Macromolecules **1985,** *18,* 2299–2304 **2299**

(20) Otsu, T.; Ushirone, J.; Imoto, M. *Kogyo Kagaku Zasshi* **1966**, *69*, 516; *Chem. Abstr.* **1966**, *65*, 15516*g*.
(21) (a) Guillet, J. E., unpublished results, (b) Ham, G., Ed. "Copolymerization"; Interscience: New York, 1964; p 791.
(22) (a) Bamford, C. H.; Norrish, R. G. W. *J. Chem. Soc.* **1938**, **1531**, 1544. (b) Yang, N. C.; Feit, E. D.; Hui, M. H.; Turro, N. J.; Dalton, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 6974. (c) Lee, L.; McAneney, B.; Guillet, J. E. *Can. J. Chem.* **1971**, *49*, 1311.
(23) (a) Guillet, J. E.; Norrish, R. G. W. *Proc. R. Soc. London, A* **1955**, **233**, 153. (b) Wissbrun, K. F. *J. Am. Chem. Soc.* **1959**, *81*, 58.
(24) Kenyon, J.; Rassoul, A.; Soliman, G. *J. Chem. Soc.* **1956**, 1774.
(25) (a) Lewis, F. D.; Hilliard, T. A. *J. Am. Chem. Soc.* **1970**, *92*, 6672. (b) Lewis, F. D.; Hilliard, T. A. *Ibid.* **1972**, *94*, 3852.
(26) Wagner, P. J.; McGrath, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 3849.

Photochemistry of Ketone Polymers. 19. Temperature and Solvent Effects in the Quenching of Ketone n–π* States by Hydroperoxy and Peroxy Groups

Howard C. Ng[†] and J. E. Guillet*

Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1.

Received July 2, 1984

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 *tert*-butyl hydroperoxide show that both the singlet and triplet n–π* states of the ketones are quenched by the peroxide at diffusion-controlled rates. Temperature and solvent effects in the quenching process were studied. The quenching constants and Arrhenius parameters for the triplet quenching are indicative of a bimolecular collisional process. The inverse dependence on temperature of the singlet quenching constant indicates a possibility of reversible exciplex formation in the quenching process. The observed solvent effects and the correlation of quenching constants with oxidation–reduction potential also seem to indicate a polar exciplex is a possible intermediate in the ketone–peroxide quenching process.

Photochemical or thermal homolysis of hydroperoxides and peroxides generates free radicals that initiate autooxidation chain reactions in lipid peroxidation[1] and in polymer oxidation.[2] This leads to the destruction of the biological membrane systems and a deterioration of polymer physical properties. Since aliphatic hydroperoxides and peroxides are only weakly absorbing in the near-ultraviolet and visible region, more efficient initiation of the free radical chain reactions could involve energy transfer from the excited states of more strongly absorbing chromophores to peroxy systems, causing cleavage of the –O–O– linkage.[3a] Both aromatic and aliphatic ketones and aldehydes, for example, have much higher extinction coefficients than do hydroperoxides[3b] in the near-UV, in which the carbonyl compounds are promoted to the n–π* excited state. Photosensitized decomposition of small-molecule peroxides by different aromatic ketones has been demonstrated experimentally.[4a,b] In a previous paper it was shown that the quenching of the aliphatic and aromatic carbonyl n–π* state by hydroperoxides and peroxides is an efficient process.[3b] Quantitative quenching measurements revealed that the rate constant of energy transfer is of the order of 10^9, i.e., close to the diffusion-controlled limit. It is known that ketonic carbonyl groups, along with other carbonyls such as ester and acid, accumulate in hydrocarbon polymer systems as the oxidation process continues,[2] while the hydroperoxide and the peroxy groups quickly reach a stationary state, usually at a relatively low concentration. Energy transfer from the photoexcited carbonyl to the peroxy groups thus may be an essential step in maintaining or accelerating the rate of degradation. Similar proposals have more recently been made by Geuskens et al. to explain certain features in the photooxidation of solid polystyrene.[4c]

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

compd	ϵ_{313},[a] M^{-1} cm^{-1}	compd	ϵ_{313},[a] M^{-1} cm^{-1}
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-BOOH	0.27[c]	acetone	4[c]
di-*tert*-butyl peroxide	0.93	3,3-dimethyl-2-butanone	10[c]

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

Stewart et al. have shown that in the case of triplet benzophenone quenching by *tert*-butyl hydroperoxide, around 65% of the quenching events involve hydrogen abstraction from the O–H group.[5] They also showed that the behavior of polymer-bound chromophores is similar to that of small molecules.

A study of the temperature and solvent effects in the hydroperoxide quenching of aliphatic and aromatic ketone n–π* states in polymers is reported in this paper. Thus study may provide information about the nature of the interactions involved in the energy-transfer step.

Experimental Section

Materials. Polymers. Poly(styrene-*co*-phenyl vinyl ketone) (7%) (pS–PVK (7%)) and poly(styrene-*co*-methy isopropenyl ketone) (6%) (pS–MIPK (6%)) copolymers were identical with those employed in the previous studies.[3b] The number-average molecular weights are 348 000 and 71 400, respectively. The polydispersity of these polymers is 1.9 and 2.9 for pS–PVK (7%) and pS–MIPK (6%), respectively, and both lie in a suitable range for viscometric determination of polymer chain scission kinetics.

Chemicals. Purification of *tert*-butyl hydroperoxide (*t*-BOOH) and di-*tert*-butyl peroxide was described in a previous paper.[3b] Hydrogen peroxide was obtained by fractional distillation of a commercial 30% solution at reduced pressure, followed by extraction in anhydrous ether. Separation of concentrated H_2O_2 was achieved by evaporation of the ether solution. A stock solution of H_2O_2 in benzene was prepared. The molarity of the H_2O_2 was determined by iodometry. The molar absorptivities of the ketone copolymers and the small molecules determined with a Cary 14 UV spectrometer at 313 nm are shown in Table I. Quantum yields

---

[†] Present address: Du Pont of Canada Ltd., Kingston, Ontario, Canada K7L 5A5.

0024-9297/85/2218-2299$01.50/0

were determined with an automatic viscometer by the procedures described in the previous paper in this series.[6]

Data Treatment. Electronic energy transfer between an excited species and a quencher in fluid media is expressed by the Stern–Volmer relationship

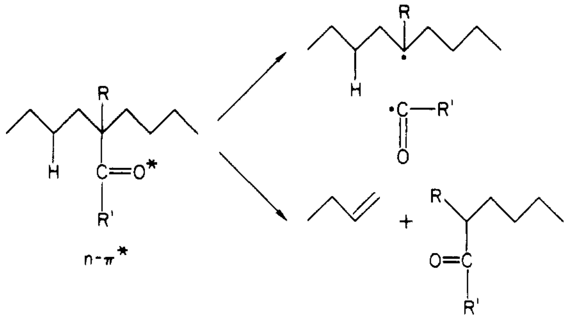
$$\Phi_0/\Phi = k_q\tau[Q] \tag{1}$$

where Φ_0 is the quantum yield in the absence of quencher, 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 $k_q\tau$. Methods of treatment of quenching data were summarized in a previous paper.[3b]

Results

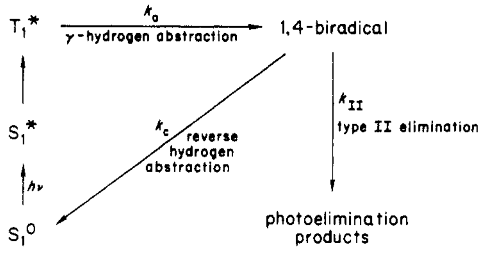
In order to further test the possibility of energy transfer between the excited carbonyl $n-\pi^*$ state and peroxy groups, experiments on the quenching of the Norrish type II photoelimination of ketone–styrene copolymers by hydroperoxides and peroxides at different temperatures and in various solvents were devised.

The major photochemical reactions originating from the carbon $n-\pi^*$ excited state in the photolysis of polymers containing pendant carbonyl chromophores will be the Norrish type I α-cleavage, giving free radicals, and the type II photoelimination to form an olefin and a lower ketone (eq 2). The type II reaction leads to polymer main-chain scission, and hence a decrease in the polymer molecular weight. The type I reaction is important only when a tertiary radical is generated and the environment permits a diffusional separation of the product radical pairs.[7a,b] Under the conditions used in these studies Φ_{II} for pS–PVK can be estimated from the changes in the polymer molecular weight since Φ_I is small and the radicals produced are not tertiary.



(2)

Temperature Dependence. Norrish Type II Elimination in pS–PVK. Aromatic ketones, upon excitation to the $n-\pi^*$ singlet state, proceed to the triplet with unit quantum yield. The triplet species is quantitatively depleted by γ-hydrogen abstraction to yield the 1,4-biradical, followed by type II elimination and reverse hydrogen abstraction to regenerate starting reactant.[7c,d] The following simplified kinetic scheme may be used to define the important rate constants for the various photochemical and photophysical steps in the mechanism:



(3)

Many of these processes are temperature dependent. Table II shows the dependence of Φ_{II}, the chain scission quantum yield, on temperature for experiments in benzene solution.

Table II
Effect of Temperature on Quantum Yield of pS–PVK (7%) Chain Scission[a]

temp, °C	Φ_{II}[b]	temp, °C	Φ_{II}[b]
8.2	0.38	36.5	0.49
15.8	0.40	55.0	0.53
25.2	0.42	70.2	0.60

[a] Irradiation at 313 nm in benzene. [b] Error estimated ≤5%.

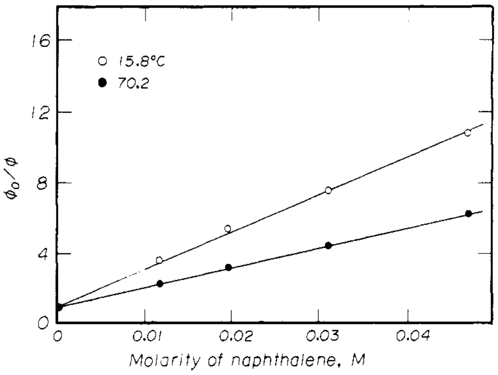


Figure 1. Stern–Volmer plot of naphthalene quenching of pS–PVK scission, in benzene, irradiated at 364 nm at 15.8 and 70.2 °C.

Exothermic triplet–triplet energy transfer is usually diffusion-controlled when the donor energy is higher than that of the acceptor by a few kilocalories per mole. The rate constant for energy transfer (k_q) can be approximated by the rate constant for diffusion given by the modified Debye expression[8]

$$k_{\mathrm{diff}} = \frac{8RT}{3000\eta} \tag{4}$$

However, there are many cases of exothermic transfer, usually in nonviscous solvents, for which the measured rates are smaller than the diffusion-controlled rate (k_{diff}).[9] In these cases, k_q is given by

$$k_q = \alpha k_{\mathrm{diff}} \tag{5}$$

where α is a measure of the efficiency of energy transfer for each encounter of donor and acceptor. Wagner and Kochevar[10] have correlated α with viscosity for a large number of solvents.

Triplet-energy acceptors, such as naphthalene, quench triplet aromatic ketones. The Stern–Volmer constants ($k_q\tau_T$) for naphthalene quenching of the pS–PVK triplet at various temperatures were determined by measurements of the retardation of photoscission in pS–PVK (Figure 1) and are listed in Table III. The $k_q\tau_T$ values are in good agreement with the literature value for the same copolymer (pS–PVK (7%)) determined at 30 °C ($k_q\tau = 183$ M^{-1}).[11,12] These values are higher than the $k_q\tau_T$ value reported for the PVK homopolymer (PPVK; $k_q\tau = 83$ M^{-1}), which corresponds to a triplet lifetime of PPVK of 7.5×10^{-9} s.[13] This lower value is presumably due to the occurrence of triplet migration in the homopolymer, resulting in a threefold reduction in the lifetime of PVK triplet.

Quenching of pS–PVK Ketone Triplet by *t*-BOOH. Quenching of the excited carbonyl $n-\pi^*$ state by hydroperoxides and peroxides has been demonstrated to be an efficient process.[3b] The excited ketone sensitizes the decomposition of the peroxy group and returns to the ground state. In the presence of hydroperoxides, the decrease in the triplet quantum yield of polymer chain scission shows

Table III
Quenching of pS-PVK (7%) Chain Scission by Naphthalene in Benzene[a]

temp, °C	$k_q\tau_T$,[b] M^{-1}	τ_T,[c] ns
8.2	238 ± 7	63.2
15.8	216 ± 10	51.4
25.2	212 ± 5	42.4
36.5	182 ± 1	29.7
55.0	151 ± 1	18.8
70.2	112 ± 1	11.4

[a] Irradiation at 364 nm. [b] From Figure 1. [c] Assuming $k_q = \alpha k_{diff}$ and $\alpha = 0.305$. Benzene viscosity from "Landolt-Bornstein Zahlenwerte und Funktionen", Vol. II, p 158.

Table IV
Quenching of pS-PVK (7%) Chain Scission at 313 nm by *t*-BOOH in Benzene

temp, °C	$k_q\tau_T$,[a] M^{-1}	$k_q \times 10^{-9}$,[b] $M^{-1}\ s^{-1}$	α[c]
8.2	23.7	0.38	0.030
15.8	22.7	0.44	0.032
25.2	21.3	0.50	0.030
36.5	15.9	0.54	0.027
55.0	11.5	0.61	0.023
70.2	9.1	0.80	0.025

[a] From Figure 3, error estimated to be <±5%. [b] From $k_q\tau_T$, using τ_T values from Table III. [c] Assuming the value of α for naphthalene is 0.305, α values for *t*-BOOH from k_{diff}.

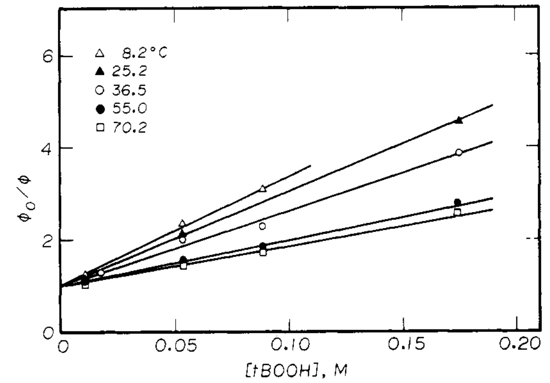


Figure 2. Quenching of pS-PVK type II scission by *t*-BOOH at different temperatures, in benzene, at 313 nm.

a Stern-Volmer relationship with the concentration of hydroperoxide. At different temperatures, a variation of the slope ($k_q\tau_T$) of the Stern-Volmer plot is observed (Figure 2), where k_q is the bimolecular quenching constant between the hydroperoxide and the pS-PVK. The $k_q\tau_T$ values derived from the slopes are listed in Table IV.

In order to determine the relationship between k_q and temperature, the τ_T values at different temperatures were estimated by assuming that quenching by naphthalene is diffusion-controlled. It is generally accepted that the bimolecular rate constant of quenching small-molecule triplet ketones in benzene by naphthalene at room temperature is about $5 \times 10^9\ M^{-1}\ s^{-1}$.[14] This gives an α value, as defined in eq 5, of 0.305. Under the assumption that the variation of α with temperature is small, the τ_T values for pS-PVK were estimated from the Stern-Volmer constants and are also given in Table III. From the observed $k_q\tau$ values for hydroperoxide quenching, the k_q values for *t*-BOOH were estimated. These values are given in Table IV. It should be mentioned that this kinetic treatment may underestimate the value of τ_T at a given temperature for chromophores in a polymer chain, since α may be less than 0.305. For this reason, the k_q values may also be underestimated. Assuming the value of α for naphthalene is 0.305, it is also possible to calculate α for the hydroperoxide quenching, which ranges from about 0.025 to 0.030, or about one-tenth of the efficiency of naphthalene. A plot of log k_q vs. $1/T$ yields a reasonable Arrhenius relationship, as shown in Figure 3. Activation parameters from the least-squares fit of the data in Figure 3 are $E_a = 2.0 \pm 0.2$ kcal/mol and $\Delta S^\ddagger = -12 \pm 1$ eu. The activation energy is of the right order of magnitude for a diffusion-controlled process. It is also clear that motion of the polymer chain is not a rate-controlling step in the quenching reaction, since this would be expected to result in a much higher activation energy.

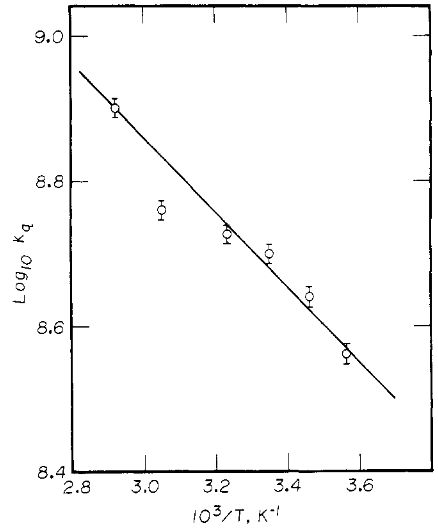


Figure 3. Arrhenius plot for the quenching of pS-PVK chain scission by *t*-BOOH in benzene.

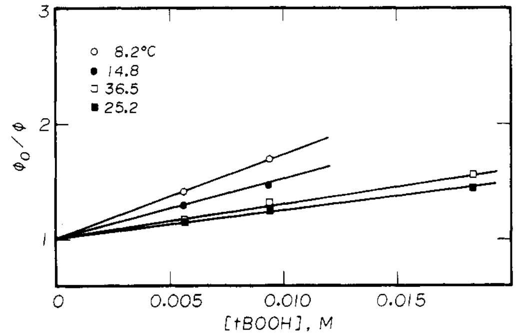


Figure 4. Quenching of pS-MIPK singlet scission by *t*-BOOH at different temperatures. [*cis*-1,3-Pentadiene] = 0.5 M, in benzene, 313 nm.

Table V
Effect of Temperature on Singlet and Triplet Quantum Yields of pS-MIPK (6%) Chain Scission[a]

temp, °C	singlet, Φ_1[b]	triplet, Φ_3	total Φ
8.2	0.06	0.12	0.18
14.8	0.06	0.12	0.18
25.2	0.06	0.12	0.18
36.5	0.07	0.15	0.22
55.5	0.06	0.22	0.28

[a] Irradiation at 313 nm in benzene. [b] Determined by using *cis*-1,3-pentadiene as triplet quencher.

Photolysis of pS-MIPK and Quenching by *t*-BOOH. In contrast to aromatic ketones, photoexcited aliphatic ketones undergo the Norrish type II elimination, which originates from both singlet and triplet states. In the presence of sufficient amounts of triplet quenchers such as *cis*-1,3-pentadiene, the triplet is completely quenched and the contribution from the singlet state can be determined.[15,16] The effect of temperature on singlet

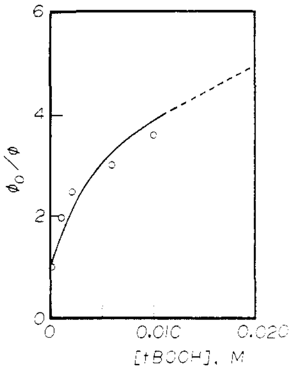


Figure 5. Predicted Stern–Volmer plot for pS–MIPK quenched by *t*-BOOH based on eq 6: open circles, experimental data; dashed line, by eq 6 at 36.5 °C. $\Phi_1{}^0 = 0.07$, $\Phi_3{}^0 = 0.15$, $k_{q1}\tau_1 = 32\ \mathrm{M}^{-1}$, $k_{q3}\tau_3 = 2300\ \mathrm{M}^{-1}$.

Table VI
Effect of Temperature on the Quenching of Chain Scission from the pS-MIPK (6%) n–π* Singlet State by *t*-BOOH[a]

temp, °C	$k_q\tau_S$,[b] M^{-1}	temp, °C	$k_q\tau_S$,[b] M^{-1}
8.2	74	25.2	26
14.8	56	36.5	32

[a] Irradiated at 313 nm in benzene, in the presence of 0.5 M *cis*-1,3-pentadiene. [b] From Stern–Volmer plot.

Table VII
Effect of Temperature on the Quenching of Chain Scission from the pS-MIPK (6%) n–π* Triplet State by *t*-BOOH[a]

temp, °C	$k_q\tau_T$,[b] M^{-1}	temp, °C	$k_q\tau_T$,[b] M^{-1}
8.2	1330	25.2	1430
14.8	1840	36.5	2300

[a] Irradiation at 313 nm in benzene. [b] Calculated from eq 5 at [*t*-BOOH] = 0.002 M; $k_{q1}\tau_1$ value and $\Phi_3{}^0/\Phi_1{}^0$ at the given temperature taken from Tables IV and V, respectively.

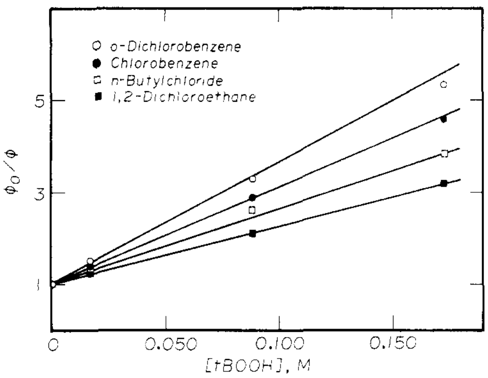


Figure 6. Stern–Volmer plot for quenching of pS–PVK by *t*-BOOH in different solvents, at 313 nm, 25.2 °C.

Table VIII
Solvent Effect on the Quenching of pS-PVK (7%) Chain Scission by *t*-BOOH[a]

solvent	$k_q\tau_T$,[b] M^{-1}	dielectric constant	viscosity,[c] cP
benzene	21.3	2.28	0.60
chlorobenzene	21.5	5.62	0.75
1,2-dichlorobenzene	26.7	9.93	1.36
1,2-dichloroethane	12.9	10.36	0.78
1-chlorobutane	16.9	7.39	0.41

[a] Irradiation at 313 nm, 25.2 °C. [b] From Figure 6. [c] Viscosity data from "Landolt-Bornstein Zahlenwerte und Funktionen", Vol. II.

and triplet quantum yields of pS-MIPK (6%) chain scission is shown in Table V. It has been shown that hydroperoxide quenches both the singlet and the triplet carbonyl n–π* states significantly.[3b] The temperature dependence of the quenching of the aliphatic ketone singlets by *t*-BOOH is shown in Figure 4. The Stern–Volmer constants ($k_{q1}\tau_1$) at various temperatures are summarized in Table VI.

The kinetic analysis for the situation in which two excited states undergo reaction and are both quenched has been derived by Dalton and Turro,[17] Shetlar,[18] and Wagner.[19] Applying the expression derived by Wagner for the condition of no equilibration between states[19]

$$\frac{\Phi_0}{\Phi} = \frac{(1 + k_{q1}\tau_1[\mathrm{Q}])(1 + k_{q3}\tau_T[\mathrm{Q}])}{1 + \{(k_{q3}\tau_T[\mathrm{Q}])/(1 + \Phi_3{}^0/\Phi_1{}^0)\}} \qquad (6)$$

a rearrangement of eq 6

$$k_{q3}\tau_T = \frac{(\Phi_0/\Phi - 1 - k_{q1}\tau_1[\mathrm{Q}])(1 + \Phi_3{}^0/\Phi_1{}^0)}{\{(1 + \Phi_3{}^0/\Phi_1{}^0)(1 + k_{q1}\tau_1[\mathrm{Q}]) - (\Phi_0/\Phi)\}[\mathrm{Q}]} \qquad (7)$$

Since $\Phi_3{}^0/\Phi_1{}^0$ and $k_{q1}\tau_1$ values were determined from singlet quenching experiments (Tables V and VI), $k_{q3}\tau_T$ value at a given temperature can be calculated from eq 7, with a relative quantum yield (Φ_0/Φ) measured at a given quencher concentration [Q]. The triplet quenching constants of *t*-BOOH on pS–MIPK chain scission at various temperatures are listed in Table VII. Figure 5 shows the predicted Stern–Volmer relation according to eq 6 using the derived $k_{q3}\tau_3$ values shown in Table VII and the measured $k_{q1}\tau_1$ and $\Phi_3{}^0/\Phi_1{}^0$ results at a given temperature (36.5 °C). The agreement of the measured Φ_0/Φ values at various [Q] with the predicted values again indicates that hydroperoxide quenches both the singlet and the triplet carbonyl n–π* states in the pS–MIPK system. The discrepancy at higher quencher concentrations may be due to the direct photodecomposition of the hydroperoxide at higher concentration of *t*-BOOH.

Solvent Effects. The quantum yields of chain scission for aromatic ketone polymers such as pS–PVK have been shown to vary with solvent polarity.[6] Whether the effect of halogenated solvents on the quantum yield is a result of the perturbation by the heavy chlorine atom on the energy levels of the n–π* and π–π* states or an effect on the rate of radiationless decay (e.g., by enhanced reverse hydrogen transfer due to spin–orbit coupling) is not yet understood, but the effect is small in any case. However, the rate of quenching of pS–PVK chain scission by *t*-BOOH does depend on solvent polarity, as shown in Figure 6. The Stern–Volmer slopes and quenching constants are summarized in Table VIII. It should be noted that in the aromatic solvents, the quenching constant increases with the dielectric constant of the medium.

Discussion

In a previous paper it has been demonstrated that the ketone n–π* state, in either singlet or triplet state, was efficiently quenched by hydroperoxides and peroxides.[3b] The electronic excitation energy was transferred from the n–π* state of the carbonyl group to the peroxy system, causing the cleavage of the peroxy bond, and the carbonyl groups returned to ground state. Results of the study on temperature and solvent effects in this interaction of photoexcited pendant carbonyl groups on a polystyrene chain with peroxides, presented in this paper, are used to define the nature of the quenching process.

The quenching constants for the pS–PVK triplet–*t*-BOOH system, presented in Table IV, are of the order of magnitude of 10^8. The values of the quenching rate constants in the temperature range studied are all higher than the rate constants for the type II elimination[20] for the polymer aromatic ketone. There are no detectable chemical products from the possible bimolecular reaction between the 1,4-biradicals and the peroxide quenchers.[3b] It is conceivable that the triplet carbonyls on the polymer chain are quenched before they can abstract a γ-hydrogen atom and lead to polymer chain scission.

The Arrhenius activation parameters were measured for the triplet ketone quenched by hydroperoxides ($E_a = 2.0 \pm 0.2$ kcal/mol, $\Delta S^* = -12 \pm 1$ eu). The positive dependence of k_q and an activation energy of 2 kcal/mol are both indications of a diffusion-controlled process. The entropy of activation (−12 eu) is also consistent with a bimolecular collisional process.

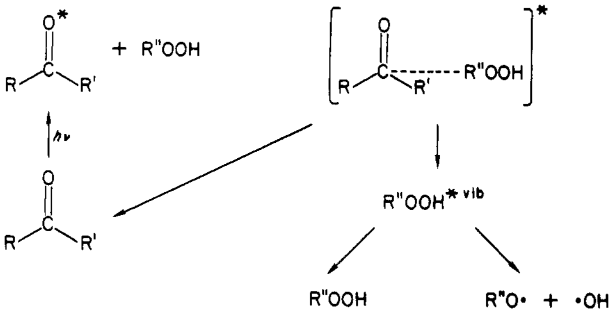
In pS–MIPK both singlet and triplet states result in type II elimination, causing polymer chain scission. The quantum yield distributions from the contribution of singlet and triplet states at different temperatures are given in Table V. Note that the singlet quantum yield is constant (0.06) between 8 and 56 °C, whereas the triplet quantum yield of MIPK scission increases with temperature. This positive dependence of Φ_{II} on triplet state is also observed in pS–PVK (Table II).

Results of the quenching of MIPK singlet by hydroperoxide at various temperatures are given in Table VI. A negative dependence of $k_q\tau_1$ on temperature was observed. The slope of the Stern–Volmer plot (i.e., $k_q\tau_1$) doubles as the temperature is decreased from 36.5 to 8.2 °C . Yang et al. have demonstrated that the singlet lifetime of acetone carbonyl n–π* state remained constant between −10 and +40 °C,[16b] and as shown in Table V the singlet quantum yield for pS–MIPK chain scission remains constant in the temperature range studied; it seems reasonable to conclude that the variation in $k_q\tau_1$ originates in a variation in k_q, while τ_1 remains essentially unchanged in the temperature range studied. Results in Table VI indicate the significant increase in the singlet quenching constant at lower temperatures.

The effect of temperature on the quenching of pS–MIPK triplet by hydroperoxide, as shown by the results in Table VII, is less obvious. The $k_q\tau_T$ term decreases at lower temperatures. It has been observed in the aromatic ketone case that the triplet lifetime is inversely dependent on temperature (Table III); the variation of $k_q\tau_T$ in Table VII indicates that the quenching constant k_q of MIPK aliphatic ketone triplet by hydroperoxides reduces rapidly at lower temperatures.

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.[21] 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 a basic requirement of the "classical" electronic energy transfer,[22] 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 peroxides 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 system might undergo bond dissociation to yield the observed peroxide decomposition products.[3b] This mechanism is illustrated in the following scheme:



(8)

Quenching of the carbonyl n–π* state by olefins,[23] dienes,[16] amines,[24] and disulfides[25,26] 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 n–π* states should be similar. The quenching constants for the pS–PVK triplet-*t*-BOOH system at various temperatures, shown in Table IV, are of the same order of magnitude as the triplet quenching constant for amines, which has been shown to involve a charge-transfer exciplex.[24]

The inverse temperature dependence of k_q in the pS–MIPK–hydroperoxide quenching indicates a possibility of reversible exciplex formation as an intermediate in the quenching process. However, the results are not conclusive because of the complexity of the MIPK system. The temperature dependence of the quantum yield data depends both on intersystem crossing–H abstraction partitioning and on biradical partitioning.[27]

The solvent effect on the quenching of pS–PVK chain scission by *tert*-butyl hydroperoxide, as shown in Table VIII, is not pronounced. In aromatic solvents there appears to be a trend that the quenching is enhanced in more polar solvents of higher dielectric constant. It is interesting to note that, according to eq 4, a reverse trend, namely a decrease in quenching efficiency, would be expected from considerations of solvent viscosity of the three aromatic solvents shown in Table VIII. The viscosity effect must be overcome by the stabilization of the possible polar intermediates in the quenching process by solvation in a medium of higher dielectric constant.

The quenching constants in the two aliphatic chlorohydrocarbon solvents do not show the same solvent polarity effect. In these two solvents the $k_q\tau_T$ values may have larger viscosity contributions. It is noted that $k_q\tau_T$ values in aliphatic solvents, with higher polarity and lower viscosity, are lower than those in aromatic solvents. These differences might arise from stabilization due to the conjugated π systems of the aromatic solvents.

Stern–Volmer constants for the quenching of the singlet and triplet carbonyl n–π* state by three different peroxide compounds, namely hydrogen peroxide, *tert*-butyl hydroperoxide, and di-*tert*-butyl peroxide, are given in Table IX. Oxidation and reduction potentials of some relevant peroxides and ketones, taken from literature, are listed in Table X. A comparison of the two tables indicates that there is a correlation between $k_q\tau$ values for both triplet and singlet quenching and the reduction potentials of these peroxide compounds. Since ketones in general have higher reduction potentials than the peroxide compounds shown in Table X, it is energetically favorable that during the quenching process the excited ketone may function as an

Table IX
Stern–Volmer Constants for Quenching of Singlet and Triplet Carbonyl n–π* States by Peroxides in Benzene[a]

quencher	singlet quenching[b] $k_q\tau_S$, M^{-1}	triplet quenching[c] $k_q\tau_T$, M^{-1}
hydrogen peroxide	48.6	23.4
tert-butyl hydroperoxide	26.3	15.9
di-*tert*-butyl peroxide	17.9	2.4

[a] Irradiated at 313 nm, 36.5 °C. [b] Quenching of pS-MIPK singlet from Stern–Volmer plot, error estimated to be ≤5%. [c] Quenching of pS-PVK triplet, error estimated to be ≤5%.

Table X
Oxidation and Reduction Potentials of Some Peroxides and Ketones

peroxide	ox. potl,[a] eV	red. potl,[b] V
hydrogen peroxide	11.5[c]	−2.15[e]
tert-butyl hydroperoxide	10.2[d]	−2.33[e]
di-*tert*-butyl peroxide	8.7[d]	
acetone	9.7[f]	−2.61[g]
acetophenone	9.5[f]	

[a] Ionization potential obtained from photoelectron spectroscopic data. [b] Polarographic reduction potential vs. a saturated calomel electrode. [c] Reference 29. [d] Reference 30. [e] Reference 31. [f] Reference 32. [g] Reference 33.

electron donor, transferring charge from the half-filled π* orbital to the lowest unoccupied MO of the peroxy system. Similar interactions have been postulated between the excited ketone and electron-deficient systems such as unsaturated nitriles.[16b,33]

In conclusion, we have shown temperature and solvent effects in the quenching of both singlet and triplet n–π* states of polymeric ketones (both aliphatic and aromatic) by alkyl hydroperoxides. The quenching constants and Arrhenius parameters for the triplet quenching are indicative of a bimolecular collisional process with an encounter complex intermediate. The inverse dependence on temperature of the singlet quenching constant indicates the possibility of reversible exciplex formation in the quenching process. The observed solvent effects and the correlation of quenching constants with oxidation–reduction potential also seem to indicate that a polar exciplex is a possible intermediate in the ketone–peroxide quenching process.

Acknowledgment. We 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) For a general review, see: Bland, J. *J. Chem. Educ.* **1976**, *53*, 274.

(2) (a) Winslow, F. H. *Pure Appl. Chem.*, **1977**, *49*, 495. (b) Carlsson, D. J.; Wiles, D. M. *J. Macromol. Sci., Rev. Macromol. Chem.* **1976**, **C14**, 65. (c) Cicchetti, O. *Adv. Polym. Sci.* **1970**, *7*, 70.

(3) (a) Guillet, J. E. *Adv. Chem. Ser.* **1978**, *No.* **169**, 11. (b) Ng, H. C.; Guillet, J. E. *Macromolecules* **1978**, **11**, 937.

(4) (a) Walling, C.; Gibian, M. J. *J. Am. Chem. Soc.* **1965**, **87**, 3413. (b) Uberreiter, K.; Bruns, W. *Makromol. Chem.* **1963**, **68**, 24. (c) Geuskens, G.; Baeyens-Volant, D.; Delaunois, G.; Lu Vinh, Q.; Piret, W.; David, C. *Eur. Polym. J.* **1978**, **14**, 299.

(5) Stewart, L. C.; Carlsson, D. J.; Wiles, D. M.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, **105**, 3605.

(6) Ng, H. C.; Guillet, J. E. *Macromolecules*, preceding paper in this issue.

(7) For reviews, see: (a) Guillet, J. E. *Pure Appl. Chem.* **1977**, *49*, 249. (b) Turro, N. J. *Ibid.* **1977**, *49*, 405. (c) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1. (d) Lamola, A. A. In "Techniques of Organic Chemistry"; Weissberger, A., Ed.; Interscience: New York, 1969.

(8) (a) Debye, P. *Trans. Electrochem. Soc.* **1942**, **82**, 265. (b) Osborne, A. D.; Porter, G. *Proc. R. Soc. London, A* **1965**, **284**, 9.

(9) (a) Backstrom, H. J. L.; Sandros, K. *Acta Chem. Scand.* **1962**, **16**, 958. (b) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, **88**, 4769.

(10) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, **90**, 2232.

(11) Tsunooka, M.; Nishino, T.; Tanaka, M. *Chem. Lett.* **1977**, 1107.

(12) Golemba, F. J.; Guillet, J. E. *Macromolecules* **1972**, **5**, 212.

(13) Faure, J.; Fouassier, J.-P.; Lougnot, D. J.; Salvin, R. *Nouv. J. Chim.* **1977**, **1**, 15.

(14) (a) Clark, W. D. K.; Litt, A. D.; Steel, C. *J. Am. Chem. Soc.* **1969**, **91**, 5413. (b) Porter, G.; Topp, M. R. *Proc. R. Soc. London, A* **1970**, **315**, 163.

(15) Wagner, P. J.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, **88**, 1245.

(16) (a) Hautala, R. R.; Turro, N. J. *J. Am. Chem. Soc.* **1971**, **93**, 5593. (b) Yang, N. C.; Hui, M. H.; Should, D. M.; Turro, N. J.; Hautala, R. R.; Dawes, K.; Dalton, J. E. *Ibid.* **1977**, **99**, 3023.

(17) Dalton, J. C.; Turro, N. J. *Mol. Photochem.* **1970**, **2**, 133.

(18) Shetlar, M. D. *Mol. Photochem.* **1973**, **5**, 311.

(19) Wagner, P. J. In "Creation and Detection of the Excited State"; Lamola, A. A., Ed.; Marcel Dekker: New York, 1971; Vol. 1, p 173.

(20) Wagner, P. J. *Acc. Chem. Res.* **1971**, **4**, 168.

(21) Evleth, E. M. *J. Am. Chem. Soc.* **1976**, **98**, 1637.

(22) For reviews, see: Lamola, A. A. "Techniques of Organic Chemistry"; Leermakers, P. A.; Weissberger, A., Ed.; Interscience: New York, 1969; Vol. 14, p 17.

(23) (a) Wagner, P. J.; Kochevar, E. I. *J. Am. Chem. Soc.* **1972**, **94**, 3859. (b) Caldwell, R. A.; Sovocool, G. W.; Gajewski, R. P. *Ibid.* **1973**, **95**, 2549.

(24) For a review, see: Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973**, **73**, 141.

(25) Wallace, W. L.; Van Duyne, R. P.; Lewis, F. D. *J. Am. Chem. Soc.* **1976**, **98**, 5319.

(26) Gruen, H.; Schott, H. N.; Byers, G. W.; Giles, H. G.; Kampmeier, J. A. *Tetrahedron Lett.* **1972**, 3925.

(27) We thank Reviewer II for constructive comments on this point.

(28) Brown, R. S. *Can. J. Chem.* **1975**, *53*, 3439.

(29) Batich, C.; Adam, W. *Tetrahedron Lett.* **1974**, *16*, 1467.

(30) Yamshchikov, A. V.; Levin, E. S. *Elektrokhimiya* **1970**, *6*, 588.

(31) Vedeneyev, V. I.; Gurvick, L. V.; Kondrat'yev, V. N.; Medvedev, V. A.; Frankevich, Ye. L. "Bond Energy, Ionization Potential and Electron Affinities"; E. Arnold Publisher: London, 1966.

(32) Powers, R.; Day, R. *J. Org. Chem.* **1959**, *24*, 722.

(33) Barltrop, J. A.; Carless, H. A. J.; *J. Am. Chem. Soc.* **1972**, *94*, 1951.