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A Steady-State and Picosecond Pump-Probe Investigation of the Photophysics of an Acyl and a Bis(acyl)phosphine Oxide

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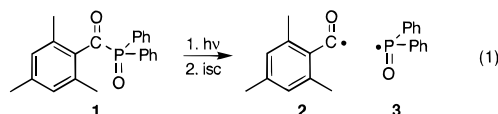
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Abstract: The photophysics (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (**1**) and bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide (**4**) have been investigated by fluorescence, phosphorescence, and low temperature time resolved electron spin resonance. Both **1** and **4** undergo α -cleavage to produce benzoyl and phosphorous centered radicals. The photochemistry of **1** and **4** has been investigated by nanosecond laser flash photolysis, picosecond pump-probe spectroscopy, and steady-state photolysis. The singlet states of **1** and **4** and the phosphorous centered radicals produced by α -cleavage were characterized directly by time resolved absorption spectroscopy. The triplet states of **1** and **4** were characterized indirectly by quenching with 1-phenylnaphthalene as a selective triplet quencher. The use of 1-phenylnaphthalene indicates that α -cleavage occurs mainly from the triplet states of **1** and **4**. However, the observed rate of formation of phosphorous centered radicals derived from picosecond investigations is experimentally indistinguishable from the rate of disappearance of the singlet states of **1** and **4**. The results are compatible with mechanisms for which the rate of intersystem crossing of the S_1 states of **1** and **4** limits the observed rate of α -cleavage, because the rate of α -cleavage is of the same order or faster than the rate of intersystem crossing. This relatively uncommon situation appears to have an analogy in the well investigated photochemistry of dibenzyl ketone.

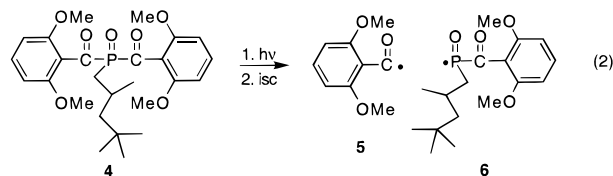
Introduction

Acyl and bis(acyl)phosphine oxides have received considerable recent attention both because of their interesting photochemistry and photophysics and because they are widely employed as photoinitiators in free radical polymerization processes.^{1–15} Most of the published research on phosphine oxides has centered on the generation of reactive phosphorus radicals and on the characterization of the structure and reactivity of these radical species. For example, it is well established^{4,6,8,12,16} that (2,4,6-trimethylbenzoyl)diphenylphosphine

oxide (**1**) undergoes rapid α -cleavage from a triplet excited state to afford the 2,4,6-trimethylbenzoyl (**2**) and diphenylphosphinoyl (**3**) radicals (eq 1).



For bis(acyl)phosphine oxides, a related class of photoinitiators that have the interesting potential to generate four radicals from a single precursor, the photochemistry is similar. As an example,^{12,17} bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide (**4**) undergoes initial α -cleavage from the triplet excited state to afford radicals **5** and **6** as shown in eq 2.



We have recently reported on measurements of the reactivity of the two phosphonyl radicals **3** and **6** toward a variety of alkyl halides, alkenes, and oxygen, and it was found that **3** was 2–6 times more reactive than **6**.¹⁷ For example, **3** adds to methylmethacrylate with a rate constant of $(11 \pm 2) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, whereas **6** has an addition rate constant for the same reaction of $(2.3 \pm 0.3) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Less attention has been paid to the photophysics of these compounds.

Reports^{4,6–8,12,16–19} of the photophysical properties of **1** and **4** have been relatively incomplete. The CIDEP produced by

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photolysis of **1** and **4** are consistent with triplet mechanism polarization.^{8,16,17} The formation of **3** produced by photolysis can be quenched by addition of naphthalene⁴ which is indicative of a triplet precursor. Fluorescence from **1** has been reported, along with an estimated singlet energy E^S of 69 kcal mol⁻¹.⁴ In this paper, we present a more complete study of the photophysics of **1** and **4** employing laser flash photolysis (LFP), picosecond pump-probe spectroscopy, as well as employing steady-state and time resolved fluorescence, phosphorescence, and low-temperature TR-ESR spectroscopy.

Experimental Section

Materials and Solvents. (2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (**1**) (BASF) was recrystallized from diethyl ether. Bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide (**4**) (Ciba Specialty Chemicals) was separated from its coinert, 2-hydroxy-2-methyl-1-phenylpropanone, by silica gel chromatography. Anthracene (Baker), benzophenone (Aldrich), and thioxanthone (Aldrich) were recrystallized from ethanol before use. 1-Phenylanthracene (Aldrich), cyclohexane (Aldrich HPLC), benzene (Aldrich spectrophotometric grade), ethanol (Aldrich spectrophotometric grade), diethyl ether (Aldrich spectrophotometric grade), toluene (Aldrich spectrophotometric grade), methylcyclohexane (Aldrich spectrophotometric grade), ethanol (Aldrich spectrophotometric grade), and acetonitrile (Aldrich spectrophotometric grade) were used as received.

General Methods. UV-vis absorption spectra were recorded on a Hewlett-Packard HP8452A UV spectrometer. Fluorescence emission and excitation spectra were recorded on a SPEX Fluorolog 1680 0.22 m double spectrometer. Low temperature phosphorescence spectra were recorded on a Perkin-Elmer LS-50 spectrofluorimeter.

Steady-State Irradiations. Relative quantum yields of phosphine oxide bleaching were determined by continuous irradiation at 380–400 nm (**1**) and 390–470 nm (**4**) employing a xenon lamp (LX300UV; Varian) and colored glass filters (KG1, UG5, GG395 (**1**) and KG1, BG3, GG400 (**4**)). The bleaching of the phosphine oxides was monitored by UV absorption spectroscopy.

Laser Flash Photolysis Experiments. Laser flash photolysis experiments employed the pulses (355 nm, ca. 8 mJ/pulse, 8 ns) from a Continuum Surelite I Nd-YAG laser or a Lambda Physik FL 3002 dye laser (Stilbene 420, 420 nm, ca. 2 mJ/pulse, 20 ns) pumped by a Lambda Physik Lextra excimer laser (308 nm, ca. 80 mJ/pulse, 20 ns) and a computer-controlled system which has been described elsewhere.²⁰ Solutions of **1** or **4** were prepared at concentrations such that the absorbance was ~0.3 at the excitation wavelength employed. Transient absorption spectra were recorded employing a Suprasil quartz flow cell (1 × 1 cm) to ensure that a fresh volume of sample was irradiated by each laser pulse. Quenching rate constants were measured using argon-saturated static samples contained in 1 × 1 cm Suprasil quartz cells. Fresh solutions were prepared at each quencher concentration.

Low-Temperature Triplet TR-ESR Experiments. Low-temperature TR-ESR experiments employed the pulses from a Lambda Physik LPX 100 excimer laser (308 nm, ca. 80 mJ/pulse, 20 ns), a Bruker ESP-300 X-band ESR spectrometer equipped with a dielectric ring cavity (ESP380-1052 DLQ-H) in a high-Q mode and an Oxford cryostat (GFS 300), and the boxcar averager and signal processor as previously described.²¹ The signals were averaged over a 5 μ s period following the laser flash. No sample depletion was detected in successive repetitions of the experiments. Solutions of **4** in toluene/ethanol mixtures (1:1 by volume) were transferred to 4 mm O.D. quartz ESR tubes and cooled to 20 K inside the ESR cavity immersed into the cryostat by a permanent flow of evaporating helium. The simulations of the experimental ESR spectra of molecular triplets in a glass are based on the theory of the ESR of randomly oriented triplet molecules developed in the literature.^{22–25} The Levenberg–Marquardt least-squares algorithm was implemented to extract the zero-field splitting

Table 1. Physical Properties of **1** and **4**^a

	1	4
E^S (kJ/mol)		
nonpolar	289	278
polar	298	281
E^T (kJ/mol)		
nonpolar	262	244
polar	263	255
Φ_f	0.0006	0.0016
τ_p (ms) at 77 K	4.0	4.6
τ_T (ps)	~100 ^b	~300 ^b
	~80 ^c	~180 ^c
ZFS		
D (cm ⁻¹)	0.1868 ± 0.0007	0.149 ± 0.001
E (cm ⁻¹)	0.00784 ± 0.0006	0.0140 ± 0.0006

^a E^S : singlet energy in nonpolar (cyclohexane) and polar (acetonitrile) solution; E^T : triplet energy in nonpolar (methylcyclohexane) and polar (ethanol) glass; Φ_f : fluorescence quantum yield in acetonitrile (fluorescence standard: 9,10-diphenylanthracene $\Phi_f = 0.95$);³⁰ τ_p : phosphorescence lifetime in ether–ethanol–toluene glass (2:1:1) at 77 K; τ_T : triplet lifetime in acetonitrile at 23 °C; zero-field splitting parameters (ZFS) D and E . ^b Determined by triplet quenching with 1-phenylanthracene using nanosecond laser flash photolysis. ^c Determined by triplet quenching with 1-phenylanthracene from ground state bleaching under steady-state irradiation.

parameters D and E and the relative populations of the three sublevels p_x , p_y , and p_z . A sharp signal in the experimental spectra at $g = 2$ decays much more slowly than the triplet spectrum. This sharp signal has been assigned to a doublet radical and was excluded from spectral simulations.^{21,22,26} Further details have been reported elsewhere.¹⁶

Picosecond Pump-Probe Experiments. A Quantel Nd:YAG actively/passively mode-locked laser was employed to generate picosecond pulses of approximately 30 ps (fwhm) at 1064 nm. These pulses were frequency doubled, tripled, or quadrupled to generate 532, 355, and 266 nm pulses. Other wavelengths such as 321.5, 396, and 460 nm were generated by Raman shifting with cyclohexane solvent at the appropriate incident laser wavelength. All absorption experiments employed a nearly collinear pump-probe scheme and a 2 mm path length cell. Solutions of **1** or **4** in aerated acetonitrile had absorbances at the excitation wavelength of approximately 2.0 when possible. Further details of the picosecond system employed have been published elsewhere.²⁷

Results

Fluorescence and Phosphorescence Spectroscopy. Phosphine oxide **4** exhibits broad structureless fluorescence emission ($\lambda_{\max} \sim 464$ nm) in cyclohexane solution upon 340 nm excitation (see Figure 1) with a low fluorescence quantum yield (see Table 1). The excitation spectrum of **4** (Figure 1b) is very similar to its UV-vis absorption spectrum (Figure 1a). The singlet excited state energy of **4**, estimated from the intersection of the emission and excitation spectra at 428 nm, is ca. 278 kJ/mol. Phosphine oxides **1** and **4** exhibit phosphorescence emission with resolvable vibrational fine structure in ether/ethanol/toluene glass at 77 K upon excitation with 400 and 410 nm light, respectively (see Figure 2). The (0,0) emission bands for **1** and **4** occur at 456 and 472 nm, corresponding to approximate triplet energies of ca. 262 and ca. 253 kJ/mol, respectively; the vibrational progression for both, **1** and **4**, is ca. 1500 cm⁻¹. The phosphorescence quantum yields at 77 K of **1** and **4** are at least 0.1 or higher, determined by comparison to the phosphorescence

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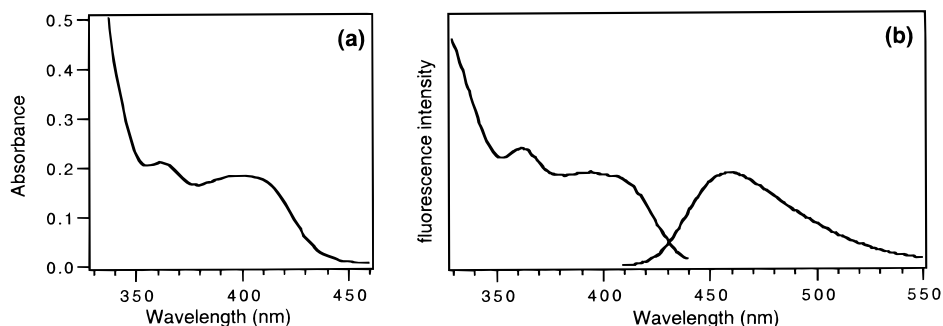


Figure 1. (a) UV-vis absorption spectrum and (b) fluorescence emission and excitation spectra of **4** in cyclohexane solution at 23 °C.

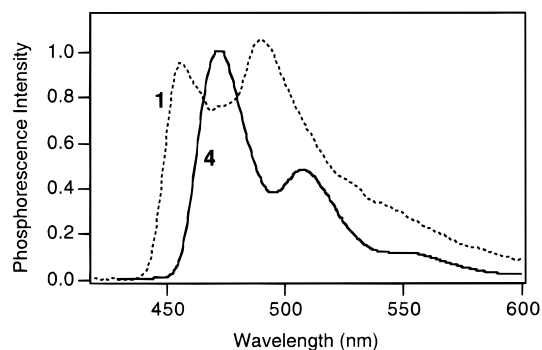


Figure 2. Phosphorescence emission spectra of **1** and **4** in ether/ethanol/toluene glass (2:1:1 by volume) at 77 K.

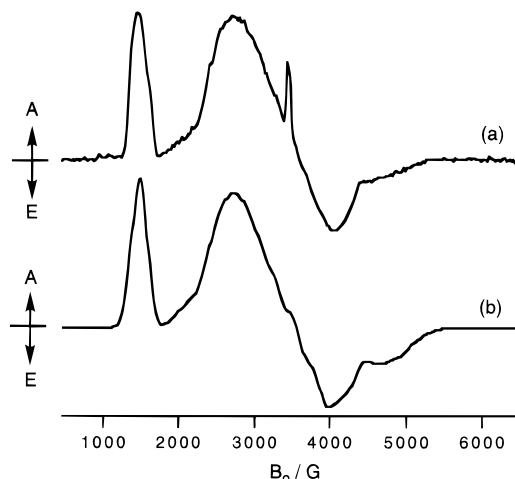


Figure 3. (a) Triplet TR-ESR spectrum recorded 1–5 μs following 308 nm laser excitation of **4** in ethanol/toluene glass (1:1 by volume) at 77 K and (b) its simulation.

of benzophenone. The phosphorescence possesses a lifetime of 4.0 and 4.6 ms for **1** and **4**, respectively, and together with the relatively high phosphorescence quantum yield suggests a $n\pi^*$ nature of the lowest triplet state. The triplet energies were determined from the (0,0) emission band using glasses of different polarity (methylcyclohexane and ethanol) (see Table 1).

Low Temperature Triplet TR-ESR. Figure 3a shows the TR-ESR spectrum recorded 1–5 μs following laser excitation (308 nm) of **4** in toluene/ethanol glass at 20 K along with its simulation Figure 3b. The simulation parameters are $D = 0.149 \pm 0.001 \text{ cm}^{-1}$, $E = 0.0140 \pm 0.0006 \text{ cm}^{-1}$, $p_X = 0.24 \pm 0.02$, $p_Y = 0.1$, $p_Z = 0.66 \pm 0.01$, and $\text{fwhm} = 230 \pm 10 \text{ G}$. The three energy levels are chosen to be in the order $X > Y > Z$.²⁸ From these values the sign of triplet polarization of the radicals

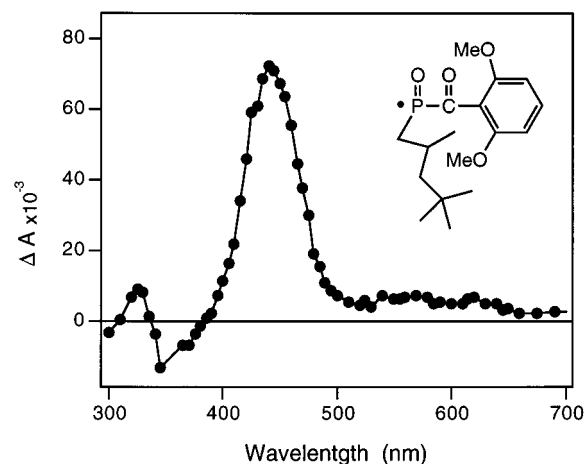


Figure 4. Transient optical absorption spectrum recorded 200–700 ns following laser excitation (355 nm, 8 ns) of **4** in argon-saturated acetonitrile solution at 23 °C.

5 and **6** can be predicted as positive (absorptive signals).¹⁶ This is in good agreement with the experimental findings. TR-ESR of **4** at room temperature after laser flash photolysis gives polarized ESR signals in absorptive mode.¹⁶

$$\frac{1}{A} = \frac{1}{A_{\text{total}}} + \frac{1/\tau_T}{A_{\text{total}}k_q[Q]} \quad (3)$$

Nanosecond Laser Flash Photolysis. Laser flash photolysis (355 nm excitation) of acetonitrile solutions of **4** affords a readily detectable transient absorption in the range of 400–500 nm (see Figure 4) which decays on the microsecond time scale with mixed kinetics. This transient has been assigned to the 2,6-dimethoxybenzoyl-2,4,4-trimethylpentylphosphinoyl radical (**6**). Similar transient absorption spectra were reported upon 420 nm excitation of **4**.¹⁷ Evidence for the formation of triplet states of **4** was obtained from experiments (420 nm excitation) with acetonitrile solutions of **4** containing different concentrations of 1-phenylanthracene (0.05 to 0.4 M) as a selective triplet quencher. With increasing concentrations of 1-phenylanthracene a corresponding increasing amount of 1-phenylanthracene triplets ($\lambda_{\text{max}} = 480 \text{ nm}$) was observed, demonstrating that triplet-triplet energy transfer was operating. The Stern-Volmer constant $k_q\tau_T$ were determined by application of experimental data ($1/A$ vs $1/[Q]$) to eq 3 a modified version of the Stern-Volmer equation.⁴ In the latter expression A is the absorbance of 1-phenylanthracene triplets observed at the end of the laser flash at 480 nm (which is proportional to the quantum yield for its formation), A_{total} is the absorbance that would be observed if all triplets of **4** were quenched by 1-phenylanthracene, τ_T is the lifetime of the phosphine oxide triplet state, k_q is the rate constant for its quenching by

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1-phenylnaphthalene, and $[Q]$ is the concentration of 1-phenylnaphthalene.

Using a value of $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for k_q ,²⁹ we obtained an estimate of 300 ps for the lifetime of the triplet excited state of **4**. The selection of 1-phenylnaphthalene as selective quencher of triplet **4** was based on the following considerations: (i) 1-phenylnaphthalene does not absorb the laser light. (ii) The triplet energy of **4** (255 kJ/mol) is higher than that of 1-phenylnaphthalene (246 kJ/mol),³⁰ and (iii) the singlet energy of **4** (281 kJ/mol) is lower than that of 1-phenylnaphthalene (379 kJ/mol).³⁰

Thioxanthone possesses a higher triplet energy ($E^T = 265 \text{ kJ/mol}$)³¹ than **4**, and its triplet state is readily quenched by **4** with a rate constant of $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile measured by laser flash photolysis (355 nm excitation). It was demonstrated by triplet sensitization of **4** with thioxanthone using laser flash photolysis that triplet states of **4** undergo α -cleavage efficiently, and it was found that **6** is generated synchronously with the decay of the thioxanthone triplet. The decay kinetic of the thioxanthone triplets matched the growth of the phosphorus radical **6**, and the amount of **6** increases with increasing concentration of **4**.

Similar laser flash photolysis experiments to those described above for **4** were performed with **1**. Laser flash photolysis (355 nm excitation) of **1** affords a readily detectable transient absorption in the range of 300–350 nm assigned to the diphenylphosphinoyl radical (**3**).^{4,32} Triplet quenching experiments (for E^T and E^S of **1** see Table 1) with 1-phenylnaphthalene (416 nm excitation) according to eq 3 lead to an estimated triplet lifetime for **1** of 100 ps (employing 1-phenylnaphthalene concentrations from 0.2–2 M). Similar to **4**, triplet sensitization with thioxanthone causes efficient α -cleavage from the triplet state of **1**, and formation of the radical **3** could be observed. The same rate constant for triplet energy transfer of thioxanthone triplets to **4** ($5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile) was observed for energy transfer to **1**.

Steady-State Photolysis. Steady-state irradiation of air saturated acetonitrile solutions of **1** and **4** causes a ground state bleaching of **1** or **4** and has been employed to determine the quantum yields of α -cleavage ($\Phi_\alpha(\mathbf{1}) = 0.56$; $\Phi_\alpha(\mathbf{4}) = 0.51$).³³ This method can be employed to study the influence of triplet quencher (1-phenylnaphthalene) on the ground state bleaching quantum yield. Air saturated acetonitrile solutions of **4** were irradiated (390–470 nm excitation) in the presence of different concentrations of 1-phenylnaphthalene (0.2–1.2 M). With increasing triplet quencher concentrations the relative bleaching quantum yield decreases. Plots of the data (Φ_o/Φ_Q vs $[Q]$; Figure 5) according to the Stern–Volmer equation (eq 4) afforded a $k_q\tau_T$ value, where Φ_o and Φ_Q are the relative bleaching quantum yields of **4** in the absence and in the presence of triplet quencher (1-phenylnaphthalene), τ_T is the lifetime of the phosphine oxide triplet state, k_q is the rate constant for its quenching by 1-phenylnaphthalene, and $[Q]$ is the concentration of 1-phenylnaphthalene.

Using a value of $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for k_q ,²⁹ an estimate of 180 ps for the lifetime of the triplet excited state of **4** is obtained.

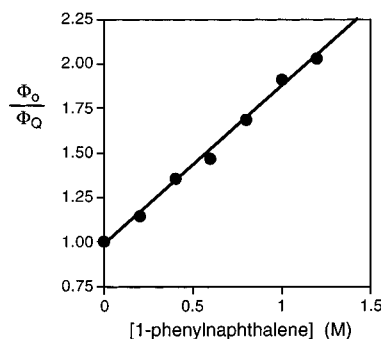


Figure 5. Stern–Volmer plot of the triplet state quenching of **4** with 1-phenylnaphthalene; steady-state irradiation (390–470 nm excitation) in air saturated acetonitrile solutions at 23 °C.

$$\frac{\Phi_o}{\Phi_Q} = 1 + \tau_T k_q [Q] \quad (4)$$

This is in good agreement with the triplet lifetime ($\sim 300 \text{ ps}$) measured by nanosecond-laser flash photolysis and 1-phenylnaphthalene quenching (see above). The linearity of the Stern–Volmer plots (eq 4; Figure 5) is consistent with the α -cleavage occurring predominantly from the triplet state rather than from an excited singlet state. If, in addition to triplet states, the singlet states would yield to phosphine oxide bleaching, the Stern–Volmer plots would be expected to display nonlinearity especially at the higher concentration of quencher where the function would reach a plateau.

Steady-state irradiation (380–400 nm excitation) of air saturated acetonitrile solutions of **1** causes bleaching of **1** similar to those described above for **4**. But in the presence of 1-phenylnaphthalene, colored products were formed with a strong optical absorption above 380 nm, preventing accurate determination of the bleaching of **1**. These colored products are presumably caused by reactions of 1-phenylnaphthalene with the radicals **2** and **3** and/or their peroxy derivatives. In the presence of the radical scavenger, *n*-butylacrylate (0.5 M), no photolysis products were detected with an optical absorption higher than 380 nm. By Stern–Volmer treatment (eq 4) of the triplet quenching of **1** with 1-phenylnaphthalene, the triplet lifetime of **1** was estimated to be 80 ps, which is in good agreement with the value ($\sim 100 \text{ ps}$) obtained by nanosecond-laser flash photolysis (see above).

Picosecond Pump–Probe Spectroscopy. In an effort to directly detect the excited states of **1** and **4**, we monitored the transient absorption kinetics of solutions of these compounds in aerated acetonitrile at room temperature through a series of picosecond pump–probe experiments. We chose to pump (excite) the molecules with 266 nm laser pulses and probe (monitor) the transient absorption kinetics at various wavelengths where one could expect the radicals **3** and **6** to absorb (absorption at 321.5 and 460 nm, respectively; no or low absorption at 396 and 355 nm). For example, the phosphinoyl radical, **3**, derived from **1**, should absorb strongly at 321.5 nm and less so at 355 nm. Indeed we were able to obtain first order growth kinetics at 321.5 nm which presumably represents the appearance of **3** as a result of α -cleavage from the triplet precursor. The data yields a growth time constant of 123 ps. At 355 nm an entirely different kinetic behavior was measured. In this case there was a fast growth of a transient absorption signal followed by a rapid partial decay to a long-lived residual transient absorption. Interestingly, the decay kinetics at 355 nm could be fit to a lifetime of 128 ps or roughly the same kinetics as the growth observed at 321.5 nm. A closer look at the transient absorption at 321.5 nm reveals a double exponential

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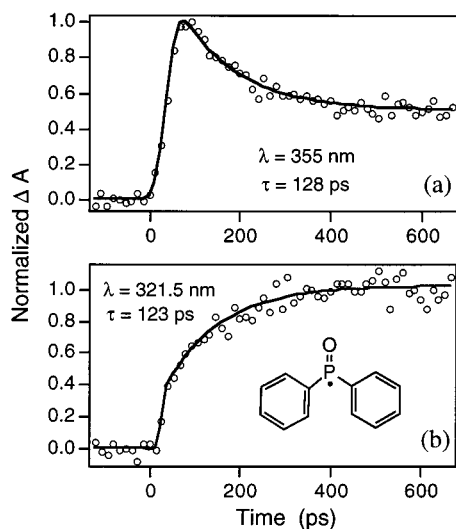


Figure 6. Transient absorption kinetics observed following picosecond photolysis (266 nm, 26 ps, pulse from a Nd:YAG laser) of **1** in aerated acetonitrile solution at room temperature monitored at (a) 355 nm and (b) 321.5 nm. The growth kinetics measured at the 321.5 nm match well with the decay kinetics monitored at 355 nm. The absorption at 321.5 nm is assigned to the phosphorus radical **3** and that at 355 nm to the S_1 of **1**. See text for details.

growth kinetic. Within the laser flash a small optical absorption is built up followed by a growth which was fit to a lifetime of 123 ps. Obviously, the first growth is belonging to the same transient observed at 355 nm with higher intensity. These results are summarized in Figure 6. The signal at 355 nm in the photolysis of **1** was monitored over a shorter time scale (80 ps) and was found to appear within the system response time.

Very similar results to those obtained for **1** were obtained in picosecond pump-probe experiments of **4** except that no residual, long-lived, absorption at 355 nm was observed. Unfortunately, at 460 nm the wavelength where the phosphorus radical **6** is expected to absorb strongly (see Figure 4), a growth matching the response time of the instrument leading to a residual was detected. This could be interpreted as an overlay of both transients, the decay of the excited state (clearly observed at 355 nm) and the growth of the radical **6** at 460 nm. Other probe wavelengths (321.5, 396, and 532 nm) were used in search for exclusive detection of the phosphorus radical **6** but without success. Another difference between the observed behavior of transients produced from **1** and **4** is the overall attenuation of the observed rate of decay at 355 nm for **4** of 1.1 ns compared to 128 ps for **1**. Like **1**, however, the short time scale growth of transient absorption due to the photolysis of **4** at 355 nm matched the response time of the system. The results are summarized in Figure 7.

We attempted to influence the kinetics of the observed transients by addition of 1-phenylnaphthalene which is expected to selectively quench triplets of **1** and **4**. This required us to choose 355 nm as the wavelength for both pump and probe for these experiments, since 1-phenylnaphthalene competes for the exciting photons at 266 nm. 1-Phenylnaphthalene has an excited state singlet energy of 379 kJ/mol, whereas it has a low lying triplet, T_1 , whose energy is 246 kJ/mol.³⁰ Thus if the transients observed at 355 nm are triplet excited states of **1** or **4**, then the observed decay rate constant should increase as a function of 1-phenylnaphthalene concentration. If the 355 nm transient absorptions are due to a singlet-singlet absorption, no quenching should be observed, since in this case the singlet excited states of **1** and **4** are lower in energy than that of 1-phenylnaphthalene. In fact no change in the 355 nm transient

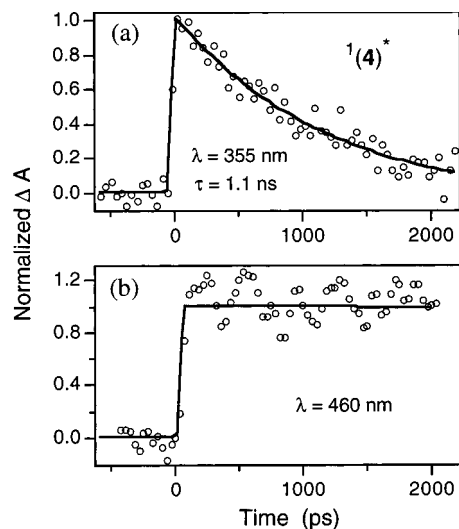


Figure 7. Kinetics of the transient absorptions observed following picosecond photolysis (266 nm, 26 ps, pulse from a Nd:YAG laser) of **4** in acetonitrile solution at room temperature are shown above, monitored at (a) 355 nm and (b) 460 nm. The growth kinetics measured at 460 nm exhibit virtually the same time constant as the decay kinetics monitored at 355 nm. The absorption at 355 nm is assigned to the S_1 of **4** and that at 460 nm to an overlay of the S_1 of **4** and the phosphorus radical **6**, see text for details.

absorption kinetics in the photolysis of **1** or **4** is observed, thereby allowing assignment of the 355 nm transient to the singlet state of **1**.

Discussion

The photochemistry of benzoylphosphine oxides is dominated by α -cleavage,^{4-7,10,12} however, comparatively little is known about their photophysics. The emission and triplet ESR spectra of **1** and **4** provide key information about the fundamental properties of their singlet and triplet excited states. The lower energy electronic singlet-singlet absorptions of bis(benzoyl)phosphine oxides (e.g., **4**) compared to mono(benzoyl)phosphine oxides (e.g., **1**) have been documented.¹⁵ Thus, it is not surprising that **4** also exhibits lower energy fluorescence compared to **1** (Figure 1). Indeed, the singlet excited state energy of **4** (278 kJ/mol) is significantly lower than that of **1** (289 kJ/mol).⁴ Bis(benzoyl) substitution in phosphine oxides also appears to lead to a reduction in the solvent dependent triplet excited state energies as demonstrated by the lower energy phosphorescence emission of **4** compared to **1** (see Table 1). Our value for the triplet energy of **1** in acetonitrile is in agreement with the previously estimated lower limit ($E^T > 251$ kJ/mol).⁴ The triplet states of **1** and **4** were assigned to a n,π^* nature because (i) the phosphorescence lifetimes of **1** and **4** at 77 K are short (4.0 and 4.6 ms, respectively) and possess relatively high phosphorescence quantum yields ($\Phi_p > 0.1$). Triplet states of π,π^* nature with quantum yields $\Phi_p > 0.1$ usually possess a phosphorescence lifetime at low temperature of several seconds.³⁴ (ii) The triplet energy increases with increasing solvent polarity (see Table 1). States of π,π^* nature usually were stabilized by polar solvents leading to a decrease in the energy of the electronic state.

The α -cleavage of **1** (eq 1) and **4** (eq 2) from their lowest triplet excited state has been established based on laser flash photolysis,⁴ TR-ESR,^{6,8,16,17} and CIDNP¹² studies. The yield of **6** detected at 450 nm, in nanosecond laser flash photolysis

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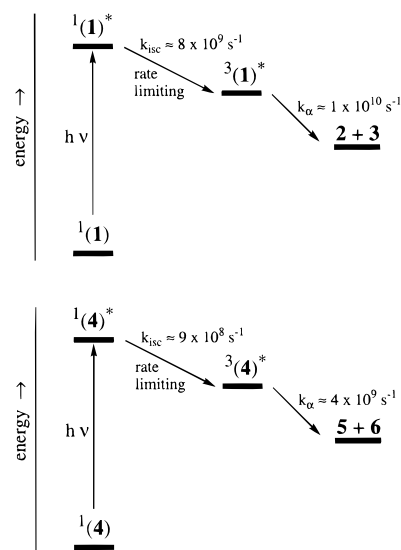
experiments, decreases upon the addition of anthracene ($E^T = 178 \text{ kJ/mol}$)³⁰ to benzene solutions of **4**; under these conditions, triplet energy transfer is competitive with cleavage of the triplet state of **4**. From Stern–Volmer quenching experiments employing 1-phenylnaphthalene it was found that the triplet lifetimes of **1** ($\tau_T \sim 100 \text{ ps}$) and **4** ($\tau_T \sim 300 \text{ ps}$) were relatively short. In addition, the bleaching quantum yield of **1** and **4** decreases under steady-state irradiation with increasing triplet quencher concentration. The linearity of the Stern–Volmer plots (eq 4) is consistent with α -cleavage occurring from the triplet state rather than from an excited singlet state. Up to this point the mechanistic picture appears to be clear and straightforward: **3** and **6** result from the α -cleavage of the respective triplet states of **1** and **4** according to eqs 1 and 2. At first, however, the picosecond results appear not to fit with this straightforward picture, because of the following unexpected feature of the assignment of the transient absorptions observed following 266 nm picosecond photolysis of **1** and **4** at 355 nm. For both **1** and **4** short-lived transients are observed whose decay kinetics matched well with the growth kinetics obtained at wavelengths where the respective phosphorus radicals should absorb (at 321.5 nm for **3** and at 460 nm for **6**).

Specifically, in the study of **1** we found a short-lived transient with a lifetime of 128 ps which decayed to a residual absorption. The residual is probably due to the radical known to absorb weakly at 355 nm³² and which decays slowly on the picosecond time scale. A likely candidate for the rapidly decaying transient species is a precursor excited state of the radical. In this case at least two possibilities exist: (i) the precursor is the triplet, T_1 , of **1** or (ii) the precursor is the excited singlet state, S_1 , of **1**. In order to assign the transient we first considered the radical growth kinetics monitored at 321.5 nm.

It is known that at 321.5 nm radical **3** absorbs strongly, so we monitored the transient absorption kinetics at this wavelength following 26 ps, pulsed laser excitation at 266 nm of an aerated acetonitrile solution of **1** at room temperature. The time constant of the growth shown in Figure 6 was found to be 123 ps and matched well with the decay lifetime of the transient at 355 nm. Thus, it appears that the transient at 321.5 nm evolves as the transient at 355 nm decays and that the first transient is a product of the decay of the latter. The transients at 355 nm were assigned to the singlet–singlet absorption of the singlet state S_1 for the following reasons: (i) the evolution of the 355 nm transient absorption at 355 nm occurs within the system response (growth occurs in less than 10 ps); and (ii) the decay kinetics at 355 nm do not change in the presence of increasing concentrations of 1-phenylnaphthalene (which quench the triplet). Completely analogous results and arguments are found and used in assigning the 355 nm transient absorption in the photolysis of **4** to its excited singlet state, S_1 , as well. In this case the singlet is roughly an order of magnitude longer-lived than that of **1**. These results are consistent with the direct formation of **3** and **6** from the S_1 states of **1** and **4** and do not require any involvement of triplet states.

Thus, it is imperative to reconcile the concomitant singlet excited state decay and the phosphorus radical growth with the involvement of the triplet as an intermediate between these two species which appear to be required by the quenching experiments. It is possible to bring consistency to all of the results if the triplets of both **1** and **4** have lifetimes that are of the same order as, or shorter than, their singlet excited state lifetimes. If the rate limiting step in producing radicals **3** and **6** is the intersystem crossing of the singlets of **1** and **4** (see Scheme 1), the measured rate of formation of **3** and **6** is that of the slow

Scheme 1. Energy Level Diagrams for α -Cleavage of **1** and **4**



step (intersystem crossing of S_1) rather than the fast step (α -cleavage of T_1).

The situation described in Scheme 1 appears to be rare but is not unique. Atkinson reported that in a picosecond investigation of the photochemistry of dibenzyl ketone (DBK) the benzyl radical growth kinetics matched that of DBK singlet excited state decay³⁵ and concluded that α -cleavage occurs in the singlet state. However, magnetic field effects³⁶ and CIDNP experiments³⁷ convincingly implicate the role of the DBK triplet as the dominant pathway for α -cleavage to produce benzoyl radicals. In addition,^{38,39} radical production from the triplet has been quenched via selective triplet–triplet energy transfer and is further evidence of the involvement of the triplet of DBK in the α -cleavage process. Thus, it is likely that the photolysis of **1** and **4** provides new examples of cases where the triplet is present but cannot be easily detected directly by time resolved methods because it decays as fast as it is formed.

A certain small fraction of α -cleavage from the excited singlet state cannot be excluded totally, but from our experiments we can conclude that most of the radicals were produced by cleavage from the triplet state. α -Cleavage in the excited singlet state may be inefficient, or since the quantum yield of α -cleavage of **1** and **4** is of the order of 0.5, recombination of the singlet radical pair is faster than separation.⁴⁰

Summary and Conclusions

The photochemistry of **1** and **4** is dominated by α -cleavage from a short lived triplet state. Direct detection of the singlet–singlet absorption on the picosecond time scale verifies rapid intersystem crossing and the short lived triplet states. The triplets are identified by triplet quenching with anthracene and 1-phenylnaphthalene by laser flash and steady-state photolysis and previous results using TR-ESR and CIDNP. Low temperature phosphorescence suggests a n,π^* nature of the lowest triplet state. The photochemistry of **1** and **4** is shown to involve a rare example, along with DBK, of systems for which intersystem crossing of S_1 , and not reaction of T , is rate limiting.

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