yields of fragment radicals, there is little correlation of the yields of radicals arising from carbon–hydrogen bond scission. In the photolysis of 2,2,4-trimethylpentane ϕ(H) is small and the octyl radicals account for only 13% of all the radicals. In the radiolysis of this alkane *G*(H) is 1.6 and 50% of the radicals are octyl radicals.[11] This contrast between radiolysis and photolysis is graphically illustrated in the radio-gas chromatograph (Figure 1). In *n*-pentane,

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[23] R. A. Holroyd and G. W. Klein, *J. Am. Chem. Soc.*, **84**, 4000 (1962).

Table IV. Comparison of Products in Radiolysis and Photolysis

	2,2,4-Trimethylpentane				*n*-Pentane[a]		
	G, molecules/100 eV				*G*, molecules/100 eV		
Product	Photolysis[b]	Radiolysis	Ref	Product	Photolysis[b]	Radiolysis	Ref
H_2	1.3	2.2	*c*	H_2	10.0	5.1	*c*
CH_4	2.2	1.1	*c*	C_2H_4	0.54	0.37	*d*
C_3H_6	0.72	0.3	*e*	C_2H_6	0.60	0.61	*d*
i-C_4H_8	5.4	2.1	*e*	C_3H_6	0.60	0.35	*d*
i-C_4H_{10}	5.8	2.8	*e*	C_3H_8	0.89	0.58	*d*
Radicals	2.4	4.8	*f*	C_5H_{10}	10.0	2.8	*d*
H atoms	0.4	1.6	*g*	Radicals	2.9	4.8	*f*
				H atoms	1.8	1.3	*g*

[a] Decanes and intermediate products of the radiolysis of pentane, and the C_9 through C_{16} products of the radiolysis of 2,2,4-trimethylpentane are not included here since those products arise chiefly by reactions of radicals. [b] Photolysis yields are expressed here in units of *G*(molecules/100 eV). At this wavelength a quantum yield of one corresponds to $G = 11.8$. [c] Reference 22. [d] R. O. Koch, J. P. W. Houtman, and W. A. Cramer, *J. Am. Chem. Soc.*, **90**, 3326 (1968). [e] Reference 19. [f] Reference 11. [g] Reference 12.

carbon–hydrogen bond cleavage is more important than in a branched alkane but still not as important as in radiolysis. In photolysis 65% of the radicals are pentyl, whereas in radiolysis 80% are pentyl.[10,23] Thus in both alkanes, decomposition of molecules excited at 1470 Å does not lead to the formation of as many parent-minus-hydrogen radicals as are observed in radiolysis. The over-all yield of radicals is also relatively less in photolysis. In the 1470-Å photolysis, only 20% of the primary process results in radical formation, whereas in the radiolysis radical formation is a major process since *G*(radicals) ~ 5.[3]

Since radical formation constitutes a small fraction of the primary process in photolysis, it is important to compare the major products of photolysis and radiolysis. In the photolysis the major products are largely molecular. In the γ radiolysis of the hydrocarbons studied the most important products are those observed in the photolysis (see Table IV). For example, in the radiolysis of pentane $G(H_2) = 5.1$ and $G(\text{pentene}) = 2.8$, and the major photochemical process is elimination of H_2, reaction 15. Ethane, ethylene, propane, and propylene are formed in the photochemical primary processes, reactions 16 and 17, and small amounts of these hydrocarbons are formed in radiolysis. It can be seen (Table IV) that the distribution of low molecular weight products of the radiolysis of pentane correlates reasonably well with the molecular products of the photolysis of pentane.

There is also a similarity of products formed in the radiolysis of 2,2,4-trimethylpentane to those formed in the photolysis. The most important photodissociation is a split into isobutane and isobutylene, reaction 8, and these are the products formed in highest yield in radiolysis (Table IV). Methane and propylene are formed in photolysis by alkane elimination (reactions 9 and 10), and corresponding amounts of these are formed in radiolysis. Thus the lower molecular weight products of the radiolysis can be accounted for by decomposition of excited molecules.

In many respects the absorption of an 8.4-eV photon has an effect similar to γ radiolysis. The relative radical yields and major molecular processes seem similar, but there are differences. The most important difference in *n*-pentane is that there are more radicals and relatively less H_2 and pentenes than in photolysis. In 2,2,4-trimethylpentane, radical formation is more important in radiolysis than in photolysis; in particular, the yield of H atoms is much greater.

It is suggested on the basis of the spectral correlation given above that excitation at higher photon energies will enhance the extent of carbon–hydrogen bond cleavage and diminish the extent of molecular processes. Radiolysis is expected to populate higher levels, and if these are the same levels that would be reached by photons more energetic than 8.4 eV, then there should be more C–H bond cleavage and relatively less of the molecular eliminations in radiolysis. Thus, for example, in *n*-pentane the fact that there is more C–H bond scission and less molecular elimination of H_2 in radiolysis compared to photolysis at 1470 Å is suggested to be due in part to the contribution of higher excited states which lead to carbon–hydrogen bond scission. It is expected that radiolysis would compare better with photolysis of liquid alkanes at wavelengths around 1200 Å. It is anticipated that further studies of the photolysis of liquid alkanes, particularly at shorter wavelengths, will be useful in elucidating excitation processes in radiolysis.

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Appendix

In the $^{14}CH_3$-radical "sampling" technique, $^{14}CH_3$ radicals are generated from $^{14}CH_3I$ solute (reaction 3) and react with the radicals (R_i) produced by the photolysis of the alkane. They may react by disproportionation (*D*), reaction 20, as well as by combination (*C*), reaction 19. The latter leads to labeled hydrocarbons.

$$R_i + {}^{14}CH_3 \longrightarrow {}^{14}CH_3R_i \qquad (19)$$

$$\longrightarrow {}^{14}CH_4 + R_i(-H) \qquad (20)$$

The relative yields of radicals are calculated from the yields of labeled hydrocarbons with the use of eq 21. The yield of each labeled hydrocarbon is

$$\phi(R_1)/\phi(R_2) = \frac{\phi({}^{14}CH_3R_1)(1 + D_1/C_1)}{\phi({}^{14}CH_3R_2)(1 + D_2/C_2)} \qquad (21)$$

multiplied by the factor $1 + D_i/C_i$ to obtain the total yield of $^{14}CH_3$ radicals which react with each radical. The values that were used for the ratios D_i/C_i were literature values based on gas-phase studies.

A necessary condition for use of the $^{14}CH_3$-radical sampling technique is that the concentration of radicals produced by the photolysis of the alkane be sufficiently high that these radicals react with one another rather than abstract from the solvent. In the photolysis the radicals are formed at a rate of about 6 × 10^{-9} mole/sec in a volume of about 10^{-7} l. or about 0.06 mole/(l. sec). At this high rate of formation little abstraction and mainly bimolecular reactions of radicals occur in a liquid alkane at 10°.[3]

The following example of the photolysis of 2,2,4-trimethylpentane is illustrative of the technique. The quantum yields of radicals are calculated from the radioactivity in each product as follows. The integrated activity in each product (column 2, Table V) is multiplied by (1 + D_i/C_i). The resulting numbers (column 4) give the relative yields of radicals. Note that the yield of CH_3 radicals is proportional to the yield of ethane formed from one *labeled* methyl radical and one *unlabeled* methyl radical. This ethane is denoted $^{14}CH_3CH_3$. The quantity measured experimentally is the total number of counts in the ethane. The fraction of this total which is $^{14}CH_3CH_3$ is calculated from eq 22. Determination of the ratio on the right-hand side of this equation is explained below.

Table V. Data for Run No. 7[a]

Labeled hydrocarbon	Counts	1 + D/C	Counts × 1 + D/C	ϕ(radical)	Radical
$^{14}CH_3CH_3$	10,230	1	10,230	0.034	CH_3
$^{14}CH_3{}^{14}CH_3$	2,060	1	2,060	0.007	$^{14}CH_3$
Isobutane	1,330	1.22	1,620	0.005	Isopropyl
Neopentane	5,840	1.9	11,100	0.037	*t*-Butyl
Isopentane	15,570	1	15,570	0.052	Isobutyl
2,2-Dimethylbutane	1,990	1	1,990	0.007	Neopentyl
Octanes	2,950	1.9	5,600	0.019	Heptyl
Nonanes	5,155	1.4	7,220	0.024	Octyl
Total			55,390	0.184	

[a] Length of photolysis, 15 min.

$$\frac{\text{counts in } ^{14}CH_3CH_3}{\text{counts in } ^{14}CH_3{}^{14}CH_3} = [CH_3]/[^{14}CH_3] \qquad (22)$$

To calculate the yields on an absolute basis, the yield of $^{14}CH_3$ radicals, which is the total activity in all products, is first calculated. In run no. 7 (Table V) the yield of $^{14}CH_3$ radicals is given by the total activity of 55,390 counts times 3.14 × 10^{-6} μmole/count = 0.174 μmole of $^{14}CH_3$. Since the absorbed light intensity in run no. 7 was 25.4 μEinsteins, $\phi(^{14}CH_3)$ = 0.0069. The factor 3.14 × 10^6 takes into account the specific activity of the methyl iodide, counter efficiency, and gas residence time in the counter. This conversion factor was obtained by irradiating a solution of $^{14}CH_3I$ in cyclopentane and measuring the $^{14}CH_4$ produced. The ratio of the mass yield of $^{14}CH_4$ to the observed number of counts in the $^{14}CH_4$ was in this case 3.14 × 10^{-6} μmole/count.

The yield of CH_3 radicals (from the photolysis of 2,2,4-trimethylpentane) is calculated from $\phi(^{14}CH_3)$ by eq 23.[3,10] The ratio $[CH_3]/[^{14}CH_3]$ was obtained

$$\phi(CH_3) = \phi(^{14}CH_3)[CH_3]/[^{14}CH_3] \qquad (23)$$

from the specific activity of the isopentane since isopentane was shown to be formed from methyl and isobutyl radicals. In this example the total (mass) yield of isopentane was 0.293 μmole.

The yield of labeled isopentane was 15,570 × 3.14 × 10^{-6} = 0.0488 μmole. Therefore, $[CH_3]/[^{14}CH_3]$ was (0.293 − 0.0488)/0.0488 = 5.0. Thus $\phi(CH_3)$ is in this case 5 × 0.0069 = 0.034. All the other radical yields can be calculated from the methyl radical yield and the relative yields in column 4. For example, ϕ(isobutyl) = $\phi(CH_3)$ × 15,570/10,230 = 0.052.