Further confirmation of the presence of H at P(1) comes from the presence of an absorption at 2320 cm^{-1} in the IR spectrum (Nujol mull).

The $^{31}P\{^1H\}$ NMR spectrum of **1** displays two somewhat broad peaks centered at 31.4 and 46 ppm and further peaks at −67.8 and −80.3 ppm. The structure of **1** shows that there are four different types of phosphorus centers, although the P(2) and P(3) environments resemble each other quite closely. It is not possible at present to assign a particular phosphorus resonance to its position in the structure, but the downfield peaks are probably due to the four-coordinate phosphorus centers, and the upfield peaks are probably due to the three-coordinate P(2) and P(3). It is notable, however, that some of the values seen here are in the same range (but with broader peaks) as those observed in other gallium–phosphorus compounds.[19] The ^1H NMR spectrum of **1** confirms the presence of 2,4,6-$(i\text{-}Pr)_3C_6H_2$ and 1-Ad groups in the ratio seen in the structure.

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Supplementary Material Available: Tables of atom coordinates, bond distances, bond angles, H coordinates, and thermal parameters for **1** (14 pages); listing of observed and calculated structure factors for **1** (43 pages). Ordering information is given on any current masthead page.

Chromophore-Assisted Peroxy Bond Breakage: Laser Flash Spectroscopic Studies of a Benzophenone Perester

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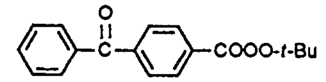
Benzoyl peroxide and, to a lesser extent, *tert*-butyl perbenzoate are widely used as thermal initiators for free radical chain reactions.[3] Like simpler peroxides such as hydrogen peroxide, these compounds do not absorb above 300 nm and are neither useful[4] nor problematic[5] sources of radicals from photolytic routes.[6] There have been a number of reports of systems that combine a long wavelength absorbing chromophore with the weak –O–O– bond of a peroxide in a single molecule. These putative unimolecular peroxide photoinitiators are said to combine the characteristics of known excited states with easily dissociated functions.[7] Our thought was that conjugation of the long-lived triplet of benzophenone with a peroxide unit susceptible to dissociation would provide an efficient source of carboxy and *tert*-butoxy radicals by combining the absorption maximum of the aromatic ketone with the function susceptible to homolysis (I). Inherent flexibility in synthesis led us to conceive of the so-called phototunable perester,[6,8] a concept that has led to substantial patent activity as well as related publications.[9-11]



I

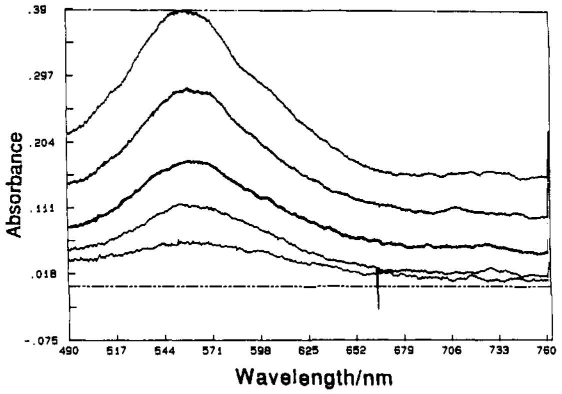


Figure 1. Transient absorption spectra resulting from absorption of a 25-ps pulse of 355-nm light in a deaerated perester I solution (7 mM) in CCl_4. Reading from top to bottom, the delay settings are 30, 462, 792, 1122, and 2442 ps.

Recently, *tert*-butyl peresters derived from fluorenone, benzophenone, and 9-methylfluorene have been investigated by laser flash photolysis experiments.[12,13] On the few hundred nanosecond time scale, the fluorenone perester entities showed transient absorptions that were assigned[12] to T_1 states of the chromophores; however, no T–T absorption in the benzophenone perester I case was found[12] in that time scale. Falvey and Schuster[13] employed picosecond laser flash techniques to investigate the 9-methylfluorene perester system. They observed growth of the 9-methylfluorenyl radical with a 55-ps time constant and inferred that energy translocation from the chromophore and fission of the peroxy bond occur within their experimental time resolution (ca. 25 ps). These limited examples show that chromophore-linked peroxides exhibit a wide range of excited-state stability prior to peroxy bond breakage. This has led us to inquire into what factors govern the dynamics of energy dissipation in chromophore-linked peresters. Our inquiry reflects, to a limited extent, the earlier work of Scaiano and Wubbels,[14] who studied the photosensitized intermolecular dissociation of di-*tert*-butyl peroxide. They concluded that energy transfer occurs to a repulsive state of the peroxide. Here we introduce our findings on the ultrafast processes that follow population of the T_1 state of a benzophenone perester.

Deaerated solutions of *tert*-butyl *p*-benzoylperbenzoate (benzophenone perester I) in CCl_4 with absorbance of unity at 355

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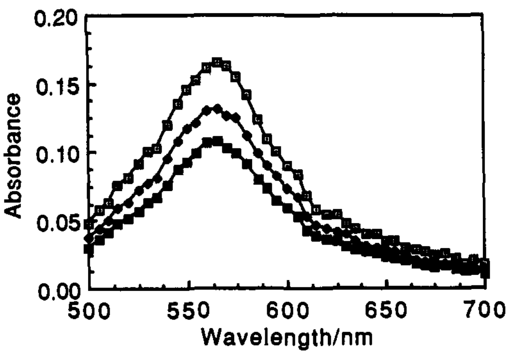
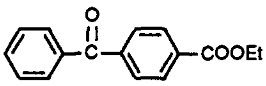


Figure 2. Transient absorption spectra taken at 1.3 (▣), 3.7 (◆), and 7.9 μs (dark square with light dot) after a 10-ns pulse of 355-nm light was incident on a deaerated CCl_4 solution of ester II (8.1 mM).

nm were exposed to 25-ps pulses of 355-nm radiation from a frequency-tripled mode-locked Nd:YAG laser (Quantel 571). The sample was flowed through a 10-mm quartz (each side) fluorescence cuvette to ensure presentation of a fresh solution each time the laser fired (5 Hz). The pump–continuum probe spectrographic system was based upon that described by Atherton et al.[15] except that the two probe beams were conducted to the cuvette and therefrom to the double diode array detector by fiber-optic cable. Figure 1 shows a series of transient absorption spectra taken with the above described perester I. The species absorbing maximally at 565 nm decayed exponentially with a lifetime of 870 ps to a nonzero base line (see below).

A similar set of experiments with a CCl_4 solution of ethyl *p*-benzoylbenzoate (ester II) which was prepared for comparison purposes showed the immediate formation of a nondecaying (over 9 ns) absorption (λ_{max} = 560 nm). The initial absorbances (at 30 ps) of the transients from I and II were both 0.29 under identical excitation conditions.



II

Extended time scale observations employed a Q-switched Nd:YAG laser (355 nm; 10 ns) and kinetic absorption spectrophotometry. When this instrument was used, ester II in CCl_4 yielded time-dependent absorption spectra as shown in Figure 2. The 562-nm peak decayed exponentially with a lifetime of several microseconds in deaerated solution. This decay was enhanced by oxygen. By analogy with benzophenone, this band is assigned to the absorption of the T_1 state of ester II. On this same instrument a flowed CCl_4 solution of perester I (A_{355} = 1.0) yielded a weak absorption (Figure 3) with λ_{max} = 570 nm. Under identical excitation conditions the initial absorbance of the perester (I) transient was only one-tenth that of the ester (II) species. The 570-nm species from I decayed exponentially with a lifetime of 254 ns.

With naphthalene (N) present as cosolute (to 1 M) in the perester solution, picosecond absorption studies showed that the 565-nm transient (Figure 1) decayed more rapidly in a manner that was first order in N concentration. Nanosecond level studies on these same solutions showed the instantaneous (at end of 10-ns pulse) presence of a new species absorbing maximally at 410 nm, where the $N(T_1)$ state absorbs.[16]

These observations allow the following conclusions:

(i) The 565-nm species, τ = 870 ps, is the $T_1 \rightarrow T_n$ absorption of perester I formed by very rapid (<25 ps) intersystem crossing from the singlet manifold (cf. benzophenone). This assignment stems from the similarities in absorption spectra at t = 30 ps of I and II, their coincident intensities, and the fact that N quenches the 565-nm species from I to produce an immediate (on nanosecond scales) formation of $N(T_1)$.[18]

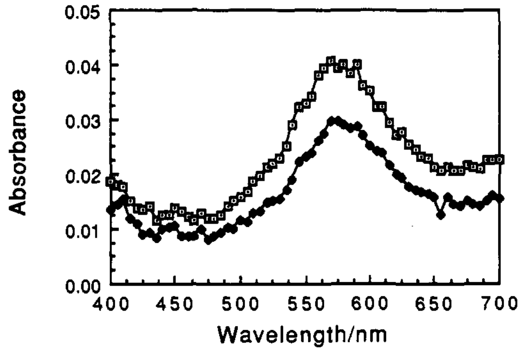


Figure 3. Transient absorption spectra resulting after excitation (10 ns, 355 nm) of a deaerated 7 mM solution of perester I in CCl_4. The two spectra are taken at delay times of 80 (▣) and 140 ns (◆).

(ii) The residual weak absorption at 570 nm at 9 ns and the immediate weak absorption at 570 nm in the multinanosecond experiment that exhibits a lifetime of 254 ns are assigned to the *p*-benzoylbenzoyloxy radical resulting from the fission of the peroxy bond. The decay (τ = 254 ns) then corresponds to the loss of CO_2 to form the benzoylphenyl radical, a species that apparently has no significant absorption in the observed spectral region. That the same spectral and lifetime features (λ_{max} = 570 nm, τ = 260 ns) were observed in benzene solution reassures us that Cl atom abstraction from CCl_4 is unimportant.

In summary, the sequence of events is

$$\mathrm{P(S_0)} + h\nu \rightarrow \mathrm{P(S_1)}$$

$$\mathrm{P(S_1)} \rightarrow \mathrm{P(T_1)} \qquad \text{very rapid}$$

$$\mathrm{P(T_1)} \rightarrow \mathrm{RCO_2^{\bullet}} + {}^{\bullet}\mathrm{OR'} \qquad k = 1.2\ \mathrm{ns^{-1}}$$

$$\mathrm{RCO_2^{\bullet}} \rightarrow \mathrm{R^{\bullet}} + \mathrm{CO_2} \qquad k = 0.004\ \mathrm{ns^{-1}}$$

where P = perester I, R = benzoylphenyl, and R′ = *tert*-butyl.

These results are supportive of the conclusions of Allen et al.,[12] who found no evidence of the T_1 state of perester I at a few hundred nanoseconds postexcitation. We also note that time-resolved EPR studies have shown[19] that the parent benzoyloxy radical ($PhCO_2^{\bullet}$) loses CO_2 in a 250 ns lifetime process although Cl- and MeO-substituted radicals were shown to have somewhat longer lifetimes. Clearly the photoinduced peroxy bond fission in I is much slower than that found for the 9-methylfluorenyl perester[13] and is much more rapid than the same process in the fluorenone peresters.[12] In all three molecules the peroxy bond is not conjugated with the chromophore and it is not unreasonable to assume that its bond-breaking rate is largely independent of the nature of the discrete chromophore. Thus we conclude that this large variance in observed rates reflects the rates at which energy can be transferred into the dissociable unit. Our current and future investigations are aimed at uncovering the nature of the barriers. Finally, we note that Scaiano and Wubbels[14] found that the T_1 state of benzophenone had a lifetime of 60 ns in neat di-*tert*-butyl peroxide at 25 °C, i.e., some 80 times longer than we find here for the T_1 state of perester I. This is clear evidence that connecting the O–O bond directly to the chromophore enhances its energy-accepting characteristics. They also showed that the same intermolecular process had a very weak activation requirement and that the Arrhenius A factor was near $1 \times 10^7\ M^{-1}\ s^{-1}$, indicating severe orientational requirements for energy transfer. It will be very interesting to measure the A factor for the T_1 decay of perester I.

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Efficient Photoinduced Generation of Radical Cations in Solvents of Medium and Low Polarity

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The electron acceptors and donors most often used in organic photoinduced electron transfer (PET) reactions are neutral molecules, in which case the initially formed intermediates are radical anion/radical cation pairs.[1] Normally, efficient product formation is observed only when diffusive separation competes effectively with return electron transfer within the radical ion pairs.[1,2] For this reason, PET reactions are usually performed in polar solvents such as acetonitrile, in which the Coulombic barrier to separation is greatly reduced compared to less polar solvents.[3]

The utility of PET reactions would be considerably extended if separated radical ions could be photochemically generated in nonpolar solvents. For example, it would permit a more direct comparison between PET chemistry and thermal electron transfer chemistry, which is usually performed in lower polarity solvents.[4] More importantly, it is becoming increasingly clear that polar solvents may react rapidly with radical ions, whereas nonpolar solvents do not.[2,5]

For these reasons we investigated the possible use of cationic acceptors[6] as sensitizers in PET reactions in nonpolar solvents. In this case, electron transfer to the excited state of the cationic acceptor from a neutral donor results in the formation of a neutral radical/radical cation pair in which there is no Coulombic barrier to separation. Therefore, the rate constants for separation of these pairs should be much less dependent on solvent polarity. In low-polarity solvents, these sensitizers are expected to benefit from an additional advantage. Because the return electron transfer reactions in the initial ion pairs are often in the Marcus "inverted" region,[7,8] their rates can be decreased if the reaction reorganization energy can be decreased.[9] Since most of the reorganization energy is associated with reorientation of the solvent, this can be achieved in less polar solvents.[9] Described herein are experiments that confirm the utility of these sensitizers in nonpolar solvents.

Table I. Quantum Yields for Formation of Separated Radical Cations in Various Solvents Using *N*-Methylacridinium (MA^+) Hexafluorophosphate and 2,6,9,10-Tetracyanoanthracene (TCA) as Excited-State Electron Acceptors and the Relative Fluorescence Efficiencies of *N*-Methylacridinium Iodide and Hexafluorophosphate

solvent (ε)[a]	biphenyl (TCA)[b]	biphenyl (MA^+)[b]	$(\Phi^f_{I^-}/\Phi^f_{PF_6^-})$[c]
acetonitrile (35.9)	0.18	0.33 (0.33)	0.97
butyronitrile (24.3)	0.17	0.39	0.97
o-dichlorobenzene (9.93)	0.08	0.62	0.47
methylene chloride (8.93)	0.06	0.89 (0.88)	0.64
tetrahydrofuran (7.58)	0.02	0.43 (0.42)	0.23
fluorobenzene (5.42)	0.01	0.52	0.05
chloroform (4.81)	0.01	0.71 (0.75)	0.03
benzene (2.27)		0.34[d]	

[a] Static dielectric constant at 25 °C. [b] The ion yields were measured by using the transient absorption method described previously,[7] except that stilbene, dimethylstilbene, dimethoxystilbene, and tritolylamine were all used as monitors for the biphenyl radical cation, to correct for ion formation resulting from reactions of triplet MA^+ and triplet TCA with the low oxidation potential monitors. The experimental details will be given elsewhere. The numbers in parentheses were measured by using photoacoustic calorimetry from $(1 - \phi_f - \alpha)E_{h\nu}/E_{ip}$, where $E_{h\nu}$ is the photon energy, ϕ_f is the fluorescence quantum yield, and α is the fraction of photon energy released as heat in the photochemical reaction. The radical ion pair energies, $E_{ip} = E_{ox}(D) - E_{red}(A)$,[7] were calculated by using the redox potentials determined in acetonitrile and were corrected for triplet MA^+ formation. The errors in the quantum yields are estimated to be ca. 15%. [c] Relative fluorescence efficiencies of *N*-methylacridinium iodide vs *N*-methylacridinium hexafluorophosphate. [d] The benzene value was measured by using the more soluble *N*-decylacridinium hexafluorophosphate as the acceptor.

The sensitizers used in this study were the salts of *N*-methylacridinium (MA^+) and *N*-decylacridinium (DA^+) hexafluorophosphate. The use of MA^+ as an electron-transfer sensitizer

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[‡] Eastman Kodak Company.

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