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ARTICLES

Ultrafast Pump−Probe Studies of *tert*-Butyl Aroylperbenzoates and Triplet Energy Interception by the O−O Bond

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Photolysis of *tert*-butyl aroylperbenzoates (BAPs) **1**−**4** in benzene and acetonitrile at 335 or 267 nm produces the S_1 states ($\lambda_{max} \approx 590$ nm) that rapidly intersystem cross ($k_{ISC} \approx 1.3 \times 10^{11}$ s^{-1}) into the triplet states ($\lambda_{max} \approx 560$ nm, $\tau_T = 0.6-0.7$ ns in benzene). Results from the 267 nm excitation experiments of **1** in acetonitrile suggest the rate of the $S_2 \rightarrow S_1$ internal conversion ($k_{S_2 \rightarrow S_1} = 1.6 \times 10^{12}$ s^{-1}) is similar to that of benzophenone and *p*-iodobenzophenone. The rate of the $S_1 \rightarrow T_1$ intersystem crossing is not affected by the solvent or the excitation wavelength. However, decay of the triplet states of **1** and *p*-iodobenzophenone is faster in acetonitrile than in benzene. Intramolecular triplet energy dissipation to a repulsive excited triplet state of the O−O bond of BAPs may be a possible mechanism. The results obtained from semiempirical and ab initio calculations have been presented.

Introduction

The photophysics of benzophenone is well understood.[2] Photoexcitation in the singlet manifold of benzophenone results in rapid intersystem crossing (ISC) with unit efficiency to the triplet state.[2,3] *tert*-Butyl aroylperbenzoates (BAPs) containing the benzophenone chromophore follow a similar photophysical pathway when irradiated.[4,5] We have recently shown the S_1 states of *tert*-butyl 4-(4′-methylbenzoyl)perbenzoate and *tert*-butyl 4-(4′-bromomethylbenzoyl)perbenzoate absorb at ~590−625 nm.[4] The lifetimes of the singlet states (τ_s) are 20 and 7 ps, respectively, in benzene. The triplet states of BAPs ($\lambda_{max} \approx 540-560$ nm) decay in less than 1 ns.[4,5]

The effects of excitation wavelength (267 and 335 nm) on the relaxation kinetics of benzophenone and *p*-iodobenzophenone have been reported from our lab recently, and the rates of the $S_2 \rightarrow S_1$ internal conversion of these compounds have been found to be 1.9×10^{12} and 1.7×10^{12} s^{-1} in acetonitrile, respectively.[6] We have extended ultrafast pump−probe studies to several other BAPs, namely, *tert*-butyl (4-benzoyl)perbenzoate (**1**), *tert*-butyl 4-(4′-chloromethylbenzoyl)perbenzoate (**2**), *tert*-butyl 4-(3′-bromomethylbenzoyl)perbenzoate (**3**), and *tert*-butyl 4-(4′-bromobenzoyl)perbenzoate (**4**) (Figure 1). The effects of solvent and excitation wavelength (267 and 335 nm) on the kinetics of formation and decay of the singlet and triplet states of BAPs are discussed in this paper. We used *p*-iodobenzophenone (*p*-IB) as a reference, and the results are included. The estimated lifetime of the triplet state of *p*-IB (0.2 ns)[7] is much shorter at room temperature than that of benzophenones that have nondissociable substituents ($\tau_T = 0.8-47$ μs in benzene).[8] This is due to dissociation of the C−I bond in the former.[7,9]

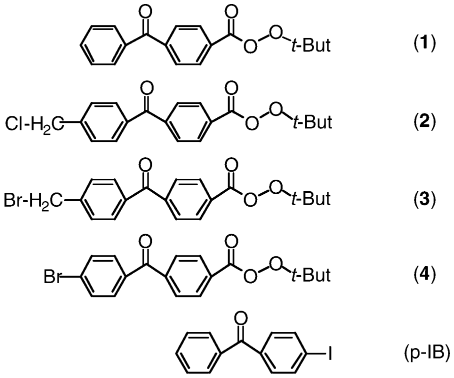

Figure 1. *tert*-Butyl aroylperbenzoates and *p*-iodobenzophenone.

Products from steady-state photolysis of BAPs indicate that homolytic dissociation of the perester (O−O) bond leads to formation of the corresponding aroylbenzoyloxyl and aroylphenyl radicals.[10,11] The quantum yields of dissociation (ϕ_{diss}) of the O−O bond are near unity for many of the BAPs.[10−12] The aroylphenyl radicals ($\lambda_{max} = 550$ nm) have lifetimes of 0.4−0.6 μs in CCl_4, and the absolute bimolecular rates of reactions of these radicals range from 7.56×10^7 to 1.68×10^9 M^{-1} s^{-1} (at 22 ± 2 °C).[4,12] BAPs are also known to induce photopolymerization of double-bond-containing monomers.[11,13]

The perester bond of BAPs dissociates as a result of the intramolecular triplet energy dissipation. A semiempirical treatment using the Morse energy potential[14] for the attractive term and the Sato−Morse potential[15,16] for the repulsive term of the perester bond suggests that energy transfer to a repulsive triplet excited state of the O−O bond is a possible mechanism in BAPs. This could lead to the experimentally observed rapid and efficient dissociation of the O−O bond.

Results

Transient spectra obtained from *p*-IB and **1** in benzene at room temperature (excitation at 335 nm) show an early broad

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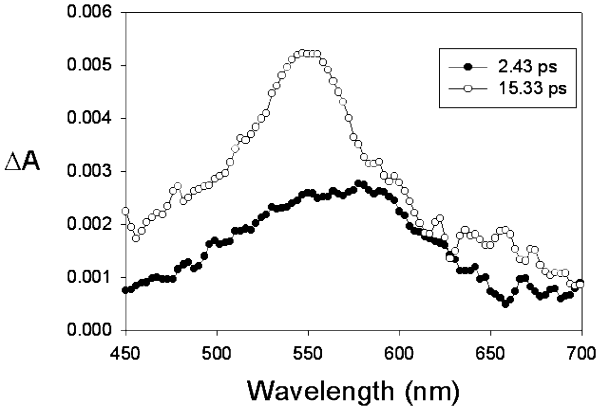

Figure 2. Transient absorption spectra obtained from ultrafast pump–probe experiments of *p*-IB (1.83×10^{-2} M) in benzene, recorded (●) 2.43 ps and (○) 15.33 ps after the laser pulse.

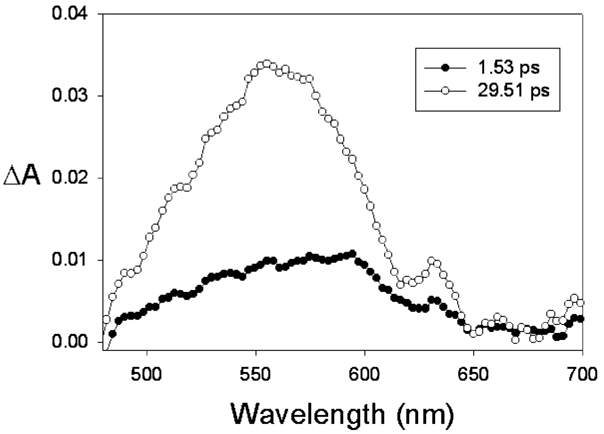

Figure 3. Transient absorption spectra obtained from ultrafast pump–probe experiments of **1** (3.28×10^{-2} M) in benzene, recorded (●) 1.53 ps and (○) 29.51 ps after the laser pulse.

absorption that forms instantaneously after the laser pulse excitation with maxima at 580 and 590 nm, respectively. The absorption shifts to 540 and 560 nm, respectively, with time as shown in Figures 2 and 3. The observation of two absorption maxima in each case suggests the presence of two species. The early broad absorption can be assigned to the $S_1 \rightarrow S_n$ transition.[4,17] A similar broad absorption ($\lambda_{max} = 570$ nm) was also obtained in pump–probe experiments of benzophenone in acetonitrile[6] and water[18] and was assigned to the singlet state.

The transient absorptions observed at longer delay times (e.g., 540 and 560 nm absorption of *p*-IB and **1**, respectively) are similar to that observed at 30 ps following 355 nm excitation of **1** in CCl_4 and assigned to the $T_1 \rightarrow T_n$ transition.[4,5,19] Similar transient absorption behaviors were recorded of *p*-IB and **1** when acetonitrile was used as the solvent (Figures 4 and 5). For these two compounds, the spectra were also recorded in acetonitrile using 267 nm excitation, which corresponds to the $\pi \rightarrow \pi^*$ transition. The nature of the spectra was found to be almost the same, except that formation of the S_1 state was not observed to be instantaneous (vide infra).[6]

There were no major differences in the transient absorption spectra obtained from **2** or **4** (335 nm excitation) when compared to that of **1**. Details of the kinetics of formation and decay of the singlet and triplet states of **3** obtained from 380 nm excitation have been previously reported.[4] It has been shown that the growth time of the triplet state and the decay time of the S_1 state are the same within experimental error.[4] It is also reasonable to assume that the quantum yield of the $S_1 \rightarrow T_1$ ISC in BAPs and *p*-IB is unity given that the same is true for benzophenone.[2,3] For all compounds the formation and decay of the triplet states were obtained by measuring kinetic traces at the wavelength maxima corresponding to the triplet states. The time profiles of formation of the triplet state of **1** in acetonitrile are shown in Figure 6. The lifetimes of the S_1 state (τ_{S_1}), the S_2 state (τ_{S_2}), and the triplet state (τ_T) of *p*-IB and **1** measured in acetonitrile are presented in Table 1. The τ_{S_1} and τ_T of **1**–**4** and *p*-IB measured in benzene are compiled in Table 2. The measured τ_T of **1** in benzene is in good agreement with that of **1** in CCl_4.[5]

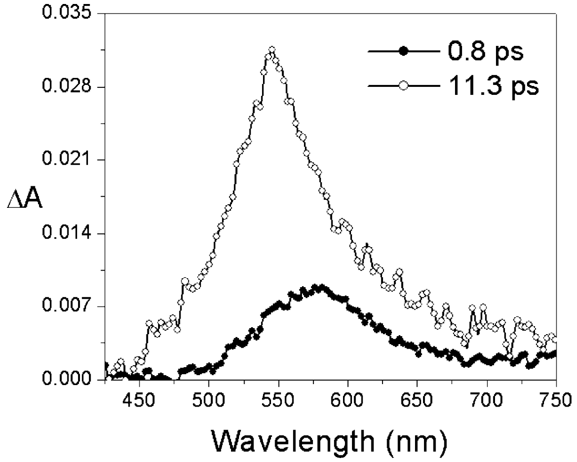

Figure 4. Transient absorption spectra obtained from ultrafast pump–probe experiments of *p*-IB (3.72×10^{-2} M) in acetonitrile, recorded (●) 0.8 ps, (○) 11.3 ps after the laser pulse.

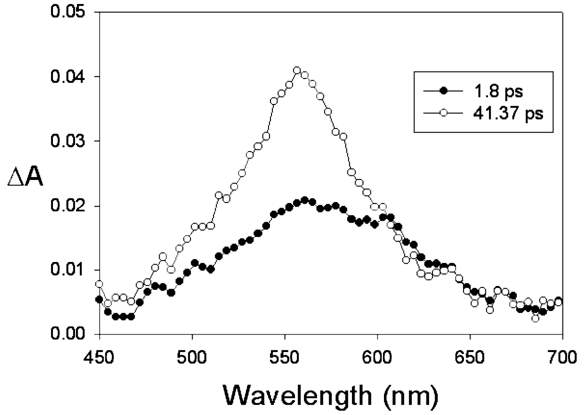

Figure 5. Transient absorption spectra obtained from ultrafast pump–probe experiments of **1** (3.50×10^{-2} M) in acetonitrile, recorded (●) 1.8 ps and (○) 41.37 ps after the laser pulse.

Discussion

Kinetics of the Singlet States. It is clear from Figures 2–5 that the absorption of the S_1 state overlaps with that of the triplet state. This is also reflected in the time profiles (Figure 6). The longer rise times represent the triplet growth and, thus, the singlet decay. The S_1 state lifetimes are similar in both solvents for **1** and *p*-IB, indicating that there is no significant effect of solvent polarity on the rate of the $S_1 \rightarrow T_1$ ISC. This is unlike the case of benzophenone—the rate of ISC of which has been considered to be slightly solvent dependent.[17a,b] Nevertheless, values of $(k_{ISC})^{-1}$ that are within experimental error in polar and nonpolar solvents have also been reported for benzophenone.[17c,20] Changing the excitation wavelength does not affect the τ_{S_1} of **1** and *p*-IB; the τ_{S_1} values obtained in acetonitrile using either 335 or 267 nm excitation are within experimental error for each compound (Table 1).

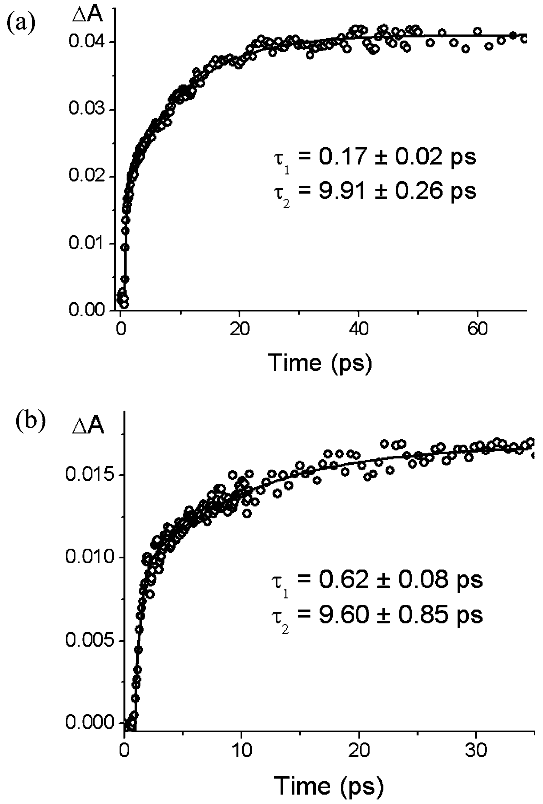

Figure 6. Time profiles monitored at 560 nm during ultrafast pump−probe experiments of **1**: (a) 3.50 × 10^{-2} M in acetonitrile, excitation at 335 nm; (b) 6.69 × 10^{-4} M in acetonitrile, excitation at 267 nm.

TABLE 1: Lifetimes of the S_2 State (τ_{S_2}), the S_1 State (τ_{S_1}), and the Triplet State (τ_T) of *p*-IB and 1 in Acetonitrile

compd	concn (M)	excitation wavelength (nm)	τ_{S_2} (ps)	τ_{S_1} (ps)	τ_T (ps)
p-IB[a]	3.72 × 10^{-2}	335		4.38 ± 0.10	68.50 ± 0.60
	7.10 × 10^{-4}	267	0.59 ± 0.07	4.29 ± 1.81	58.46 ± 0.89
1	3.50 × 10^{-2}	335		9.91 ± 0.26	322.32 ± 2.93
	6.69 × 10^{-4}	267	0.62 ± 0.08	9.60 ± 0.85	330.14 ± 5.62

[a] Reference 6.

TABLE 2: Lifetimes of the S_1 State (τ_{S_1}) and the Triplet State (τ_T) of BAPs and *p*-IB[a]

compd	concn (M)	τ_{S_1} (ps)	τ_T (ps)
1	3.28 × 10^{-2}	9.11 ± 0.48	743.11 ± 105.01
2	3.15 × 10^{-2}	8.55 ± 0.48	645.58 ± 32.62
3[b]	3.26 × 10^{-2}	7.87 ± 0.17	737.86 ± 38.17
4	2.57 × 10^{-2}	7.24 ± 0.28	638.34 ± 24.84
p-IB	1.83 × 10^{-2}	4.26 ± 0.29	98.46 ± 2.16

[a] Solvent = benzene, excitation at 335 nm. [b] Reference 4, excitation at 380 nm.

Excitation at 267 nm initially generates the S_2 state ($\pi \rightarrow \pi^*$ transition). This is unlike the case with 335 nm excitation in which the compounds are excited to the S_1 state ($n \rightarrow \pi^*$ transition). However, the similar S_1 state lifetimes obtained from experiments at both excitation wavelengths indicate that the triplet states are populated exclusively from the S_1 state. Thus, other pathways, e.g., involvement of the T_2 state or direct S_2 to T_1 conversion, may not occur for these compounds in solution (vide infra).[6,7,20,21]

It has been postulated for benzophenone that ISC from the S_1 state takes place to the T_2 state that is π,π^* in character and almost isoenergetic to the S_1 state (77 kcal/mol).[2] The T_2 state then undergoes internal conversion to the T_1 state (n,π^*, ∼5 kcal/mol lower than the S_1 state).[2] However, the results of ab initio calculations suggest that such a T_2 state is not involved in the cases of BAPs. Similar to the observation made for benzophenone in [bis(*p*-bromophenyl)ether] at 1.6 K, the direct $S_1(n,\pi^*) \rightarrow T_1(n,\pi^*)$ ISC seems to occur.[22] Configuration interaction singles (CI Singles) calculation of **1** using 6-31+G(d) basis sets indicated that the T_2 state is 24 kcal/mol higher in energy than the T_1 state. The triplet energy of BAPs (68−69 kcal/mol)[23] is similar to that of benzophenone (69 kcal/mol), and the singlet energy of BAPs can also be considered to be similar to that of benzophenone, given that BAPs show the characteristic absorption behavior of the benzophenone chromophore.[10,11] Thus, in the cases of BAPs the T_2 state may energetically lie well above the S_1 state.

Formation of the S_1 state should be instantaneous following 335 or 380 nm excitation ($S_0 \rightarrow S_1$ transition). Indeed, the kinetic fits of growth curves (e.g., Figure 6a) revealed this to be so. The early rise times representing the absorption of the singlet state are within or close to the instrument response function (∼0.15 ps). This is true for all the growth data obtained from the 335 or 380 nm excitation experiments. The early rise time observed for **1** (0.62 ps) following the 267 nm excitation experiment is, however, significantly longer than the instrument response function (Figure 6b); similar observations were made earlier in the case of benzophenone and *p*-IB.[6] Thus, the early rise time represents the $S_2 \rightarrow S_1$ internal conversion. The observed rate of the $S_2 \rightarrow S_1$ internal conversion ($k_{S_2 \rightarrow S_1} = 1.6 \times 10^{12}\ s^{-1}$) of **1** is similar to those of benzophenone and *p*-IB.[6]

It is well-known that spin−orbit interaction of heavy atoms may increase rates of ISC.[24] Decay of the S_1 state becomes faster as a heavy atom is introduced in BAPs (Table 2). For example, the τ_{S_1} values of **1** (which does not have any heavy atom in its molecule) and **4** (which has a bromine atom in its molecule) are 9.11 and 7.24 ps, respectively. It further drops to 4.26 ps for *p*-IB. Thus, these data show a long-range internal heavy atom effect in these compounds.[25]

Kinetics of the Triplet State. The most significant observations with respect to the lifetimes of the triplet states are (i) there is a significant solvent dependence (the τ_T values of both *p*-IB and **1** are shorter in acetonitrile than in benzene) and (ii) the magnitudes of the τ_T values are hundreds of picoseconds. That the τ_T values of BAPs are less than 1 ns whereas the τ_T values of nonperester derivatives of benzophenone are in the microsecond regime indicates that the most likely process that is responsible for the decay of the triplet state is fission of the O−O bond to produce radicals.[4,5,12] To achieve this result, the electronic energy initially resident on the benzophenone moiety needs to become resident on the peroxy moiety as a result of intramolecular energy transfer (IET). Two questions that arise from the observations are the following: (i) What is the nature of the solvent effect? (ii) Why is the IET process not instantaneous?

The τ_T of **1** remains essentially the same (τ_T = 0.32 and 0.33 ns, respectively) in acetonitrile following either 267 or 335 nm excitation. Thus, the different τ_T values of **1** in acetonitrile and benzene seem mostly related to the nature of the solvent. Although solvent viscosity might affect radical-producing processes, the small difference in the viscosities of benzene ($\eta = 0.603 \times 10^{-3}$ Pa•s at 25 °C)[26] and acetonitrile ($\eta = 0.345 \times 10^{-3}$ Pa•s at 25 °C)[26] seems unable to account for the large differences observed in τ_T.

The possibility of a relatively nonpolar geometry of the triplet state of **1** that would be more stabilized in benzene than in

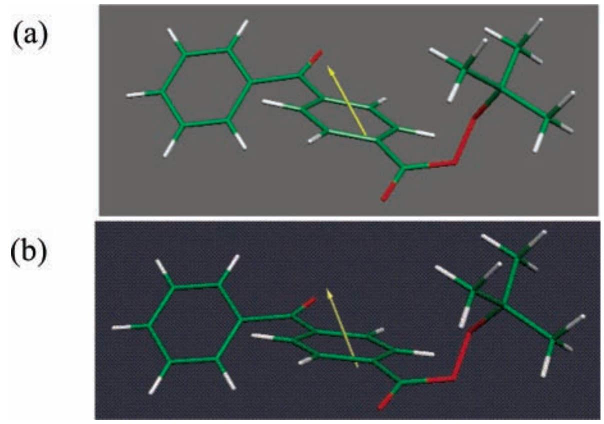

Figure 7. (a) Structure of **1** optimized by DFT/6-31G(d). (b) Structure of the triplet state of **1** optimized by CI Singles/6-31+G(d). The yellow arrows indicate the direction of the dipole moment.

acetonitrile does not seem to be the case either, as indicated by ab initio calculations. The geometry of the ground state of **1** was optimized by the density functional theory (DFT) method using 6-31G(d) basis sets, while that of the triplet state was optimized by the CI Singles/6-31+G(d) method. It is observed that the triplet state is flatter than the ground state; especially the benzophenone and perester carbonyl groups, as well as the phenyl ring between them, are more planar in the triplet state than in the ground state (Figure 7). The calculated dipole moment of the triplet state (2.2210 D) is larger than that of the ground state (2.0876 D). This indicates that the polarity, in fact, increases in the transition from the ground state to the triplet state. Similar calculations have also indicated a higher dipole moment of the triplet state of *tert*-butyl 3-(4′-methylbenzoyl)perbenzoate (2.6360 D) than that of its ground state (1.6205 D).

The differences observed in τ_T could be rationalized in terms of a transition state that may form prior to dissociation of the O−O bond.[27] Since the polarity increases on going from the ground state to the triplet state, it may be possible that the transition state is more polar even than the triplet state. In such a case, its formation would be more favored in a polar solvent such as acetonitrile than in benzene, resulting in the faster decay of the triplet state in acetonitrile.

The τ_T values of **2**−**4** have been found to be in the same vicinity as the reported τ_T of **1**.[5] It seems that 0.6−0.7 ns (in benzene) is the general lifetime of the triplet states of BAPs that have the perester moiety at the position para to the benzophenone carbonyl group. It is also noted that decay of the triplet states of these BAPs is not affected by the nature of the substituents in that no systematic variations were observed in the τ_T values of **1**−**4**. The observations were similar in benzene and acetonitrile. Since decay of the triplet state is associated with dissociation of the O−O bond, the substituents may be too distant to affect the dissociation.

Possible Mechanism of Triplet Energy Interception. In general, the Förster type of mechanism is considered for IET processes,[2,28] and triplet excitation transfer probably takes place through an exchange mechanism.[28,29] IET processes are considered to be structure and distance dependent.[2] However, no differences in the efficiencies of excitation energy transfer were observed in benzophenone-$(CH_2)_n$-naphthalene[30] and anthracene-$(CH_2)_n$-naphthalene systems,[31] where $n = 1-3$. Triplet excitation energy transfer has been found to be faster than singlet excitation energy transfer.[2,30] Although a little higher value (1×10^{10} s^{-1}) has been estimated for the IET process in benzophenone-$(CH_2)_{1-3}$-naphthalene molecules,[30] the rate of such an energy transfer ($k_T = 1/\tau_T$) in BAPs can be considered to be ∼1.5×10^9 s^{-1} in benzene.

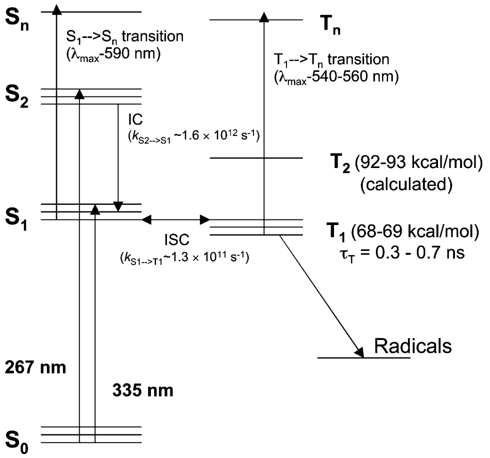

Figure 8. Jablonski diagram representation of BAPs.

Given the lower triplet energy of BAPs (68−69 kcal/mol) than the energy required for the vertical electronic excitation of the O−O bond,[32] emission from the benzophenone chromophore and absorption by the perester moiety leading to vertical excitation of the latter can be ruled out. After the benzophenone carbonyl group is excited initially, the excitation will be passed on from one excited state to another until the lowest excited state is reached.[2,33] Lewis and Calvin proposed a similar theory in which energy can be transferred within a molecule until it reaches a “loose-bolt” group which efficiently dissipates the energy.[34] The O−O bond may provide such a loose bolt in the molecules of BAPs. A semiempirical treatment does provide evidence that the triplet energy may efficiently transfer to a dissociative excited triplet state of the O−O bond.[35,36]

Potential energy profiles for the cleavage of the O−O bond were calculated using a Morse potential (eq 1) for the bonding interaction and a Sato−Morse function (eq 2) for the repulsive triplet state. In eqs 1 and 2, V and V_{tr} are the attractive and repulsive terms, respectively, r is the displacement from the equilibrium bond distance, D_e is the bond energy, and β is the Morse parameter.

$$V = D_e[\exp(-2\beta r) - 2\exp(-\beta r)] \tag{1}$$

$$V_{tr} = D_e/j[\exp(-2\beta r) + 2\exp(-\beta r)] \tag{2}$$

D_e was taken as 37 kcal/mol[37] for the perester (O−O) bond of BAPs, and β was taken as 2.69 Å^{-1}.[38] j (a Sato parameter) in eq 2 was taken as 4; the choice was derived from the fact that it gave better repulsive curves for several other cases.[16] The plots obtained are shown in Figure 9. As can be seen, the energy difference between the attractive and repulsive plots (ΔE_{r-a}) even at the equilibrium bond distance is 64.75 kcal/mol, which is ∼3 kcal/mol less than the triplet energy of BAPs. This indicates that the triplet energy can collapse once it reaches the repulsive triplet state of the O−O bond. The efficiency of such an energy transfer can be 100%,[30] resulting in efficient dissociation of the O−O bond.

The smaller ΔE_{r-a} value than the triplet energy of BAPs may suggest that no activation energy is required for the photochemical dissociation of the O−O bond. While such plots provide a better basis for mechanistic discussion, they can only be regarded as a coarse approximation. A slight change in the j

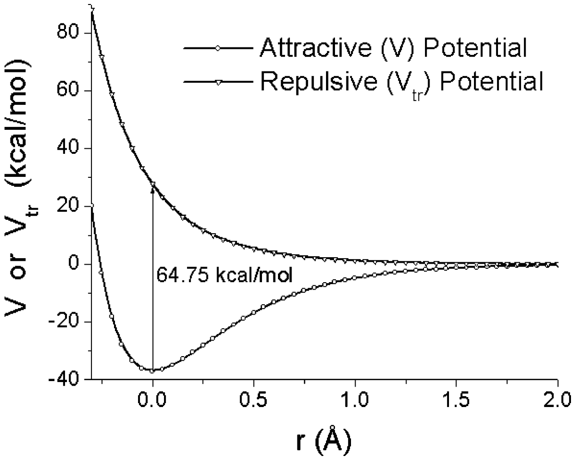

Figure 9. Calculated attractive and repulsive potentials of the O−O bond of BAPs.

value or in the bond dissociation energy, which is in the range of 35−39 kcal/mol for the perester bond,[37] can alter the ΔE_{r-a} value. In a crude sense, the IET process in BAPs can be considered equivalent to the bimolecular benzophenone triplet energy transfer to di-*tert*-butyl peroxide, major differences being in the efficiencies and rates of the two processes. A value of $j = 2.9$ was found to correlate the theoretically predicted and experimentally observed energy of activation in the case of bimolecular energy transfer from several triplet sensitizers including benzophenone to di-*tert*-butyl peroxide.[35] In our case, the use of $j = 2.9$ in eq 2 yielded a value of $\Delta E_{r-a} = 75$ kcal/mol, which is higher than the triplet energy of BAPs. Thus, the presence of a potential barrier for triplet energy dissipation to the repulsive triplet excited state of the O−O bond cannot be ruled out.

Cleavage of the C−I bond of *p*-IB from the triplet manifold is 4 kcal/mol exothermic, given the ~64 kcal/mol bond energy of a phenyl−iodine bond and ~68 kcal/mol triplet energy of *p*-IB.[7] Nonetheless, it has been calculated that a minimum of 3 kcal/mol of activation energy is required for the n,π^* triplet state to pass into either a π_I,σ^* or σ,σ^* state, both of which are irreversibly dissociative.[7] The fact that cleavage is an activated process is in accord with the triplet state being a well-defined bound state as indicated by its multiple picosecond lifetime. The cases of BAPs are similar. From the semiempirical calculations, the upper limit of such an activation energy for BAPs seems to be ~7−8 kcal/mol. The presence of such a potential barrier could also explain the existence of the transition state that is more polar in nature than the triplet state, as suggested by ab initio calculations.

Experimental Section

Materials. The synthesis of **1**−**4** has been provided previously.[10,11] *p*-IB (Trans World Chemicals) was twice recrystallized from methanol before use. Spectrometric grade benzene and twice distilled acetonitrile were used as the solvents.

Ultrafast Spectrometry. The setup used for the ultrafast transient absorption spectrometric experiments has been detailed elsewhere.[6] In brief, the output of a Ti:sapphire laser (Spectra-Physics, Hurricane) (fwhm ≈ 150 fs) was steered into a third harmonic generator (CSK Super Tripler) to obtain the 267 nm excitation wavelength. An optical parametric amplifier (OPA-800C, Spectra-Physics) was used to obtain the 335 nm excitation wavelength. The energy of the probe pulses was <1 μJ/cm^2 at the sample. The pump beam was typically arranged to be 5 μJ/pulse with a spot size of 1−2 mm diameter at the sample. Both beams were coupled into 200 μm fiberoptic cables after the sample cell and thereafter input into a CCD spectrograph (Ocean Optics, S2000-UV−vis) for time-resolved spectral information (425−800 nm). Typically, 5000 excitation pulses were averaged to obtain the transient spectrum at a particular delay time. Kinetic traces at appropriate wavelengths were assembled from the accumulated spectral data. The sample flow-through cell had an optical path of 2 mm and was connected to a solution reservoir and flow system. Sample solutions were prepared to have an absorbance of 0.8−1.2 at the excitation wavelength and were used without deaeration. All measurements were conducted at room temperature, 22 ± 2 °C.

Ab Initio Calculations. Geometry optimizations of the ground and triplet states of **1** were carried out with the DFT variant B3LYP and CI Singles methods, respectively. The Gaussian 98 program package[39] was used for the calculations in which the 6-31G(d) and 6-31+G(d) basis sets, respectively, were employed for the ground and triplet states.

Conclusions

Excitation of the BAPs **1**−**4** at 335 or 267 nm revealed that the S$_1$ states have lifetimes of 7−9 ps. The rates of the S$_1$ → T$_1$ ISC in these compounds remained the same in benzene and acetonitrile. During the 267 nm excitation experiments of **1** in acetonitrile, the S$_1$ state was found to form in 0.62 ps, which is the time of the S$_2$ → S$_1$ internal conversion. The data obtained as well as ab initio calculations indicate that there is no involvement of the T$_2$ state in the photophysical relaxation pathway of BAPs in solution. In benzene, the τ_T values of **1**−**4** were measured to be 0.6−0.7 ns, while that of *p*-IB was found to be ~0.1 ns. The triplet decay was observed to be faster in acetonitrile than in benzene for both **1** and *p*-IB. The semiempirical and ab initio calculations suggest that intramolecular triplet energy dissipation in BAPs that results in efficient dissociation of the O−O bond may take place to the repulsive excited triplet state of the latter and involve a transition state that is probably more polar than the triplet state.

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Supporting Information Available: Various transient spectra and lifetime curve fittings (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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