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Triplet Energy Distribution in Photoinitiators Containing Two Dissociable Groups

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Suitable probe molecules containing the benzophenone chromophore and one dissociable bond [perester **1** or C−X (**4**, **5**)] or two such bonds (**2**, **3**) have been synthesized and studied to examine intramolecular triplet energy dispersion. Triplet energies and phosphorescence quantum yields as well as quantum efficiencies of bond scissions have been studied, and the flow of triplet energy in such molecules is discussed. Upon irradiation at 350 nm in either benzene or methanol, the target peresters undergo dissociation of both cleavable groups, producing a pair of radicals. The presence of a benzylic chloride function has little influence on the efficiency of perester dissociation. However, the presence of a benzylic bromide function was found to decrease the quantum yield of decomposition of the perester function of **3**. This can be explained by taking into account the effect of the heavy atom and the rate of cage geminate radical pair recombination. The nature of the heavy atom perturbation, however, was found to be different in **5** as compared with **3**.

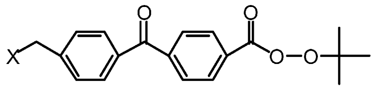
Introduction

Benzophenone is a widely used triplet sensitizer. Its n → π^* transition produces the triplet state exclusively due to the unit quantum yield of the $S_1 \rightarrow T_1$ intersystem crossing (ISC).[2] The triplet energy of benzophenone can be transferred, though inefficiently, to dialkyl peroxides to cause homolytic scission of the peroxy bond.[3] In contrast, such triplet energy transfer may be made highly efficient by linking the perester bond directly to the benzophenone chromophore. This is clearly reflected by much higher rates and quantum yields of decomposition of benzophenone peresters.[4]

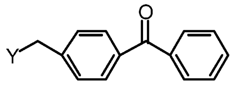
The lifetime of the triplet state of benzophenone in neat di-*tert*-butyl peroxide at 25 °C is 60 ns.[5] This is about 80 times longer than the lifetime of the triplet state of *tert*-butyl *p*-benzoylperbenzoate.[6] In fact, the quantum efficiency of photodecomposition of the *tert*-butyl aroylperbenzoates was found to be at least three times that of benzophenone-sensitized decomposition of benzoyl peroxide, clearly indicating the efficacy of the intramolecular process in contrast to bimolecular energy transfer.[4]

Intramolecular triplet energy transfer from the benzophenone chromophore can also enhance dissociation of the C−Cl and C−Br bonds.[7] However, the rates and quantum yields of photolytic C−X bond dissociation in appropriately substituted benzophenones have not been reported. The free radicals generated following intramolecular energy dispersion have been shown to have application in polymerization[7,8] as well as in photo-cross-linking and photografting.[9]

CHART 1. Photodissociable Peresters and Substituted Benzophenones.



1. X = H
2. X = Cl
3. X = Br



4. Y = Cl
5. Y = Br

Though the observations are relatively old, a detailed, systematic investigation of the factors affecting this process has not been provided. We synthesized suitably designed probe molecules in order to understand the mechanism and chemical consequences of the intramolecular dispersion of the benzophenone triplet energy, especially when two cleavable groups are available in the same molecule. We selected the C−X and perester bonds which have different homolytic bond dissociation energies. The compounds studied (Chart 1) are *tert*-butyl 4-(4′-

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(1) Contribution no. 467 from the Center for Photochemical Sciences. This paper is dedicated to Prof. Dr. J. W. Neckers on the occassion of his 100th birthday.

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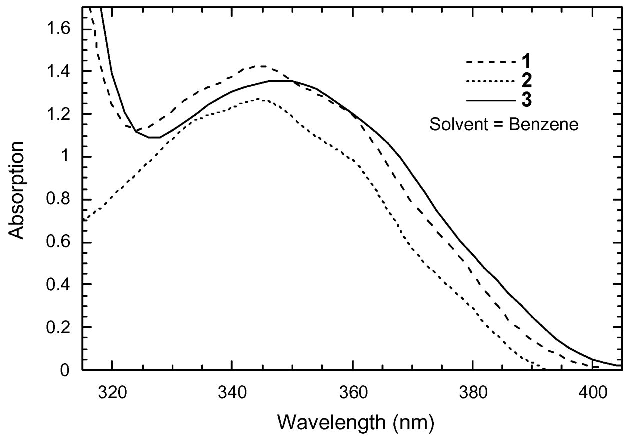

FIGURE 1. UV−vis absorption spectra of peresters. Concn: **1** = 6.88×10^{-3} M, **2** = 6.96×10^{-3} M, and **3** = 7.18×10^{-3} M.

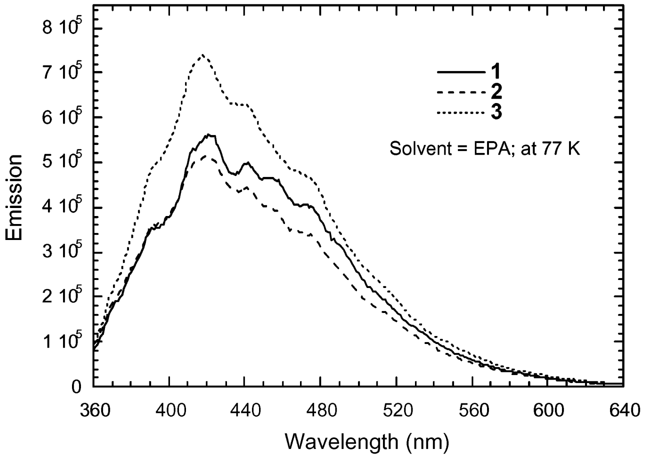

FIGURE 2. Phosphorescence spectra of peresters. Excitation wavelength = 350 nm.

methylbenzoyl)perbenzoate (**1**), *tert*-butyl 4-(4′-chloromethylbenzoyl)perbenzoate (**2**), *tert*-butyl 4-(4′-bromomethylbenzoyl)perbenzoate (**3**), 4-(chloromethyl)benzophenone (**4**), and 4-(bromomethyl)benzophenone (**5**). In **2** and **3**, the C−X and perester bonds are at the remote para positions of the benzophenone chromophore. Similar compounds with only one dissociable group [either perester **1** or C−X (**4**, **5**)] were studied for comparison. The rates, quantum efficiencies, and a mechanism of decomposition of these peresters are reported herein. The phosphorescence quantum yields are presented, and the intramolecular flow of the triplet energy is discussed.

Results and Discussion

Spectra and Product Analysis. UV−vis spectra (Figure 1) of peresters **1**−**3** show the characteristic absorption of the benzophenone chromophore with an absorption corresponding to the $n \rightarrow \pi^*$ transition of the carbonyl group with a maximum at 346−348 nm. The ϵ_{350} values in benzene are found to be 197, 175, and 188 M^{-1} cm^{-1} for **1**, **2**, and **3**, respectively. Phosphorescence spectra of the peresters are relatively structureless (Figure 2) as well as broader and blue shifted compared to that of benzophenone. This may be due to the presence of the perester side chain that renders the molecule more flexible. Triplet energies determined from the 0−0 band of the phosphorescence spectra are given in Table 1. The triplet energy of benzophenone is 68 kcal/mol,[10] while those of the peresters are higher (77 kcal/mol). Thus, the presence of a *tert*-butyl perester side chain causes an increment of about 9 kcal/mol in the triplet energy.

TABLE 1. Triplet Energy of Peresters[a]

perester	triplet energy (kcal/mol)
1	77.0
2	77.2
3	77.5

[a] Solvent = EPA; temperature at 77 K; excitation at 350 nm.

Each perester undergoes homolytic bond dissociation, forming radical products upon irradiation at 350 nm in benzene (Table 2). The thermal and primary photolytic products were similar for **1** and **2** except that the corresponding acids and phenyl esters were also obtained during photolysis. The products of the thermolysis of **3** do not include those formed by cleavage of the C−Br bond. On the other hand, photolysis of this perester yields mainly those products in which the Br atom is no longer retained. This is because the flow of the triplet energy takes place in both directions in the molecule, causing scission of each dissociable group. Thus, only the perester bond dissociates during thermolysis, while both the C−Br and perester bonds dissociate during photolysis.

This is also true for **2**, in which dissociation of both the C−Cl and perester bonds was observed. Products from cleavage of the C−Cl bond were found from NMR studies. We observed only one product derived from dissociation of the C−Cl bond in **2** as a primary photoproduct (during GC/MS analysis) when photolysis was carried out in benzene. Most of the products observed after 2 min of irradiation retained the Cl atom. Nevertheless, dissociation of the C−Cl bond was clearly observed when photolysis was carried out in methanol. Those photoproducts that formed because of coupling of the $^{\bullet}CH_2{-}OH$ radical (formed after H-abstraction from the methanol molecule) with the $^{\bullet}CH_2{-}Ar$ radicals (generated by dissociation of the C−X bond) were observed from both **2** and **3**.

Mechanism. The mechanism of photolysis of simple peresters is well established.[4] A similar mechanism is proposed for the photodecomposition of peresters that contain two dissociable groups (Scheme 1). The mechanism is based on the analysis of the primary photolysis products obtained within 1−2 min of irradiation at 350 nm in benzene. The homolytic bond dissociation energies of benzylic C−Br and C−Cl bonds are 55 and 59 kcal/mol, respectively, while that of a perester bond is 30 kcal/mol.[10] It is unlikely that dissociation of both the C−X and perester bonds occurs simultaneously in **2** or **3**, given that the triplet energy of these molecules is about 77 kcal/mol. The possibility of a one-photon−two-bond-dissociation mechanism can be discarded on energy grounds.

Dissociation of the perester bond is the only photochemical option in **1**. Thus, rapid intramolecular triplet energy transfer leads to scission of that bond. The formed

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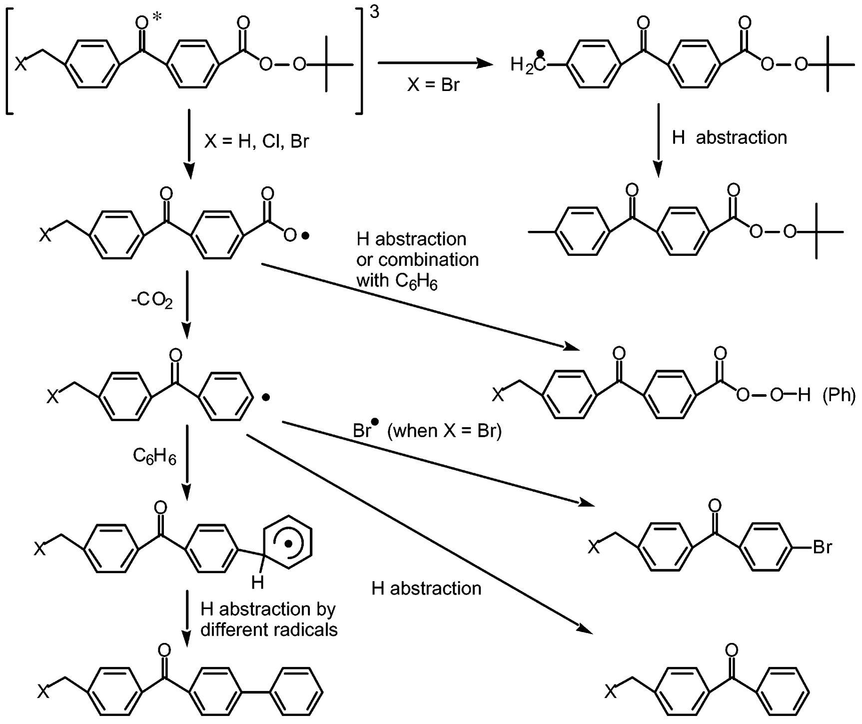
[10] Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1993.

TABLE 2. Thermal and Primary Photoproducts

perester	thermal products[a]	photoproducts[a]	photoproducts[b]
1	CH_3–Ph–CO–Ph CH_3–Ph–CO–Ph–Ph	CH_3–Ph–CO–Ph CH_3–Ph–CO–Ph–Ph CH_3–Ph–CO–Ph–COOH CH_3–Ph–CO–Ph–CO–OPh	CH_3–Ph–CO–Ph CH_3–Ph–CO–Ph–CO–OCH_3 CH_3–Ph–CO–Ph–COOH
2	$ClCH_2$–Ph–CO–Ph $ClCH_2$–Ph–CO–Ph–Ph	CH_3–Ph–CO–Ph $ClCH_2$–Ph–CO–Ph $ClCH_2$–Ph–CO–Ph–Ph $ClCH_2$–Ph–CO–Ph–COOH $ClCH_2$–Ph–CO–Ph–CO–OPh	$ClCH_2$–Ph–CO–Ph CH_3–Ph–CO–Ph–CH_2OH $ClCH_2$–Ph–CO–Ph–COOH HO–CH_2–CH_2–Ph–CO–Ph HO–CH_2–CH_2–Ph–CO–Ph–CO–OCH_3
3	$BrCH_2$–Ph–CO–Ph $BrCH_2$–Ph–CO–Ph–Ph	CH_3–Ph–CO–Ph CH_3–Ph–CO–Ph–Ph CH_3–Ph–CO–Ph–COOH $BrCH_2$–Ph–CO–Ph–Br CH_3–Ph–CO–Ph–$COOOCMe_3$	CH_3–Ph–CO–Ph CH_3–Ph–CO–Ph–CH_2OH CH_3–Ph–CO–Ph–COOH HO–CH_2–CH_2–Ph–CO–Ph HO–CH_2–CH_2–Ph–CO–Ph–CO–OCH_3

[a] Solvent = benzene; during photolysis, biphenyl, phenyl *tert*-butyl ether, acetone, and *tert*-butyl alcohol were also observed in all cases. [b] Solvent = methanol.

SCHEME 1. Mechanism of Photodissociation of Peresters



4-(4′-methylbenzoyl)benzoyloxy radical may abstract an H atom or combine with solvent to yield the corresponding carboxylic acid or phenyl ester. Dissociation of carbon dioxide from the 4-(4′-methylbenzoyl)benzoyloxy radical results in the formation of the corresponding aryl radical, which, in turn, may abstract an H atom or combine with solvent. Since benzene is not a good H donor, it might be possible that these radicals abstract an H atom from the intermediate radical that forms when the aroyloxyl and aryl radicals trap benzene, as depicted in the mechanism. The trapping of the aroyloxyl and aryl radicals by benzene is well established.[11]

Compound **3** produces the usual radical derived products due to cleavage of the perester bond. In addition, it also forms **1** in an observable amount. Evidence for its formation was obtained by NMR studies.[12] The formation of **1** during the photolysis of **3** can take place when the C–Br bond dissociates prior to the perester bond. However, given the higher bond dissociation energy of a benzylic C–Br bond relative to a perester bond, the preference for dispersion of the triplet energy should be toward the perester moiety in **3**. This does not seem to be the case. Formation of **1** as a major photolytic product suggests that dissociation of the C–Br bond is favored. This is further supported by the observed quantum efficiency data described below.

4-(Bromomethyl)-4′-bromobenzophenone was observed as one of the products during irradiation of **3**. Thus, it is

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[11] Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2886.

[12] The chemical shift of the methyl peak of **1** in C_6D_6 is 1.997 ppm. During the irradiation of **1**, we observed disappearance of the peak at 1.997 ppm and appearance of a new peak at 2.020 ppm. The methyl peak of 4-methylbenzophenone appears at 1.991 ppm. Thus, the peak at 2.020 ppm may correspond to the methyl group of the solvent (benzene) incorporated product, which is one of the major primary photolytic products in all cases. During the irradiation of **3**, we recorded the appearance of two peaks exactly at 2.022 and 1.997 ppm. The peak at 1.997 ppm corresponds to the methyl group of **1**, a primary photolytic product in this case. We observed no peak at 1.997 ppm during the irradiation of **2**. (See the Supporting Information.)

TABLE 3. Quantum Yields of Bond Dissociation[a]

compound	ϕ_{diss} −O−O−	C−X
1	0.82	
2	0.63	0.26
3	0.22	0.41
4		0.61
5		0.37

[a] (a) Intensity (I_0) = 9.2 × 10^{16} quanta L^{-1} s^{-1}; (b) solvent = C_6D_6; (c) concn = 8.3 × 10^{-3} M.

also possible that the corresponding aryl radical formed during decomposition of **3** abstracts a Br atom from the starting material, forming the corresponding benzyl radical and 4-(bromomethyl)-4′-bromobenzophenone. However, such an abstraction was not observed in the case of **2**. If it were one of the pathways of decomposition, an abstraction of a Cl atom from **2** would also have been observed.

The situation is different in the case of **2**, where the formation of **1** was not observed. Retention of the C−Cl bond in the majority of the photoproducts indicates that cleavage of the perester bond rather than the C−Cl bond is a favored path. The bond dissociation energy of a benzylic C−Cl bond is lower than the triplet energy of **2**. Despite this, the triplet energy prefers to disperse in the direction of the perester moiety. This is not surprising, given that the perester bond is much weaker than the C−Cl bond.

Rates and Quantum Yields. The quantum efficiency of dissociation (ϕ_{diss}) values of the C−X and perester bonds were obtained by ^{1}H NMR (Table 3). The quantum yield of the decomposition of **1** in C_6D_6 was found to be 0.82, in the same range of quantum yields previously found for decomposition of similar peresters in benzene.[4] There is little difference in the ϕ_{diss} values of the dissociation of the perester bonds in **1** and **2**. However, there is a sharp drop in the ϕ_{diss} values of the perester bonds from **1** to **3** (0.82 to 0.22). Thus, in the case of **3**, a larger fraction of the triplet energy finds other ways to disperse rather than toward the perester bond. This is in complete agreement with the observed photoproducts. The ϕ_{diss} (0.41) of the C−Br bond is nearly twice the ϕ_{diss} (0.22) of the perester bond in **3**, indicating the favorable cleavage of the C−Br bond over the perester bond. The opposite pertains to **2**, in which the ϕ_{diss} (0.26) of the C−Cl bond was found to be less than half of the ϕ_{diss} (0.63) of the perester bond.

We also measured and compared the rates and ϕ_{diss} values of **4** and **5** with those of **2** and **3**.[13] Cleavage of the C−X bond is the only possible photochemical dissociation process in **4** and **5**. To our knowledge, the rates and ϕ_{diss} values for the photolysis of these compounds are not reported, although rates of polymerization of certain monomers using these compounds as photoinitiators have been previously presented.[7] The k_{obs} of the C−Cl bond dissociation in **4** was found to be 4.8 × 10^{-5} M s^{-1}. This is similar to the k_{obs} (4.6 × 10^{-5} M s^{-1}) of the C−Cl bond dissociation of **2**. Similarly, the k_{obs} values of the C−Br bond dissociations of **3** (2.7 × 10^{-5} M s^{-1}) and **5** (1.9 × 10^{-5} M s^{-1}) were also found to be nearly the same. The ϕ_{diss} values which reflect the fraction of the triplet energy utilized in dissociating the C−X bond are, as expected, different for these compounds. Thus, the similarity in the rate constants of the corresponding C−X bond dissociation may be a strong indication that these are the individual rates.

TABLE 4. Quantum Yields of Bond Dissociation in Methanol

perester[a]	ϕ_{diss} −O−O−	C−X
1	1.44	
2	1.02	0.23
3	0.16	0.45

[a] Concn = 7.5 × 10^{-3} M.

Induced Decomposition. The peresters show similar UV−vis absorptions in methanol. The observed photoproducts in methanol (Table 2) are normal radical products that are formed, following the general mechanism of homolytic dissociation of the C−X and perester bonds. The $^{\bullet}CH_2{-}OH$ radical was found to couple with the corresponding phenyl radicals (formed after perester bond dissociation followed by decarbonylation) in **1**, **2**, and **3**. Coupling of the $^{\bullet}CH_2{-}OH$ radical with the corresponding benzyl radicals was also observed for **2** and **3**. For simple peresters,[4] a significant increase in the quantum yield of decomposition has been found in methanol. To test the possibility of such solvent-assisted decomposition, we measured the ϕ_{diss} in CD_3OD (Table 4) and observed induced decompositions of **1** and **2**.

The ϕ_{diss} of the perester bond in **1** and **2** was found to be much higher than in benzene and higher than unity. The ϕ_{diss} of the C−Cl bond, however, remained the same in **2**, indicating the solvent-induced dissociation of only the perester bond. This may be because the triplet energy favors dispersion toward the perester bonds in these molecules. There was no such a solvent effect on the decomposition of **3**. The ϕ_{diss} values of both the C−Br and perester bonds were almost the same either in C_6D_6 or in CD_3OD. This may be because of the favoribility of the triplet energy dispersion toward the C−Br bond, dissociation of which is not induced by the solvent.

Unlike photodecomposition of the peresters in benzene in which formation of both acetone and *tert*-butyl alcohol was observed during NMR studies, formation of only *tert*-butyl alcohol was observed in methanol. The corresponding benzoyloxy and aryl as well as *tert*-butyl radicals easily abstract hydrogen from methanol. The $^{\bullet}CH_2{-}OH$ radical can induce the decomposition of the peresters, as shown in the Scheme 2.

An analysis of the ϕ_{diss} (either in benzene or methanol) demonstrates that the decomposition of **3** is not as efficient as that of **1** or **2**. After 5 min of irradiation in C_6D_6, the decomposition of **1** and **2** was almost complete, as indicated by the disappearance of the peak belonging to the *tert*-butyl group (see the Supporting Information). However, a considerable amount of **3** was not decom-

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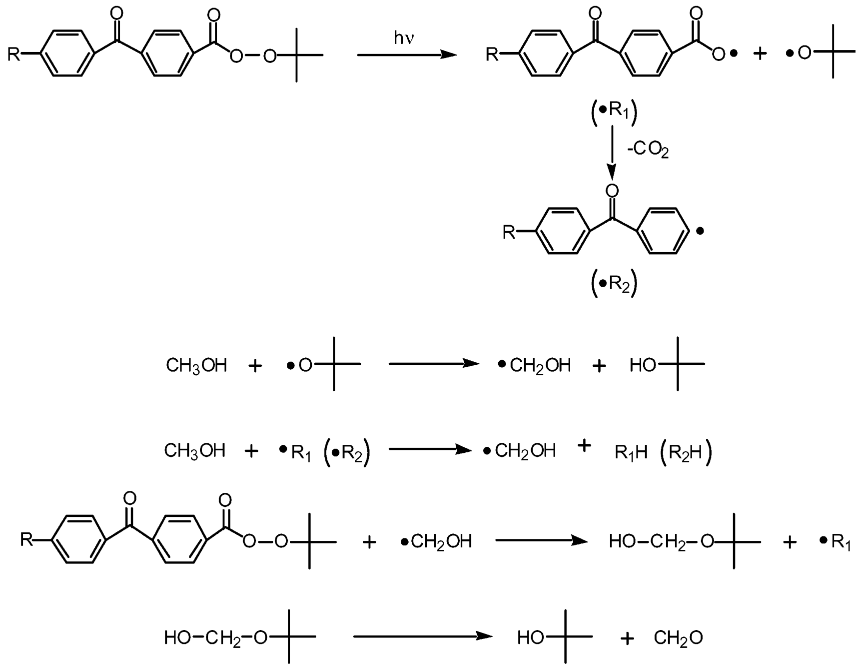
(13) It should be noted that, in **2** or **3**, when any one of the C−X or perester bonds dissociates during irradiation, the overall concentration of the starting material changes. Thus, it appears that the higher observed rate and the ϕ_{diss} may be the limiting rate and quantum yield of the dissociation of each of these peresters. Even if this is the case, we clearly see that dissociation of the C−Br bond is the favorable path of the triplet energy dispersion in **3**. The opposite is true in **2**. However, given the nature of appearance and disappearance of the peaks observed during NMR studies and the nature of the data, we believe that these data reflect rates and ϕ_{diss} values of the individual bonds.

SCHEME 2. Possible Mechanism of Induced Decomposition



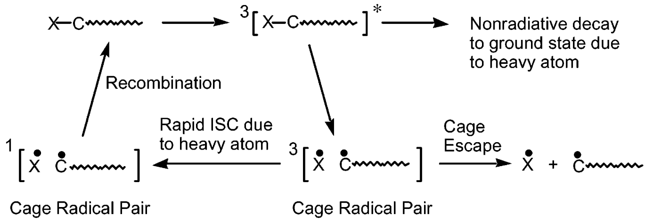
posed, even after 5 min of irradiation. The slow decomposition is also reflected in rates of photopolymerization which were found to be much lower for **3** than for other simple peresters when they were used as photoinitiators.[14]

The more facile dissociation of the C−Br bond into a stable benzyl radical was previously considered to be the reason.[14] For this, the rate of dissociation of the C−Br bond has to be considerably higher than that of the perester bond in the same molecule. However, the observed rate constants of the C−Br bond (2.7×10^{-5} M s^{-1}) and the perester bond (2.0×10^{-5} M s^{-1}) were found to be nearly the same in **3**. The bimolecular termination rate constant for benzyl radicals in benzene at 25 °C was also reported to be 1.8×10^{-9} M s^{-1}.[15] Thus, the reasoning presented previously does not seem sufficient.

It is also noted that the ϕ_{diss} (0.37) of the C−Br bond of **5** in benzene is much lower than the ϕ_{diss} (0.61) of the C−Cl bond of **4**. The excited states of these molecules have sufficient energy to easily cleave either bond. Even if we consider the bond dissociation energy, the opposite should have been the case because the C−Cl bond is stronger than the C−Br bond. However, the C−Br bond seems to cause a decrease in the ϕ_{diss} values in both **3** and **5**. The reason for such a low ϕ_{diss} of the C−Br bond can be explained by taking into account the heavy atom effect and the cage radical pair recombination.

Reason for Low ϕ_{diss} of 3 and 5. We propose that there are at least two possible ways of energy dissipation that can result in the observed low ϕ_{diss} values of **3** and **5** (Scheme 3). The presence of a heavy atom in the molecule may have an effect on the triplet state as well as on the radical pairs that form following triplet energy dispersion. The effect of a heavy atom in enhancing the nonradiative decay of the triplet states by spin−orbit coupling is well established.[16] A heavy atom may enhance the depopulation of the triplet state by inducing the radiationless $T_1 \rightarrow S_0$ decay and, hence, may also decrease the phosphorescence quantum yield (ϕ_{Ph}). Direct spectroscopic observation of a decrease in ϕ_{Ph} values has been made in iodo and bromo polymethine dyes at 77 K.[17]

SCHEME 3. Reason of Low Quantum Yield of Dissociation



In the case of peresters, a triplet radical pair is selectively generated from a triplet precursor. Typically, triplet−singlet ISC in a radical pair takes $\sim 10^{-8}$ s.[18] The time scale for the formation of secondary cages is on the order of 10^{-8} s in nonviscous ($n < 10$ cP) homogeneous solutions at room temperature.[18,19] Thus, there is a probability that the spin correlation of RPs (RP = radical pair) can change in the secondary cages. In such a situation, a competition may arise between ISC of the type $^3\mathrm{RP} \rightarrow {}^1\mathrm{RP}$ within the solvent cage and the escape of the RP from the cage. The heavy atom spin−orbit interaction can have a dramatic effect on such a competition between diffusion and ISC. In many cases, an external[20] or internal[21]heavy atom has been found to significantly enhance the rates of ISC in the primary and

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[19] Turro, N. J.; Weed, G. C. *J. Am. Chem. Soc.* **1983**, *105*, 1861.

TABLE 5. Phosphorescence Quantum Yields

compound	ϕ_{Ph}
1	0.055
2	0.051
3	0.069
4	0.566
5	0.025

secondary cage pairs. Experimental evidence of a large influence of even a single solvent atom on the photodissociation process in which a bromine atom itself is involved has also been obtained.[22]

We measured the ϕ_{Ph} of the probe molecules using 350 nm as the excitation wavelength (Table 5). It is clear that the ϕ_{Ph} of **4** (0.566) is comparable to that of benzophenone ($\phi_{Ph} = 0.74$).[10] However, the ϕ_{Ph} of **5** (0.025) is remarkably decreased. This can be attributed to the bromine atom induced enhancement of the $T_1 \rightarrow S_0$ radiationless decay. The deactivation of the triplet state into the ground state causes fewer triplet states to undergo chemical decomposition. Consequently, the quantum yield of chemical decomposition is decreased.

We, however, found no significant difference in the ϕ_{Ph} values of the peresters. The ϕ_{Ph} of **3** was found comparable to the ϕ_{Ph} of **1** that has no heavy atom. This indicates that, in the case of **3**, the heavy atom may have little or no effect on the triplet state. This is also supported by the nature of the triplet states of the peresters that are assumed to be a very short-lived species. The absence of an observable heavy atom perturbation on the triplet state of **3** may also be due to a relatively larger energy gap between T_1 and S_0 states that minimizes the spin–orbit interaction in the triplet state.

Thus, in the case of **3**, the heavy atom probably affects the triplet RP and induces its rapid spin inversion in the solvent cage. As a result, the singlet RP is generated which may recombine rapidly, causing a decrease in the quantum yield of photodissociation processes. The magnitude of this effect will be none or negligible in the case of **1** or **2**, respectively, where cage escape of the triplet RP may take place prominently. Thus, it is the chemical recombination of the geminate pairs that manifests in the form of the low ϕ_{diss} of **3**. The bromine atom enhanced geminate radical pair recombination may also be contributing to the low ϕ_{diss} of **5**. However, this seems to be the only path that is causing the low ϕ_{diss} of **3**.

Experimental Section

Materials and Equipment. Reagents and solvents were obtained from commercial suppliers and used as received unless otherwise noted. Benzene and cyclohexane were dried over sodium/benzophenone under argon before use. Solvents were used without purification if they were either spectrophotometric or HPLC grade. Column chromatography and thin-layer chromatography (TLC) were performed using standard grade silica gel (32–63 μm, 60 Å) and silica gel plates (200 μm). Melting points are uncorrected. Elemental analyses were performed at Atlantic Microlab, Inc., Atlanta, GA. Nuclear magnetic resonance (NMR) spectra were recorded on a 200 MHz spectrometer. $CDCl_3$ was the solvent for NMR unless otherwise noted. Chemical shifts relative to TMS at 0.0 ppm are reported in parts per million (ppm) for ^1H NMR on the δ scale. UV spectra were obtained on a UV–vis diode array spectrometer. GC/MS data were collected using spectrometers having 30 m × 0.25 mm × 0.25 μm columns. A phosphorimeter coupled to a 1680 0.22m double spectrometer was used to record phosphorescence spectra.

Synthesis. The peresters were synthesized following a literature procedure.[4]

(A) *tert*-Butyl 4-(4′-Methylbenzoyl)perbenzoate (1). 1,4-Dimethyl terephthalate was selectively hydrolyzed and treated subsequently with $SOCl_2$.[23] The Friedel–Craft acylation[24] reaction of the resulting 4-(carbomethoxy)benzoyl chloride with toluene and saponification and acidification of the product gave 4-(4′-methylbenzoyl)benzoic acid, which was refluxed with an excess of $SOCl_2$ to obtain 4-(4′-methylbenzoyl)benzoyl chloride. To a solution of 4-(4′-methylbenzoyl)benzoyl chloride (7 mmol, 1.8 g) in 20 mL of dry ether was added a solution of *tert*-butyl hydroperoxide (8–9.6 mmol of 5.0–6.0 M solution in decane, 1.6 mL) and triethylamine (8 mmol, 1.1 mL) in 10 mL of ether in ~10 min at the ice-bath temperature. The reaction mixture was stirred for 1 h more at the same temperature and then filtered. Crude **1** was obtained from the evaporation of the filtrate. The crude product was chromatographed over silica gel using CH_2Cl_2 as eluent and recrystallized twice from ether/hexane (1.4 g, yield 64%). ^1H NMR ($CDCl_3$) δ 7.23–8.09 (4d, 8H), 2.46 (s, 3H), 1.44 (s, 9H). Anal. Calcd for $C_{11}H_{20}O_4$: C, 73.06; H, 6.45; O, 20.48. Found: C, 73.17; H, 6.13; O, 20.57. Mp = 78–79 °C (lit.[4] 80–81 °C).

(B) *tert*-Butyl 4-(4′-Chloromethylbenzoyl)perbenzoate (2). 4-(4′-Methylbenzoyl)benzoyl chloride (7 mmol, 1.8 g) was chlorinated[25] in benzene, and 4-(4′-chloromethylbenzoyl)benzoyl chloride (1.37 g) was obtained in 67% yield. This was recrystallized from dry cyclohexane. The solid obtained after evaporating cyclohexane still contained some dichloro product and unreacted starting material. This was converted without further purification to **2** by the same procedure described for **1**. Chromatography of the product was carried out using cyclohexanes/ether (3.5:1) as eluent to separate the dichloro product. The resulting solid was recrystallized twice from hexanes/ether to yield (49%) pure **2**. ^1H NMR ($CDCl_3$) δ 7.52–8.10 (4d, 8H), 4.66 (s, 2H), 1.45 (s, 9H). ^{13}C NMR (APT, $CDCl_3$) δ 142.4, 141.44, 136.56, 130.86, 130.52 (2C), 129.9 (2C), 129.12 (2C), 128.61 (2C), 84.35, 45.25, 26.23 (3C). Anal. Calcd for $C_{11}H_{19}O_4$: C, 65.8; H, 5.52; O, 18.45. Found: C, 64.78; H, 5.61; O, 18.04. Mp = 98–99 °C.

(C) *tert*-Butyl 4-(4′-Bromomethylbenzoyl)perbenzoate (3). 4-(4′-Methylbenzoyl)benzoyl chloride (7 mmol, 1.8 g) was brominated by refluxing it in benzene with NBS (8 mmol, 1.42 g) using benzoyl peroxide as initiator for 3 h. NBS was added in three portions at intervals of 45 min. The resulting 4-(4′-bromomethylbenzoyl)benzoyl chloride (1.2 g, yield 51.4%) was recrystallized from dry cyclohexane, and the same procedure applied for the preparation and purification of **2** was followed to obtain the pure perester (yield 41.6%). ^1H NMR ($CDCl_3$) δ 7.51–8.09 (4d, 8H), 4.54 (s, 2H), 1.44 (s, 9H). ^{13}C NMR (APT, $CDCl_3$) δ 142.84, 141.47, 136.54, 130.92, 130.59 (2C), 129.88 (2C), 129.18 (4C), 84.35, 31.99, 26.25 (3C). Anal. Calcd for $C_{11}H_{19}O_4$: C, 58.33; H, 4.89; O, 16.35. Found: C, 58.79; H, 4.92; O, 16.08. Mp = 91–93 °C.

(D) 4-(Chloromethyl)benzophenone (4) and 4-(bromomethyl)benzophenone (5) were prepared by chlorination[25] with SO_2Cl_2 and bromination with NBS in benzene of

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4-methylbenzophenone, respectively. Compound **4** was purified by chromatography using ethyl acetate/hexane (1:15) as eluent and recrystallized twice from ethanol; mp = 93−94 °C (lit.[26] 95−96 °C). To separate **5** from the dibromo product and unreacted starting material, the crude product was chromatographed using cyclohexanes/ether (3.5:1) and recrystallized twice from ethanol; mp = 107−108 °C (lit.[27] 109−110 °C).

Primary Photoproducts. Irradiations were carried out using a photochemical reactor equipped with a jacketed beaker and 8 W × 16 RPR 3500 Å lamps. Quartz cuvettes (3.5 mL) well dried and then sealed with a rubber septum were used as photolysis vessels. All samples were degassed with argon for at least 20 min. Disappearance of the starting material and appearance of products were monitored by TLC and GC/MS. The peresters undergo thermolysis when passed through the column of the GC/MS. Thus, the GC/MS data of the peresters were recorded before irradiation, which established the nature of the thermolytic products. For the primary products from photolysis, GC/MS spectra were recorded consecutively after 30 s, 1 min, and 2 min of irradiation. The analysis of the GC/MS data taken before and after irradiation in combination with the TLC observation established the structure of the primary photoproducts. Comparison with the GC/MS data of authentic samples was also made where it was applicable.

Rate and Quantum Yield Measurements. Quartz NMR tubes were used for quantum yield measurements. The solvents used were either CD_3OD or C_6D_6, containing 0.03% v/v TMS. Hexamethyldisiloxane was used as the internal standard. The degassed and sealed samples were irradiated, and spectra were recorded in 15 or 10 s intervals within 60−90 s of the total irradiation time. The rate and ϕ_{diss} of perester dissociation were obtained from the disappearance of the peak belonging to the *tert*-butyl group at 1.44 ppm. Similarly, the disappearance of the peak corresponding to CH_2-X was monitored to obtain rates and ϕ_{diss} values of C−X bond dissociation. For rate measurement, data points collected up to 60−90 s were considered. In this period, the change in concentration was within 50%. For quantum yield calculations, only the data recorded within 30−35 s (less than 15% conversion) were used. The starting concentration of the samples was chosen such that the absorption of the starting material remained >1 at 350 nm after 20% conversion. The initial absorptions of the molecules were 1.3−1.4, and thus, all the light was absorbed by the starting material even after 15% conversion. Benzophenone−benzhydrol actinometry[10] was used to determine the intensity of light. The phosphorescence spectra were recorded in EPA glass at 77 K; the excitation wavelength was 350 nm. Phosphorescence quantum yields were determined according to the general procedure[2] using benzophenone as reference, and the reported ϕ_{Ph} measurements are normalized values.

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Supporting Information Available: Figures S1−2 (zero order curve fit for rate constants), Figure S3 (NMR study of decomposition of 4-(bromomethyl)benzophenone, Figure S4 (NMR spectra comparison of decomposition of peresters), Table S1 (GC/MS peaks of photoproducts), and ^{1}H and ^{13}C NMR spectra of **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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