Triplet Quenching by *tert*-Butyl Hydroperoxide[1]

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Abstract: Laser flash photolysis studies show that *tert*-butyl hydroperoxide is an excellent triplet quencher. For example, the rate constants for benzophenone and phenanthrene in benzene at 300 K are 1.8×10^8 and 2.3×10^7 M^{-1} s^{-1}, respectively. In the case of benzophenone, around 65% of the quenching events involve hydrogen abstraction from the O–H group. The rate constants are reduced in the presence of hydroxylic solvents, reflecting a drop in hydroperoxide reactivity associated with hydrogen bonding. The behavior of polymer-bound chromophores is similar to that of small molecules; the sensitized cleavage of hydroperoxides and hydrogen abstraction from the O–H group are suggested as possible contributors to the photooxidative degradation of polymers.

The interaction of peroxides and hydroperoxides with excited states is a subject of current interest. The problem is of practical relevance because of its potential role in polymer systems.[3-5] Further, the quenching of excited states by di-*tert*-butyl peroxide has been shown to provide an example of energy transfer to a repulsive state.[6]

It has been observed that hydroperoxides are usually better quenchers of carbonyl triplets than peroxides, but no unequivocal explanation has been offered.[3,7] By contrast, in the case of excited singlets, the rate constants derived from fluorescence quenching studies indicate that, in some systems, di-*tert*-butyl peroxide is a slightly better quencher than *tert*-butyl hydroperoxide.[8]

The high rates of triplet quenching by hydroperoxides have been suggested to reflect the intermediacy of an exciplex although no direct evidence of this species has been presented.[3] An alternative explanation that has been previously discarded is the possibility of carbonyl triplet photoreduction by hydrogen abstraction from the hydroperoxide O–H bond.[9] Several reports published in the last few years make this possibility not just an attractive one but, in fact, almost a predictable result. For example, a recent study on the interaction of carbonyl triplets with phenols, where the same bond and similar thermochemistry is involved, has shown that photoreduction is the predominant reaction path.[10] Further, Wagner and Puchalski[11] have recently reported that in the photoreaction of acetophenone with 1-phenylethanol ~50% of the reaction involves attack at the O–H position. In the case of *tert*-butoxy radicals, which are generally accepted as good analogues of carbonyl triplets, the rate of H abstraction from the OH group of *tert*-butyl hydroperoxide has been measured at 2.5×10^8 M^{-1} s^{-1} at 295 K in a 1:2 mixture of benzene and di-*tert*-butyl peroxide.[12] Even in the case of alcohols, the reaction with *tert*-butoxy radicals involves some attack at the O–H site.[13] Semiempirical calculations have also predicted high rate constants for the reaction of carbonyl triplets with hydrogen peroxide.[14]

In this paper we report the results of a laser flash photolysis study of the quenching of a variety of triplet photosensitizers by *tert*-butyl hydroperoxide. The aspects examined include the kinetics, solvent and isotope effects, and, in the case of benzophenone, the temperature dependence and the yield of photoreduction. In the case of carbonyl chromophores we have also compared the behavior of free and polymer-bound chromophores.

Results

The unambiguous interpretation of quenching data requires confirmation that interfering, direct chemical reactions between the chromophore and quencher are not occurring prior to photoexcitation. Hydroperoxides and ketones are known to react (especially in the presence of trace catalysts such as acidic groups, SeO_2, etc.) to give peroxyketals,[15] which are anticipated to display a complex photochemistry of their own. The extent of any product formation in hydroperoxide–ketone solutions was investigated by UV and FTIR spectroscopy. At the highest concentration used in quenching experiments (5×10^{-3} M ketone, 0.3 M hydroperoxide) only very small (≤5 nm) red shifts were noted both in the intense UV absorptions and in the long-wavelength UV tails of benzophenone, 4-methoxyacetophenone, acetophenone, and 4-methylbenzophenone. No spectral changes were observed over several days after preparing these mixtures, implying that no reaction takes place at ambient temperatures during storage. The possibility of the small UV shifts resulting from direct ketone–hydroperoxide reactions was investigated by FTIR spectroscopy. A comparison of the IR spectra of ketone–hydroperoxide mixtures with those of individual components showed no loss in carbonyl absorption (only a small shift from 1682 to 1680 cm^{-1}), no decrease in free –OH absorption, and no formation of new bands even at high scale expansions. These IR data clearly imply negligible (≤1%) reaction at the highest ketone with hydroperoxide levels used in our work.

Kinetic Studies. The kinetics of triplet quenching by *tert*-butyl hydroperoxide were monitored by following the decay of the T–T absorptions of the different sensitizers with nanosecond laser flash photolysis techniques. The pulses from a nitrogen laser (337.1 nm, ~8 ns, up to 10 mJ) were used for excitation, and the transient absorptions were monitored at or near the absorption maxima of the triplet species involved.

All the kinetic studies were carried out following essentially the same approach as exemplified here for the case of benzophenone. A series of samples containing 0.0052 M benzophenone in chlorobenzene and variable amounts of *tert*-butyl hydroperoxide were examined at seven different temperatures in the 230–343 K range. Triplet benzophenone was detected by its T–T absorption at 525 nm. The formation and decay of this absorption are shown in Figure 1. In the presence of *tert*-butyl hydroperoxide, the 525-nm absorption decays more rapidly and, in addition, does not

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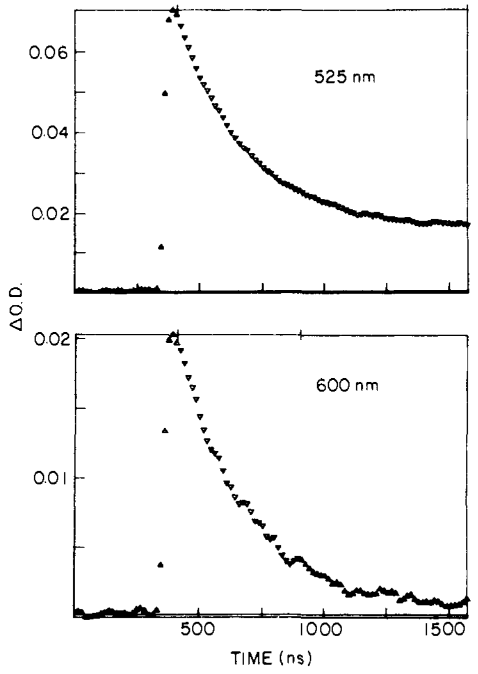

Figure 1. Transient absorptions monitored at 525 (top) and 600 nm (bottom), upon excitation of a sample containing benzophenone (0.005 M) and *tert*-butyl hydroperoxide (0.0205 M) in chlorobenzene at 238 K.

decay to the prepulse level (Figure 1). A spectroscopic study after the triplet decay is complete (e.g., in the 1000–1500-ns region of the trace as shown in Figure 1) indicates that the residual optical density is due to the ketyl radical, $(C_6H_5)_2\dot{C}OH$, which shows a maximum at 540 nm. Within the time scale of these experiments the ketyl radical can effectively be regarded as a stable product; its spectrum was in full agreement with that reported earlier.[16] When the optical absorptions were monitored at 600 nm where the triplet signals (although weak) are substantially stronger than those arising from the ketyl radical, the decay traces return to essentially the prepulse level, as shown in Figure 1. The kinetics for triplet decay measured at 525 or 600 nm were in excellent agreement. The ketyl radicals can reasonably be expected to result from reaction 1.[17]

$$(C_6H_5)_2CO^* + Bu^tOOH \rightarrow (C_6H_5)_2\dot{C}OH + Bu^tOO\cdot \quad (1)$$

It is important to establish quantitatively the role played by reaction 1. In other words, what fraction of the triplet quenching events involves photoreduction by the hydroperoxide? It is possible to answer this question by using the quantitative photoreduction of benzophenone triplets by triethylamine as an actinometer; the technique was developed by Linschitz et al.[18] and has been used before in our laboratories.[16,19] These experiments were carried out at 525 nm in order to use the same traces employed for the kinetic studies. We find that between 230 and 343 K in chlorobenzene, the fraction of quenching events that lead to photoreduction remains essentially constant (within ±10%) at about 65%. Thus, only ~35% of the quenching events do not lead to ketyl radicals; these may involve sensitized O–O cleavage, cage disproportionation of the initially formed radical pair, or perhaps triplet deactivation via an exciplex mechanism as suggested previously.[3,5] However, it is clear that the main reaction path involves hydrogen abstraction; the excellent agreement between the kinetics for benzophenone triplets and for alkoxyl radicals[12] suggests that this process should be treated as a simple, radical-like abstraction.

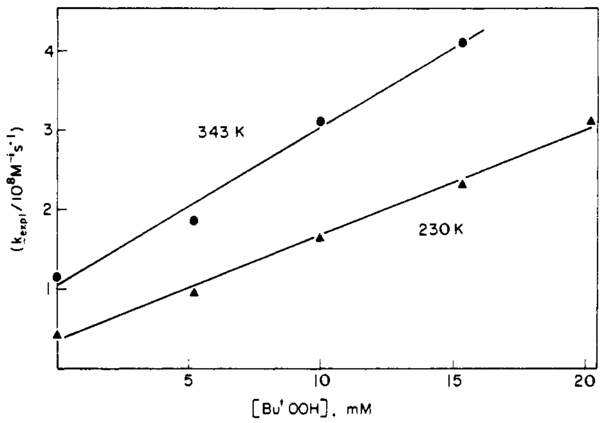

Figure 2. Quenching of triplet benzophenone (0.005 M) in chlorobenzene by *tert*-butyl hydroperoxide, according to eq 2.

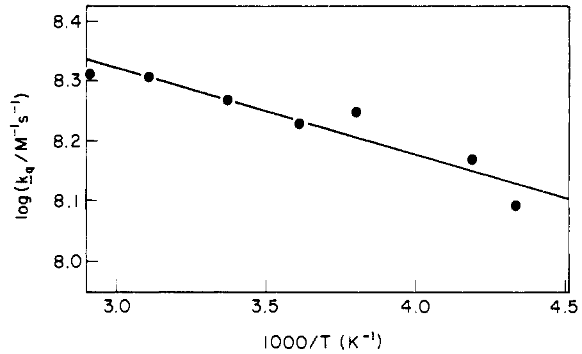

Figure 3. Arrhenius plot for the quenching of triplet benzophenone by *tert*-butyl hydroperoxide in chlorobenzene. Each point results from a plot similar to those shown in Figure 2.

In the presence of low concentrations of the hydroperoxide the decay of the triplet state followed clean pseudo-first-order kinetics.[20] The experimental rate constant for triplet decay, k_{expt}, can be related to the bimolecular rate constant for triplet quenching, k_q, according to eq 2

$$k_{expt} = k_0 + k_q[Bu^tOOH] \quad (2)$$

were k_0 is the first-order rate constant for triplet decay in the absence of hydroperoxide and includes processes such as phosphorescence, radiationless decay, reaction with the solvent, and impurity quenching. Figure 2 shows two representative plots according to eq 2, obtained at the two extreme temperatures. Arrhenius analysis of the data (see Figure 3) leads to

$$\log (k_q/M^{-1}\,s^{-1}) = (8.75 \pm 0.17) - (0.66 \pm 0.21)/(2.3RT)$$

with RT in kcal mol^{-1} and where the errors correspond to 95% confidence limits. Interpolation leads to $k_q = 1.85 \times 10^8$ M^{-1} s^{-1} at 300 K. It should be noted that given the observation that triplet quenching involves several reaction paths, the use of an Arrhenius expression should be regarded simply as a formal way of reporting the temperature dependence of the overall quenching process.[22]

Other ketones, such as acetophenone and *p*-methoxyacetophenone, also showed transient decays consistent with hydrogen abstraction (i.e., ketyl formation), but in these cases the quantitative determination of radical yields was more difficult because

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(20) A detailed analysis of the kinetic treatment of data from systems where reagents and products absorb in the same spectral region has been described elsewhere.[21]

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(22) Though in this particular case the temperature independence of the yields suggests that the overall activation energy is approximately the same as for hydrogen abstraction.

Table I. Kinetic Data for the Quenching of Triplet States by *tert*-Butyl Hydroperoxide at 300 K

substrate	solvent	λ-(monit)[a]	k_q/M^{-1} s^{-1}
benzophenone	benzene	525	$(1.8 \pm 0.3) \times 10^8$
benzophenone	hexadecane	525	$(1.5 \pm 0.3) \times 10^8$
benzophenone	acetonitrile–H_2O (95:5 v/v)	525	$(6.8 \pm 1.1) \times 10^7$
benzophenone	acetonitrile–D_2O (95:5 v/v)	525	$(5.6 \pm 1.2) \times 10^7$
p-methyl-benzophenone	benzene	525	$(4.1 \pm 0.6) \times 10^8$
p-methyl-benzophenone	acetonitrile–H_2O (95:5 v/v)	525	$(5.9 \pm 0.6) \times 10^7$
acetophenone	chloroform	365	$(7.7 \pm 2.2) \times 10^8$
p-methoxy-acetophenone	benzene	400	$(1.9 \pm 0.4) \times 10^9$
p-methoxy-acetophenone	acetonitrile–H_2O (95:5 v/v)	525	$(1.3 \pm 0.1) \times 10^8$
p-methoxy-acetophenone	acetonitrile–D_2O (95:5 v/v)	525	$(1.05 \pm 0.15) \times 10^8$
phenanthrene	benzene	483	$(2.3 \pm 0.2) \times 10^7$
phenanthrene	acetonitrile	483	$(1.06 \pm 0.2) \times 10^7$
phenanthrene	acetonitrile–H_2O (90:10 v/v)	483	$(0.70 \pm 0.1) \times 10^7$
anthracene	benzene	420	$\leqslant 2 \times 10^6$

[a] Wavelength (nm) at which triplet decay was monitored.

Table II. Quenching of Polymer-Bound Carbonyl Triplets at 300 K by *tert*-Butyl Hydroperoxide[a]

substrate[b]	solvent	λ(monit)[c]	k_q/M^{-1} s^{-1}
PPMA	benzene	400	$(5.5 \pm 1.0) \times 10^8$
co(Sty-VBP)	benzene	525	$(3.1 \pm 0.5) \times 10^8$
co(Sty-PMA)	benzene	400	$(8.1 \pm 2.2) \times 10^8$
co(MMA-PMA)	benzene	400	$(6.3 \pm 0.2) \times 10^8$

[a] [Bu^tOOH] = 1–0.1 M. [b] Abbreviations used for the monomers: PMA = *p*-methoxyacrylophenone; Sty = styrene; VBP = 4-vinylbenzophenone; MMA = methyl methacrylate. [c] Wavelength (in nm) at which the triplet decay kinetics were monitored.

Table III. Quenching of Sensitizers Containing Benzoyl Chromophores by *tert*-Butyl Hydroperoxide at Low Temperature

sensitizer[a,b]	solvent	*T*, K	k_q/M^{-1} s^{-1}
1,5-diphenyl-1,5-pentanedione	chloroform	220	$(2.4 \pm 0.4) \times 10^8$
co(MMA-PVK)[c]	chloroform	229	$(1.02 \pm 0.30) \times 10^8$
PPVK	chloroform	229	$(1.4 \pm 0.3) \times 10^8$
PPVK	toluene-d_8	217	$(4.4 \pm 2.0) \times 10^8$

[a] See footnote *b* in Table II for abbreviations. [b] All monitored at 365 nm, in static samples. [c] PVK = phenyl vinyl ketone.

Table IV. Effects of Alcohols on the Lifetime of Triplet Macrocarbonyls in the Presence of *tert*-Butyl Hydroperoxide

polymer	alcohol	alcohol concn, M	τ, ns, at 300 K
co(Sty-VBP)[a] (3200)[b]	methanol	0	199
		0.23	245
		0.46	323
		1.12	374
co(Sty-PMA)[c] (1650)	Bu^tOH	0	1130
		0.021	1207
		0.053	1297
		0.48	1500

[a] In benzene plus Bu^tOOH (0.02M). [b] Triplet lifetime in the absence of hydroperoxide (in ns). [c] In chloroform plus Bu^tOOH (1.6×10^{-3} M).

of the low extinction coefficient for the ketyl radicals as compared to the triplet species. Table I summarizes k_q values obtained at 300 K for several monoketones and polynuclear aromatics.

Both hydroperoxides and carbonyl chromophores are believed to be important initiators of polymer photodegradation and photooxidation processes.[3-5] Consequently, we examined the quenching by *tert*-butyl hydroperoxide in the case of polymer-bound sensitizers. Table II summarizes the quenching data at 300 K.

Unfortunately, in the case of poly(phenyl vinyl ketone), PPVK, it was not possible to carry out studies at room temperature, because the signals due to the triplet state and the Norrish Type II biradical (produced during degradation, $\lambda_{max} = 410$ nm) overlap extensively in both wavelength and time. This problem can be overcome by working at low temperatures, where the triplet lifetime is substantially longer than that for the 1,4-biradical. Table III summarizes the data obtained in the 217–229 K temperature range, for a series of molecules containing benzoyl chromophores.

In the case of the polynuclear aromatic photosensitizers in general, and phenanthrene in particular (Table I), it was important to determine if the quenching of the sensitizer(s) involved the cleavage of the O–O bond, (reaction 3) as in the case of di-*tert*-butyl peroxide reported earlier, or physical quenching (reaction 4). To this end, diphenylmethanol in concentrations of up to 0.6 M was added as a scavenger for both HO· and $Bu^tO\cdot$ (reactions 5 and 6) and the formation of $(C_6H_5)_2\dot{C}OH$ easily monitored at 540 nm.[16] While these experiments clearly showed that good yields of ketyl radicals are formed, quantitative interpretation is complicated by the possibility of HO· and $Bu^tO\cdot$ trapping by the hydroperoxide (reactions 7 and 8). In fact, the sequence of reactions 3–8 should be regarded only as a very oversimplified one as it ignores other possible reaction paths for HO· and all radical–radical reactions. In view of these complications all we could really establish is that in benzene at 300 K, between 20% (reactions 5 and 6 predominating) and 70% (reactions 7 and 8 also allowed for) of the phenanthrene quenching events lead to O–O bond cleavage.

$$S^* + Bu^tOOH \rightarrow S + Bu^tO\cdot + OH\cdot \quad (3)$$

$$S^* + Bu^tOOH \rightarrow S + Bu^tOOH \quad (4)$$

$$Bu^tO\cdot + (C_6H_5)_2CHOH \rightarrow Bu^tOH + (C_6H_5)_2\dot{C}OH \quad (5)$$

$$HO\cdot + (C_6H_5)_2CHOH \rightarrow H_2O + (C_6H_5)_2\dot{C}OH \quad (6)$$

$$Bu^tO\cdot + Bu^tOOH \rightarrow Bu^tOH + Bu^tOO\cdot \quad (7)$$

$$HO\cdot + Bu^tOOH \rightarrow H_2O + Bu^tOO\cdot \quad (8)$$

In the case of phenanthrene we also observed the formation of a weaker transient at ca. 430 nm that, unfortunately, could not be characterized in detail. This transient might possibly result from the reactions of HO· with the sensitizer and/or solvent. It was also observed that while the addition of *tert*-butyl hydroperoxide reduced the lifetime of phenanthrene triplets, it did not have a significant effect on the yield of triplet formation; thus, the quenching of phenanthrene singlets is relatively inefficient in the concentration range examined ([Bu^tOOH] ≤ 0.017 M). This result is entirely consistent with the kinetic parameters (for the singlet state) reported by Encinas and Lissi.[8]

Solvent Effects in Polymer Systems. Solvent effects in the case of small molecules have already been illustrated in Table I, where it is clear that the reactivity of the hydroperoxide is lower in hydrogen bonding as compared to nonpolar media.

Because the ketone copolymers are insoluble in polar hydrogen-bonding media, a somewhat different approach was adopted involving quenching with hydroperoxide in predominantly nonpolar media containing small portions of hydroxylic substrates. If the reactivity of the hydroperoxide is strongly dependent upon the media, the triplet-state quenching should be partially suppressed by addition of substrates such as alcohols. For example, when a sample of co(Sty–PMA) in chloroform containing 0.0016 M hydroperoxide was irradiated at 300 K, we measured a triplet lifetime of 1130 ns. When *tert*-butanol was added, the triplet lifetime increased significantly, as shown in Table IV. A similar effect was observed by addition of methanol to a solution of co(Sty–VBP) in benzesne (Table IV). The "true" effect is probably somewhat larger than suggested by the data in Table

Table V. Comparison of the Rates of Triplet Quenching by Several Substrates Capable of Generating *tert*-Butoxyl Radicals[a]

		$k_q/M^{-1}\ s^{-1}$		
sensitizer	E_T	Bu^tOOH	Bu^tOOBu^t [b]	Bu^tON_2-OBu^t [c]
$RCOC_6H_5$	73.7	7.7×10^8 [d]	9.6×10^6 [e]	
$RCO(4\text{-}CH_3OC_6H_4)$	72.5	1.9×10^9 [f]	7.9×10^6 [e]	1.4×10^8 [f]
benzophenone	68.6	1.8×10^8	3.4×10^6	1.7×10^7
phenanthrene	61.9	2.3×10^7	1.8×10^6	4.3×10^6
anthracene	42	$\leqslant 2 \times 10^6$	9.7×10^4	$\leqslant 5 \times 10^5$

[a] In benzene, at 300 K unless otherwise specified. [b] Reference 6. [c] From: Mendenhall, G. D.; Stewart, L. C.; Scaiano, J. C. *J. Am. Chem. Soc.* 1982, *104*, 5109–5114. [d] In chloroform, R = CH_3–. [e] Propiophenone, R = C_3H_7–. [f] R = CH_3–.

IV, since the methanol may also be acting as a (reactive) triplet quencher.[17] Lacking reactive CH's α to the –OH group, *tert*-butanol cannot quench by this mechanism and displays only a polarity effect.

Discussion

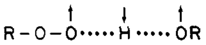
It is important to establish that reaction between *tert*-butyl hydroperoxide and the sensitizers does not occur and to determine the extent of complex formation under our experimental conditions. Both the UV and IR spectral data imply negligible direct reaction. However, Walling and Heaton have shown that *tert*-butyl hydroperoxide dimerizes readily.[7] At concentrations below 0.1 M hydroperoxide in low-polarity solvents at room temperature, only minor (≤10%) dimer formation occurs. In fact, with concentrations above 0.1 M in benzene or toluene-d_8 at temperatures below 260 K, deviations from eq 2 were found, presumably due to reduction in the free hydroperoxide levels. The measurement of the activation energy was carried out in chlorobenzene, where concentrations below 0.02 M were sufficient to measure the rate constants over the complete temperature range. Under these conditions, quenching plots were linear, thus confirming that dimerization does not need to be taken into consideration.

As indicated in Table V, *tert*-butyl hydroperoxide is a better quencher than di-*tert*-butyl peroxide or di-*tert*-butyl hyponitrite. In the case of aromatic sensitizers such as phenanthrene, the process leads to the formation of some *tert*-butoxyl radicals. In the di-*tert*-butyl peroxide system we have established that the quenching process does not require the intermediacy of an exciplex, as had been suggested earlier,[3,5] but rather, it is sufficient to invoke the transfer of the triplet excitation energy into a repulsive state. This mechanism has now received support from independent experiments.[8]

The increase of reactivity of the hydroperoxide as compared to the peroxide in the case of phenanthrene may be partially due to a decrease in steric hindrance although the contribution of polar effects, or even the intermediacy of an exciplex, cannot be ruled out. In fact, *tert*-butyl hydroperoxide shows some tendency to form complexes with aromatics in the ground state;[7] presumably one can expect this tendency to be enhanced in the excited state.

When we compare the reactivity of the peroxide and hydroperoxide in the case of benzophenone triplets we find a marked increase (over a factor of 50). Considering the high reactivity in the case of benzophenone triplets, one could have anticipated less reactivity difference than for phenanthrene. However, the dramatic increase in reactivity can be explained by a change in reactive mechanism, since the dominant process, in the case of benzophenone, is hydrogen abstraction, reaction 1. If the fraction due to hydrogen abstraction is subtracted, the remaining reactivity accounts for a rate constant of ca. 6 × 10^7 $M^{-1}\ s^{-1}$; the changes in reactivity are now in line with those observed in the case of phenanthrene. Ng and Guillet have also observed the quenching of ketone copolymers in the liquid phase in the presence of di-*tert*-butyl peroxide and *tert*-butyl hydroperoxide.[3] Their data were derived from an indirect method, involving the measurement of polymer chain scission as an indicator of ketone triplet decomposition, and lead to k_q values for poly[styrene–co(phenyl vinyl ketone)] of 1.2 × 10^9 (hydroperoxide) and 1.7 × 10^8 $M^{-1}\ s^{-1}$ (peroxide) in benzene at 309 K (cf. our hydroperoxide–PPVK data in Table III). Ng and Guillet invoked an exciplex mechanism based on the erroneous assumption that hydrogen transfer from an –OH group was too slow to account for the observed k_q values and on the experimental result that benzophenone was not consumed in model experiments with *tert*-butyl hydroperoxide. This latter fact would would imply that there is extensive back-reaction in reaction 1. While other examples of efficient primary photoreduction leading to no detectable products are available in the literature, it is perhaps significant that in the case of cumene hydroperoxide quenching of benzophenone Geuskens and Lu-Vinh[5] report relatively efficient product formation in sharp contrast with Guillet's observations.

The high reactivity of hydroperoxides can be anticipated by using bond energy–bond order calculations.[14,23] This technique provides a clear explanation as to why O–H bonds are considerably more reactive than C–H bonds with similar dissociation energy. In exothermic hydrogen transfer reactions, a major contribution to the activation energy is due to repulsion involving the two end atoms between which the hydrogen atom is being transferred. Naturally, this arises from the spin configuration, as shown in the transfer between a hydroperoxide and an alkoxy radical.



$$R{-}O{-}\overset{\uparrow}{O}\cdots\cdots\overset{\downarrow}{H}\cdots\cdots\overset{\uparrow}{O}R$$

In the case of the O–O end atom interaction, the Morse parameter is 2.29 $Å^{-1}$ and the O–O bond is only 35–40 kcal mol^{-1}. As a general rule, end atoms that form weak bonds also lead to small repulsive terms. Thus, the high reactivity of the O–H bond in these reactions is directly related to the weakness of the peroxide bond.

Our solvent studies indicate that the reactivity of hydroperoxides drops substantially in the presence of good hydrogen bonding agents (see Tables I and IV). This aspect of the problem clearly parallels the case of phenols, the reactivity of which is also decreased by hydrogen-bonding solvents.[10,24] A reasonable explanation is that when the O–H bond is engaged in hydrogen bonding it becomes less available for external reagents. Similar effects could be expected at very high hydroperoxide concentrations.

It is interesting that Encinas and Lissi[8] have observed that *tert*-butyl hydroperoxide is less reactive toward excited aromatic singlets than di-*tert*-butyl peroxide; however, most of their experiments were carried out in acetonitrile, and given the purification procedure they describe, their hydroperoxide was unlikely to be water free. Further, quenching of singlets requires higher hydroperoxide concentrations than for excited triplets (because of their intrinsically shorter lifetimes). Thus, since their hydroperoxide data has been obtained in hydrogen-bonding media, it is not inconsistent with our own results (see Table I).

Another intriguing aspect of quenching by *tert*-butyl hydroperoxide is the case of *p*-methoxyacetophenone. This ketone is well-known to have a low-lying π,π^* triplet state[25,26] and is expected to lack the radical-like characteristics that play a dominant role in the photochemistry of other ketones, such as benzophenone. In fact, *p*-methoxyacetophenone triplets are quite unreactive when the reaction involves the cleavage of CH bonds.[27] In the case of phenols,[10,24] we also measured an unusually high reactivity for *p*-methoxypropiophenone and it would thus seem that the high reactivity of O–H bonds toward π,π^* triplets is a rather general phenomenon. The reasons for this high reactivity are so far unclear, and while we have suggested that charge transfer interactions may play an important role and that the reaction may

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occur via the intermediacy of an exciplex,[10] these explanations are, at this point, tentative.

It is possible that the higher reactivity of *p*-methylbenzophenone, compared with benzophenone triplets, is also the result of a decrease in the π,π^*–n,π^* energy gap even if, in this case, the n,π^* state is expected to remain the low-lying one.

Finally, our studies with polymer systems show that the same type of behavior is observed as with small molecules. In general, the rate constants are somewhat smaller for the macromolecules, as could be expected from the change in diffusion coefficients. Solvent effects (see Table IV) seem to parallel those in small molecules; however, one should be aware that the addition of alcohols to polymer solutions in nonpolar solvents will also result in conformational changes in the macromolecule and that these must also contribute to the reactivity changes observed.

The quenching of macroketones by hydroperoxides has been suggested to be an inportant additional route for the photoinitiation of the oxidative degradation of polymers,[3,4] and the possibility of reactive quenching has been recognized.[5] This reaction may add to direct hydroperoxide photolysis as a source of radicals in photooxidizing solid polymers where ketones and hydroperoxides are produced during processing and UV exposure.[28] The solid-state analogue of reaction 1 can be expected to occur in solid polymers, but the efficiency of initiation of propagating oxidation chains will be reduced by the high probability of cage reactions of the macroradicals.[29] Polynuclear aromatics such as naphthalene, phenanthrene, and anthracene, have frequently been detected as impurities in polyolefins[30] and have been shown to sensitize photooxidative degradation;[31] hydroperoxide quenching of the excited aromatic triplets may contribute to the photoinitiation in these systems.

Experimental Section

Materials. Aqueous *tert*-butyl hydroperoxide (Aldrich; 70% hydroperoxide, 30% water) was purified by azeotropic distillation using a Dean-Stark trap to remove the water-rich distillate, dried over $MgSO_4$, and fractionally distilled. Iodometry showed ≥98% purity, and GC analysis showed the following impurity limits: acetone ≤0.01 M, Bu^tOH ≤0.02M, and Bu^tOOBu^t ≤0.05 M. Repeated distillation and further purification steps such as fractional crystallization had no effect on the quenching data.

All sensitizers were commercially available and were recrystalized or sublimed. Benzene (Aldrich, Gold Label) was purified by treatment with sulfuric acid, washed with water, then refluxed over CaH_2 under nitrogen, and distilled. All other solvents were of the highest purity commercially available and were used as received.

The polymer samples were prepared by free radical polymerization of the corresponding monomer or monomer mixtures in benzene. Conversions were kept below 20%. Further details on the purification are the same as in earlier work.[27b,32] The abundances of each monomer in the copolymers were determined by UV spectroscopy. Co(sty–VBP) contained 23% of 4-vinylbenzophenone units; co(Sty–PMA) had 39% *p*-methoxyacrylophenone units; co(MMA–PMA) contained 22% *p*-methoxyacrylophenone, and co(MMA–PVK) had 21.3% phenyl vinyl ketone moieties.

Spectra. UV spectra were recorded on a Hewlett-Packard 8450A spectrophotometer with 0.1 cm path cells. IR spectra were recorded on a Nicolet 7199 FTIR spectrophotometer, equipped with a mercury cadmium telluride detector. Solutions for IR were prepared in carbon tetrachloride, and a spectral subtraction routine used to study difference spectra.

Laser Flash Photolysis. The samples, usually 1 mL, where contained in Suprasil cells (3-mm path length, 7-mm width). They were deaerated by bubbling with oxygen-free nitrogen.

Our laser facility uses a Molectron UV-24 nitrogen laser for excitation. The data, initially acquired by an R-7912 Tektronix transient digitizer, were processed by a PDP-11/23 computer, which also provided suitable control for the experiment, as well as processing, storage, and hard-copy facilities. Further details have been given elsewhere.[33]

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Registry No. *tert*-Butyl hydroperoxide, 75-91-2; benzophenone, 119-61-9; *p*-methylbenzophenone, 134-84-9; acetophenone, 98-86-2; *p*-methoxyacetophenone, 100-06-1; phenanthrene, 85-01-8; anthracene, 120-12-7; 1,5-diphenyl-1,5-pentanedione, 6263-83-8; poly(phenyl vinyl ketone), 26742-84-7; hydrogen, 1333-74-0.

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Phenyl Radical Kinetics[1]

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Abstract: The reactions of phenyl radicals with 17 substrates have been examined by using laser flash photolysis techniques. Absolute rate constants were determined for all the reactions in Freon 113 at 298 K by using iodobenzene or benzoyl peroxide as radical precursors. The following are some representative rate constants, which include all possible modes (or sites) of attack on each substrate: benzene, $(4.5 \pm 0.3) \times 10^5\ M^{-1}\ s^{-1}$; chlorobenzene, $(1.18 \pm 0.13) \times 10^6\ M^{-1}\ s^{-1}$; methyl methacrylate, $(1.8 \pm 0.3) \times 10^8\ M^{-1}\ s^{-1}$; carbon tetrachloride, $(7.8 \pm 0.7) \times 10^6\ M^{-1}\ s^{-1}$; tetrahydrofuran, $(4.8 \pm 0.6) \times 10^6\ M^{-1}\ s^{-1}$; toluene $(1.7 \pm 0.7) \times 10^6\ M^{-1}\ s^{-1}$.

The reactions of phenyl radicals in solution have been the subject of many studies that have led to numerous measurements of relative rate constants.[3-7] However, virtually no absolute rates have been reported. In fact, the only direct, time resolved measurement of their reactions deals with *p*-carboxyphenyl radicals

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