where I is the rate of initiation, and k_2, k_3, k_4 and k_5 are the rate constants for reactions 2, 3, 4 and 5. The above reaction scheme was made to fit the experimental observations, so that only 3-methyl-1-butene is formed as a product of the chain reaction. As pointed out before, a distribution between this isomer and 1-pentene should be expected, but this would not affect the general form of the reaction scheme.

Applying the usual steady-state treatment to the above mechanism, the rate of consumption of acetylene is given by

$$\frac{-\mathrm{d}(\mathrm{C_2H_2})}{\mathrm{d}t} = k_3(I/k_5)^{1/2}(\mathrm{C_2H_2}) \qquad (1)$$

This rate equation, which also yields the rate of product formation, predicts that the reaction rate should be first order in the acetylene concentration. Since the chain length L is equal to the rate of propagation divided by the rate of initiation, it follows that

$$L = \frac{k_3}{(k_5 I)^{1/2}}(\mathrm{C_2H_2}) \qquad (2)$$

Equation 2 shows that the chain length is inversely proportional to the intensity of radiation. Therefore, the simple chain mechanism accounts for the observed reaction order and intensity dependence. It is also interesting that the assumed mechanism and the experimental data can be used for estimating the activation energy of the addition of the isopropyl radical to acetylene. The value of the activation energy based on the above reaction mechanism is really an average for a mixture of propyl and isopropyl radicals in which isopropyl radicals are more abundant. However, the error introduced in this portion should be negligible since no significant difference is expected between the activation energies for addition of propyl and isopropyl radicals to acetylene.

The rate of initiation at a dose rate of 48×10^6 rad./hr. is 4.05×10^{14} radicals cc.$^{-1}$ sec.$^{-1}$, at 240° and 10.0 atm. total pressure. Therefore, from the experimentally measured rate of disappearance of acetylene, $k_3/k_5^{1/2} = 1.25 \times 10^{-11}$ molec.$^{-1/2}$ cc.$^{1/2}$ sec.$^{-1/2}$.

Since the activation energy for reaction 3 is calculated from the measured rate and not from the temperature dependence of the rate constant, the value of the steric factor must be assumed. Mandelcorn and Steacie[5] found the value of the steric factor to be of the order of 10^{-4} for the addition of methyl radicals to acetylene. This rather low value seems to be characteristic of radical additions to multiple bonds.[6]

Using the value of $P_3 = 10^{-4}$ for the addition of isopropyl radicals to acetylene and assuming the pre-exponential factor for k_5 is the normal collision number, it follows that $E_3 - E_5/2 = 4.5$ kcal. Since the activation energy E_5 for the recombination of radicals is estimated to be about 1 kcal., the agreement with the value of 5.5 kcal. found by Mandelcorn and Steacie for the addition of methyl radicals to acetylene[5] is remarkably good. This agreement also tends to favor a free radical chain mechanism for the radiation-induced alkylation of acetylene with propane. If this mechanism is correct, radiation offers a powerful new tool for exploring a free radical hydrocarbon reaction that is exceptionally difficult to study thermally.

[5] L. Mandelcorn and E. W. R. Steacie, *Can. J. Chem.*, **32**, 474 (1954).

[6] N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Vol. I, Princeton University Press, Princeton, N. J. 1958.

LINDEN, NEW JERSEY

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, HUMBLE OIL & REFINING COMPANY]

High Energy Electron Irradiation of *n*-Hexane

BY JEAN H. FUTRELL*

RECEIVED JUNE 1, 1959

A study of the radiation chemistry of normal hexane in gas and liquid phase as the pure compound and in admixture with radical scavengers in the gas phase is reported. The radiolysis products which were determined are hydrogen, propane, ethylene, *n*-butane, ethane, methane, propane, acetylene, hexane isomers, isobutane, butene, isopentane and *n*-pentane, listed in order of decreasing "*G*"-values. The nature and yields of these products and the effect of radical scavengers are rationalized with satisfactory precision from the assumption that initial ionization processes, followed by very fast ion-molecule reactions of the hydride ion transfer type, dominate the reaction process. It is therefore tentatively suggested that such a partial mechanism has considerable validity for normal hexane and related compounds.

Introduction

It is well known that hydrocarbons yield a great variety of products on radiolysis and little attempt has been made to establish detailed quantitative yields for a representative system. The early work by Lind[1] and co-workers established for the first members of the paraffin series that the gaseous products consist chiefly of hydrogen and of smaller amounts of saturated compounds. A number of subsequent papers have added very little to this generalization, with many investigations reporting only such data as total gas yields, or yields of "polymer" remaining after distillation of reactant. Until very recently experimental difficulties in detecting and measuring these products have discouraged a detailed repetition of the pioneering work.

The development of modern analytical techniques, particularly of gas-liquid partition chromatography, has rendered a detailed study feasible.[2] Hexane appeared attractive for this purpose as a representative paraffin hydrocarbon. The radiol-

---

* Headquarters, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[1] S. C. Lind and D. C. Bardwell, THIS JOURNAL, **48**, 2355 (1926).

[2] H. A. Dewhurst, *J. Chem. Phys.*, **24**, 1254 (1956).

ysis of this compound in the liquid phase has been studied in great detail by Dewhurst[3-5] under a variety of experimental conditions. It is the purpose of this paper to extend this work to include a study of the low molecular weight products from liquid *n*-hexane radiolysis and to report a similar study for *n*-hexane vapor.

Experimental

The radiation source, radiation vessels and general procedures have been described by Lampe.[6] The general approach to the dosimetry problem for gas phase radiolysis also has been described.[7] It consisted essentially of referring the measured product yields to the yield of ethane from methane radiolysis, assuming "G"(C_2H_6) = 2.1,[6] or to the polymerization yield from acetylene radiolysis[8] conducted in a reactor under conditions identical to those used in the hexane work. The usual corrections for relative stopping power were applied. Several variations of this approach were used and best results were obtained when the reactor was surrounded by a Faraday cage and the irradiation current was monitored as the total current incident on the system.

Dosimetry for liquid phase radiolysis is somewhat simpler, as the incident beam is easily stopped by small sample thicknesses. In this case the hydrogen yield from cyclohexane, "G" = 5.3,[9] was used as the dosimetry standard to determine scattering and window absorptions corrections for the Pyrex irradiation vessel used. Less than 10^7 ergs per gram dose was used in the standardization runs, so that no correction for non-linearity of hydrogen yield was required.[10]

Materials.—Phillips Research Grade hydrocarbons were used without further purification. The hexane was carefully degassed by repeated freeze-pump-melt cycles and by trap-to-trap distillation during evacuation. Matheson cylinder oxygen was used directly in the added oxygen runs.

Analysis.—Gas-liquid partition chromatography was used to analyze for all products except hydrogen. An 8 meter hexadecane column and a 4 meter benzyl cellosolve column were required to resolve all products boiling below hexane. Mass spectrometer analysis was used for hydrogen, and instrumental difficulties introduced fairly large errors for some samples.

Gaseous products from liquid hexane radiolysis were recovered quantitatively by refluxing for several hours under vacuum.[11] The gas fraction was further subdivided into fractions volatile at −196° and at −80° for analysis by gas chromatography and mass spectrometry.

Discussion of Results

Radiolysis of Pure Hexane.—The radiolysis products were determined for some twenty experiments with hexane vapor at various pressures and irradiation intensities, and the results were extrapolated to zero dose in the usual manner. The resulting values are given in Table I. No effect of intensity or pressure was noted over a threefold range of intensities at pressures from 50 to 140 mm. Instrumental factors made it impossible to measure all products for each run, the hydrogen value being determined in only five experiments. Hence it is subject to greatest experimental uncertainty, and it is estimated that the hydrogen "G"-value is reliable only to ±1.5 molecules per hundred electron volts. The yields of the other products are considered accurate to ±20% except for those which are formed in rather low abundances. Dosimetry is thought to be the major source of error, so that the relative yields are probably somewhat better than absolute values. The results are compared to those of Henri and coworkers,[12] and the agreement is considered quite satisfactory. The discrepancies noted may be attributed to the conditions of their experiment in which a radon gas α-particle source was used and in which apparent "G"-values were calculated after approximately 40% of the hexane was decomposed.

TABLE I

HUNDRED ELECTRON VOLT YIELDS FROM GAS AND LIQUID PHASE RADIOLYSIS OF *n*-HEXANE

	Gas phase		Liquid phase		
	Henri[a]	This research	Dewhurst[b]	Krenz[d]	This research
H_2	3.5	4.3	5.0	4.9	4.95
CH_4	0.44	0.5	0.15	0.4	0.13
C_2H_2	..	0.2	..	..	.15
C_2H_4	0.08	1.1	.22[c]	..	.63
C_2H_6	.90	0.9		.7	.63
C_3H_6	.06	0.3	.10[c]	..	.49
C_3H_8	1.35	1.4		..	.67
i-C_4H_{10}	1.1	0.1		..	Not detectible <0.005
n-C_4H_{10}		1.1	.24[c]	..	.8
C_4H_8	..	0.1		..	.46
i-C_5H_{12}	0.23	.1	.10[c]	..	Trace, >0.05
n-C_5H_{12}		.1		..	Trace, >0.05
C_6'	..	.15	..	..	....
C_6''	..	.1	..	..	....
−*n*-C_6	8.2	9.5	..	..	....

[a] Reference (12). Radon gas α-particle source, approximately 40% of hexane decomposed in this experiment. [b] Reference (4); 800 kvp. electrons. [c] Probably represent lower limits; see original reference. [d] Reference (13).

The liquid phase hundred electron volt yields were determined in an analogous fashion and are also presented in Table I. The hydrogen and methane yields from this research are in excellent agreement with the values obtained by Dewhurst.[4] Values for hydrogen and ethane are in agreement with Krenz,[13] although his methane yield is apparently in error. Dewhurst has suggested that the "G"-values he determined for the C_2-C_5 products are probably lower limits because of evaporation losses prior to analysis; hence we feel that our data are more reliable.

The data in columns 2 and 5 of Table I are of interest as a comparison of the radiolysis yields from gas phase and liquid phase irradiation of an organic compound analogous to similar comparisons by Burton[14,15] for several substances. Within experimental accuracy, it appears that there is no effect of phase on hydrogen and acetylene yields. Propylene and butene are formed in greater amounts in the liquid and formation of all other compounds is somewhat depressed. Although isobutane is a minor product, it is particularly striking that this compound is not observed as a

---

(3) H. A. Dewhurst and E. H. Winslow, *J. Chem. Phys.*, **26**, 969 (1957).

(4) H. A. Dewhurst, *J. Phys. Chem.*, **61**, 1466 (1957).

(5) H. A. Dewhurst, *ibid.*, **62**, 15 (1958).

(6) F. W. Lampe, THIS JOURNAL, **79**, 1055 (1957).

(7) F. W. Lampe, *J. Phys. Chem.*, **61**, 1015 (1957).

(8) L. M. Dorfman and F. J. Shipko, THIS JOURNAL, **77**, 4723 (1955).

(9) R. H. Schuler and A. O. Allen, *ibid.*, **77**, 507 (1955).

(10) W. S. Guentner, T. J. Hardwick and R. P. Nejak, *J. Chem. Phys.*, **30**, 601 (1959).

(11) A. S. Newton, *Anal. Chem.*, **28**, 1214 (1956).

(12) V. P. Henri, C. R. Maxwell, W. C. White and D. C. Peterson, *J. Phys. Chem.*, **56**, 153 (1952).

(13) F. H. Krenz, *Nature*, **176**, 1113 (1955).

(14) J. P. Manion and M. Burton, *J. Phys. Chem.*, **56**, 560 (1952).

(15) M. Hamashima and M. Burton, *ibid.*, **62**, 246 (1958).

liquid phase product. The significance of these observations is not apparent in our current state of knowledge of radiolytic processes.

It is clear that the radiolysis of normal hexane is an exceedingly complex process. This is especially so when one considers that in the gas phase work the products detected represent only some 27% of the hexane decomposed. An atom material balance indicates the undetected higher boiling liquids have the empirical formula C_nH_{2n}. A few drops of liquid were observed to form near the reactor window which could not be removed by flaming during evacuation; but such a small amount was formed from the vapor that attempts at further analysis proved impractical. Normal hexane in liquid phase radiolysis gives at least 13 products boiling above hexane,[4] and there is every reason to expect the condensation products from gas phase work to be equally complex.

Scavenger Experiments.—Table II summarizes the data obtained in experiments in which ethylene or oxygen was added in various amounts to normal hexane vapor before radiolysis. With both scavengers the hydrogen yield drops rapidly to some 50% of the pure hexane value. With added ethylene the energy yield values remain essentially constant except for ethane and *n*-butane, and the changes in these values may be reasonably attributed to the coupling and disproportionation of ethyl radicals resulting from the scavenging of hydrogen atoms by the added ethylene. Except for hydrogen there is no marked change in the product distribution on adding oxygen to the radiolysis system. There is an apparent diminution of butane and pentane yields and possibly of propane, although the changes do not greatly exceed probable experimental error. The only oxidation products detected were carbon monoxide and carbon dioxide, which overlapped the methane and acetylene peaks in the chromatograms. Water and small amounts of peroxides probably would have escaped detection by our techniques.

TABLE II

EFFECT OF SCAVENGERS ON RADIOLYSIS YIELDS

	Pure *n*-hexane	Added ethylene	Added oxygen
H_2	4.3	1.9	2.0
CH_4	0.5	0.5	..
C_2H_2	0.2	0.2	..
C_2H_4	1.1	..	1.1
C_2H_6	0.9	1.6	0.9
C_3H_6	0.3	0.5	0.4
C_3H_8	1.4	1.4	1.2
i-C_4H_{10}	0.1	0.1	0.05
n-C_4H_{10}	1.1	1.4	.9
C_4H_8	0.1	0.1	.2
i-C_5H_{12}	.1	.1	.05
n-C_5H_{12}	.1	.1	.05

Mechanism.—It was pointed out in earlier discussion that the radiolysis of hexane represents an exceedingly complex process. The production of at least 27 compounds in readily detectible amounts virtually precludes any critical considerations of possible mechanisms. Nevertheless, it is constructive to consider certain features of the radiolytic behavior, and we have chosen to do so in terms of reactions of the ion–molecule type whose importance in radiation chemistry recently has been emphasized.[16] Since no studies of these reactions for *n*-hexane have been reported, we shall consider reactions which have been demonstrated for a number of related hydrocarbons.

In particular we shall consider ion–molecule reactions of the hydride-ion transfer type, whose general occurrence in hydrocarbon systems and whose probable importance in radiation chemistry has been suggested by Field and Lampe.[17] With these authors we assume that this reaction competes favorably with other possible ion–molecule reactions and that it will occur for all ions for which the reaction

$$R^+ + C_6H_{14} \dashrightarrow RH + C_6H_{13}^+ \qquad (1)$$

is approximately thermoneutral or is exothermic. For the purpose of calculation it will be assumed that thermodynamically allowed decompositions of RH will occur. That is, the heat of reaction is distributed between the reaction products by the requirement of conservation of momentum, and the neutral product is considered to decompose if its share of energy is equal to or greater than the endothermicity of the decomposition reaction.

The mass spectral fragmentation pattern for *n*-hexane[18] is taken as a measure of the initial distribution of ions formed in the radiolysis system. The ionization mechanisms which have been postulated corresponding to the appearance potentials of each ion are used as an indication of the uncharged fragments resulting from the initial ionization processes,[19] and the same mechanisms are assumed to apply at the higher electron voltages used in establishing the hexane mass spectrum. There results an initial distribution of ions, free radicals and molecules assumed to be formed instantaneously in the system. The ions are further examined as possible reactants for the hydride transfer reaction 1 above, using the tabulated data for heats of formation.[19] It appears probable that $C_5H_{11}^+$, $C_4H_9^+$, $C_4H_8^+$, $C_4H_7^+$, $C_3H_7^+$, $C_3H_6^+$, $C_3H_5^+$, $C_3H_3^+$, $C_2H_5^+$ (C_2H_4 + H_2), $C_2H_4^+$, $C_2H_3^+$ (C_2H_2 + H_2), $C_2H_2^+$ and CH_3^+ will react. The products in parentheses indicate further decomposition of the neutral entity RH.

If these assumptions are correct, very fast ion–molecule reactions will convert essentially all the ions to $C_6H_{13}^+$ before neutralization can occur. In the absence of specific information concerning neutralization, it may reasonably be assumed for calculation purposes that reactions (2) and (3) represent this process

$$C_6H_{13}^+ + e \dashrightarrow C_6H_{13}^* \dashrightarrow C_6H_{12} + H \qquad (2)$$

$$H + C_6H_{14} \dashrightarrow C_6H_{13} + H_2 \qquad (3)$$

On neutralization the C_6H_{13} radical will be highly excited, possessing energy equal to its ionization potential, and it is likely that fragmentation will occur. The simplest process conceptually ac-

---

[16] D. P. Stevenson, *J. Phys. Chem.*, **61**, 1454 (1952).

[17] F. H. Field and F. W. Lampe, THIS JOURNAL, **80**, 5587 (1958).

[18] "Catalog of Mass Spectral Data," API Project 44, Carnegie Institute of Technology, Pittsburgh, F. D. Rossini, Ed., Serial 9, contributed by National Bureau of Standards, October 31, 1947.

[19] J. L. Franklin and F. H. Field, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

cessible is the expulsion of a hydrogen atom, which by momentum conservation will carry essentially all the energy. Atoms formed in this manner presumably would react to produce a hydrogen molecule and a hexyl radical, as indicated in equation 3, either as hot atoms or after thermalization by collision. Alternative neutralization mechanisms might include molecular elimination of hydrogen, carbon–carbon bond scission or some combination of these.

In considering reactions of the free radicals formed by all these processes, it is assumed that at 300°K. hydrogen abstraction is not important, so that only disproportionation and combination need be considered. Only ethyl, propyl and hexyl radicals are formed in significant quantities, and they are assumed to react at each radical–radical collision[20] as shown

$$\text{I.}\quad 2C_2H_5\cdot \begin{cases} \rightarrow C_2H_4 + C_2H_6 & (4) \\ \rightarrow C_4H_{10} & (5) \end{cases}$$

$$\text{II.}\quad 2C_3H_7\cdot \begin{cases} \rightarrow C_3H_6 + C_3H_8 & (6) \\ \rightarrow C_6H_{14} & (7) \end{cases}$$

$$\text{III.}\quad 2C_6H_{13}\cdot \longrightarrow C_6 + C_{12}\ \text{products} \qquad (8)$$

$$\text{IV.}\quad C_2H_5\cdot + C_3H_7\cdot \begin{cases} \rightarrow C_2H_4 + C_3H_8 & (9) \\ \rightarrow C_2H_6 + C_3H_6 & (10) \\ \rightarrow C_5H_{12} & (11) \end{cases}$$

$$\text{V.}\quad C_2H_5\cdot + C_6H_{13}\cdot \begin{cases} \rightarrow C_2H_4 + C_6H_{14} & (12) \\ \rightarrow C_2H_6 + C_6H_{12} & (13) \\ \rightarrow C_8H_{18} & (14) \end{cases}$$

$$\text{VI.}\quad C_3H_7\cdot + C_6H_{13}\cdot \begin{cases} \rightarrow C_3H_6 + C_6H_{14} & (15) \\ \rightarrow C_3H_8 + C_6H_{12} & (16) \\ \rightarrow C_9H_{20} & (17) \end{cases}$$

Results of recent kinetic studies[21] were used to estimate $k_4/k_5 = 0.14$; $k_6/k_7 = 0.5$; $k_9/k_{11} = 0.05$, $k_9 = k_{10}$; $k_{12}/k_{14} = 0.05$, $k_{12} = k_{13}$; and $k_{15}/k_{17} = 0.05$, $k_{15} = k_{16}$.

The results of these calculations are summarized in Table III, which normalizes the results to the basis of molecules produced per hundred ions initially formed. These quantities are converted to G-values by dividing by W, the energy required to form an ion pair. Columns 5 and 6 compare the calculated and experimental energy yields for gas phase hexane irradiations, based on an estimated value of $W = 26$ e.v.[22] The agreement achieved is remarkable.

There are many objections which may be raised to this partial mechanism. According to current concepts, the mass spectrum of a compound represents the extent of unimolecular decomposition of the parent molecule–ion in some 10^{-6} to 10^{-5} sec. after formation, while the rates of ion–molecule reactions are such that they will occur in the order of 10^{-10} sec. at the pressures used in this research. Hence it is not certain that the initial distribution of ion, radical and molecular products is properly represented by the mass spectral fragmentation pattern. Secondly, general types of ion–molecule reactions of hydrogen atom or proton transfer or of carbon–carbon bond synthesis have not been considered. Essentially all hydrogen atom transfer reactions may be ruled out on energetic grounds, but ignorance of the proton affinity of hexane and of condensation reactions for this system prohibits drawing definitive conclusions about the other reaction types. Finally, no attempt has been made to account for the radiation energy degraded in non-ionizing excitation modes.

TABLE III

COMPARISON OF CALCULATED AND EXPERIMENTAL G-VALUES

	Basis of 100 ions formed				G-values	
	From initial fragmentation	From ion–molecule reactions	From radical interactions	Total	Calcd.[a]	Obsd.
H_2	19.8	22.2	100	142	5.4	4.3
CH_4	4.5	1.5	...	6.0	0.2	0.5
C_2H_2	..	10	...	10.0	0.4	0.2
C_2H_4	11.8	11.8	2.3	25.9	1.0	1.1
C_2H_6	20.3	..	2.3	22.6	0.9	0.9
C_3H_6	..	13.9	3.0	16.9	0.6	0.3
C_3H_8	7.6	15.3	3.0	25.9	1.0	1.4
C_4H_8	..	1.4	...	1.4	0.05	0.1
C_4H_{10}	2.6	18.7	5.6	26.9	1.0	1.1
C_5H_{12}	..	0.9	8.9	9.8	0.4	0.2

[a] Assuming $W = 26$ e.v./ion pair.

Nevertheless the striking agreement between calculated and experimental yields strongly suggests that this sort of mechanism has some degree of validity for n-hexane. It explains the predominance of ethylene, propane and butane among the radiolysis products. It predicts that more than 30% of the hydrogen is formed independent of scavengers, the exact amount depending on assumptions about the details of the neutralization step. It predicts that scavengers will have a noticeable effect only on hydrogen, butane and pentane among lower molecular weight products. This appears to be confirmed by the data in Table II, although the observed diminution in butane may be within experimental error. Finally, it satisfactorily explains the anomaly noted by Dewhurst[5] that the predominant radiolysis products are formed from C_6 species despite the very low abundance of C_6 positive ion fragments in the electron impact spectra.

Acknowledgments.—The author is indebted to Messrs. C. W. Bell and T. P. Gorman for assistance with the experiments and to Dr. F. W. Lampe for many stimulating discussions.

BAYTOWN, TEXAS

---

(20) Hence the probabilities of these reactions may be calculated by simple statistics: $P_{\text{I}} \propto (C_2H_5)^2$, $P_{\text{II}} \propto (C_3H_7)^2$, $P_{\text{III}} \propto (C_6H_{13}\cdot)^2$, P_{IV} $2(C_2H_6)(C_3H_7\cdot)$, $P_{\text{V}} \propto 2(C_2H_6)(C_6H_{13}\cdot)$, and $P_{\text{VI}} \propto 2(C_3H_7\cdot)(C_6H_{13}\cdot)$

(21) D. G. L. James and E. W. R. Steacie, *Proc. Roy. Soc.* (*London*), **244A**, 19 (1958); R. W. Durham and E. W. R. Steacie, *Can. J. Chem.*, **31**, 377 (1953); C. A. Heller, *J. Chem. Phys.*, **28**, 1255 (1958).

(22) G. J. Hine and G. L. Brownell, "Radiation Dosimetry," Academic Press, Inc., New York, N. Y., 1956, p. 38.