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α-Bond Dissociation of *p*-Phenylbenzoyl Derivatives in the Higher Triplet Excited State Studied by Two-Color Two-Laser Flash Photolysis

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Photochemical properties in the lowest singlet and triplet excited states (S_1 and T_1) and in the higher triplet excited states (T_n) of *p*-phenylbenzoyl derivatives (PB-X) having C−O and C−S bonds were investigated in solution using a stepwise two-color two-laser flash photolysis technique. PB-Xs (X = OPh and SPh as a leaving group) undergo α-bond dissociation in the S_1 state, while the C−O bonds in PB-OH and -OMe were stable upon the 266-nm laser flash photolysis. The $T_1(\pi,\pi^*)$ states of PB-X were efficiently produced during the 355-nm laser flash photolysis of PB-X in the presence of benzophenone as a triplet sensitizer. The $T_1(\pi,\pi^*)$ states of PB-Xs deactivate to the ground-state without producing any intermediates. However, when PB-Xs (X = OPh and SPh) in the T_1 states (PB-X(T_1)) were excited upon the 430-nm laser flash photolysis, their disappearance was observed. These observations indicate that PB-X(T_1) (X = OPh and SPh) is excited to PB-Xs in the T_n states which decompose through the C−X bond cleavage. From the transient absorption measurements, quantum yields (Φ_{dec}) of the disappearance of PB-X(T_1) were determined while bond dissociation energies (BDE) of the C−X bonds of PB-X were calculated by computations. On the basis of the Φ_{dec} and the BDE values, it was shown that the rates of the decomposition process of PB-X in the T_n states were expressed in an energy gap low form as a function of BDE. Features of the C−X bond cleavage of PB-X in the T_n states were discussed.

Introduction

There is a considerable amount of photochemical studies of bond dissociation taking place from aromatic carbonyl compounds in the excited states. Norrish type I and II reactions and carbon−heteroatom bond cleavage occurring at the α- and β-positions of aromatic carbonyl compounds have been widely studied by means of product analysis and time-resolved transient measurements.[1−4] Homolytic α-cleavage of C−C, −O, −S, −P, and −N bonds in carbonyl compounds leading to formation of radicals has been used for initiating photopolymerizable formulations that can be activated by UV irradiation.[5] After α-cleavage of these molecules in solution, photo-Fries rearrangement is one of typical successive intramolecular reactions.[6] It has been shown that photo-Fries rearrangement occurs for carbonyls in the lowest singlet excited states, S_1.[6] For instance, phenyl acetates[7−9] and acetanilides,[10−14] respectively, undergo C−O and C−N α-bond scission in the S_1 state to provide corresponding photo-Fries products. In these cases, the occurrence of efficient photoreactions in the S_1 states prevents intersystem crossing to the lowest triplet excited state, T_1. Thus, photochemical reactions of the T_1 states are not uncovered. Conversely, it is reported that photoproducts of S-phenyl thiobenzoates due to photo-Fries rearrangement are absent upon photoexcitation of the $S_0 \rightarrow S_1$ transition and that photochemistry of S-phenyl thiobenzoates was concluded to proceed via the C−S bond scission in the T_1 state by the laser flash photolysis measurement.[15,16]

Triplet sensitization technique using triplet energy transfer has been widely used to investigate properties of various molecules in the T_1 state, when the molecules have the low formation quantum yields of the T_1 state. Acetone, acetophenone, or benzophenone (BP) whose triplet excitation energies (E_T) are ca. 76, 74, or 69 kcal mol^{-1}, respectively, are typical triplet sensitizers.[2] However, because of the larger E_T of acetyl and benzoyl derivatives than those of these triplet sensitizers, we are unable to elucidate properties of acetyl and benzoyl derivatives in the T_1 states by means of the triplet sensitization. Supposing that a phenyl group is attached to the phenyl ring of benzoyl moieties to form one of biphenyl derivatives whose E_T values are known to be ca. 65 kcal mol^{-1},[17,18] the triplet sensitization can be applied for formation of the T_1 states by using appropriate triplet sensitizers, which enable us to directly investigate whether α-bond dissociation of aromatic carbonyls proceeds in the triplet manifold.

For occurrence of the bond dissociation in the excited states, electronic character of the dissociative states and the corresponding bond dissociation energy, BDE, are important factors as well as the excitation energy of the reactive states. Generally, higher singlet and triplet excited states (S_n and T_n, with n of 2 and larger) are expected to be reactive more than the S_1 and T_1 states.[2] Therefore, some chemical reactions, which will not proceed in the S_1 and T_1 states, are expected to occur alternatively in the S_n or T_n state. Thus, we have been seeking new photochemically reactive states in the T_n states by means of two-color two-laser flash photolysis techniques.[19−41] The method of multistep excitation has been widely used to

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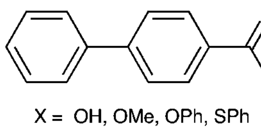
SCHEME 1: Structures of PB-X Used in the Present Study



investigate photophysical and photochemical processes in the S_n or T_n states by other researchers.[42−49] Previously, we reported photochemical properties of β-bond cleavage of some biphenyls in the T_n states, naphthalenes and aromatic carbonyls in which carbon−halide, −oxygen, and −sulfur bonds are at the benzylic position of the aromatic moieties or at the β-position of the carbonyl group.[28,30,37,41] The energy levels of the reactive species in the T_n states were evaluated, and a relationship between rates of the bond cleavage and the bond dissociation energies of the scissile bonds was formulated.[37,41] Now, it is of our interest whether α-cleavage of aromatic carbonyls proceeds in the T_1 and T_n states.

In the present work, we investigate α-cleavage processes of *p*-phenylbenzoyl derivatives (PB-X; X = OH, OMe, OPh and SPh) not only in the S_1 and T_1 states but also in the T_n states (PB-X(T_n)) by means of steady-state and laser flash photolyses. The structures of PB-X studied in this work are shown in Scheme 1. As was expected, the α-bond dissociation was not seen in the T_1 states whereas PB-X(T_n) was found to decompose. The quantum yields toward disappearance of PB-X(T_n) were determined by stepwise two-color two-laser flash photolysis techniques. On the basis of the quantum yields and BDE of cleavable C-X bonds estimated by DFT calculation, rates of α-cleavage processes in PB-X(T_n) are formulated as a function of BDE, and the photochemical profiles of PB-X(T_n) are discussed.

Experimental Section

4-Phenylbenzoic acid (PB-OH) was purchased from Aldrich. 4-Phenylbenzoic methylester (PB-OMe) was prepared by methylation of PB-OH in boiling methanol in the presence of sulfuric acid. 4-Phenylbenzoyl phenol (PB-OPh) and 4-phenylbenzoyl phenyl sulfide (PBSPh) were synthesized by a reaction of 4-phenylbenzoyl chloride with phenol and thiophenol, respectively. PB-Xs were all purified by repeated recrystallizations from hexane or ethanol. BP was purchased from Nacalai Tesque and recrystallized from ethanol before use. Acetonitrile (ACN, spectroscopy grade from Nacalai Tesque) and ethanol (spectroscopy grade from Kishida) were used as the solvents without further purification. ACN was used as the solvent at room temperature, whereas ethanol was used for phosphorescence measurement at 77 K. Sample solutions were freshly prepared and deoxygenated by bubbling with Ar. All experiments were carried out at room temperature. Absorption and emission spectra were recorded on a JASCO model U-best 50 spectrophotometer and a Hitachi model F-4010 fluorescence spectrophotometer, respectively. Nanosecond fluorescence lifetimes were determined by using a time-correlated single-photon counting fluorimeter (Edinburgh Analytical Instrument, FL-900CDT) while picosecond fluorescence lifetimes were determined with a femtosecond laser system equipped with a mode-locked Ti:sapphire laser (Spectra-Physics, Tsunami; the center wavelength 800 nm, pulse width ca. 70 fs, repetition rate 82 MHz) pumped by a CW green laser (Spectra-Physics, Millenia V; 532 nm, 4.5 W). The details of the photon counting system have been reported elsewhere.[40] Steady-state photolysis was carried out by using a low-pressure mercury lamp (254 nm). The photonflux at 254 nm was determined by using *N*-methyldiphenylamine in aerated methylcyclohexane as a chemical actinometer. The quantum yield for the formation of *N*-methylcarbazol from *N*-methyldiphenylamine has been established as 0.42.[50] The procedure to determine the quantum yields of photodecomposition of PB-X was the same as that described in the literature.[51] Fourth harmonics (266 nm) and third harmonics (355 nm) of a Nd^{3+}:YAG laser (JK Lasers HY-500; pulse width 8 ns) were used as light sources for the direct excitation and triplet sensitization, respectively. The details of the detection system for the time profiles of the transient absorption upon single-color laser flash photolysis have been reported elsewhere.[52] Third harmonics (355 nm) from a Nd:YAG laser (Brilliant, Quantel; 5-ns full width at half-maximum (fwhm)) and the laser light at 430 nm (6 mJ pulse^{-1}) from an OPO laser (Continuum, Surelite OPO) which was pumped by another Nd:YAG laser (Continuum, Surelite II-10; 5-ns fwhm) were used as excitation light sources for stepwise two-color two-laser flash photolysis. The details of the detection system for the time profiles of the transient absorption upon two-color two-laser flash photolysis have been reported elsewhere.[53]

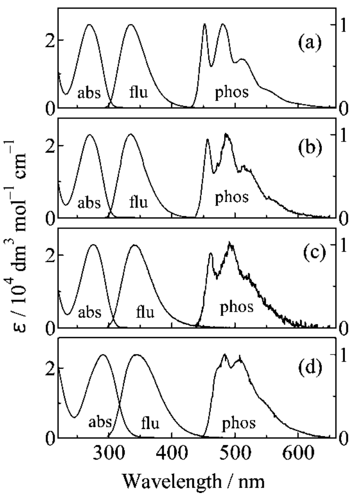


Figure 1. The UV absorption and fluorescence spectra of PB-X (X = OH (a), OMe (b), OPh (c), and SPh (d)) in ACN at 295 K and the phosphorescence spectra in ethanol at 77 K.

Results and Discussion

Absorption and Emission Spectra of PB-X. Figure 1 shows the absorption and phosphorescence spectra of PB-X.

The shape of the UV absorption and fluorescence spectra is similar to each other. The similarity in the UV spectra indicates that the ground-state absorption is attributed to the 4-phenylbenzoyl moiety, irrespective of the substituent groups, X. From the observation of fluorescence from PB-X, it is inferred that the electronic character of PB-X in the S_1 state, S_1, is of π,π^*. The lifetimes of fluorescence were determined by the time-correlated single photon counting method. Fluorescence of PB-OH and -OMe decayed according to a single exponential function although that of the others showed a multiexponential decay profile. The data of the fluorescence lifetime are listed in Table 1. The obtained phosphorescence spectra are similar to each other in the shape, indicating that triplet excitation energy of PB-X is localized on the *p*-phenylbenzoyl, PB, moiety. On the basis of the lifetimes, τ_p of phosphorescence in second time region and similarity in the shape of the phosphorescence spectra, electronic character of PB-X(T_1) used in the present

TABLE 1: Photophysical and Photochemical Parameters Obtained in the Present Work

X	$\tau_f{}^a$ /ps	$E_T{}^b$/ kcal mol^{-1}	$\tau_p{}^c$/s	$\varepsilon^{T\text{-}T}(\lambda_{max}^{T-T}$/nm)^d/ dm^3 mol^{-1} cm^{-1}	$k_q{}^e$/10^9 dm^3 mol^{-1} s^{-1}	$\Phi_{254}{}^f$	$\Phi_{rad}{}^g$	$\Phi_{dec}{}^h$	BDE(C−X)^i/ kcal mol^{-1}
OH	201	63.3	1.6	28000 (402)	3.9	∼0	∼0	∼0	105.5
OMe	1100	62.4	3.0	28000 (402)	4.2	∼0	∼0	∼0	92.9
OPh	< 20 (21%)	61.8		30000 (412)	4.8	0.14	0.30	0.22	69.6
	247 (27%)		1.0						
	2300 (52%)								
SPh	< 20 (10%)	60.6		23000 (448)	7.0	0.09	0.20	0.72	56.3
	234 (44%)		< 0.5						
	2900 (46%)								

[a] Lifetimes of fluorescence in ACN at 295 K. [b] Triplet energies determined from the 0−0 origin of the phosphorescence spectrum obtained in ethanol at 77 K. [c] Lifetimes of phosphorescence in ethanol at 77 K. [d] Molar absorption coefficients of PB-X in the T_1 state determined by the triplet sensitization. Errors ± 5%. [e] Quenching rate constants of BP(T_1) by PB-X. [f] Quantum yields of decomposition upon 254-nm steady-state photolysis of PB-X in ACN. Errors ± 10% [g] Quantum yield of decomposition upon the 266-nm laser flash photolysis of PB-X in ACN. Errors ± 10% [h] Quantum yield of decomposition upon the 430-nm laser flash photolysis of PB-X in the T_1 state in ACN. Errors ± 10% [i] BDE(C−X) values were obtained by eq 5 using heats of formation ($\Delta_f H$) of corresponding species computed by using B3LYP/6-31Gd level using Gaussian 03 package (see data in Supporting Information).

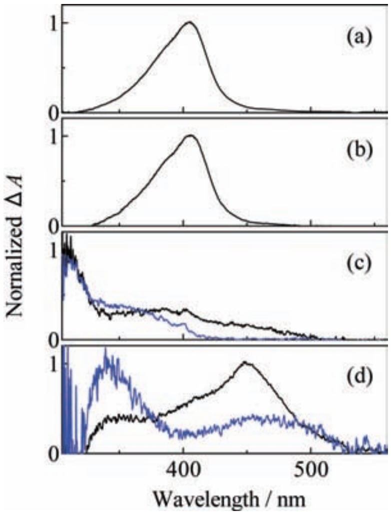


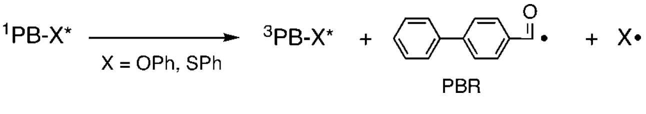
Figure 2. Transient absorption spectra (solid line) observed at 100 ns upon the 266-nm laser flash photolysis of PB-X (X = OH (a), OMe (b), OPh (c), and SPh (d)) in aerated ACN at 295 K and ones (blue line) taken at 4.0 μs (c) and 2.5 μs (d).

study is of π,π*. The lifetime of phosphorescence from PB-SPh shorter than that of other PB-Xs may be due to heavy atom effect of sulfur atom in PB-SPh. The T_1 state energies, E_T of PB-X(T_1) were determined from the 0−0 origin of the phosphorescence spectra, and the values are listed in Table 1 along with τ_p values.

Steady-State Photolysis of PB-X at 254 nm. Absorption spectral changes during the photolysis of PB-X at 254 nm were measured in ACN at 295 K. The spectral data are deposited in Supporting Information. PB-OH and -OMe showed little changes in the absorption spectra after several-minute irradiation while decomposition of PB-OPh and -SPh was seen from the changes of the corresponding absorption spectra. Quantum yields, Φ_{254} of initial decomposition upon 254-nm photolysis were determined to be 0.14 ± 0.01 for PB-OPh and 0.09 ± 0.01 for PB-SPh. These values were not affected by the amount of dissolved oxygen, indicating that the S_1 states are involved in the photodecomposition of PB-OPh and -SPh. From appearance of isosbestic points during the 254-nm light irradiation, it was inferred that a definite photochemical reaction proceeds to form the products. However, unfortunately, they were not isolated by column chromatography, presumably, due to small product yields. To investigate the initial photochemical reactions of PB-X, we carried out nanosecond laser flash photolysis of PB-X.

266-nm Laser Photolysis of PB-X. During the 266-nm laser flash photolysis of PB-X in Ar-saturated ACN, transient absorption spectra with a broad absorption around 440 nm were observed (Figure 2).

The transient absorption spectra at 100 ns for PB-OH, -OMe, and -SPh having lifetimes of a few tens of microseconds in degassed ACN were quenched by the amount of the dissolved oxygen, indicating that they are ascribable to the corresponding triplet−triplet absorption. After quenching of the triplet excited states by the dissolved oxygen, no residual absorption was seen in the transient absorption for PB-OH and -OMe while an absorption spectrum having the maximum at 450 nm was obtained for PB-SPh (Figure 2d). The residual absorption spectrum with PB-SPh is due to the phenyl thiyl radical.[54,55] As with PB-OPh, an absorption band at 398 nm, the shape of which is similar to that of the phenoxyl radial,[56] can be seen at 4.0 μs in the presence of the dissolved oxygen (Figure 2c). The transient absorption spectrum at 100 ns consists of that of the phenoxyl radical and one having small absorption at 410 nm. The absorption band at 410 nm is due to the PB-OPh(T_1) as shown later by the triplet sensitization. Since steady-state photolysis of PB-OPh and -SPh revealed that both PB-Xs undergo photodecomposition in the S_1 state, the corresponding T_1 states are competitively formed via intersystem crossing from the S_1 states where C−O and C−S bonds at the α-position efficiently cleave.



Unfortunately, we were unable to observe the absorption spectrum of *p*-phenylbenzoyl radical (PBR), which may locate in the shorter wavelength region than 300 nm.[57]

Quantum yields, Φ_{rad} for the formation of the phenoxyl and phenyl thiyl radicals, X$^\bullet$ upon the 266-nm photolysis of PB-OPh and -SPh were determined with eq 1

$$\Phi_{rad} = \Delta A_{X^\bullet}(1 - 10^{-A_{266}})^{-1} C_\infty^{266^{-1}} \varepsilon_\lambda^{X^{\bullet -1}} l^{-1} \qquad (1)$$

where $\Delta A_{X^\bullet}$, A_{266}, C_∞^{266}, $\epsilon_\lambda^{X^\bullet}$, and l, respectively, represent an absorbance change at the peak wavelengths, 398 and 450 nm for the phenoxyl and phenyl thiyl radicals, the absorbance of PB-X at 266 nm, the concentration of the S_1 state of PB-X produced upon the 266-nm laser excitation of PB-X having the

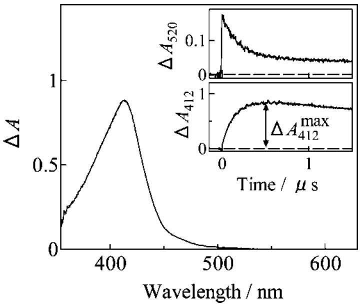


Figure 3. A transient absorption spectrum obtained at 800 ns upon the 355-nm laser flash photolysis in ACN solution of BP (1.0×10^{-2} mol dm^{-3}) in the presence of PB-OPh (1.1×10^{-3} mol dm^{-3}). Insets are the temporal absorbance changes at 520 nm (upper) and 412 nm (lower).

infinite absorbance at 266 nm with a fixed laser intensity on the assumption of the absence of photochemical reactions of PB-X in the S_n states with n over 2, the molar absorption coefficient of the phenoxyl radical at 398 nm (2000 dm^3 mol^{-1} cm^{-1}),[56] the phenyl thiyl radicals at 450 nm (2000 dm^3 mol^{-1} cm^{-1}),[58] and the optical path length (1 cm). The value of C_∞^{266} was determined to be 3.3×10^{-5} mol dm^{-3} by using absorption of BP in the T_1 state (BP(T_1)) in ACN as a chemical actinometer expressed with eq 2 for $\lambda = 266$ nm

$$\Delta A_{\mathrm{T}}^{\mathrm{BP}} = \varepsilon_{\mathrm{T}}^{\mathrm{BP}} l(1 - 10^{-A_\lambda^{\mathrm{BP}}})\mathrm{C}_\infty^\lambda \Phi_{\mathrm{ISC}}^{\mathrm{BP}} \qquad (2)$$

where $\Delta A_{\mathrm{T}}^{\mathrm{BP}}$, $\epsilon_{\mathrm{T}}^{\mathrm{BP}}$Z, A_λ^{BP}, and $\Phi_{\mathrm{ISC}}^{\mathrm{BP}}$ are, respectively, the initial absorbance at 520 nm for the formation of BP(T_1) obtained immediately after laser pulsing, the molar absorption coefficient of BP(T_1) at 520 nm in ACN (6500 dm^3 mol^{-1} cm^{-1}),[59] the absorbance of BP(T_1) at the excitation wavelength λ, and the formation quantum yield of BP(T_1) (1.0).[17] According to eqs 1 and 2, the Φ_{dec} values were determined to be 0.3 ± 0.03 for PB-OPh and 0.20 ± 0.02 for PB-SPh.

Formation of PB-X(T_1) from the Triplet-Sensitized Energy Transfer. To efficiently produce PB-X(T_1), we performed triplet sensitization by using BP as a triplet energy donor upon the 355-nm laser flash photolysis. Since the E_T of BP(T_1) (69.1 kcal mol^{-1})[17] is larger than those of PB-X (ca. 62 kcal mol^{-1}), the triplet energy is efficiently transferred from BP(T_1) to PB-X, giving PB-X(T_1). Upon the 355-nm laser flash photolysis of BP/PB-X systems where only BP absorbs 355-nm laser light, the absorption spectra of the corresponding PB-X(T_1) were observed.

Figure 3 shows a transient absorption spectrum obtained upon the triplet sensitization using a 355-nm laser pulse in an BP/PB-OPh system. The shape of the obtained absorption spectrum is similar to those of PB-OH and -OMe in the T_1 states, as shown in Figure 2. The obtained absorption spectrum is, thus, due to PB-OPh(T_1). The decay rate of BP(T_1) was 5.4×10^6 s^{-1}, which was the same as that of the growth of PB-OPh(T_1). These observations indicate that the triplet excitation energy transfer from BP(T_1) efficiently proceeds to PB-OPh(T_1). Upon the 355-nm laser flash photolysis of other BP/PB-X systems, transient absorption spectra due to the corresponding PB-X(T_1) were obtained after triplet energy transfer from BP(T_1). Upon the triplet sensitization, only the formation of PB-X(T_1) was clearly observed in the transient absorption spectra. After the absorption of PB-X(T_1) had decayed, no residual absorption was observed in the wavelength region, 350 − 700 nm. These observations indicate that PB-X(T_1) does not dissociate.

Figure 4a shows rates, k_{obsd}, of the decay of BP(T_1) in the presence of PB-OPh plotted as a function of the concentration [PB-OPh] of PB-OPh.

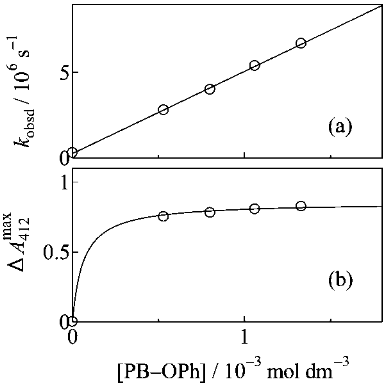


Figure 4. The decay rate (k_{obsd}) of BP(T_1) (a) and the maximum absorbance change ($\Delta A_{412}^{\max}$) at 412 nm (b) plotted as a function of [PB-OPh] obtained upon the 355-nm laser flash photolysis of a BP (1.0×10^{-2} mol dm^{-3})/PB-OPh system.

Since the plots give a straight line, the k_{obsd} can be formulated by eq 3.

$$k_{\mathrm{obsd}} = k_0 + k_{\mathrm{q}}[\text{PB-OPh}] \qquad (3)$$

where k_0 and k_{q}, respectively, represent the decay rate of BP(T_1) in the absence of PB-OPh and the rate constant for quenching of BP(T_1) by PB-X. From the intercept and the slope of the line, the values of k_0 and k_{q} were determined to be 3.0×10^5 s^{-1} and 4.8×10^9 dm^3 mol^{-1} s^{-1}.

Figure 4b shows the maximum absorbance, $\Delta A_{412}^{\max}$ at 412 nm of PB-OPh(T_1) (see the lower inset in Figure 3) produced by the triplet sensitization plotted as a function of [PB-OPh]. The value of $\Delta A_{412}^{\max}$ increases with increasing [PB-OPh], but the increase is not linear with [PB-OPh]. The quantity of $\Delta A_{412}^{\max}$ of PB-OPh(T_1) produced by the triplet sensitization can be formulated by eq 4

$$\Delta A_{412}^{\max} = k_{\mathrm{q}}[\text{PB-OPh}]\alpha_{\mathrm{TET}}\varepsilon^{\mathrm{T-T}} l \Phi_{\mathrm{ISC}}^{\mathrm{BP}}(1 - 10^{-A_{355}^{\mathrm{BP}}})C_\infty^{355}(k_0 + k_{\mathrm{q}}[\text{PB-OPh}])^{-1} \qquad (4)$$

where α_{TET}, $\epsilon^{\mathrm{T\text{-}T}}$, $\Phi_{\mathrm{ISC}}^{\mathrm{BP}}$, A_{355}^{BP}, and C_∞^{355} are, respectively, an efficiency of triplet energy transfer from BP(T_1) to PB-OPh, the molar absorption coefficients of PB-OPh(T_1) at the absorption maximum wavelength (412 nm), the formation quantum yield of BP(T_1) (1.0),[17] the concentration of the S_1 state of BP formed upon the 355-nm laser flash excitation of BP having the infinite absorbance at 355 nm at a fixed laser intensity. The value of C_∞^{355} was determined to be 3.1×10^{-5} mol dm^{-3} by using triplet absorption of BP (eq 2 with $\lambda = 355$ nm). By use of eq 4 and the determined values of k_0, k_{q}, and C_∞^{355} and by assumption that the efficiency of α_{TET} is unity, the $\epsilon^{\mathrm{T-T}}$ value of PB-OPh(T_1) was determined to be 30000 ± 1500 dm^3 mol^{-1} cm^{-1} at 412 nm. The same procedures were used to determine the $\epsilon^{\mathrm{T-T}}$ values of PB-X(T_1), which are listed in Table 1 along with the maximum wavelength of the triplet−triplet absorption peak, $\lambda_{\max}^{\mathrm{T-T}}$.

Photodecomposition upon the 430-nm Laser Flash Photolysis of PB-X(T_1). Since PB-X(T_1) has absorbance at 430 nm where ground-state PB-Xs have no absorbance, the 430-nm laser flash photolysis of PB-X(T_1) produces PB-X(T_n) with n over 2 of the corresponding PB-X. Figure 5 shows time profiles of PB-SPh(T_1) at 448 nm obtained upon the 355-nm flash laser photolysis of a BP/PB-SPh system in the absence and the presence of the second 430 nm laser pulsing.

Upon the 430-nm laser flash photolysis of PB-SPh(T_1) at 250 ns after the first 355-nm laser pulsing, we observed an abrupt

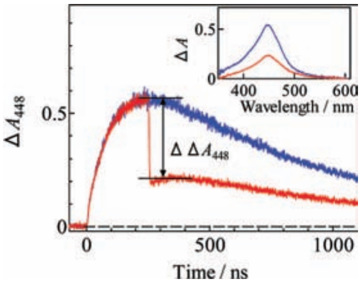


Figure 5. Temporal absorbance changes (ΔA_{448}) at 448 nm observed after 355-nm laser pulsing in a BP (1.0×10^{-2} mol dm^{-3})/ PB-SPh (1.1×10^{-3} mol dm^{-3}) system in the absence (blue color) and presence (red color) of a 430-nm laser pulse at the laser power of 3 mJ at 250 ns. Inset; transient absorption spectra at 350 ns in the absence (blue color) and presence (red color) of a 430-nm laser pulse.

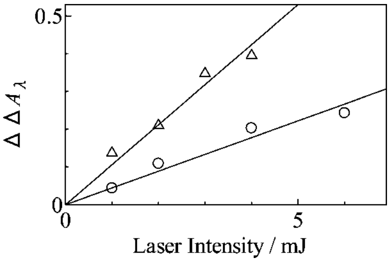


Figure 6. Changes ($\Delta\Delta A_\lambda$) in the transient absorption change of PB-X(T_1) at the transient absorption maximum wavelength (λ: 412 nm for PB-OPh (○) and 448 nm for PB-SPh (Δ)) plotted as a function of the intensity of the second incident 430-nm laser pulse.

decrease in the absorbance change, ΔA_{448}, at 448 nm of the triplet absorption. The observation of bleaching in the absorption spectra of PB-X(T_1) indicates occurrence of photodecomposition of PB-SPh(T_n), presumably, due to α-cleavage during the second 430-nm laser flash photolysis although the formed phenyl thiyl radical was not recognized in the transient absorption due to their small molar absorption coefficient compared with that of PB-SPh(T_1) (inset in Figure 5). Bleaching of the absorption spectrum of PB-OPh(T_1) was also obtained upon sequential 430-nm laser pulsing after the 355-nm laser flash photolysis in a BP/PB-OPh system, whereas with PB-X(T_1) (X = OH and OMe) bleaching was not observed. From these observations, it is inferred that PB-OH(T_n) and PB-OMe(T_n) deactivate to the PB-X(T_1) (X = OH and OMe), respectively, via rapid internal conversion without any photochemical reactions.

Quantum yields, Φ_{dec} of decomposition of PB-X(T_n), upon 430-nm laser pulsing were estimated from the change, $\Delta\Delta A_\lambda$, in the transient absorbance change at $\lambda_{\max}^{\mathrm{T-T}}$ due to the decomposition of PB-X(T_1) and the 430-nm laser intensity. Figure 6 shows the $\Delta\Delta A_\lambda$ values obtained for PB-OPh and -SPh plotted as a function of the 430-nm laser intensity.

As the laser intensity increases, the $\Delta\Delta A_\lambda$ value linearly increases, showing that the decomposition monophotonically proceeds in PB-X(T_n). According to the determining procedures for Φ_{dec} reported previously,[24,30,31] the Φ_{dec} values were determined to be 0.22 ± 0.02 for PB-OPh and 0.72 ± 0.05 for PB-SPh. Although we tried to identify the photoproducts upon stepwise two-color laser photolysis of PB-OPh and -SPh, we were unable to isolate them from the parent molecules, presumably, because of the relatively large amount of the parent molecules, PB-X and BP.

Estimation of BDE of α-Bond of PB-X. On the basis of the heats of formation, $\Delta_f H$ of PB-X, PBMR, and $^{\bullet}$X computed by using the B3LYP/6-31Gd level using Gaussian 03 package, bond dissociation energies, BDE(C−X), of α-bonds in PB-X were estimated by eq 5

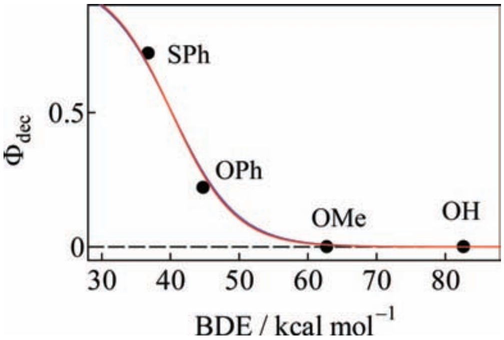


Figure 7. Quantum yields Φ_{dec} of decomposition of PB-X(T_n) plotted as a function of the corresponding BDE. The solid curves were drawn according to eq 8 with best-fitted parameters of α and β by assuming that the E_R values are 62 kcal mol^{-1} (red line) and 130 kcal mol^{-1} (blue line).

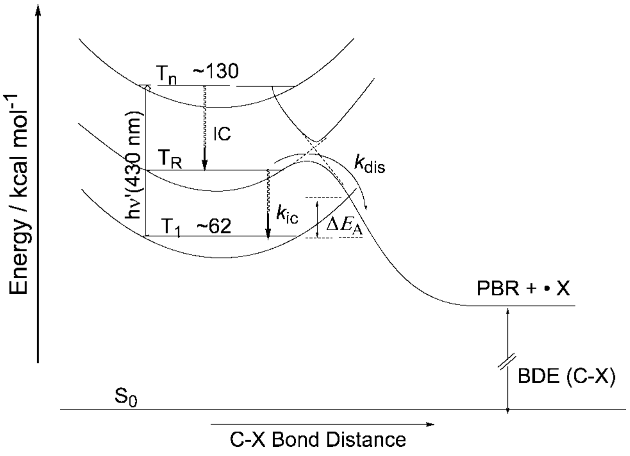
$$\mathrm{BDE(C{-}X)} = \Delta_f H(\mathrm{PBR}) + \Delta_f H(^{\bullet}\mathrm{X}) - \Delta_f H(\mathrm{PB\text{-}X}) \quad (5)$$

The values of $\Delta_f H$(PB-X), $\Delta_f H$(PBR), and $\Delta_f H$($^{\bullet}$X) are found in Supporting Information. The obtained values of BDE(C−X) are listed in Table 1.

Photochemical Features of PB-X in the Excited States. In the present study, we have shown occurrence of decomposition of PB-OPh and -SPh in the S_1 and T_n states and determined the quantum yields Φ_{254} and Φ_{rad} for the S_1 and Φ_{dec} for the T_n state. The $T_1(\pi,\pi^*)$ states of these two molecules are found to be inert to α-cleavage. According to the spin-conservation rule, a singlet radical pair, ^{1}(PBR + $^{\bullet}$X)$_{\mathrm{cage}}$ of PBR and the corresponding radical, $^{\bullet}$X would be formed in the solvent cage immediately after the C−X bond cleavage in the S_1 state. Some of the singlet radical pairs may undergo geminate recombination to reform the parent molecule or in-cage radical reactions, and the others will escape from the solvent cage to be free radicals. Thus, the quantum yield, $\Phi_{\mathrm{dis}}(S_1)$ of the actual bond dissociation in the S_1 state of those two PB-Xs must be larger than the determined Φ_{rad} values. With PB-SPh, intersystem crossing to PB-SPh(T_1) is clearly competitive with the dissociation process in the S_1 state since absorption of PB-SPh(T_1) is obtained in the transient absorption measurement upon photolysis of PB-SPh. In contrast, little absorption of PB-OPh(T_1) was seen in the transient absorption, indicating that very little intersystem crossing from the S_1 state of PB-OPh is operative in the quenching of the S_1 state. Consequently, the $\Phi_{\mathrm{dis}}(S_1)$ values can be estimated to be $1 > \Phi_{\mathrm{dis}}(S_1) > 0.30$ for PB-OPh and $1 > \Phi_{\mathrm{dis}}(S_1) > 0.20$ for PB-SPh. The difference between Φ_{rad} and Φ_{254} may be corresponding to total quantum yields for in-cage and out-of-cage radical reactions (0.08 for PB-OPh and 0.11 for PB-SPh).

Lifetime measurements of fluorescence of PB-OPh and -SPh revealed that the decay profiles of the S_1 states were analyzed with multiexponential functions while PB-OH and PB-OMe, both of which are inactive for photodecomposition, showed single exponential decay profiles with nanosecond lifetimes. On the basis of the result that the decay profiles of the fluorescence of PB-OPh and -SPh consist of picosecond and nanosecond lifetimes, the shorter lifetimes of a few hundreds of picoseconds and/or less than 20 ps could be derived from the α-cleavage process that quenched the S_1 state. The rates, $k_{\mathrm{dis}}(S_1)$, of the bond dissociation in the S_1 state of PB-OPh and -SPh are thus estimated to be larger than 10^{10} s^{-1}. On the other hand, the quantum yields, Φ_{dec} for decomposition of PB-OPh(T_n) and PB-

SCHEME 2: Schematic Energy Diagram of PB-X (X = OPh and SPh) in the T_1, T_R, and T_n States, Including an α-Cleavage Pathway



SPh(T_n) can be regarded to be corresponding to those $\Phi_{dis}(T_R)$ for the bond dissociation in a higher triplet excited state, T_R state which is reactive for the C−X bond dissociation since the triplet biradical, $^3(PBR + {}^{\bullet}X)_{cage}$ in the solvent cage, which are formed upon the C−X bond cleavage in the T_R state, is free of geminate recombination. The residual quantum yield, $1 - \Phi_{dis}(T_R)$ must correspond to that for internal conversion, $\Phi_{ic}(T_R)$ from the T_R to the T_1 state with a rate, $k_{ic}(T_R)$ which should be competitive with the dissociation rate, $k_{dis}(T_R)$. In the present work, the lifetime of the dissociative T_R state cannot be determined since no emission from PB-X(T_n) could be observed at room temperature. The C−O bond rupture in the T_R state seemed to occur within the pulse duration (ca. 7 ns) of the second 430-nm laser irradiation. By consideration of the general rate of internal conversion processes in triplet manifolds in solution, the magnitude of the lifetime of the T_R state will be as large as 10^{12} s^{-1}. Therefore, the $k_{dis}(T_R)$ value can be estimated to be located in the range of $10^{11}-10^{12}$ s^{-1}.

A schematic energy diagram of PB-X(T_n) (X = OPh and SPh) along with the α-cleavage pathway is depicted in Scheme 2.

Upon the 430-nm laser flash photolysis of PB-X in the $T_1(\pi,\pi^*)$ state, PB-X(T_n) at an energy level of ca. 130 kcal mol^{-1} is formed. PB-X(T_n) will deactivate through internal conversion to PB-X(T_R). It is originally suggested that the bond dissociation in the excited states proceeds by avoided crossings between the reactive excited-state with dissociative potential surfaces of the same overall symmetry (avoided crossing).[60] The electronic configuration of the dissociative state, which strongly interacts with PB-X(T_n) in the n,π^* states, is $^3(\pi,\sigma^*)$ of the C−X bond of PB-X. When the electronic character of the T_R states is of a π,π^* type, the electronic configuration of the interactive potential surface is of $^3(\sigma,\sigma^*)$. In both cases, it is considered that the α-bond dissociation proceeds without activation energies from the T_R state along the corresponding dissociative surface. On the other hand, we have observed that all PB-X(T_1) studied in the present work deactivate to the corresponding ground-state without decomposition. The absence of chemical reactions indicates that the presence of an activation energy, ΔE_A from the $T_1(\pi,\pi^*)$ state to a $^3(\sigma,\sigma^*)$ dissociative potential. A large thermal barrier between the T_R state and the corresponding dissociative potential would disable to promote the decomposition of PB-OH(T_n) and PB-OMe(T_n), resulting in efficient internal conversion from the T_R to the T_1 state.

Figure 7 shows the quantum yields, Φ_{dec} of decomposition for PB-X(T_n) obtained in the work plotted as a function of the corresponding BDE.

As the BDE decreases, the Φ_{dec} value increases. Since the shape of the triplet absorption spectra of PB-Xs resembles each other, electronic features of PB-X(T_n) formed upon the second laser excitation of PB-X(T_1) are also similar to each other. In this sense, the energy level, E_R of PB-X(T_R), T_R, that has interaction with the corresponding dissociative potential with a little or large energy barrier would be the same as those of all PB-Xs. Here, we assume that the dissociation process of PB-X(T_n) obeys to an energy-gap law. That is, the rate, $k_{dis}(T_R)$ is proportional to an exponential expression of an energy gap, ΔE (E_{RT} − BDE) between the state energy, E_{RT} of the T_R and the bond dissociation energy, BDE.

$$k_{dis}(T_R) = A \exp(\alpha \Delta E) \tag{6}$$

Here, A and α represent, respectively, a pre-exponential factor and a constant in unit of mol kcal^{-1}. Conversely, the decomposition yield, Φ_{dec} is formulated in eq 7 by using the rates, $k_{dis}(T_R)$ and $k_{ic}(T_R)$, both of which are rates of the deactivation processes in the T_R state shown above

$$\Phi_{dec} = k_{dis}(T_R)(k_{dis}(T_R) + k_{ic}(T_R))^{-1} \tag{7}$$

By use of eq 6, eq 7 can be expressed as

$$\Phi_{dec} = \beta(\beta + \exp(-\alpha \Delta E))^{-1} \tag{8}$$

where $\beta = Ak_{ic}(T_R)^{-1}$. An energy level of the T_R of PB-Xs must be located between the lowest E_T levels (ca. 62 kcal mol^{-1}) and the maximum E_T level (130 kcal mol^{-1}) promoted by the second laser photolysis. By use of eq 8, best-fitted values of α and β were, respectively, obtained to be 0.218 mol kcal^{-1} and 8.68×10^{-3} for E_{RT} = 62 kcal mol^{-1} and 0.210 mol kcal^{-1} and 6.57×10^{-9} for E_{RT} = 130 kcal mol^{-1}. The simulated curves resemble each other, and the α values are very close irrespective of the E_{RT} value. Although we are unable to determine the definite E_{RT} value from these simulations, it is noteworthy that the dissociation rate of PB-X(T_n) is expressed in an energy-gap-law form of eq 6.

In the present work, we have shown by using the triplet sensitization techniques that α-cleavage is absent for PB-X(T_1). Out of concern for spin multiplicity of α-cleavable excited states for C−S bond in aromatic carbonyls, it is notable that our finding contrasts with the reported result that S-phenyl thiobenzoates in the T_1 state are dissociative.[15,16] Since quantum yields for radical formation from S-phenyl thiobenzoates in the T_1 state were not reported, they cannot be compared with our data, Φ_{rad} (0.20) and Φ_{dec} (0.72) for PB-SPh. Sulfur-centered radicals have been shown as efficient initiating agents in radical photopolymerization reaction.[61−64] Thus, PB-SPh could be promising as a highly efficient initiator for photopolymerization using double light excitation procedures. In contrast, PB-OPh(T_n) provides a radical yield (Φ_{dec} = 0.20) smaller than that (Φ_{rad} = 0.30) in the S_1 state. From the viewpoint of radical yields, PB-OPh should be utilized as a photoinitiator under single light excitation.

Conclusion

By means of single color and stepwise two-color two-laser photolysis techniques, photochemical profiles of PB-X in the excited states have been investigated. α-Bond cleavage of PB-OPh and -SPh in the S_1 state was recognized. No photochemical reactions occur in PB-X(T_1) used in the present study. 430-nm laser photolysis of PB-X(T_1) demonstrates that decomposition of PB-X(T_n) (X = OPh and SPh) occurs with definite quantum yields, Φ_{dec} via a single-photonic process. The mechanism for the α-cleavage of PB-X(T_n) (X = OPh and SPh) is interpreted in terms of avoided crossing of a T_R state with a dissociative potential surface. The rate of α-cleavage of PB-X(T_R) is shown to be formulated in an energy-gap-law equation (eq 6) as a function of ΔE (E_{RT} − BDE). To the best of our knowledge, the value (0.73) of Φ_{dec} for PB-SPh(T_n) is the largest among the quantum yields for decomposition of aromatic compounds in the T_n states. α-Cleavage of C−S bond in the T_n states where benzoyl and S-centered radicals are efficiently produced may be feasible as photoinitiating systems for radical photopolymerization reactions.

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Supporting Information Available: Absorption spectrum changes upon the steady-state photolysis of PB-OPh and -SPh at 254 nm and elemental heats of the formation for determining the BDE by eq 5 are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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