

ing and extremely helpful discussions during the 3rd International Conference in Quantum Chemistry, Uppsala, Sweden. Thanks are due to Dr. F. P. Lossing for providing results of his experimental determinations

of ionization potentials. The author also wishes to thank her colleague at RIAS, Dr. Ruth Aranow, for reading this manuscript prior to submission for publication.

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## The Free Radical, High Pressure Polymerization of Ethylene. II. The Evidence for Side Reactions from Polymer Structure and Number Average Molecular Weights

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RECEIVED JANUARY 26, 1963

Polyethylene polymerized isothermally in batch reactors at about 130 and 250° and at pressures of 800 to 3,000 atm. was characterized with respect to certain structural parameters and number average molecular weight. The methyl and vinylidene contents (per 1,000 CH<sub>2</sub>) both decrease with pressure, and increase with temperature, but the vinylidene content is more strongly affected by these parameters than is the methyl content. Under most conditions the unsaturation occurs largely in the form of vinylidene groups, but the vinyl content becomes competitive at high temperatures and pressures. There is a close correspondence between vinylidene content and molecular weight. The data indicate, in fact, that under the conditions of this study the major molecular weight-controlling step is associated with the formation of vinylidene groups. The decomposition ( $\beta$ -elimination) of a tertiary radical could lead to this result and is a step which has already been suggested as participating in the thermal degradation of polyethylene at higher temperatures. This step, together with Roedel's "backbiting" mechanism, as subsequently modified, can account for most of the data on polymer structure and molecular weights reported in this study. Some difficulty is experienced, however, in accounting quantitatively for all experimental facts, and some doubt remains as to the adequacy of the steps which have been proposed.

### Introduction

Several workers have attempted to gain information on the propagation and termination steps in the free radical polymerization of ethylene, yielding high molecular weight products, through kinetic studies carried out under isothermal conditions.<sup>1-3</sup> The existence in polyethylene, polymerized by free radical mechanisms, of branches and of unsaturation<sup>4</sup> testifies to the importance of isomerization reactions and of radical decomposition reactions.<sup>5</sup> In most cases the conclusions have been based on examination of commercial high pressure polyethylene, polymerized under conditions which are either unknown or not well defined, particularly with respect to temperature. The present study was undertaken to study branching, unsaturation and molecular weights of polyethylenes polymerized isothermally in batch reactors under known and well defined conditions, in an attempt to define more precisely some of the more important side reactions in the free radical high pressure polymerization of ethylene.

Polymerization rates are often strongly dependent on phase composition and their interpretation in heterogeneous systems is open to question.<sup>2</sup> Some doubt exists as to whether all samples for which data will be presented were polymerized under single-phase conditions. There was, however, no evidence that any heterogeneity which may have existed had any effect on the polymer properties measured.

### Experimental

**Sample Preparation.**—The polymer samples used for the infrared measurements were prepared at two temperatures. The low temperature (130°) synthesis was represented by samples prepared in the presence of 15 to 30 mole % propane in an earlier kinetic study.<sup>2</sup> The (varying) amounts of propane had no measurable effect on the methyl and vinylidene contents. It may be concluded in view of this, and of unpublished data, that the values of methyl, vinyl and vinylidene concentrations

are, within experimental error, independent of the propane concentration, from undiluted monomer to the highest propane concentrations employed.

The high temperature samples (250°) were prepared in the absence of propane and without adding initiator to the ethylene. Under these conditions reproducible polymerization rates could not be obtained, especially at the higher pressures, and it must be concluded that most or all of the initiation was the result of interaction of the ethylene with the trace amounts of oxygen contained in it.<sup>6</sup>

The number average molecular weights were determined for several samples made in the high temperature (250°) synthesis just described. The samples made at 130° in the presence of propane were unsuitable for a molecular weight study, since the objective was to study molecular termination in the absence of added transfer agent. Several samples were, however, available which had been polymerized, using di-*t*-butyl peroxide at 140° in the absence of propane and at pressures of 1,600 to 1,800 atm., as well as a sample polymerized elsewhere under similar conditions and by a similar technique.<sup>7</sup> In spite of the small difference in synthesis temperature, comparison of the molecular weights of these samples with the vinylidene contents of those polymerized at 130° in the presence of propane is relevant (see under Results). It will be for the 140° samples that the molecular weights, judged to be characteristic of the low temperature synthesis, in the absence of added transfer agent, will be reported. Reliable infrared determinations for the identical series could not be obtained because of difficulties in the sample preparation with this particular series, owing largely to the high molecular weights and limited amounts of polymer available.

The number average molecular weights were determined by osmotic pressure measurements.

**Infrared Analyses.**—Determinations of methyl, vinylidene, vinyl and *trans*-vinylene contents were made using a Beckman IR-7 spectrophotometer. Methyl content was determined from the 1378 cm.<sup>-1</sup> absorption, after compensating for methylidene absorptions at 1368 and 1352 cm.<sup>-1</sup>, by means of a wedge of linear polyethylene containing less than 0.3 methyl/10<sup>3</sup>CH<sub>2</sub>. Absorptions due to vinylidene, vinyl and *trans*-vinylene were measured at 888, 909 and 965 cm.<sup>-1</sup>, respectively. In the case of the first two of these, corrections for the absorption by the RCH<sub>2</sub>CH<sub>2</sub> group at 894 cm.<sup>-1</sup> had to be made, using the appropriate value of the methyl content measured at 1378 cm.<sup>-1</sup>.

Although the absorptivity for the symmetrical C-H bending mode of methyl groups at 1378 cm.<sup>-1</sup> is known to decrease with increasing length of the pendant alkyl branch, this variation occurs only as the branch changes from methyl to butyl.<sup>8</sup> Since the pendant branches are known to be primarily ethyl and butyl,<sup>9,10</sup> the absorptivity of a hydrocarbon with a long alkyl chain was

(1) R. K. Laird, A. G. Morrell and L. Seed, *Discussions Faraday Soc.*, **22**, 126 (1957).

(2) R. O. Symcox and P. Ehrlich, *J. Am. Chem. Soc.*, **84**, 53 (1962).

(3) R. H. Wiley, N. T. Lipscomb and F. J. Johnston, *J. Polymer Sci.*, **57**, 867 (1962); H. N. Friedlander, *ibid.*, **58**, 455 (1962); Z. Laita and Z. Machacek, *ibid.*, **38**, 459 (1959).

(4) J. J. Fox and A. E. Martin, *Proc. Roy. Soc. (London)*, **A175**, 226 (1940); T. F. Rugg, J. J. Smith and L. H. Wartman, *J. Polymer Sci.*, **11**, 1 (1953); L. H. Cross, R. B. Richards and H. A. Willis, *Discussions Faraday Soc.*, **8**, 235 (1950).

(5) L. Nicolas, *J. chim. phys.*, 177 (1958).

(6) P. Ehrlich and R. N. Pittilo, *J. Polymer Sci.*, **43**, 389 (1960).

(7) G. A. Mortimer and W. F. Hamner, paper presented before the Southwestern section of the American Chemical Society, Dallas, Tex., December 6, 1962; *J. Polymer Sci.*, in press.

(8) F. P. Reding and C. H. Lovell, *ibid.*, **21**, 157 (1956).

(9) A. H. Willbourn, *ibid.*, **34**, 569 (1962).

(10) D. A. Boyle, W. Simpson and J. D. Waldron, *Polymer*, **2**, 335 (1961).

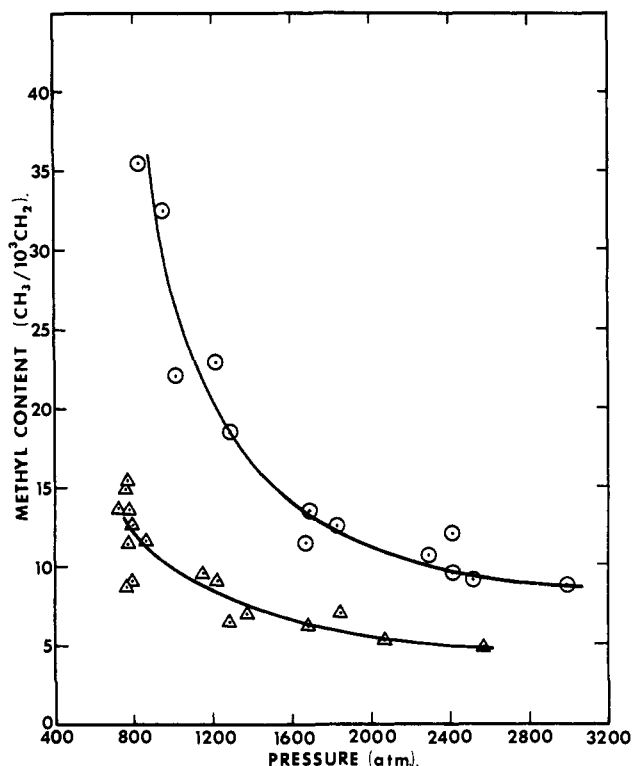


Fig. 1.—Methyl content as a function of polymerization pressure at polymerization temperatures of 130° ( $\Delta$ ) and 250° ( $\circ$ ).

used as standard. This standard was 1-tetradecene with a measured absorptivity of  $1.27 \pm 0.03 \text{ cm.}^2 \text{ g.}^{-1} 10^3 \text{CH}_2(\text{CH}_2)^{-1}$ . At ethyl/butyl ratios typical for high pressure polyethylene, use of this absorptivity might lead to an overestimate of about 15% in total methyl.

The absorptivities for the  $\text{RCH}_2\text{CH}_3$  absorption near  $894 \text{ cm.}^{-1}$  in several different polyethylene samples were measured after elimination of the interfering unsaturation by bromination. The values found, in units of  $\text{cm.}^2 \text{ g.}^{-1} 10^3 \text{CH}_2(\text{CCH}_2\text{CH}_3)^{-1}$ , were  $0.032 \pm 0.003$  at  $888 \text{ cm.}^{-1}$  and  $0.018 \pm 0.001$  at  $909 \text{ cm.}^{-1}$ .

The absorptivities for the C-H out-of-plane bending modes at 888, 909 and  $965 \text{ cm.}^{-1}$  for vinylidene, vinyl and *trans*-vinylene were evaluated from standard solutions in *n*-tetradecane of 2-ethyl-1-hexene, 1-tetradecene and 1-octadecene, and *trans*-4-octene, respectively, using *n*-tetradecane in the reference beam. The absorptivities, in units of  $\text{cm.}^2 \text{ g.}^{-1} 10^3 \text{CH}_2(\text{C}=\text{C})^{-1}$ , for vinylidene, vinyl and *trans*-vinylene were  $8.2 \pm 0.5$ ,  $9.3 \pm 0.2$  and  $7.5 \pm 0.3$ , respectively. These values are somewhat higher than the average values obtained by Anderson and Seyfried<sup>11</sup> for a series of model compounds whose structures were closely similar to those of the compounds used here.

### Results

Figure 1 presents the concentration of methyl groups of polyethylene samples polymerized at 130° and at 250°. All of the low temperature samples, obtained in the course of an earlier study,<sup>2</sup> had been polymerized in the presence of 15 to 30% propane, but the reproducibility of the results is not sufficient to establish the anticipated small increase in methyl content with propane concentration in this range. It is possible, therefore, to ignore this variable. The increase in methyl content with increasing temperature and decreasing pressure is clear. The high temperature data are sufficiently reproducible to indicate that the logarithm of the methyl concentration depends approximately linearly on pressure. The same general trends of methyl content with temperature and pressure have been noted before.<sup>1,7</sup> Polyethylenes with methyl contents too low to be observed by the methods employed have been synthesized at 60 to 80° and pressures of 5,000 to 7,000 atmospheres.<sup>12</sup> Figure 2 presents data

(11) J. A. Anderson and W. D. Seyfried, *Anal. Chem.*, **20**, 998 (1949).

(12) R. A. Hines, W. M. D. Bryant, A. W. Larchar and D. C. Pease, *Ind. Eng. Chem.*, **49**, 1071 (1957).

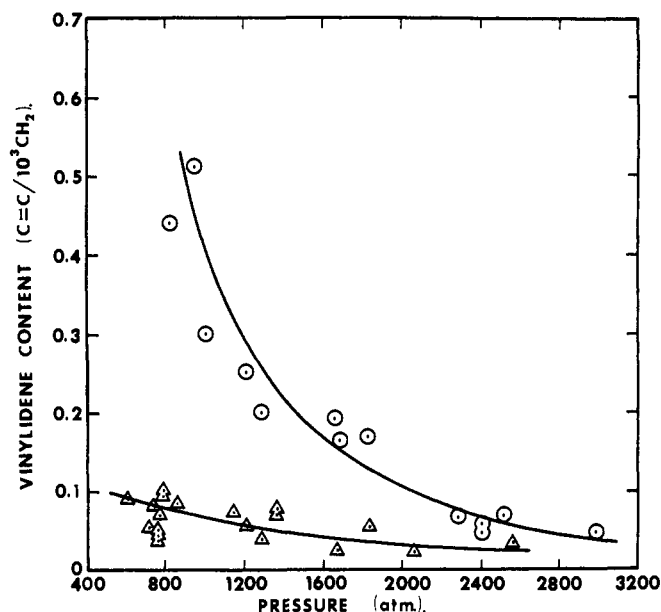


Fig. 2.—Vinylidene content as a function of the polymerization pressure at polymerization temperatures of 130° ( $\Delta$ ) and 250° ( $\circ$ ).

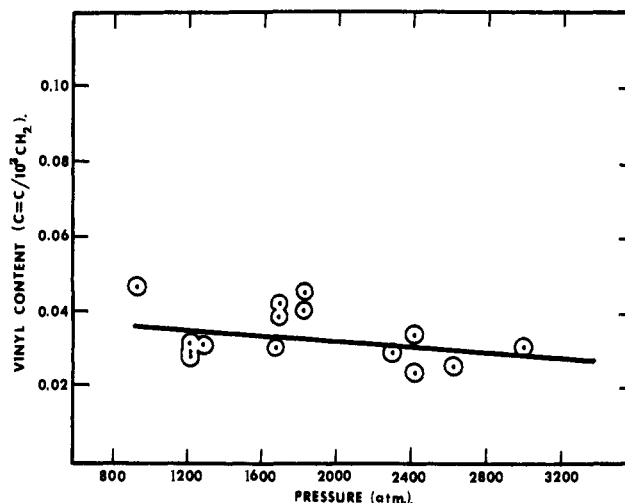


Fig. 3.—Vinyl content as a function of the polymerization pressure at a polymerization temperature of 250°.

for the concentration of vinylidene groups. Again, an increase with temperature and a decrease with pressure is to be noted. The vinylidene contents for the low temperature samples are of insufficient magnitude and reproducibility to establish the functional dependence on pressure. At the higher polymerization temperature this dependence can again be seen to be roughly semi-logarithmic, but greater than that of the methyl groups.

The vinyl contents of the 130° samples were less than  $0.015/10^3 \text{CH}_2$ . The values obtained were of doubtful significance and will not be reported. Results for the 250° samples are presented in Fig. 3. A small decrease in vinyl content with pressure seems indicated, although the reproducibility is insufficient to resolve the question with certainty.

*trans*-Vinylene measurements for samples polymerized at both polymerization temperatures gave values of  $0.01/10^3 \text{CH}_2$  or less and are considered to be of doubtful significance.

The processes leading to vinylidene groups are presumably also responsible for molecular termination, *i.e.*, they are chain transfer steps (see below). A relationship between vinylidene content and number average

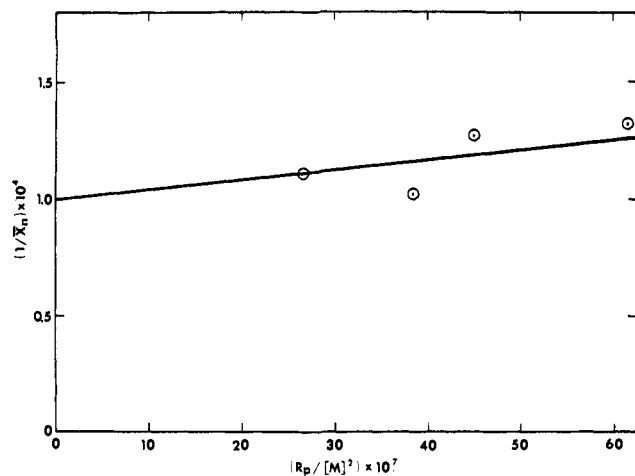


Fig. 4.—Reciprocal number average degree of polymerization vs.  $R_p/[M]^2$  for polymer prepared at 140°.

molecular weight might, accordingly, be expected, if these processes play an important role in molecular termination. The most convenient test for the presence and relative importance of chain transfer in molecular termination makes use of the equation  $1/\bar{X}_n = 1/\bar{X}_n^0 + (k_t/k_p^2)R_p/[M]^2$ . Figure 4 is a plot of  $1/\bar{X}_n$  vs.  $R_p/[M]^2$  where  $\bar{X}_n$  is the number average degree of polymerization,  $R_p$  the polymerization rate and  $[M]$  the monomer concentration.<sup>13</sup> The samples represented had been polymerized in the absence of propane at pressures of 1,600 to 1,800 atm. at 140°. This choice of samples was made in order to eliminate chain transfer to propane which is the main step responsible for molecular termination under the conditions of synthesis of the low temperature samples used for the infrared analysis.<sup>2</sup> Since the probability of vinylidene formation must be independent of the molecular chain length, it is legitimate to compare the molecular weights of the samples represented by Fig. 4 with the vinylidene contents of those represented by Fig. 2 (see also Sample Preparation). Figure 4 shows that the molecular weights are nearly independent of the polymerization rate and that the plot has a positive intercept on the y-axis. The slope, which represents  $k_t/k_p^2$ , is too small to be established with reasonable accuracy and is drawn in to be consistent with a value of 0.50 for  $k_p/k_t^{1/2}$ , obtained in the kinetic study carried out in the presence of propane.<sup>2</sup> The intercept,  $1/\bar{X}_n^0$ , is not very sensitive to the choice of  $k_p/k_t^{1/2}$ , and the strong dominance of a chain transfer process over bimolecular radical termination seems established. The limiting molecular weight is 280,000. Absence of termination by disproportionation has been assumed. If radical-radical termination occurred by disproportionation only, the limiting molecular weight would be reduced by about 20% and the limiting transfer constant would be increased correspondingly.

Figure 5 shows the number average molecular weight as a function of the polymerization pressure of samples polymerized at 250°. Reproducible polymerization rates could not be obtained in the preparative step because of the dominance of irreproducible amounts of oxygen initiation. Termination by radical-radical reactions should nonetheless be negligible and all molecular weights reported should correspond to the limiting molecular weights, corresponding to  $\bar{X}_n^0$ . This can be verified readily by comparing the number of molecules arising from coupling reactions, and equal to  $(k_t/k_p^2) \cdot R_p/[M]^2$ , with the total number created, and equal to  $1/\bar{X}_n$ . By extrapolating  $k_p/k_t^{1/2}$  found at 130° with an activation energy of 6 kcal., one obtains values of about

(13) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 4.

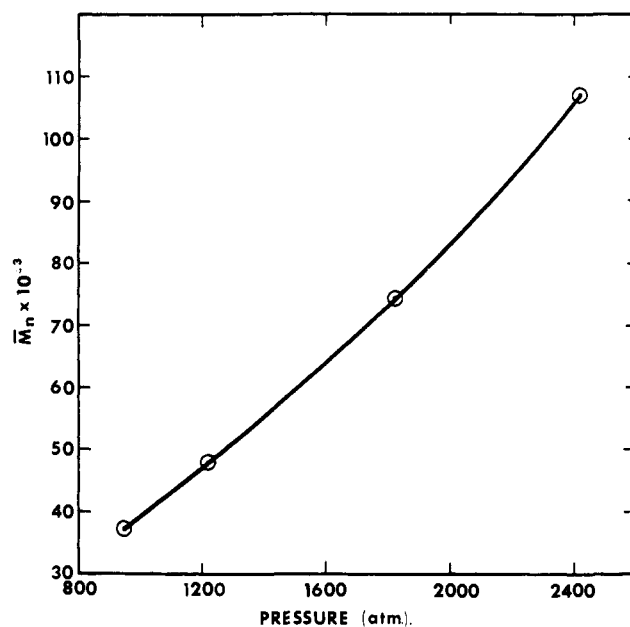


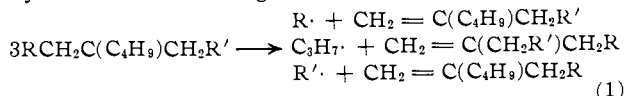
Fig. 5.—Number average molecular weight of polymer vs. polymerization pressure for polymer prepared at 250°.

1.5 to 4.0  $l^{1/2}$  mole<sup>-1/2</sup> sec.<sup>-1/2</sup> covering the range of 1,000 to 2,500 atm. Values of  $R_p$  are in the range of  $10^{-6}$  to  $5 \times 10^{-4}$  mole  $l^{-1}$  sec.<sup>-1</sup> and the monomer concentrations are 13 to 18 moles/l., leading to the result that  $(k_t/k_p^2)R_p/[M]^2$  is negligible compared to  $1/\bar{X}_n$ . This conclusion receives further support from the fact that Fig. 5 is a smooth curve, in spite of large and irregular variations in polymerization rates.

A calculation of vinylidene groups per molecule now becomes possible. The vinylidene content of the low temperature samples at the mid-point of the pressure range is about 0.5 vinylidene groups/ $10^3CH_2$ . At similar pressures, and in the absence of propane, the limiting molecular weight has been shown to be about 280,000, or somewhat lower, if allowance for disproportionation is made. This corresponds to about 1 vinylidene group per molecule. For the high temperature samples the vinylidene values correspond to from about 1.1 vinylidene groups per molecule at 1,000 atm. to 0.45 at 2,400 atm. If a vinyl value of 0.04 group/ $10^3CH_2$  is assumed valid at all pressures, one obtains a total unsaturation of about 1/molecule throughout the pressure range. Allowing for some experimental uncertainty, one may conclude that the chain transfer-controlled molecular termination, already found to be characteristic of the polymerization on the basis of the molecular weight data, is associated with the formation of unsaturated, primarily vinylidene, groups. Radical decomposition ( $\beta$ -elimination) reactions would therefore appear to be the dominant molecular weight-controlling steps in the absence of transfer agent, although a significant contribution due to transfer with monomer must not be ruled out at 250°.

#### Reaction Mechanism

Vinylidene in polyethylene may arise from the decomposition ( $\beta$ -elimination) of a tertiary polymer radical, by two of the following routes.

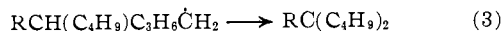


where R represents a long chain, and R' a short chain, branch. It has already been suggested that this reaction occurs during the thermal degradation of polyethylene at temperatures above 290°,<sup>14</sup> and that it may

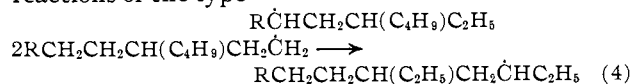
also be active in the synthesis of high pressure polyethylene.<sup>5</sup> Tertiary radicals might be formed simply as the result of a sequence including two intramolecular hydrogen abstraction ("backbiting")<sup>15</sup> steps. Considering only 1-5 shifts, we have



followed by two addition steps and a second abstraction step

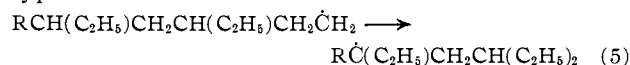


Such a mechanism cannot account for the origin of ethyl branches. Recent work has indicated that the ratio of ethyl to butyl groups in commercial high pressure polyethylene is probably at least unity, and may be as great as two.<sup>9,10</sup> It was therefore suggested that reactions of the type

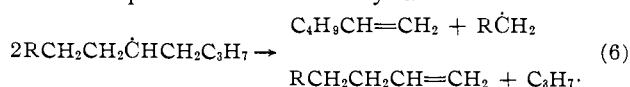


occur with a probability far greater than the isomerization of an unbranched radical (reaction 2). It was suggested further that reaction 4 followed by a simple addition step may repeat through several cycles, leading to the formation of several closely spaced branches.<sup>16</sup> There is some evidence that the structure of commercial high pressure polyethylene does indeed conform to this picture.<sup>10</sup>

We must examine to what extent the  $\beta$ -elimination and hydrogen abstraction reactions discussed account for the data on branching, unsaturation and number average molecular weights. As indicated, branches arise by several alternate paths involving side reactions 2, 2 followed by 3, and 2 followed by 4. Methyl groups at the end of long chain branches, and formed by intermolecular hydrogen abstraction, need not be considered because of their infrequent occurrence. Vinylidene formation involves side reactions 2, followed by 3 and 1, or 2 followed by 4, 5 and 1, where 5 is a reaction of the type



which leads to tertiary radicals. Vinyl can result from the decomposition of a secondary radical



preceded by reaction 2, or it can result from the disproportionation of two radicals, or from transfer with monomer. Neglecting the latter two possibilities, the concentration of methyl, vinylidene and vinyl groups can therefore be written in terms of the probabilities,  $P_i$ , of reactions 1 through 6 compared to the propagation reaction, *i.e.*, as  $k_i/(k_i + k_p[M])$ , where  $k_i$  stands for the rate constants of reactions 1 through 6,  $k_p$  stands for the propagation constant which can, and probably does, differ for primary, secondary and tertiary radicals, and  $[M]$  stands for the monomer concentration. The change in structure with temperature and pressure must also be accounted for in terms of these probabilities.

Qualitatively, this picture accounts for many of the experimental data. The moderate over-all activation energy for branching (2-3 kcal./mole) is accounted for by the small magnitude of the terms  $E_2 - E_p$ ,  $E_3 - E_p$  and  $E_4 - E_p$ , in accordance with accepted ideas. The logarithm of the methyl, vinylidene and vinyl contents should be approximately linear in pressure, as is indeed indicated by the data of Fig. 1 and 2, and the slope of

the semi-logarithmic plots should be given approximately by the appropriate combination of  $\Delta V^\ddagger$  terms, the volumes of activation for the respective reaction steps. If all branches were formed by Roedel's simple "backbiting" mechanisms,<sup>16</sup> one would have simply  $\partial \ln (\text{CH}_3/\text{CH}_2)/\partial P + \partial \ln [M]/\partial P = (\Delta V_p^\ddagger - \Delta V_2^\ddagger)/RT$ , where  $[M]$  stands for the monomer concentration and the subscript  $p$  for the propagation step. Analyzing the data in this manner, about -19 cc./mole is obtained for  $\Delta V_p^\ddagger - \Delta V_2^\ddagger$ , a value algebraically only slightly larger than that obtained previously<sup>2</sup> for  $\Delta V_p^\ddagger$ . This indicates that the absolute value of  $\Delta V_2^\ddagger$  is considerably smaller than that of  $\Delta V_p^\ddagger$ , as is true for many hydrogen abstraction reactions,<sup>17</sup> but quantitative conclusions concerning individual reaction steps should not be drawn, because a significant proportion of the branches arises presumably *via* a succession of backbiting steps. A more negative value in the over-all activation volume should be the result, but a definite assignment for the probabilities of the competitive paths seems premature (see below). The greater pressure dependence of the vinylidene content, compared to the methyl content, is readily accounted for by the requirement that more consecutive reactions have to take place, each of which has to compete with the propagation reaction which should have the larger pressure coefficient.

Some of the other data are more difficult to explain in terms of this simple mechanism. The temperature dependence of the vinylidene content is such as to yield an over-all activation energy of only 6 kcal. Since the activation energies of secondary radical decomposition reactions are believed to be in the range of 25-35 kcal./mole,<sup>18</sup> one has to conclude that the probability of decomposition of a tertiary radical is high, *i.e.*, substantially greater than 0.1 at 130° and unity at 250°. As will be seen, this seems in conflict with the methyl/vinylidene content. The apparent constancy of vinyl content with pressure at 250° is not readily explainable by means of the mechanism discussed, since a pressure dependence intermediate between that for the methyl and vinylidene contents should be observed, and since disproportionation reactions should make a negligible contribution. It is possible that a pronounced pressure dependence does exist, but is masked by the poor sensitivity of the vinyl measurements. Alternatively, hydrogen transfer to monomer could play a significant role at 250°.

We proceed to a more quantitative examination of the data. Although the writing of analytical expressions for the structural parameters in terms of the rate constants for reactions 1 to 6 involves some difficulties, one can readily estimate sets of approximate probabilities  $P_i$ . Table I describes the structure of poly-

TABLE I  
POLYETHYLENE STRUCTURE AND PROBABILITIES  
OF SIDE REACTIONS

Methyl/10 <sup>3</sup> CH <sub>2</sub>	14	$P_1$	0.2	0.04
Vinylidene/10 <sup>3</sup> CH <sub>2</sub>	0.17	$P_2$	.007	.009
Vinyl/10 <sup>3</sup> CH <sub>2</sub>	0.04	$P_3$	.007	.07
Ethyl/butyl	1	$P_4$	.1	.1
		$P_5$	.1	.5
		$P_6$	.004	.003

ethylene synthesized at 250° and 1,600 atm. and lists two possible sets of approximate probabilities satisfying such a structure, assuming an ethyl/butyl ratio of one. The  $P_i$  represent probabilities of abstraction reactions per active hydrogen or of  $\beta$ -scission per C-C bond, the

(14) W. G. Oakes and R. B. Richards, *J. Chem. Soc.*, 2929 (1949).

(15) M. J. Roedel, *J. Am. Chem. Soc.*, **75**, 6110 (1953).

(16) W. Simpson and J. M. Turner, as quoted in ref. 9.

(17) K. E. Weale, *Quart. Rev.*, **16**, 267 (1962); A. C. Toohy and K. E. Weale, *Trans. Faraday Soc.*, **58**, 2446 (1962).

(18) J. G. Calvert, *Ann. Rev. Phys. Chem.*, **11**, 41 (1960).

left column referring to the case of equal reactivity for tertiary and secondary hydrogen abstraction, the right column to the more realistic case.<sup>19</sup> We find that with either set of values the probability that a side chain ethyl radical abstracts a secondary hydrogen,  $P_4$ , must exceed  $P_2$  greatly if the substantial proportion of ethyl groups is to be accounted for. This was already noted by Willbourn, who did not consider the decompositions of secondary and tertiary radicals, however. If  $P_4$  is made greater than 0.1, a succession of ethyl branches spaced two chain carbons apart results and simple solutions become inadequate. It can be seen qualitatively that  $P_4$  must, however, be allowed to exceed 0.1 if ethyl/butyl values of 2, as reported by Willbourn, are to be accounted for. Note that in either column of Table I,  $3P_1$  is substantially less than unity. If set equal to unity, as required by the low temperature coefficient of the vinylidene content, hydrogen abstraction would have to proceed with greater ease from a secondary than from a tertiary hydrogen radical ( $P_2 > P_3$ ,  $P_4 > P_5$ ). It would therefore appear that the low experimental activation energy for vinylidene formation together with accepted data of relative rates of secondary and tertiary hydrogen abstractions

(19) K. O. Kutschke and E. W. R. Steacie in "Vistas in Free Radical Chemistry," Pergamon Press, New York, N. Y., 1959, p. 176.

cannot be satisfied simultaneously. One possible rationalization for  $P_1$  being less than unity over the entire temperature range would, however, be provided if the activation energy for vinylidene formation in the present case were far less than that for  $\beta$ -elimination in a simple system as indicated in reaction 1. Conceivably,  $\beta$ -elimination and monomer addition to the radical which is split off is a concerted process, resulting in a lowering of the activation energy.

The data of this study, therefore, although not necessarily in disagreement with previous ideas on the origin of branching and unsaturation in high pressure polyethylene, cannot provide a quantitative confirmation for the mechanisms which have been proposed, without additional postulates which at the moment appear to be of doubtful validity. It is quite possible that these difficulties will be resolved with a more detailed knowledge of polymer structure. The conclusion that, under the conditions described, vinylidene formation is associated with the principal mechanism responsible for molecular termination is, however, independent of these uncertainties.

**Acknowledgments.**—We are indebted to C. Crofoot for the molecular weight measurements, to Dr. G. A. Mortimer for providing data on one of his samples, and to Prof. W. H. Urry for discussions.

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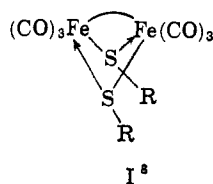
## Organosulfur Derivatives of the Metal Carbonyls. IV. The Reactions between Certain Organic Sulfur Compounds and Iron Carbonyls<sup>1</sup>

By R. B. KING<sup>2</sup>

RECEIVED NOVEMBER 6, 1962

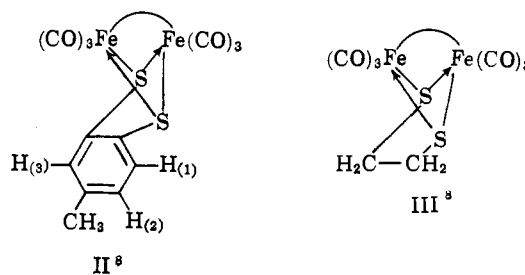
Iron pentacarbonyl was found to react with the sulfur derivatives 3,4-toluenedithiol, 1,2-ethanedithiol and bis-(trifluoromethyl)-dithietene to give the compounds  $C_7H_8S_2Fe_2(CO)_6$ ,  $C_2H_4S_2Fe_2(CO)_6$  and  $C_4F_6S_2Fe_2(CO)_6$ , respectively. Triiron dodecacarbonyl reacted with either  $(CF_2)_2S_4$  or  $(CF_2)_4S_3$  to give  $C_2F_4S_2Fe_2(CO)_6$ . These new iron complexes are red, volatile, crystalline, diamagnetic and air-stable solids. The reaction between  $C_3F_7Fe(CO)_4I$  and  $CF_3SAg$  in benzene solution was found to give yellow crystalline volatile  $[C_3F_7Fe(CO)_3SCF_3]_2$ . The structures of these new compounds are discussed.

Recently a variety of organosulfur derivatives of general formula  $[Fe(CO)_3SR]_2$  (I) (R = methyl, ethyl, isopropyl, phenyl, or naphthyl)<sup>3-7</sup> have been prepared by reactions between triiron dodecacarbonyl and appropriate mercaptans, sulfides, or disulfides. In



view of the existence of these compounds it seemed of interest to synthesize related compounds such as II or III in which the two sulfur atoms are joined by a carbon chain. Such compounds might be expected to be especially readily formed and to exhibit special stability due to an effect similar to that responsible for the stabilization of various chelate derivatives.

The most obvious route for the synthesis of compounds such as II and III is the reaction between an appropriate 1,2-dithiol derivative and iron pentacar-



bonyl or triiron dodecacarbonyl. In this connection the reaction between the commercially available 3,4-toluenedithiol and iron pentacarbonyl was investigated and found to give stable, volatile red crystals of the composition  $C_7H_8S_2Fe_2(CO)_6$  expected for II. The yield was about 20% when iron pentacarbonyl was used. In order to obtain yields of this order of magnitude in the preparation of the  $[Fe(CO)_3SR]_2$  compounds where the R group does not act as a bridge between the two sulfur atoms, it is necessary to use the more reactive triiron dodecacarbonyl.

The properties of this new organosulfur derivative

(8) Recent X-ray studies on  $[Fe(CO)_3SC_2H_5]_2$  have indicated the presence of a bent iron-iron bond and a molecular geometry similar to that of  $Co_2(CO)_8$ .<sup>10</sup> The analogous compounds described in this paper undoubtedly possess a similar structure and are therefore depicted in the structures with bent iron-iron bonds.

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