Laser Flash Photolysis of *tert*-Butyl Aroylperbenzoates: Kinetics of the Singlet and Triplet States and the Aroylphenyl Radicals[1]

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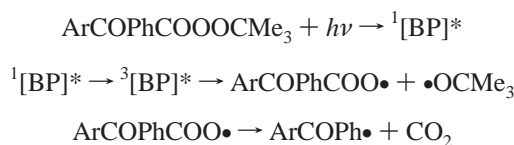Received April 15, 2003; E-mail: neckers@photo.bgsu.edu

Abstract: *tert*-Butyl aroylperbenzoates (**1**−**4**) were studied by laser flash photolysis (LFP). LFP (380 nm, pulse width ~350 fs) of **2** and **3** allowed direct observation of their singlet states, which showed broad absorption ($\lambda_{max} \sim 625$ nm; $\tau \sim 20$ and ~7.9 ps, respectively). The triplet state of each ($\lambda_{max} \sim 530-560$ nm) rapidly dissociates by O−O cleavage as indicated by the short triplet lifetimes (e.g., triplet lifetime of **3** ~0.74 ns). The ~550 nm absorption obtained from the 355 nm LFP (pulse width ~7 ns) of **1**, **2**, and **4** has been assigned to the corresponding aroylphenyl radicals. Two representative radicals (4-benzoylphenyl **5** and 3-(4′-methylbenzoyl)phenyl **6**) investigated in detail showed solvent-dependent lifetimes. Absolute bimolecular rate constants of reactions of these radicals with various quenchers including double-bond-containing monomers have been observed to range from 7.56×10^7 to 1.68×10^9 M^{-1} s^{-1} in CCl_4 at room temperature. A possible structure of the aroylphenyl radicals and the transition responsible for the 550 nm absorption are discussed.

Introduction

Diaroyl peroxides and peroxyesters are important *thermal initiators* for the formation of vinyl polymers in a number of commodity applications. For instance, most commercial polystyrene is made from styrene monomer with benzoyl peroxide as the initiator in a thermal reaction. Peroxide initiators also stimulate the free radical reactions that provide relatively high molecular weight polymers from many other vinyl monomers including butadiene and acrylonitrile.[2] Photoinitiators for vinyl polymerization, in contrast, almost always differ from their thermal counterparts. Bond homolysis initiation of monomer to polymer conversions by photochemical processes most often involve aromatic ketones that initiate chains either via radicals produced from a Norrish type I cleavage or by bimolecular electron-transfer processes that also produce chain-initiating radicals.[3] Save for those reported here, there are virtually no commercially employed photoinitiators that are also peroxides, either diaroyl or dialkyl, or peresters. Thus, the work below was initially undertaken to develop methodology to produce radical intermediates directly by the photodecomposition of selected peresters.

tert-Butyl aroylperbenzoates (BP) efficiently produce aroyl-benzoyloxyl and aroylphenyl radicals when irradiated at ~355

nm (n → π* transition).[4,5] These radicals have been found to initiate polymerization of double-bond-containing monomers[4,6] and to cause photo-cross-linking and photografting.[7,8] Rapid intramolecular triplet energy dissipation accounts for the efficient dissociation of the perester bond and the attendant high quantum yields of cleavage. Laser flash photolysis (LFP) of *tert*-butyl (4-benzoyl)perbenzoate [**1**] revealed a relatively short-lived triplet state (~0.87 ns).[9] The following steps are, in principle, involved in the photodissociation of BPs:

$$ArCOPhCOOOCMe_3 + h\nu \rightarrow {}^1[BP]^*$$

$$^1[BP]^* \rightarrow {}^3[BP]^* \rightarrow ArCOPhCOO\bullet + \bullet OCMe_3$$

$$ArCOPhCOO\bullet \rightarrow ArCOPh\bullet + CO_2$$

Reports dealing with the kinetics of the singlet and/or triplet states of organic peresters are limited.[9,10] Furthermore, though the rate of intersystem crossing (ISC) of benzophenone is often quoted (~3.33×10^{10} s^{-1} measured in aromatic solvents such

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Chart 1

(1) R₁ = H, R₂ = H
(2) R₁ = CH₃, R₂ = H
(3) R₁ = Br-CH₂, R₂ = H

(4)
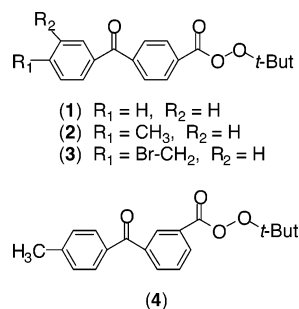
as benzene)[11] and multitudes of data are available on the triplet state of benzophenones,[11,12] there are limited reports on the spectroscopic observation of the singlet state of benzophenones.

We recently carried out LFP studies of **1**, *tert*-butyl 4-(4′-methylbenzoyl)perbenzoate [**2**], *tert*-butyl 4-(4′-bromomethyl-benzoyl)perbenzoate [**3**], and *tert*-butyl 3-(4′-methylbenzoyl)-perbenzoate [**4**] (Chart 1). Transient spectroscopy provided insights into the kinetics of their photophysical and photochemi-cal processes. LFP at 380 nm (pulse width ∼350 fs) of **3** allowed direct observation of its singlet state. We report here the kinetics of decay of the singlet and triplet states of **2** and **3**.

Photoinduced peroxy bond fission and the decarboxylation of the aroyloxyl radical so obtained have been studied in detail and different rates of peroxy bond fission have been obtained for various perester systems.[13] Detailed spectroscopic studies of photochemically generated aroyloxyl radicals and their absolute rate constants have also been reported.[14] However, the same cannot be said of phenyl radicals. A detailed study of the relative reactivities of the thermally produced phenyl radical toward a number of substrates has been reported earlier.[15] Because of their weak UV–visible signals in solution at ambient temperature, indirect approaches have been applied to obtain absolute rates of reactions of the phenyl radical in solution.[16] Their UV–vis,[17] IR,[18] and Raman[19] spectra have, however, been reported and interpreted in the gas phase and in an argon matrix at low temperatures.

This work first shows that aroyl substitution conveys a strong and easily detectable mid-UV absorption to phenyl radicals,

demonstrating the virtue of attaching a chromophore to an otherwise difficult to observe transient species.[4,20] We also report here the kinetics of decay processes of the 4-benzoylphenyl and 3-(4′-methylbenzoyl)phenyl radicals obtained by the 355 nm LFP of **1** and **4**.

Experimental Section

Chemicals and solvents required were obtained from commercial suppliers. Compounds **1**–**3** were synthesized as previously reported,[4,5] and **4** was synthesized from methyl 3-(4′-methylbenzoyl)benzoate that had been itself synthesized by a modified literature method[21] (see Supporting Information). Solvents used for LFP experiments were either spectrometric-grade or distilled over benzophenone/sodium as required.

The laser system and apparatus for the ultrafast transient absorption spectroscopy experiments has been described elsewhere.[22] It included a Ti:sapphire seed laser pumped with a diode-pumped 5 W cw Nd: YAG laser. The excitation pulse (380 nm) was the second harmonic of the tuned fundamental frequency (760 nm). The energy of the pump beam was arranged to be ∼150 µJ/pulse. Typically, 500 excitation pulses were averaged to obtain the transient spectrum at a particular delay time. In-house LabVIEW (National Instruments) software allowed automatic spectral acquisition over a series of delay line settings. Kinetic traces at appropriate wavelengths were assembled from the accumulated spectral data. The instrument rise time was ∼350 fs. Sample solutions were prepared to have an absorbance of 0.7–0.8 at the excitation wavelength in the 2 mm flow cell and were used without deaeration.

Nanosecond flash photolysis studies were performed on a kinetic spectrometric detection system previously described.[23] The excitation pulse (355 nm, 12–19 mJ/pulse) was the third harmonic of a Q-switched Nd:YAG laser. The excitation pulse width was ∼7 ns. Transients produced were followed temporally and spectrally by a computer-controlled kinetic spectrophotometer. The sample solutions showing an absorbance in the range of 0.15–0.33 at the excitation wavelength in 1-cm² quartz cuvettes were used and degassed continu-ously with argon during experiments. Fresh samples were used for obtaining each kinetic trace. All measurements have been made at room temperature.

Results and Discussion

Absorption and Kinetics of Singlet and Triplet States. LFP of **2** in benzene at room temperature (380 nm excitation, pulse width ∼350 fs) resulted in a broad absorption having a maximum at ∼560 nm (Figure 1). The triplet states of benzophenones have been known to show absorption at ∼530 nm.[12a,c] A similar 560 nm transient absorption obtained from **1** has been assigned to its triplet state.[9] Thus, the 560 nm transient obtained from **2** can be assigned to its triplet state, the rise time of which was found to be ∼20 ps.

In fact, time-resolved transient absorption spectra of **2** indicate that, in the early time (∼2 ps), the broad absorption has a maximum at ∼625 nm that later shifts to ∼560 nm. This suggests that there may be two species involved, though it is not that clear in the case of **2**. An attempt to extract kinetic

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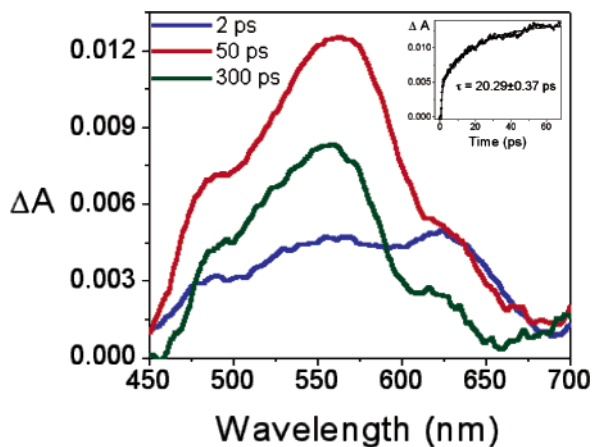(23) Ford, W. E.; Rodgers, M. A. J. *J. Phys. Chem.* **1994**, *98*, 3822.

Figure 1. Transient absorption spectra obtained from the 380 nm laser flash photolysis of **2** in benzene, recorded (blue) 2 ps, (red) 50 ps, and (green) 300 ps after the laser pulse. Inset: kinetic trace (triplet growth) monitored at 570 nm.
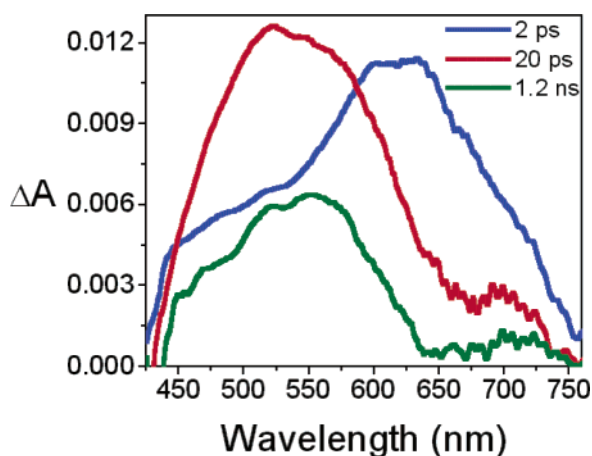

Figure 2. Transient absorption spectra obtained from the 380 nm laser flash photolysis of **2** in benzene, recorded (blue) 2 ps, (red) 20 ps, and (green) 1200 ps after the laser pulse.

data at ∼625 nm failed because of the weak signal. However, under similar experimental conditions, LFP of **3** resulted in two clearly distinguishable transients having absorption maxima at ∼530 and ∼625 nm (Figure 2). The 530 nm transient can be unequivocally assigned to the triplet state of **3** and its lifetime was found to be ∼0.74 ns.

The 625 nm transient from **3** appears instantly after the laser pulse excitation and decays rapidly. Since the singlet state of benzophenone has been suggested to have absorption at ∼580 nm, at a higher wavelength than that at which its triplet state absorbs,[24] we assign the 625 nm absorption to the singlet state of **3**.[25] Conclusive evidence for this assignment comes from kinetic analysis. Decay of the 625 nm transient and the rise time of the triplet state of **3** were found to be the same (∼7 ps) within the error range (Figure 3). Thus, it is clear that the 625 nm transient is the precursor of the 530 nm transient (the triplet state). The rate of ISC increases from 4.93×10^{10} s^{-1} to 1.27×10^{11} s^{-1} going from **2** to **3**. This can be attributed to the

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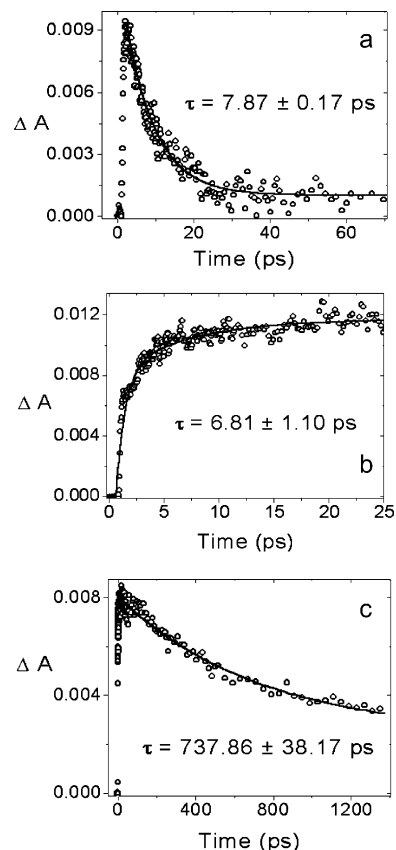
Figure 3. Kinetic traces showing growth and decay of the singlet and triplet states of **3**. (a) Decay of the singlet state monitored at 675 nm. (b) Growth of the triplet state monitored at 525 nm. (c) Decay of the triplet state monitored at 475 nm.

heavy atom-enhanced ISC (S$_1$ → T$_1$) in **3** that contains a bromine atom.[26]

The steady-state photolysis of the BPs has revealed that the corresponding aroylbenzoic acid and benzophenones are always the major products in a H-donating solvent like methanol or cyclohexane.[4,5] When benzene was used as the solvent, adduct products such as ArCOPh-Ph and ArCOPh-COOPh were also observed in addition.[5] Biphenyl, phenyl *tert*-butyl ether, acetone, and *tert*-butyl alcohol were observed as minor products.[5] In the case of CCl$_4$ as the solvent, the major product, however, was found to be the corresponding chlorobenzophenones. The decay of the triplet state of BPs, thus, represents dissociation of the perester bond and the resulting radicals give rise to different photoproducts. Both concerted (simultaneous scission of the O−O and R−C bonds) and stepwise (scission of the O−O bond followed by scission of the R−C bond) mechanisms have been reported and debated for photodissociation of peresters.[6,13c,14b,27] Thus, the triplet state of BPs can dissociate either to the aroylbenzoyloxyl radical or to a combination of the aroylbenzoyloxyl and aroylphenyl radicals.

In both **2** and **3**, the absorption at ∼530−560 nm does not go to the baseline over the data accumulation time (1.4 ns). This likely indicates the triplet state produces a species that also absorbs at these wavelengths. In our case we cannot distinguish whether the residual absorption at ∼560 nm is due to the

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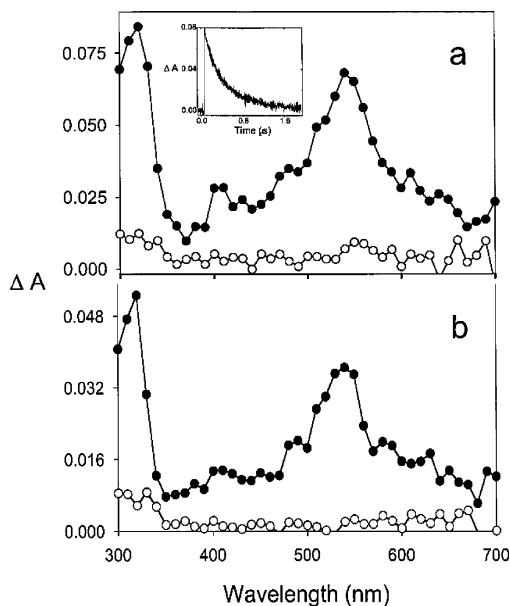
Figure 4. (a) Transient absorption spectra obtained from laser flash photolysis of **1** (1.18×10^{-3} M) in CCl_4, recorded (●) 20 ns and (○) 2 μs after the laser pulse. Inset: kinetic trace monitored at 550 nm. (b) Transient absorption spectra obtained by laser flash photolysis of *p*-iodobenzophenone (1.15×10^{-3} M) in CCl_4, recorded (●) 20 ns and (○) 2 μs after the laser pulse. (Excitation at 355 nm.)

aroylbenzoyloxyl or the aroylphenyl radical. Nevertheless, after ~7 ns of laser excitation (355 nm), we observe transient absorption having a maximum at ~550 nm that is convincingly due to the aroylphenyl radicals (vide infra). Thus, if these BPs undergo stepwise decomposition, decarboxylation seems to take place between ~1 and ~7 ns.[28]

Characterization and Kinetics of Aroylphenyl Radicals. Two absorption bands having maxima at 320 and 550 nm were obtained from each of **1**, **2**, and **4** when they were laser flash photolyzed at room temperature in CCl_4 with 355 nm excitation (pulse width ~7 ns). The 550 nm transient showed a single-exponential decay in each case and has been assigned to the corresponding aroylphenyl radical on the basis of the following observations: (a) similar 550 nm transients were obtained during LFP of **1** and *p*-iodobenzophenone in CCl_4 (Figure 4);[29] (b) the 550 nm transients were chemically quenched by oxygen, indicating they were carbon-centered radicals;[30] (c) when

p-iodobenzophenone was photolyzed in benzene, the well-established absorption of the iodine–benzene complex[16] having a maximum at ~470 nm was obtained in addition to the 550 nm absorption; (d) the 550 nm transients were quenched by a H-atom-donating quencher like 1,4-cyclohexadiene and an analysis of the reaction mixture revealed formation of an increased amount of products formed by hydrogen abstraction (corresponding benzophenones); and (e) the corresponding chlorobenzophenones were the major photoproducts in all cases, indicating chlorine abstraction by the aroylphenyl radicals from the solvent.

Aroylbenzoyloxyl, *tert*-butoxyl, and trichloromethyl radicals are also formed in the reaction, though none contributes to the 550 nm absorption. Aroylbenzoyloxyl radicals are not the absorbing species because the 550 nm absorption is also observed from *p*-iodobenzophenone, a compound that cannot produce the benzoylbenzoyloxyl radical.[31] The *tert*-butoxyl radical absorption at 320 nm is neglible.[32] Similar absorptions were obtained during LFP of **2** in either benzene or CCl_4, ruling out contribution by any solvent-derived radicals such as the $ArCOC_6H_4C_6H_6$● adduct radical[5,33] or the trichloromethyl radical. Similar spectra were also obtained from **4** in both CCl_4 and acetonitrile. There were no differences in the spectra recorded on either flowing or static samples, indicating that there is no involvement of any product of a secondary photoreaction.

The triplet states of benzophenones have also long been known to abstract available H-atoms, forming ketyl radicals that show absorption at ~535 nm.[34] However, since the lifetimes of the triplet state of these BPs are in the picosecond regime, formation of a ketyl-type radical seems unlikely. The solvent (CCl_4) also cannot furnish such an H-atom. In fact, intramolecular triplet energy transfer causing scission of the perester bond is much faster than are the bimolecular rates of H-abstraction by the triplet states of benzophenones.[35] Consequently, no ketyl radical-derived product was observed when BPs were irradiated at 350 nm in either benzene or methanol.[5] The estimated lifetime of the triplet state of *p*-iodobenzophenone is ~0.2 ns, and no ketyl radical-derived product was observed during its photolysis either, even when an H-donor solvent like cyclopentane was used.[36,37] This along with the picosecond lifetime of the triplet state rules out the 550 nm transient being a ketyl-type radical.

(28) The aroyloxyl radicals are known to show absorption in the 600–800 nm range and their reported lifetimes are 0.2–0.5 μs (ref 14). However, we observed no absorption in that range during our experiments, and attempts to observe the aroylbenzoyloxyl radicals were unsuccessful. Ingold and co-workers (ref 14b) had studied a single aroylbenzoyl peroxide and, as was the case with the system we report in this paper, saw no aroylbenzoyloxyl radical absorption. One of the reviewers has pointed out that two-photon absorption could be responsible for extremely fast decarboxylation of the aroylbenzoyloxyl radicals, and we believe this could be the case. The aroyloxyl radicals are known to decarboxylate faster, leading to the formation of the aryl radicals when they absorb at either 308 or 700 nm (ref 14a). It has also been shown that the benzoyloxyl radical that has been stabilized by preparation at low temperatures (67 K) can be photodecarboxylated with light of 550–1300 nm (Karch, N. J.; Koh, E. T.; Whitsel, B. L.; McBride, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 6729).

(29) In optically matched experiments, the lifetimes of the 550 nm transient obtained from both **1** and *p*-iodobenzophenone were found to be same within experimental error. The initial OD obtained in the case of *p*-iodobenzophenone was, however, much smaller than in the case of **1**. The quenching rate constant of the benzoylphenyl radical with *p*-iodobenzophenone was found to be 1.7×10^9 M^{-1} s^{-1} (the error involved in this measurement is large due to the low OD at 550 nm).

(30) Since the triplet states are also quenched by oxygen, the 550 nm absorption might be mistakenly assigned to the triplet state of BPs, as was done by Allen et al. (ref 6), who assigned the 550 nm absorption obtained from the nanosecond LFP of **1** in acetonitrile to its triplet state.

(31) The only common radical that can be obtained from both **1** and *p*-iodobenzophenone is the 4-benzoylphenyl radical. The similar ~560 nm absorption observed previously during nanosecond LFP of **1** was tentatively assigned to the 4-benzoylbenzoyloxyl radical on the basis of the resemblance of its lifetime to that of the benzoyloxyl radical (ref 14). However, the lifetimes of the aroylphenyl radicals have also been found to be in a similar range (~0.4 μs) and depend on the solvent and concentration of the precursor BPs. The evidence presented in the text clearly suggests that the 550 nm absorption is due to the aroylphenyl radicals.

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(35) The possibility that a bimolecular rate constant of H-abstraction by the triplet state of the BPs in the concentration range as low as 8×10^{-4} mol/L could be 10^9 M^{-1} s^{-1} or faster seems to be very unlikely. The rates of reactions of the triplet state of benzophenone with benzene and toluene have been found to be 0.8×10^4 and 2×10^4 M^{-1} s^{-1}, respectively (ref 34a).

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(37) We have recently measured the triplet lifetime of *p*-iodobenzophenone and it was found to be 98.46 ± 2.16 ps in benzene (detailed results will be published elsewhere).

solvent	**5**[a] (τ, μs)	**6**[b] (τ, μs)
C_6H_6	0.66 ± 0.03	0.68 ± 0.04
CCl_4	0.41 ± 0.01	0.62 ± 0.02
CH_3CN	0.21 ± 0.01	0.29 ± 0.01

[a] Concentration of the precursor BP (**1**): 1.18×10^{-3} M. [b] Concentration of the precursor BP (**4**): 1.41×10^{-3} M.

Scheme 1
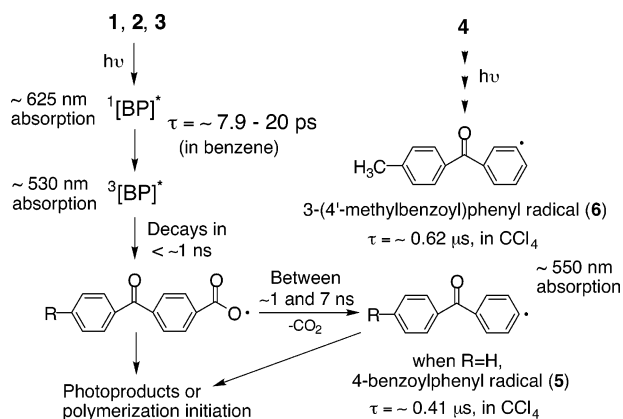
When experiments were carried out at ~2 and ~6 mJ/pulse, similar spectra were obtained from a 1.20×10^{-3} M solution of **1** in CCl_4. The initial ODs at 550 nm were observed to be lower than those obtained from the experiment when ~12 mJ/pulse energy was employed. The lifetime monitored at 550 nm, however, was essentially the same (0.42 μs). A similar 550 nm transient was obtained from LFP of *tert*-butyl 4-(4′-bromobenzoyl)perbenzoate in CCl_4. Since each of the BPs studied, as well as *p*-iodobenzophenone, gave the 550 nm transient, this transient seems generic to this class of radicals. Transients that form during the photodissociation of BPs are presented in Scheme 1.

Lifetimes of the 4-benzoylphenyl (**5**) and 3-(4′-methylbenzoyl)phenyl (**6**) radicals were recorded in different solvents (Table 1) and reflect the reactivity of these radicals toward the solvents employed. The lifetime of **5** was observed to be higher in benzene (0.66 μs) than in CCl_4 (0.41 μs) and it is consistent with the higher rate of chlorine abstraction (7.8×10^6 M^{-1} s^{-1}) by the phenyl radical from CCl_4 than the rate of its quenching (4.5×10^5 M^{-1} s^{-1}) by benzene.[16] However, the rate of quenching of the phenyl radical by acetonitrile (1.05×10^5 M^{-1} s^{-1}) has been found to be nearly comparable with that by benzene,[16] while we observed lower lifetimes of both **5** (0.21 μs) and **6** (0.29 μs) in acetonitrile.

Solvent polarity may influence the stability of these radicals. So we tried to deduce their lifetimes in cyclohexane and methanol. However, in such H-donating solvents, the kinetics became complex at 550 nm, and other unidentified transients having very long lifetimes were observed. Given the nonpolar nature of their ground states (vide infra), it is clear that polarity and H-donating incapability of a solvent is critical in observing such radicals.

Absolute bimolecular rate constants of quenching (k_q) of the two representative radicals (**5** and **6**) by various additives were obtained by monitoring the absorption at 550 nm. The k_q values were calculated by plotting 1/lifetime against concentration of

	$k_q \times 10^8$ (M^{-1} s^{-1})	
quencher	5	6
BP	16.8 ($\pm$1.40)	9.43 ($\pm$0.69)
1,4-CHD	15.8 ($\pm$1.10)	8.75 ($\pm$0.12)
toluene	5.59 ($\pm$0.46)	4.14 ($\pm$0.16)
MMA[b]	0.76 ($\pm$0.03)	1.07 ($\pm$0.05)
MMA	3.14 ($\pm$0.19)	2.86 ($\pm$0.11)
LAC	3.57 ($\pm$0.12)	2.07 ($\pm$0.18)
NVP	8.67 ($\pm$0.29)	9.59 ($\pm$0.47)

[a] Solvent, CCl_4; concentration of the radical sources, 7.82×10^{-4} to 2.41×10^{-3} M; abbreviations, 1,4-CHD = 1,4-cyclohexadiene, MMA = methyl methacrylate, LAC = lauryl acrylate, NVP = 1-vinyl-2-pyrrolidinone. [b] The commercially available sample of MMA containing monomethyl ether hydroquinone as the radical inhibitor was used; in all other cases of monomers, radical inhibitor removed samples were used.

Scheme 2
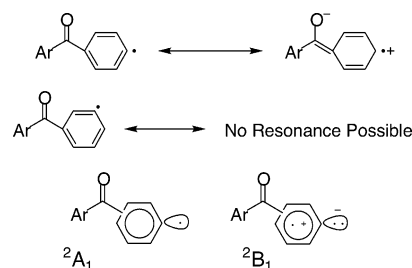
the quencher and are given in Table 2. The radicals were quenched by precursor BPs with comparatively high rate constants. Electron spin resonance studies have shown that substituted phenyl radicals with para and meta carboxyl groups have high reactivity.[38] Although it was difficult to distinguish whether the quenching was due to oxidation by the peroxyester bond or H-abstraction, it is suggested that quenching by the precursor BP primarily occurs by H-abstraction. When benzoyl peroxide was used as quencher, it showed no measurable quenching in the concentration range of $10^{-2}-10^{-4}$ M. The addition of these radicals to the aromatic rings of BP can also be one possible mode of the quenching. However, products from such an adduct were not observed during product analysis.[4,5,36]

Although **6** is a little longer lived than **5**, there are not many differences in their reactivities as reflected by their similar k_q of reactions with all the studied quenchers. Both radicals showed higher reactivity toward 1-vinyl-2-pyrrolidinone than toward acrylate monomers. It is also noted that the k_q did not change significantly in the presence of monomethyl ether hydroquinone (MMEH, the commercially used radical inhibitor).

Possible Structure and Transitions of the Aroylphenyl Radicals. The odd electron is localized in the σ orbital in the ground (doublet) state ($^2A_1$) of the phenyl radical.[17c,38,39] A similar σ radical structure can be assumed for aroylphenyl radicals; so one might expect a contribution from the resonance structures shown in Scheme 2 for the 4-aroylphenyl radicals. However, this does not seem to be the case because such resonance is not possible for the 3-aroylphenyl radical. Since both of these radicals show the 550 nm absorption, they should have similar structures in their ground states.

(38) Zemel, H.; Fessenden, R. W. *J. Phys. Chem.* **1975**, *79*, 1419.
(39) (a) Porter G.; Ward, B. *Proc. R. Soc. Ser. A* **1965**, *287*, 457. (b) Johnson, R. P. *J. Org. Chem.* **1984**, *49*, 4857. (c) Kim, G.; Mebel, A. M.; Lin, S. H. *Chem. Phys. Lett.* **2002**, *361*, 421.

The lowest energy optical transition of phenyl radicals has been assigned as $^2A_1 \rightarrow {}^2B_1$ (σ radical $\rightarrow \pi$ radical).[39a] The $^2B_1$ state is the next low-lying electronic state in which one of the π electrons has moved to the unpaired σ orbital, creating a radical cation center in the aromatic ring. The existence of the σ ground state and low-lying π radical state of the phenyl radical has been confirmed by several ab initio calculations.[39b,c]

Low-temperature matrix studies have shown phenyl radical bands at 534, 288, and 235 nm,[40] and recently, the low-energy band ($\sim$511 nm) has been assigned to the $^2A_1 \rightarrow {}^2B_1$ transition.[17c] It is possible that the $^2A_1 \rightarrow {}^2B_1$ transition is responsible for the 550 nm absorption of the aroylphenyl radicals. The contribution of the electron density on the carbonyl group may be shifting absorption to higher wavelengths. Substituents such as carboxylic acid or aldehyde groups have long been known to shift and usually intensify the UV absorption of benzene.[41] Investigation by up-to-date methods of ab initio calculations might shed some theoretical light on electronic excitation energies of the aroylphenyl radicals.

Conclusion

LFP (380 nm, 350 fs) allowed observation of the singlet and triplet states of BPs. The singlet states of BPs (**2**, **3**) showed broad absorption having a maximum at $\sim$625 nm and the rates of ISC were observed to be 4.93×10^{10} s^{-1} and 1.27×10^{11} s^{-1} in **2** and **3**, respectively. The triplet states, which show absorption at $\sim$530$-$560 nm, have been confirmed to be short-lived species ($\tau < \sim$1 ns in benzene). This is due to rapid intramolecular triplet energy dissipation to cause efficient scission of the perester bond forming reactive aroylbenzoyloxyl and aroylphenyl radicals. The latter absorbs in the mid-UV$-$visible region ($\sim$550 nm) and shows solvent-dependent lifetimes. Both the 4-benzoylphenyl and 3-(4'-methylbenzoyl)-phenyl radicals obtained from the 355 nm LFP of **1** and **4**, respectively, have been found to rapidly react with various substrates including double-bond-containing monomers, the bimolecular rate constants for which have been observed to be 7.56×10^7 to 1.68×10^9 M^{-1} s^{-1} in CCl$_4$ at room temperature. The symmetrically allowed $^2A_1 \rightarrow {}^2B_1$ transition seems to account for the 550 nm absorption of aroylphenyl radicals.

Supporting Information Available: Synthetic procedure and 41 figures showing NMR spectra of **4**, various transient spectra, lifetimes, and quenching rate constant graphs and fittings. This material is available free of charge via the Internet at http://pubs.acs.org.

JA030231G

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(41) Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy;* John Wiley & Sons: New York, 1962; p 257.