

Radical Formation in the Radiolysis of Branched Hydrocarbons¹

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Abstract: The individual alkyl radical yields in irradiated 2,4-dimethylpentane and 2,2,4-trimethylpentane have been measured with the C-14-labeled methyl radical "sampling" technique. Also, certain of the fragment alkyl radical yields from some branched hexanes and 2,3,4-trimethylpentane are reported. Fragmentation, which represents only a small fraction of the over-all radical yield in *n*-alkanes, becomes more important in branched alkanes, accounting for 48% of the total in 2,4-dimethylpentane and 64% in 2,2,4-trimethylpentane. This dependence of the fragment radical yields on molecular structure can be expressed by a single empirical relationship, $G(R) = (1.0C_1 + 2.8C_2 + 8.6C_3 + 29C_4)/(n - 1)^2$, where *n* is the number of carbon-carbon bonds and the *C_i*'s are the number of bonds (whose cleavage leads to the radical R) with *i* adjacent carbon-carbon bonds. As a corollary to the above the bond most likely to break in a molecule is the one with the most adjacent carbon-carbon bonds. A correlation of radical yields with the electron distribution in the highest occupied molecular orbital of alkanes is noted. The yield of parent-minus-hydrogen radicals decreases with increased branching of the molecule. The removal of a secondary hydrogen atom is more likely than removal of a primary hydrogen atom for these alkanes. However, the tertiary hydrogen atoms are less likely to be removed than the secondary in primary processes, a fact which is attributed to steric hindrance. Such an effect would be expected if the parent-minus-hydrogen radicals are formed in a bimolecular step. Evidence is presented to show that in the case of 2,2,4-trimethylpentane about 40% of the radicals formed initially react with radicals in the spurs.

Symmetrical molecules such as cyclohexane, benzene, or neopentane have frequently been chosen as model compounds for studying the radiation chemistry of liquid hydrocarbons. In these compounds all carbon-carbon and carbon-hydrogen bonds are equivalent, and consequently fewer products are formed. However, to obtain a better understanding of the primary processes responsible for radical formation, it is important to study molecules in which there are several nonequivalent bonds, which may exhibit varying susceptibility to rupture. Unfortunately, for such cases, the number of products formed is large and a complete product analysis is difficult. However, a determination of the yields of radical intermediates for such hydrocarbons gives information about the primary cleavage of the molecule without the necessity of inferring this from the products formed.

Previous work² on branched hydrocarbons has shown that in the radiolysis of hexanes there is a greater probability for rupture of the molecule at a site adjacent to the side chains and, further, that the yields of complementary radicals are not always equal. The latter fact indicates that in fragmentation more than one bond may rupture. Recently, the profound role of the molecular structure of the hydrocarbon was emphasized by determinations of the yields of methyl radicals for a large number of different hydrocarbons.³ This yield was found to obey an empirical relationship in which $G(\text{CH}_3)$ is related to the number of methyl groups attached at any one site in the molecule and is inversely proportional to the square of the number of carbon-carbon bonds.³ A similar dependence has been shown to exist for the yield of ethyl radicals from normal alkanes.⁴

The aim of this investigation was to examine the

effect of molecular structure on the yields of radical intermediates and to search for a general relationship for predicting radical yields. This included studying the yields of fragment radicals arising from carbon-carbon bond scission as well as the yields of parent-minus-hydrogen-atom radicals. Molecules containing tertiary, as well as primary and secondary hydrogen atoms were studied to determine the relative susceptibility of different carbon-hydrogen bonds. Specifically, the yields of all the radical intermediates in the radiolysis of 2,4-dimethylpentane and 2,2,4-trimethylpentane were determined. Also, certain fragment radical yields, such as ethyl and isopropyl, were measured for several other branched chain alkanes.

Experimental Section

The hydrocarbons (Phillips Research Grade) used were purified to remove unsaturates by passage through a silica gel column. 3-Methylpentane was further purified by gas chromatography. The methyl-C-14 iodide (Volk Radiochemical Co.) was diluted with unlabeled methyl iodide to a specific activity of ~0.5 mcurie/mmole and then purified by gas chromatography. The iodine used was Mallinckrodt reagent grade.

Samples were prepared by degassing the required volume (0.3 to 0.5 ml) of hydrocarbon, which was delivered into the vacuum system through a silicone septum. Measured amounts of ¹⁴CH₃I vapor were added as solute to the hydrocarbon in the irradiation cell.

The irradiation cells were made of copper and were cylindrical in shape with inside dimensions of 0.5 in. diameter and 0.5 in. deep. The 2.0-mev electron beam from a Van de Graaf type generator entered the cell vertically through a 1-mil brass window on the flat face. The cells could be mounted reproducibly with respect to the beam exit window. The electron beam was defined by a 0.25-in. diameter slit. An aluminum pneumatic high-vacuum valve (Consolidated Engineering Co. Model VCS-23A) was used to turn the electron beam on and off. The effect of bremsstrahlung from the beam hitting the shutter during warmup periods was found to be negligible. Samples received a dose of $2-5 \times 10^{19}$ ev/g. The beam current was 5-10 μ a. The relative dose given to each sample was determined by integrating, with an Elcor (Model A310B) current integrator, the current to the irradiation cell. Absolute dosimetry was based on the yield of H₂ ($G = 5.2$) from cyclopentane irradiated in the same position in an identical cell. Irradiation periods were from 0.5 to 2.0 sec.

Irradiated samples were analyzed with a gas chromatograph. The column employed was 40 ft long and contained GC-22 support

(1) This paper is based on studies conducted for the U. S. Atomic Energy Commission under Contract AT(11-1)-GEN-8.

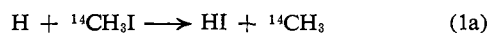
(2) H. A. Dewhurst, *J. Am. Chem. Soc.*, **80**, 5607 (1958).

(3) R. H. Schuler and R. R. Kuntz, *J. Phys. Chem.*, **67**, 1004 (1963).

(4) R. A. Holroyd in "Advances in Chemical Research," T. Gäumann, Ed., North-Holland Publishing Co., Amsterdam, 1966.

coated with silicon grease. The effluent from the chromatograph passed directly into a proportional counter. Pulses from this counter were amplified and counted, providing a measure of the radioactivity yield in each component.⁵ With this technique a lower limit of approximately 2 nmoles of product could be detected.

Radical Sampling. Radical yields were determined with the ¹⁴CH₃-radical sampling technique.^{6,7} In this technique the ¹⁴CH₃ radicals are generated during radiolysis from ¹⁴CH₃I solute which is present at a concentration of from 0.5 to 1.0 mM. This may occur by a reaction of hydrogen atoms



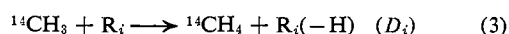
or by dissociative electron capture⁸



Since, in general, the yield of ¹⁴CH₃ radicals is small ($G \sim 0.2$), whatever the mode of their generation, the perturbation caused by the presence of ¹⁴CH₃I to the over-all radiolysis of the hydrocarbon is minimal. The ¹⁴CH₃ radicals "sample," *i.e.*, react with some of the radicals produced from the radiolysis of the hydrocarbon, forming labeled hydrocarbons



which on analysis characterize the radicals and serve as a measure of their yields as well. It has been shown⁶ that the relative yields of these labeled hydrocarbons when corrected for disproportionation (D)



are proportional to the radical yields; that is

$$\frac{G(\text{R}_1)}{G(\text{R}_2)} = \frac{{}^{14}\text{CH}_3\text{R}_1(1 + D_1/C_1)}{{}^{14}\text{CH}_3\text{R}_2(1 + D_2/C_2)} \quad (I)$$

Iodine Scavenging. Iodine was also employed as a scavenger in certain cases in order to measure the absolute yield of a certain fragment radical from an alkane. Nonradioactive iodine was employed at a concentration of between 0.5 and 1.0 mM. It is believed that at concentrations less than ~ 1 mM complications with the use of I₂ are minimal and iodine serves primarily as a radical scavenger.⁴ This method was used only to determine the yields of either methyl, ethyl, or isopropyl radicals.

Irradiated iodine solutions were analyzed by gas chromatography and the yield of the corresponding alkyl iodide formed was determined with an electron capture detector (Wilkins Instrument and Research, Inc.). Product yields as low as 0.01 to 0.1 nmole were readily measured to within 10% accuracy with this method.

Results

2,4-Dimethylpentane. In Table I are listed the radicals which were identified, on the basis of the labeled hydrocarbons observed, as intermediates in the radiolysis of 2,4-dimethylpentane. To calculate yields of R_i from the yields of labeled hydrocarbons, ¹⁴CH₃R_i, the relative yields of radicals were calculated with eq I. The disproportionation to combination ratios, D/C , used are given in the table (column 3).^{9,10}

Absolute radical yields given in Table I are based on $G(\text{CH}_3) = 0.283$.³ $G(\text{CH}_3)$ is proportional to $G({}^{14}\text{C}_2\text{H}_6)^*$, the yield of labeled ethane formed by combination of one labeled methyl radical with a methyl radical formed from the radiolysis of 2,4-dimethylpentane. However, the observed radioactive

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

(6) R. A. Holroyd and G. W. Klein, *Intern. J. Appl. Radiation Isotopes*, **15**, 644 (1964).

(7) R. A. Holroyd and G. W. Klein, *J. Phys. Chem.*, **69**, 194 (1965).

(8) W. G. Burns, R. A. Holroyd, and G. W. Klein, *ibid.*, **70**, 910 (1966).

(9) J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1609 (1960).

(10) Whenever available, gas-phase ratios of disproportionation to combination were used, but frequently such ratios have not been measured and in these cases estimates were made from an empirical relationship based on the entropy of the products; *cf.* R. A. Holroyd and G. W. Klein, *J. Phys. Chem.*, **67**, 2273 (1963).

Table I. Radical Yields in 2,4-Dimethylpentane^a

Radical	Rel yield of ¹⁴ CH ₃ R	D/C	G(R)
Methyl	0.66	0	0.28 ^b
Methyl- ¹⁴ C	~ 0.9	0	~ 0.4
Ethyl	0	0.12	0
Isopropyl	1.0	0.22 ^c	0.53
Isobutyl	1.26	0	0.54
2,4-Dimethylpentyl	1.58	0.1 ^d	0.74
1-Isopropyl-2-methylpropyl	0.98	0.3 ^d	0.54
1,1,3-Trimethylbutyl	1.06	0.5 ^d	0.68
G(¹⁴ CH ₄)			0.34

^a Yields are in molecules/100 ev. ¹⁴CH₃I concentration was ~ 0.8 mM. ^b Assumed value from ref 3. ^c Reference 9. ^d Reference 10.

ethane yield also includes $G(\text{C}_2\text{H}_6)^{**}$, the ethane formed by recombination of two labeled methyl radicals. It has been shown that the yield of the former, $G(\text{C}_2\text{H}_6)^*$, can be obtained by multiplying the ethane activity yield by $G(\text{CH}_3)/[G(\text{CH}_3) + G({}^{14}\text{CH}_3)]$.⁶ This ratio was calculated in each run from $G(\text{CH}_3)$ which is 0.283 and $G({}^{14}\text{CH}_3)$, which is the sum of the yields of all labeled hydrocarbons, including that fraction of the methane-C-14 which is formed by disproportionation reactions.

The yield of ¹⁴CH₄ formed is in excess of that expected from disproportionation, D_i . The origin of this excess methane-¹⁴C is uncertain but probably arises principally from cage recombination of ¹⁴CH₃ and HI formed in reaction 1a.

2,2,4-Trimethylpentane. The results for 2,2,4-trimethylpentane are shown in Table II. A total of eight radical species were observed to be present. The relative radical yields were calculated with eq I from the observed yields of the corresponding labeled hydrocarbons in a manner analogous to that used for 2,4-dimethylpentane. The absolute yields of radicals (column 4) were derived from the relative yields and the value of $G(\text{isopropyl})$ which was determined with the iodine scavenging technique. At 1.4 mM iodine the average yield of isopropyl iodide was found to be 0.133 ± 0.013 based on five determinations.

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

Radical (R)	Rel yield of ¹⁴ CH ₃ R	D/C	G(R) ^b
Methyl	7.96	0	0.87
Methyl- ¹⁴ C	1.0-2.7	0	0.1-0.3
Isopropyl	1.0	0.22 ^c	0.13
<i>t</i> -Butyl	2.63	0.9 ^d	0.54
Isobutyl	7.37	0	0.80
Neopentyl	1.6	0	0.17
2,2,4-Trimethylpentyl	4.11	0	0.45
2,4,4-Trimethylpentyl	2.70	0.1	0.32
1-Isopropyl-2,2-dimethylpropyl	5.96	0.4	0.91
1,1,3,3-Tetramethylbutyl	2.13	0.4	0.56

^a ¹⁴CH₃I concentration was ~ 1 mM. ^b Yields are relative to $G(\text{isopropyl iodide}) = 0.13$. ^c Reference 9. ^d Reference 11.

In this case the yields of the two types of ethane-¹⁴C were separated by determining the ratio $G(\text{CH}_3)/G({}^{14}\text{CH}_3)$ from the ratio of the yield of unlabeled to

labeled isopentane. Absolute dose measurements were not made. The value of $G(\text{CH}_3)$, arrived at by this method, is 0.87 which is higher than the value of 0.69 reported by Schuler and Kuntz.³

Other Branched Hydrocarbons. Several other branched hydrocarbons were investigated primarily to determine the yield of fragment alkyl radicals resulting from carbon-carbon bond scission. The results are shown in Table III.

Table III. Fragment Radical Yields

Hydrocarbon	Radical	Yield, radicals/100 ev	
		Exptl	Empirical eq IIIb
2,2-Dimethylbutane	CH_3	0.99 ^a	1.07
	C_2H_5	1.2	1.16
2,3-Dimethylbutane	CH_3	0.34 ^a	0.45
	<i>i</i> - C_3H_7	1.9	2.3
2-Methylpentane	CH_3	0.27 ^a	0.26
	C_2H_5	0.12	0.11
	<i>i</i> - C_3H_7	0.38	0.34
3-Methylpentane	CH_3	0.15 ^a	0.19
	C_2H_5	1.2	0.69
2,4-Dimethylpentane	CH_3	0.28 ^a	0.31
	<i>i</i> - C_3H_7	0.53	0.48
3,3-Dimethylpentane	CH_3	0.34 ^a	0.50
	C_2H_5	?	1.6
	CH_3	0.69, ^a 0.87	0.64
2,2,4-Trimethylpentane	<i>i</i> - C_3H_7	0.13	0.18
	<i>i</i> - C_4H_9	0.80	0.59
	CH_3	0.19, ^a 0.17	0.29
2,3,4-Trimethylpentane	<i>i</i> - C_3H_7	1.2	1.18
	CH_3	0.48 ^a	0.49

^a Data from ref 3.

For 2,2-dimethylbutane, iodine was used to measure the yield of ethyl radicals. This was found to be 1.2 ± 0.1 at 0.8 mM I_2 . The yield of ethyl radicals is nearly the same as that of methyl ($G = 0.99$)³ even though there is only one ethyl group and four methyl groups in the molecule. A few sampling experiments with $^{14}\text{CH}_3$ indicated that in addition to methyl and ethyl radicals the other major fragment radical is *t*-butyl whose yield is 0.50 molecule/100 ev. A small yield of isobutyl radicals ($G = 0.07$) is also present.

In the radiolysis of 2,3-dimethylbutane, isopropyl is a major fragment radical. Its yield, as determined with iodine at a concentration of 0.4 mM, is 1.9 ± 0.1 based on two determinations.

2-Methylpentane and 3-methylpentane were studied to determine the effect of the position of the methyl side chain on the fragment radical yields and on the ethyl radical yield in particular. For 3-methylpentane, the yield of ethyl iodide at 1.2 mM I_2 was found to be 1.2 ± 0.08 and the yield of methyl iodide to be 0.16; the latter agrees with an earlier value of 0.154.³ The $^{14}\text{CH}_3$ radical "sampling" experiments indicated the only other fragment radical present is *sec*-butyl, and its yield is 0.89 relative to the above value of $G(\text{C}_2\text{H}_5)$.

For 2-methylpentane, the radical sampling technique was used. Relative yields of radicals were determined from the relative yields of labeled hydrocarbons with eq I. Absolute yields were obtained by assuming that the total radical yield is 5.0.⁴ The

fragment radicals found and their yields were: ethyl, 0.12; *n*-propyl, 0.58; isopropyl, 0.5 molecule/100 ev.

For 2,3,4-trimethylpentane, the yield of isopropyl iodide at 0.7 mM I_2 was found to be 1.2 ± 0.08 and the yield of methyl iodide was 0.17. The yield of the latter agrees (to within the experimental accuracy) with the value of 0.187 reported by Schuler and Kuntz.³

Discussion

Carbon-Carbon Bond Scission. The results reported here provide quantitative information on fragmentation, that is, carbon-carbon bond rupture, and bear out the earlier generalization that branching enhances fragmentation.² It is our purpose to show a correlation in the data on fragment radical yields.

In 2,4-dimethylpentane fragmentation occurs most readily at the two central carbon-carbon bonds giving isobutyl ($G = 0.54$) and isopropyl ($G = 0.53$) radicals. These yields are approximately 2.5 times larger than the yields of propyl and butyl radicals from isomeric *n*-heptane.⁴ This enhancement is attributed to the presence of the methyl groups which are adjacent to the cleaved carbon-carbon bond in 2,4-dimethylpentane. A similar effect is noticed in 2,2,4-trimethylpentane. There are two central carbon-carbon bonds and it can be seen from the results in Table II that cleavage to form isobutyl and *t*-butyl radicals is much more probable than cleavage into isopropyl and neopentyl. These results suggest that the *bond most likely to cleave is the one with the most adjacent carbon-carbon bonds*. This seems to be true for the other hydrocarbons studied as well. For example, in 2,3-dimethylbutane, $G(\text{isopropyl})$ (four adjacent C-C bonds) is 1.9 whereas $G(\text{CH}_3)$ (two adjacent C-C bonds) is 0.34.³ Similarly, in 2-methylpentane $G(\textit{n}$ -propyl) is approximately five times $G(\text{ethyl})$.

Since the yield of a radical appears to be a function of the number of carbon-carbon bonds adjacent to the bond dissociating, these and other results were used to derive an equation expressing the yield of a fragment radical in these terms. First it is necessary to know by how much the yield of a radical will be enhanced due to the presence of each adjacent carbon-carbon bond. A point of departure is provided by the recent compilation of methyl radical yields by Schuler and Kuntz.³ They found that the yield of methyl radicals from normal paraffins is given by

$$G(\text{CH}_3) = 2.04/(n - 1)^2$$

where n is the number of carbon atoms in the molecule. This can also be expressed as

$$G(\text{CH}_3) = 1.02C_1/(n - 1)^2 \quad (\text{II})$$

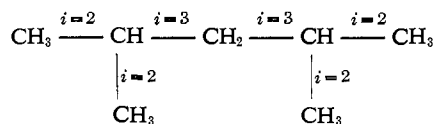
where C_1 is the number of carbon-carbon bonds in the molecule which have one adjacent carbon-carbon bond. We shall assume that we can express the yield of any radical, $G(\text{R})$, from an alkane by an equation in which, by analogy with eq II, the yield is inversely proportional to $(n - 1)^2$ and increases with the number of carbon-carbon bonds, i , adjacent to the bond which will break to produce the radical. Thus, there will be several terms in the equation

$$G(\text{R}) = \frac{1}{(n - 1)^2} \sum_i A_i C_i \quad (\text{IIIa})$$

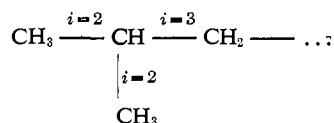
(11) G. R. McMillan, *J. Am. Chem. Soc.*, **82**, 2422 (1960).

where the coefficients A_i are to be derived from the data.

The value of A_1 has been shown to be 1.02, or approximately 1.0, based on the yield of methyl radicals from normal alkanes. For the evaluation of the coefficient A_2 , we must examine cases where there are two carbon-carbon bonds adjacent to the one dissociating. In 2,4-dimethylpentane, there are four bonds of this type; *i.e.*, $C_2 = 4$, and dissociation of these bonds gives methyl radicals.



Since the yield of methyl radicals is 0.28, substitution in eq IIIa results in $0.28 = (1/6^2) \times A_2 \times 4$; therefore, $A_2 = 2.5$. All of the carbon-carbon bonds except the terminal ones in n -alkanes also have two adjacent carbon-carbon bonds. It has been shown that in the particular case of the ethyl radical yield from n -alkanes, a relationship similar to eq II is obeyed,⁴ *i.e.*, $G(\text{C}_2\text{H}_5) = 7.0/(n-1)^2$. Since $C_2 = 2$, this corresponds to a value of A_2 of 3.5. For 2-methyl paraffins it has been shown³ that the yield of methyl radicals from the site where there is one adjacent methyl group (and consequently $i = 2$ since there are two adjacent carbon-carbon bonds)



is given by $2.79C_2/(n-1)^2$. Since this equation was shown to fit a large number of cases and is intermediate between the other two values derived here for less general cases, we have taken this as the value of A_2 , *i.e.*, $A_2 = 2.8$.

For the evaluation of the coefficient A_3 the data reported here provide three measurements. A_3 is given by $G(\text{R}) \times (n-1)^2/C_3$. For 2,4-dimethylpentane, $G(\text{isopropyl}) = 0.53$ and $G(\text{isobutyl}) = 0.54$. In both cases $C_3 = 2$; thus, $A_3 = 9.6$. The value of A_3 calculated in a similar fashion from the yield of isopropyl radicals from 2,2,4-trimethylpentane is 6.4. The yield of methyl radicals from this hydrocarbon may also be used to evaluate A_3 . The yield of methyl radicals expected to be formed from the end of the molecule with two methyl groups is 0.11 based on the values of A_2 and eq IIIa. Since the total yield of methyl radicals is 0.69,³ the yield of methyl radicals from the end of the molecule with three methyl groups is 0.58. From this yield a value of $A_3 = 9.4$ may be derived. Another measure of this quantity is provided by the yield of methyl radicals ($G = 2.3$) from neopentane.¹² The bond which dissociates to give CH_3 has three adjacent carbon-carbon bonds, $C_3 = 4$, thus $A_3 = 9.2$. The average value of A_3 from these four determinations is 8.6.

In the two hydrocarbons which were given intensive study there is one case, the central bond in 2,2,4-trimethylpentane, where there are four adjacent carbon-carbon bonds ($i = 4$). The observed yields of *t*-butyl and isobutyl radicals, which are formed by scission at this point, lead to values of $A_4 = 26$ and 39. However, three more values of A_4 were obtained by measuring

(12) R. A. Holroyd, *J. Phys. Chem.*, **65**, 1352 (1961).

$G(\text{C}_2\text{H}_5)$ from 2,2-dimethylbutane, $G(i\text{-C}_3\text{H}_7)$ from 2,3-dimethylbutane,¹³ and $G(i\text{-C}_3\text{H}_7)$ from 2,3,4-trimethylpentane, which lead to values of A_4 of 29, 24, and 29, respectively. The average value of A_4 based on these five determinations is 29. Thus from these data eq III becomes

$$G(\text{R}) = \frac{1}{(n-1)^2} (1.0C_1 + 2.8C_2 + 8.6C_3 + 29C_4) \quad (\text{IIIb})$$

This gives the yield of any one radical species R in terms of the number of carbon-carbon bonds, the cleavage of which yields the radical R. The coefficients A_i increase regularly by about a factor of 3 with the addition of each adjacent carbon-carbon bond. In fact eq IIIb could equally well be written

$$G(\text{R}) = \frac{1}{(n-1)^2} \sum_{i=1}^6 3^{(i-1)} C_i \quad (\text{IIIc})$$

The values for $G(\text{CH}_3)$ which would be derived from eq III for the normal and isoalkanes are essentially the same values as would be predicted by eq IV of ref 3 since the first two coefficients are identical in the two equations. As was shown these values are in good agreement with experiment. Values calculated from eq IIIb for fragment radical yields from various branched chain hydrocarbons are compared with the experimental data in Table III. All compounds have been included for which radical yield data are available up through the nonanes. The empirical values for more than half of the cases are within 10% of experimental, nearly all are within 30%, and the worst case is $G(\text{C}_2\text{H}_5)$ from 3-methylpentane.

The yields of ethyl radicals from 2- and 3-methylpentane were obtained to test the effect of the location of the side methyl group on the ethyl radical yield, and a dramatic difference was observed in that $G(\text{C}_2\text{H}_5)$ for 3-methylpentane is ten times larger than $G(\text{C}_2\text{H}_5)$ for 2-methylpentane. Equation IIIb predicts that the yields should differ by a factor of about 6.

Equation IIIb can be used to estimate radical yields in hydrocarbons where no data are presently available. For example $G(\text{C}_2\text{H}_5)$ from 3,3-dimethylpentane is predicted to be 1.8. An electron spin resonance study has indicated that a split at this position is the most likely since 1,1-diethylpropyl radical is very prominent in the esr spectrum of the irradiated liquid.¹⁴

The radical yields for cases where there are five and six adjacent carbon-carbon bonds could also be estimated if one assumes that the coefficients in eq IIIb increase by roughly a factor of 3 in each term. Thus $G(\text{isopropyl})$ and $G(t\text{-butyl})$ from 2,2,3-trimethylbutane would each be about 2.4. Since $G(\text{CH}_3)$ is estimated to be about 0.9 for this compound this would lead to a fragment alkyl radical yield larger than 5.0. Since total radical yields are generally about 5 it is expected that mainly fragment radicals will be formed in this case.

In principle, eq IIIb may be used to predict the yield of any fragment radical from any alkane. It

(13) In this case C_4 is taken to be 2; actually only one bond of this type is present, but there are two isopropyl radicals formed when it dissociates.

(14) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

should be kept in mind, however, that this is an empirical correlation with certain limitations. An accuracy of no better than 10% in predicting radical yields is expected. Also it does not apply to the yields of the fragments remaining after loss of a methyl or ethyl radical because of unsymmetrical fragmentation.¹⁵ Equation IIIb also predicts that a break at any carbon-carbon bond except the terminal ones in a *n*-alkane has equal probability. In reality these yields differ somewhat in a long-chain *n*-alkane.¹⁶

Theoretical Considerations. A complete explanation of eq IIIb in terms of the primary processes involved is not evident at the present time. This is partially because the precursor of fragment alkyl radicals in the radiolysis of alkanes cannot be completely specified. Possibilities include electronically excited (and superexcited) species and activated ions and molecules. Little information about the fate of such species in the liquid phase is available. However, it has been shown in a set of significant experiments that ethane dissolved in liquid N₂, when irradiated with a 1470-Å light, does decompose in condensed phase.¹⁷ Final interpretation of our results will be facilitated when more information becomes available on the decomposition of excited and activated species in the liquid phase.

Any theoretical explanation of the results obtained on fragment radical yields must account for the following. The yield of a radical varies with molecular weight as $(n - 1)^{-2}$. The yield is enhanced approximately threefold for each additional adjacent carbon-carbon bond; thus the bond most likely to cleave is the one with the most adjacent carbon-carbon bonds. An explanation which accounts for these effects is given below.

Several authors^{18,19} have applied molecular orbital theory to obtain an understanding of the fragmentation observed in mass spectrometers. In considering their results we observed that there is a correlation between fragment radical yields and the calculated electron distribution of the electrons in the highest occupied molecular orbital of an alkane molecule. Recently the molecular orbitals of several *n*-alkanes and the six isomeric hexanes have been calculated.¹⁹ The electrons in the highest occupied orbital are delocalized but are principally between carbon-carbon atoms. In branched hydrocarbons the greatest electron density²⁰ is calculated¹⁹ to be at the carbon-carbon bond which has the most adjacent carbon-carbon bonds, and this is the one most likely to dissociate. In *n*-alkanes the fragment radical yields closely parallel the calculated electron distribution in this highest orbital. Further, the calculated fraction of the electron density at the terminal carbon-carbon bond in *n*-alkanes decreases with increasing molecular weight according to $(n - 1)^{-2}$, satisfying an important experimental finding. The factor of 3 in eq IIIc also is explained at least for the difference in probability of scission of bonds with

(15) R. A. Holroyd and G. W. Klein, *J. Am. Chem. Soc.*, **87**, 4983 (1965).

(16) R. H. Schuler and R. W. Fessenden, presented at the Third International Congress on Radiation Research, Cortina, Italy, 1966.

(17) J. A. Pirog and J. R. McNesby, *J. Chem. Phys.*, **42**, 2490 (1965).

(18) K. Fueki and K. Hirota, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **81**, 212 (1960).

(19) J. C. Lorquet, *Mol. Phys.*, **9**, 101 (1965).

(20) It should be noted that in MO theory the positive charge distribution in the molecular ions is the same as the electron distribution in the highest occupied molecular orbital.

two compared to one adjacent carbon-carbon bonds. The electron density of the highest occupied orbital in the second carbon-carbon bond in *n*-alkanes is much greater than in the first bond. For *n*-hexane, for example, this factor is calculated to be 3.0.¹⁸

It appears that the principal empirical findings on radical yields can be correlated with this theory. It is therefore suggested that the probability of dissociation of a particular bond is proportional to the electron distribution of the electrons in the highest occupied molecular orbital. This would be expected if the precursor were an excited state and the electron in the highest molecular orbital were the one excited. Then if excited states of hydrocarbons are repulsive states, the probability of dissociation of a particular carbon-carbon bond could be strongly coupled to the electron distribution in the highest occupied orbital of the ground-state molecule.

The molecular structure effect on radical yields may also be rationalized as a bond-strength effect. It has been shown that the energy of dissociation of a carbon-carbon bond, E_D in kcal/mole, is approximately given by the relationship²¹

$$E_D = 84.5 - 2.1i \quad (\text{IV})$$

where i is as before the number of carbon-carbon bonds adjacent to the given carbon-carbon bond. The constants in eq IV were evaluated from the experimental values of ΔH_f for the radicals: methyl, ethyl, isopropyl, and *t*-butyl²² and ΔH_f for the appropriate hydrocarbons. Thus the bond which has the most adjacent carbon-carbon bonds is the weakest and it is the bond which is also the most likely to cleave. A bond energy difference of 2 kcal is associated with a factor of about 3 in radical yield.²³

Formation of Parent-Minus-Hydrogen Radicals. One purpose of this study was to measure the yields of the parent-minus-hydrogen radicals and to determine the effect of molecular structure on these yields.

The yield of parent-minus-hydrogen radicals was found to decrease with increased branching of the molecule. For a normal alkane this yield is about 4.0,⁴ whereas for 2,4-dimethylpentane it is 2.0, for 2,2,4-trimethylpentane, 2.2, and for neopentane, 2.4.¹⁵ Thus the extent of carbon-hydrogen scission is reduced by increased branching. It was pointed out above that branching enhances fragment radical yields. These two effects are complimentary in that the overall radical yield remains constant at about 5.^{4,24} Thus the yield of parent-minus-hydrogen radicals is given approximately by

$$G_P = 5.0 - G(\text{fragments}) \quad (\text{V})$$

The results reported here also provide information on the position of hydrogen atom loss in the formation of parent-minus-hydrogen radicals. It has already been demonstrated that this process is not random but that there is a dependence on carbon-hydrogen bond energy. In the case of isopentane it was found that the secondary

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(22) D. P. Stevenson, *Discussions Faraday Soc.*, **10**, 35 (1951).

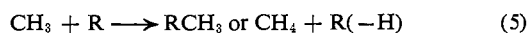
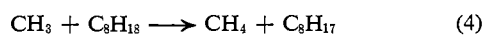
(23) A very similar bond strength effect on the fragmentation of squalene by radiolysis has been noted; cf. H. Yamazaki and S. Shida, *J. Chem. Phys.*, **32**, 950 (1960).

(24) R. H. Schuler, *J. Phys. Chem.*, **63**, 925 (1959).

hydrogens are more reactive than the primary; however, the tertiary hydrogen atoms are most reactive and in pure isopentane $G(t\text{-pentyl}) = 2.5$.¹⁵ Similar results were obtained in this work except that the tertiary species were formed in much lower yield, *i.e.*, $G(1,1,3\text{-trimethylbutyl}) = 0.68$ and $G(1,1,3,3\text{-tetramethylbutyl}) = 0.56$. In both cases a large fraction of the radicals must be formed by abstraction since it is known that thermal hydrogen atoms abstract principally the tertiary hydrogen atoms.²⁵ Consequently, the yield of tertiary parent-minus-hydrogen radicals in 2,4-dimethylpentane and 2,2,4-trimethylpentane formed directly in primary processes may be quite small. This reduced reactivity at the tertiary hydrogen position, compared to isopentane, is attributed to steric factors. That is, from a geometrical standpoint the tertiary hydrogen atoms can be shown to be blocked by surrounding methyl groups. It is therefore tentatively concluded that there is a primary process involving a bimolecular step in the formation of parent-minus-hydrogen radicals.

Evidence for Inhomogeneous Energy Deposition.

The radical yields reported here can be used to calculate what products may be expected under various experimental conditions. Further, the calculated yields can be compared with the experimentally observed yields. For 2,2,4-trimethylpentane it is known that at typical dose rates most of the radicals disappear bimolecularly by combination. The methyl radical is an exception; it abstracts hydrogen forming methane at dose rates less than 10^{16} ev ml⁻¹ sec⁻¹, but combines at higher dose rates.³



If significant amounts of combination products of methyl with the other radicals present are observed at dose rates less than 10^{16} ev ml⁻¹ sec⁻¹, it is evidence that regions of high dose rate, *i.e.*, spurs, exist. The yields of such products (usually called the molecular yield by analogy with aqueous radiation chemistry) allow an estimation of the amount of radical combination occurring in spurs.

The products formed in the radiolysis of 2,2,4-trimethylpentane have been the subject of some rather extensive studies.²⁶⁻²⁸ The products formed through the nonanes have been identified and their yields have been measured. Most of the saturated products are those which one would expect to be formed by combination reactions among the radical intermediates observed to be present in the irradiated liquid. At

(25) R. A. Holroyd and G. W. Klein, *J. Phys. Chem.*, **67**, 2273 (1963).

(26) J. A. Knight, R. L. McDaniel, and F. Sicilio, *ibid.*, **67**, 921 (1963).

(27) J. A. Knight, R. L. McDaniel, R. C. Palmer, and F. Sicilio, *ibid.*, **65**, 2109 (1961).

(28) S. Munari and F. Cocchi, *Atti Accad. Ligure Sci. Lettere* (Genoa), **20**, 396 (1964).

the dose rate employed by Knight, *et al.*, of 0.9×10^{16} ev ml⁻¹ sec⁻¹, abstraction (reaction 4) would predominate and account for approximately 83% of the methyl radicals if there were a homogeneous distribution of radicals. If methyl radicals combined with other radicals (reaction 5) we would expect the following products (observed G value in parenthesis): ethane (0.05), isobutane (1.6), 2-methylbutane (0.05), 2,2-dimethylpropane (0.20), 2,2-dimethylbutane (0.02), 2,2,4-trimethylhexane (0.07), 2,4,4-trimethylhexane (0.06), 2,2,3,4-tetramethylpentane (0.05), and 2,2,4,4-tetramethylpentane (0.04). These products with the exception of isobutane and neopentane are all considered to be formed by combination reactions of methyl radicals. Note also that no significant yield of any of these products could have been formed by combination of pairs of radicals if methyl were not one of the pair.²⁹ These products represent a total yield of methyl radicals reacting *via* reaction 5 of 0.59 radical/100 ev. This includes those methyl radicals which disproportionate when reacting with a radical, R. The amount of isobutane and 2,2-dimethylpropane assumed to be formed by the radical combination was calculated to be 0.02 and 0.04, respectively, by considering the yields of the other products and the relative radical yields. Of the molecular yield of 0.59 only a yield of $G = 0.12$ (17% of the methyl radical yield) would have resulted from combination reactions in the homogeneous case at the dose rate employed. This leaves an excess yield of 0.47 methyl radical/100 ev. This excess yield can be explained only if we postulate that energy is absorbed inhomogeneously and that radicals are formed close together in spurs, which are instantaneous regions of high dose rate where reaction 5 is favored. The molecular yield³⁰ of methyl radicals is thus ~ 0.47 compared to the radical yield of 0.69. Thus, of all the methyl radicals formed, approximately 60% escape the spur. It is expected that other radicals will behave similarly. These results thus give an estimate of the magnitude of track effects in low LET radiolysis. Also they support previous work which indicated that spur combination of radicals occurs in other organic liquids such as methyl acetate,³¹ methyl iodide,³² ethyl iodide,³³ as well as hydrocarbons.¹⁵

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(29) The only exception is 2,2,4,4-tetramethylpentane, a small yield ($G \sim 0.01$) would be formed by combination of *t*-butyl with neopentyl radicals.

(30) We have neglected the contribution of $\text{H} + \text{CH}_3 \rightarrow \text{CH}_4$ which may also occur in the spur.

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(32) J. Sturm and H. A. Schwarz, *ibid.*, **17**, 531 (1962).

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