

# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. © Copyright, 1965, by the American Chemical Society

VOLUME 87, NUMBER 22

NOVEMBER 19, 1965

## Physical and Inorganic Chemistry

### Radical Yields in the Radiolysis of Hydrocarbons. II.<sup>1a</sup> Neopentane, Isopentane, and Cyclopentane<sup>1b</sup>

Richard A. Holroyd and George W. Klein

Contribution from the Mellon Institute, Pittsburgh, Pennsylvania 14213,  
and Atomics International, A Division of North American Aviation, Incorporated,  
Canoga Park, California. Received June 21, 1965

Individual radical yields from neopentane, isopentane, and cyclopentane have been determined using the  $^{14}\text{C}_2\text{H}_5$ -radical-sampling method. In neopentane only four alkyl radicals are present whereas in isopentane nine are observed. Fragment alkyl radicals, arising from the scission of carbon-carbon bonds, account for 79 and 41%, in neopentane and isopentane, respectively, of the alkyl radicals formed in primary processes. The relative probability (per bond) of rupture of primary, secondary, and tertiary carbon-hydrogen bonds in isopentane is 1:3:9. The observations that  $G(\text{CH}_3)$  exceeds  $G(\text{C}_4\text{H}_9)$  in both neopentane and isopentane and that fragmentation is more probable for branched structures are attributed to the fact that decomposition of molecular ions is more probable for highly branched structures. In cyclopentane 90% of the radicals are cyclopentyl though small amounts of three additional  $\text{C}_5$  radicals are observed. In neopentane a small yield of isobutyl radicals ( $G = 0.16$ ) is observed which is believed to result from ionic isomerization. Evidence is cited which suggests that considerable combination of radicals occurs in tracks for low LET radiolysis. The fraction of methyl radicals which escape the track,  $N(\text{CH}_3)/N(\text{CH}_3)_0$ , is estimated to be  $\leq 0.66$  for neopentane.

#### Introduction

A few years ago it was shown in a study of the radiolysis of several liquid alkanes in which iodine was used as a scavenger that carbon-carbon bond rupture is

more likely in branched-chain alkanes than in *n*-alkanes.<sup>2</sup> A recent detailed investigation has elucidated the effect of structure on the yield of methyl radicals from saturated hydrocarbons. For any hydrocarbon  $G(\text{CH}_3)$  can be calculated from an empirical relationship in which the important consideration is the number of methyl groups attached at a particular carbon atom.<sup>3</sup> It is clear that more studies of this type, probing the effect of structural factors on the yields of individual radicals, will be useful in arriving at an understanding of the primary processes by which radicals are initially formed. The present study is concerned with the radical yields from various pentanes of different structure.

In the radiolysis of neopentane  $G(\text{CH}_3)$  (based on the yield of  $\text{CH}_3\text{I}$  from a solution saturated with iodine<sup>4</sup>) is 2.3. The product distribution in the radiolysis of the neat hydrocarbon indicated that the other major radical species present are *t*-butyl and neopentyl. In a study of radical yields in cyclopentane using iodine-131 as a scavenger,<sup>5</sup> normal and secondary pentyl iodides were found in addition to cyclopentyl iodide. Dauphin found six different fragment alkyl iodides in isopentane but only one radioactive pentyl iodide peak. He reported that the results were complicated by the decomposition of *t*-pentyl iodide during distillation. In an earlier study of isopentane using iodine-131 to scavenge radicals gas chromatography was used to analyze the alkyl iodides and several pentyl iodides were found but again *t*-pentyl iodide was absent.<sup>6</sup>

(1) (a) Part I: R. A. Holroyd and G. W. Klein, *J. Am. Chem. Soc.*, **84**, 4000 (1962). (b) Supported in part by the Atomic Energy Commission. Portions of this paper were presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962.

(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, *ibid.*, **65**, 1352 (1961).  
(5) J. Dauphin, *J. chim. phys.*, **59**, 1207 (1962).  
(6) K. H. Napier and J. H. Green, "Radiation Biology," Academic Press Inc., New York, N. Y., 1959, p. 87.

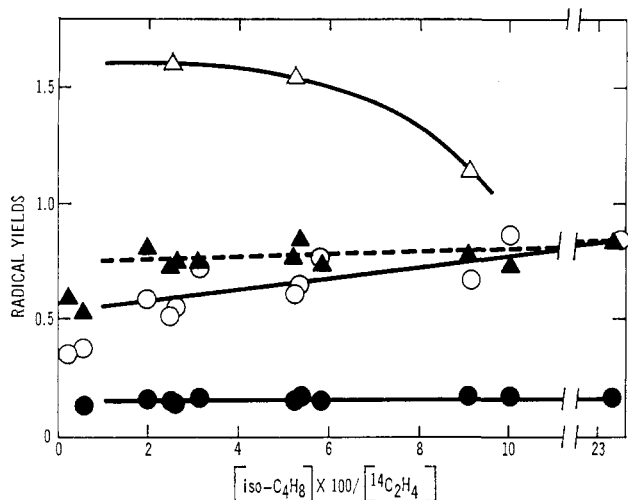
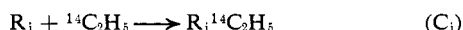
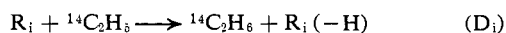


Figure 1. Neopentane, radical yields in molecules/100 e.v. vs. the ratio of the concentrations isobutene-ethylene-<sup>14</sup>C: —Δ—,  $G(^{14}\text{C}_2\text{H}_5)$ ; --▲--,  $G(\text{neopentyl})$ ; —○—,  $G(t\text{-butyl})$ ; —●—,  $G(\text{isobutyl})$ .

For the purpose of determining the yields of individual radicals, particularly tertiary radicals, from various pentanes the <sup>14</sup>C<sub>2</sub>H<sub>5</sub> radical sampling method<sup>7,8</sup> is well suited. In this method the <sup>14</sup>C<sub>2</sub>H<sub>5</sub> radicals are generated during radiolysis by addition of hydrogen atoms to solute ethylene-<sup>14</sup>C. The fraction of hydrogen atoms scavenged will depend on the concentration of ethylene-<sup>14</sup>C. *We wish, however, to emphasize that in general only a small fraction of the hydrogen atoms need be scavenged to detect radicals.* This is readily seen from the fact that in the previously reported studies<sup>8</sup>  $G(^{14}\text{C}_2\text{H}_5)$  is typically 0.1 to 0.2. The <sup>14</sup>C<sub>2</sub>H<sub>5</sub> radicals "sample" or combine with radicals produced



by the radiolysis of the hydrocarbon without affecting their concentration. The labeled hydrocarbons formed are stable so that in this case tertiary radicals can be readily detected. The relative yields of these labeled hydrocarbons when corrected for disproportionation



are proportional to the radical yields, that is

$$\frac{G(\text{R}_i)}{G(\text{R}_2)} = \frac{\text{R}_i^{14}\text{C}_2\text{H}_5[1 + \text{D}_i/\text{C}_i + \text{D}_i'/\text{C}_i']}{\text{R}_2^{14}\text{C}_2\text{H}_5[1 + \text{D}_2/\text{C}_2 + \text{D}_2'/\text{C}_2']} \quad (\text{I})$$

Where available, gas phase ratios of  $D/C$  are used. Since frequently such ratios have not been measured it has been necessary to use estimates calculated from an empirical relationship based on the entropy of the products.<sup>9</sup> Where the relative amount of disproportionation is small the relative radical yields will be only slightly dependent on the estimates of these ratios.

### Experimental Section

The pentanes (Phillips Research Grade) were purified by passage through a silica gel column. The

(7) R. A. Holroyd and G. W. Klein, *Intern. J. Appl. Radiation Isotopes*, **13**, 493 (1962).

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

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

specific activity of the <sup>14</sup>C-labeled ethylene was ~0.1 Mc./mmole.

Samples were prepared for irradiation by adding a measured (PVT) amount of <sup>14</sup>C<sub>2</sub>H<sub>4</sub> to the degassed hydrocarbons contained in "Pyrex" vials. The neopentane samples were 0.1 to 0.3 ml. and the isopentane and cyclopentane samples were either 0.5 or 1.0 ml. Irradiation of the samples with a pulsed beam of 2.8-Mev. electrons from the Van de Graaff accelerator has been described.<sup>8</sup> The beam current was 1–10 μa., and samples received a total dose of approximately  $2 \times 10^{20}$  e.v./g.<sup>10</sup> The samples were maintained at the desired temperature by a stream of nitrogen gas pre-cooled to either 0 or -78°. Further details of the experimental methods used are given elsewhere.<sup>7,8</sup>

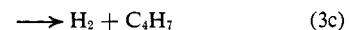
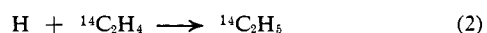
Samples were analyzed by gas chromatography. The identity of each labeled hydrocarbon produced was determined by comparison of retention times with those of authentic samples.

### Results

*Neopentane.* Since absolute yields were not determined for neopentane, the yields reported are relative to  $G(\text{CH}_3) = 2.3$ .<sup>4</sup> The radical yields were calculated using eq. I and disproportionation to combination ratios of 0.06 for methyl, 0.80 for *t*-butyl,<sup>9,11</sup> 0.05<sup>11</sup> for neopentyl, and 0.07<sup>11</sup> for isobutyl radicals.

A major difficulty in the application of the <sup>14</sup>C<sub>2</sub>H<sub>5</sub> radical sampling method to neopentane was the build-up of isobutene, a major product, which is a better scavenger for hydrogen atoms than ethylene. Therefore in order to be certain that butyl radicals were not being formed from isobutene, unusually high concentrations of ethylene-<sup>14</sup>C (~20 mM) were employed and consequently  $G(^{14}\text{C}_2\text{H}_5)$  was not negligible but of the order of unity. The observed yields of radicals calculated as described above are plotted in Figure 1 vs. the ratio  $[i\text{-C}_4\text{H}_8]/[^{14}\text{C}_2\text{H}_4]$ . The concentration of <sup>14</sup>C<sub>2</sub>H<sub>4</sub> was determined from the amount added; the concentration of isobutene is an average based on the amount found in the sample after radiolysis.

It is clear from Figure 1 that the yield of *t*-butyl radicals increases with increasing values of the abscissa, indicating the occurrence of reaction 3a. In this system hydrogen atoms are expected to react as follows.



From a plot of the ratio of yields  $G(t\text{-C}_4\text{H}_9)/G(^{14}\text{C}_2\text{H}_5)$  vs.  $[i\text{-C}_4\text{H}_8]/[^{14}\text{C}_2\text{H}_4]$ ,  $k_{3a}/k_2$  was found to be 3.5. Observed values for  $k_3/k_2$  in the gas phase vary from 4.4<sup>12</sup> to 14.5.<sup>13</sup> Hydrogen atom addition to isobutene also

(10) Due to an error in dosimetry the radical yields reported in ref. 8 are 10% too high.

(11) For the reaction of <sup>14</sup>C<sub>2</sub>H<sub>5</sub> with *t*-C<sub>4</sub>H<sub>9</sub>, neopentyl, and isobutyl, the ratios  $D'/C$  are 0.26, 0.05, and 0.05,<sup>9</sup> respectively, calculated from eq. III of ref. 9. Entropy data were obtained from American Petroleum Institute Project 44 data or estimated from partial group considerations as tabulated by S. Benson in "Foundations of Chemical Kinetics," McGraw Hill Book Co., Inc., New York, N. Y., 1960, p. 667.

(12) R. J. Cvetanović in "Advances in Photochemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1963.

(13) K. Yang, *J. Am. Chem. Soc.*, **84**, 3795 (1962).

**Table I.** Radical Yields in Neopentane<sup>a</sup>

Radical R	Primary yields
Methyl	2.3 <sup>b</sup>
<i>t</i> -Butyl	0.55
Isobutyl	0.16
Neopentyl	0.78
<sup>14</sup> C <sub>2</sub> H <sub>5</sub>	1.6
Total	5.4

<sup>a</sup> Values observed at low values of the ratio [*i*-C<sub>4</sub>H<sub>8</sub>]/[<sup>14</sup>C<sub>2</sub>H<sub>4</sub>].  
<sup>b</sup> Assumed value from ref. 4.

leads to isobutyl radicals (reaction 3b) but only in small amounts since  $k_{3a}/k_{3b} \cong 10$ . Since it has been reported that  $(k_{3a} + k_{3b})/k_1$  is  $3.3 \times 10^4$  for neopentane<sup>4</sup> we can calculate that  $k_1/k_2$  is approximately  $10^{-4}$ . The data points shown in Figure 1 for values of the abscissa less than 0.10 were obtained using solutions in which a considerable fraction of the energy was absorbed in the ethylene thus reducing the over-all yields of radicals. It is clear from Figure 1, however, that isobutyl radicals are produced as a primary product and do not result solely from reaction 3b.<sup>14</sup>

The yields of radicals observed in neopentane at low values of the ratio [*i*-C<sub>4</sub>H<sub>8</sub>]/[<sup>14</sup>C<sub>2</sub>H<sub>4</sub>] are summarized in Table I. A small yield of 2-methyl-1-pentene-<sup>14</sup>C is also observed corresponding to a small yield of 2-methylallyl radicals ( $G \cong 0.05$ ). Since very little of this species is formed it is difficult to state whether or not it is a primary radical species. Clearly part of this yield may be attributed to reaction 3c. It has been suggested<sup>15</sup> that 2-methylallyl radicals are produced in tracks by reaction of hydrogen atoms with isobutene and constitute evidence for the existence of tracks. Since the yield of 2-methylallyl radicals is relatively small and since they could be formed directly from the hydrocarbon by loss of two hydrogen atoms and a methyl radical (such processes in which allyl radicals are formed do occur; see section on cyclopentane below) the extent of track reactions cannot be reliably assessed from its yield.

**Isopentane.** A total of nine radical intermediates was identified in isopentane, all of which can be visualized as being formed by bond scission without rearrangement. The results obtained at 10 and  $-70^\circ$  are shown in Table II. Again difficulty was encountered in measuring absolute yields; the yields given are relative to  $G(\text{CH}_3) = 0.39$ .<sup>3</sup> The 2-methylhexane-<sup>14</sup>C and 2,3-dimethylpentane-<sup>14</sup>C, formed from 3-methylbutyl and 1,2-dimethylpropyl radicals, respectively, were not separated completely by gas chromatography and therefore, in order to calculate the yield of 1,2-dimethylpropyl, it was assumed that the yield of 3-methylbutyl was 50% of the yield of 2-methylbutyl. This procedure is justified by the results for 2,2,4-trimethylpentane<sup>16</sup> where it is observed that the ratio of yields of primary-type radicals is proportional to the number of primary carbon-hydrogen bonds whose scission would lead to that radical. Disproportionation factors used are given in the table.

(14) The presence of isobutyl radicals was indicated in an earlier study.<sup>4</sup> 2,2,4-Trimethylpentane and 2,2,5-trimethylhexane are minor products and are presumably formed by combination of isobutyl with *t*-butyl and neopentyl radicals.

(15) J. W. Falconer, *Nature*, **198**, 985 (1963).

(16) R. A. Holroyd, to be published.

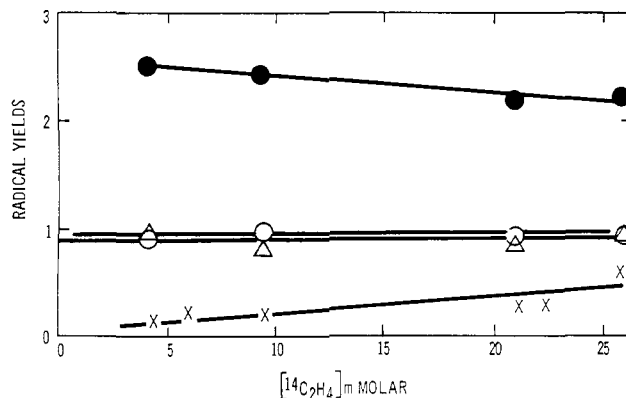


Figure 2. Isopentane, radical yields in molecules/100 e.v. vs. the concentration of ethylene-<sup>14</sup>C at  $10^\circ$ : ●,  $G(t\text{-pentyl})$ ; ○,  $G(1,2\text{-dimethylpropyl})$ ; △,  $G(2\text{-methylbutyl})$ ; ×,  $G(^{14}\text{C}_2\text{H}_5)$ .

For the purpose of obtaining the yields of radicals formed in primary processes a few irradiations were done at  $-70^\circ$ . It was hoped that by adding sufficient ethylene at  $-70^\circ$  to suppress abstraction by thermal hydrogen atoms, the yields of pentyl radicals observed would represent the yields of pentyl radicals formed in primary processes (assuming primary processes are temperature independent). The values taken for  $D/C$  and  $D'/C$  were the same as for  $10^\circ$ .<sup>17</sup> At  $-70^\circ$  the

Table II. Isopentane. Dose Rate  $\sim 5 \times 10^{19}$  E.v. ml.<sup>-1</sup> Sec.<sup>-1</sup>

	[ <sup>14</sup> C <sub>2</sub> H <sub>4</sub> ], mM					
	5-10	~30	10°	~30	10°	-70°
Relative yield of R- <sup>14</sup> C <sub>2</sub> H <sub>5</sub> , %	1 + D/C		G(R)		G(RI) <sup>a</sup>	
$G(\text{methyl})$	7.1	6.5	1.06	(0.39) <sup>b</sup>	(0.39) <sup>b</sup>	0.71
$G(\text{ethyl})$	13.5	13.3	1.12	0.81	0.84	0.91
$G(\text{isopropyl})$	8.4	7.9	1.34 <sup>c</sup>	0.58	0.60	0.66
$G(\text{isobutyl})$	0.5	0.5	1.0	0.03	0.03	
$G(\text{sec-butyl})$	2.4	2.0	1.4 <sup>c</sup>	0.18	0.16	0.18
$G(2\text{-methylbutyl})$	13.8	15.5	1.2 <sup>d</sup>	0.86	1.05	1.44
$G(3\text{-methylbutyl})$	6.9	7.8	1.2	0.43	0.53	
$G(1,2\text{-dimethylpropyl})$	13.7	17.8	1.3 <sup>d</sup>	0.92	1.31	
$G(t\text{-pentyl})$	22.6	13.1	2.0 <sup>e</sup>	2.42	1.48	
$G(^{14}\text{C}_2\text{H}_5)$	2.8	15.7	1.12	0.16	1.0	
$G(\text{total})$				6.8	7.4	

<sup>a</sup> Reference 5. <sup>b</sup> Reference 3. <sup>c</sup>  $D/C$  ref. 9,  $D'/C$  ref. 11.  
<sup>d</sup> Reference 11. <sup>e</sup> The yield of this radical is assumed to be half the yield of 2-methylbutyl (see text).

*t*-pentyl radical yield is  $\sim 1.5$  and  $G(^{14}\text{C}_2\text{H}_5)$  is 1.0 thus  $G_H \geq 1.0$ . The data are self-consistent to the extent that the sum of yields  $G(t\text{-pentyl}) + G(^{14}\text{C}_2\text{H}_5)$  at  $-70^\circ$  is 2.48, approximately equal to the sum of these yields at  $10^\circ$ , 2.58. The yields of 2- and 3-methylbutyl and 1,2-dimethylpropyl radicals are higher at  $-70^\circ$  than at  $10^\circ$ . Based on these yields the probability (per bond) of rupture of primary, secondary, and tertiary bonds in isopentane is found to be 1:4:8.

For further confirmation of these results primary yields of pentyl radicals also were estimated from the data obtained at  $10^\circ$ . The concentration of <sup>14</sup>C<sub>2</sub>H<sub>4</sub> was varied and the effect on the yields is shown in Figure 2. Only the *t*-pentyl radical yield is affected

(17) The effect of temperature on these ratios is not known for all cases and has therefore been neglected.

by ethylene and over the range studied the decrease in its yield is approximately equal to the increase in  $G(^{14}\text{C}_2\text{H}_5)$ . If it is assumed that all thermal hydrogen atoms abstract to form *t*-pentyl and that  $G(\text{H})$  is 1.6, the primary yield of *t*-pentyl radicals is  $2.58 - 1.6 = 0.98$ . This is a lower limit since hydrogen atoms may abstract from other sites as well.

Another estimate of the primary pentyl radical yields was obtained by using the data in Figure 2 and an extrapolation procedure. If a steady-state approximation is assumed for hydrogen atoms it can be shown that

$$G(\text{C}_5\text{H}_{11})/G(^{14}\text{C}_2\text{H}_5) = \frac{G(\text{C}_5\text{H}_{11})^0}{G(\text{H})} + A \frac{(\text{RH})}{(\text{C}_2\text{H}_4)} \quad (\text{II})$$

where  $A$  is constant. From kinetic plots of the ratios  $G(\text{C}_5\text{H}_{11})/G(^{14}\text{C}_2\text{H}_5)$  vs.  $(\text{RH})/(\text{C}_2\text{H}_4)$  for each of the pentyl radicals the following primary yields,  $G(\text{C}_5\text{H}_{11})^0$ , were obtained from the intercepts:  $G(2\text{-methylbutyl})^0 \cong 0.8$ ,  $G(3\text{-methylbutyl})^0 \cong 0.4$ ,  $G(1,2\text{-dimethylpropyl})^0 \cong 0.8$ , and  $G(t\text{-pentyl})^0 \cong 1.2$ . This analysis also indicated that  $k_1/k_2$  for isopentane is  $\sim 4 \times 10^{-3}$ .

In the final column of Table II are listed the alkyl iodide yields reported by Dauphin.<sup>5</sup> The agreement with our radical yields is reasonable except for the methyl and pentyl iodides. The pentyl iodides were not resolved and as mentioned earlier *t*-pentyl iodide could not be detected because of its instability. Clearly the most important intermediate in isopentane is the *t*-pentyl radical. It has been observed (along with methyl, ethyl, and isopropyl radicals) to be present in irradiated isopentane at  $-125^\circ$  in e.s.r. studies.<sup>18</sup>

**Cyclopentane.** Although the e.s.r. spectrum of irradiated cyclopentane at  $-80^\circ$  shows only cyclopentyl radicals,<sup>18</sup> in the present study three additional  $\text{C}_5$  alkyl radicals are observed to be formed in significant yields. The relative yields of labeled hydrocarbons observed at  $10^\circ$  are given in Table III, column 2. The

Table III. Cyclopentane at  $10^\circ$

Radical R	Relative yield of $\text{R}^{14}\text{C}_2\text{H}_5$ , %	1 + $D/C$	$G(\text{R})^a$	$G(\text{RI})^b$
Methyl	0.506	1.06	(0.019)	0.21
Ethyl	...	...	0	0.06
Propyl	...	...	0	0.09
Cyclopentyl	88.7	1.3	4.1	2.86
Cyclopentenyl-3	4.7	1.0	0.17	...
4-Pentenyl	2.6	1.1	0.10	...
1-Methylbutyl	0	...	...	0.1
<i>n</i> -Pentyl	3.6	1.1	0.14	0.22

<sup>a</sup> Results normalized to  $G(\text{CH}_3) = 0.019$ , see ref. 3. <sup>b</sup> Ref. 5.

ratio  $(D + D')/C$  for the reaction ethyl + cyclopentyl is taken as 0.31.<sup>9,11</sup> Disproportionation for cyclopentenyl-3 since it is allylic, is assumed to be negligible;  $(D + D')/C$  for 4-pentenyl is the same as for *n*-pentyl. About 1% of the activity was found in a product identified to be 3-methylhexane. Increasing the ethylene concentration suppressed the yield of this product indicating it was largely a secondary product. 3-

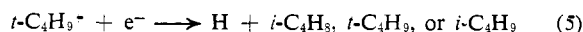
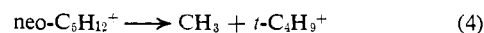
(18) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

Methylhexane corresponds to 1-methylbutyl radicals which would be expected to be formed by hydrogen atom addition to pentene-1 which is a product of cyclopentane radiolysis.<sup>19</sup>

**2,2-Dimethylbutane and 2,4-Dimethylpentane.** Preliminary results obtained using the  $^{14}\text{CH}_3$ -radical sampling method<sup>16</sup> to determine radical yields indicated that isobutyl radicals are formed to a very small extent in 2,2-dimethylbutane:  $G(i\text{-C}_4\text{H}_9) = 0.06$ , whereas  $G(t\text{-butyl}) \cong 0.43$ . A search for *t*-butyl radicals in 2,4-dimethylpentane indicated that they were not present.

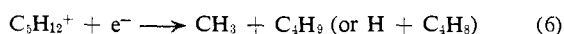
## Discussion

**Fragmentation Processes.** In *n*-alkanes it has been observed that in many cases the yields of alkyl radical pairs are approximately equal, e.g.,  $G(\text{C}_2\text{H}_5) = G(\text{C}_4\text{H}_9)$  in *n*-hexane and  $G(\text{C}_3\text{H}_7) = G(\text{C}_4\text{H}_9)$  in heptane.<sup>8</sup> However in this work a nonequivalence of radical pair yields is observed in neopentane and isopentane. In the former  $G(\text{CH}_3) \gg G(\text{C}_4\text{H}_9)$ ; in isopentane both  $G(\text{CH}_3)$  exceeds  $G(\text{C}_4\text{H}_9)$  and  $G(\text{C}_2\text{H}_5)$  exceeds  $G(\text{C}_3\text{H}_7)$ . This disparity of yields suggests that there is a primary process in which a radical group is removed from the excited state or molecular ion and then the fate of the larger remaining fragment is not always a stable alkyl radical. Instead this fragment may, e.g., lose a hydrogen atom from a carbon atom adjacent to the site of radical loss. In the case of neopentane it has been suggested that this process proceeds through elimination of a methyl radical from the molecular ion leaving a *t*-butyl carbonium ion<sup>20</sup> (eq. 4 and 5).



The latter upon neutralization may be stabilized to *t*-butyl (or possibly isobutyl radicals) or may subsequently lose a hydrogen atom from the excited radical forming an olefin. The large yield of methyl radicals ( $G = 2.3$ ) and isobutene ( $G = 2.4$ )<sup>4</sup> suggests this is a major process in neopentane.

Similar processes may be visualized for isoparaffins and *n*-paraffins. The over-all reaction yielding methyl in isopentane or *n*-pentane would be



In isopentane, 2-butene and *sec*-butyl radicals would be the products of reaction 6, and the yields:  $G(\text{CH}_3) = 0.39$ ,  $G(\text{C}_4\text{H}_9) = 0.21$  indicate this process is less important here than in neopentane. In *n*-pentane the yields of methyl radicals<sup>3</sup> and 1-butene<sup>21</sup> are even less.

The importance of the ionic process will be dependent on the heat of dissociation,  $\Delta H$ , of the molecular ion into  $\text{CH}_3$  and  $\text{C}_4\text{H}_9^+$ . In neopentane where  $G(\text{CH}_3)$  is 2.3,  $\Delta H$  for this reaction is  $+0.35$  e.v.; in isopentane where  $G(\text{CH}_3) = 0.39$ ,  $\Delta H$  is  $+0.52$  e.v.; and in *n*-pentane where  $G(\text{CH}_3) = 0.14$ ,  $\Delta H$  is  $+1.48$  e.v.<sup>22</sup> There seems to be a correlation of the yield with the ease of dissociation of the molecular ion. If the molecular ions were initially formed with a small amount of excitation energy, this ionic process could account for

(19) A. R. Lepley, *Anal. Chem.*, **34**, 322 (1962).

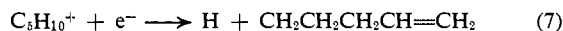
(20) T. F. Williams, *Trans. Faraday Soc.*, **57**, 755 (1961).

(21) A. E. de Vries and A. O. Allen, *J. Phys. Chem.*, **63**, 879 (1959).

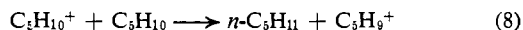
(22) Data taken from J. L. Franklin and F. W. Lampe, *Trans. Faraday Soc.*, **57**, 1449 (1961).

the fact that the yield of methyl radicals increases with the extent of branching.<sup>23</sup>

Ring opening occurs to a small extent in cyclopentane forming straight-chain radicals whose formation may involve an analogous ionic decomposition. The over-all process may be represented in this case by



This could occur by carbon-carbon bond scission of the excited molecule-ion followed by elimination of a hydrogen atom upon neutralization. An alternate reaction of this radical ion may be



which is suggested to explain the observed small yield of *n*-pentyl radicals.

**Primary Yields of Alkyl Radicals.** The primary yields of radicals are the yields formed in all processes except abstraction reactions such as reaction 1, which leads to additional parent alkyl radicals. The yields of parent pentyl radicals produced in primary processes in isopentane are 37% primary, 25% secondary, and 37% *t*-pentyl radicals. The total yield of pentyl radicals produced in primary processes is 3.2 and the total yield of fragment alkyl radicals is 2.0/100 e.v. so that 41% of the radicals produced initially are fragments. In neopentane the percentage of fragmentation increases to 79%. This decrease in the yield of parent pentyl radicals in going from isopentane to neopentane is consistent with the process, just discussed, that branching enhances the likelihood of fragmentation.

**Isomerized Radicals.** The observation of a significant yield ( $G = 0.16$ ) of isobutyl radicals in neopentane prompted an investigation of other hydrocarbons in which such rearrangements might be important. 2,2-Dimethylbutane was investigated to see if isomerization of isobutyl radicals was general for this type of structure. 2,4-Dimethylpentane was studied to see if the isomerization process is reversible. In the latter case only isobutyl radicals are found even though *t*-butyl radicals are considered to be more stable than isobutyl. The absence of *t*-butyl radicals here tends to rule out a mechanism involving rearrangements of excited radicals.

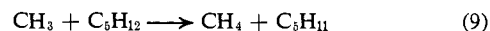
Alternately it has been suggested that isobutyl radicals may be formed by addition of hydrogen atoms to isobutene in the spur.<sup>15</sup> If these hydrogen atoms were thermal, isobutyl radicals would be produced with one-tenth of the yield of *t*-butyl radicals. In neopentane the ratio  $G(\text{isobutyl})/G(\text{t-butyl})$  is 0.28, three times higher than expected. Thus a process involving thermal hydrogen atoms is inconsistent with the data.

As discussed above *t*-butyl carbonium ions may be important intermediates in neopentane. Upon neutralization of this ion one might expect that both isobutyl and *t*-butyl radicals would be formed, since the *t*-butyl ion may be in equilibrium with an isobutyl carbonium ion.<sup>24</sup>

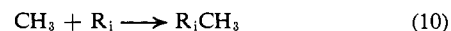
(23) However, an alternate explanation involving decomposition of the neutral excited species formed by neutralization of  $\text{C}_5\text{H}_{12}^+$  can readily be visualized and such a process cannot be completely ruled out: cf. P. Ausloos and G. Lias, *J. Chem. Phys.*, **41**, 3962 (1964).

(24) Sufficient time for equilibration would be available if geminate recombination of ions requires  $10^{-9}$  to  $10^{-7}$  sec. as suggested by recent theoretical considerations: cf. T. F. Williams, *J. Am. Chem. Soc.*, **86**, 3954 (1964).

**Extent of Track Reactions in Neopentane.** The availability of the radical yields for neopentane makes it possible to calculate what yields of stable products are expected to be formed under various conditions and to compare them to the actual observed yields. The comparison is given here for the purposes of assessing the extent of track reactions in neopentane. The argument is based on the known effect of dose rate on the reactions of methyl radicals in neopentane.<sup>4</sup> At sufficiently low dose rates methyl radicals only abstract



and do not combine with other radicals ( $R_1$ ) to form products,  $R_1\text{CH}_3$ . Since the dose rate in the particle



tracks would be high enough to favor combination reactions, the formation of combination products of methyl radicals with other radicals at low dose rates would be evidence that tracks exist in irradiated hydrocarbons.

The yields of stable products that would be expected considering the radicals present in neopentane were calculated by assuming radicals combine statistically and the results are compared here with the observed yields of stable products reported earlier for neat neopentane<sup>4</sup> (see Table IV). At low dose rates methyl

Table IV. Product Yields from Neopentane

Product	Low dose rates ( $\text{Co}^{60}$ $\gamma$ values)		High dose rates	
	Exptl. <sup>a</sup>	Calcd. <sup>b</sup>	Exptl.	Calcd. <sup>b</sup>
Ethane	0.42	0	0.97	0.49
Isopentane	0.04	0	0.27	0.07
2,2-Dimethylbutane	0.28	0	0.75	1.02
2,2,3,3-Tetramethylbutane	0.05	0.03	0.10	0.03
2,2,4-Trimethylpentane	0.03	0.02	0.08	0.02
2,5-Dimethylhexane	...	0.00	...	0.00
2,2,4,4-Tetramethylpentane	0.40	0.48	0.17	0.24
2,2,5-Trimethylhexane	0	0.13	0.06	0.07
2,2,5,5-Tetramethylhexane	1.53	2.03	0.14	0.53

<sup>a</sup> Reference 4. <sup>b</sup> See text for details.

radicals as well as hydrogen atoms abstract in pure neopentane. For each hydrogen atom and each methyl radical a neopentyl radical would therefore be formed, and there would be a total yield of neopentyl radicals of  $G(\text{CH}_3) + G(\text{H}) + G(\text{neopentyl})_0$  of 4.7. Products would then be formed by combination of neopentyl, *t*-butyl, and isobutyl radicals. The product distribution expected under such conditions is shown in column 3, Table IV. Disproportionation has been neglected in the calculation and would, if considered, decrease the expected yields of products such as 2,2,3,3-tetramethylbutane and 2,2,4,4-tetramethylpentane.

In calculating product yields at high dose rates it was assumed that products are formed by combination reactions of methyl, neopentyl, isobutyl, and *t*-butyl radicals, and that the hydrogen atoms formed additional neopentyl radicals by abstraction. The results are shown in the final column of Table IV. The observed yield of 2,2,5,5-tetramethylhexane is lower than expected for both low and high dose rates presumably because hydrogen atoms reacted to some extent with the isobutene thus lowering the yield of neopentyl radicals and products derived therefrom.

This comparison shows that the products ethane, isopentane, and 2,2-dimethylbutane are observed to be formed in both cases in yields in excess of the calculated values, in fact they are not expected at all at low dose rates. On the other hand these are exactly the products one would expect to form in reaction 12 considering that the radicals present are methyl, isobutyl, and neopentyl. Further the yields of ethane, isopentane, and 2,2-dimethylbutane observed at low dose rate are in the ratio 1:0.12:0.67 and in light of the radical yields we would expect the ratio of these yields to be 1:0.14:0.67 if methyl radicals were combining with the other radicals at this dose rate. Since at these low dose rates methyl radicals are known to predominantly abstract we conclude that regions of high dose rate exist; that is these products are formed by combination of methyl and other radicals in the tracks of the ionizing particle. Further evidence of the molecular nature of these products comes from the observation that the yield of ethane in 30 mM iodine solution is 0.35,<sup>4</sup> and the yield of 2,2-dimethylbutane is 0.20 in the presence of 1 mM oxygen, only slightly below the yields in neat neopentane.<sup>4</sup> This reduction of yields is characteristic and to be expected at high concentrations of scavenger.

It is of interest to use this data to calculate the fraction of methyl radicals formed initially which escape the track,  $N(\text{CH}_3)/N(\text{CH}_3)_0$ ;  $N(\text{CH}_3)$  is the methyl radical yield and is observed to be 2.3 and  $N(\text{CH}_3)_0$  is the sum of the methyl radical yield plus the molecular methyl radical yield, the latter is the yield of methyl radicals which combine with other radicals in the track. The molecular methyl radical yield is  $\geq 2G(\text{C}_2\text{H}_6) + G(\text{isopentane}) + G(2,2\text{-dimethylbutane}) = 1.2$ ; it may be larger than this to the extent that methyl radicals also combine with hydrogen atoms in the track. The yield of methyl radicals which react with *t*-butyl radicals has been neglected since this represents a back reaction to neopentane, the extent of which cannot be directly measured. Thus the molecular methyl radical yield is equal to or greater than 1.2 or  $N(\text{CH}_3)/N(\text{CH}_3)_0$  is  $\leq 0.66$ . This value is remarkably close to the corresponding value of 0.62 for OH radicals observed in low LET radiolysis of water.<sup>25</sup> If this interpretation is correct it would be extremely interesting to measure the yields of these characteristic products as a function of solute concentration and LET and compare the experimental results with the expectations of diffusion theory.

(25) P. J. Dyne and J. M. Kennedy, *Can. J. Chem.*, **36**, 1518 (1958).

## Photoisomerization of 1,6-Heptadiene Sensitized by Mercury 6(<sup>3</sup>P<sub>1</sub>) Atoms<sup>1</sup>

R. Srinivasan and K. A. Hill

Contribution from the IBM Watson Research Center,  
Yorktown Heights, New York 10598. Received May 28, 1965

The decomposition of 1,6-heptadiene photosensitized by mercury 6(<sup>3</sup>P<sub>1</sub>) atoms has been studied in the pressure range from 3 to 65 mm. In addition to free-radical products and a polymer which accounted for 95% of the decomposition, six isomers were observed. Four of these were identified as 4-cyclopropylbutene-1, bicyclo[3.2.0]heptane, bicyclo[3.1.1]heptane, and 1-methyl-2-vinylcyclobutane. Thus, in this system, an isomerization which gives rise to a cyclopropyl derivative (as in other unconjugated diolefins) as well as a parallel process which gives a cyclobutyl derivative (as in monoolefins) are observed. It is tentatively suggested that the present system may not be unique in this respect and that two such pathways may be operative in the mercury-photosensitized isomerization of other unconjugated diolefins as well.

### Introduction

The photoisomerization of mono- and diolefins sensitized by mercury 6(<sup>3</sup>P<sub>1</sub>) atoms has been the subject of many recent studies. In monoolefins, the process generally proceeds with the migration of a hydrogen. Avrahami and Kebarle<sup>2</sup> proposed that in a molecule

in which several kinds of protons are available the migratory aptitude will be determined by the order 1,4 > 1,3 > 1,2. Placzek and Rabinovitch<sup>3</sup> have reviewed all of the results to which this hypothesis is applicable and come to the conclusion that it is, in general, a valid statement although not a highly selective one. These authors have also pointed out that the mercury-sensitized isomerizations of diolefins seem to be exceptional in that the 1,2 migration of hydrogen atoms is the only process that is to be observed, although 1,3 and 1,4 migrations are equally possible. The three examples that are known to date are: 1,4-pentadiene,<sup>4</sup> 1,5-hexadiene,<sup>5</sup> and 1,5-cyclo-octadiene.<sup>4</sup> If the cyclic compound is dropped from the discussion (since it is almost the only one for which data are available), there are only two exceptions. Of these 1,4-pentadiene may be really thought of as in a class by itself. In this molecule, apart from the 1,2 transfer which is observed, the other possibility is a 1,3 transfer which would give a product with a conjugated diene system. This product may undergo secondary reactions more rapidly than the reactant. This limits the exceptional behavior to 1,5-hexadiene.

(3) D. W. Placzek and B. S. Rabinovitch, *Can. J. Chem.*, **43**, 820 (1965).

(4) R. Srinivasan, *J. Am. Chem. Soc.*, **86**, 3318 (1964).

(5) R. Srinivasan, *J. Phys. Chem.*, **67**, 1367 (1963).

(1) Paper IV on "Mercury Photosensitized Reactions in Diolefins."  
(2) M. Avrahami and P. Kebarle, *J. Phys. Chem.*, **67**, 354 (1963).