[CONTRIBUTION FROM THE REFINING TECHNICAL AND RESEARCH DIVISIONS, HUMBLE OIL & REFINING COMPANY]

High Energy Electron Irradiation of Methane. Remarks on the Reaction Mechanism

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Methane, at pressures of 50 and 150 mm., has been irradiated with two million-volt electrons from a Van de Graaff electrostatic accelerator. In all experiments the gaseous products of the reaction were hydrogen, ethane, propane, butane and ethylene formed with "G" of 5.7, 2.1, 0.14, 0.04 and 0.05, respectively, while "G" for methane consumption was 7.6. The identity of $G(CH_4)$ and $G(H_2)$ with those reported by previous investigators employing α-particles and deuterons and much higher pressures seems to afford additional evidence that the radiation-induced reaction is independent of the intensity of the radiation and the pressure. Some polymeric material with the approximate empirical formula of C_nH_{2n} also is formed. Ethane, propane and presumably higher paraffins are formed simultaneously. This fact and the non-dependence of the energy yields on intensity and pressure are difficult to reconcile with a completely free radical nature of the reaction.

Introduction

Probably the first experiments concerning the radiation chemistry of methane were those of Mund and Koch[1] in which they irradiated methane with α-particles from radon and observed that a reaction took place which resulted in a slightly reduced pressure. Somewhat later, the same types of experiment, but in more detail, were carried out by Lind and Bardwell[2,3] who confirmed the absence of appreciable pressure change and in addition found as products, hydrogen, ethane, propane, butane and pentanes. They reported no unsaturation in the gas phase, but did find evidence of a small amount of liquid with the empirical formula of C_nH_{2n}.

The work of McLennan and Glass,[4] which most likely represents the first investigation of the electron irradiation of methane, showed again that no significant pressure change occurred, that hydrogen, ethane and higher hydrocarbons were formed, and that, therefore, the reaction was qualitatively, at least, similar to that induced by α-particles.

Honig and Sheppard[5] published a study of α-particle and deuteron irradiations of methane and butane in which they found essentially the same products as Lind and Bardwell[3] but, in addition, found small amounts of unsaturation in the gas phase. The energy yields found by Honig and Sheppard were in reasonably good agreement with those of Lind and Bardwell.

No direct studies of the radiation chemistry of pure methane have been reported since the work of Honig and Sheppard and no detailed investigations of electron irradiations seem ever to have been reported, although some investigations that have shed light on reactions that must be highly probable in irradiated hydrocarbon systems have appeared fairly recently. The results of these studies, which consist of interpretation of mass spectra, free-radical identification in irradiated systems,[6] pressure dependence of mass spectra[7,8a,8b,9] and ion-electron recombination measurements[10] will be considered in more detail later.

Experimental

Radiation Source.—The source of high-energy electrons was a 2-million volt Van de Graaff electrostatic accelerator. In all experiments the accelerating voltage was maintained at 2.0 million volts and the electron beam current at approximately 5 amperes.

Radiation Vessels.—The vessels in which the gaseous irradiations were carried out consisted of cylindrical Pyrex tubes, of 22 mm. outside diameter and 19 mm. inner diameter to one end of which was sealed an optically flat Pyrex window of 1 mm. thickness. In the other end of the tube was sealed a $^1/_{16}$ inch diameter tungsten wire which supported and made electrical contact with a stainless steel disk of 17 mm. diameter and 3 mm. thickness located about 800 mm. from the Pyrex window. This disk served to collect those electrons that managed to make their way through the entire path of gas and, hence, afforded some measure of the average beam current traversing the tube. A high-vacuum stopcock connected to a 14/35 ₮ was sealed to the tube between the disk and the tungsten-glass seal for filling and evacuation purposes.

Only about one-quarter to one-half of the electrons incident on the Pyrex window of the reaction vessel reach the collector disk and in order to determine the average current in the tube a slightly modified vessel was used. This vessel was exactly similar to those described above except that the stainless steel collector disk was made movable by sealing to the tungsten wire support a thin flexible wire 800 mm. long which when extended placed the collector disk about 1 mm. from the entrance window. Measurements of collected current could thus be made at distances of 1 to 800 mm. from the entrance window of the reaction vessel.

Materials.—Phillips Research Grade methane, stated to have a purity of 99.58 mole %, was frozen out in liquid nitrogen in such a way that three times as much methane as required to fill the storage bulb on the vacuum system was contained in the trap. The gas was allowed to boil off in such a manner that approximately the middle third of the frozen mixture was collected and stored in a three-liter bulb that had previously been evacuated to about 10^{-6} mm.

Matheson acetylene was bubbled through concentrated sulfuric acid and then passed slowly through a trap immersed in a Dry Ice-acetone mixture from which it was collected and stored in a previously evacuated storage bulb. The absolute purity is not known but from mass spectral analysis, it is estimated that its purity was not less than 99 mole %.

Procedures.—In carrying out an irradiation the reaction vessel was first evacuated to about 10^{-6} mm. and gently flamed. It was filled to the desired pressure with the gas to be irradiated and the generator preset to deliver 5.0 μ-amperes at the entrance window of the reaction tube. The reaction tube was then placed in the predetermined position, the irradiation begun, and the collected current measured as a function of time. At frequent intervals during the irradiation period, the reaction tube was moved away from the generator window, the incident current checked, and, if necessary, reset to 5.0 μamperes. After the irradiation the final pressure was measured and the residual gases transferred to evacuated (10^{-6} mm.) sample bulbs by means of a Toepler pump. The analyses of the resulting gas mixtures

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[1] W. Mund and W. Koch, *Bull. soc. chim. belg.*, **34**, 120 (1924).

[2] S. C. Lind and D. C. Bardwell, *Science*, **62**, 422 (1925).

[3] S. C. Lind and D. C. Bardwell, THIS JOURNAL, **48**, 2335 (1926).

[4] J. C. McLennan and J. V. S. Glass, *Can. J. Research*, **3**, 241 (1930).

[5] R. E. Honig and C. W. Sheppard, *J. Phys. Chem.*, **50**, 119 (1946).

[6] L. H. Gevantman and R. R. Williams, Jr., *J. Phys. Chem.*, **56**, 569 (1952).

[7] V. L. Tal'roze and A. K. Lyubimova, *Doklady Akad. Nauk, S.S.S.R.*, **86**, 909 (1952).

[8] (a) D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **23**, 1353 (1955); (b) D. O. Schissler and D. P. Stevenson, *ibid.*, **24**, 926 (1956).

[9] F. H. Field, J. L. Franklin and F. W. Lampe, forthcoming publication.

[10] M. A. Biondi and S. C. Brown, *Phys. Rev.*, **76**, 1697 (1949).

were done in triplicate on a Consolidated Mass Spectrometer previously calibrated with Phillips Research Grade hydrocarbons. Because of the nature of the radiation-induced reaction of acetylene, it was sufficient to measure only the final and initial pressures in the dosimetry experiments.

Dosimetry.—It has been demonstrated[11–13] that acetylene, when subjected to a high-energy radiation, polymerizes to cuprene and benzene at a rate which is dependent only upon the rate of absorption of energy by the acetylene. If we make the approximation, which is probably valid within the uncertainty of the measurement of the average electron beam current in the reaction vessel, that the energy lost per electron per unit distance traveled is simply proportional to the number of electrons per cm.[3] that the gas molecules present to the electron beam, and integrate the first-order rate equation we get

$$\ln \frac{(C_2H_2)_0}{(C_2H_2)} = \frac{\alpha G Z L \bar{I}}{Ve} t$$

In the preceding equation $(C_2H_2)_0$ is the initial acetylene concentration, (C_2H_2) is the acetylene concentration at time t, G is the 100 e.v. yield of acetylene disappearance, Z is the number of electrons in acetylene, L is the distance traveled by the electrons traversing the gas, $\bar{I}$ is the average beam current in the reaction vessel, e is the charge on the electron in coulombs, V is the volume occupied by the gas, and α is the proportionality constant between energy loss per electron per unit distance and the number of bound electrons per cm.[3]. α is determined from the slope of a plot of the left-hand side of the above equation *versus* time and is employed in energy absorption calculations in the methane irradiations.

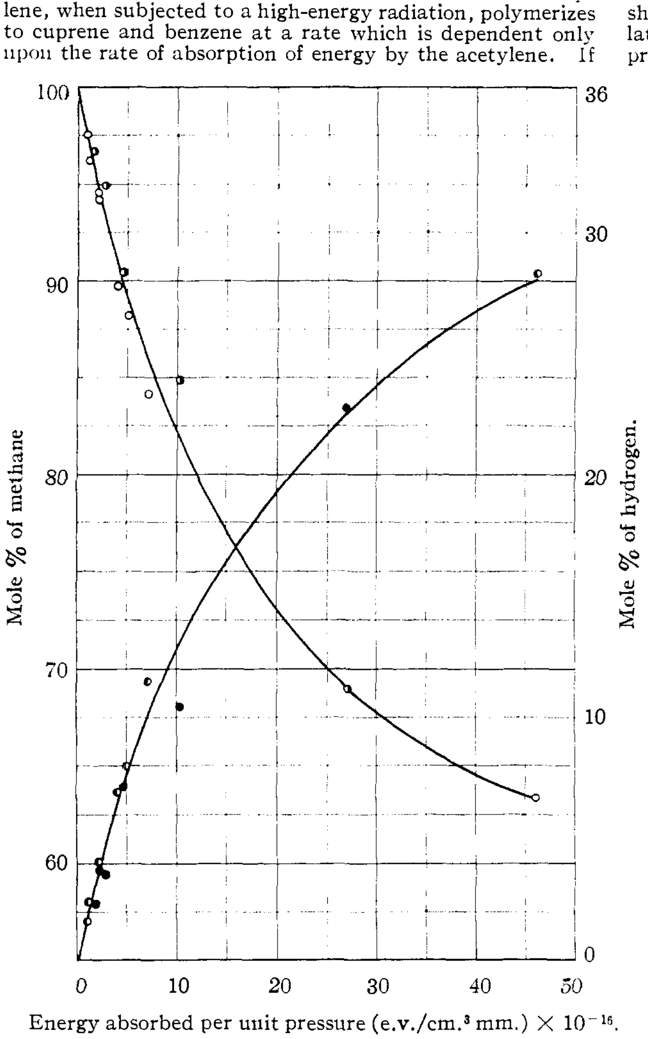

Fig. 1.—Methane consumption and hydrogen formation: O, methane 50 mm.; ◑, methane 150 mm.; ◐, hydrogen 50 mm.; ●, hydrogen 150 mm.

The acetylene irradiation data at 50 mm. pressure are shown in Table I. Acetylene concentrations were calculated directly from the pressure after correcting the final pressure for the benzene which is formed with a "G" of 5.1.[11]

Results

The results of the irradiations of methane at 50 and 150 mm. are shown in Figs. 1 and 2. Ethylene and butane data are not shown in the figures because of the low level of their concentrations and resulting poor precision in their analyses. In all of the reactions investigated no change of pressure, outside of the uncertainty involved in its measurement, was found. This was not unexpected in view of the results of previous investigations with other types of radiation.[1–5]

From material balances on the irradiated systems it was apparent that some polymeric material is formed. The amount of polymer produced (material lost) increases smoothly with increasing dosage but always such that the ratio of hydrogen lost to carbon lost is about 2. In the experiment of longest duration 85% of the original carbon and 93% of the original hydrogen were found in the gas phase.

In the absorbed energy calculations the most important property of the molecules that governs this absorption is the number of electrons per cubic centimeter that the gas presents to the beam of high energy electrons. Since little or no pressure change is observed, the number of molecules per unit volume must be unchanged and, if no material disappears from the gas phase, the average number of electrons per molecule must also be the same. Actually, however, there must be some liquid formed because material balances on the gas phase show that the very small amount of material disappearing increases smoothly with increasing dosage and always in the same ratio of hydrogen to carbon of about 2. If some liquid is formed, the statement that the average number of electrons per molecule remains unchanged is not strictly true but, at the conversions of methane under consideration here and with the material balances obtained, the assumption of a constant average gas composition, with respect to the number of electrons, introduces no error that is not well within the uncertainties of the measurement of the average beam current in the reaction vessel.

Table I

1.7 Mev. Electron Irradiation of Acetylene at 50 Mm. Pressure and 300°K.

Time (min.)	Av. current (μa.)	ΔP (mm.)
30	1.4	2.5
60	1.2	4.0
89	1.1	6.2
150	1.3	11.2

The initial slopes of Figs. 2 and 3 are, of course, related to the energy yields for the various components. The 100-electron-volt yields are tabulated in Table II, where they are compared with the values obtained in irradiations with α-particles[3]

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(11) L. M. Dorfman and F. J. Shipko, This Journal, **77**, 4723 (1955).

(12) S. C. Lind, D. C. Bardwell and J. H. Perry, *ibid.*, **48**, 1556 (1926).

(13) C. Rosenblum, *J. Phys. Chem.*, **52**, 474 (1948).

and deuterons.[5] It is considered that the agreement for $G(CH_4)$ and $G(H_2)$, is evidence that these energy yields are independent of radiation intensity over a wide range. The "G" values for α-particles were computed from their ion-pair yields[3] by using a value of 30.1 electron-volts as the energy required for an α-particle to produce an ion-pair in methane.[14]

TABLE II

Component	This work (1.7 mev. electrons)	Lind and Bardwell[3] 6 mev. α (Rn)	Honig and Sheppard[5] 12 mev. D^+
CH_4	−7.6	−7.3	−8.3
H_2	5.7	5.5	
C_2H_6	2.1	1.1	
C_3H_8	0.14	0.38	
C_2H_4	0.05	..	
C_4H_{10}	0.04	0.22	

One other important point can be obtained from the data and this concerns the relative rates of formation of ethane and propane. Figure 3 shows quite conclusively that ethane and propane are formed simultaneously rather than the propane formation occurring only through the action of the radiation on ethane already produced. The data for butane and ethylene indicate that these substances are also formed simultaneously with the other products.

Discussion

It has been well established that the passage of high energy radiation through a chemical system causes ionization and electronic excitation of the molecules comprising the system. Furthermore, it is generally accepted that about one-half of the energy transferred to the molecules goes into ionization processes and the remaining energy into electronic and vibrational excitation processes. The fate of an ion produced in the primary act is to decompose to a smaller ion and neutral fragment, to react with molecules present, or be neutralized by an electron to form an excited molecule. If the latter reaction dominates, the effect is the same as if excitation rather than ionization had occurred in the primary act. The excited molecules are generally believed to decompose to atoms and/or free radicals and the thought is widespread that these agents are the principal cause of reaction in irradiated systems.

There is some evidence that CH_3, C_2H_5, CH_2 and H are formed in irradiated methane.[6] The simultaneous ethane, propane and butane formation could then be explained on the basis of radical-radical combinations. However, the C_2H_5 must be formed simultaneously with the others before this explanation is valid. Conceivably, the C_2H_5 could be formed by the reaction

$$CH_3 + CH_2 \longrightarrow C_2H_5 \qquad (1)$$

but in the experiments of Gevantman and Williams,[6] where the radicals were "scavenged" by iodine, no change in the relative concentrations of CH_3, C_2H_5 and CH_2 was found upon changing the iodine concentration. This observation would appear to rule out (1). Another possibility would be the reaction

$$CH_3 + CH_4 \longrightarrow C_2H_5 + H_2 \qquad (2)$$

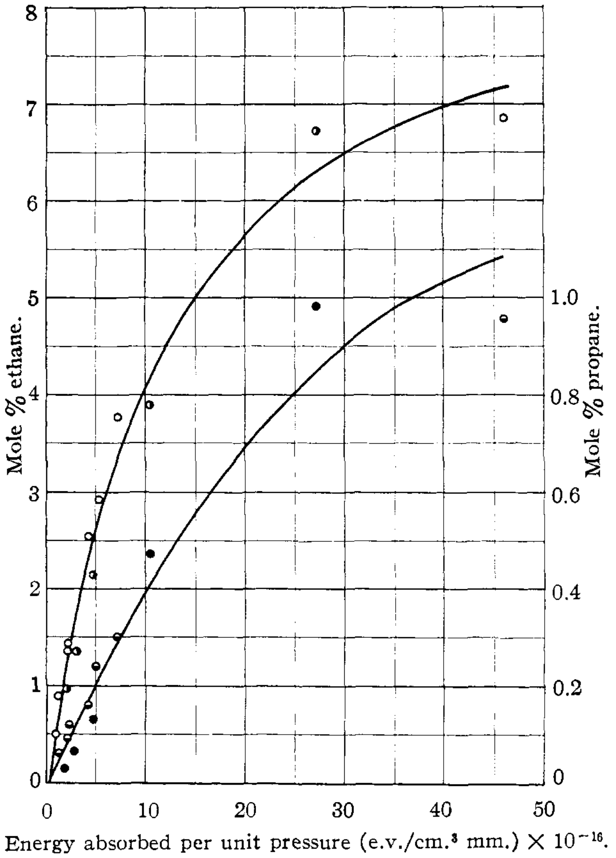

Fig. 2.—Ethane and propane formation: ○, ethane 50 mm.; ◑, ethane 150 mm.; ●, propane 150 mm.; ⊖, propane 50 mm.

However, this reaction has an activation energy of at least 12 kcal. and never has been reported.

The large majority (~85%) of the ions in the methane mass spectrum are CH_4^+ and CH_3^+ and recent evidence cited below indicates these species can react readily with methane in the following way

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \qquad (3)$$

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2 \qquad (4)$$

Tal'roze and Lyubimova[7] reported the existence of CH_5^+ and somewhat later Stevenson and Schissler[8a] reported the specific rate of the reaction

$$CD_4^+ + CD_4 \longrightarrow CD_5^+ + CD_3 \qquad (3a)$$

to be 1.4×10^{-9} cm.³ molecule⁻¹ sec.⁻¹. At this Laboratory, we[9] have found the specific rate of (3) to be of the order of 1×10^{-9} cm.^{3} molecule^{-1} sec.$^{-1}$. The form and magnitude of the rate for this type reaction was derived theoretically 20 years ago.[15]

In a recent paper, Schissler and Stevenson[8b] have shown that (4) could be expected to have a cross-section of the order of 2×10^{-14} cm.^{2} for ions of thermal energy at 300°K., which corresponds to a rate constant of about 2×10^{-9} cm.^{3} molecule^{-1} sec.$^{-1}$. We[9] have also observed the formation of $C_2H_5^+$ to proceed with an apparent rate constant equal to that found by Schissler and Stevenson.

The magnitudes of the rate constants for (3) and (4) are such that these reactions must be con-

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[14] W. P. Jesse and J. Sadauskis, *Phys. Rev.*, **97**, 1668 (1955).

[15] H. Eyring, J. O. Hirschfelder and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936).

sidered extremely probable in irradiated methane with (4) very likely accounting for the observed simultaneous hydrocarbon buildup. The buildup by this path would be possible, however, only if electron neutralization of CH_4^+ and CH_3^+ did not occur before (3) and (4) could take place. While there are no data available on neutralization rates in ionized methane, the results of Biondi and Brown[10] on neutralization rates in ionized hydrogen, if extrapolated to ionized methane, suggest that, at the radiation intensities and pressures used in this work and in most high energy radiations, electron neutralization of CH_3^+ and CH_4^+ will be slow compared with (3) and (4) and that these reactions may indeed be occurring.

The energy yields are independent of pressure over a threefold range. This fact is difficult to reconcile with a purely free radical scheme (which would be required if CH_4^+ and CH_3^+ were neutralized before reaction with methane) because of the competition between free radical abstraction and recombination reactions.

The results of this work are not strictly comparable to those of Lind and Bardwell[3] (see Table II) because these authors used higher intensities and higher pressure which would tend to operate in opposite directions on the energy yields. However, it seems quite improbable that the two effects would so exactly counterbalance each other as to give the striking agreement in $G(H_2)$ and $G(CH_4)$. Rather, it seems easier to believe that $G(H_2)$ and $G(CH_4)$ are independent of pressure and intensity over a wide range.

These facts suggest that ion-molecule reactions in irradiated methane may be playing a much larger part than has been generally believed. When the ions are neutralized they may fragment in many ways and so no detailed mechanism can be written without complete speculation as to the neutralization reactions. A detailed scheme would require, in addition, an understanding of the reactions leading to the polymeric material of which at the present time nothing is known.

Acknowledgments.—The author wishes to acknowledge fruitful discussions with Drs. W. E. Doering, F. H. Field and J. L. Franklin and the assistance of Messrs. T. P. Gorman and J. P. Keller in carrying out the experimental work.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA)]

Organic Ions in the Gas Phase. III. $C_6H_5^+$ Ions from Benzene Derivatives by Electron Impact

BY SEYMOUR MEYERSON AND PAUL N. RYLANDER

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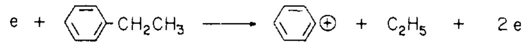
Alkylbenzenes and alkylbenzene derivatives under electron impact give rise to $C_6H_5^+$ ions. They have been assumed to be phenyl ions formed by cleavage of the side chain from the ring. Spectra of labeled molecules furnish evidence that the $C_6H_5^+$ ions derived from phenyl alkyl ketones and 2-methyl-2-phenylalkanes do have the phenyl structure. On the other hand, those derived from α-chloroethylbenzene and ethylbenzene are formed by a process involving ring cleavage.

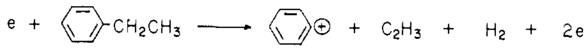
Introduction

The known stability of the benzene ring to chemical attack has led mass spectrometrists to assume that this ring is also stable to electron bombardment. Thus the $C_6H_5^+$ ions found in the mass spectra[1] of all alkylbenzenes heavier than toluene have been assumed to contain the original ring, and to be phenyl ions formed by cleavage of the side-chain from the ring. Similarly, the $C_6H_7^+$ ions have been assumed implicitly to be benzenium[2] ions formed by the same cleavage with concomitant transfer of hydrogen from the side-chain to the ring.

Identification of $C_6H_5^+$ as phenyl has seemed obvious. So firmly was this notion accepted that even the measured appearance potential of 16.3 e.v. for the $C_6H_5^+$ ion from ethylbenzene,[3] which leads to a heat of formation of phenyl ion 61 kcal. higher than the known heat of formation,[4] did not suggest that this ion was other than phenyl. Instead, this high value led to the suggestion[4] that the process could not be represented simply as



but more probably as



The last reaction gives a heat of formation of the phenyl ion more nearly in agreement with the known value.

The spectra of labeled compounds furnish evidence that the $C_6H_5^+$ ion is frequently not a phenyl ion. The precursor of the $C_6H_5^+$ ion in these cases is the $C_6H_7^+$ ion, which is not benzenium. However, some benzene derivatives do yield $C_6H_5^+$ and $C_6H_7^+$ ions that almost certainly are phenyl and benzenium.

Phenyl Ions

$C_6H_5^+$ ions from electron impact of phenyl alkyl ketones and 2-methyl-2-phenylalkanes apparently retain the original ring intact.

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[1] American Petroleum Inst., Research Project 44, "Catalog of Mass Spectral Data," Carnegie Inst. of Technology, Pittsburgh, Pa., 1947-1956.

[2] L. W. Pickett, N. Muller and R. S. Mulliken, *J. Chem. Phys.*, **21**, 1400 (1953).

[3] F. H. Field and J. L. Franklin, *ibid.*, **22**, 1895 (1954).

[4] J. L. Franklin and F. H. Field, *ibid.*, **21**, 2082 (1953).