(15) R. D. Mair and A. J. Gaupner, *Anal. Chem.*, **361**, 194 (1964).
(16) A. D. Awtrey and R. E. Connick, *J. Am. Chem. Soc.*, **73**, 1842 (1951).
(17) R. A. Stein and V. Slawson, *Anal. Chem.*, **35**, 1008 (1963).
(18) T. Kilp, W. Panning, B. Houvenaghel-Defoort, and J. E. Guillet, *Rev. Sci. Instrum.*, **47**, 1496 (1976).
(19) Similar results were reported with different product ratios by J. Chaineaux and C. Tanielian, "Singlet Oxygen Reaction with Organic Compounds and Polymers", B. Rånby and J. F. Rabek, Ed., Wiley, Chichester, 1978.
(20) K. Gollnick, ref 10a.
(21) (a) M. A. Golub, M. L. Rosenberg, and R. V. Gemmer, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, 17, 699 (1976); (b) M. A. Golub, M. L. Rosenberg and R. V. Gemmer, *Rubber Chem. Technol.*, **50**, 704 (1977).
(22) (a) Y. Amerik and J. E. Guillet, *Macromolecules*, **4**, 375 (1971); (b) T. L. Nemzek and J. E. Guillet, *ibid.*, **10**, 94 (1977).
(23) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).
(24) E. R. Bell, F. F. Rust, and W. E. Vaughn, *J. Am. Chem. Soc.*, **72**, 337 (1950).
(25) D. J. Carlsson and D. M. Wiles, *Macromolecules*, **2**, 597 (1969).
(26) R. F. Reinisch and H. R. Gloria, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **9**, 349 (1968).
(27) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966, p 651.
(28) A. Factor, C. A. Russell, and T. G. Traylor, *J. Am. Chem. Soc.*, **87**, 3692 (1965).
(29) O. Cicchetti, *Adv. Polym. Sci.*, **7**, 70 (1970).
(30) C. Walling, *Pure Appl. Chem.*, **15**, 69 (1967).
(31) D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **89**, 4891 (1967).
(32) J. D. Bacha and J. K. Kochi, *J. Org. Chem.*, **30**, 3272 (1965).
(33) C. Walling, "Free Radicals in Solution", Wiley, New York, N.Y., 1957, p 422.

Photochemistry of Ketone Polymers. 13. Quenching of Excited Ketone Carbonyls by Hydroperoxides and Peroxides[1]

Howard C. Ng and J. E. Guillet*

Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1.
Received May 19, 1978

ABSTRACT: Studies of the photolysis of ketone-containing polymers such as poly(styrene-*co*-phenyl vinyl ketone) and poly(styrene-*co*-methyl isopropenyl ketone) in the presence of di-*tert*-butyl peroxide and *tert*-butyl hydroperoxide show that both the singlet and triplet n–π^* state of the ketones are quenched by the peroxides at diffusion-controlled rates. The energy transfer results in the ketone-sensitized decomposition of the hydroperoxides and is best explained by proposing the formation of an intermediate exciplex between the excited state of the ketone and the ground state of the peroxide. In view of the simultaneous presence of keto, hydroperoxy, and peroxy groups in the photooxidation of hydrocarbons generally, and hydrocarbon polymers in particular, this phenomenon should be considered in all attempts to establish detailed mechanisms of photodegradation.

Photooxidation of hydrocarbon polymers yields oxygenated species such as hydroperoxide, peroxide, and ketones, usually with a concomitant deterioration of polymer physical properties.[2,3] In view of the intense activity in the study of the mechanism and kinetics of the photooxidation of polymers, it is surprising that there are few reports in the literature concerning the mutual interactions of these key species in photooxidation. Acyl peroxides and benzoyl peroxides, for example, are known to undergo photosensitized decomposition sensitized by polynuclear hydrocarbons such as anthracene and toluene.[4,5] Walling and Gibian showed that the decomposition of benzoyl peroxide and *tert*-butyl hydroperoxide (*t*-BuOOH) could also be photosensitized by aromatic ketones such as acetophenone and benzophenone.[6] Überreiter and Bruns[7] have reported that tetralin hydroperoxide undergoes photosensitized decomposition in the presence of fluorenone, and Nakata and Tokumaru[8] reported the singlet sensitized decomposition of benzoyl peroxide by aromatic hydrocarbons such as chrysene, anthracene, and naphthalene.

This paper concerns the quantitative study of energy transfer from polymeric ketones (aromatic and aliphatic) to hydroperoxides and peroxides, and from small molecular ketones to polymeric hydroperoxides. It serves to demonstrate that interaction between these species is significant and may be expected during the photooxidation of many polymers.

Experimental Section

Polymers. Three polymers were used in this study. *cis*-1,4-Polyisoprene hydroperoxide was prepared by singlet-oxygen oxidation by the microwave discharge method and characterized by the method described previously.[9] The resultant polymer is of low hydroperoxide content (ca. 0.1%) and is unchanged in molecular weight. Poly(styrene-*co*-phenyl vinyl ketone) with 7.6 mol % ketone (PS–PVK, 7.6%) and poly(styrene-*co*-methyl isopropenyl ketone) (PS–MIPK, 6%) were prepared by emulsion polymerization as described previously.[10] The ketone content of the copolymers was determined by measuring the absorbance of the copolymer at 313 nm, adopting an extinction coefficient of the ketone chromophore measured from the corresponding vinyl ketone homopolymers. The polymers were reprecipitated three times into cool methanol and freeze–dried before use. The purified polymers were characterized by spectroscopic methods such as UV, IR, and NMR. The number average molecular weight, $\bar{M}_n$, was determined by osmometry, and the viscosity average molecular weight, $\bar{M}_v$, was determined using the corresponding Mark–Houwink constants for polystyrene[11] and *cis*-1,4-polyisoprene (*cis*-PIP).[12] The molecular weights of these polymers are summarized in Table I.

Chemicals. *tert*-Butyl hydroperoxide (Lucidol, 90%) was purified using Piette's procedure[13] to a purity of >99%. Recrystallized Luperox 2.5, 2.5 crystal (2,5-dimethyl-, 2,5-dihydroperoxyhexane) was obtained as a research sample from Lucidol Corp. and further purified to >99 mol % by Professor T. Tidwell. Di-*tert*-butyl peroxide (D-*t*-BuP) (MC & B practical grade) was vacuum distilled twice (30 °C (12 mm)). Decanoyl peroxide was recrystallized from a 3:1 mixture of methanol and chloroform and vacuum dried for 48 h. Spectroscopic grade acetone (Fisher) was used without further purification. 3,3-Dimethyl-2-butanone (pinacolone) (Baker, practical grade) was distilled before use. Spectroscopic grade benzene (Fisher) was used as solvent without further purification. Reagent grade 1,2-dichloroethane (Fisher) was dried over $CaCl_2$ and freshly distilled before use. The molar absorptivity of the ketone copolymers and the small molecules determined using a Cary 14

0024-9297/78/2211-0937$01.00/0

Table I
Molecular Weights of Polymers Investigated in This Study

polymer	mol wt		$\overline{M}_w/\overline{M}_n$[c]
	$\overline{M}_v$[a]	$\overline{M}_n$[b]	
cis-1,4-polyisoprene (*cis*-PIP)	296 000	126 000	2.4[d]
poly(styrene-*co*-phenyl vinyl ketone) (PS-PVK, 7.6%)	670 000	348 000	2.6
poly(styrene-*co*-methyl isopropenyl ketone) (PS-MIPK, 6%)	174 000	71 400	2.9

[a] Viscosity determined in benzene, 30 °C. [b] From osmometry, determined in toluene, on a Hewlett-Packard Model 502 high-speed membrane osmometer, using Arro 08 S & S membrane. [c] Polydispersity determined from gel-permeation chromatography data on a Waters Anaprep GPC instrument. [d] Assuming $\overline{M}_v \approx \overline{M}_w$.

Table II
Structure and Molar Absorptivity (313 nm) of Polymers and Reagents

compd	M^{-1} cm^{-1}[a]	compd	M^{-1} cm^{-1}[a]
PS-PVK (7.6%)	87[b]	decanoyl peroxide	1.45[c]
PS-MIPK (6%)	19[b]	Luperox 2.5, 2.5	0.36[c]
t-BuOOH	0.27[c]	acetone	4[c]
D-*t*-BuP	0.93	3,3-dimethyl-2-butanone	10[c]

[a] Molarity in ketone units. [b] In benzene. [c] In 1,2-dichloroethane.

UV spectrometer at 313 nm are shown in Table II.

Apparatus and Procedure. The optical train arrangement for the photolysis has been described previously.[14] A digital pyroelectric radiometer (Molectron Corp. Model PR 200) was used at the end of the optical train to give a relative value of the incident and transmitted light intensity. The absolute value of light intensity at 313 nm was determined by ferrioxalate actinometry. The photolysis cell consisted of a cylindrical quartz tube with plane quartz end plates. The 25-mL cell was 2.5 cm in length and 3.5 cm in diameter. The photolysis cell was connected to a continuous line with the automatic viscometer described by Kilp et al.,[15] which was synchronized to a shutter attached to the lamp housing to control the time of irradiation. The polymer solution (usually <0.5 g/dL of polymer) in the cell was saturated with dry nitrogen before irradiation. Molecular weight changes during photolysis were determined periodically after each exposure.

1,2-Dichloroethane was used as the solvent for the photolysis of *cis*-1,4-polyisoprene hydroperoxide at 30 °C, and benzene was used as the solvent for the styrene–ketone copolymers photolysis at 35 °C. The calculation of quantum yield for polymer chain scission, ϕ_s, was performed according to the procedures described by Nemzek and Guillet.[16] Since the initial polydispersities, γ_0, of the polymer samples in this study fall close to the favorable range of $1.5 < \gamma_0 < 2.5$, an accuracy of better than ±10% can be expected in the quantum yields.

Results and Discussion

Photosensitized Decomposition of Hydroperoxide by Ketones. Photolysis of *cis*-1,4-polyisoprene hydroperoxide at 313 nm irradiation causes a homolytic cleavage of the RO–OH bond and leads to a subsequent polymer chain scission with a relatively low quantum efficiency (ca. 10^{-2})[12,17] by the following reaction scheme:

$$\sim\!\sim CH_2C(CH_3)(HOO)CH{=}CHCH_2\!\sim\!\sim \xrightarrow{h\nu}$$
$$\sim\!\sim CH_2C(CH_3)(O\cdot)CH{=}CHCH\!\sim\!\sim \xrightarrow{\beta\ \text{scisson}}$$
$$\sim\!\sim CH_2\cdot + CH_3C({=}O)CH{=}CHCH_2\!\sim\!\sim \quad (1)$$

In the presence of alkanones such as acetone or 3,3-dimethyl-2-butanone, the rate of chain scission of the polymer is increased. Figure 1 shows the nearly linear relationship between the relative rate of polymer chain scission, R_k/R_0, with the amount of ketone added. Since the carbonyl group has a much higher extinction coefficient than the hydroperoxide group at 313 nm (Table II), the increase in the rate of chain scission is probably due to the sensitization of the hydroperoxide decomposition by energy absorbed initially by the ketone. Although Walling and Wagner have shown that polar solvents do enhance β scission of alkoxy radicals,[18] the low concentration of hydroperoxides (ca. 10^{-3} M)[17] and ketones (ca. 10^{-1} M) made the preferential solvation less likely.

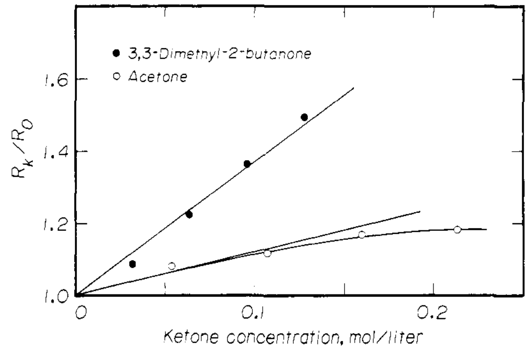


Figure 1. *cis*-1,4-Polyisoprene hydroperoxide degradation sensitized by aliphatic ketones: irradiated at 313 nm in 1,2-dichloroethane.

Prolonged irradiation (20 h) of an equimolar mixture of benzophenone and *t*-BuOOH in benzene at 360 nm, where the hydroperoxide is transparent and only the aromatic ketone absorbs, showed complete decomposition of the *t*-BuOOH and virtually total retention of the starting benzophenone. The *t*-BuOOH decomposition yielded predominantly *tert*-butyl alcohol (90%) and a small amount of acetone, isobutylene oxide, and methanol. This is consistent with the product distribution from direct photolysis of *t*-BuOOH.[19] Ninety percent of the benzophenone sensitizer was recovered. A small amount of photoreduction products (e.g., benzpinacol) might arise from the secondary photoreactions.

These findings are consistent with the fact that both singlet sensitizers (anthracene and other polynuclear hydrocarbons)[4,5,8] and triplet sensitizers (benzophenone and others)[6,7] can act as photosensitizers for the decomposition of acyl peroxides, alkyl and aromatic peresters, and hydroperoxides. It is possible that this occurs by means of electronic energy transfer from the excited sensitizer to the peroxide and the hydroperoxide acceptor systems.

In order to test the possibility of this energy transfer mechanism, experiments on the quenching of the Norrish type II photoelimination of ketone–styrene copolymers by hydroperoxides and peroxides were devised. Upon electronic excitation, phenyl or alkyl ketones with γ hydrogen undergo characteristic intramolecular hydrogen abstraction which yields both cleavage and cyclization products.[20] In PS-PVK and PS-MIPK the type II reaction results in polymer chain scission.[21a–e] In the case of aromatic ketones, the reactions originate only from the n–π^* carbonyl, in which case the reaction depends on the structure of the carbonyl triplet,[20] whereas in aliphatic ketones, both singlet and triplet n–π^* states participate in the reaction.[22] Styrene copolymers with low content of ketone were chosen to minimize energy migration along the polymer chain.[21a,c] The quantum yields of the type II elimination from the singlet and triplet states for PS–MIPK were obtained using *cis*-1,3-pentadiene as a triplet quencher (0.5 M)[23] and corrected for singlet quenching.[24] Table III shows the type II scission quantum yields which are in good agreement with corresponding Φ_{II} values of their small molecule analogues.

Table III
Quantum Yields of Type II Photoelimination of Styrene-Vinyl Ketone Copolymers and Small Molecule Analogues

compd	Φ_{II} singlet	triplet	total	ref
PS-PVK (7.6%)		0.49	0.49[a]	this study
PS-MIPK (6%)	0.07	0.15	0.22[a]	this study
γ-phenylbutyrophenone		0.50	0.50	20
2-hexanone	0.097	0.155	0.252	22a
5-methyl-2-heptanone	0.07	0.14	0.21	22c

[a] In benzene at 26.5 °C, irradiated at 313 nm.

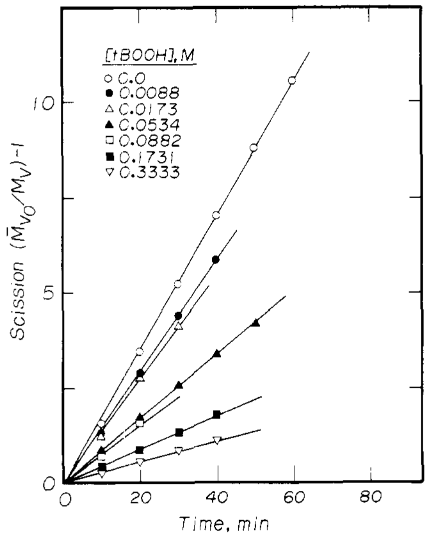


Figure 2. Quenching of PS–PVK scission by t-BuOOH: irradiated at 313 nm, 36.5 °C, in benzene.

It is noteworthy that the value in Table III for PS–PVK is higher than the values reported by Golemba and Guillet[21d] (Φ_{II} = 0.18). Their low Φ_{II} values might be derived from the quenching of the excited triplets by the photoproduct, namely the styrene functional groups at the polymer chain ends.[25] Application of automatic viscometric measurements enables one to monitor polymer chain scission at the very early stage of the process, thus the product quenching problem could be avoided. This is shown by the linearity of the plot of $[(\bar{M}_{v,0}/\bar{M}_v) - 1]$ vs. time in Figure 2. This quantity represents the number of scissions per polymer molecule.

Quenching of PS–PVK by t-BuOOH and D-t-BuP. Triplet Quenching. Electronic energy transfer between an excited species and a quencher in fluid media is usually expressed by the Stern–Volmer relationship:

$$\phi_0/\phi = 1 + k_q\tau[Q] \quad (2)$$

where ϕ_0 is the quantum yield in the absence of quencher and ϕ is the quantum yield at quencher concentration [Q], τ is the lifetime of the excited state in the absence of the quencher, and k_q is the rate constant for energy transfer. Under typical experimental conditions a plot of ϕ_0/ϕ vs. [Q] will produce a straight line with slope $k_q\tau$.

Figure 2 shows the relative rate of scission of PS–PVK in the presence of various concentrations of t-BuOOH. The addition of the hydroperoxide to the PS–PVK solution definitely quenches polymer chain scission derived from the type II photoelimination. In this case the photoreaction is derived completely from the triplet phenyl ketone. The Stern–Volmer plot from these data is linear, as shown in Figure 3. This is direct evidence for electronic energy transfer from the ketone triplet to the hydroperoxide systems. From the slope of the Stern–Volmer plot, the $k_q\tau$ value is determined to be 15.9 M^{-1}.

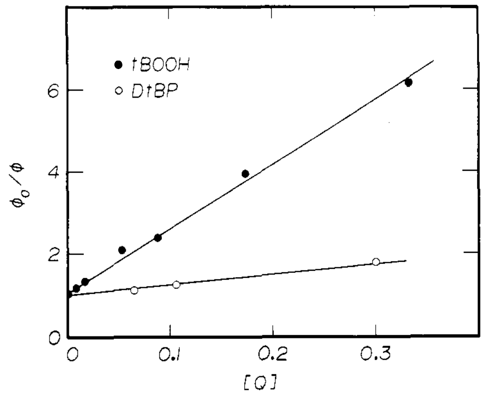


Figure 3. Stern–Volmer plot for PS–PVK scission quenched by t-BuOOH and D-t-BuP.

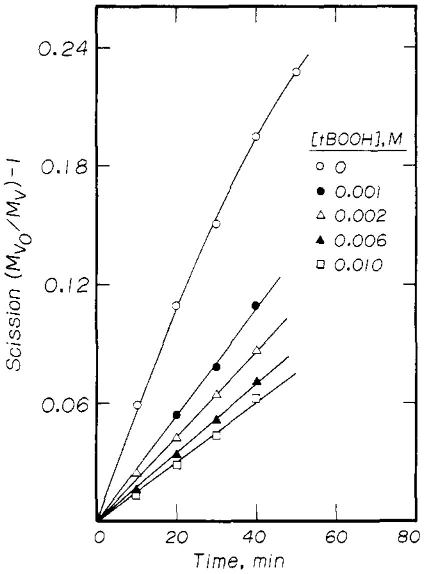


Figure 4. Quenching of PS–MIPK by t-BuOOH: irradiated at 313 nm, 36.5 °C, in benzene.

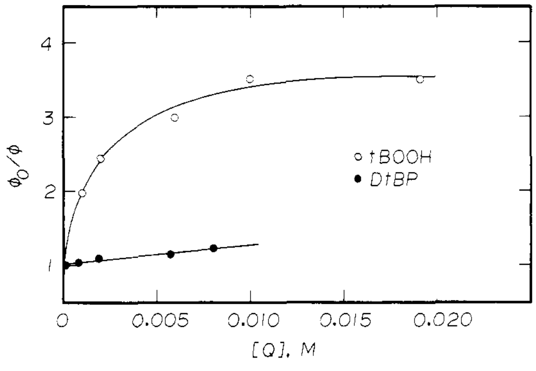


Figure 5. Stern–Volmer plot for PS–MIPK scission quenched by t-BuOOH and D-t-BuP.

Di-*tert*-butyl peroxide also quenches the type II chain scission of the PS–PVK, although with less efficiency than the hydroperoxide ($k_q\tau_T$ = 2.34 M^{-1}).

Quenching of PS–MIPK by t-BuOOH and D-t-BuP. The type II reaction of aliphatic ketones occurs from both the singlet and the triplet n–π^* state.[14,21b,22] For PS–MIPK, 32% of the type II chain scission results from the singlet state and the remaining 68% from the triplet state (Table III). *tert*-Butyl hydroperoxide quenches this chain scission as shown in Figure 4. The ratio of the total type II scission quantum yield ϕ_0/ϕ plot against the concentration of hydroperoxide gives a curve which levels

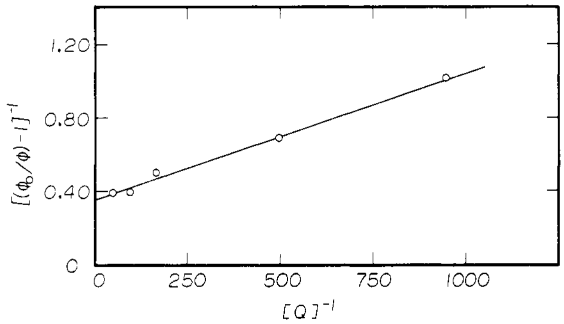


Figure 6. Modified Stern–Volmer plot for PS–MIPK triplet quenched by *t*-BuOOH.

off at high quencher concentration (Figure 5). If the hydroperoxide is assumed to quench the triplet n–π* state only, the kinetic expression should be:[26]

$$\phi_0/\phi = \frac{k_{q_3}\tau_3[Q]}{1 + (\phi_1^0/\phi_3^0)(1 + k_{q_3}\tau_3[Q])} \qquad (3)$$

Rearrangement of eq 3 gives

$$\left(\frac{\phi_0}{\phi} - 1\right)^{-1} = \frac{\phi_1^0}{\phi_3^0} + \frac{1 + (\phi_1^0/\phi_3^0)}{k_{q_3}\tau_3}[Q]^{-1} \qquad (4)$$

where ϕ_1^0/ϕ_3^0 is the ratio of the quantum yields derived from singlet and triplet, respectively, in the absence of the quencher, and k_{q_3} and τ_3 are the triplet quenching constant and lifetime, respectively. A plot of $[(\phi_0/\phi) - 1]^{-1}$ vs. $[Q]^{-1}$ is depicted in Figure 6. A straight line is obtained as described by eq 4. This confirms the assumption that the hydroperoxide quenches only the triplet excited state or, alternatively, the triplet quenching process is much more efficient than the singlet process. From the intercept of the straight line ϕ_1^0/ϕ_3^0 is equal to 0.36 (27% singlet, 73% triplet, which agrees well with the ratio 32% singlet, 68% triplet determined from the values listed in Table III). From the intercept of the slope, the $k_{q_3}\tau_3$ value is determined to be 2×10^3 M^{-1}. Quenching of the PS–MIPK scission by D-*t*-BuP also gives a linear Stern–Volmer plot, as shown in Figure 5. From the slope, a $k_q\tau$ value of 27.8 M^{-1} is obtained, which is much lower than that determined for the hydroperoxide quenching. Thus D-*t*-BuP is shown to quench the n–π* state, but with lower efficiency.

Quenching of PS–MIPK Singlet by *t*-BuOOH and D-*t*-BuP. To study singlet energy transfer to hydroperoxides and peroxides, *cis*-1,3-pentadiene was used as triplet quencher to suppress all reaction from the triplet state. *cis*-1,3-Pentadiene quenches the carbonyl n–π* triplet at a diffusion-controlled rate but only quenches the singlet with $k_q\tau = 0.19$ M^{-1}.[24] Thus, with 0.5 M of pentadiene, almost all the triplet and only 9% of the singlet are quenched under these conditions. Straight lines were again obtained in the Stern–Volmer plot for both the *t*-BuOOH and D-*t*-BuP (Figure 7). From the slopes of the straight lines, $k_{q_1}\tau_1$ is determined to be 26.3 M^{-1} for *t*-BuOOH and 17.9 M^{-1} for D-*t*-BuP. This is strong evidence that singlet energy transfer occurs between the carbonyl n–π* singlet and both hydroperoxide and peroxide groups, with approximately equivalent efficiency.

To illustrate the generality of the quenching of ketone excited states by hydroperoxides and peroxides, further studies were carried out. The Stern–Volmer plot for Luperox 2.5, 2.5 and PS–MIPK is curved (Figure 8), but a plot of $[(\phi_0/\phi) - 1]^{-1}$ vs. $[Q]^{-1}$ yields a straight line which provides $\phi_1^0/\phi_3^0 = 0.32$ and $k_q\tau = 1940$ M^{-1}, in good agreement with values for *t*-BuOOH obtained previously. Similarly, the Stern–Volmer plot for the decanoyl peroxide gives a straight line with slope equal to $k_q\tau = 18.1$ M^{-1} (Figure 8), again in good agreement with values obtained in the D-*t*-BuP case (Table IV).

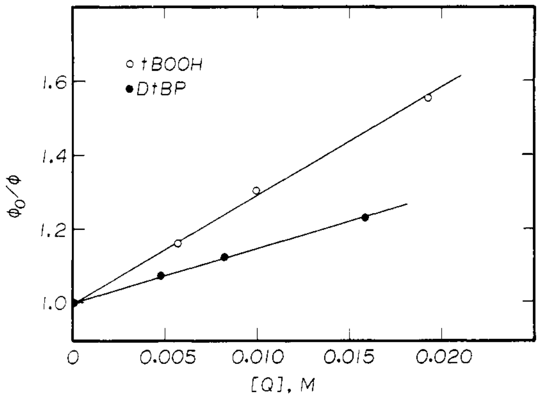


Figure 7. Stern–Volmer plot for PS–MIPK singlet quenched by *t*-BuOOH and D-*t*-BuP.

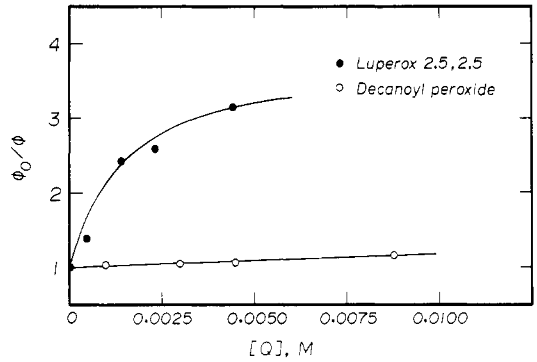


Figure 8. Stern–Volmer plot for PS–MIPK scission quenched by different peroxides.

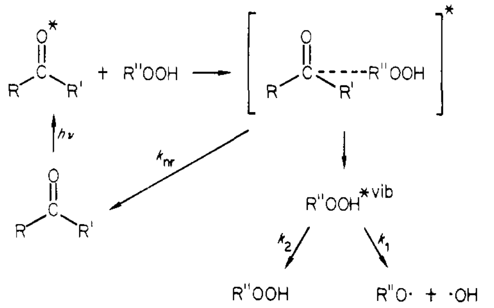
All evidence supports the hypothesis that energy transfer from both singlet and triplet carbonyl n–π* states to hydroperoxides and peroxides is a general phenomenon. The results of the quenching studies are summarized in Table IV. Quenching constants for PS–PVK were calculated using a triplet lifetime of 13.6 ns for this polymer.[27] Calculation of quenching constants for PS–MIPK is hindered by the lack of information on singlet and triplet lifetimes of this copolymer. However, a singlet lifetime of 1.6 ns has been reported for MIPK homopolymer.[21e] Adopting this value for PS–MIPK copolymer gives a bimolecular rate constant $k_q = 1.5 \times 10^{10}$ M^{-1} s^{-1}, i.e., a value reaching the diffusion-controlled limit for hydroperoxide quenching the MIPK singlet.

Polystyrene in solution does not undergo molecular weight change when irradiated at 313 nm with or without hydroperoxides or peroxides. Furthermore, carbonyl compounds, both aromatic and aliphatic, do not form ground-state complexes with hydroperoxides or peroxides, as no new absorption peak was observed for the mixture. The possibility of quenching by chemical reaction, namely the carbonyl n–π* hydrogen abstraction from ROO–H, is ruled out for the following reasons: (1) Benzophenone, was quantitatively recovered in the photosensitized decompostion of *t*-BuOOH. (2) The reported rate constants for photoreduction, k_r, of carbonyl compounds are much lower than k_q observed, e.g., k_r for benzophenone in isopropyl alcohol, 5×10^6 M^{-1} s^{-1},[28a] in alkane, 1×10^5 M^{-1} s^{-1}.[28b] The strength of the ROO–H bond has been estimated to be 88 kcal/mol,[29] which is weaker than a C–H bond in a saturated hydrocarbon. Thus from bond energy consideration, k_r is expected to lie between 5×10^6 and 1×10^5 M^{-1} s^{-1}.[30] (3) The deactivation of n–π* carbonyl by hydrogen abstraction cannot account for the high k_q values for D-*t*-BuP.

The type II photoelimination of carbonyl compounds proceeds via a 1,4-biradical intermediate. The first-order rate constant for this biradical formation is usually of the order of 10^8 s^{-1}.[20] Since the peroxides quench the type II reaction with rate constants of the order of 10^9, the quenching process must precede the formation of the biradical. This means that the peroxides interact with the carbonyl n–π* state and cause the deactivation of the excited species directly from that state.

The excess electronic excitation energy supplied to the peroxy system presumably leads to the decomposition of the peroxy linkage. Hydroperoxides and peroxides are transparent at wavelengths $\lambda > 340$ nm. Semiempirical computations have shown that the peroxy system has no low-lying stable excited states and that the potential energy surfaces of the first four excited states are dissociative.[31] Aromatic and aliphatic ketones emit, if at all, at a wavelength $\lambda > 360$ nm with low efficiency in solution. Therefore the overlap of donor (ketone singlet or triplet) emission and acceptor (hydroperoxide and peroxide) absorption spectra, which is the basic requirement of the "classical" electronic energy transfer, i.e., Dexter exchange and Förster resonance mechanisms,[32] is negligible. Electronic energy transfer from carbonyl n–π* state to hydroperoxides and peroxides thus calls for a nonclassical interpretation.

A likely mechanism for this energy transfer is the formation of an encounter complex of finite lifetime between the excited carbonyl and the ground state hydroperoxide or peroxide as an intermediate in the quenching process. Coupling of the carbonyl n–π* electronic energy and the peroxy vibrational energy then occurs in the "exciplex" intermediate and leads to subsequent deactivation of the n–π* species. The resultant vibrationally excited peroxy systems might undergo bond dissociation to yield the observed products. This mechanism is illustrated in the following scheme:



(5)

Our experimental data on the rate of disappearance of peroxy groups during the ketone-sensitized photolysis of *cis*-polyisoprene hydroperoxide, *t*-BuOOH, and the results of Walling and Gibian,[6] suggest that a significant portion of the energy transferred from the excited ketone to the hydroperoxide results in direct scission of the peroxy linkage as depicted in eq 5. Due to the fact that hydroperoxides decompose by a radical chain mechanism, it is difficult to determine how efficient this process is, but from other experiments we would predict an efficiency close to unity (i.e., $k_1 >> k_2$ in eq 5).[17] The value may depend on solvent viscosity due to cage recombination of the primary radicals.

Quenching of the carbonyl n–π* state by olefins,[33] dienes,[24] amines,[34] and disulfides[35,36] has been postulated to involve an exciplex intermediate. Peroxide has an electronic configuration similar to that of the disulfide; therefore, the nature of the interaction for these systems toward carbonyl n–π* should be similar. The quenching constants for *t*-BuOOH–PS–PVK and D-*t*-BuP–PS–PVK systems are close to the values reported for rate constants of amine–triplet carbonyl quenching, which is a process generally believed to involve an exciplex intermediate.[34] Detailed studies on the solvent and temperature effects as well as the donor–acceptor oxidation–reduction potential correlation on k_q for the peroxide–carbonyl quenching were reported by Ng and Guillet.[27] Results from such studies also support a quenching mechanism involving a charge-transfer exciplex intermediate.

Table IV
Quenching Studies of PS-PVK and PS-MIPK Type II Photoelimination by Peroxides

polymer	quencher	$k_q\tau$, M^{-1}[a]	k_q, M^{-1} s^{-1}	remarks
PS-PVK (7.6%)	*t*-BuOOH	15.9	1.17×10^9	*b*
PS-PVK (7.6%)	D-*t*-BuP	2.34	1.72×10^8	*b*
PS-MIPK (6%)	*t*-BuOOH	2000		*c*
PS-MIPK (6%)	*t*-BuOOH	26.3		*d*
PS-MIPK (6%)	D-*t*-BuP	27.8		
PS-MIPK (6%)	D-*t*-BuP	17.9		*d*
PS-MIPK (6%)	decanoyl peroxide	18.1		
PS-MIPK (6%)	Luperox 2.5, 2.5	1940		*c*

[a] In benzene, 36.5 °C, irradiated at 313 nm. [b] Triplet lifetime of PS-PVK (7.6%) is 13.6 ns at 36.5 °C (see ref 27). [c] Triplet quenching, $k_q\tau$ value derived from a $[(\phi_0/\phi) - 1]^{-1}$ vs. $[Q]^{-1}$ plot. [d] Singlet quenching, in the presence of 0.5 M *cis*-1,3-pentadiene.

The large difference in $k_q\tau$ values for singlet and triplet quenching reflects a difference in lifetime for the two excited states. Quenching constants for hydroperoxides are always higher than those for peroxides, indicating an unfavorable steric effect exerted by the bulky alkyl substituent on peroxide during the quenching process as compared to a hydrogen atom on hydroperoxide counterparts. This also supports a quenching mechanism in which the bimolecular collision of the excited carbonyl and the peroxy system leading to an encounter complex of appropriate geometry is the rate-determining step. Interestingly, one might ascribe a factor of 1.5 to steric effects in the singlet quenching, whereas a factor of 7 was found in the triplet reaction. The large difference shows that the two different multiplicities may undergo different types of charge-transfer quenching.[37]

In conclusion, we have shown that energy transfer occurs between both singlet and triplet n–π* states of polymeric ketones (both aliphatic and aromatic) and alkyl peroxides and hydroperoxides. The process occurs at rates which are close to diffusion controlled and results in the sensitized decomposition of the peroxy linkage. Since classical energy transfer by Förster or Dexter mechanisms seem unlikely, the most reasonable explanation for this effect is that it proceeds via an exciplex formed between the excited carbonyl and the ground state hydroperoxide or peroxide molecule. In view of the primary role that peroxy and ketone groups play in photodegradation mechanisms in polymers, this phenomenon should be considered in any attempt to quantify mechanisms of photooxidation.

Acknowledgment. The authors gratefully acknowledge financial support of this work from the National Research Council of Canada and a University of Toronto Open Fellowship (to H.C.N.).

References and Notes

(1) Presented in part at the International Conference on Singlet Oxygen and Related Species in Chemistry and Biology, Pinawa,

Manitoba, Canada, August, 1977.
(2) For a general review, see B. Rånby and J. F. Rabek, "Photodegradation, Photooxidation and Photostabilization of Polymers", Wiley, New York, N.Y., 1975.
(3) O. Cicchetti, *Adv. Polym. Sci.*, **7**, 70 (1970).
(4) C. Luner and M. Szwarc, *J. Chem. Phys.*, **23**, 1978 (1955).
(5) I. N. Vasilev and V. A. Kronganz, *Kinet. Katal.*, **4**, 204 (1963).
(6) C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **87**, 3413 (1965).
(7) K. Überreiter and W. Bruns, *Makromol. Chem.*, **68**, 24 (1963).
(8) T. Nakata and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **43**, 3315 (1970).
(9) H. C. Ng and J. E. Guillet, "Singlet Oxygen Reaction with Organic Compounds and Polymers", B. Rånby and J. F. Rabek, Ed., Wiley, Chichester, 1978.
(10) A. C. Somersall, E. Dan, and J. E. Guillet, *Macromolecules*, **7**, 233 (1974).
(11) J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook", Interscience, New York, N.Y., 1975.
(12) H. C. Ng and J. E. Guillet, *Photochem. Photobiol.*, in press.
(13) L. H. Piette and W. C. Landgraf, *J. Chem. Phys.*, **32**, 1107 (1960).
(14) M. Heskins and J. E. Guillet, *Macromolecules*, **3**, 224 (1970).
(15) T. Kilp, B. Houvenaghel-Defoort, W. Panning, and J. E. Guillet, *Rev. Sci. Instrum.*, **47**, 1496 (1976).
(16) T. L. Nemzek and J. E. Guillet, *Macromolecules*, **10**, 94 (1977).
(17) H. C. Ng and J. E. Guillet, *Macromolecules*, in press.
(18) C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, **86**, 3386 (1964).
(19) J. T. Martin and R. G. W. Norrish, *Proc. R. Soc. London, Ser. A*, **220**, 322 (1953).
(20) For a general review, see P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).
(21) (a) J. E. Guillet and R. G. W. Norrish, *Proc. R. Soc. London, Ser. A*, **233**, 153 (1955); (b) G. H. Hartley and J. E. Guillet, *Macromolecules*, **1**, 165, 413 (1968); (c) Y. Amerik and J. E. Guillet, *ibid.*, **4**, 375 (1971); (d) F. J. Golemba and J. E. Guillet, *ibid.*, **5**, 212 (1972); (e) E. Dan, A. C. Somersall, and J. E. Guillet, *ibid.*, **6**, 228 (1973).
(22) (a) D. R. Coulson and N. C. Yang, *J. Am. Chem. Soc.*, **88**, 4551 (1966); (b) N. C. Yang, S. P. Elliott, and B. Kim, *ibid.*, **91**, 7551 (1969); (c) N. C. Yang and S. P. Elliott, *ibid.*, **91**, 7550 (1969).
(23) P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 1245 (1966).
(24) (a) R. R. Hautala and N. J. Turro, *J. Am. Chem. Soc.*, **93**, 5593 (1971); (b) N. C. Yang, M. H. Yui, D. M. Shold, N. J. Turro, R. R. Hautala, K. Dawes, and J. C. Dalton, *ibid.*, **99**, 3023 (1977).
(25) P. J. Wagner and K. C. Liu, *J. Am. Chem. Soc.*, **97**, 7189 (1975).
(26) P. J. Wagner, "Creation and Detection of the Excited State", Vol. 1, Part A, A. Lamola, Ed., Marcel Dekker, New York, N.Y., 1971, Chapter 4.
(27) H. C. Ng and J. E. Guillet, manuscript in preparation.
(28) (a) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1971); (b) L. Giering, M. Berger, and C. Steel, *ibid.*, **96**, 953 (1974).
(29) L. R. Mahoney and M. A. DaRooge, *J. Am. Chem. Soc.*, **92**, 4063 (1970).
(30) One of the referees (reviewer II) pointed out that the protonated ketyl radical from benzophenone is known to reduce many species, including peroxide. However, in neutral organic solvent, the significance of this process is doubted.
(31) E. M. Evleth, *J. Am. Chem. Soc.*, **98**, 1637 (1976).
(32) For reviews, see A. A. Lamola, "Technique of Organic Chemistry", Vol. 14, P. A. Leermakers and A. Weissberger, Ed., Interscience, New York, N.Y., 1969, p 17.
(33) (a) P. J. Wagner and E. I. Kochevar, *J. Am. Chem. Soc.*, **94**, 3859 (1972); (b) R. A. Caldwell, G. W. Sovocool, and R. P. Gajewski, *ibid.*, **95**, 2549 (1973).
(34) For a review, see S. G. Cohen, A. Parola, and G. H. Parsons, *Chem. Rev.*, **73**, 141 (1973).
(35) W. L. Wallace, R. P. Van Duyne, and F. D. Lewis, *J. Am. Chem. Soc.*, **98**, 5319 (1976).
(36) H. Gruen, H. N. Schott, G. W. Byers, H. G. Giles, and J. A. Kampmeier, *Tetrahedron Lett.*, 3925 (1972).
(37) We thank reviewer II for pointing this out to us.

Relative Reactivities in Oxidations of Polypropylene and Polypropylene Models

Frank R. Mayo

SRI International, Menlo Park, California 94025.

Received May 3, 1978

ABSTRACT: The oxidations of solid polypropylene in bulk and solution and of its liquid models, 2,4-dimethylpentane and 2,4,6-trimethylheptane, give ratios of rate constants for propagation and termination, $k_p/(2k_t)^{1/2}$, at several temperatures that fall clearly into three groups. This ratio is highest for bulk atactic polypropylene where propagation is limited to radicals that escape from the cage and can be scavenged, intermediate for polymer in both bulk and solution if all the initiating radicals are considered, and smallest for the models. Differences are due mostly to changes in termination constants but also to steric effects on inter- and intramolecular propagation. Difficulties in radical separation and combination are compensating. Sequence lengths in oxidations of polypropylene are discussed.

In 1973, Niki, Decker, and Mayo[1] reported rates and rate constants for oxidations of bulk atactic polypropylene (APP) and compared them with the corresponding relations for the model, 2,4-dimethylpentane (DMP)[2], at 45 to 55 °C. This comparison requires an appreciation of the very low efficiency of chain initiation in unplasticized bulk APP (formation and separation of two $PPO_2\cdot$ radicals) and the related very low termination constant for the combination of two free $PPO_2\cdot$ radicals. The low efficiency of initiation arises from both the low efficiency of utilizing initiator radicals to make $PP\cdot$ radicals and the low probability (~16% at 45 °C)[3] that the resulting $PPO_2\cdot$ radicals will separate and propagate before they terminate. The comparison also requires an appreciation of the importance of sequence lengths. In the oxidation of bulk DMP at 50 °C, intramolecular propagation is so much faster than intermolecular propagation that 83% of the DMP reacting gives dihydroperoxide.[2] Similarly, 2,4,6-trimethylheptane (TMH) appears to give a high proportion of trihydroperoxide, but only at <1% conversion.[4] In APP, sequence lengths are not well known,[5] in spite of claims to the contrary,[6,7] and comparisons with models must be based on averages of unknown proportions of slower intermolecular and faster intramolecular propagations in APP.

A 1975 paper by Chien and Wang[8] presents new data on the oxidation of bulk APP and purports to show that the ratios $k_p/k_t^{1/2}$ (rate constants for propagation and termination) for bulk APP, isotactic polypropylene (IPP), and their models, DMP and TMH, all fall on the same Arrhenius plot. My present paper shows that this conclusion is the result of misunderstanding or misinterpretation of published data, which I admit are somewhat confusing. When an early draft of this manuscript was sent to known contributors to the field, their responses produced some additional data and corrections of old data. Incorporation of these, together with some corrections and additions to our previous work, now leads to a consistent

0024-9297/78/2211-0942$01.00/0