

Radiolysis of Ethylene. II. Primary Free Radicals and Their Reactions¹

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The effects of pressure and dose rate on the radiolytic production of C₃ to C₈ hydrocarbons from ethylene have been evaluated. The effects of oxygen and iodine on product distribution indicated that butenes, cyclobutane, acetylenes, and 2-hexenes do not require radicals as precursors for their formation. The major initial radical species are hydrogen atom and methyl radical while *n*-propyl, *sec*-propyl, and *sec*-butyl radicals are produced in small quantities by direct processes not involving radical reactions, presumably by higher order ion-molecule reactions. A quantitative kinetic treatment was developed employing the following simplifying assumptions: (1) the steady-state concentration of all radicals is determined only by hydrogen atom and its sequent radicals; (2) initial radical yields are constant; (3) all radicals add to ethylene or combine with ethyl radicals. Analysis of the data employing kinetic relationships derived in this treatment demonstrates the applicability of a free-radical mechanism for the formation of the higher, normal alkanes. Rate constants were derived for a number of reactions of methyl, ethyl, and *n*-butyl radicals and are in good agreement with the literature. An extension of the reaction mechanism leads to a quantitative description of the dose rate and pressure dependences of the γ -ray-initiated polymerization of ethylene at room temperature which is in good agreement with published experimental data.

Introduction

The radiolysis of ethylene has received considerable attention²⁻⁸ largely because there is much information available from mass spectrometry,⁹⁻¹⁵ photochemistry,¹⁶⁻¹⁸ and from pertinent studies of free radical reactions.¹⁹ The formation of hydrogen and ace-

tylene from ethylene has been ascribed to ionic and excited species and, in part, to an excited intermediate which dissociates only at lower pressures.⁵ Methane and methyl radicals probably result from reactions of ions,^{5,8} while the production of ethyl radicals has been shown to proceed only *via* hydrogen atom addition to ethylene.⁷

Investigators of radiation-induced ethylene polymerization have suggested that radical addition to ethylene occurs at low dose rates.²⁰ Further evidence for such processes was obtained from qualitative studies of the pressure and dose rate dependence of hexanes and octanes.⁶ However, experimental conditions which favor free-radical addition to ethylene will also increase the chain length of ionic polymerization because in both cases the termination step involves two reactive intermediates. It should be possible to distinguish between the two modes of polymerization by comparing rate constants with those already known for the reactions of radicals¹⁹ or ions.^{10,21} The results of such a study are reported in this paper.

Experimental

The source of radiation was a 1-Mev. Van de Graaff accelerator. The techniques and dosimetry were reported earlier^{7,22}; a cylindrical cell *ca.* 0.75 in. deep and 2 in. o.d., fitted with two 0.005-in. thick aluminum windows was employed at ambient temperature (23°). Gas chromatographic analyses were carried out on aliquots of the irradiated sample using a Perkin-Elmer Model 154-DG vapor fractometer, and retention volumes were determined for all C₁ to C₆ hydrocarbons, *n*-heptane, 3-methylheptane, and *n*-octane using authentic samples. Flame detection was used for the determination of the hydrocarbons. The response of the detector was checked frequently and found to be reproducible within $\pm 4\%$ or better. In order to assure positive identification of all components, and to resolve overlap of certain peaks, two sets of experiments were performed using partition columns of different characteristics: (a) 2-m. silver nitrate in ethylene glycol (Perkin-Elmer No. H) in series with 6-m. bis-(2-methoxyethyl) adipate (Perkin-Elmer No. BMEA) at 40° (this column retains alkynes and was used for most analyses); (b) 2-m. squalane (Perkin-Elmer No. U) in series with 2-m. diethylhexyl sebacate-BMEA (Perkin-Elmer No. V) at 50°. Confirmation of the olefinic character of the identified hydrocarbons was also obtained by qualitative experiments in which all

(1) Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 1964.

(2) (a) S. C. Lind, D. C. Bardwell, and J. H. Perry, *J. Am. Chem. Soc.*, **48**, 1556 (1926); (b) B. M. Mikhailov, V. G. Kiseley, and V. S. Bogdanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 545 (1958).

(3) F. W. Lampe, *Radiation Res.*, **10**, 691 (1959).

(4) K. Yang and P. J. Manno, *J. Phys. Chem.*, **63**, 752 (1959).

(5) M. C. Sauer, Jr., and L. M. Dorfman, *ibid.*, **66**, 322 (1962).

(6) M. C. Sauer, Jr., Abstracts of the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961.

(7) G. G. Meisels and T. J. Sworski, Abstracts of the 141st National Meeting of the American Chemical Society, Washington, D. C., March 1962.

(8) P. Ausloos and R. Gordien, Jr., *J. Chem. Phys.*, **36**, 5 (1962).

(9) F. H. Field, J. L. Franklin, and F. W. Lampe, *J. Am. Chem. Soc.*, **79**, 2419 (1957).

(10) C. E. Melton and P. S. Rudolph, *J. Chem. Phys.*, **32**, 1128 (1960).

(11) F. H. Field, *J. Am. Chem. Soc.*, **83**, 1523 (1961).

(12) R. Fuchs, *Z. Naturforsch.*, **16a**, 1026 (1961).

(13) A. G. Harrison, *Can. J. Chem.*, **41**, 236 (1963).

(14) P. Kebarle and E. W. Godbole, *J. Chem. Phys.*, **39**, 1131 (1963).

(15) S. Wexler and R. Marshall, *J. Am. Chem. Soc.*, **86**, 781 (1964).

(16) R. J. Cvetanović and A. B. Callear, *J. Chem. Phys.*, **23**, 1182 (1955); *ibid.*, **24**, 873 (1956).

(17) M. C. Sauer, Jr., and L. M. Dorfman, *ibid.*, **35**, 497 (1961).

(18) H. Okabe and J. R. McNesby, *ibid.*, **36**, 601 (1962).

(19) J. A. Kerr and A. F. Trotman-Dickenson in "Progress in Reaction Kinetics," Vol. 1, G. Porter, Ed., Pergamon Press, New York, N. Y., 1961, p. 105.

(20) J. C. Hayward and R. H. Bretton, *Chem. Eng. Progr. Symp. Ser.*, **50**, 73 (1954).

(21) P. J. Nawrocki and R. Papa, "Atmospheric Processes," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963.

(22) G. G. Meisels, *J. Chem. Phys.*, **41**, 51 (1964).

unsaturated hydrocarbons were removed before analysis by passing them through 0.5 m. of mercuric acetate and mercuric nitrate in ethylene glycol, adsorbed on firebrick, at room temperature.²³ Alkyl iodides were determined using a 2-m. column of diethylhexyl sebacate (Perkin-Elmer No. B) at 100°.

Results

At 100 torr ethylene pressure and at an average dose rate of 3×10^{14} e.v. cc.⁻¹ sec.⁻¹, product formation was found to be linear with total dose; decomposition did not exceed 1.5%. The yields of products expressed in molecules/100 e.v. (*G* values) are summarized in Table I. Only those exceeding 0.01 are listed; lower values were too uncertain to be meaningful. In addition to the compounds listed in Table I a number of unidenti-

Table I. Product Yields in the Radiolysis of 100 Torr of Ethylene^a

Product ^b	—Yield, molecules/100 e.v.—	
	Pure ethylene	Ethylene and 10 torr of oxygen
Hydrogen	1.2	c
Methane	0.22	c
Ethane	0.85	c
Acetylene	3.5	3.6
Propane	0.56	c
Cyclopropane	c	0.11
<i>n</i> -Butane	2.32	...
Isobutane	0.11	c
Butene-1 and isobutylene	0.094	0.090
<i>trans</i> -Butene-2	0.030	0.039
<i>cis</i> -Butene-2	0.033	0.042
Cyclobutane	0.10	0.042
Butadiene	~0.003	~0.010
<i>n</i> -Pentane	0.041	...
Isopentane	0.013	...
Pentene-1	0.053	...
<i>n</i> -Hexane	0.31	...
2-Methylpentane ^d	0.019	...
3-Methylpentane	0.048	...
Hexene-1	0.046	...
<i>trans</i> -Hexene-2	0.030	0.021
3-Methylpentene-2	0.010	...

^a At a mean dose rate of 3×10^{14} e.v. cc.⁻¹ sec.⁻¹. ^b Also produced and identified, but with yield too small to be reasonably accurate under these conditions, were 2-methylbutene-1, 2-methylbutene-2, pentene-2, 2-methylpentene-2, *cis*-3-hexene, *n*-heptane, 3-methylheptane, and *n*-octane. Analysis for alkynes higher than acetylene was not attempted. ^c Not determined. ^d Or 2,3-dimethylbutane.

fied heptanes, heptenes, octanes, and octenes were also produced as judged by their relative retention times. In order to identify the products which have free radicals as precursors, an irradiation was carried out in the presence of 10 torr of oxygen. The acetylenes, butenes, cyclobutane, butadiene, and hexene-2 persist under these conditions although some of their yields are affected.

The dose rate dependence of the formation of the saturated hydrocarbons was evaluated by carrying out single irradiations at beam currents differing by a factor of 500. Ethane, heptane, and octane yields were not determined, and *n*-pentane and cyclobutane were not separated and their yields are reported jointly.

(23) J. A. Kerr and A. F. Trotman-Dickenson, *Nature*, **182**, 466 (1958).

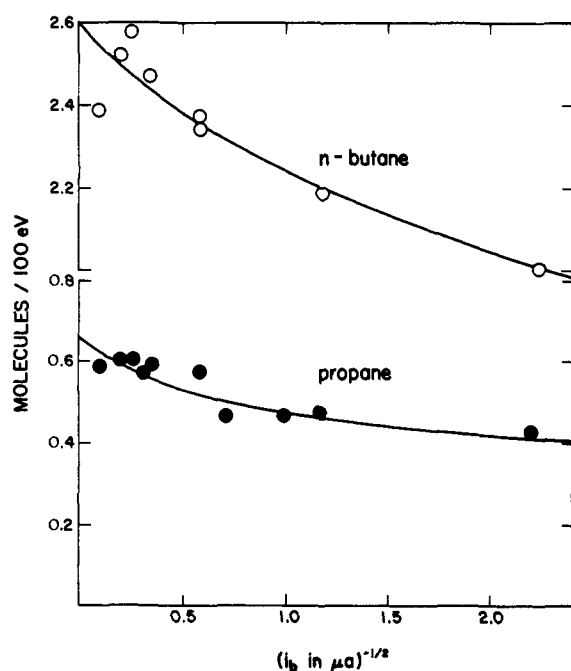


Figure 1. Dose rate dependence of product yields at 100 torr ethylene pressure: propane and *n*-butane.

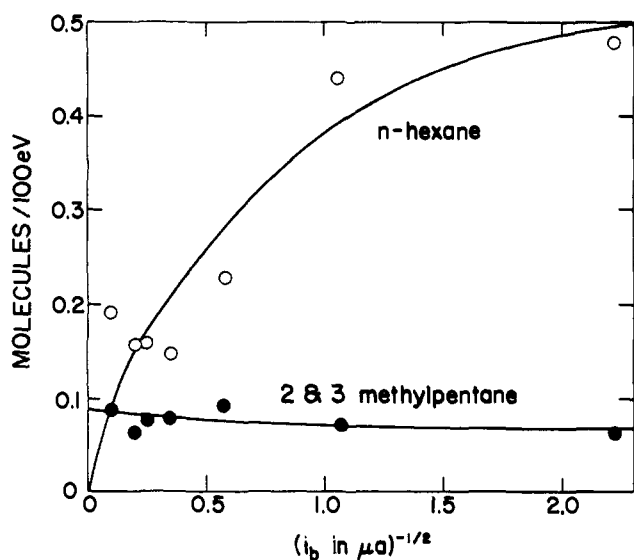


Figure 2. Dose rate dependence of product yields at 100 torr ethylene pressure: hexanes.

The yields are shown in Figures 1 to 3 as a function of the reciprocal square root of the beam current, so that increasing values of the abscissa represent conditions favoring radical addition to ethylene. Independence of beam current indicates the absence of radical addition processes; yields increasing with current demonstrate that precursors may be formed by radical addition to ethylene; decreasing yields suggest that a radical precursor of the product is removed by addition; intercepts represent the yields one would observe if no radical addition were to take place.

A series of experiments was carried out in which pressure was varied between 10 and 700 torr and beam current between 10 and 1 μ . Typical results are shown in Figures 4 and 5. The variation of the butene

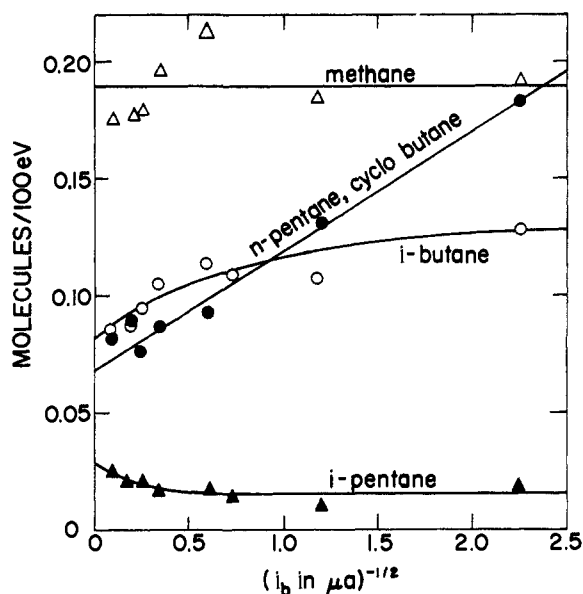


Figure 3. Dose rate dependence of product yields at 100 torr ethylene pressure: methane, isobutane, isopentane, and *n*-pentane and cyclobutane combined.

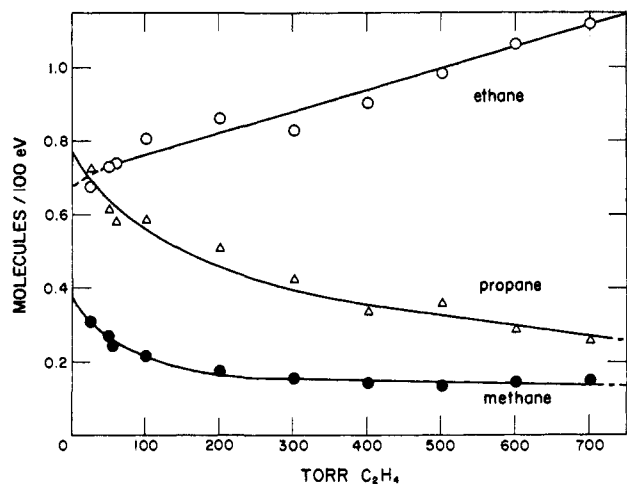


Figure 4. Pressure dependence of product yields: methane, ethane, and propane.

and the pentene-1 yields resembles that of the propane yield. The yields of cyclobutane, isopentane, 2-methylpentane and 3-methylpentane, the *n*-hexenes, and 3-methylpentene-2 appeared to be relatively independent of pressure while butadiene showed a slight increase with pressure, but experimental error was too great (15 to 25% depending on the compound) to permit further conclusions. The yields of *n*-hexane and *n*-octane increased with pressure. Since pressure changes affect not only free-radical processes but also collisional stabilization or quenching of energetic species, the simple distinctions given in the preceding paragraph cannot be applied here.

It should be possible to measure primary radical yields by adding iodine as a radical scavenger and analyzing for the product alkyl iodides after irradiation. This technique is complicated by the possibility of electron capture and by the thermal formation of ethylene diiodide and its subsequent thermal

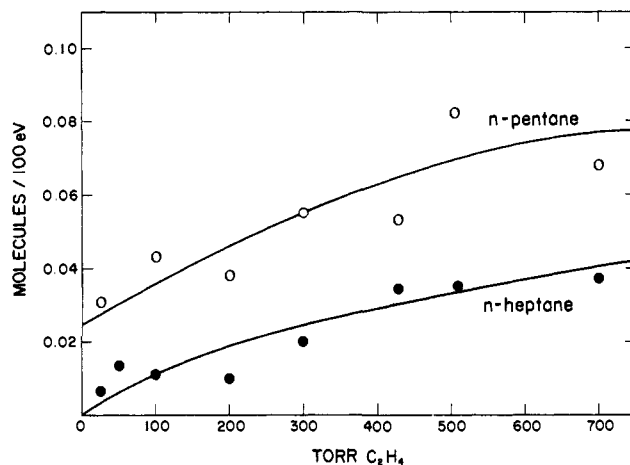


Figure 5. Pressure dependence of product yields: *n*-pentane and *n*-heptane.

and iodine atom catalyzed decomposition.^{24,25} Poor reproducibility of results was observed (Table II).

Table II. Iodine Scavenging in Ethylene Radiolysis^a

Product	Yield, ^b molecules/100 e.v.—		
	Pressure, torr		
	28	52	149
Acetylene	4.5	4.1	3.9
Propane	0.0	0.0	0.17
<i>n</i> -Butane	0.0	0.0	0.35
Methyl iodide	1.3	1.2	0.8
Ethyl iodide	3.3	5.1	2.3
2-Iodopropane	0.03	0.02	0.02
1-Iodopropane	0.08	0.02	0.02
2-Iodobutane	0.07	0.21	0.02
1-Iodobutane	0.00	0.00	0.04

^a Irradiation vessel contained iodine at equilibrium vapor pressure (ca. 0.5 torr). ^b Yields are only approximate.

The formation of alkyl iodides demonstrates the existence of a number of primary radicals since blank samples of similar composition, maintained under identical conditions for reference analysis, never showed any alkyl iodides or other products without irradiation.

Discussion

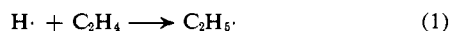
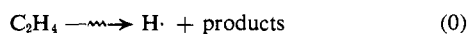
The effects of nitric oxide⁵⁻⁷ and oxygen (Table I) suggest that all the alkanes formed in the radiolysis of ethylene, except methane, have free-radical precursors. However, they cannot arise solely from the reactions of primary hydrogen atoms and methyl radicals^{6,7} because the yields of the isomeric hexanes did not depend on pressure and because propyl and butyl iodides were found when radical addition to ethylene is inhibited by iodine. The mechanism of product formation can be discussed conveniently in terms of the reactions initiated by primary radicals, *i.e.*, those produced by radiation impact on ethylene without involving radical addition to ethylene.

(1) *Hydrogen Atom and Its Sequent Radicals.* It has been shown that radiolysis of ethylene leads to the formation of 6.8 hydrogen atoms per 100 e.v.,⁷

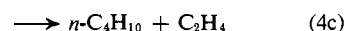
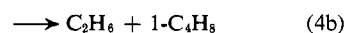
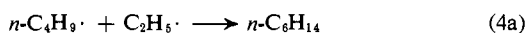
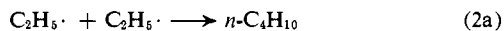
(24) R. B. Mooney and H. G. Reid, *J. Chem. Soc.*, 2597 (1931).

(25) L. B. Arnold and G. B. Kistiakowsky, *J. Chem. Phys.*, 1, 166 (1933).

followed by the almost immediate addition of hydrogen atoms to ethylene.^{7,26}



No other reactions of hydrogen atoms need be considered under our experimental conditions since the radical steady-state concentration is too low to permit radical reactions with hydrogen atoms.⁷ Further sequences must include the following reactions.



A large number of reactions involving other primary radicals and secondary radicals such as $\text{C}_4\text{H}_9\cdot$ produced in step 3 will also contribute to product formation.

The free radical reaction scheme can be tested quantitatively if a number of simplifying assumptions are made: (1) the steady-state concentration of all radicals is determined only by radicals sequent to hydrogen atoms; (2) the initial yield of primary radicals is independent of pressure; and (3) all radicals react either with ethylene or with ethyl radicals. Hydrogen atoms are the most abundant primary radicals and probably constitute 85% of the primary radical yield.⁷ They are probably produced predominantly by the dissociation of ethylene into acetylene and two hydrogen atoms ($\text{C}_2\text{H}_4 \xrightarrow{\text{H}\cdot} \text{C}_2\text{H}_2 + 2\text{H}\cdot$) and their formation is essentially independent of pressure.²⁷ The yield of methyl radicals, which accounts for most of the other 15%, varies by a factor of two over the pressure range employed here²⁷; therefore, the yield of primary radicals probably varies less than 8% between 25 and 700 torr. Statistical considerations of radical combination reactions¹⁹ show that more than 90% of methyl and *n*-butyl radicals will combine with ethyl radicals except when the relative extent of addition exceeds 25% of combination.

The absorption of high energy radiation by small samples of gases at low pressure leads essentially to a uniform distribution of primary radicals in the reaction volume. Therefore, one may employ reactions 0 to 4 and the steady-state approximation to derive the relationship

$$[\text{C}_2\text{H}_5\cdot]_{\text{ss}} = \frac{k_3 E}{2k_2} \left(\sqrt{\frac{2k_2 d G_{\text{H}}}{k_3^2 E^2 100N} + 1} - 1 \right) \quad (I)$$

where d is the dose rate in e.v. cc.⁻¹ sec.⁻¹, E is the concentration of ethylene in moles cc.⁻¹, G_{H} is the yield of hydrogen atoms per 100 e.v., and N is Avogadro's number.

n-Butane. Kinetic analysis of the *n*-butane yield is simpler than that of the ethane yield because it is produced only by reactions 2a and 4c. It should be given by

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

(27) G. G. Meisels, *Trans. Am. Nucl. Soc.*, **7**, 308 (1964).

$$G(n\text{-C}_4\text{H}_{10}) = \frac{k_{2a} G_{\text{H}}}{2k_2} - \left(\frac{k_{2a}}{k_2} - \frac{k_{4c}}{k_4} \right) \frac{k_3^2 E^2}{2k_2 d} \left(\sqrt{\frac{2k_2 d G_{\text{H}}}{k_3^2 E^2 100N} + 1} - 1 \right) \quad (II)$$

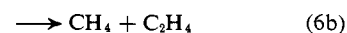
The first term on the right-hand side of eq. II is the yield of *n*-butane when addition reactions are absent, G^0 , and it follows that

$$[G^0(n\text{-C}_4\text{H}_{10}) - G(n\text{-C}_4\text{H}_{10})] \frac{d}{E^2} = \left(\frac{k_{2a}}{k_2} - \frac{k_{4c}}{k_4} \right) \frac{k_3^2}{2k_2} \left(\sqrt{\frac{2k_2 d G_{\text{H}}}{k_3^2 E^2 100N} + 1} - 1 \right) \quad (III)$$

Ethane. This product may arise not only from reactions 2b, 4b, and 6b but also from the combination of two methyl radicals.



Correction for this reaction can be made since propane arises primarily from reaction 6a.



The contribution of reaction 5 to the ethane yield can thus be evaluated from the relationship $k_6^2/(k_2 k_5) = 4$, and values for k_{2a}/k_2 and k_{6a}/k_6 are found in the literature.¹⁹

One may derive a relationship similar to eq. III for the corrected ethane yield, but a direct test of these relationships has little significance because the factor d/E^2 varies by several orders of magnitude. However, the ratio of the changes in butane yields to the corrected ethane yields should be constant and is indeed found to be 1.5 ± 0.5 .

It is convenient at this point to consider the numerical values in the square root term. The minimum value of d/E^2 employed in this work was 2.5×10^6 e.v. cc. mole⁻¹ sec.⁻¹ corresponding to 1.5×10^{-3} $\mu\text{a. torr}^{-1}$. Insertion of $k_2 = 10^{14}$ mole⁻¹ cc. sec.⁻¹ and $k_3 = 1.5 \times 10^6$ mole⁻¹ cc. sec.⁻¹¹⁹ shows that neglect of the term +1 introduces a 14% error into the calculated steady-state concentration of ethyl radicals under these least favorable conditions. The error at greater ratios of d/E^2 will be correspondingly less and eq. I may be simplified to

$$[\text{C}_2\text{H}_5\cdot]_{\text{ss}} \cong \frac{k_3 E}{2k_2} \left(\sqrt{\frac{2k_2 d G_{\text{H}}}{k_3^2 E^2 100N}} - 1 \right) \quad (IV)$$

n-Hexane is formed by reaction 4a, and use of eq. IV leads to the expression

$$G(n\text{-hexane})d/E^2 = -\frac{k_{4a} k_3^2}{k_4 2k_2} + \frac{k_{4a}}{k_4} k_3 \sqrt{\frac{d G_{\text{H}}}{2k_2 E^2 100N}} \quad (V)$$

The applicability of this relationship is demonstrated in Figure 6. In spite of considerable scatter there is no systematic deviation from a straight line. From intercept and slope one may estimate $(k_{4a}/k_4)(k_3^2/2k_2) \cong 0.010$ mole⁻¹ cc. sec.⁻¹ and $(k_{4a}/k_4)(k_3/\sqrt{2k_2}) \cong 0.053$ mole^{-1/2} cc. sec.^{-1/2}, respectively, and $k_{4a}/k_4 \cong 0.28$. This is more than a factor of two lower than that commonly found for two *n*-alkyl radicals. Use of the established value $k_2 = 10^{14}$ mole⁻¹ cc. sec.⁻¹

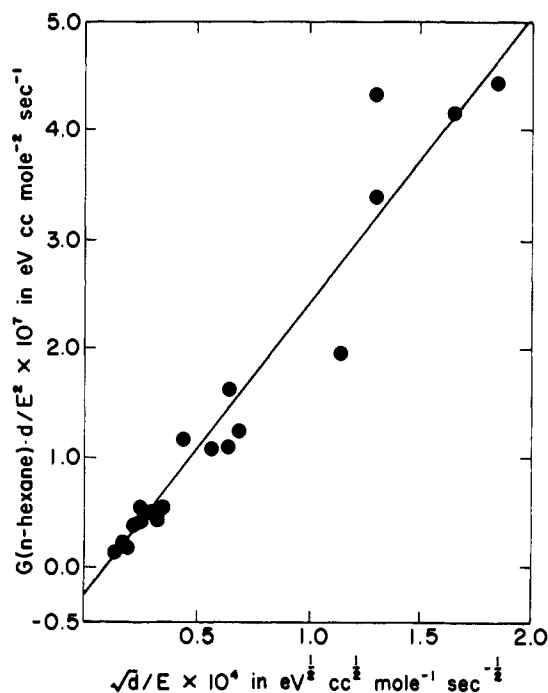


Figure 6. Dependence of *n*-hexane yields on kinetic parameters demonstrating applicability of eq. V.

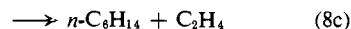
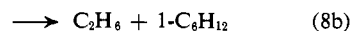
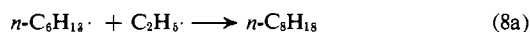
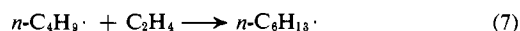
leads to $k_3 \approx 2.6 \times 10^6 \text{ mole}^{-1} \text{ cc. sec.}^{-1}$, in acceptable agreement with values reported in the literature (Table III).

Table III. Rate Constants at 23° Derived from Ethylene Radiolysis^a

Constant	This work	Lit. value ^b
k_3	2.9×10^6	$0.8 \times 10^6 - 2 \times 10^6$
k_7	4×10^6	2.6×10^6
k_9	1.4×10^6	$0.8 \times 10^6 - 1.0 \times 10^6$

^a All values in $\text{mole}^{-1} \text{ cc. sec.}^{-1}$. ^b From ref. 19.

n-Octane. A plausible reaction sequence for *n*-octane is



The butyl radical concentration is too small for self-reactions. These steps have not been considered earlier to avoid unnecessary complications, and since *n*-octane formation never exceeds 7% of butane and hexane yields, their effect on the lower products is negligible. The radical mechanism for octane formation may now be tested using the relationship

$$\frac{[n\text{-hexane}]}{[n\text{-octane}]} = \frac{k_{8c}}{k_{8a}} - \frac{k_{4a}k_8k_3}{k_7k_{8a}2k_2} + \frac{k_{4a}k_8}{k_7k_{8a}} \sqrt{\frac{dG_H}{2k_2E^2100N}} \quad (VI)$$

The yields involved are quite small and consequently considerable scatter is observed (Figure 7), but from intercept and slope one may estimate $k_{8c}/k_{8a} \leq 2$ and $k_7 \leq 4 \times 10^6 \text{ mole}^{-1} \text{ cc. sec.}^{-1}$ in reasonable

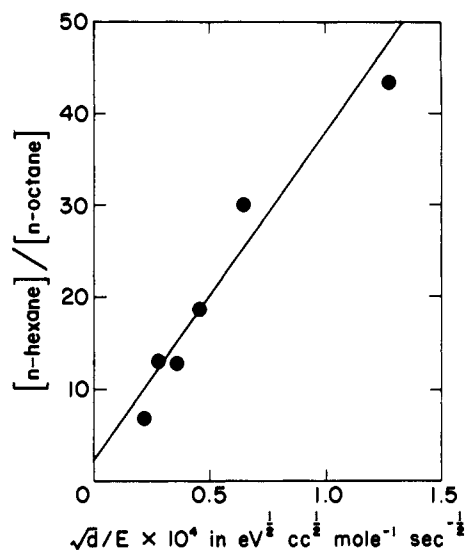
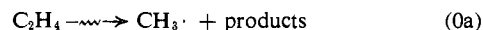


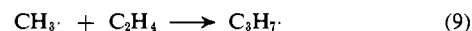
Figure 7. Dependence of *n*-hexane/*n*-octane product ratio on kinetic parameters demonstrating applicability of eq. VI.

agreement with a previously reported value (Table III).

(2) *Methyl Radical and Its Sequent Radicals.* The primary yield of methyl radicals shows an appreciable pressure dependence,²⁷ and it follows that radical reactions in the formation of the odd-numbered *n*-alkanes can be studied only by varying the dose rate. The formation of methyl radicals occurs by a sequence of reactions⁷ which can be summarized by



The assumptions listed in section (1) require that subsequent reactions of the methyl radical include only reaction 6 and



Thus, reactions of the methyl radical are considered as a minor perturbation of the original mechanism and without effect on the steady-state concentration of ethyl radicals. It follows that

$$\frac{G(\text{propane})}{G^0(\text{propane}) - G(\text{propane})} = \frac{k_3k_6}{2k_2k_9} + \frac{k_6}{k_9} \sqrt{\frac{G_H d}{2k_2E^2100N}} \quad (VII)$$

where G^0 is the yield of propane if process 9 were not occurring. The applicability of this equation is shown in Figure 8. Although the large scatter is to be expected from the use of yield differences, it is possible to evaluate $k_9 \sim 1.4 \times 10^6 \text{ mole}^{-1} \text{ cc. sec.}^{-1}$, using the accepted relationship $k_6 = k_2$. The agreement of k_9 with values determined for this rate constant by other methods is again quite good (Table III).

(3) *Validity of the Rate Constants.* The numerical values of the rate constants summarized in Table III depend not only on the validity of the assumptions in section (1) (principally that the sum of all the radical yields can be approximated by the hydrogen atom yield), but also on the absence of wall reactions and on the homogeneity of the radical concentration throughout the irradiation vessel. The relatively large values of the rate constant for addition may be due to the regions of reduced dose rate. Although the rates of energy

absorption have been shown to vary by an order of magnitude in different sections of the cell,²² radical concentrations would not be expected to be so dissimilar. Even at the highest steady-state concentrations radicals may be expected to survive 10^7 collisions before combination occurs, so that the displacement by diffusion is on the order of the dimensions of the irradiation vessel.²⁸

An alternate reaction scheme involving ionic species should lead to similar kinetic relationships. Here the formation of higher alkyl radicals by multiple order ion-molecule reactions would compete with ion-electron recombination as electron attachment to ethylene does not occur under our experimental conditions.^{21,29} Bimolecular rate constants for thermal ion-molecule reactions are of the order of 10^{15} mole⁻¹ cc. sec.⁻¹.³⁰⁻³² The rate constants for ion-electron combination have not been measured for ethylene but analogous reactions in atmospheric gases^{21,29} indicate that these constants must be of the order of 6×10^{16} mole⁻¹ cc. sec.⁻¹ and 2.5×10^{21} mole⁻² cc.² sec.⁻¹ for the second- and third-order processes, respectively. It is clear that below atmospheric pressure the rate constant of the terminating ion destruction is at most 10^2 times that of the chain lengthening ion-molecule reactions. This contrasts sharply with the present observation that the rate constant for chain termination is 10^7 times that for propagation. Although it is possible that in macroscopic systems ion-molecule reactions occur which are unobservable in the mass spectrometer by virtue of an appreciable activation energy, their participation is improbable because of the existence of rapid, competitive reactions. Therefore, it appears that the formation of the higher normal alkanes can be ascribed to a chain of reactions which includes only free radicals as secondary species.

(4) *Other Primary Radicals.* Although hydrogen atom and methyl radical appear to be the most important primary radicals, there is ample evidence that others are produced as well without requiring intermediate radical addition to ethylene. The minor formation of vinyl radicals is indicated from the presence of scavengable terminal olefins, in particular hexene-1. The virtual absence of scavengable butene-1 suggests that vinyl radicals add very rapidly to ethylene yielding 1-butenyl, in agreement with earlier observations.^{33,34} It is doubtful that $G(\text{vinyl})$ is much greater than 0.1 and thus is considerably smaller than that found in the liquid phase.³³

Vinyl radical cannot arise from the neutralization of vinyl ion because of the efficient ion-molecule reaction with ethylene.¹⁰ Its precursor is probably an excited ethylene molecule dissociating into vinyl radical and a hydrogen atom. The small yield of this reaction and the enhancement of vinyl radical produc-

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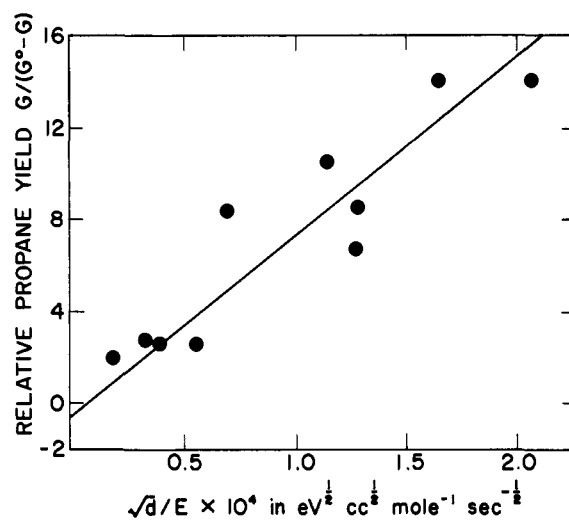
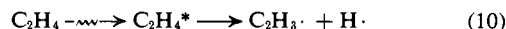


Figure 8. Kinetic plot of propane yield demonstrating applicability of eq. VII.

tion by electric fields⁷ suggest that a forbidden transition is involved such as the singlet at 6.5 e.v.^{35,36}



Possible explanations for the considerably greater probability of vinyl radical formation in the liquid phase are faster neutralization and the enhanced probability of internal conversion. Effects of environment on forbidden transitions have previously been observed.³⁷

The addition of iodine results in the formation of methyl iodide, ethyl iodide, iodopropanes, and 2-iodobutane (Table II). The variation in ethyl iodide yields at the lower pressures can be ascribed to competition for hydrogen atoms between ethylene and iodine. The complete absence of propane and butane at the lower pressures indicates that all radical-radical and all radical addition reactions are inhibited. It follows that propyl and 2-butyl radicals must be produced as primary species. Radical recombination and radical addition to ethylene become competitive at 149 torr as demonstrated by the appearance of propane, butane, and 1-iodobutane. A simplified kinetic scheme considering only radical-radical combination and radical reaction with iodine can be used in conjunction with the data at this pressure to estimate a collision efficiency of approximately 50% for the action of iodine as a scavenger. This value is in good agreement with liquid phase studies, where an efficiency of approximately 30% was found.³⁸

The formation of *n*-propyl radicals is suggested both from the iodine scavenging experiment and from the appearance of *n*-pentane when methyl radical addition to ethylene should be insignificant (Figures 3 and 5). $G^0(n\text{-propyl})$ is probably about 0.02. Similarly, the formation of isopentane and that of 2-iodopropane suggests $G^0(\text{isopropyl}) \sim 0.02$, and the yield of 2-iodobutane and the pressure independence of 3-methylpentane (Figure 2) indicate $G^0(\text{sec-butyl}) \sim$

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0.02. Isobutyl radical is probably also a "primary" radical because of the appearance of 2-methylpentane and its lack of variation with pressure (Figure 2).

The formation of these radicals must involve only excited or ionized entities because they are not sequent to any other radical species. A possible source of propyl radicals is the reaction suggested by Field.¹¹



Similar mechanisms for the formation of butyl radicals are possible in view of the fragmentation patterns of hexenes and octenes³⁹ which indicate that 7% of parent hexene ions and 17% of parent octene ions yield fragment ions whose complement is a butyl radical. Although there is no assurance that unimolecular dissociation of intermediate ions yields radicals of such a complex structure,^{40,41} some successful correlations have been carried out in the past.⁴²

Alternate ionic reaction schemes involve the formation of propyl and butyl ions by ion-molecule reactions with subsequent neutralization; however, mass spectrometric studies have indicated that saturated ions of low molecular weight are not important,^{11,15} ions of composition $\text{C}_n\text{H}_{2n+1}^+$ becoming predominant only at higher masses.¹⁴ Moreover, a mechanism must be provided for dissipation of the ion-electron recombination energy without dissociation processes.

Several other primary radicals are probably produced also; for example, the formation of cyclopropane in the presence of oxygen may indicate methylene insertion. However, these studies do not provide sufficient information to establish their nature or their behavior.

(5) *Nonscavangeable Products.* Several products, subsequently referred to as "molecular" products, apparently do not have free radicals as precursors since they persist in the presence of nitric oxide or oxygen. The formation of hydrogen, methane, and acetylene has been discussed previously.^{5,7-9} In the liquid phase cyclobutane formation has been ascribed to reaction of a higher excited ethylene molecule or an ionic reaction³³ while the "molecular" formation of butene-1 and *trans*-hexene-2 has been observed in the solid and the liquid and has been attributed to ionic processes.^{33,43} The formation of butenes in the gas phase has previously been observed by Mikhailov, *et al.*,^{2b} and by Lampe.³

The yield of cyclobutane is reduced by the addition of 10% oxygen. Such behavior has been attributed to the physical quenching of triplet state species,⁴⁴ and we suggest that this mechanism applies here. The state involved must be a high-lying one as production of cyclobutane by low energy electron swarms has not been observed⁷ nor is cyclobutane a product in vacuum ultraviolet and mercury-photosensitized photolysis of ethylene. The absence of a phase effect may be attributed to paucity of excitation processes leading to

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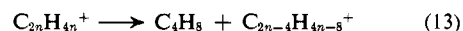
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high-lying optically allowed states near the ionization threshold.

The molecular butenes show a strong pressure dependence. Their yields are not reduced by oxygen and, in fact, a slight increase is apparent. Moreover, enhancement of excitation processes by application of electrostatic fields⁷ does not influence their formation. This differs sharply from cyclobutane, and we suggest that the molecular butenes are produced by ionic reactions although the possibility of a high-lying allowed transition cannot be eliminated. One possible scheme supported by mass spectrometric findings^{11,14} and the observation of charge transfer from butene ion to nitric oxide⁴⁵ involves the ionic polymerization of ethylene and unimolecular dissociation of intermediate ions



Part of the butadiene may have acetylene ion as its precursor and be formed by a reaction scheme similar to eq. 12 and 13.

(6) *Polymerization at High Pressures and Very Low Dose Rates.* It is generally accepted that radical-radical reactions occur with collision frequency, *i.e.*, with a rate constant k_c of approximately 10^{14} mole⁻¹ cc. sec.⁻¹. The rate constant for radical addition to ethylene, k_a , is of the order of 2×10^6 mole⁻¹ cc. sec.⁻¹ at room temperature.¹⁹ The applicability of these constants for radiation conditions has been shown in this investigation. Now the disappearance of ethylene by a free-radical-initiated chain reaction may be described by a restatement of the classical polymerization equation^{46,47} in terms of *G* values.

$$G(-\text{C}_2\text{H}_4) = G^i(-\text{C}_2\text{H}_4) + G_R^P k_a \sqrt{2E/(k_c d I_\gamma)} \quad (\text{VIII})$$

where I_γ is the γ -flux expressed in Mrads/hr. and d is a proportionality factor of 6.05×10^6 sec.⁻¹ hr. Mrad⁻¹. $G^i(-\text{C}_2\text{H}_4)$ is the yield of ethylene disappearance when no radical addition to ethylene occurs and has been found to be approximately 20.^{5,7} G_R^P is the total of all primary radical yields and is about 7.3 radicals/100 e.v. at pressures greater than 1 atm.^{7,27} Equation VIII can now be stated numerically

$$G(-\text{C}_2\text{H}_4) = 20 + 0.9 \times 10^3 \sqrt{E/I_\gamma}$$

This is in excellent agreement with the results of Hayward and Bretton,²⁰ who obtained the empirical relationship

$$G(-\text{C}_2\text{H}_4) = 16 + 1.0 \times 10^3 \sqrt{E/I_\gamma}$$

by following the decrease of ethylene pressure during irradiation. The intercept is smaller than 20 because of the formation of gaseous products such as acetylene, hydrogen, ethane, etc. The agreement suggests strongly

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(47) A. Charlesby, "Atomic Radiation and Polymers," Pergamon Press, New York, N. Y., 1960, p. 373.

that the radiation-induced polymerization of ethylene at ambient temperature is adequately described by a free-radical mechanism.

(7) *The Role of Neutralization.* In the preceding discussion, charge neutralization has been ignored completely. The use of electron attachment coefficients for ethylene or oxygen^{21,29} allows one to predict that $C_2H_4^-$ will not be formed under our experimental conditions. Since the positive charge survives more than 10^4 collisions, neutralization by free electrons will occur when it resides either on a highly complex polymeric ethylene unit as formed by reactions 12 and 13, or on a highly unsaturated radical as formed by reaction 10 and its higher analogs. In either case the resultant, neutralized species would be of such a complexity that it would not be detectable by the experimental techniques employed in this investigation.

Since free-radical-induced polymerization is insignificant under our conditions, one can estimate the extent of the contribution of ionic processes from the lack of material balance. The products listed in Table I account for 61.5% of the consumed ethylene units (carbon balance); the missing components have an average empirical composition $C_nH_{1.7n}$, supporting the conclusion that neutralization involves highly complex and unsaturated species.

Conclusions

The most important primary radical in the radiolysis of ethylene is the hydrogen atom. Its reactions and those of its sequent radicals largely determine the dose rate and pressure dependence of all products which have simple radicals as precursors. An approximate kinetic scheme can be employed to arrive at a quantitative description of the yield dependence on kinetic parameters. Other primary radicals, formed without radical addition to ethylene, include methyl, *n*-propyl, *sec*-propyl, and *sec*-butyl radicals. Their formation must be ascribed to higher order ion-molecule reactions.

A molecular mechanism is established for the formation of the butenes and cyclobutane. Higher order ionic association steps are suggested as an explanation for the former, while dimerization of an excited species is invoked to interpret the formation of the latter.

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Free Radicals by Mass Spectrometry.

XXXIII. Ionization Potentials of CF_2 , CF_3CF_2 , CF_3CH_2 , *n*- C_3F_7 , and *i*- C_3F_7 Radicals

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The vertical ionization potentials of three perfluoralkyl radicals are found to be 9.98, 10.06, and 10.5 v. for C_2F_5 , *n*- C_3F_7 , and *i*- C_3F_7 , respectively. The increase in ionization potential with CF_3 substitution is in contrast with the decrease found along the alkyl series and accounts for certain features of the mass spectra of perfluoroparaffins. These results suggest that $I(CF_3)$ should be <9.5 v. and that $I_{vert}(CF_3) = 10.1$ v. measured by direct electron impact includes >0.6 v. of excitational energy. $I(CF_3CH_2)$ is found to be 10.6 v., appreciably higher than $I(CF_3CF_2)$. The CF_2 radical has been produced by the thermal decomposition of the C_2F_5 radical, and $I_{vert}(CF_2)$ is 11.7 v. With appearance potential data this gives $\Delta H_f(CF_2) \sim -36$ kcal./mole.

Introduction

Experimental measurements of the ionization potential of the CF_3 radical have fallen into two groups: values of 10.1–10.2 v. from direct electron impact on CF_3 radicals produced by thermal reactions in a mass spectrometer,^{2–4} and values of 8.9–9.5 v. from dis-

sociative ionization of CF_3 derivatives by the indirect electron impact method.^{5–7} The situation, with regard to the “high” and “low” values for $I(CF_3)$, the heats of formation of CF_3 and CF_3^+ derived from appearance potentials, and the thermodynamic properties of CF_3 derivatives, has been reviewed recently^{8–10} and will not be discussed here except to comment that, although the inconsistencies in the appearance potential data for CF_3^+ from different compounds are large, these data can more easily be reconciled with $I(CF_3) \sim 9.5$ v. than with $I(CF_3) \sim 10.1$ v.

It is difficult to predict on theoretical grounds

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