TABLE I
QUANTUM YIELD OF CHAIN BREAKING IN ETHYLENE–CO COPOLYMERS

Concentration of COD, mol/l.	ϕ, mol/einstein
0.000	0.0505
0.038	0.0430
0.079	0.0355
0.092	0.0350
0.122	0.0326
0.207	0.0281
0.387	0.0283
0.410	0.0270

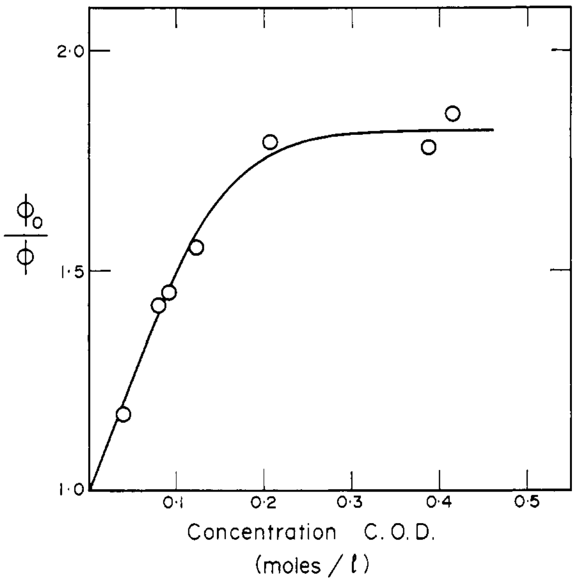

Figure 1.

quantum yield for chain breaking (ϕ) was determined from the initial slope of the line obtained by plotting $[(\bar{M}_n)_0/\bar{M}_n] - 1$ as a function of the light absorbed by the system. The results of experiments using a 1.8% solution (6×10^{-3} mol/l. of CO) are shown in Table I. Under the conditions of the experiment (at 3130 Å), all the light is absorbed by the polymer and none by the COD. We attribute the reduction in the quantum efficiency to the quenching of the triplet (n–π^*) state of the ketone by transfer of the electronic energy to the COD. Such a process has been shown to occur in simple aliphatic ketones in solution by Wagner and Hammond[6,7] and by Dougherty[8] using piperylene as the acceptor.

Figure 1 shows a plot of ϕ_0/ϕ against the concentration of COD. Since the decrease in molecular weight is due to both type I and type II processes, it is not expected that a simple linear Stern–Volmer relationship will be observed. However, studies of quenching in simple ketones[6,7] show a similar effect, which has been ascribed to the fact that some of the type II reaction arises from the excited singlet state and is not quenched. Complete quenching of all reaction is therefore not possible and ϕ will remain at a finite value independent of the concentration of quencher after a certain concentration has been reached.

The initial slope of this curve is equal to $k_q/\Sigma k_r$, where k_q is the bimolecular rate constant for quenching and Σk_r is the sum of the rate constants for all the reactions quenched. From these experiments we do not have sufficient information to evaluate the magnitude of the individual rate constants, but from the maximum quenching observed we can estimate that about 45% of the total reaction involves the triplet state of the carbonyl group. This is somewhat less than that observed with the lower aliphatic ketones at 30° (65%). (The latter figure however refers to type II products only.)

This mechanism of energy transfer is evidently not particularly effective in the present example, since only a 45% reduction in the rate of degradation can be obtained even with quite high stabilizer concentrations. However, it may well be possible to find additives which will quench both the singlet and triplet states, in which case more effective stabilizing action could be expected. It may well be that the effectiveness of carbon black as a weathering stabilizer is related to its ability to accept electronic excitation energy directly from the polymer molecule. The conjugated double bonds present in most forms of carbon black are not unlike those in COD and the structural variations would ensure that almost any desired energy levels would be available for quenching.

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(9) To whom all correspondence should be addressed.

A Mechanism for the Oxidative Photodegradation of Polyethylene

Several studies of the fundamental processes occurring in the oxidative photodegradation of polyethylene have been reported.[1] While the later stages of the photooxidation evidently involve radical chains similar to those of thermal oxidation, the primary stages are less clearly understood. This paper proposes a new mechanism for the oxidative photodegradation of polyethylene and presents experimental evidence supporting it. The mechanism is consistent with (1) known photochemistry of model systems resembling polyethylene and with (2) known products of polyethylene photooxidation. In addition, the formation and role of *electronically excited* oxygen molecules in the photodegradation is described.

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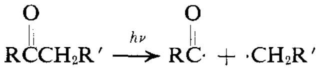
(1) (a) M. B. Neiman, Ed., "Aging and Stabilization of Polymers," Consultants Bureau, New York, N. Y., 1965, Chapter 4; (b) W. L. Hawkins, *Oxidn. Combust. Rev.*, **1**, 170 (1965); (c) G. Scott, "Atmospheric Oxidation and Antioxidants," Elsevier Publishing Co., New York, N. Y., 1965, Chapter 3.

The proposed mechanism has four steps: (1) absorption of light by carbonyl groups; (2) Norrish type II cleavage involving n–π* excited states of carbonyl groups; (3) formation of *singlet* oxygen molecules by quenching of the n–π* triplet state of carbonyl groups; and (4) reaction of *singlet* oxygen molecules with vinyl groups formed in the type II cleavage. Each step will be discussed in turn.

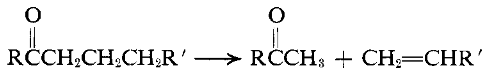
1. Absorption of Light by Carbonyl Groups. Since little or no radiation with a wavelength shorter than 300 mμ is transmitted by the earth's atmosphere[2] and since "pure" polyethylene would have a paraffinic structure $-(CH_2CH_2)_n-$ not capable of absorbing light of wavelength longer than 300 mμ, previous workers[3,4] have suggested that carbonyl groups formed during polymerization or processing of the polymer are responsible for the initial absorption. The ketone group $>C{=}O$ shows a relatively weak absorption band with a maximum at 270–290 mμ and extending into the region above 300 mμ. This absorption is a n–π* transition[5] and involves promotion of an electron from a nonbonding n orbital localized on the oxygen atom to a more delocalized antibonding π* orbital distributed over the entire carbonyl group.

2. Norrish Type II Cleavage. The known photochemistry of aliphatic ketones[6–10] suggests that the principal routes available for chain scission are the Norrish type I reaction (eq 1)



$$\overset{O}{\overset{\|}{R C}}CH_2R' \xrightarrow{h\nu} \overset{O}{\overset{\|}{RC}}\cdot + \cdot CH_2R' \qquad (1)$$

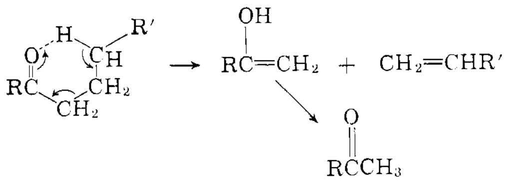
and the Norrish type II reaction (eq 2).



$$\overset{O}{\overset{\|}{RC}}CH_2CH_2CH_2R' \longrightarrow \overset{O}{\overset{\|}{RC}}CH_3 + CH_2{=}CHR' \qquad (2)$$

The quantum yields of these reactions have been measured for a variety of aliphatic ketones[11] and the type I cleavage appears to be much less important than the type II process where the quantum yields are in the range 0.2–0.3. Also, Guillet[12] has presented strong evidence that the main source of chain scission in photooxidation of model systems, such as the copolymer of carbon monoxide and ethylene, is the type II process. Additional evidence favoring this view comes from several studies[13] of the photolysis of polyethylene, where infrared studies indicated the presence of vinyl groups in the oxidized polymers.

Rice and Teller[14] and Noyes and Davis[15] have considered alternative mechanisms for the Norrish type II cleavage of ketones, but present evidence strongly favors their suggestion of a cyclic, six-membered-ring intermediate[16]



(3)

The nature of the excited states which participate in the Norrish type II cleavage has been a subject of considerable controversy.[17–21] However, Wagner and Hammond[21] recently showed that both excited n–π* singlet states and n–π* triplet states take part in the type II cleavage of several aliphatic ketones. It will be shown in the next section that n–π* carbonyl triplets can be quenched efficiently by molecular oxygen. Therefore, in the oxidative photodegradation of polyethylene, we suggest that a *main source of chain scission is the unquenched Norrish type II cleavage which may occur via the excited n–π* singlet state of the ketone group.*

3. Quenching of n–π* Triplets to Form Singlet Oxygen Molecules. The suggestion that electronically excited states of O_2 can be produced by physical quenching of excited states of sensitizers appears to have been made first by Kautsky.[22] He studied the photooxidation of spatially separated sensitizer and acceptor molecules and found that, at low oxygen pressure, it was possible to excite selectively a sensitizer and to produce oxidation of distant acceptor molecules. He concluded that this long-range oxidation was due to diffusion of *excited* oxygen molcules produced by the quenching of the phosphorescence of the sensitizer.[22] Kearns[23] has reviewed the evidence in support of singlet O_2 production by quenching of excited triplet state molecules.

The formation of endoperoxides has served as a useful criterion for the detection of singlet O_2 molecules produced in a given reaction.[24] It has been shown

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(12) J. E. Guillet, J. Dhanray, F. J. Golemba, and G. H. Hartley, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

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(14) F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938).

(15) W. Davis, Jr., and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **69**, 2153 (1947).

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(19) D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

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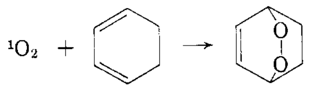
(22) For a review of these early experiments, see, H. Kautsky, *Trans. Faraday Soc.*, **35**, 216 (1939).

(23) K. Kawaoka, A. V. Khan, and D. R. Kearns, *J. Chem. Phys.*, **46**, 1842 (1967).

(24) C. S. Foote and S. Wexler, *J. Amer. Chem. Soc.*, **86**, 3880 (1964); E. J. Corey and W. C. Taylor; *ibid.*, **86**, 3881 (1964); T. Wilson, *ibid.*, **88**, 2898 (1966).

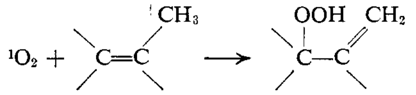
recently[25] that ketones such as benzil and benzophenone can be used to sensitize the formation of singlet oxygen. In these reactions, cyclohexadiene-1,3 was oxidized to the endoperoxide (eq 4) and no dimers of cyclohexadiene



(4)

were produced, even though these are the major products in the oxygen-free reaction.[26] In the absence of the ketone sensitizer, no endoperoxide was formed. We, therefore, suggest that in the oxidative photodegradation of polyethylene, *the n–π* triplet states of ketone groups are quenched by molecular oxygen resulting in production of electronically excited O_2 molecules.*[27,28]

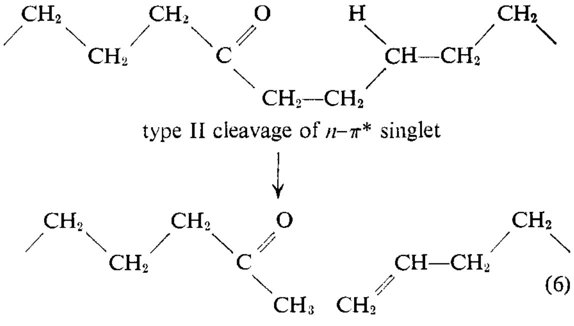
4. Reaction of Singlet Oxygen with Vinyl Groups. Another reaction characteristic of singlet O_2 molecules is the attack on olefins to form hydroperoxides.[24,29]



$$ {}^1O_2 + \;\rangle C{=}C\langle^{CH_3} \longrightarrow \;\rangle \overset{OOH}{C}{-}C{\overset{CH_2}{\diagup\!\!\diagup}}\;\;\; (5) $$

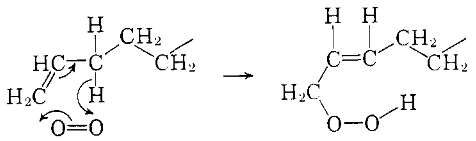
Since vinyl groups are formed in the Norrish type II cleavage, we suggest that in oxidative photodegradation of polyethylene, singlet O_2 molecules, formed by quenching of n–π* carbonyl triplets, react with vinyl groups to form hydroperoxides.

Further reactions of the hydroperoxide would lead to additional carbonyl groups which could undergo type II cleavages. These reactions are now being studied. The formation of the hydroperoxide by singlet oxygen attack is also attractive from a steric point of view since the ketone and vinyl groups in the polymer system would be separated only slightly by type II cleavage.



(6)

$$(\text{ketone})^{3n-\pi^*} + O_2 \longrightarrow \text{ketone} + {}^1O_2 \qquad (7)$$



(8)

Additional support for the mechanism is given by data obtained in the photolysis of polyethylene which indicate that rather little autocatalysis occurs and that chain lengths are quite short. This behavior would be expected if the rate-determining step is the diffusion of oxygen.

It should be mentioned that, if the above mechanism is valid, it would then appear that a mechanism for stabilization based upon quenching of the triplet n–π* state of the carbonyl group would not have significant effectiveness for two reasons: (1) type II cleavage can still occur *via* the singlet n–π* state and (2) oxygen could compete effectively with the added quenchers and produce singlet O_2 molecules which would promote oxidation.

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(27) There are two states of singlet O_2 which can be produced by quenching of the triplet sensitizer: the $^1\Sigma_g{}^+$ state which lies 37.5 kcal above the $^3\Sigma_g{}^-$ ground state and the $^1\Delta_g$ state which lies 22.5 kcal above the ground state. Recently, Kearns has presented evidence[28] that both excited states participate in dye-sensitized photooxygenation reactions and that the relative amounts of each vary with the triplet energy of the sensitizer. Since n–π* carbonyl triplet energies are usually above 50 kcal, it is very probable that the singlet O_2 produced from these species would have a substantial $^1\Sigma_g{}^+$ contribution.

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