Irradiation of Polyethylene. II. Kinetics of Unsaturation Effects

By MALCOLM DOLE, D. C. MILNER[1] AND T. F. WILLIAMS[2]

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By studying three different types of polyethylene, it can be shown that the original unsaturation in the material whether vinyl or vinylidene disappears initially according to a first-order law and that the rate then becomes less than first order as the *trans*-vinylene concentration builds up. A protective action of vinyl groups by vinylene groups is postulated to explain the pronounced departure from first-order kinetics. Formation of vinylene unsaturation is accurately described by the equation $c - c_0 = (c_\infty - c_0)(1 - e^{-kD})$ which is based on a linear increase of concentration with dose followed by a first-order elimination, both effects being independent of vinyl unsaturation. The limiting concentration attained is greater, the greater the crystallinity of the polyethylene. At liquid nitrogen temperatures vinyl destruction is virtually suppressed, but vinylene formation is scarcely affected. Approximately half of hydrogen elimination results in vinylene formation, probably by molecular detachment because of its zero temperature coefficient. A post-irradiation heating of the polyethylene to room temperature causes a significant amount of vinyl or vinylidene destruction, thus proving the existence of free radical reactions in the solid state. Evidence from infrared data for cyclization or ring link formation is given. Production of ring links is linear with time, and the greater the crystallinity of the polyethylene. The yield of ring links is less at liquid nitrogen temperature than at room temperature. The first-order kinetics observed for vinyl, vinylidene and vinylene elimination together with the high initial value of G_0 for vinyl decay, 9.6, can only be explained on the basis of activation of the double bond by energy of excitation released in localized regions corresponding to the spurs of fast electron tracks. Thus this paper describes the kinetics of decay in the solid phase of a specific group whose chemical structure and concentration are both known.

Introduction

As a result of the practical importance of the cross linking of polyethylene by high energy radiations, the statement often has been and is still being made[3] that hydrogen evolution and cross linking are the major processes taking place in the irradiation of polyethylene by ionizing radiations. This is despite the fact that the production of unsaturation was shown many years ago to be a significant factor.[4-6] Although Charlesby[7] later estimated from indirect evidence that the production of unsaturation was negligible, the early observation[4,5] of this Laboratory on the formation of vinylene unsaturation during the irradiation has since been abundantly confirmed.[6,8,9-12] However, there still exists disagreement[6,8] concerning the magnitude of the production of unsaturation relative to that of cross linkages.

For the purpose of understanding the kinetic effects of irradiation it is important to have quantitative information on the efficiency of vinylene group production by the ionizing radiations. Thus, Pearson[13] has proposed kinetic mechanisms based on the reduction of the rate of formation of double bonds with time, as have also Simha and Wall.[14] Pearson's mechanism has been criticized

by Collyns, Fowler and Weiss.[15] Another theoretical paper is that of Okamoto and Isihara.[16]

In addition to the formation of vinylene-type double bonds, the initial irradiation causes the disappearance of vinylidene[6,12,17] and vinyl unsaturation[12] but, hitherto, the kinetics of such effects has not been thoroughly studied. These phenomena are important from the standpoint of illuminating the mechanism of energy transfer and of reactions in the solid state.

Finally, it is necessary to obtain accurate G values (olefinic groups per 100 e.v.) for vinyl and vinylidene disappearance as well as for vinylene production in order to approach the goal of achieving material balance in the irradiation of polyethylene.[18]

Apparatus and Methods

A. Radiation Source.—In May of 1956, 234 curies of cobalt-60 were obtained from the Oak Ridge National Laboratory in the form of nickel-plated wafers, one cm. in diameter. These were sealed into compartments on the front faces of two stainless steel blocks as illustrated in Fig. 1 and then placed into a recessed well into the bottom of which the mechanism holding the cobalt-60 was fastened as shown in Fig. 1. The well was surrounded on the sides and bottom by nine inches of lead. A worm gear and pinion arrangement enabled the stainless steel blocks to be moved a short distance back and forth in the horizontal direction by means of removable rods which passed through the upper protective housing.

The upper lead chamber,[19] which rolled on wheels in a track, also contained a recessed well opening downwards. The equipment to be irradiated could be lifted up and fastened into the upper well on a long rod after the upper tank had been moved forward.

B. Radiation Cells and Holder.—A brass holder was constructed with a rectangular tongue that fitted into the space between the cobalt-60 blocks. Into the holder could be placed a special Dewar vessel containing the irradiation cell. Although the Dewar vessel was necessary only at liquid nitrogen temperatures, it was used in all experiments

(1) Fulbright Fellow, 1956.

(2) On leave from A. E. R. E., Harwell, England.

(3) See, for example, abstract of paper by A. A. Miller and E. J. Lawton, presented before the Polymer Division at the September Meeting of the American Chemical Society, New York, N. Y., 1957.

(4) D. G. Rose, M.S. Thesis, Northwestern University, 1948.

(5) M. Dole, Report of Symposium IV. "Chemistry and Physics of Radiation Dosimetry," Army Chemical Center, Md., 1950, p. 120.

(6) M. Dole, C. D. Keeling and D. G. Rose, THIS JOURNAL, 76, 4304 (1954).

(7) A. Charlesby, Proc. Roy. Soc. (London), 215A, 187 (1952).

(8) E. J. Lawton, P. D. Zemany and J. S. Balwit, THIS JOURNAL, 76, 3437 (1954).

(9) A. Charlesby and W. H. T. Davison. Chem. and Ind., 232 (1957).

(10) W. C. Sears and W. W. Parkinson, Jr., J. Polymer Sci., 21, 325 (1956).

(11) D. S. Ballentine, G. J. Dienes, B. Manowitz, P. Ander and R. B. Mesrobian, ibid., 13, 410 (1954).

(12) A. A. Miller, E. J. Lawton and J. S. Balwit, J. Phys. Chem., 60, 599 (1956).

(13) R. W. Pearson, Chem. and Ind., 903 (1956); 209 (1957); J. Polymer Sci., 25, 189 (1957).

(14) R. Simha and L. A. Wall, J. Phys. Chem., 61, 425 (1957).

(15) B. G. Collyns, J. F. Fowler and J. Weiss, Chem. and Ind., 74 (1957).

(16) H. Okamoto and A. Isihara, J. Polymer Sci., 20, 115 (1956).

(17) M. Dole and C. D. Keeling, THIS JOURNAL, 75, 6082 (1953).

(18) M. Dole, D. C. Milner and T. F. Williams, ibid., 79, 4809 (1957).

(19) We are indebted to Mr. R. E. Betterley of the Mechanical Engineering Department of Northwestern University for assistance in the design of the steel framework and tanks which held the lead.
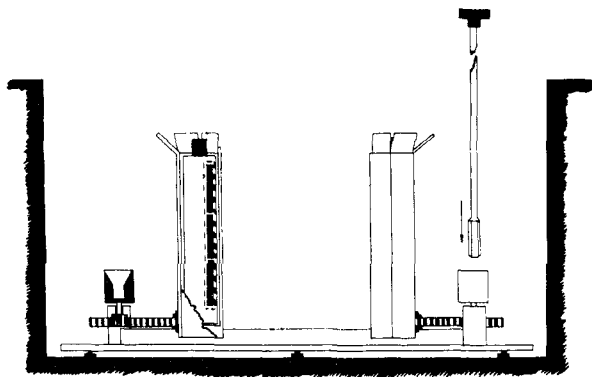
Fig. 1.—Schematic diagram of holder for the radioactive cobalt.

(filled with water at room temperature) in order that the radiation intensity might be maintained as constant as possible. The γ-ray intensity was reduced about 25% by the use of the Dewar flask. This reduction was mainly due to the fact that the irradiation cell within the Dewar was necessarily raised up about 1 to 1.5 cm. into a radiation region of smaller intensity.

The glass irradiation cells were of various types. Figure 2 illustrates a cell designed for two special purposes: (1) to measure by means of the Pirani gauge the rate of gas evolution at low pressures of hydrogen and (2) to enable the polyethylene film to be irradiated at liquid nitrogen temperature and then to be transferred to an infrared cell without warming to room temperature. Usually, a mercury manometer took the place of the Pirani gauge, and a cylindrical tube of glass of volume about 100 cc. took the place of the glass bubble. One type of glass cell had a detachable top which made possible the intermittent irradiation of the same film. This cell was used in the studies of the growth of the vinylene unsaturation and of the decrease in the vinyl group concentration.

Figure 3 illustrates a square aluminum frame for holding the polyethylene film which was used in connection with the special cell of Fig. 2. With the lower part of the glass cell immersed in liquid nitrogen, the glass bubble could be broken
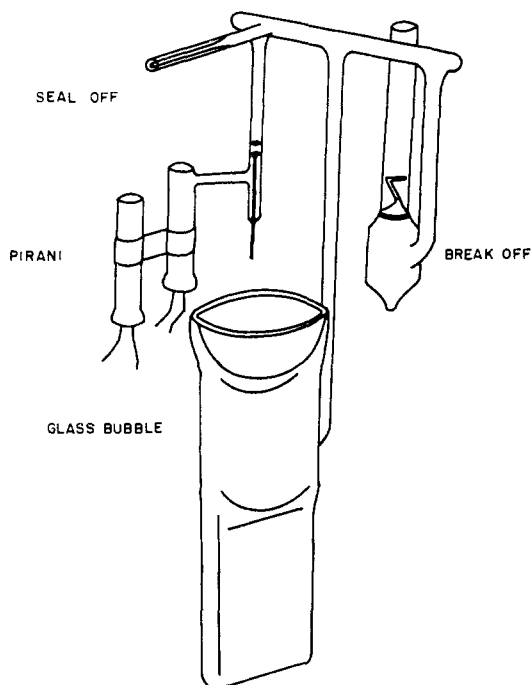

Fig. 2.—Cell for irradiation of polyethylene film at liquid nitrogen temperature.

and pierced by the plunger and the end of the plunger gripped by the spring clips as illustrated in Fig. 3. In this way the irradiated film could be removed from the irradiation cell and transferred to the infrared beam within the infrared cell illustrated in Fig. 4 without warming the film to room temperature.
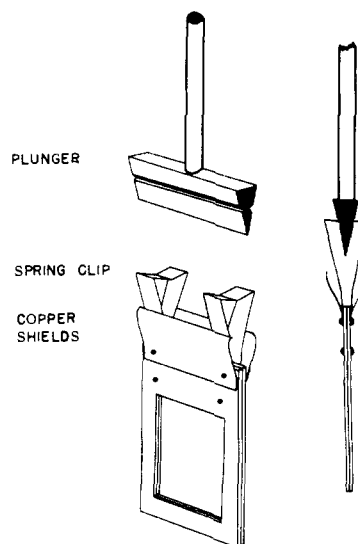

Fig. 3.—Details of film holder for use at liquid nitrogen temperature.

C. Dosimetry.—The determination of the absorption of the energy of the cobalt-60 γ-rays within the polyethylene in the cells was carried out using the $FeSO_4$ dosimeter taking $G(Fe^{+++})$ to be 15.6 ferric ions produced per 100 electron volts of energy absorbed. This value is intermediate between that found by Lazo, Dewhurst and Burton,[20] 15.8, and by Schuler and Allen,[21] 15.45.

Ferric ion concentrations were determined with a Beckman spectrophotometer taking 2,160 as the decadic molar extinction coefficient[20] for light of 304 mμ wave length and at 22.5°. A temperature correction[22] of 0.72% per degree (positive) was applied to the spectrophotometric measurements not at 22.5°. The half-life of cobalt-60 was taken to be 5.3 years in estimating the change of the intensity with time.

D. Infrared Cells and Equipment.—The polyethylene film was always attached to its support so that the bottom edge (bottom with respect to the cobalt-60 radiation cell) lined up with the bottom of the opening in the Masonite support.

The inner rock salt windows of the special infrared cell illustrated in Fig. 4 were attached to a glass ring according to the method of Frank and Stow.[23] The glass rings holding the windows were then sealed to the cell by means of the Shell Chemical Company's epoxide resin No. 828 using their curing agent U. The outer rock salt windows were sealed to a brass ring with Apiezon grease Type N, the force of the atmospheric pressure being sufficient to hold them in place. The vacuum jacket could be attached to a vacuum line for evacuation. When small leaks developed, they were eliminated by painting the rock salt to glass seals with a rubber solution. In Fig. 4, the horizontal arrow indicates the path of the infrared beam. In actual operation it was found that the temperature of the polyethylene film after removal from the liquid nitrogen bath and insertion into the infrared beam was about −125°.

E. Analytical Methods for Determination of Unsaturation.—Most of the measurements of the concentration of vinyl, vinylene and vinylidene unsaturation in the polyethylene were carried out by the infrared technique. The accuracy of this method depends on a knowledge of the

(20) R. M. Lazo, H. A. Dewhurst and M. Burton, J. Chem. Phys., 22, 1370 (1954).
(21) R. H. Schuler and A. O. Allen, ibid., 24, 56 (1956).
(22) W. Wild, Disc. Faraday Soc., 12, 113 (1952).
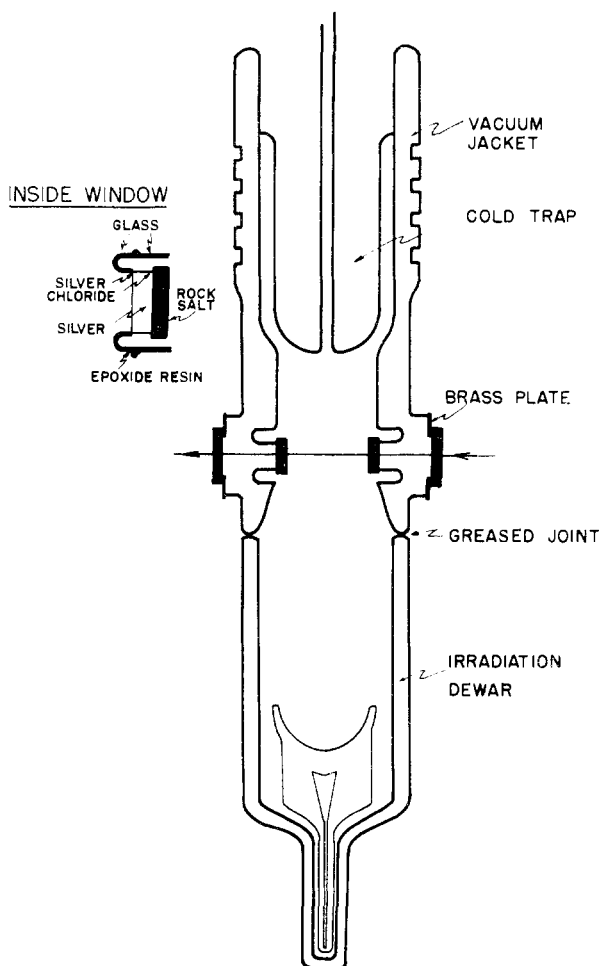(23) R. Frank and R. L. Stow, Rev. Sci. Instru., 25, 514 (1954).

Fig. 4.—Infrared cell and irradiation Dewar used at liquid nitrogen temperature.

thickness of the film and of the molar extinction coefficient. The film thicknesses were determined easily by weighing a known area of the film of known density. The vinyl group molar extinction coefficient ϵ was calculated from the equation

$$\epsilon = \frac{\log_{10}(T_0/T)\nu_{max}}{cl} \tag{1}$$

where c is concentration in moles/liter, l the film thickness in cm. and $\log_{10} T_0/T$ the apparent optical density at the maximum of the absorption band. If the true integrated absorption intensity A in the equation

$$A = \frac{\pi}{2cl} \ln \left(\frac{T_0}{T}\right)_{\nu_{max}} \Delta\nu^{1/2} \tag{2}$$

is known[24] as well as T_0/T and $\Delta\nu_{1/2}$, which is the width of the band at half intensity, the concentration c can be calculated. Richardson and Sacher[25] made a careful study of the integrated absorption intensity of a number of 1-olefins and concluded that A was equal to 4580 l. cm.$^{-2}$ mole^{-1} at the frequency 909 cm.$^{-1}$ (10.98 μ). By determining the optical density at the peak of the 10.98 μ band and by measuring its half width, 8.25 cm.$^{-1}$, for the high density polyethylene Marlex-50, we calculated that c for the vinyl group was 0.99 × 10^{-4} mole/g. or 0.095 mole/liter. Smith[26] found 1.00 × 10^{-4} mole/g. for the vinyl group concentration in Marlex-50. The molar extinction coefficient of the vinyl group calculated from eq. 1 using our c value was 153 l.cm.$^{-1}$mole^{-1}. Richardson and Sacher[25] recommend 149

(24) D. A. Ramsay, THIS JOURNAL, 74, 72 (1952).
(25) W. S. Richardson and A. Sacher, J. Polymer Sci., 10, 353 (1953).
(26) D. C. Smith, Ind. Eng. Chem., 48, 1161 (1956).

for polymers, Hampton[27] found 155 and Reynolds,[28] 150. We have adopted our estimate 153 for the calculations of this paper. For the other olefinic groups, the *trans*-vinylene and the vinylidene, we have used the extinction coefficients of 139 given by Hampton[27] and of 159 given by Richardson and Sacher,[25] respectively. All of these extinction coefficients as well as similar ones by Reynolds and by Shreve[29] are considerably greater than those based on the calculations of Cross, Richards and Willis[30] used in the first paper of this series.[6] This means that the unsaturation values of this paper are 40% lower in the case of the *trans*-vinylene group and 35% lower in the case of the vinylidene group than the values of our first paper. Our first research was not concerned with vinyl unsaturation.

In order to check the infrared results, an independent chemical method similar to that described by Mayo[31] was used to measure unsaturation both in unirradiated and irradiated samples. In the case of Marlex-50 the unirradiated film did not dissolve in CCl$_4$ solvent so that the vinyl concentration could be determined by the infrared method both before and after bromination. The average of two experiments gave a decrease in vinyl group concentration of 0.48 ± 0.05 × 10^{-4} mole/g. by the bromination method and 0.48 ± 0.08 × 10^{-4} by the infrared method. Such good agreement is fortuitous. In the case of a low density polyethylene, the entire film dissolved at the CCl$_4$ boiling point, and it was assumed that bromination completely saturated the olefinic groups. Total unsaturation measured by this method was 0.60 × 10^{-4} mole/g. while the infrared gave 0.414, 0.061 and 0.087 × 10^{-4} mole/g. for the vinylidene, *trans*-vinylene and vinyl groups, respectively. Adding, the total unsaturation as determined by the infrared method becomes 0.56 × 10^{-4} mole/g., in good agreement with the chemical method.

In the case of the irradiated films, the chemical results were much less reliable for a number of reasons. The films failed to dissolve completely in the carbon tetrachloride solvent; the correction for bromine substitution became very large and depended upon the length of time the KBrO$_3$ solution stood in contact with the film after titration with standard thiosulfate solution to the first end-point, or even to the second end-point; after bromination infrared studies demonstrated that this technique failed to brominate completely the olefinic groups. For these reasons the chemical method was not used to measure unsaturation in the irradiated films.

F. Materials.—The studies of unsaturation described in this paper were carried out on three types of polyethylene; (1) a low density, high pressure polyethylene (du Pont Code No. B-3125) containing initially vinylidene unsaturation; (2) high density Marlex-50 containing a relatively high concentration of vinyl groups; and (3) a Ziegler type polyethylene (Dow Code No. Q911) containing vinyl, vinylene and vinylidene unsaturation. Table I summarizes the properties of these samples.

TABLE I

PROPERTIES OF POLYETHYLENE SAMPLES

Name	B-3125	Marlex-50	Q-911
Concn., moles/g. × 10^{+4}			
Vinyl	0.087	0.99	0.207
trans-Vinylene	.061	.058	.064
Vinylidene	.414		.06
Density	.909	.956	.954
Ash content, %	.18	.11	.19
$\overline{M}_w$	266,000	74,990	
$\overline{M}_n$	17,500	12,300	53,000
Long chain branching index	12.0		

The concentrations of the olefinic groups and the densities given in Table I were determined in this Laboratory. The

(27) R. R. Hampton, Anal. Chem., 21, 923 (1949).
(28) J. G. Reynolds, Disc. Faraday Soc., 9, 323 (1950).
(29) O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, Anal. Chem., 22, 1261 (1950).
(30) L. H. Cross, R. B. Richards and H. A. Willis, Discs. Faraday Soc., 9, 235 (1950).
(31) F. R. Mayo, THIS JOURNAL, 75, 6133 (1953).

molecular weights and long chain branching index were determined by the suppliers while the molecular weights of Marlex-50 were taken from the paper by Tung.[32] In the determination of the vinylidene concentration the absorbance due to the ethyl group was corrected for by brominating the unirradiated film with bromine vapor to eliminate the vinylidene group so that the ethyl group absorbance could be directly measured. 75% of this absorbance was assumed to be present, following Bryant and Voter,[33] at a wave length of 11.25 μ, the wave length of the vinylidene group absorbance peak. The Dow Ziegler polyethylene, Q911, may have contained 0.1% catalyst impurities, mainly aluminum and titanium compounds. The molecular structure of Marlex-50 has been described by Smith.[26]

All of the materials were used as received except that for most of the infrared studies a slab of polyethylene 0.02 to 0.05 cm. thick was prepared in order to increase the sensitivity of the infrared measurements. This slab was made by heating and fusing together 4 to 10 thicknesses of 2 mil film under the pressure of an electric heater. This technique gave a clear thick film of good uniformity. All films were evacuated for 48 hr. before being irradiated in order to remove dissolved oxygen.

Results and Interpretation

A. Reduction in Vinyl, Vinylene and Vinylidene Unsaturation.—Figure 5 illustrates the decrease of the vinyl concentration of Marlex-50 with radiation dose during irradiation *in vacuo* and at room temperature. Most of the points on the graph were obtained in an experiment using a radiation cell with a removable top so that the thick film of Marlex-50 could be removed periodically for an infrared examination. Inasmuch as the film thus became exposed intermittently to oxygen of the air, some integral experiments were performed with no exposure to oxygen until the film was removed at the end of the experiment. The resulting vinyl concentration observed in these latter experiments agreed well with those obtained in the intermittent one. Similar curves were obtained for the disappearance of vinylidene unsaturation in B-3125 as shown in Fig. 5 and of vinyl unsaturation in the Ziegler polyethylene, Q-911.

The data for the decrease in concentration of the vinyl groups follow a first-order relationship up to about 50% reduction in concentration and to higher doses in the case of the vinylidene group. Uncertainty in the correction due to the ethyl group absorbance prevents us from concluding to what dose the first-order law is obeyed in the latter case.

Table II gives the constants of the equation

$$\ln \frac{[Vi]_0}{[Vi]} = k_1 D \qquad (3)$$

Table II

DECAY CONSTANTS AND G-VALUES FOR INITIAL VINYL AND VINYLIDENE GROUP DISAPPEARANCE

Polyethylene type	C_0, moles/g. $\times 10^4$	k_1, g./e.v. $\times 10^{21}$	$-G_0$(initial), molecules/ 100 e.v.
		Vinyl	
Marlex-50	0.99	1.61	9.6
Q-911	.21	1.43	1.8
		Vinylidene	
B-3125	.414	1.49	3.7

where [Vi] represents the vinyl group concentration in units of moles/g. after the accumulated

(32) L. H. Tung, *J. Polymer Sci.*, **24**, 333 (1957).

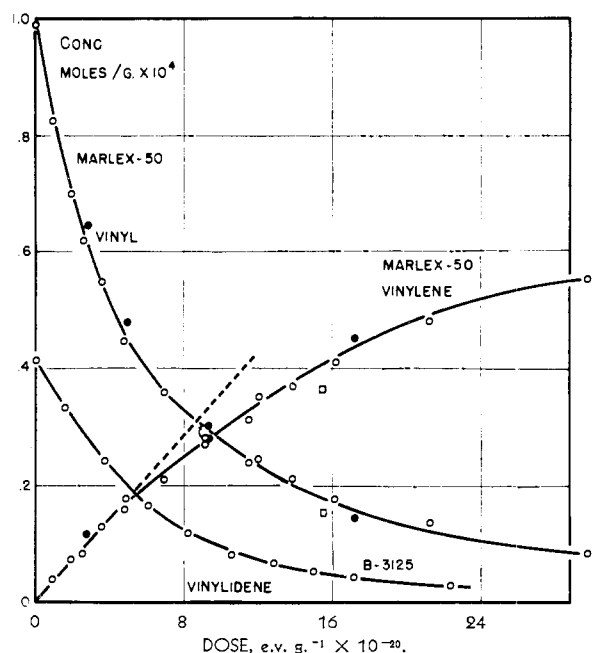(33) W. M. D. Bryant and R. C. Voter, This Journal, **75**, 6113 (1953).

Fig. 5.—Changes in unsaturation as a function of dose. Open circles represent intermittent irradiation; closed circles, continuous irradiation to the dose indicated and squares, continuous irradiation in presence of 0.9 atm. pressure of hydrogen gas. The vinyl and vinylene curves are for Marlex-50 and the vinylidene curve for B-3125 polyethylene.

dose D, $[Vi]_0$ the vinyl concentration at zero time and k_1 the first-order law decay constant.

Inasmuch as $G(-vinyl)$ is given by the expression

$$G(-[Vi]) = -100Nd [Vi]/dD \qquad (4)$$

where G is in units of molecules per 100 e.v. and N is Avogadro's number, $G_0 (-[Vi])$, the initial rate of vinyl group elimination, can be calculated from the equation

$$G_0(-[Vi]) = 100k_1 [Vi]_0 N$$

Thus, the initial G_0 is proportional to the initial vinyl group concentration, at least over the 5-fold concentration range studied.

In the kinetic papers previously mentioned,[13-16] there has been no discussion of the mechanism of vinyl group disappearance, although Pearson[13] adopted an earlier suggestion[6] of one of us that the vinylidene group reacts with a free radical center on a neighboring chain to form a cross link. Other possible mechanisms for the disappearance of vinyl or vinylidene groups include (1) isomerization in the case of vinyl to form a vinylene group, (2) reduction with atomic hydrogen to form a free radical, activation with subsequent reaction by (3) "sub-excitation" electrons,[34] (4) excitation energy or (5) positive charges. Because of the low concentration of the vinyl or vinylidene groups, about 0.1 mole/liter, a significant number of these groups cannot become activated by direct ionization in the primary event.

Although an extensive study has not been carried out by us at liquid nitrogen temperature, it is clear from the first results obtained that there is a defi-

(34) R. L. Platzman, *Radiation Research*, **2**, 1 (1955); see also J. Weiss, *Nature*, **174**, 78 (1954).

nite reduction in the rate of vinyl and vinylidene group disappearance at this low temperature. Charlesby and Davison[9] have noted a "slight" temperature dependence for vinylidene elimination. Table III contains infrared absorbance data taken with a Perkin–Elmer spectrophotometer on thin films, all measurements at about $-130°$. From the curve of Fig. 5, the vinyl concentration after an irradiation of 30×10^{20} e.v.g.$^{-1}$ at room temperature would have been 0.1 of its initial value; however, in the low temperature irradiation the value fell only to 0.91 of its initial value. A postirradiation heating to room temperature followed by cooling to $-130°$ for the infrared measurement showed a further decrease in the vinyl concentration to 0.71 of its initial value. This experiment indicates that free radicals are mobile enough in the solid polyethylene at room temperature to produce chemical changes.

TABLE III

OPTICAL DENSITIES OF POLYETHYLENES IRRADIATED AT LIQUID NITROGEN TEMPERATURE

All Infrared Measurements at about $-130°$

$\log I_0/I$

	Marlex-50			
Wave length, μ	10.05	10.35	11.00	11.25
Group	Vinyl	Vinylene	Vinyl	Vinylidene
Unirradiated	0.047	0.013	0.146	0
Irradiated to 32 $\times 10^{20}$ e.v./g.	.039	.1051	.133	0
Warmed to r.t. and recooled	.024	.1051	.104	0
	B-3125			
Unirradiated		0.016	0.02	0.129
Irradiated to 30 $\times 10^{20}$ e.v./g.		.100	.045	.098
Warmed to r.t. and recooled		.115	.032	.080

Similar to the decay of vinyl groups with irradiation is the decay of vinylene unsaturation produced by the irradiation. For this process the over-all equations are proposed

$$-CH_2CH_2- \leadsto \longrightarrow -CH=CH- + H_2 \qquad (5)$$
$$-CH=CH- \leadsto \longrightarrow x \qquad (6)$$
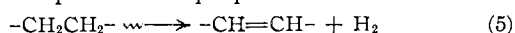
where (5) represents a zero-order process of vinylene growth and (6) a first-order elimination or decay of the vinylene group leading to the formation of an activated state x which reacts further. Equations 5 and 6 lead to the kinetic equation

$$\frac{d[V1]}{dD} = \varphi' - k_2[V1] \qquad (7)$$

where [V1] represents concentration of the vinylene group, and φ', the observed quantum yield of reaction 5 when [V1] equals [V1]$_0$. Integrating

$$[V1] = \frac{\varphi'}{k_2} (1 - e^{-k_2 D}) + [V1]_0 e^{-k_2 D} \qquad (8)$$

At infinite dose

$$[V1]_\infty = \varphi'/k_2 \qquad (9)$$

hence (8) can be written

$$\frac{[V1] - [V1]_0}{[V1]_\infty - [V1]_0} = 1 - e^{-k_2 D} \qquad (10)$$

Equation 10 is similar to one deduced by Pearson[13] and Simha and Wall.[14]

Pearson's postulated mechanism has to be rejected for the following reasons: the rate of hydrogen production at zero time should equal that of vinylene formation. This prediction is not verified as $G_0(H_2)$, the initial yield, equals ca. 4.0 (a paper on hydrogen production will be submitted for publication later) and G_0 (trans-CH=CH-) is only half as great. From the infrared data there is no detectable evidence of cis-vinylene formation. Pearson assumes that vinylene formation arises from the reaction

$$2 -CH_2CHCH_2- \longrightarrow -CH_2CH=CH- + -CH_2CH_2CH_2-$$
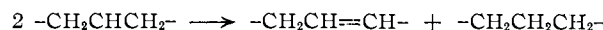
This cannot be the case; otherwise the vinylene production would be frozen out at liquid nitrogen temperatures because of the high viscosity of the solid, whereas its rate of formation is scarcely affected by temperature (ref. 9 and Table III).

Pearson's mechanism predicts that cross linking for the same total dose will be a function of the intensity for the ionizing radiations, contrary to observation.[35]

Simha and Wall[14] based their mechanism in part on a reaction of a free radical with atomic hydrogen to form the vinylene group, followed by a further reaction with atomic hydrogen to eliminate it. If by atomic hydrogen they refer to "thermalized" hydrogen atoms, their mechanism has to be rejected because of inability to conform with the observed temperature effects. The second mechanism for vinylene formation proposed by Simha and Wall is the same as Pearson's which has already been discussed. Both Pearson and Simha and Wall ignore ion–molecule type reactions or reactions involving molecular detachment of hydrogen like eq. 5. A further general criticism of their mechanism is that they treat the problem throughout from the standpoint of homogeneous solution kinetics without consideration of the existence of crystalline and amorphous regions within the polyethylene and without consideration of the high viscosity of the solid.

Equation 10 was tested by making a provisional estimate of k_2 from a plot of the change in rate of vinylene production versus [V1] and then plotting [V1] $-$ [V1]$_0$ as a function of $(1 - e^{-k_2 D})$. All of the vinylene growth data over the whole dose range and for all three types of polyethylene agreed within the experimental limits of error with this relationship, thus proving the validity of eq. 10. From the slopes of the straight lines [V1]$_\infty$ was calculated. The decay constants k_2 and the limiting vinylene concentrations at infinite dose are given in Table IV. The k_2 constants are nearly equal for all these polyethylenes, but the [V1]$_\infty$'s are not. This fact suggests that the reaction of eq. 5 is more efficient the more crystalline the polyethylene.

The first-order kinetics observed for both the vinylene and vinyl group decay requires that the excitation energy be localized; that is, all the excitation energy cannot be imagined to seek out the vinyl and vinylene groups until degraded, otherwise the decay would be zero order. We imagine the vinyl and vinylene groups to become activated

(35) A. Chapiro, J. chim. phys., 52, 246 (1955).

TABLE IV

DECAY CONSTANTS, G-VALUES FOR FORMATION AND LIMIT-
ING CONCENTRATIONS OF *trans*-VINYLENE GROUPS

Polyethylene type	k_2, g./e.v. $\times 10^{21}$	$[Vl]\infty$, moles/g. $\times 10^4$	G_6, obsd.	G_0,[a] no initial vinylene
Marlex-50	0.52	0.707	2.2	2.4
Ziegler, Q-911	.52	.57	1.8	2.0
B-3125	.58	.42	1.5	1.7

[a] These G_0 values were obtained by adding to G_0 (obsd.) $100k_2[Vl]_0\ N$ to allow for the small rate of destruction of vinylene groups at zero time.

in regions of localized excitation produced by the high energy recoil electrons as they traverse the polymer.[36,37] The probability of vinyl group activation thus becomes proportional to their concentration. Let E represent the number of excitation spheres or regions produced per 100 e.v. of energy absorbed, each of which may bring about the activation of a single vinyl group. Let n equal the number of chain segments, CH_2 units, any one or more of which will be excited, within the excitation sphere or spur; and let N_0 be the total number of CH_2 units per gram of polymer. We equate the fraction of vinyl groups reacting in dose dD, $d[Vi]/[Vi]$, to the ratio of CH_2 groups within all the spurs to N_0. If α is the probability of an activated vinyl group reacting, then

$$\frac{d[Vi]}{[Vi]} = \frac{\alpha E}{100} \times \frac{n}{N_0}\, dD \qquad (11)$$

The number n is the number of CH_2 groups in close enough proximity to a vinyl group so that the excitation energy absorbed by any one or more of the CH_2 groups can travel to the vinyl group. Hence

$$k_1 = \frac{\alpha E}{100}\, \frac{n}{N_0} \qquad (12)$$

The minimum value of αE for $G(\text{-vinyl})$ value of 9.6 is 9.6, and the minimum possible value of E must also be 9.6 (minimum value on the basis of one vinyl group reacting per excitation sphere). For this value of αE, n becomes equal to 720 segments. The diameter of a sphere containing 720 segments is 32 Å. or the length of one side of a cube of 720 segments is 26.0 Å. On the average, a sphere of this diameter in Marlex-50 initially will contain one vinyl group since we have used a value of αE corresponding to the initial G-value for vinyl decay.

The maximum possible value of E is set by energetics. Thus, in 100 e.v. absorbed, probably three or four ion pairs are produced, requiring about 30 to 40 e.v. inasmuch as the ionization potential of straight chain paraffinic hydrocarbons approaches 10 e.v. as the chain increases in length.[37] It is estimated that approximately 60 to 70 e.v. are then available for excitation. The thermal activation energy[38] of the vinyl group is about 2.16 e.v.; hence the maximum possible number of ex-

(36) This point of view bears certain analogies to the target theory which has been extensively developed by D. E. Lea "Actions of Radiations on Living Cells," 2nd Ed., Cambridge Univ. Press, 1955, Chap. III, but for ionizations, not for excitations.

(37) J. Lennard-Jones and G. G. Hall, *Disc. Faraday Soc.*, **10**, 18 (1951).

(38) P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 130.

citation spheres is 70/2.16 or 32. This yields a value of n equal to 174 and an effective excitation sphere diameter of 20 Å. However, if electronic excitation energy be considered, about 6.5 e.v. for olefinic type groups,[39] then the maximum possible number of excitation spheres per 100 e.v. is 70/6.5 or about 11. This is not much greater than the observed value of 9.6, a fact which suggests that $G(\text{-vinyl})$ cannot become greater than 11 even at much higher vinyl group concentrations.

In this treatment we have considered each excitation sphere as leading to the possible activation of one vinyl group. It has been estimated by Lea[36] and Pollard[40] that only one spur is produced per 100 e.v., so it is necessary to postulate that a multiple number of vinyl groups may disappear in each sphere up to a maximum value of E as considered above. The volume of such a spur is, therefore, equal to the volume which initially contains 9.6 vinyl groups in Marlex 50, or a volume containing 6.9×10^3 segments.

There is a possibility that the deviation of vinyl decay from the first-order law might be due to a slow production of vinyl groups from chain scission followed by disproportionation. If the latter can be expressed by a zero-order growth law, then eq. 10 should be applicable to the vinyl decay data. However, it was impossible to obtain agreement between data and theory, so this postulate for vinyl decay must be rejected. Instead, we postulate a deactivating process whereby vinylene groups can deactivate the activated vinyl groups before the latter can react. Let q be the number of chain segments associated with each activated vinyl group that can bring about the transfer of energy from vinyl to vinylene, then the fraction of vinyl groups which are deactivated by this process is proportional to $q[Vl]/N_0$, and the equation for the disappearance of vinyl unsaturation may be written

$$\frac{-d[Vi]}{[Vi]} = \frac{\alpha E}{100} \times \frac{n}{N_0}\left(1 - q\beta\frac{[Vl]}{N_0}\right) dD \qquad (13)$$

where β is a proportionality constant. The data suggest that at infinite time $d[Vi]/dD$ but not $[Vi]$ is zero; hence $q\beta[Vl]_\infty/N_0$ must equal unity and

$$1 - q\beta\frac{[Vl]}{N_0} = 1 - \frac{[Vl]}{[Vl]_\infty}$$

Substituting for $[Vl]/[Vl]_\infty$ from eq. 10 and integrating

$$\ln\frac{[Vi]_0}{[Vi]} = \frac{k_1}{k_2}\left(1 - \frac{[Vl]_0}{[Vl]_\infty}\right)(1 - e^{-k_2 D}) \qquad (14)$$

Equation 14 can be shown to describe the data within the experimental uncertainties for vinyl decay in both Marlex-50 and Ziegler Q-911 polyethylene. The requirement of eq. 14 that the vinyl concentration approach a non-zero value at infinite time cannot be rigorously tested because of the possible independent production of vinyl groups by the γ-radiation and because it is difficult to measure low vinyl group concentrations by the infrared technique. Nevertheless calculated predictions appear reasonable.
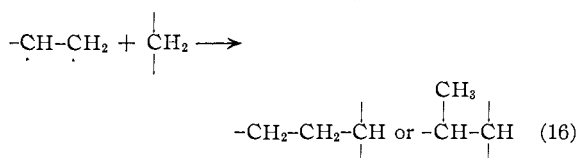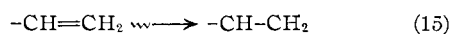
(39) E. P. Carr and H. Stücklen, *J. Chem. Phys.*, **4**, 760 (1936); THIS JOURNAL, **59**, 2138 (1937).

(40) E. Pollard, *Advances in Biol. and Med. Phys.*, **39**, 53 (1953).

An equation based on homogeneous kinetics for the competitive reactions of vinyl deactivation and vinyl decay failed to agree with the data.

In their ultraviolet absorption studies Carr and Stücklen[39] found four absorption bands for *trans*-butene-2 between 48,500 and 51,500 cm.$^{-1}$ which are all below the first absorption band for butene-1 at 53,000 cm.$^{-1}$. Overlapping bands also exist in this range. If the vinyl and vinylene groups in solid polyethylene have similar electronic energy states, then it is clear that the higher excitation energy of the vinyl group can be transferred to the lower or equally energetic electronic states of the vinylene group. The lower decay constant of vinylene groups and their low initial concentration coupled with the rapid disappearance of vinyl groups may explain in part why the rate law for vinylene growth appears to be independent of the vinyl concentration.

Charlesby[41] defined end-linking in terms of a scission of the carbon to carbon bonds along the main chain, followed by a reaction of these end groups with other chains to form C–C links and to eliminate atomic hydrogen. Such a reaction would have a large activation energy and appears, therefore, unlikely. Our definition of the term end-linking refers to activation of the vinyl group, followed by reaction with a saturated hydrocarbon chain

$$-CH{=}CH_2 \text{ \tiny{wv}} \longrightarrow -CH\text{-}CH_2 \qquad (15)$$

$$-CH\text{-}CH_2 + CH_2 \longrightarrow$$

$$-CH_2\text{-}CH_2\text{-}CH \text{ or } -CH\text{-}CH \qquad (16)$$

Reaction 16 is exothermic with a low activation energy ($\sim$ 8 kcal./mole) in comparison to the highly endothermic reaction of Charlesby.

$$R\cdot + CH_2 \longrightarrow R\text{-}CH + H \qquad (17)$$
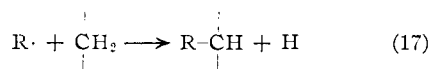
Referring to Tables II and IV it will be noted that the k for vinyl disappearance is nearly 3 times that for vinylene elimination. This is in line with the results of Charlesby[42] who obtained greater G-values for the cross-linking of 1-olefins than for other types. Because of the validity of eq. 10 over the whole irradiation period, there is no evidence for isomerization of vinyl to vinylene unsaturation. Furthermore, vinyl groups cannot be reacting with atomic hydrogen to any significant extent inasmuch as the hydrogen yield does not increase as the vinyl groups disappear. The initial G-value for vinyl disappearance, approximately $2G(H_2)$ seems to be too high to be explicable on the basis of elimination of vinyl unsaturation by reaction with free radicals. Thus, at least half of the hydrogen evolution occurs probably by molecular detachment, because of the zero temperature coefficient of vinylene formation. If the remaining hydrogen evolution resulted in free radicals, $G(R\cdot)$

would then equal four. But two free radicals would be required to combine with one vinyl group, so that a $G(R\cdot)$ equal to 19.2 would be necessary to account for the high value of $G_0(\text{-vinyl})$. These calculations are correct only if a chain reaction does not ensue. There is no evidence for chain reactions in solid polyethylene.

The high $G_0(\text{-vinyl})$ also would be difficult to explain on any mechanism involving sub-excitation electrons. Platzman[34] has estimated that 20% of the energy absorbed can be attributed to sub-excitation electrons. As the energy[39] required to excite the vinyl group is about 6.5 e.v., the energy content of the sub-excitation electrons is insufficient to give a $G_0(\text{-vinyl})$ of 9.6.

We also have considered the influence of a heterogeneous molecular weight distribution on the vinyl group decay law. If the assumption is made that excitation energy cannot pass branch points but can be localized anywhere along the whole length of a linear molecule, it is possible to explain the data on the basis of Tung's molecular weight distribution.[32] However, the assumption of the branch point barrier is inconsistent with the data for vinylidene decay in B-3125 which has many branch points.

In each unit of 100 e.v. of energy absorbed by the polyethylene there are possibly three ion pairs produced. The ionization potential is only of the order of 10–11 e.v., hence two-thirds of the absorbed energy is available for molecular excitation. This is more than enough energy to activate both the vinyl and vinylene groups. The sequence of reactions for the elimination of unsaturation may be postulated, therefore, as

a. Activation

$$-CH{=}CH_2 \text{ \tiny{wv}} \longrightarrow -CH\text{-}CH_2\cdot$$

$$-CH{=}CH\text{-} \text{ \tiny{wv}} \longrightarrow -CH\text{-}CH\text{-}$$

b. Reaction

$$-CH\text{-}CH_2\cdot + CH_2 \longrightarrow -CH_2\text{-}CH_2\text{-}CH \quad \text{(end-linking)}$$

$$-CH\text{-}CH\text{-} + CH_2 \longrightarrow -CH_2\text{-}CH\text{-}CH \quad \text{(cross-linking)}$$

The difference in the rates of vinyl and vinylene disappearance probably is to be found in the difference in the steric effects or frequency factors of the last two reactions.

Transfer of excitation energy is well known to occur,[43] but the interesting problem arises as to whether the transfer is along or across the polyethylene chains, i.e., intra- or intermolecular. A recent paper by Avivi and Weinreb[44] gives strong evidence in favor of intermolecular transfer which is also supported by the facts of this paper that the vinyl decay is not zero order.

B. Growth of Vinylene Unsaturation.—Inasmuch as the formation of vinylene unsaturation, apart from its elimination, is linear with radiation dose as clearly demonstrated by the data and practically independent of temperature, it is reasonable

(41) A. Charlesby, *Proc. Roy. Soc. (London)*, **A231**, 521 (1955).

(42) A. Charlesby, *Radiation Res.*, **2**, 96 (1955), as calculated by B. M. Talbert and R. M. Lemmon, *ibid.*, **3**, 52 (1955).
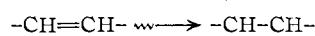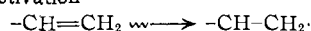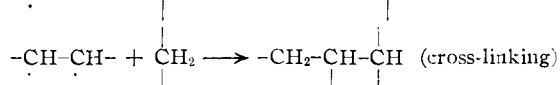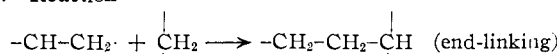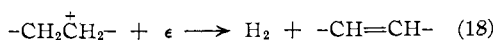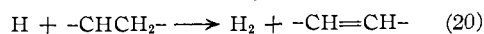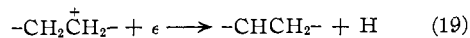
(43) For a review and discussion of this subject see J. Franck and R. Livingston, *Rev. Modern Phys.*, **21**, 505 (1949).

(44) P. Avivi and A. Weinreb, *J. Chem. Phys.*, **27**, 716 (1957).

to conclude that the vinylene group is formed in the primary act. By primary act we mean the first chemical process occurring on neutralization of the ions produced by the ionizing radiation. Such an equation could be

$$-CH_2\overset{+}{C}H_2- + \epsilon \longrightarrow H_2 + -CH=CH- \quad (18)$$

or

$$-CH_2\overset{+}{C}H_2- + \epsilon \longrightarrow -\overset{\cdot}{C}HCH_2- + H \quad (19)$$

$$H + -\overset{\cdot}{C}HCH_2- \longrightarrow H_2 + -CH=CH- \quad (20)$$

As long as the hydrogen atom produced in reaction 19 reacts immediately to abstract an H-atom from the same hydrocarbon chain according to reaction 20, it is meaningless to try to distinguish between the above two mechanisms. There is good evidence that the hydrogen atoms, if produced by reaction 19, do not exist as such long enough to become thermalized. Thus, one of us in collaboration with Livingston and Taylor attempted to detect atomic hydrogen at liquid nitrogen temperature by means of the paramagnetic resonance absorption method[45] after a heavy irradiation of low-density polyethylene at $-196°$, but without success.

Evidence that vinylene production occurs in the primary act is seen in the data obtained at $-196°$ given in Table III. Charlesby and Davison[9] observed only a slight decrease of $G(Vl)$ with reduction of temperature to $-196°$. If the elimination of vinylene unsaturation has a temperature coefficient, as is reasonable to suppose because vinyl elimination clearly does, then the net production of vinylene unsaturation at liquid nitrogen temperature would be expected to be greater than at room temperature. Actually, $G(Vl)$ does fall slightly at $-196°$ according to infrared measurements made at room temperature subsequent to the irradiation. The data of Table III demonstrate that warming to room temperature does not significantly alter the trans-vinylene concentration.

The decrease in trans-vinylene production at $-196°$ is paralleled by a decrease in $G(H_2)$, but the latter decrease is slightly greater, as would be expected on the basis of the reduction in vinylene elimination at $-196°$. Table V gives the ratio of G at $25°$ at $-196°$ for net hydrogen and vinylene production as measured in both cases after warming to room temperature. Although sufficient data do not exist to calculate the φ' and k_2 constants of eq. 8 for $-196°$, the relatively high $G(Vl)$ values indicate that production of $G(Vl)$ is probably linear with dose.

C. Cyclization.—Although the formation of ring links[18] (cyclization) does not increase the un-

TABLE V

INFLUENCE OF TEMPERATURE ON INTEGRAL G-VALUES FOR NET HYDROGEN AND VINYLENE PRODUCTION

Material	Marlex-50		B-3125	
Dose, e.v./g $\times 10^{-20}$	10	12.5	10	12.5
$G(H_2)_{25°}/G(H_2)_{-196°}$	1.47		1.21	
$G(Vl)_{25°}/G(Vl)_{-196°}$		1.21		1.14

(45) R. Livingston, H. Zeldes and E. H. Taylor, *Phys. Rev.*, **94**, 725 (1954).

saturation, nevertheless the two effects are related in the sense that whereas vinylene formation requires the splitting out of adjacent hydrogen atoms on the same chain, ring-link formation requires the splitting out of hydrogen atoms from the same chain but from positions separated by one or more CH_2 groups; hence cyclization will be discussed in this paper.

A preliminary announcement already has been made.[18] Figure 6 illustrates the growth in the infrared absorbance at 10.1 μ, which we have attributed to trans-1,2-disubstituted cyclopentanes or cyclohexanes. Concomitantly the vinyl peaks at 10.01 and 10.98 μ decline with the irradiation. Correcting for the overlap of the absorption band
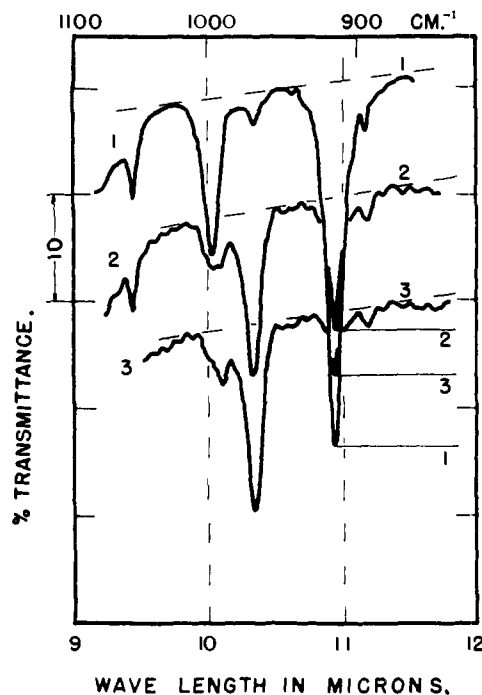

Fig. 6.—Infrared curves showing growth in peaks at 10.1 and 10.34 μ and decrease in peaks at 10.0 and 10.98 μ as a function of irradiation dose. Curves 1, 2, 3 were obtained after doses of zero, 14.4 $\times 10^{20}$ and 26.6 $\times 10^{20}$ e.v.g^{-1}, respectively.

due to the 10.01 μ vinyl absorbance, which can be done readily by making use of the fact that the optical density at 10.01 μ decreases with irradiation in the same proportion as does the 10.98 μ vinyl band, it is possible to calculate the increase in optical density at 10.1 μ with the irradiation dose. The results of this estimate show that except for the very early points, which are difficult to determine accurately, the optical density at 10.1 μ increases linearly with irradiation dose.

This absorption band cannot be due to post-irradiation oxidation,[10] because it does not increase or change in magnitude on standing in air after the irradiation in contrast to the carbonyl absorbance at 5.8 μ which grows slowly with time. The data for two integral experiments agreed fairly well with those of the intermittent experiment.

If the assumption is made that the absorbance at 10.1 μ is due to a 1,2-disubstituted cyclohexane

ring and if the extinction coefficient can be assumed to be equal to that of *trans*-1,2-dimethylcyclohexane, namely, 25 l. cm.$^{-1}$ mole^{-1} as calculated[46] from infrared spectra, then G (ring-link) can be estimated from the slope of the curve of optical density *versus* radiation dose for Marlex-50 to be 1.5. This is a surprisingly high value as it is the same order of magnitude as G(Vl), but it may be without quantitative significance because of the uncertainty concerning the nature of the absorbing group. For example, the absorbing group might possibly be a disubstituted cyclopropane.

It is difficult to measure the temperature coefficient of the optical density at 10.1 μ inasmuch as the much larger and overlapping absorbance due to the vinyl group does not disappear with irradiation at liquid nitrogen temperature. Some of this absorbance does disappear on warming to room temperature; hence a rough estimate can be made of the growth of the optical density at 10.1 μ. Two estimates for liquid nitrogen temperature irradiations of Marlex-50 (infrared spectra studied at room temperature) agreed fairly well with each other and demonstrate a temperature effect about equal to that for cross-linking (cross-linking will be discussed in a later paper). Thus, from this standpoint ring-link formation is more akin to cross-linking than to vinylene formation.

The slope of the curve for Marlex-50 is 1.35 times as great as that for the Ziegler polyethylene Q-911. As the increase in absorbance at 10.1 μ cannot be measured in the case of B-3125, if indeed, it exists at all, one thus sees a good correlation between the crystallinity of the polyethylene and rate of formation of ring-links. This trend is opposite to that of cross-linking inasmuch as Miller and Lawton[47] have noted a lower cross-linking effi-

(46) "Catalog of Infrared Spectral Data" of the Amer. Petroleum Institute Research Project, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

(47) A. A. Miller and E. J. Lawton, Preprints of Papers, Division of Paint, Plastics and Printing Ink Chemistry, A. C. S., Vol. XVII, No. 2, Sept. 1957.

ciency (as determined from solubility measurements) for highly crystalline Marlex-50 than for a low density polyethylene.

D. Comparison with Results of Others.— In this paper we shall not attempt a material balance calculation; instead a comparison with results of others will be given. Miller and Lawton[47] adopt Miller, Lawton and Balwit's[12] value of G(*trans*-CH=CH-) equal to 2.2 and state that it is independent of temperature and crystallinity. They assume that the rate of *trans*-vinylene production is linear up to 50 megaroentgen/g. (29.0 $\times$ 10^{20} e.v./g.). From the data of Fig. 5 and Table IV it is clear that the linear rate of vinylene production occurs only to about 8 megaroentgen/g. and that the efficiency of vinylene formation increases with the crystallinity. Charlesby and Davison[9] found 1.3 for G(*trans*-CH=CH-), an integral value for 20 megaroentgen.

The values of G(*trans*-Vl) given in Table IV are intermediate between the values of Charlesby and Davison, and Miller, *et al.* However, it should be noted that Miller and Lawton[47] take 5.7 for G(H$_2$) while Charlesby and Davison[9] found 3.1 and we, 4.0 (details to be published later). Miller and Lawton neglect the destruction of the initial unsaturation in computing a material balance. Charlesby and Davison give 0.74 for G(-vinylidene) while our result from Table II is 3.7 for the initial value. Charlesby and Davison's result represents an average value over 20 megaroentgen.

EVANSTON, ILLINOIS

A Magnetic Study on the Photodecomposition of p-(N,N-dimethylamino)-benzenediazonium Chloride

BY E. A. BOUDREAUX AND E. BOULET

A study of the mechanism of photodecomposition for the inorganic stabilized diazonium salt, p-(N,N-dimethylamino)-benzenediazonium chloride–zinc chloride dihydrate, in both buffered and non-buffered aqueous solutions has been investigated by magnetic susceptibility measurements. These measurements were conducted on the samples during the time of irradiation with ultraviolet light. The results indicate the presence of free radicals as intermediates in the formation of the products. The molar concentrations of free radicals calculated from the data are approximately 7.3×10^{-4}, 1.1×10^{-3} and 1.8×10^{-3} mole per liter, respectively, for two buffered solutions having pH 1.7 and 3.5 and for a non-buffered solution with pH 3.5.

The mechanism of the decomposition of diazonium salts has remained in a controversial state for some time.[1] Waters and his followers[2] present

(1) K. H. Saunders, "The Aromatic Diazo Compounds," Edward Arnold and Co., London, 1949, p. 105.

(2) W. A. Waters, *J. Chem. Soc.*, 113, 2007, 2014 (1937); 1077 (1938); 864, 1805 (1939).

very strong evidence for a free radical mechanism, but Hodgson and his co-workers[3-6] give evidence for an ionic mechanism. However, the views of

(3) H. H. Hodgson, S. Birtwell and J. Walker, *ibid.*, 770 (1941).

(4) H. H. Hodgson, *ibid.*, 348 (1948).

(5) H. H. Hodgson, *Chem. and Ind.*, 774 (1947).

(6) H. H. Hodgson, *J. Soc. Dyers Colourists*, 64, 99 (1947).