

[CONTRIBUTION FROM THE RADIATION RESEARCH LABORATORIES, MELLON INSTITUTE, PITTSBURGH, PA.]

## Detection of Radical Intermediates in the Radiolysis of Hydrocarbons with the Ethylene-C<sup>14</sup> Scavenging Technique<sup>1</sup>

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The ethylene-C<sup>14</sup> scavenging method has been used to determine individual radical yields in the radiolysis of *n*-pentane, *n*-hexane and *n*-heptane. Secondary alkyl radicals are the predominant radical type observed in all cases. Rearrangement is absent; that is, only radicals that can be derived from the parent by loss of a hydrogen atom or an alkyl radical are formed. Only minor amounts of unsaturated radicals are observed. At 10° the total radical yields are 5.4, 5.6 and 4.8 for *n*-pentane, *n*-hexane and *n*-heptane. Lowering the temperature to -70° decreases all secondary alkyl radical yields but does not affect the normal alkyl radical yields. Hydrogen abstraction reactions do not contribute to the radical yield at -70°; thus the results represent primary radical yields. The maximum observed value of  $G_{C_2^{14}H_5}$ , the yield of scavenged hydrogen atoms, indicates  $G_H$  must be greater than or equal to 1.4.

Recently a new technique has been described for detecting radicals in the radiolysis of hydrocarbons.<sup>2</sup> The scavenger used in this method is the labeled ethyl radical which is generated during radiolysis by addition of hydrogen atoms to C<sup>14</sup><sub>2</sub>H<sub>4</sub>, present in low concentrations. At the high dose rates employed, the C<sup>14</sup><sub>2</sub>H<sub>5</sub> radicals scavenge the radical intermediates of the radiolysis of the hydrocarbon thus forming labeled hydrocarbon products. The relative yields of these labeled hydrocarbons after a small correction has been made for disproportionation may be equated to the relative yields of radicals.

The specific labeled hydrocarbons produced serve to identify the radicals from which they were formed. Thus this technique is similar to the use of iodine as a scavenger since individual radical intermediates can be identified as well as their yields determined. In the case of *n*-pentane it has been shown that very similar results are obtained with the two methods.<sup>2</sup> A unique characteristic of the C<sup>14</sup><sub>2</sub>H<sub>4</sub> scavenging technique is that the over-all radiolytic decomposition of the hydrocarbon is largely unperturbed. That is, the 0.1 mole per cent ethylene-C<sup>14</sup> that is added will scavenge only a small fraction of the hydrogen atoms but still produce a sufficiently large yield of labeled hydrocarbons. Therefore the yields of products are only slightly affected by the presence of the scavenger.

Before a complete understanding of the mechanism of radiolysis of hydrocarbons is possible, much more detailed information is needed on the yields of radicals from a variety of hydrocarbons under different experimental conditions. Results for *n*-pentane, *n*-hexane and *n*-heptane at 10° and -70° are presented here.

### Experimental

All hydrocarbons used were Phillips research grade and were purified previous to use by passage through a silica gel column to remove unsaturates. Only the first fraction eluted was used and in all cases the unsaturated impurity was < 0.003 mole per cent. The ethylene-C<sup>14</sup> was obtained from New England Nuclear Corp. and purified twice by gas chromatography to remove C<sup>14</sup><sub>2</sub>H<sub>6</sub> and higher boiling impurities. The specific activity of the C<sup>14</sup><sub>2</sub>H<sub>4</sub> was ≅ 0.1 mc./mmole.

Samples were prepared for irradiation by adding a measured amount of ethylene-C<sup>14</sup> to approximately 1 ml. of degassed hydrocarbon. For *n*-pentane at 10° the amount of

ethylene in the liquid phase was found to be two-thirds of the total added. It was assumed that this same fraction was dissolved in the other hydrocarbons. The concentration of ethylene in the samples at -70° was calculated by assuming that all the ethylene was dissolved in the liquid.

Most of the details of the experimental procedure and analytical technique are described elsewhere.<sup>2</sup> The method of irradiating samples has been modified by operating the Van de Graaff at high beam currents, using an intermittent feature<sup>3</sup> to minimize heating of the sample. Samples were irradiated with a pulsed beam of 5-10 μamp. The duration of each pulse was 0.03 sec. and the ratio of "light" to "dark" periods was 1 to 15. Under these conditions the pulse length was more than 100 times the lifetime of the alkyl radicals<sup>3</sup>; thus in effect each sample received several successive doses.

For low temperature irradiations the sample was cooled to -78° and then placed in a polystyrene dewar which was flushed continuously with a stream of nitrogen gas, pre-cooled to -78°. The temperature of the sample during irradiation was approximately -70°.

All samples were analyzed by gas chromatography. Each labeled hydrocarbon was identified by addition of non-radioactive carrier to the sample for comparison of retention times.

**Kinetic Analysis.**—The assertion made earlier that the relative yields of labeled hydrocarbons measure the relative radical yields can be justified if one first assumes that radicals (excluding hydrogen atoms) react only with other radicals under the conditions of the experiment. Then for the steady state approximation

$$G_{R_m}D/100N = \sum_i a_i k_{mi}(R_m)(R_i) \quad (I)$$

where

$G_{R_m}$  is the 100 e.v. yield of radical  $R_m$

$D$  is the absorbed dose rate in e.v.l<sup>-1</sup> sec.<sup>-1</sup>

$k_{mi}$  is the spec. rate const. for reacn. of radical  $R_m$  with radical  $R_i$

$a_i$  is a const. ( $= 1$ ) except when 2 ident. radicals are combining, then  $a_i = 2$

thus the ratio of yields of two labeled hydrocarbons is given by

$$\frac{G_{R_m C_2^{14} H_5}}{G_{R_n C_2^{14} H_5}} = \frac{G_{R_m}}{G_{R_n}} \times \frac{\sum_i \frac{a_i k_{ni}}{k_{nE}} (R_i)}{\sum_i \frac{a_i k_{mi}}{k_{mE}} (R_i)} \quad (II)$$

where  $k_{nE}$  is the spec. rate const. for reac. of radical  $R_n$  with C<sup>14</sup><sub>2</sub>H<sub>5</sub>,  $G_{R_m C_2^{14} H_5}$  is the yield of the labeled hydrocarbon formed from  $R_m$ . Thus a sufficient condition that the relative yields of labeled hydrocarbons measure the relative radical yields is that the coefficients in the summations are equal; *i.e.*

$$a_i k_{ni}/k_{nE} = a_i k_{mi}/k_{mE}$$

In other words, the ratio of the reactivity of radical  $R_n$  with another radical  $R_i$  to the reactivity of  $R_n$  with C<sup>14</sup><sub>2</sub>H<sub>5</sub> is the same as the ratio of the reactivity of radical  $R_m$  with  $R_i$  to the reactivity of  $R_m$  with C<sup>14</sup><sub>2</sub>H<sub>5</sub>. Equation III will be obeyed if the relative rate constants are in proportion to the relative collision frequencies in the liquid phase. That this is the

(1) Supported, in part, by the U. S. Atomic Energy Commission.

(2) R. A. Holroyd and G. W. Klein, *J. Appl. Radiation and Isotopes*, in press (1962).

(3) R. W. Fessenden, Mellon Institute Quarterly Report, March 1962.

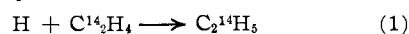
case in the gas phase has been shown for a series of combination reactions of alkyl radicals<sup>4</sup> where the ratio  $k_{nm^2}/k_{nn}k_{mm} \cong 4$ . Therefore the method gives relative radical yields; for example

$$G_{C_4H_9}/G_{C_3H_7} = \frac{(1 + D/R)G_{\text{hexane-C}^{14}}}{(1 + D/R)G_{\text{pentane-C}^{14}}}$$

where  $D/R$  is the ratio of disproportionation to combination in each reaction.

### Results and Discussion

Ethyl- $C^{14}$  radicals are generated during radiolysis by hydrogen atom addition to ethylene (reaction 1). Since all  $C^{14}_2H_5$  radicals react with other radicals,



the total yield of labeled hydrocarbons corrected for losses due to disproportionation is equal to  $G_{C_2^{14}H_5}$ . Values for  $G_{C_2^{14}H_5}$  observed for *n*-pentane, *n*-hexane and *n*-heptane are given in Table I. It is found that  $G_{C_2^{14}H_5}$  increases with ethylene concentration; at 0.017*M* ethylene,  $G_{C_2^{14}H_5} = 0.22$  for *n*-pentane. Thus only a fraction of the hydrogen atoms is scavenged by ethylene under these conditions.

The concentration of  $C^{14}_2H_5$  radicals thus produced ( $\sim 10^{-7}M$ ) is insufficient to scavenge all radicals and the yield of a specific labeled hydrocarbon cannot be equated directly to the radical yield. However, absolute radical yields may be calculated from the relative yields if any individual radical yield is known. Since  $G_{C_2^{14}H_5}$  is experimentally observable,  $G_{C_2H_5}$  can be determined from the relationship:  $G_{C_2H_5} = G_{C_2^{14}H_5}((C_2H_5)/(C^{14}_2H_5))$ .<sup>5</sup> The yields of ethyl radicals calculated

TABLE I  
ETHYL RADICAL YIELDS AT 10°

Hydrocarbon	( $C_2^{14}H_4$ ), moles/l. $\times 10^2$	Labeled hydrocarbon, formed, $\mu\text{mole}$	Dose, e.v./ml. $\times 10^{-19}$	$G_{C_2^{14}H_5}$	$C_2H_5/C^{14}_2H_5$	$G_{C_2H_5}$
<i>n</i> -Pentane <sup>a</sup>	1.7	0.425	21.0	0.222	2.36	0.53
<i>n</i> -Hexane	0.7	.215	21.0	.114	2.90	.33
<i>n</i> -Hexane	.6	.232	21.0	.123	2.68	.33
<i>n</i> -Heptane	.7	.276	21.0	.145	1.30	.19
<i>n</i> -Heptane	.4	.126	50.4	.039	4.58	.18

<sup>a</sup> Data of ref. 2.

in this way for *n*-pentane, *n*-hexane and *n*-heptane are given in the final column of Table I. Although  $G_{C_2^{14}H_5}$  increases, the ratio  $(C_2H_5)/(C^{14}_2H_5)$  decreases with increasing ethylene concentration and the product  $G_{C_2H_5}$  is a constant. The value of  $G_{C_2H_5}$  is observed to decrease in this series from 0.53 for *n*-pentane to 0.19 for *n*-heptane. A very similar effect has been noted for  $G_{CH_3}$  which decreases monotonically with increasing molecular weight for *n*-alkanes.<sup>5</sup>

The observed relative yields of labeled hydrocarbons, in terms of percentage of the total yield, are given in the second column of Tables II, III and IV for *n*-pentane, *n*-hexane and *n*-heptane,

(4) J. A. Kerr and A. F. Trotman-Dickenson, *Chemistry & Industry*, 125 (1959); M. H. J. Wijnen, *J. Am. Chem. Soc.*, **83**, 3752 (1961).

(5) The ratio  $(C_2H_5)/(C^{14}_2H_5)$  is readily obtained; for example in the case of *n*-pentane,  $(C_2H_5)/(C^{14}_2H_5)$  is the ratio of yields of non-labeled to labeled 3-methylhexane. The yield of the former is obtained from the total yield of 3-methylhexane as measured with the thermal conductivity detector.

(6) R. R. Kuntz and R. H. Schuler, Abstracts 139th Meeting Am. Chem. Soc., St. Louis, Mo., 1961.

respectively. Each number is the average of several determinations. The average deviation found in most cases was less than 5%. The labeled hydrocarbons derived from the various *sec*-pentyl, *sec*-hexyl and *sec*-heptyl radicals were observed to decrease slightly with increasing ethylene concentration (see Fig. 1). Therefore

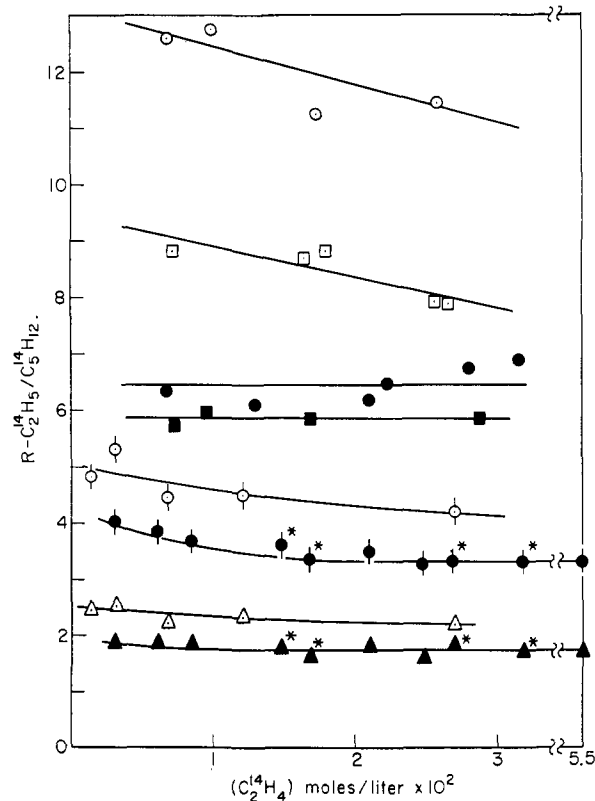


Fig. 1.—Ratios of  $RC_2^{14}H_5/n-C^{14}_5H_{12}$  vs. ethylene- $C^{14}$  concentration. Open points are results at 10°; filled points are results at -70°:  $\circ, \bullet$ , *n*-heptane;  $RC^{14}_2H_5$  is the sum of the yields of 3-ethyl- and 4-ethyl-heptane and 3-methyl-octane;  $\square, \blacksquare$ , *n*-hexane;  $RC^{14}_2H_5$  is the sum of the yields of 3-methylheptane and 3-ethylhexane;  $\circ, \bullet$ , *n*-pentane;  $RC^{14}_2H_5$  is 3-methylhexane;  $\triangle, \blacktriangle$ , *n*-pentane,  $RC^{14}_2H_5$  is 3-ethylpentane. An asterisk denotes conversion is  $<0.005\%$ .

the values reported are those obtained at the lowest ethylene concentration. The labeled butane may contain either one or two  $C^{14}_2H_5$  radicals. The reported relative yields of butane- $C^{14}$  have been corrected so as not to include the butane formed from two  $C^{14}_2H_5$ 's. Again this is done by making use of the observed ratio  $(C_2H_5)/(C^{14}_2H_5)$ .<sup>5</sup>

The relative yields, when adjusted for disproportionation losses, represent the relative radical yields. These are given in column 3 of Tables II through IV. The following values based on gas phase studies have been used for disproportionation/recombination ratios: ethyl + *n*-alkyl, 0.147; ethyl + *sec*-alkyl, 0.41. The latter value is assumed since data on ethyl + *sec*-pentyl, *sec*-hexyl and *sec*-heptyl are unavailable; but this

(7) R. K. Brinton and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1840 (1955).

TABLE II  
*n*-PENTANE

Radical (R)	Relative yield of RC <sup>14</sup> H <sub>5</sub>		G(10°)	G(-70°)
	Obsd.	Corr.		
CH <sub>3</sub>	2.3	1.9	0.10	..
C <sub>2</sub> H <sub>5</sub>	11.0	9.6	.51	0.56
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	7.7	6.8	.36	(0.36) <sup>a</sup>
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	0.7	0.7	.04	..
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	1.4	1.2	.065	..
1-Methylbutyl	37.8	41.5	2.21	1.47
1-Ethylpropyl	18.9	20.8	1.10	0.77
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	21.0	18.4	0.98	1.04

<sup>a</sup> This value is assumed to be the same as at 10°.

TABLE III  
*n*-HEXANE

Radical (R)	Relative yield of RC <sup>14</sup> H <sub>6</sub>		G(10°)	G(-70°)	G <sub>R1</sub>
	Obsd.	Corr.			
CH <sub>3</sub>	1.40	1.13	0.06	..	0.077 <sup>a</sup>
C <sub>2</sub> H <sub>5</sub>	6.7	5.9	.33	0.35	.40 <sup>c</sup>
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	6.5	5.7	.32	(.32) <sup>b</sup>	.70 <sup>c</sup>
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	5.7	5.0	.28	.34	.30 <sup>c</sup>
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	1.2	1.1	.06	.05	..
1-Methylpentyl } 1-Ethylbutyl }	58.4	63.7	3.58	2.35	2.60 <sup>c</sup>
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	20.1	17.6	0.99	0.92	0.70 <sup>c</sup>

<sup>a</sup> Ref. 6. <sup>b</sup> This value is assumed to be the same as at 10°. <sup>c</sup> Ref. 13.

TABLE IV  
*n*-HEPTANE

Radical (R)	Relative yield of RC <sup>14</sup> H <sub>7</sub>		G(10°)	G(-70°)
	Obsd.	Corr.		
CH <sub>3</sub>	0.74	0.6	0.03	..
C <sub>2</sub> H <sub>5</sub>	4.4	3.8	.18	..
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	4.8	4.1	.20	(0.20) <sup>a</sup>
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	5.5	4.75	.23	.22
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	4.2	3.7	.18	.18
<i>n</i> -C <sub>6</sub> H <sub>13</sub>	0.91	0.8	.04	.03
1-Propylbutyl } 1-Methylhexyl } 1-Ethylpentyl }	51.0	55.1	2.67	1.31
<i>n</i> -C <sub>7</sub> H <sub>15</sub>	17.1	14.8	0.72	0.50

<sup>a</sup> This value is assumed to be the same as at 10°.

value is reasonable since a ratio of 0.30 has been reported for methyl + *sec*-butyl.<sup>8</sup>

The radical yields are listed in the fourth column of each table. These are based on the relative yields and the values for  $G_{C_2H_5}$  in Table I. The total radical yields observed here are 5.4, 5.6 and 4.8 for *n*-pentane, *n*-hexane and *n*-heptane, respectively. For *n*-hexane the iodine scavenging technique gave a value of 5.60 for the total radical yield<sup>9</sup> and from the rate of iodine uptake it has been shown that the total radical yield is similar for a series of aliphatic hydrocarbons.<sup>10</sup> For *n*-heptane, values of 6.1 and 6.0 were obtained using *n*-butyl mercaptan<sup>11</sup> and DPPH,<sup>12</sup> respectively,

(8) B. S. Rabinovitch and R. W. Diesen, *J. Chem. Phys.*, **30**, 735 (1959).

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

(10) E. N. Weber, P. F. Forsyth and R. H. Schuler, *Radiation Research*, **3**, 58 (1955).

(11) J. D. Nevitt, W. A. Wilson and H. S. Seelig, *Ind. Eng. Chem.*, **51**, No. 3, 311 (1959).

(12) L. Bouby and A. Chapiro, *J. Chem. Phys.*, **52**, 645 (1955).

as scavengers. Thus the total radical yield observed with ethylene-C<sup>14</sup> for *n*-pentane and *n*-hexane agrees well with other determinations, but the value found for *n*-heptane appears to be approximately 15% low. This may mean that disproportionation is more important in this case than has been assumed. Since a fraction of the hydrogen atoms are removed by reaction 1 ( $G_{C_2H_5} \sim 0.1$ ), the total radical yield observed with ethylene-C<sup>14</sup> is expected to be only 2 to 3% low. Data on individual radical yields are available for comparison for *n*-hexane and the methyl radical yields. The yields of alkyl iodides for *n*-hexane<sup>6,13</sup> (Table III) are very nearly the same as the yields determined with ethylene-C<sup>14</sup> with the exception of the *n*-propyl iodide which is more than twice the yield of propyl radical observed here.

Certain generalizations regarding radical formation are obvious from the data. The major radicals observed are not rearranged (or isomerized). That is, the radicals formed are those that can be derived by loss of a hydrogen atom or alkyl group from the parent hydrocarbon. One exception to this was noted in that a small yield of isopropyl ( $G = 0.04$ ) is observed for *n*-pentane. The yields of secondary alkyl radicals are proportional to the number of hydrogen atoms available at each position.<sup>14</sup> Thus, for example, the yield of 1-methylbutyl is exactly twice the yield of 1-ethylpropyl for *n*-pentane. For *n*-heptane the sum of the yields of 1-methylhexyl and 1-ethylpentyl is 4.5 times the yield of 1-propylbutyl, whereas the ratio of available hydrogen atoms is 4 to 1. Unfortunately the octanes derived from secondary hexyl radicals were not resolved with the columns used.

There appears to be a one-to-one correspondence between the yield of a radical and the yield of its complementary radical for *n*-hexane and *n*-heptane, as if the mode of formation of fragment radicals were carbon-carbon bond scission. For *n*-pentane, however,  $G_{CH_3} > G_{C_2H_5}$  and  $G_{C_3H_7} > G_{C_4H_9}$ . Such non-equivalence of radical fragments was observed for *n*-butane<sup>15</sup> and is very common for branched alkanes.<sup>16</sup> Although only saturated alkyl radicals are reported in the tables, very small amounts (~1% of the total radical yield) of pentenyl and hexenyl radicals were observed for *n*-pentane and *n*-hexane. These were relatively more important at -70°. One may conclude that the formation of unsaturated radicals is a minor process. It is possible, however, that some unsaturated radicals would not be detected efficiently by this technique. We have assumed that radicals react only with other radicals, but if a radical reacts with the substrate its steady state concentration is thereby lowered and its apparent yield thus decreased. Any very reactive radical such as vinyl or a substituted vinyl radical, if formed, might therefore not be observed.

**Results at -70°.**—The treatment of the data obtained at -70° was analogous to that used for

(13) H. A. Dewhurst, *J. Phys. Chem.*, **62**, 15 (1958).

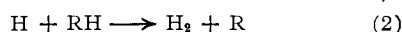
(14) C. D. Wagner, *ibid.*, **64**, 231 (1960).

(15) C. E. McCauley and R. H. Schuler, *J. Am. Chem. Soc.*, **79**, 4008 (1957).

(16) H. A. Dewhurst, *ibid.*, **80**, 5607 (1958).

the 10° results. That is, the ratios of the yields of all labeled hydrocarbon products were obtained relative to the yield of labeled pentane for each hydrocarbon studied. In most cases these ratios were again independent of ethylene concentration in the range studied, *i.e.*, from 0.005 to 0.05 *M*. The only exceptions were the ratios 3-methylhexane-C<sup>14</sup>/pentane-C<sup>14</sup> and possibly 3-ethylpentane-C<sup>14</sup>/pentane-C<sup>14</sup>. In these cases a more detailed study indicated that the ratios showed a tendency to increase at low ethylene concentrations (Fig. 1). The value of these ratios used in calculating radical yields was that obtained in the concentration independent region, that is, > 0.01 mole/l. ethylene.

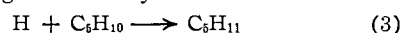
The radical yields at -70° are shown in column 5 of each table. These were calculated from the relative radical yields by assuming  $G_{C_3H_7}$  was the same as at 10°. No dose measurements were attempted at -70°. The yields observed for the *n*-alkyl radicals are very nearly the same as at 10° for all three hydrocarbons. On the other hand, the yields of all secondary alkyl radicals are from 30 to 50% lower at -70° than at 10°. (This can also be seen from the ratios in Fig. 1.) For example, for *n*-hexane the sum of the yields of the two *sec*-hexyl radicals is reduced from 3.58 to 2.35, the later value agreeing more closely with the yield of secondary hexyl iodide observed in saturated iodine solutions. This suggests that the yields observed at -70° are primary radical yields and that reaction 2 does not contribute to the hexyl radical yield under these conditions. That is, at



ethylene concentrations greater than 0.01 *M* reaction 2 cannot be important at -70°.

The apparent temperature dependence of the secondary alkyl radical yields requires that  $E_2 > E_1$ . Further, if reactions 1 and 2 are competing for hydrogen atoms at 10°, the yield of H<sub>2</sub> should decrease with increasing ethylene concentration and  $k_1/k_2$  must be approximately 400. Hardwick,<sup>17</sup> in an extensive study of hydrogen yields from various hydrocarbons, has shown  $G_{H_2}$  decreases as expected with increasing olefin concentration. Back<sup>18</sup> has found that the rate constant for addition of hydrogen atoms to pentene is 419 times the rate constant for abstraction from pentane at 21°. From gas phase data the activation energy,  $E_2$ , has been shown to be equal to  $4.4 + E_1$  kcal./mole and  $k_1/k_2 = 710$  at 56°,<sup>19</sup> when RH is propane. If  $E_2$  for *n*-pentane, *n*-hexane and *n*-heptane is also the same as for propane, then reaction 2 can compete with reaction 1 at 10° but cannot be important above 0.01 *M* ethylene at -70°. Therefore, as was asserted above, the yields observed at -70° are primary yields.

At high conversions secondary alkyl radicals might also be generated by reaction 3. To check

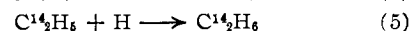


this point several runs were carried out with *n*-pentane at very low conversion (<0.005%) where the average pentene concentration was low enough

so that reaction 3 could not compete with reaction 1. The results (Fig. 1, points with asterisks) show that ratios under these conditions were the same as observed under normal conditions. Accepting therefore that these data represent the primary radical yields, the results should be comparable to the yields of alkyl iodides from concentrated iodine solutions. The observed total primary radical yields here are 4.3, 4.4 and 3.0. The total yield of alkyl iodides is 4.5 for *n*-butane,<sup>15</sup> 4.5 for *n*-pentane<sup>20</sup> and 4.8 for *n*-hexane.<sup>13</sup>

An alternate explanation for the decrease in *sec*-alkyl radical yields at low temperatures is to assume that the rate of disproportionation relative to combination is temperature dependent for secondary alkyl radicals and temperature independent for normal alkyl radicals. However, this is unlikely from a consideration of gas phase results, and also we have observed that the yield of C<sup>14</sup><sub>2</sub>H<sub>6</sub> relative to the yield of labeled pentane is the same at -70° and 10° for *n*-pentane.

In this regard it is found that the yield of C<sup>14</sup><sub>2</sub>H<sub>6</sub>, in cases where it has been measured, is somewhat in excess of that expected to be formed as a result of disproportionation reactions. Depending on the hydrocarbon studied, the excess amount represents from 5 to 25% of the total number of C<sup>14</sup><sub>2</sub>H<sub>6</sub>'s formed. Thus either disproportionation is more important than has been assumed or there is another source of C<sup>14</sup><sub>2</sub>H<sub>6</sub> such as reactions 4 and 5



For *n*-heptane  $k_4$  is 2.1 liter mole<sup>-1</sup>, sec.<sup>-1</sup> at 10° in the gas phase.<sup>21</sup> Clearly at low dose rates reaction 4 is important, but under these conditions the rate of reaction 4 is approximately  $14 \times (C^{14}_2H_6)$  moles liter<sup>-1</sup> sec.<sup>-1</sup>, and the rate of reaction 6 is > 400



$\times (C^{14}_2H_6)$  moles liter<sup>-1</sup> sec.<sup>-1</sup>.<sup>22</sup> Thus at the high dose rates employed here the fraction of C<sub>2</sub><sup>14</sup>-H<sub>6</sub> radicals abstracting is small at 10° and negligible at -70°.

TABLE V  
YIELDS OF C<sup>14</sup><sub>2</sub>H<sub>6</sub> AT -70°

Hydrocarbon	(C <sup>14</sup> <sub>2</sub> H <sub>6</sub> ),		$G_{C^{14}_2H_6}$
	moles/l. $\times 10^2$	(C <sup>14</sup> <sub>2</sub> H <sub>6</sub> )/ (C <sub>2</sub> H <sub>6</sub> )	
<i>n</i> -Pentane	0.3	0.57	0.3
<i>n</i> -Pentane	0.9	1.28	0.7
<i>n</i> -Pentane	1.8	1.85	1.1
<i>n</i> -Pentane	2.0	2.27	1.3
<i>n</i> -Pentane	3.4	2.47	1.4
<i>n</i> -Pentane	5.6	2.27	1.3
<i>n</i> -Hexane	0.7	0.64	0.2
<i>n</i> -Hexane	1.0	1.58	0.6
<i>n</i> -Hexane	1.7	3.34	1.2
<i>n</i> -Hexane	2.6	3.89	1.4
<i>n</i> -Hexane	2.9	3.86	1.4
<i>n</i> -Heptane	1.3	3.95	0.7
<i>n</i> -Heptane	2.8	9.7	1.8

(20) R. H. Schuler and G. Buzzard, private communication.

(21) D. G. L. James and E. W. R. Steacie, *Proc. Roy. Soc. (London)*, **A244**, 289 (1958).

(22) At 10°  $k_6$  should be greater than  $4 \times 10^3$  l. mole<sup>-1</sup> sec.<sup>-1</sup>, the value for ethyl radicals in liquid ethane; R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **33**, 935 (1960).

(17) T. J. Hardwick, *J. Phys. Chem.*, **66**, 291 (1962).

(18) R. A. Back, *Trans. Faraday Soc.*, **54**, 512 (1958).

(19) Kang Yang, *J. Am. Chem. Soc.*, **84**, 719 (1962).

Reactions 5 as well as 7 may be important, however, and may compete with reactions 1 and 2. The data at  $-70^\circ$  shown in Table V suggest this to



be the case. The yield of  $\text{C}_2^{14}\text{H}_5$ 's is calculated indirectly from the measured value of  $G_{\text{C}_2\text{H}_5}$  for each hydrocarbon and the ratio  $(\text{C}_2^{14}\text{H}_5)/(\text{C}_2\text{H}_5)$ . The value of  $G_{\text{C}_2^{14}\text{H}_5}$  is much larger than at  $10^\circ$  and for *n*-hexane increases from 0.2 to 1.4 in the concentration region where the yield of secondary hexyl radicals is observed to be constant. Since reaction 2 is unimportant here, some reaction such as 7 must be competing with 1 for hydrogen atoms.

The limiting value of  $G_{\text{C}_2^{14}\text{H}_5}$  at high ethylene concentration should be  $G_{\text{H}}$ . The highest values observed so far are 1.4 and 1.8. Therefore  $G_{\text{H}}$  must be equal to or greater than these values.

Reported values of  $G_{\text{H}}$  vary from  $2.0^{13}$  to  $3.16^{23}$  for *n*-hexane; Meshitsuka and Burton<sup>24</sup> measured  $G_{\text{HI}}$  from *n*-hexane as a function of irradiation time with iodine present and by extrapolation found the initial value of  $G_{\text{HI}}$  to be 2.5. Values of 4.25 and 3.70 have been reported for  $G_{\text{HI}}$  for *n*-pentane and *n*-heptane.<sup>23</sup>

Thus the use of this ethylene- $\text{C}^{14}$  scavenging method not only provides a measure of the radical yields but also of the yield of scavenged hydrogen atoms in  $G_{\text{C}_2^{14}\text{H}_5}$ . A great deal of information may be obtained in experiments employing ethylene- $\text{C}^{14}$  scavenging. Comparison of the results obtained with other results using various scavengers further justifies the assertion that relative radical yields are determined.

(23) T. J. Hardwick, *J. Phys. Chem.*, **65**, 101 (1961).

(24) G. Meshitsuka and M. Burton, *Rad. Research*, **10**, 499 (1959)

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## Vacuum Ultraviolet Photochemistry. V. Photolysis of Isobutane

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The photolysis of isobutane was carried out at room temperature at 1470 Å. and 1236 Å. Certain specifically labeled deuterium compounds were used to gain information on the mechanisms of product formation. From isotopic analysis of products, hydrogen, methane and ethane, in the photolysis of an equimolar mixture of isobutane + isobutane- $d_{10}$  the following conclusions were drawn: (1) Hydrogen is formed both from atomic and molecular processes. The atomic process becomes more important at the shorter wave length (1236 Å.). From scavenger experiments, it was found that approximately half the hydrogen is formed by the atomic process at 1470 Å. (2) Methane is predominantly formed by a molecular process at 1470 Å. and 1236 Å. (3) Ethane is formed primarily by the combination of methyl radicals. From the photolysis of isobutane-2- $d$ , it was concluded that (a) there is no apparent preference of the position (primary or tertiary) for the expulsion of atomic hydrogen at 1470 Å. However there is some discrimination with regard to position for the hydrogen produced by molecular elimination. (b) The primary and tertiary hydrogen participate almost equally in the intramolecular production of methane. Reactions responsible for the formation of other products, ethylene, propane, propylene, isobutene, neopentane and isopentane, are discussed.

### Introduction

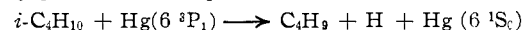
The photolyses of some alkanes, such as methane,<sup>1</sup> ethane,<sup>2</sup> propane<sup>3</sup> and butane,<sup>4</sup> have been carried out recently in the vacuum ultraviolet region.

From isotopic analysis of the products of certain specifically deuterium labeled hydrocarbons it has been established that molecular detachment processes play a major role in the formation of hydrogen<sup>1-4</sup> and methane.<sup>3</sup> The relative importance of the molecular *vs.* free radical process depends on wave length.<sup>3</sup> Molecular detachment processes also have been observed in the radiolysis of gaseous hydrocarbons.<sup>5</sup>

Since isobutane contains a tertiary CH bond whose energy is lower than that of the primary CH bond by almost 10 kcal./mole,<sup>6</sup> it is of interest to know whether the tertiary hydrogen preferentially participates in the formation of products.

The mercury sensitized photolysis of isobutane

has been studied<sup>7</sup> and it was found that the primary process is the split of a C-H bond.



The radiolysis of isobutane has been studied over the temperature range from  $-20$  to  $50^\circ$ .<sup>8</sup> The dependence of the yield of products on temperature suggests that hydrogen was formed primarily by an atomic process while methane was formed partly by a molecular process.

### Experimental

**Light Source.**—A water-cooled rare gas resonance lamp with a LiF window was used as the light source. Tantalum electrodes were employed. Detailed descriptions of the construction and operation of this lamp have been reported.<sup>2-4</sup> The lamp produced radiation mainly at 1470 Å. (Xe) or 1236 Å. (Kr).

In the later part of this work an air-cooled electrodeless discharge lamp operated with a Raytheon 2450-MC unit (125 w.) was used to excite the resonance lines. Approximately 500  $\mu$  of pure rare gas was used. It was found that the microwave discharge powered lamp has several advantages: (1) it is free from impurities originating in the electrodes, (2) the LiF window can be replaced easily, (3) it has more intensity than the a.c. operated lamp.

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- (3) H. Okabe and J. R. McNesby, *ibid.*, to be published.
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- (5) E.g., K. Yang and P. J. Manno, *J. Am. Chem. Soc.*, **81**, 3507 (1959); L. M. Dorfman, *J. Phys. Chem.*, **60**, 826 (1956).
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