out the differences between branched and linear depolymerizing systems. What is obviously needed now are kinetic studies on polymers with known branch concentrations and lengths. At this time two types of structures look promising to us, namely, copolymers of diazomethanes with higher diazo derivatives and polymers of deuteroethylene.

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NOTES

Gases Liberated during the High Voltage Electron Irradiation of Polyethylene

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The irradiation of polyethylene with high energy electrons causes a liberation of hydrogen and volatile hydrocarbons, presumably due to the breaking of C–H and C–C bonds. The radicals and ions thus formed are capable of reacting further to form, (1) cross-linked material and (2) depolymerization products. Both reactions occur simultaneously in the material. The predominant reaction appears to favor the formation of cross-linked material.[1] Usually the nature of the reactions are deduced by the physical properties of the remaining bulk irradiated material. However, the gaseous products that are concomitantly produced in the reactions can be examined and will lead to a further understanding of the mechanism. Both approaches should result in the same deductions.

Charlesby has reported similar findings for polyethylene irradiated in an atomic pile.[2] He reported that hydrogen accounted for 98% of the total volume of the gas liberated and that the remaining gas consisted almost entirely of methane and ethane with smaller amounts of propane and butane.

The experiments described in this note were undertaken to determine the nature of the gases liberated from polyethylene when bombarded with high energy electrons in order to confirm some of the previous findings.[1,2]

Experimental

The source of high energy electrons used in the experiments was the General Electric Research Laboratory 800 kv. (peak) resonant transformer cathode ray unit.[3,4]

The gas liberated during the irradiation was subsequently analyzed with a mass spectrometer.

The polyethylene was of commercial grade and had a molecular weight of about 19,000. The test sample consisted of a stack of four 1-inch squares cut from 0.003 inch thick sheet and had an initial weight of 0.1988 g.

The test sample was sealed into a thin-wall glass bulb that could be connected to the spectrometer vacuum system through a ground glass taper joint. Attached to the thin bulb were two side arms, one of which served as a cold trap and the other contained a pressure gage.

The bulb was blown to a diameter of about 5 cm. from AO fernico sealing type glass. The volume of the total system was 140 cc. The polyethylene samples were first loaded through the glass side arm, and the bulb then sealed to the rest of the system. The equivalent absorber thickness of the combined bulb wall and polyethylene sample was about 76 mg./cm.^{2}, which value is in the range of penetration of the electron beam where the irradiation dose is nearly uniform throughout the thickness.

Condensable products liberated during irradiation were collected in the cold trap, which was held at liquid nitrogen temperature during the irradiation.

Preliminary to each irradiation exposure, the sample and glassware were outgassed by heating them while connected to the vacuum system. The thin bulb was heated to approximately 90° by means of infrared lamps. The bulb and sample were usually heated for several hours. In addition, most of the remainder of the glassware was vigorously heated by torching. At the end of the outgassing cycle, the pressure was usually zero, both with the trap at room temperature and at liquid nitrogen temperature. Gas pressure was measured with a thermistor type gage.[5]

During the irradiation period the trap was held at liquid nitrogen temperature so that the gas pressure indicated was that of the non-condensable fraction. By comparing the pressure readings with and without coolant on the traps, it was possible to determine the total pressure and the pressure corresponding to the volatile hydrocarbon products.

Irradiation dose measurements were made with a specially constructed air ionization chamber. The dose is expressed in roentgen units. The roentgen by definition is the amount of irradiation to produce 1 e.s.u. of charge in one cc. of standard air. The absorption of one roentgen corresponds to the liberation of 1.6×10^{12} charges, or ion pairs, in one gram of air, and it is assumed in one gram of polymer. On the basis of 32.5 e.v. per ion pair, this is equivalent to the absorption 83.8 ergs./g.

Discussion and Results

The pressure of the non-condensable gas, which was found to be hydrogen, was observed to increase linearly with the amount of irradiation. This is to be expected as the number of cross-links, as determined by swelling and tensile measurements, was found to increase nearly linearly with irradiation.[1] The data also indicates that the pressure of both the non-condensable and condensable gases is nearly a linear function of the irradiation dose up to a total dose of 16×10^6 roentgen. The pressure of the gases liberated by an irradiation dose of 16×10^6 roentgen was 1660 μ and 360 μ for the non-condensable and the condensable fractions, respectively. The near linear relationship holds in the case of the non-condensable fraction for irradiation doses up to 200×10^6, but not for the condensable fraction, as the yield of condensable gas was considerably less than expected. The decrease may in part be due to reabsorption of condensables by the polyethylene during the pressure measurement

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[1] E. J. Lawton, A. M. Bueche and J. S. Balwit, *Nature*, **172**, 76 (1953).

[2] A. Charlesby, *Proc. Roy. Soc.* (*London*), **A215**, 203 (1952).

[3] E. J. Lawton, W. D. Bellamy, *et al.*, *Tappi*, **34**, 113 (1951).

[4] J. A. Knowlton, G. R. Mahn and J. W. Ranftl, *Nucleonics*, **11**, 64 (Nov. 1953).

[5] S. Dushman, "Vacuum Technique," p. 329.

which in this case required a longer time to make because the pressure was high.

The mass spectrometer analysis of the non-condensable and condensable fractions indicated that the non-condensable gas was hydrogen and the condensable fraction was made up of volatile hydrocarbons, which in some instances included compounds up to C_{11}. The gaseous products liberated by an irradiation dose of 4×10^6 roentgen are indicated in Fig. 1, which shows relative amounts of gas *vs.* the number of carbon atoms in each hydrocarbon product. Hydrogen is the predominant gas and for this particular run accounted for about 85% of the total volume liberated. Both saturated and unsaturated products are evolved during the irradiation. In both cases, volatile compounds containing C_2, C_3 and C_4 carbon atoms were the predominant ones liberated. The yield of methane in most cases was relatively low. This is somewhat different from that reported by Charlesby in which hydrogen accounted for about 98% of the gas, and the remaining gas consisted almost entirely of methane and ethane.[2] This may be due to the different type of irradiation source used. In general, the spectrum of Fig. 1 was the same whether the gases were collected during the early stages of the irradiation or after the sample had an accumulated irradiation dose of approximately 10^9 roentgen. Likewise, the same general spectrum was obtained whether the irradiation dose was accumulated at either a fast or at a slow dose rate.

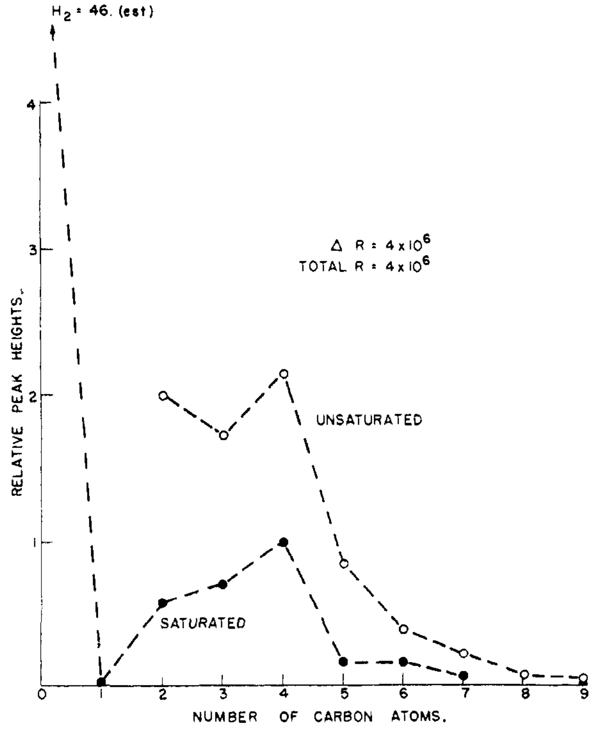

Fig. 1.—Mass spectrograph analysis of gases liberated from polyethylene irradiated with 800 kv.(peak) electrons. Relative spectrometer peak heights *vs.* number of carbon atoms in the hydrocarbon product.

The presence of *trans*-unsaturation in the polymer produced by the irradiation also has been detected by changes in the infrared absorption peak 10.35. It was found that this type of unsaturation increases with increasing irradiation, see Table I.

TABLE I

INCREASE IN *trans*-UNSATURATION IN POLYETHYLENE IRRADIATED WITH 800 KV.(PEAK) ELECTRONS. INFRARED ABSORPTION AT 10.35μ

Irradiation dose, roentgen	Absorbance
0	0.007
20×10^6	.037
50×10^6	.069
100×10^6	.102
250×10^6	.184
500×10^6	.243

The polyethylene in this case was irradiated in a nitrogen atmosphere. Unsaturation of this type may be due to the removal of hydrogen by atomic hydrogen at sites adjacent to the point of origin of the hydrogen atom. A small fraction of the total hydrogen liberated then may be due to this reaction.

Because of its small size, hydrogen would be expected to diffuse readily to the surface of the polyethylene so that the total amount of this gas collected should be proportional to the volume of the polyethylene. The relatively large hydrocarbon molecules, on the other hand, would diffuse with difficulty through the polymer so that the hydrocarbon gases collected would be mainly those that originated near the surface, and the total amount should be proportional to the surface rather than to the volume of the sample. Heating the sample caused liberation of additional hydrocarbon volatiles. The sample was not always heated after each run so that a good quantitative measure of the amount of volatile hydrocarbon depolymerization products was not obtained. Although the hydrocarbon portion of the spectrum of Fig. 1 is probably distorted slightly because of different diffusion rates, it is indicative, however, in a qualitative way of the kinds of gases liberated and also that there is a preferred liberation of compounds containing C_2, C_3 and C_4 carbon atoms. The preferential liberation of C_3 and C_4 compounds could possibly be connected with the short chain branches found in polyethylenes. The branches are reported to be from two to thirty carbon atoms long, the most probable length being C_3 to C_5 atoms. These occur on an average of about 30 carbon atoms along the chain.[6] There is no clear picture, however, as to the reason why the ionization act would prefer to disrupt the C–C bond at the branch point rather than any other point along the chain aside from the possible lower C–C bond energy at the tertiary position. The existence of a specific type of side reaction, such as the hydrogen transfer "back biting" mechanism[6] thought to be responsible for branching in the polymerization reaction may be one step in the formation of C_3 and C_4 products. Further experimental results using an unbranched material and short chain paraffins should shed light on this problem.

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(6) M. J. Roedel, "The Molecular Structure of Polyethylene, Long and Short Chain Branching in Polyethylene," paper presented 123rd Meeting ACS, Los Angeles, California, March, 1953.

Loss of hydrogen and volatile compounds is accompanied by a loss in weight of the sample. Likewise, as the supply of these gases is decreased by increased cross-linking and unsaturation, the amount of gas evolved per given irradiation dose increment was observed to decrease. For example, the evolution of hydrogen decreased from 106 μ per million roentgen when the sample was first irradiated to 86 μ per million roentgen after the sample had absorbed an accumulated dose of 1037 $\times$ 10^6 roentgen. The corresponding decrease in volatile compounds was from 30 to 12 μ per million roentgen. The total weight decrease was from 0.1988 to 0.1947 g.

Cross-linking Efficiency.—If it is assumed that each hydrogen molecule evolved is indicative of one C–C cross-link, then it is possible from the above hydrogen data to calculate the concentration of cross-links and the efficiency of the irradiation in producing cross-links. The initial pressure change corresponds to a loss of 2×10^{-6} g. of hydrogen, or a decrease of about 0.007% of the available hydrogen. The concentration of cross-links computed from this would be $C = 3.33 \times 10^{18}$ per cubic centimeter. The efficiency of the irradiation in producing cross-links is defined as the concentration C, divided by the number of electrostatic charges, or ion pairs, per cubic centimeter of polymer produced by the irradiation. In the case of the above concentration which corresponds to an irradiation dose of 10^6 roentgen, the efficiency is found to be equal to 1.87. This is in agreement with other values as determined from tensile and swelling data.[7] The efficiency of production of cross-links decreased with increasing amounts of accumulated irradiation. The decrease as determined from the above hydrogen data was from the initial value of 1.87 to 1.51 after the sample had received an accumulated dose of 1037 $\times$ 10^6 roentgen.

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[7] E. J. Lawton, J. S. Balwit and A. M. Bueche, *Ind. Eng. Chem.*, in press.

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The Addition of Methyl Radicals to Benzene

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In an interaction involving radicals and aromatic hydrocarbons, as *e.g.*, benzene, two reactions need to be considered as the most probably primary processes: I, the hydrogen atom abstraction, represented by equation 1

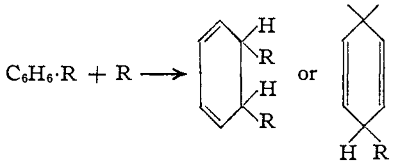
$$C_6H_6 + R\cdot \longrightarrow C_6H_5\cdot + R\cdot H \qquad (1)$$

and II, the radical addition reaction, shown symbolically by equation 2

$$C_6H_6 + R\cdot \longrightarrow C_6H_6R\cdot \text{ complex} \qquad (2)$$

It appears[1] that the hydrogen atom abstraction prevails in reactions taking place in gaseous phase and it is favored by higher temperatures, while the radical addition predominates in reactions proceeding in solution. Of course, the primary complex, like $C_6H_6\cdot R$, cannot be the final product of the over-all reaction. It has to react further with radicals, yielding eventually the final addition product (see *e.g.*, equation 3) or the product of substitution (see equation 4).

addition



(3)

substitution

$$C_6H_6\cdot R + R \longrightarrow C_6H_5\cdot R + H\cdot R \qquad (4)$$

The stoichiometry of the over-all reaction represented by equations 2 followed by (4) is identical with the stoichiometry of the process described by equation 1 followed by a recombination of phenyl and R radicals. Nevertheless, there are means for distinguishing between these two alternatives (see ref. 1).

On the other hand, reactions (2) followed by (3) lead to a different stoichiometry of the over-all process, and to entirely different products. Such products have been reported recently in publications by Magat and Bonême,[2] by Stockmayer and Peebles,[3] and by Marvel and Anderson.[4] These workers demonstrated that growing polymeric radicals may be added to aromatic hydrocarbons, the products of such reactions being copolymers which incorporate the aromatic compounds in their chains. Essentially the same conclusion has been drawn by Mayo[5] who studied the chain transfer reaction in bromobenzene. Our present work furnishes the evidence that methyl radicals are added to benzene, and the relevant observations are described in this communication.

Experimental

Methyl radicals were generated by the thermal decomposition of acetyl peroxide. The compound was synthesized by the conventional method described, *e.g.*, in a paper by Price and Morita,[6] and it was purified by crystallization. Most of our experiments were carried out in solutions concentration of which varied from 7×10^{-2} molar to 4×10^{-3} molar and at a temperature of 65.0°. The investigated samples of solution were deaerated thoroughly in a special glass reaction vessels, and then immersed in a bath maintained at a temperature constant to $\pm 0.1°$. At the end of a predetermined period of time the samples were removed from the bath, frozen in acetone–solid carbon dioxide mixture and analyzed. The method of analysis[7] enables us to determine the amounts of carbon dioxide, methane and ethane, produced in the reaction, while the amount of undecomposed peroxide was determined by iodometric titration. The reliability of our analytical procedure was checked by special blank runs and it was found entirely satisfactory. The decomposition experiments were carried out in benzene, in cyclohexane, and in isoöctane. All these solvents were carefully purified.

Results

The decomposition of acetyl peroxide in isoöctane or in cyclohexane solution yielded carbon dioxide,

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[1] M. T. Jaquiss and M. Szwarc, *Nature*, **170**, 312 (1952).

[2] M. Magat and R. Bonême, *Compt. rend.*, **232**, 1657 (1951).

[3] W. H. Stockmayer and L. H. Peebles, THIS JOURNAL, **75**, 2279 (1953).

[4] C. S. Marvel and W. S. Anderson, *ibid.*, **75**, 4600 (1953).

[5] F. K. Mayo, *ibid.*, **75**, 6133 (1953).

[6] C. C. Price and H. Morita, *ibid.*, **75**, 3686 (1953).

[7] The details of our analytical methods as well as the full account of this work will be published in a later communication.