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ARTICLES

Photodecomposition Profiles of β-Bond Cleavage of Phenylphenacyl Derivatives in the Higher Triplet Excited States during Stepwise Two-Color Two-Laser Flash Photolysis

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Photochemical properties of *p*-phenylphenacyl derivatives (PP-X) having C−halide, C−S, and C−O bonds in the lowest (T_1) and higher (T_n) triplet excited states were investigated in solution by using single-color and stepwise two-color two-laser flash photolysis techniques. PP-Xs (X = Br, SH, and SPh) undergo β-bond dissociation in the lowest singlet excited states (S_1) while the C−X bonds of other PP-Xs are stable upon 266-nm laser photolysis. The $T_1(\pi,\pi^*)$ states of PP-X were efficiently produced during 355-nm laser photolysis of benzophenone as a triplet sensitizer. Triplet PP-Xs deactivate to the ground state without photochemical reactions. Upon 430-nm laser photolysis of the T_1 states of PP-X (X = Br, Cl, SH, SPh, OH, OMe, and OPh), decomposition of PP-X in the T_n states was found. On the basis of the changes in the transient absorption, quantum yields (Φ_{dec}) of the decomposition of PP-X in the T_n states were determined, while bond dissociation energies (BDE) of the C−X bonds were calculated by computations. According to the relationship between the Φ_{dec} and BDE values, it was shown that the decomposition of PP-X in the T_n state is due to β-cleavage of the corresponding C−X bond, and that the state energy of the reactive T_n for the C−O bond cleavage differs from that for the C−halide and C−S bond cleavage. The reaction profiles of the C−X bond cleavage of PP-X in the T_n states were discussed.

Introduction

Photoinduced bond dissociation is one of the most fundamental processes in photochemistry and photobiology.[1] Homolytic and heterolytic cleavage of chemical bonds in the lowest singlet (S_1) or triplet (T_1) excited states of arylmethyl compounds have been widely studied.[2] With aromatic carbonyl compounds, Norrish type I and type II reactions are well-known photochemical reactions where bond dissociation occurs at the α- and β-positions of the carbonyl groups, respectively. Beside them, a new-type bond cleavage (ω-cleavage) of carbonyl compounds has been recently reported from the viewpoint of the spin multiplicity and electronic character of the dissociative states.[3−8] The electronic character of the dissociative states and the corresponding bond dissociation energy (BDE) are important factors for the occurrence of the bond rupture as well as the excitation energy of the reactive states. Generally, the higher singlet and triplet excited states (S_n and T_n, with $n = 2$ and over) have the potential to show higher reactivities than the lowest excited states.[1] 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. For example, based on the transient absorption measurements using the double excitation method, the formation of the carbazyl radical from carbazole in the S_n and T_n states has been reported.[9,10] A number of studies of the properties and correlated reactions of the T_n states have been reported by using further excitation of the T_1 state to the T_n state.[11−17] We have been studying energy transfer, electron transfer, and bond dissociation processes in the T_n states.[18−39] As with photoinduced bond cleavage, we have reported that C−O bond dissociation occurs only in the T_n states of methoxy- or phenoxy-methylnaphthalene and 4-(methoxy- or phenoxy-methyl)benzophenone in which the C−O bond is benzylic of the aromatic moieties.[27,29] Conversely, it is of our interest whether carbonyl molecules having C−O β-bonds undergo the bond dissociation in the T_n states.

From the viewpoint of the deactivation mechanisms in the triplet excited state, photochemistry of carbonyl compounds having a β-phenyl ring has been studied.[40−51] The lifetimes of the triplet states of phenacyl derivatives, such as β-phenylpropiophenones and α-phenoxylacetophenones, are shorter than those of corresponding molecules without a β-phenyl ring. The mechanism has shown that the carbonyl in the n,π^* triplet excited state is efficiently quenched by through-space intramolecular interactions with the β-phenyl ring. For occurrence of this quenching, a *gauche* conformation is necessary where the π-system of the β-phenyl ring can overlap with the n-orbital of the carbonyl group.[43]

In the cases of α-phenoxyl acetophenone (X = O) derivatives, it is shown that fragmentation due to β-cleavage of the C−O bond occurs in the n,π^* triplet excited state in competition with

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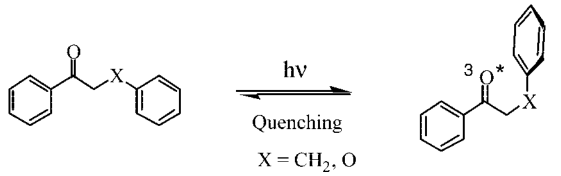


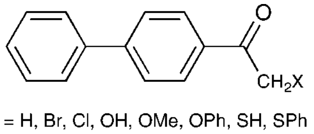
this quenching.[48,49] In polar media, the electronic character of the T_1 state of these ketones was shown to be of π,π^*, whose state energy of ca. 74 kcal mol^{-1} was suggested to be closely located to that of the $T_2(n,\pi^*)$ state.[50] It was found that the efficiencies for the β-cleavage for α-phenoxylacetophenone (X = O) derivatives in the π,π^* triplet excited state having relatively smaller C−O bond energies in polar solvent are much larger than those previously reported in benzene.[50] This observation indicated that in the absence of the deactivation pathway due to triplet n,π^* interaction with the β-phenyl ring, it can be shown that the reactivity of the β-cleavage of phenacyl derivatives in the triplet excited states having cleavable bonds (C−X) may be governed by the BDE of the C−X bond. To examine this hypothesis, *p*-phenylacetophenone derivatives are candidates since these T_1 states are expected to have the electronic character of π,π^* and to suffer little contribution from the $T_2(n,\pi^*)$ on the deactivation. However, the reactivity of β-cleavage may be reduced insomuch as the triplet excitation energies of those compounds are much smaller (e.g. ca. 61 kcal mol^{-1} for acetyl biphenyl)[52] than those of α-substituted acetophenones (ca. 74 kcal mol^{-1}).[50,51]

In this context, we investigate the β-bond dissociation of *p*-phenylphenacyl derivatives (PP-X; X = Br, Cl, SH, SPh, OH, OMe, and OPh) not only in the T_1 state but also in the T_n states by using transient absorption measurements. The structures of PP-X studied in this work are shown in Scheme 1. As was expected, the β-bond dissociation was not seen in the T_1 states whereas PP-X in the T_n states was found to decompose. The quantum yields toward the disappearance of PP-X in the T_n states were determined by stepwise two-color two-laser flash photolysis techniques. According to the relationship between the quantum yield and the BDE, the profiles of β-bond dissociation of PP-X in the T_n states of PP-X are discussed.

Experimental Section

4-Acetylbiphenyl (PP-H) was purchased from Aldrich. α-Bromo- and α-chloro-4-phenylacetophenones (PP-Br and PP-Cl) were purchased from TCI. α-Hydroxy-4-phenylacetophenone (PP-OH) was synthesized by a reaction of PP-Br and sodium formate in refluxed ethanol. α-Thiohydroxy-4-phenylacetophenone (PP-SH) was synthesized from PP-Cl by using an ion-exchange resin (IRA-400 from Aldrich). 4-Phenylphenacyl phenyl sulfide (PP-SPh) and α-phenoxyl-4-phenylacetophenone (PP-OPh) were synthesized by a reaction of PP-Br with thiophenol or phenol in acetone in the presence of K_2CO_3. α-Methoxyl-4-phenylacetophenone (PP-OMe) was prepared according to the literature.[53] PP-Xs were all purified by repeated recrystallizations from hexane. Benzophenone was purchased from Nacalai Tesque and recrystallized from ethanol before use. Acetonitrile (ACN, spectroscopy grade from Nacalai Tesque), methanol (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 a mixture of methanol and ethanol (1:1 v/v) was used as a matrix 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. Fourth harmonics (266 nm) of a Nd^{3+}:YAG laser (JK Lasers HY-500; pulse width 8 ns) were used as light sources for direct excitation. The details of the detection system for the time profiles of the transient absorption have been reported elsewhere.[54] 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 triplet sensitization and stepwise two-color two-laser flash photolysis. Two laser flashes were synchronized by a pulse generator with a delay time of 10 ns−10 μs. The probe light was obtained from a 450-W Xe-lamp (Osram XBO-450). The transmitted probe light was focused on a monochromator (Nikon G250). The output of the monochromator was monitored with a photomultiplier tube (PMT, Hamamatsu Photonics, R928). The signal from the PMT was recorded on a transient digitizer (Tektronix TDS 580D). A multichannel analyzer system (Hamamatsu Photonics, C5967) was used for the measurement of the transient absorption spectra. The total system was controlled with a personal computer via GP-IB interface. To avoid any damage of the sample solution by the probe light, a suitable cutoff filter was used in front of the sample.

SCHEME 1: Molecula Structures of *p*-Phenylphenacyl Derivatives (PP-X) Used in the Present Study



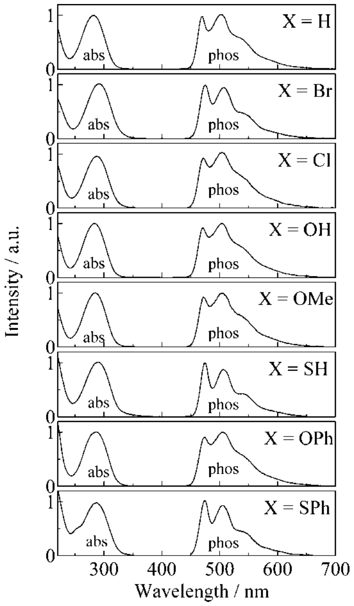


Figure 1. The UV absorption spectra of PP-X in ACN at 295 K and the phosphorescence spectra in a mixture of methanol and ethanol (1:1 v/v) at 77 K.

Results

Absorption and Phosphorescence Spectra of PP-X. Figure 1 compares the absorption and phosphorescence spectra of PP-X. The features of the UV absorption spectra are similar to each other with a peak around 290 nm. The similarity in the UV

TABLE 1: Triplet Energies (E_T), Wavelengths of the Absorption Peak (λ_{max}^{T-T}), and the Molar Absorption Coefficients (ϵ_{max}) of PP-X in the T_1 state at λ_{max}^{T-T}, Bond Dissociation Energies (BDE(C−X)) for β C−X Bonds of PP-X, and Quantum Yields (Φ_{dec}) of the Decomposition of PP-X in the T_n State

X	E_T/kcal mol^{-1}	λ_{max}^{T-T}/nm	ϵ_{max}/10^4 dm^3 mol^{-1} cm^{-1}	BDE(C−X)[a]/kcal mol^{-1}	Φ_{dec}
H	60.8	420	2.6	87.4	0
Br	60.2	460	1.0	50.8	0.65
Cl	60.5	438	2.0	65.2	0.17
SH	60.2	433	1.4	62.6	0.28
SPh	60.2	442	1.3	49.8	0.53
OH	60.8	432	2.6	77.9	0.08
OMe	60.6	430	2.2	56.2	0.11
OPh	60.4	434	2.1	47.4	0.14

[a] BDE(C−X) values were obtained by eq 1, using heats of formation ($\Delta_f H$) of corresponding species computed by using a semiempirical PM3 program contained in MOPAC'97 (see data in the Supporting Information).

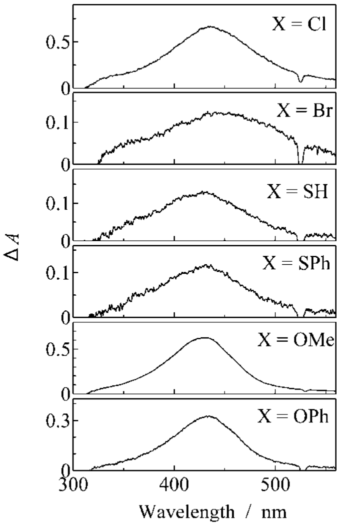
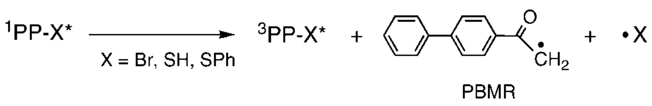


Figure 2. Transient absorption spectra obtained at 100 ns after a laser pulse during the 266-nm laser photolysis of PP-X. The spikes at 532 nm are due to scattering of the second harmonics (532 nm) of the used YAG laser system.

spectra indicates that the ground state absorption is attributed to the 4-phenylphenacyl moiety, irrespective of the substituent groups (X). From the absence of fluorescence from PP-X, it is inferred that the electronic character of PP-X in the singlet excited state (S_1) is of n,π*. The obtained phosphorescence spectra are similar to each other, indicating that triplet excitation energy of PP-X is localized on the phenylphenacyl (PP) moiety. Since it is known that the electronic character of PP-H in the triplet excited state is of a π,π* type, that of PP-Xs in the triplet excited state used in the present study is considered to be of π,π*. The T_1 state energies (E_T) of PP-X were determined to be ca. 60 kcal mol^{-1} from the 0−0 origin of the phosphorescence spectra, and the values are listed in Table 1.

266-nm Laser Photolysis of PP-X. During the 266-nm laser flash photolysis of PP-X in Ar-saturated ACN, transient absorption spectra with a broad absorption around 440 nm were observed (Figure 2). The absorption spectra having lifetimes of several microseconds were quenched by the amount of dissolved oxygen, indicating that they are ascribable to triplet−triplet absorption of the corresponding PP-X. From the similarity in the shape of these absorption spectra, it is inferred that the triplet excitation energy is localized on the PP moiety. Observation of the long-life transient absorption of PP-X in the π,π* triplet excited state indicates that the T_1 states are free of quenching by the β-phenyl ring of PP-X (X = OPh and SPh). After depletion of these transient absorption spectra, no appreciable absorption was seen except for PP-Xs (X = Br, SH, and SPh, see the Supporting Information). With PP-SPh, the residual absorption spectrum having the absorption maximum at 450 nm was due to the phenylthiyl radical, indicating that PP-SPh unambiguously undergoes β-cleavage of the C−S bond in the singlet excited state (S_1). Very week absorption bands at 320 nm seen for PP-Br and PP-SH are considered to be due to the *p*-phenylbenzoylmethyl radical (PBMR). Therefore, the S_1 states of these PP-Xs competitively undergo deactivation to the T_1 state via intersystem crossing and β-bond cleavage.



Unfortunately, we were unable to determine the quantum yields of radical formation for these PP-Xs because of the very small transient absorbance. Conversely, the absence of the residual absorption spectra indicates that PP-Xs in the singlet excited states except for X = Br, SH, and SPh are inert to the photodecomposition.

Formation of PP-X in the Triplet Excited State from the Triplet Sensitized Energy Transfer. It has been established that upon 355-nm laser photolysis of benzophenone (BP), BP in the triplet excited state is formed via a fast intersystem crossing from the lowest singlet excited state according to the El-Sayed rule with unitary quantum yield.[1] Since the triplet excitation energy of BP (69.1 kcal mol^{-1}) is larger than those of PP-X (ca. 60 kcal mol^{-1}), the triplet excitation energy is efficiently transferred from BP in the triplet excited state to PP-X. Upon 355-nm laser flash photolysis of BP/PP-X systems where only BP absorbs 355-nm laser light, the absorption spectra of the corresponding PP-X in the triplet excited state were observed (dotted lines in Figure 3). The time profiles of the growth of the transient absorption for the triplet excited state in the time region of 0−500 ns demonstrate the triplet excitation energy transfer from BP in the triplet excited state to PP-X (see insets in Figure 3). The molar absorption coefficients (ϵ_{max}) of PP-X in the triplet excited state at the absorption peak were estimated by comparing with the absorption of BP in the triplet excited state at 525 nm (ϵ_{525} = 6500 dm^3 mol^{-1} cm^{-1}) as the reference.[52,55] No residual absorption band appeared after the decay of PP-Xs in the triplet excited state to PP-Xs in the ground state. These observations indicate that decomposition of PP-X is absent in the lowest triplet excited states (T_1). The maximum wavelength of PP-X for the triplet−triplet absorption peak (λ_{max}^{T-T}) and the determined values of the molar absorption coefficient (ϵ_{max}) are listed in Table 1.

Photodecomposition upon 430-nm Laser Photolysis of PP-X in the Triplet Excited State. Since PP-Xs in the triplet excited states have large absorbance at 430 nm where ground state PP-Xs have no absorbance, 430-nm laser photolysis of the T_1 state produces the corresponding PP-X in a higher triplet excited state (T_n). Upon 430-nm laser photolysis of PP-X in the triplet excited state at 600 ns after the first 355-nm laser flash, we observed an abrupt decrease in the absorbance change (ΔA) of the triplet absorption (Figure 3 (solid line)). With PP-H in the triplet excited state, bleaching was not observed, indicating that PP-H deactivates in the T_n state to those in the T_1 state via

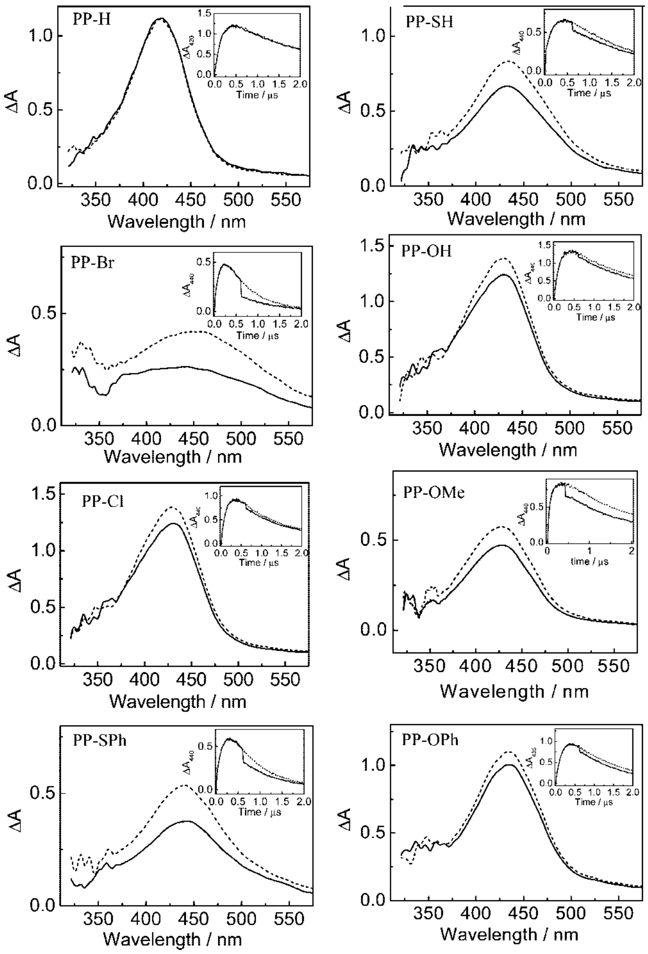


Figure 3. The transient absorption spectra obtained at 1 μs after a laser pulse during the 355-nm laser flash photolysis (dotted line) and 355- and 430-nm two-color two-laser flash photolysis (solid line) of PP-X (1.0×10^{-3} mol dm^{-3}) in Ar-saturated ACN in the presence of BP (6.0×10^{-3} mol dm^{-3}). The insets display the decay profiles of transient absorption of PP-X in the T_1 state during 355-nm laser (dotted line) and 355- and 430-nm two-color two-laser flash photolysis (solid line). The delay time between the 355- and 430-nm two-color two-laser pulses is 600 ns.

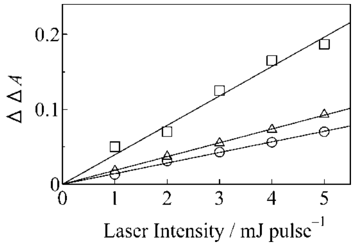


Figure 4. Changes ($\Delta\Delta A$) in absorption change at the absorption peak of PP-X (X = Cl (○), OPh (Δ), and SPh (□)) in the T_1 state plotted as a function of the intensity of the second incident 430-nm laser pulse.

rapid internal conversion (IC) without any photochemical reactions. Conversely, the observation of bleaching in the absorption spectra of other triplets indicates occurrence of photodecomposition of PP-X in the triplet excited state, presumably due to β-cleavage during the second 430-nm laser photolysis although the formed radicals were not recognized in the transient absorption due to their small molar absorption coefficients compared with those of the corresponding T_1 state (see the Supporting Information for the absorption properties of the radicals).

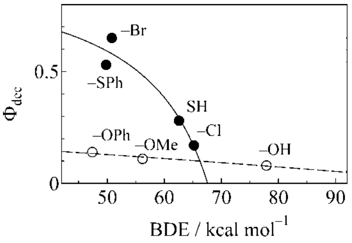


Figure 5. The Φ_{dec} values plotted as a function of BDE(C−X). The solid and broken curves were calculated according to eq 4.

Quantum yields (Φ_{dec}) of decomposition of PP-X in the triplet excited state upon 430-nm laser pulsing were estimated from the change ($\Delta\Delta A$) in the transient absorbance change at λ_{max}^{T-T} due to the decomposition of the T_1 state and the 430-nm laser intensity. Figure 4 shows the $\Delta\Delta A$ values obtained for some PP-Xs plotted as a function of the 430-nm laser intensity. As the laser intensity increases, the $\Delta\Delta A$ value linearly increases, showing that the decomposition monophotonically proceeds in the T_n state. According to the determining procedures for Φ_{dec} reported previously,[23,29,30] the Φ_{dec} values were estimated, and summarized in Table 1.

Estimation of Bond Dissociation Energy of the β-Bond of PP-X. On the basis of the heats of formation ($\Delta_f H$) of PP-X, PBMR, and $^{\bullet}$X computed by using a semiempirical PM3 program contained in MOPAC'97, bond dissociation energies (BDE(C−X)) of the β-bond in PP-X were estimated by eq 1.

$$\mathrm{BDE(C{-}X)} = \Delta_f H(\mathrm{PBMR}) + \Delta_f H(^{\bullet}\mathrm{X}) - \Delta_f H(\mathrm{PP\text{-}X}) \quad (1)$$

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

Discussion

Nature of the Photodecomposition of PP-X in the T_n States. Generally, for occurrence of bond dissociation of molecules in the excited states, the dissociative state energy must be larger than the BDE of the cleavable bond. In a previous work, we suggested (1) formulation of a dissociation rate (k_{dis}) as a function of BDE for β-bond cleavage of aromatic compounds in the higher triplet excited states and (2) the relationship between Φ_{dec} and BDE.[36] That is, the k_{dis} value for bond cleavage in a reactive higher triplet excited state (T_R) having the excitation energy (E_{RT}) is simply proportional to the energy difference, ΔE (= E_{RT} − BDE) between the E_{RT} and the corresponding BDE.

$$k_{dis} = \alpha \Delta E \quad (2)$$

Here, α is a constant. Furthermore, by using a rate (k_{ic}) of internal conversion from the T_R to the T_1 state, quantum yields (Φ_{dec}) of the bond cleavage in the T_R state can be defined by eq 3.

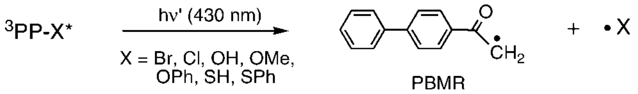
$$\Phi_{dec} = k_{dis}(k_{dis} + k_{ic})^{-1} \quad (3)$$

The yield is transformed by using eq 2 and a constant, β (= αk_{ic}^{-1}).

$$\Phi_{dec} = \beta \Delta E (1 + \Delta E)^{-1} \quad (4)$$

Figure 5 shows the Φ_{dec} values plotted as a function of BDE(C−X) of PP-X. As a decrease of the BDE value, the Φ_{dec} value tends to increase, but with PP-X having C−O bonds, the Φ_{dec} value shown as an open circle in Figure 5 gradually increases compared to those of others plotted as a closed circle.

By using eq 4, best-fitted values of E_{RT} and β were obtained to be 114.5 kcal mol^{-1} and 0.0023 for one group of PP-Xs (X = OH, OMe, and OPh) and 67.6 kcal mol^{-1} and 0.0822 for the other group of PP-Xs (X = Br, Cl, SH, and SPh). The calculated curves from the best-fitted values follow the plots of quantum yields for photodecomposition of PP-X in the triplet excited state well, indicating that the decomposition in the triplet excited state is due to C−X bond cleavage in the T_R states.



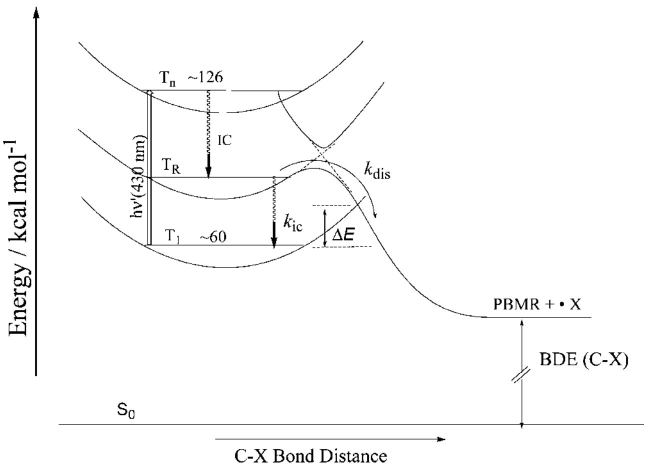
The different E_{RT} values indicate that PP-X has, at least, two channels for β-bond dissociation of PP-X in the T_n states. The energy level of the T_R thus estimated (ca. 68 kcal mol^{-1}) for PP-Xs (X = Br, Cl, SH, and SPh) will correspond to that of the $T_2(n,\pi^*)$ of PP-X because it is as large as the lowest n,π^* triplet energy level (73−74 kcal mol^{-1}) of acetophenone derivatives.[50,51] Conversely, the energy level (ca. 115 kcal mol^{-1}) estimated for PP-Xs (X = OH, OMe, and OPh), which corresponds to 248-nm photon energy, may be responsible to PP-Xs in the T_n state with n over 2. Unfortunately, the electronic character cannot be definite in the present work. Elucidation that α-bond cleavage in PP-X is inefficient in the decomposition of PP-X in the T_n state is described in the Supporting Information.

The quantum yields, Φ_{dec}, for decomposition of PP-X in the triplet excited state can be regarded to be corresponding to those (Φ_{dis}) for the C−X bond dissociation in the T_R state since the triplet biradical, $^3(\text{PBMR} + {}^{\bullet}\text{X})_{cage}$ in the solvent cage, which are formed upon C−X bond cleavage in the T_R state, is free of geminate recombination. The residual quantum yield, $1 - \Phi_{dis}$ must correspond to that for internal conversion, Φ_{ic}, from T_R to the T_1 state with a rate, k_{ic}, that should be competitive with the dissociation rate, k_{dis}. In the present work, the lifetime of the dissociative T_R state cannot be determined. The C−X bond rupture in the T_R state seemed to occur within the pulse duration (ca. 5 ns) of the second 430-nm laser irradiation. Considering the general rate of internal conversion processes in the triplet manifolds in solution, the magnitude will be as large as 10^{12} s^{-1}.[1] Therefore, the k_{dis} value of PP-X can be estimated to be equivalent to that of k_{ic} (10^{12} s^{-1}).

β-Bond Dissociation Mechanism of PP-X in the T_n State. A schematic energy diagram of PP-X in the triplet excited states along with the β-cleavage pathway is depicted in Scheme 2. Upon 430-nm laser photolysis of PP-X in the $T_1(\pi.\pi^*)$ state, that in a higher triplet excited state, T_n, at an energy level of 126 kcal mol^{-1} is formed. The molecule in the T_n state will deactivate through internal conversion to a dissociative state, T_R. It was 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.[56] The electronic configuration of the dissociative state, which strongly interacts with the $T_2(n,\pi^*)$ state of PP-X, is $^3(\pi,\sigma^*)$ of the C−X bond of PP-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 β-bond dissociation proceeds without activation energies from the T_R state along the corresponding dissociative surface.

In the present study, we have systematically varied the heteroatoms of the C−X bond and the substituted group of PP-X. On the basis of the relationship between the Φ_{dec} and BDE values (eq 4), it is shown that the p-phenylphenacyl (PP) moiety is equipped with dual channels for β-cleavage of PP-X in the T_n states. The E_{RT} value (ca.115 kcal mol^{-1}) for PP-X having a C−O bond will be equivalent to a photon energy of 530-nm light as the second laser pulse plus the triplet energy (ca. 60 kcal mol^{-1}). It is considered that if we could use a longer wavelength laser pulse than 530 nm, β-cleavage of PP-X (X = OH, OMe, and OPh) might not occur upon excitation of the triplets. By replacing the O atom of PP-X (X = OH, OMe, and OPh) with an S atom, the channel for β-cleavage will change to one for PP-X (X = SH and SPh) at the lower energy level (E_{RT} = ca. 68 kcal mol^{-1}). It is crucial to reveal the mechanism of switching the channel by changing the leaving group. However, we have no ideas to solve this issue at present.

SCHEME 2: A Schematic Energy Diagram of PP-X in the Triplet Excited States, Including a β-Cleavage Pathway



On the other hand, we have observed that PP-X deactivates in the triplet excited states decayed to the corresponding PP-X in the ground state without breaking the β-bond. The absence of bond rupture indicates the presence of an activation energy (ΔE) from the $T_1(\pi,\pi^*)$ state to a $^3(\sigma,\sigma^*)$ dissociative potential. As we expected, PP-Xs (X = OPh and SPh) in the π,π^* triplet excited states are free of quenching by the β-phenyl ring. One of the aims in the present work was to elucidate how the BDE of the C−X bond affects the reactivity toward β-cleavage in the T_1 state. Unfortunately, because of the absence of chemical reactions in the T_1 state, we were unable to make clear the relationship.

Conclusion

By means of single-color and stepwise two-color two-laser photolysis techniques, photochemical profiles of PP-X in the excited states have been investigated. It seemed that β-bond dissociation of PP-Xs (X = Br, SH, and SPh) proceeds in the S_1 state. No photochemical reactions occur in the T_1 state of PP-X used in the present study. The 430-nm Laser photolysis of PP-X in the T_1 state demonstrates that PP-X in the T_n state undergoes decomposition with definite quantum yields, Φ_{dec}, via a single photonic process. According to eq 4, the obtained Φ_{dec} values are successfully related to the BDE(C−X), indicating that photodecomposition of PP-X in the T_1 state is due to β-cleavage of PP-X. The mechanism for the β-cleavage of PP-X in the T_n states is interpreted in terms of avoided crossing of the T_R state with a dissociative potential surface. From the different E_{RT} values determined for PP-X, it is inferred that reaction channels for β-cleavage of PP-X in the T_n states depend on the type of heteroatoms of the C−X bond on the leaving group. From the systematic investigation of photodecomposition of PP-X in the T_n state, it is noteworthy that the T_n states have the potential to provide various channels for photochemical reactions although we have no evidence to explain the mechanism for the switching of the reaction channels for β-cleavage of PP-X.

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Supporting Information Available: The transient absorption spectra after depletion of PP-Xs (X = Br, SH, and SPh) in the T_1 state upon 266-nm laser flash photolysis, absorption spectral properties of the radicals produced by β-cleavage, heats of formation for determining the BDE by eq 1, and elucidation for the possibility of α-cleavage. This material is available free of charge via the Internet at http://pubs.acs.org.

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