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# On the Mechanism of Autoxidation of Three Vinyl Polymers: Polypropylene, Ethylene–Propylene Rubber, and Poly(ethyl acrylate)

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The rates of oxygen absorption and chain scission have been measured for the benzoyl peroxide initiated oxidation of atactic polypropylene, an ethylene–propylene rubber (35 mole % propylene), and poly(ethyl acrylate) at 85–110°. Evidence is presented to show that, at all kinetic chain lengths, one initiating radical produces one-chain scission in the absence of side-chain oxidation. This is consistent with the proposal that in certain cases the interaction of two peroxy radicals is the rate-determining step for scission, and that scission does not in certain cases produce propagating radicals.

## Introduction

The generally accepted scheme for the initiated oxidation of hydrocarbons is given by[1–4]

$$\begin{aligned}
&\text{Initiation:} && \text{initiator} \xrightarrow{k_d} 2R'\cdot \\
& && R'\cdot + RH \xrightarrow{k_1} R'H + R\cdot \\
&\text{Propagation:} && R\cdot + O_2 \xrightarrow{k_2} RO_2\cdot \\
& && RO_2\cdot + RH \xrightarrow{k_3} ROOH + R\cdot \\
&\text{Termination:} && \left.\begin{aligned} R\cdot + R\cdot &\xrightarrow{k_4} \\ R\cdot + RO_2\cdot &\xrightarrow{k_5} \\ RO_2\cdot + RO_2\cdot &\xrightarrow{k_6} \end{aligned}\right\} \text{nonradical products}
\end{aligned}$$

At high oxygen pressures (usually above 200 mm., depending on temperature and the reactivity of the substrate), the rates of oxygen absorption become pressure independent indicating that all termination occurs by the interaction of peroxy radicals.[5,6]

Making the usual steady-state assumptions gives the expression

$$d(O_2)/dt = k_3[2e_ik_d(I)]^{1/2}(RH)/k_6^{1/2} + x2e_ik_d(I) \quad (1)$$

where $e_i$ is the efficiency of initiation, the fraction of radicals from the initiator I that attack the hydrocarbon and initiate oxidation chains, and $x$ is the number of molecules of oxygen absorbed in the initiation and termination reactions. The value of $x$ will depend on the initiator used and on the mechanism of termination.

Liquid hydrocarbons containing allylic or benzylic hydrogens and initiated by azobisisobutyronitrile or benzoyl peroxide have been the subjects of most kinetic studies.[7–11] Considerable effort also has been devoted to the initiated oxidation of natural rubber.[12,13] In such a system, studies of the changing molecular weight of linear polymers or chemical stress relaxation for cross-linked polymers provide additional information concerning the oxidation mechanism, giving the rate of cleavage of the carbon–carbon bond along the backbone of the polymer.[14] In work on model compounds this rate is obtainable only by spectral studies or product studies which become inaccurate at low conversions.[7]

In natural rubber oxidation, attempts were made to associate the scission reaction with a definite kinetic step. High yields of peroxides and hydroperoxides that can initiate new chains and the possibility of numerous side reactions have complicated some results leaving the problem open to further investigation.[15]

In the present work we have studied at 85–105° the kinetics of oxygen absorption and chain scission for the benzoyl peroxide initiated oxidation of atactic polypropylene which is the simplest saturated polymeric hydrocarbon with a tertiary hydrogen. The results are compared with similar work on an ethylene–propylene rubber containing 35 mole % propylene and on poly(ethyl acrylate).

## Experimental

**Materials.**—Amorphous polypropylene (Hercules Powder Co. X13532-47) with a density of 0.87 and a $\bar{M}_n$ of 50,000 as determined by osmometry[16] (Mechrolab 501) was used as provided in the oxygen absorption runs and was cross linked as described below for stress relaxation measurements.

Two samples of ethylene–propylene rubber (Goodyear Rubber Co. EP440 and EP179) were provided as cross-linked 10-mil. sheets. These had a reported propylene content[17] of 35 mole % and a density of 0.85. The samples had been dicumyl peroxide cured (4.0 and 3.5 wt. % of peroxide, 20 min. at 160°). These were extracted with benzene (Soxhlet extractor) for 6 hr., dried *in vacuo* at room temperature for 2 days, and then heated *in vacuo* for 1 hr. at 120° to destroy any hydroperoxides that may have formed during the extraction.

Ethyl acrylate and 1 mole % ethylene glycol dimethacrylate (Borden Chemical Co.) were photopolymerized into 15-mil sheets as previously described.[18]

Benzoyl peroxide (Borden Chemical Co.) was recrystallized from chloroform–methanol, m.p. 104–105°.

**Cross Linking.**—The amorphous polypropylene was pressed into 15-mil sheets under 40,000 p.s.i. (Pasadena hydraulic press) for 15 min. at 100°, swollen in saturated benzoyl peroxide–benzene for 3 hr. at room temperature, and then placed *in vacuo* for 24 hr. The sample containing peroxide was then pressed into 8-mil sheets at 95° for 2 hr., extracted with benzene, dried, and heat treated as were the ethylene–propylene rubber samples. Dicumyl peroxide at 120–140°, incorporated into the sample by similar methods, did not give a satisfactorily cross-linked sample. Eight sheets of slightly different cross-link densities were prepared.

**Incorporation of Peroxide.**—Weighed pieces of cross-linked polymer were swollen in benzoyl peroxide–benzene solutions. After 2 days *in vacuo*, weighings gave the amount of incorporated

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[1] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 418–427.

[2] L. Bateman, *Quart. Rev.* (London), **8**, 147 (1954).

[3] N. Grassie, "The Chemistry of High Polymer Degradation Processes," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 175–190.

[4] N. Uri in "Autoxidation and Antioxidants," Vol. I, W. O. Lundberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, pp. 65–77.

[5] H. J. L. Backstrom, *Z. physik. Chem.*, **B25**, 99 (1934).

[6] E. J. Bowen and E. L. Tietz, *J. Chem. Soc.*, 234 (1930).

[7] H. S. Blanchard, *J. Am. Chem. Soc.*, **81**, 4548 (1959).

[8] H. Boardman, *ibid.*, **84**, 1376 (1962).

[9] L. Bateman and A. L. Morris, *Trans. Faraday Soc.*, **48**, 1149 (1952).

[10] J. L. Bolland, *ibid.*, **44**, 669 (1948).

[11] G. A. Russell, *J. Am. Chem. Soc.*, **77**, 4583 (1955).

[12] E. M. Bevilacqua, ref. 4, Vol. II, 1962, pp. 867–869.

[13] A. V. Tobolsky and A. Mercurio, *J. Am. Chem. Soc.*, **81**, 5535 (1959).

[14] A. V. Tobolsky, "Properties and Structure of Polymers," John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 223–265.

[15] E. M. Bevilacqua and E. S. English, *J. Polymer Sci.*, **49**, 495 (1961).

[16] Experiment by Mr. H. Horton.

[17] R. M. Pierson, private communication.

[18] A. V. Tobolsky, D. W. Carlson, and N. Indictor, *J. Polymer Sci.*, **54**, 175 (1961)

benzoyl peroxide. A linear relation was obtained between the benzoyl peroxide concentration in the benzene solutions and the benzoyl peroxide incorporated per gram of sample for a given cross-link density. This relation could be used to determine low levels of incorporated peroxide when weighing errors could be considerable.

**Stress Relaxation.**—The techniques have been described previously.[19] Oxygen was flushed through the relaxometer until the continuous and intermittent rates[14] of scission were the same, indicating that no cross linking (termination by steps 4 and 5 of the mechanism presented in the Introduction) was taking place. The flow rate was about 200 cc./min. Runs were made at constant elongations of *ca.* 10%.

**Oxygen Absorption.**—Rates of oxygen absorption on 0.1 and 0.2 g. of cross-linked sample were run in 10-cc. tubes attached to a single water-jacketed manometer–buret (0.4-mm. glass tubing). Dioctyl phthalate was used as the indicating fluid. The tube was half-filled with calcium oxide to absorb volatiles.[20] Glass wool was placed between the CaO and the sample which was stuck to the side of the tube. The system was evacuated, and then filled with oxygen which had been passed through silica gel. This was found to be necessary to eliminate apparent absorption on blank runs. The cell was immersed in a silicone oil constant-temperature bath whose temperature was maintained ±0.2° by a heating mantle around the bath and an intermittent heater immersed in the oil. The latter heater was controlled by a bimetal thermoregulator and supersensitive relay (American Instrument Co.). Temperature equilibration was reached within 200 sec. All runs were made at constant pressure at 1 atm. of oxygen. Rates on uncross-linked samples were made by casting films (2 mils) of the polypropylene–benzoyl peroxide from benzene on the inside of 50-ml. round-bottom flasks which were used in place of the tubes. A small vial of CaO was placed inside the flask to absorb volatiles. Cross-linked polypropylene gave rate constants similar to the linear samples, although the vial of CaO was not so efficient as the CaO in the tube in trapping the volatiles. CaO was found superior to silica gel, Ascarite, KOH, Drierite, and various combinations. Rates were shown to be independent of oxygen pressure above 230 mm. at 100° for a sample containing $7.5 \times 10^{19}$ molecules of benzoyl peroxide/cc. of polypropylene. Nitrogen was used as the diluent for oxygen. Rates were also shown to be independent of sample thickness in the range 2 to 15 mils. Absolute rates of oxygen absorption with the tube apparatus were found to agree within 10% with rates taken on identical samples at the Hercules Research Center.[21] The tube apparatus was also used for determining under nitrogen the rates of volatile evolution from benzoyl peroxide in poly(ethyl acrylate).

Densities were determined by water displacement in a Weld pycnometer at 25°.

## Results

In the presence of oxygen the much studied radical-induced decomposition of benzoyl peroxide becomes negligible.[22–24] More certain rates of radical production are expected in the initiation of oxidations than in polymerizations; yet Hammond and Nandi[25] have reported that benzoyl peroxide is an inefficient initiator in tetralin oxidation and hardly an initiator at all for cumene unless the oxidation is carried out in nonaromatic solvents. However, Bolland[10] found benzoyl peroxide a suitable initiator for ethyl linoleate, and recently Boardman[8] reported that it initiates the oxidation of *p*-cymene.

We have found benzoyl peroxide a good initiator for polypropylene, ethylene–propylene rubber, and poly(ethyl acrylate) with initiation efficiencies comparable to those found in polymerizations, as we will show subsequently.

The unimolecular decomposition rate constant $k_d$ for benzoyl peroxide used in this study was arrived at by compiling the values obtained by numerous authors[22–34] at a variety of temperatures on an Arrhenius plot. A best straight line was drawn giving the values at various temperatures listed in Table I. These values were confirmed by following the rates of volatile evolution from benzoyl peroxide in poly(ethyl acrylate) in the absence of oxygen. In this polymer, hydrogen abstraction by the benzoyloxy radical should be slow because of the electron-withdrawing nature of the carbethoxy group. A majority of the benzoyloxy radicals will decompose into $CO_2$ and phenyl radicals which will abstract hydrogen.[31,35] Above 85° benzene and $CO_2$ will appear as volatile products. Plots of the log of the rate of volatile evolution *vs.* time for benzoyl peroxide concentrations less than $2.0 \times 10^{20}$ molecules/cc. gave straight lines for over several half-lives. From the slope, $k_d$ could be evaluated assuming a constant ratio of volatiles per cleaved peroxide throughout the reaction (about 1.8, as discussed later). These values are listed for comparison in Table I.

TABLE I

DECOMPOSITION RATE CONSTANT[a] FOR BENZOYL PEROXIDE

| Temp., °C | Our value[b] | Volatile evolution | Lit. range |
|---|---|---|---|
| 85 | 0.61 | 0.55 | 0.30–1.5 |
| 90 | 1.10 | 1.08 | 0.55–2.6 |
| 95 | 1.90 | . . | 0.95–4.2 |
| 100 | 3.30 | 3.10 | 1.5 –7.2 |
| 105 | 5.60 | . . | 2.9 –10.2 |
| 110 | 9.10 | . . | 4.0 –18.3 |

[a] $k_d$ (sec.$^{-1}$) $\times 10^4$. [b] Best straight line from Arrhenius plot ($E_{act}$ = 29.6 kcal./mole).

**Kinetics of Oxygen Absorption.**—If the terms of eq. 1 are divided by $2k_d(I)$ we get

$$\frac{d(O_2)/dt}{2k_d(I)} = \frac{k_3 e_i^{1/2}(RH)/k_6^{1/2}}{(2k_d(I))^{1/2}} + xe_i \qquad (2)$$

The concentration of initiator in the polymer and $k_d$ are known. $d(O_2)/dt$ is easily measured and this rate can be extrapolated to zero time so that the initial value of the initiator can be used in eq. 2. This also avoids complications of hydroperoxide decomposition initiating new chains at higher conversions.

If $(dO_2/dt)_0/(2k_d(I)_0)$ is plotted against $(2k_d(I)_0)^{-1/2}$, the slope is $k_3 e_i^{1/2}(RH)/k_6^{1/2}$ and the intercept should be $xe_i$.

The data for the three polymers demonstrate that oxygen absorption for the three is in agreement with the accepted scheme.

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(19) A. V. Tobolsky, I. B. Prettyman, and J. H. Dillon, *J. Appl. Phys.*, **15**, 380 (1944).

(20) J. E. Wilson, *Ind. Eng. Chem.*, **47**, 2201 (1955).

(21) J. C. W. Chien, private communication.

(22) G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1044 (1956).

(23) K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946).

(24) R. Rado and M. Lazar, *J. Polymer Sci.*, **62**, S186 (1962).

(25) G. S. Hammond and U. S. Nandi, *J. Am. Chem. Soc.*, **83**, 1213 (1961).

(26) B. Barnett and W. E. Vaughan, *J. Phys. Chem.*, **51**, 926 (1947).

(27) C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950).

(28) P. F. Hartman, H. G. Sellers, and D. Turnbull, *ibid.*, **69**, 2416 (1947).

(29) G. S. Hammond, *ibid.*, **72**, 3737, 4711 (1950).

(30) D. J. Brown, *ibid.*, **62**, 2657 (1940).

(31) J. C. Bevington and J. Toole, *J. Polymer Sci.*, **28**, 413 (1958); **29**, 17 (1958).

(32) S. Cohen, *J. Am. Chem. Soc.*, **73**, 1691 (1951).

(33) W. R. Foster and G. H. Williams, *J. Chem. Soc.*, 2862 (1962).

(34) H. C. Haas, *J. Polymer Sci.*, **39**, 493 (1959); **54**, 287 (1961); **55**, 33 (1961).

(35) C. G. Swain, L. T. Schaad, and A. J. Kresge, *J. Am. Chem. Soc.*, **80**, 5313 (1958).

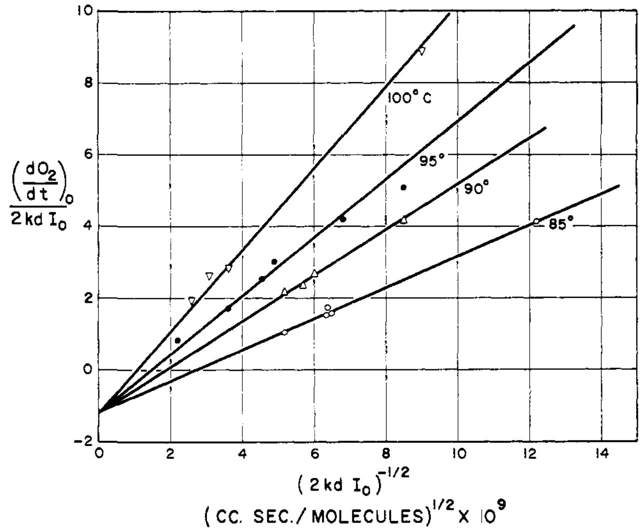

Fig. 1.—Oxygen absorption data for polypropylene.

The hidden assumption is that the measured volume change in our oxidation absorption apparatus reflects only the chemical uptake of molecular oxygen, and that all the volatile products are trapped.

However, in this work, small or negative intercepts were observed. Figure 1 shows a value of −1.2 for polypropylene. Similar plots[36] for ethylene–propylene rubber and poly(ethyl acrylate) give intercepts of 0 and 0.15. In a similar treatment of his data on the benzoyl peroxide initiated oxidation of *p*-cymene, Boardman[8] also found a negative intercept. When the CaO is removed from the oxidation tube, identical slopes but somewhat lower intercepts are observed, indicating from eq. 2 that volatiles are evolved only in the initiation and/or the termination steps. Our measured value of $(d(O_2)/dt)_0$ reflects oxygen absorption minus a relatively small amount of untrapped volatiles.

The values for $k_3e_i^{1/2}(RH)/k_6^{1/2}$ obtained from Fig. 1 for polypropylene, and from similar plots for the ethylene–propylene rubber and poly(ethyl acrylate), are presented in the Arrhenius plot, Fig. 2. These composite constants may be expressed as (molecules/cc. sec.)$^{1/2}$

| | |
|---|---|
| polypropylene | $1.13 \times 10^{19} \exp(-17{,}000/RT)$ |
| ethylene–propylene rubber | $5.10 \times 10^{18} \exp(-17{,}000/RT)$ |
| poly(ethyl acrylate) | $1.02 \times 10^{16} \exp(-13{,}000/RT)$ |

**Kinetic Chain Lengths.**—The kinetic chain length, the ratio of the rate of propagation to the rate of initiation, at any rate of initiation is obtainable from Fig. 1 for polypropylene and similar plots for ethylene–propylene rubber and poly(ethyl acrylate) if the value for the efficiency of initiation is known. Taking a value of 0.6 for $e_i$, which we will show to be a reasonable one, it can be calculated that for the rates of initiation used in this study, kinetic chain lengths fall roughly in the range of 4 to 18 for polypropylene, 3 to 11 for ethylene–propylene rubber, and 1 to 3.5 for poly(ethyl acrylate).

**Kinetics of Chain Scission.**—It has been shown[37] that in a rubber network with $N_0$ network chains/cc. supporting stress $f_0$ (force per unit area of the unstretched cross-sectional area) at temperature $T$

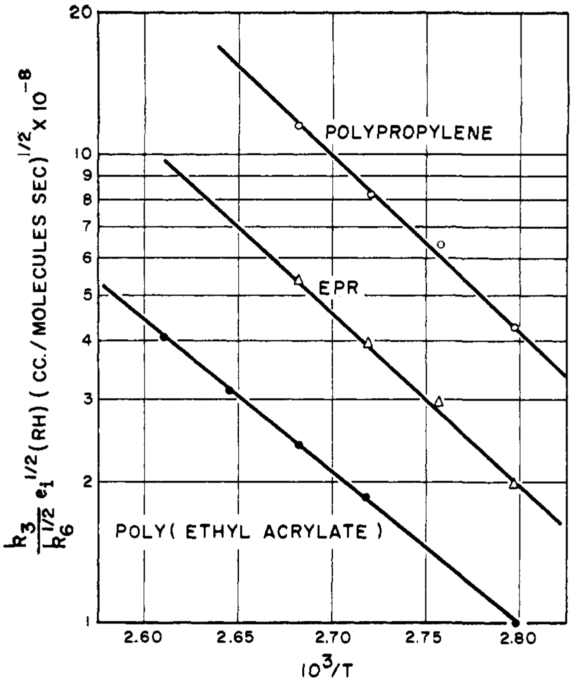

Fig. 2.—Temperature dependence of the composite rate constants for the polymers.

$$f_0 = N_0kT[(l/l_0) - (l_0/l)^2] \quad (3)$$

where $k$ is the Boltzmann constant and $l/l_0$ is the ratio of stretched to unstretched length. The amount of chain scission, the number of cuts/cc. that have occurred up to time $t$, is calculated from the equation[38]

$$q(t) = -N_0 \ln (f_t/f_0) \quad (4)$$

where $f_t/f_0$ is the ratio of the stress on the sample at time $t$ to that at time zero. Equation 4 assumes that (1) scission is random, (2) scission at the cross-link sites is negligible compared to scission along the chain, and (3) network chains are of uniform length.[39–41]

These three assumptions are valid in this study. Benzoyl peroxide should initiate oxidation chains randomly, and, as will be shown, propagation is a random process. Tertiary hydrogens along the chain greatly outnumber those at cross-link sites, and since cross linking was accomplished by decomposing peroxides throughout the sample, a random distribution of chain lengths is not to be expected. Furthermore at the low levels of scission in this study, the rates of scission calculated from the formula based on a random distribution of chain lengths,[39,40] instead of uniform chains, do not vary from the values reported here by more than 10%.

The decay in the stress on the benzoyl peroxide containing rubber samples held at constant elongation was followed with time. A rapid but small initial relaxation (200–400 sec.), independent of initiator concentration, followed by a decay dependent on peroxide concentration was observed; *e.g.*, it occurs even in uninitiated samples. The rapid relaxation is attributed to attainment of thermal and mechanical equilibrium (with re-

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(36) These plots with the complete data in tabular form are presented in N. H. Frick, Ph.D. Thesis, Princeton University, 1964, and P. M. Norling, Ph.D. Thesis, Princeton University, 1964.

(37) A. V. Tobolsky, "Properties and Structure of Polymers," John Wiley and Sons. Inc., New York, N. Y., 1960, p. 25.

(38) (a) A. V. Tobolsky, *J. Appl. Phys.*, **27**, 673 (1956); (b) A. V. Tobolsky, D. J. Metz, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **72**, 1942 (1950).

(39) A. M. Bueche, *J. Chem. Phys.*, **21**, 614 (1953).

(40) J. P. Berry and W. F. Watson, *J. Polymer Sci.*, **18**, 201 (1955).

(41) A. V. Tobolsky, *Polymer Letters*, in press.

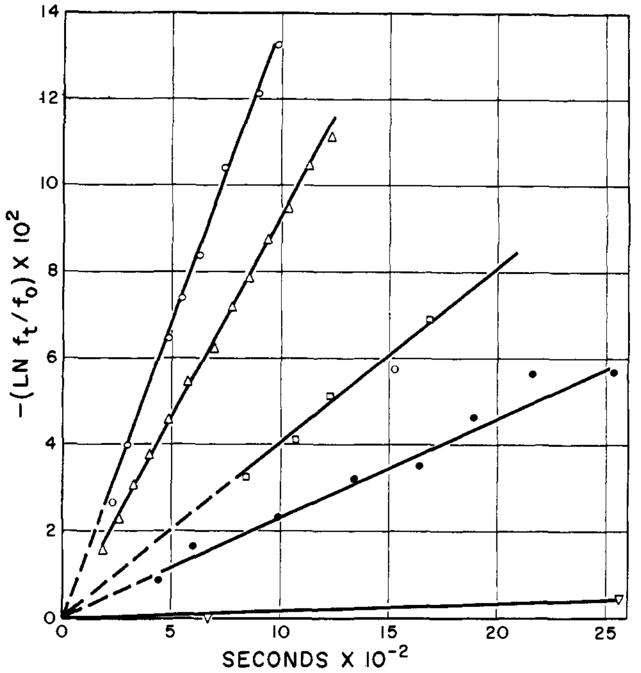


Fig. 3.—Stress decay for ethylene–propylene rubber samples at 95° and $N_0$ = 2.4 × $10^{20}$ chains/cc. The values for $(I)_0$ (molecules/cc. × $10^{-19}$) are: ▽, 0.0; ●, 1.1; □, 3.4; △, 8.6; ○, 13.2.

spect to the clamping) as well as a possible slipping of chain entanglements that act as temporary cross links. The peroxide-dependent decay was extrapolated to zero time to give $f_0$ and the initial rate of scission. The total time of the stress decay studies ranged from 1000 to 4000 sec. Figure 3 shows the stress decay observed for several ethylene–propylene samples at 95°. Measurements were started after 300 sec.

Chain scission data for polypropylene are given in Fig. 4. From these data, it can be seen that the kinetics of chain scission are not the same as for oxygen absorption. The initial rate of scission is linearly proportional to the initial concentration of benzoyl peroxide and hence to the rate of radical production by the initiator. This can be expressed as

$$(\mathrm{d}q/\mathrm{d}t)_0 = e_s(2k_d(\mathrm{I})_0) + (\mathrm{d}q/\mathrm{d}t)_{\mathrm{th}} \qquad (5)$$

where $e_s$, termed the efficiency of scission, is constant for a given polymer *and is independent of kinetic chain length*, and $(\mathrm{d}q/\mathrm{d}t)_{\mathrm{th}}$ is the extrapolated scission rate in the absence of initiator, *i.e.*, at $(\mathrm{I})_0$ = 0. Table II presents the values of $e_s$ for the three polymers. For simplicity's sake, and to avoid complications from hydroperoxide buildup, we have employed initial rates of scission. In poly(ethyl acrylate), however, where kinetic chain lengths are low and hydroperoxide accumulation is slow, the rate of scission may be followed with time and remains equal to $2e_sk_d(\mathrm{I})_0 \exp(-k_dt)$ with constant $e_s$ over a period of two half-lives.

Table II

Efficiency of Scission in the Benzoyl Peroxide Initiated Oxidation of Vinyl Polymers

| Temp., °C. | Polypropylene | Ethylene-propylene rubber | Poly(ethyl acrylate) |
|---|---|---|---|
| 85 | . . | . . | 0.23 |
| 90 | 0.59 | 0.68 | . . |
| 95 | 0.60 | 0.65 | 0.14 |
| 100 | 0.59 | 0.64 | 0.16 |
| 105 | 0.82 | 0.63 | 0.18 |
| 110 | . . | . . | 0.19 |

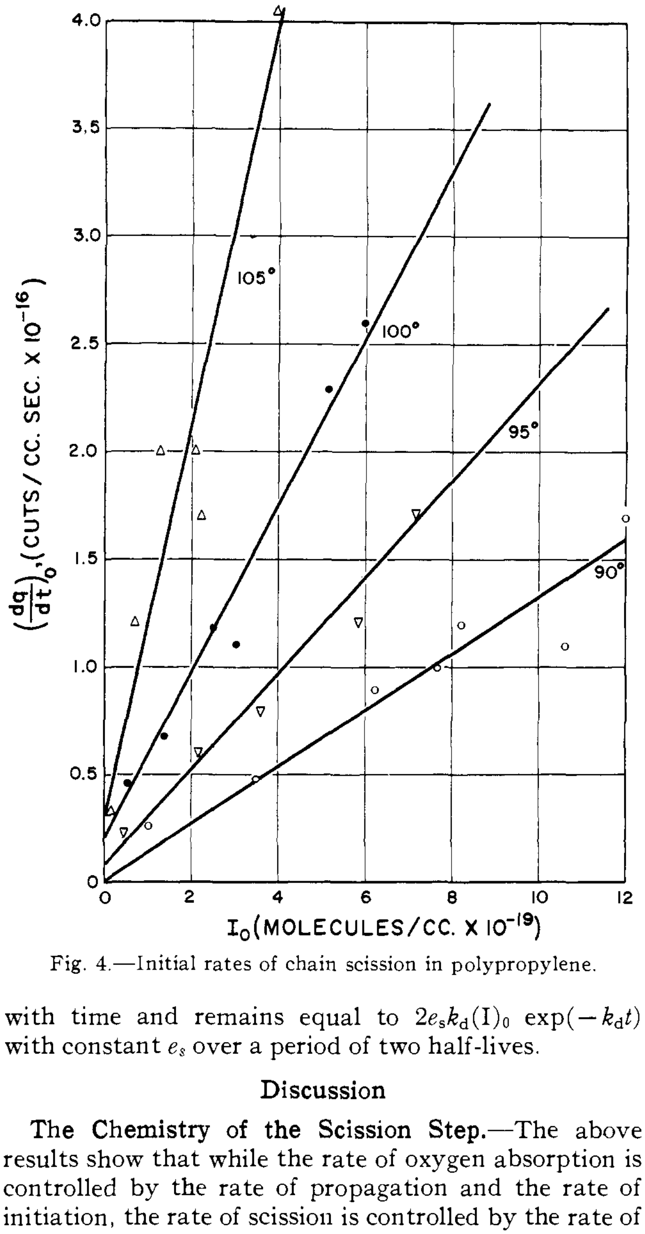
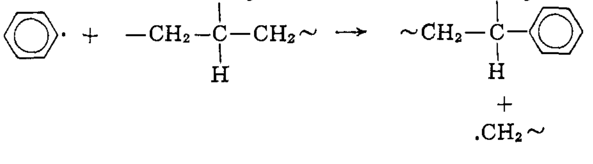


Fig. 4.—Initial rates of chain scission in polypropylene.

## Discussion

**The Chemistry of the Scission Step.**—The above results show that while the rate of oxygen absorption is controlled by the rate of propagation and the rate of initiation, the rate of scission is controlled by the rate of initiation or termination (since these are equal). The scission reaction then must be associated either with the initiation of oxidation chains by the benzoyl peroxide or with the interaction of two peroxy radicals.

A scission mechanism might involve the direct attack of a phenyl or benzoyloxy radical on a saturated carbon to give scission and a free radical.



Such free-radical displacement (SH2)[42] reactions on carbon have been observed only in strained systems[43] and compete very poorly with hydrogen-abstraction processes. Since we found that the rate of scission under flowing nitrogen is 0.16 of that in oxygen for

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[42] W. A. Pryor and T. L. Pickering, *J. Am. Chem. Soc.*, **84**, 2705 (1962).

[43] D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *ibid.*, **82**, 2368 (1960).

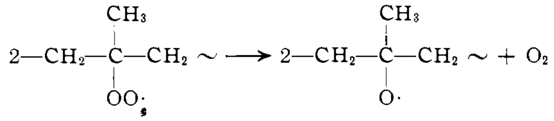
polypropylene, this mechanism cannot account for more than one-sixth of the total scissions.

Scission from an alkyl-radical precursor is highly unlikely since such a radical would be formed in both initiation and propagation reactions and should add oxygen before it can cleave.

Several authors[44,45] have suggested that scission occurs by isomerization of the peroxy radical. Since the peroxy radical concentration is proportional to $(\mathrm{I})^{1/2}$ eq. 5 argues against this interpretation.

It is quite reasonable to view the bimolecular interaction of tertiary peroxy radicals as the rate-determining step for scission, especially in light of recent work on the reactions of peroxy radicals. If termination of the oxidation chain occurred concomitantly with this reaction, this would neatly explain our result embodied in eq. 5.

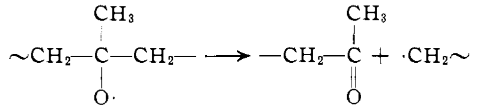
Bartlett and Traylor[46] have shown that cumylperoxy radicals interact to give cumyloxy radicals and oxygen, the reaction taking place 1.7 to 2.6 times for each termination reaction depending on the kinetic chain length. In polypropylene we should expect



$$2\mathrm{{-}CH_2{-}}\underset{\mathrm{OO\cdot}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2}\sim\ \longrightarrow 2\mathrm{{-}CH_2{-}}\underset{\mathrm{O\cdot}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2}\sim + \mathrm{O_2}$$

Numerous authors[3,13,15] have viewed the tertiary alkoxy radical thus formed as the immediate precursor to scission, and such cleavage reactions have been the subject of a study by Kochi.[47]

The cleavage would produce a ketone and a primary alkyl radical.



$$\sim\mathrm{CH_2{-}}\underset{\mathrm{O\cdot}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2{-}} \longrightarrow \mathrm{{-}CH_2{-}}\underset{\mathrm{O}}{\overset{\mathrm{CH_3}}{\underset{\|}{\mathrm{C}}}} + \mathrm{\cdot CH_2}\sim$$

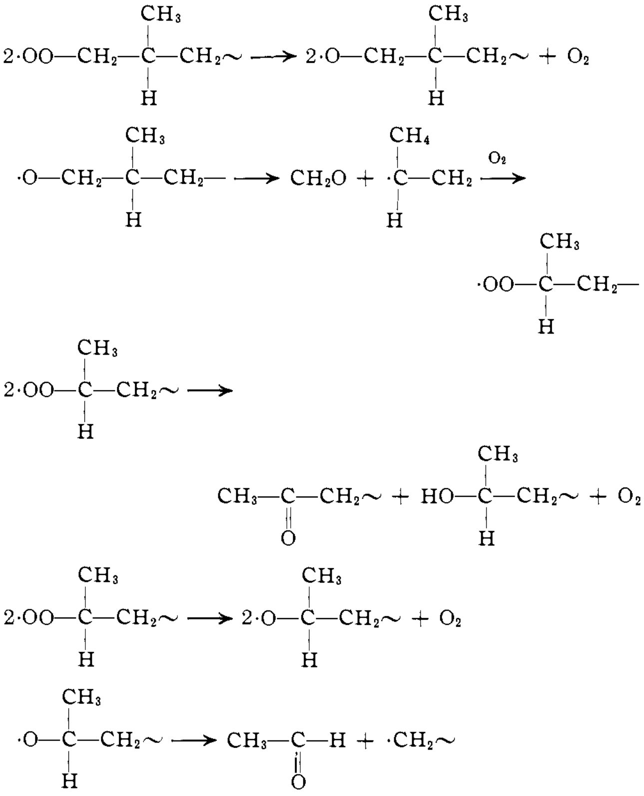
In the presence of oxygen the alkyl radicals will rapidly add oxygen to give primary peroxy radicals. Our kinetic results on scission require that such radicals terminate before abstracting hydrogens to continue the chain. A simple mechanism for termination of primary peroxy radicals has been presented by Russell[48] (see the

$$2\sim\mathrm{CH_2OO\cdot} \longrightarrow \sim\mathrm{CH_2OH} + \sim\mathrm{CH{=}O} + \mathrm{O_2}$$

transition state proposed in ref. 48).

Russell has also shown that primary and secondary peroxy radicals terminate much more readily than do tertiary peroxy radicals. The secondary tetralylperoxy radical terminates 500 times faster than cumylperoxy radicals at 90°.[11] An even greater ratio might be expected between the primary and tertiary radicals in polypropylene. If one primary peroxy radical in 1000 or even in 100 were to propagate rather than terminate as might be predicted from Russell's work, this would not be observed at kinetic chain lengths of 10 to 20.

Volatile products are evolved during the oxidation in proportion to initiation and termination. Under nitrogen, 1.8 molecules of volatiles were evolved for each molecule of benzoyl peroxide decomposed in poly(ethyl acrylate). The intercept in Fig. 1 demands that additional volatiles be evolved. This is also predicted from the work of Miller, *et al.*,[45] who found that formaldehyde and acetaldehyde were primary oxidation products in the autoxidation of isotactic polypropylene. These volatile aldehydes can be accounted for by the following reactions.[49]



$$2\mathrm{\cdot OO{-}CH_2{-}}\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2}\sim\ \longrightarrow 2\mathrm{\cdot O{-}CH_2{-}}\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2}\sim + \mathrm{O_2}$$

$$\mathrm{\cdot O{-}CH_2{-}}\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2{-}} \longrightarrow \mathrm{CH_2O} + \mathrm{\cdot}\underset{\mathrm{H}}{\overset{\mathrm{CH_4}}{\mathrm{C}}}\mathrm{{-}CH_2} \xrightarrow{\mathrm{O_2}} \mathrm{\cdot OO{-}}\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2{-}}$$

$$2\mathrm{\cdot OO{-}}\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2}\sim\ \longrightarrow \mathrm{CH_3{-}}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}CH_2}\sim + \mathrm{HO{-}}\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2}\sim + \mathrm{O_2}$$

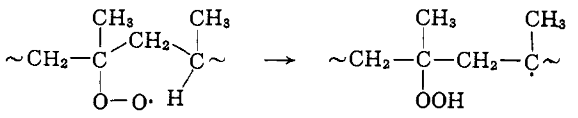
$$2\mathrm{\cdot OO{-}}\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2}\sim\ \longrightarrow 2\mathrm{\cdot O{-}}\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2}\sim + \mathrm{O_2}$$

$$\mathrm{\cdot O{-}}\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{{-}CH_2}\sim\ \longrightarrow \mathrm{CH_3{-}}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}H} + \mathrm{\cdot CH_2}\sim$$

This oxidative unzipping reaction may be rapid enough to form several molecules of aldehydes before two primary, two secondary, or a primary and a secondary peroxy radicals interact to give termination.

The interaction of a primary or a secondary with a tertiary peroxy radical to give a tertiary alcohol, oxygen, and a ketone or aldehyde is also possible, but if this is an important interaction we should expect lower efficiencies of scission for higher rates of initiation since one radical chain is terminated without scission by this interaction.

**The Propagation Reaction.**—The ratio of $k_3e_i^{1/2}(\mathrm{RH})/k_6^{1/2}$ for the ethylene-propylene rubber to that for polypropylene is 0.45 compared to a mole ratio of 0.35 for propylene units. To a first approximation the (RH) in our kinetic expression is the polymerized propylene unit with its tertiary hydrogen. The fact that the ratio is not considerably lower indicates that propagation down the polymer chain through the popular six-membered transition state is no more favored than interchain random propagation. The ratio 0.45 is in fact somewhat *higher* than the expected value of 0.35. Steric factors may be coming into play in the initiation



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[44] A. P. Zeelenberg and A. F. Bickel, *J. Chem. Soc.*, 4014 (1961).

[45] V. B. Miller, M. B. Neiman, V. S. Pudov, and L. I. Lafer, *Polymer Sci.* (USSR), **2**, 121 (1961).

[46] P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **85**, 2407 (1963).

[47] J. K. Kochi, *ibid.*, **84**, 1193 (1962).

[48] G. A. Russell, *ibid.*, **79**, 3871 (1957).

[49] P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

and propagation steps in the polypropylene oxidation. Bridger and Russell[50] have shown that tertiary hydrogens in a 1,3 arrangement are less reactive to hydrogen abstraction by phenyl radicals than are tertiary hydrogens with a 1,4 (or greater) separation. The lower efficiency of scission in polypropylene than in ethylene-propylene rubber may be a reflection of a lower initiation efficiency in the polypropylene.

If only tertiary hydrogens along the backbone are reacting according to the manner we suggest, then $e_s$ should equal $e_i$. Our values of $e_s$ for polypropylene and ethylene-propylene rubber are close to the initiation efficiencies for benzoyl peroxide in polymerizations.[51] In poly(ethyl acrylate), however, the scission efficiency is much lower. It has been observed that ester hydrogens are susceptible to oxidation,[52] so it is most reasonable to suppose that $RO_2\cdot$ radicals form on the side chain as well as on the backbone in poly(ethyl acrylate). If $RO_2\cdot$ radicals on the side chain interact and terminate, this will not contribute to the backbone scission that we measure.

The lower value for the composite rate constant $k_3e_i^{1/2}(RH)/k_6^{1/2}$ for poly(ethyl acrylate) is expected because of the electron-withdrawing nature of the carbethoxy group. The propagating peroxy radical has been shown to be electrophilic.[53] The carbethoxy group might be expected to stabilize a radical formed at the tertiary center. This may be reflected in the lower activation energy for the composite rate constant for poly(ethyl acrylate). Bolland[54] has reported that resonance stabilization of alkyl radicals formed in the propagation reaction lowers the activation energy for $k_3$.

It may prove fortuitous that in the cases we have examined, the efficiency of scission approximates the efficiency of initiation of the oxidation chains. Cases may be envisioned in which this might not be so. Termination could occur without scission. Two alkoxy radicals could couple to form a stable peroxide, or secondary peroxy radicals could form along the chain and terminate by a hydrogen-transfer mechanism. Alternatively, scission could occur without termination. The radicals produced by the cleavage of the tertiary alkoxy radical could conceivably have sufficient stability so that propagation reactions, such as hydrogen abstraction or radical addition to reactive double bonds, could compete with termination reactions. Thus in polymers quite different from the vinyl systems studied here, it would not prove surprising if values for $e_s$ are found to be dependent on the kinetic chain length or are found to be much higher or much lower than 0.6.

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[50] R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963).

[51] A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954.

[52] A. Fish and A. Waris, *J. Chem. Soc.*, 4513 (1962); 120 (1963).

[53] G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956).

[54] J. L. Bolland, *Quart. Rev.* (London), **3**, 1 (1949); *Trans. Faraday Soc.*, **46**, 358 (1950).

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# Ionization Potentials of Substituted Benzenes and Their Charge-Transfer Spectra with Tetracyanoethylene

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The relation between energy of charge-transfer absorption and ionization potential of the donor molecule in substituted benzene–tetracyanoethylene complexes shows apparent anomalies in the reported literature. By careful analysis of both the previously reported and new data in terms of band width and shape, it is shown that many of the anomalies can be explained. The relationship between the more satisfactory empirical relationship resulting and theoretical expressions which have been put forward is discussed.

## Introduction

The energy required for optically induced intermolecular charge transfer (Mulliken[1]) has been discussed theoretically by a number of authors.[2-4] Using the notation of Mulliken and Person,[3] it may be expressed as

$$h\nu_{CT} = W_1 - W_0 + X_1 - X_0 \qquad (1)$$

Here $W_0$ is the energy of the pure "no-bond" state (D, A) including all interaction terms (electrostatic and van der Waals) except that ($X_0$) resulting from mixing with the dative state $D^+A^-$. Similarly $W_1$ is the energy of the pure dative state, including van der Waals, and the now very considerable electrostatic term. $X_1$ represents the additional stabilization resulting from the interaction of the dative with the no-bond state.

We can write $W_0$ as $W_\infty - G_0$,[5] where $W_\infty$ is the energy of the separated molecules and $G_0$ includes all but the no-bond–dative interaction.

Similarly after electron transfer, $W_1$ is expressed as

$$W_\infty + I_D^v - E_A - G_1$$

Here $I_D^v$ is the vertical ionization potential of the donor, $E_A$ is the electron affinity of the acceptor, and $G_1$ is again the term involving all $D^+$–$A^-$ interactions except the "resonance" interaction with the "no-bond" state.

Using various simplifying assumptions discussed in

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[1] R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600, 4493 (1950); **74**, 811 (1952); *J. Chem. Phys.*, **19**, 514 (1951); *J. Phys. Chem.*, **56**, 801 (1952).

[2] G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer Verlag, Berlin, 1961.

[3] R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

[4] S. P. McGlynn, *Radiation Res. Suppl.*, **2**, 300 (1960).

[5] There is a change from eq. 1 of ref. 3.