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Photoinduced ω-Bond Dissociation in the Higher Excited Singlet (S_2) and Lowest Triplet (T_1) States of a Benzophenone Derivative in Solution

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Photochemical properties of photoinduced ω-bond dissociation in *p*-benzoylbenzyl phenyl sulfide (BBPS) in solution were investigated by time-resolved EPR and laser flash photolysis techniques. BBPS was shown to undergo photoinduced ω-bond cleavage to yield the *p*-benzoylbenzyl radical (BBR) and phenyl thiyl radical (PTR) at room temperature. The quantum yield (Φ_{rad}) for the radical formation was found to depend on the excitation wavelength, i.e., on the excitation to the excited singlet states, S_2 and S_1 of BBPS; $\Phi_{rad}(S_2) = 0.65$ and $\Phi_{rad}(S_1) = 1.0$. Based on the CIDEP data, these radicals were found to be produced via the triplet state independent of excitation wavelength. By using triplet sensitization of xanthone, the efficiency (α_{rad}) of the C−S bond fission in the lowest triplet state (T_1) of BBPS was determined to be unity. The agreement between $\Phi_{rad}(S_1)$ and α_{rad} values indicates that the C−S bond dissociation occurs in the T_1 state via the S_1 state due to a fast intersystem crossing from the S_1 to the T_1 state. In contrast, the wavelength dependence of the radical yields was interpreted in terms of the C−S bond cleavage in the S_2 state competing with internal conversion from the S_2 to the S_1 state. The smaller value of $\Phi_{rad}(S_2)$ than that of $\Phi_{rad}(S_1)$ was proposed to originate from the geminate recombination of singlet radical pairs produced by the bond dissociation via the S_2 state. Considering the electronic character of the excited and dissociative states in BBPS showed a schematic energy diagram for the ω-bond dissociation of BBPS.

Introduction

Aromatic carbonyl compounds, such as benzophenone and acetophenone have been widely studied to understand the mechanism of bimolecular photochemical processes in condensed phase such as H-atom, electron and energy transfer reactions since they are essential processes in photochemistry and photobiochemistry.[1−3] The photophysical processes of benzophenone are well understood through pico- and nanosecond time-resolved measurements.[4] The energy level of the lowest excited singlet state, $S_1(n,\pi^*)$ is very close to that of the second lowest excited triplet state, T_2 (π,π^*),[1] which provides a fast intersystem crossing, according to the El-Sayed rule, to produce the lowest excited triplet state, $T_1(n,\pi^*)$ within 10 ps.[4] Therefore, the T_1 state is usually reactive for bimolecular reactions via a diffusion process in solution. A large number of studies on bimolecular reactions of triplet benzophenones in solution have been performed.[1−3,6−8]

On the other hand, as a unimolecular photoreaction of aromatic carbonyl compounds, photoinduced bond cleavage, namely, Norrish type I and II reactions where carbon−carbon bond fission occurs at the α and β positions of the carbonyl, respectively, has been widely subjected.[9−20] However, little photochemical investigation of bond dissociation in benzophenone derivatives where α and β bonds are both absent has been reported. By means of product analysis, Wagner et al. studied photodecomposition mechanisms of *p*-halobenzophenones originated from the halide−carbon bond cleavage[21] when the formation of the benzoylbenzene radical was expected. Necker et al. studied photodecomposition processes of *tert*-butyl aroylperbenzoates and observed the formation of the benzoylbenzene radical by means of the ultrafast transient spectroscopy.[22] Recently, two-color two-laser flash techniques were successfully applied to cleave carbon−oxygen and carbon−silicon bonds of benzophenone derivatives which are inert to one-photon excitation.[23] In our previous papers, by using chemically induced dynamic electron polarization (CIDEP) and laser photolysis techniques, a new-type photoinduced homolytic bond cleavage which occurs neither at the α nor β positions, but at the position far of a carbonyl group, i.e., the ω position, in benzophenone derivatives was reported.[24,25] ω-Bond cleavage of benzophenone derivatives having C−S, C−Cl, and C−Br bonds was characterized to occur mainly in the $T_1(n,\pi^*)$ state. In general, for the occurrence of bond dissociation in excited states, the enthalpy of the cleaving bond must be smaller than the excited energy of the reactive excited state. The estimated bond enthalpies for the breaking C−Cl, C−S, and C−Br bonds in the benzophenone derivatives were smaller than the corresponding triplet energies,[24,25] whereas *p*-hydroxymethylbenzophenone having an enthalpy for the C−O bonding larger than the triplet energy was indeed inert to photoexcitation.[24] Interestingly, with a benzophenone having the C−Br bond, the $S_1(n,\pi^*)$ state was also shown to be reactive for ω cleavage.[25] It seemed that the spin multiplicity and electronic character of the excited states

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reactive for ω cleavage may be closely related to the breaking bond enthalpy and nature of dissociative energy potentials.

In the present work, based on CIEDP and transient absorption measurements, we show a reaction profile of photoinduced ω-bond dissociation in *p*-benzoylbenzyl phenyl sulfide (BBPS) which provides a clear dissociation yield dependence on the excitation wavelength. The novel wavelength dependence was interpreted by considering the ω-cleavable $S_2(\pi,\pi^*)$ state of BBPS competing with an internal conversion from the S_2 to the S_1 state, in contrast to the efficiently dissociative $T_1(n,\pi^*)$ state.

Experimental Section

p-Benzoylbenzyl phenyl sulfide (BBPS) was synthesized by the reaction of *p*-bromomethyl benzophenone (Aldrich) with thiophenol in the presence of K_2CO_3 in acetone. BBPS was purified by repeated recrystallizations from hexane. Acetonitirile (ACN), methanol, ethanol, and butyronitrile were distilled for purification. Diethyl ether (spectroscopy grade, Kanto) and isopentane (spectroscopy grade, Fluka) were used as supplied. ACN and butyronitrile were used as the solvents at 295 K, whereas EPA (diethyl ether-isopentane-ethanol, 5:5:2 v/v/v) and a mixture of methanol and ethanol (1:1 v/v) were used as matrixes at 77 K. Absorption and emission spectra were recorded on a U-best 50 spectrophotometer (JASCO) and a Hitachi F-4010 fluorescence spectrophotometer, respectively.

Time-resolved EPR measurements were carried out by using an X-band EPR spectrometer (Varian E−109E) without magnetic field modulation as reported previously.[26] Third harmonics (355 nm) of a Nd:YAG laser (Continuum Minilite, 6mJ, 15 Hz) and a XeCl excimer laser (Lumonics HyperEx 400, 10 Hz) were used as pulsed light sources. Sample solutions for the CIDEP measurements were constantly deoxygenated by argon gas bubbling and flowed into a quartz cell in the EPR resonator.

All of the samples for transient absorption measurements were degassed in a quartz cell with a 1 cm path length by several freeze−pump−thaw cycles on a high vacuum line. The concentration of BBPS for direct laser photolysis was adjusted to achieve the optical density at the excitation wavelength (266 or 355 nm) being ca. 0.7 in ACN. Transient absorption measurements were carried out at 295 K unless noted, or in the temperature range between −22 and 57 °C. The temperature of the sample in a quartz dewar was kept with hot water (> 295 K) or a mixture of methanol and liquid nitrogen (<295 K) within a precision of ±0.5 °C during the measurement. A XeCl excimer laser (308 nm, Lambda Physik, Lextra 50) and third (355 nm) and fourth harmonics (266 nm) of a Nd^{3+}:YAG laser (JK Lasers HY-500; pulse width 8 ns) were used as light sources for flash photolysis. The number of the repetition of laser pulsing in a sample was less than four pulses to avoid excess exposure. The details of the detection system for the time profiles of the transient absorption have been reported elsewhere.[27] The transient data obtained by laser flash photolysis was analyzed by using the least-squares best-fitting method. The transient absorption spectra were taken with a USP-554 system from Unisoku with which one can take a transient absorption spectrum with one-shot laser pulse.

Results and Discussion

Figure 1 shows absorption and phosphorescence spectra of BBPS in ACN at 295 K and in a glass matrix of a mixture of methanol and ethanol (1:1 v/v) at 77 K, respectively.

The profiles of both spectra are similar to those of benzophenone. The absorption band at 260 nm having a molar absorption coefficient of the order of 10^4 dm^3 mol^{-1} cm^{-1} can be classified to be the $S_2(\pi, \pi^*)$ absorption band, whereas that at 350 nm can be assigned to the $S_1(n, \pi^*)$ band. It was confirmed that the phosphorescence excitation spectrum of BBPS agreed well with the corresponding absorption spectrum. The energy level of the lowest triplet (T_1) state of BBPS was determined to be 68.4 kcal mol^{-1} from the phosphorescence origin, which is close to that of benzophenone (69.1 kcal mol^{-1}).[28] From the similarity in vibrational structures of the phosphorescence spectrum of BBPS to those of benzophenone, it is inferred that the electronic character of the T_1 state of BBPS is of n,π^*.

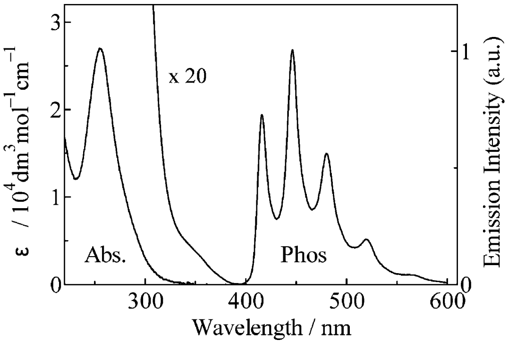


Figure 1. Absorption spectra of BBPS in ACN at 295 K and a phosphorescence spectrum of BBPS in a mixture of methanol and ethanol (1:1 v/v) at 77 K.

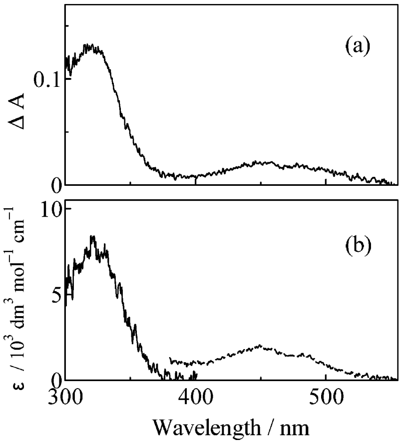
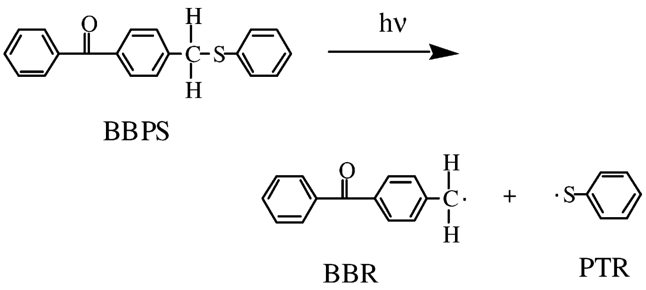


Figure 2. (a) Transient absorption spectra observed at 500 ns after 266 nm laser pulsing in an ACN solution of BBPS at 295 K. (b) Reference absorption spectra of BBR (solid line) and PTR (broken line) in ACN.

The absorption spectrum of BBPS was almost the same as a superposition of those of *p*-methylbenzophenone (MBP) and thioanisol (TA). The molar absorption coefficient (ϵ) of BBPS at 266 nm was 20 000 dm^3 mol^{-1} cm^{-1}, whereas those of MBP and TA were 17 300 and 2800 dm^3 mol^{-1} cm^{-1} at 266 nm, respectively. A sum of ϵ values of MBP and TA at 266 nm is close to that of BBPS, indicating that electronic conjugation between the benzoylbenzyl and phenyl thiyl moiety in BBPS is appreciably negligible. Therefore, it can be considered that, upon 266 nm photolysis of BBPS, the benzoylbenzyl moiety mainly absorbs the light. Figure 2a shows a transient absorption spectrum observed at 100 ns after 266 nm laser pulsing in the degassed ACN solutions of BBPS at 295 K, whereas Figure 2b displays reference absorption spectra of the *p*-benzoylbenzyl radical (BBR) having a molar absorption coefficient (ϵ) of 7600 ± 400 dm^3 mol^{-1} cm^{-1} at 320 nm[24] and the phenyl thiyl radical (PTR; $\epsilon = 2000 \pm 100$ dm^3 mol^{-1} cm^{-1} at 450 nm).[29]

The obtained transient absorption spectrum can be reproduced by using those of BBR and PTR in a 1:1 concentration ratio, indicating that BBPS undergoes photoinduced ω-bond dissociation to produce BBR and PTR.



Upon 355 and 308 nm laser photolysis of BBPS in ACN, it was confirmed that a transient absorption spectrum of PTR appeared. Observation of BBR in transient absorption at 320 nm was impossible due to the large ground-state absorption of BBPS in the wavelength region shorter than 350 nm.

The quantum yield (Φ_{rad}) of the radical formation upon laser pulsing of BBPS was determined with the use of eq 1

$$\Phi_{rad} = \Delta A_{450} \epsilon_{450}^{-1} I_{abs}^{-1} \tag{1}$$

where ΔA_{450}, ϵ_{450}, and I_{abs} are respectively the absorption change at 450 nm due to radical formation at 100 ns after laser pulsing, the molar absorption coefficient of PTR at 450 nm (2000 dm^3 mol^{-1} cm^{-1}),[29] and the number of the photon flux of a laser pulse at the excitation wavelength. The quantity of I_{abs} was determined by using the absorption of triplet benzophenone (BP) in ACN as an actinometer[30]

$$\Delta A_T^{BP} = \epsilon_T^{BP} \Phi_{ISC}^{BP} I_{abs} \tag{2}$$

where ΔA_T^{BP}, ϵ_T^{BP}, and Φ_{ISC}^{BP} are, respectively, the initial absorbance at 525 nm for the formation of triplet benzophenone obtained immediately after laser pulsing, the molar absorption coefficient of triplet BP at 525 nm in ACN (6500 dm^3 mol^{-1} cm^{-1}),[31] and triplet yield of benzophenone (1.0).[28] By using eqs 1 and 2, the Φ_{rad} values were determined to be 0.65 ± 0.03, 0.64 ± 0.03, and 1.0 ± 0.03 upon 266, 308, and 355 nm laser photolyses, respectively. The wavelengths of 266 and 308 nm are located in the S_2 absorption band of BBPS, whereas 355 nm light is absorbed by the S_1 band. The obtained results clearly indicate that the Φ_{rad} value does depend on the excitation wavelength or absorption bands of BBPS ($\Phi_{rad}(S_2) = 0.65$ and $\Phi_{rad}(S_1) = 1.0$). It was confirmed that the $\Phi_{rad}(S_2)$ and $\Phi_{rad}(S_1)$ values are independent of the ambient temperatures from −22 to 57 °C.

Figure 3 shows the time-resolved EPR spectrum observed at 500 ns after 355 nm laser pulsing in a butyronitrile solution of BBPS (0.1 mol dm^{-3}) at 295 K and simulated one.

The CIDEP spectrum with the triplets of triplet was well reproduced by the computer simulation with a g value of 2.0026 and the splitting constants of $a^H(CH_2) = 1.537$, $a^H(o\text{-H}) = 0.467$ and $a^H(m\text{-H}) = 0.176$ mT for BBR (see inset in Figure 3). The EPR parameters obtained are close to those of the BBR reported previously ($a^H(CH_2) = 1.52$, $a^H(o\text{-H}) = 0.50$, $a^H(m\text{-H}) = 0.175$ mT, and $g = 2.0029$).[25] Therefore, the hyperfine structure observed is shown to arise from BBR produced upon ω-bond cleavage of BBPS. The counter radical, PTR was hard to detect in fluid solutions, presumably, the EPR signal of PTR may show remarkable broadening due to the spin−orbit interaction. Quite the same CIDEP spectrum was obtained upon 308 nm laser excitation. The net-emissive CIDEP spectrum observed due to the triplet mechanism clearly suggests that the free radicals, BBR and PTR, obtained in the nanosecond time domain are generated via the triplet state of BBPS independent of the photoexcited absorption bands (S_1 and S_2).

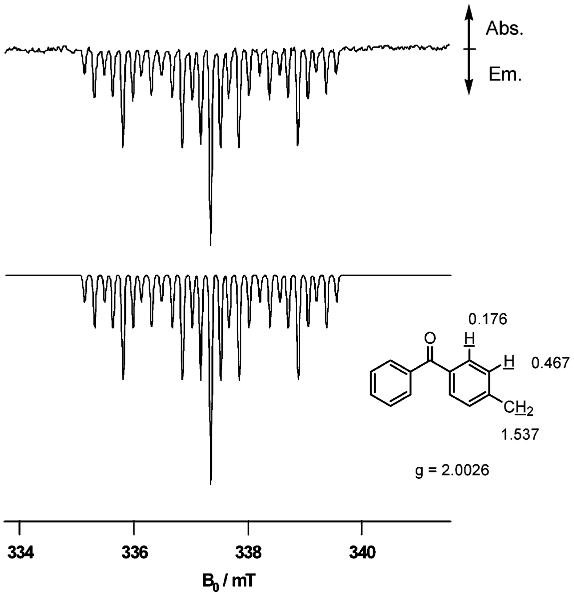


Figure 3. Time-resolved EPR spectrum obtained at 500 ns after 355 nm laser pulsing in the butyronitrile solution of BBPS (0.1 mol dm^{-3}) at 295 K (upper) and the simulated one (lower) with the splitting constants shown herein.

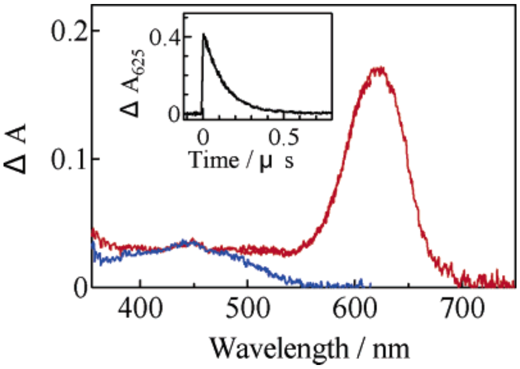


Figure 4. Transient absorption spectra obtained at 100 ns (red line) and 720 ns (blue line) upon 355 nm laser photolysis of a XT (0.01 mol dm^{-3})/BBPS (8.0 × 10^{-4} mol dm^{-3}) system in ACN. Inset; a temporal absorbance change at 625 nm for triplet XT.

To investigate photochemical profiles in the triplet state of BBPS, triplet sensitization by using xanthone (XT) was carried out by transient absorption measurements. The triplet energy of XT (74.0 kcal mol^{-1})[28] larger than that of BBPS (68.7 kcal mol^{-1}) enables efficient triplet energy transfer. Transient absorption spectra at 100 and 720 ns after 308 nm laser pulsing in a XT (0.01 mol dm^{-3})/BBPS (8.0 × 10^{-4} mol dm^{-3}) system is shown in Figure 4.

The transient absorption at 100 ns is due to triplet XT.[32] The intensity of the absorption at 625 nm for triplet XT decreases with a first-order rate of 1.0 × 10^7 s^{-1}, giving the absorption spectrum of PTR at 720 ns. These observations indicate that the C−S bond cleaves in the triplet state of BBPS immediately after triplet energy is transferred from triplet XT to BBPS. The observed rates (k_{obsd}) for the decay of triplet XT are plotted as a function of the concentration of BBPS, [BBPS] in Figure 5a.

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

$$k_{obsd} = k_0 + k_q[\text{BBPS}] \tag{3}$$

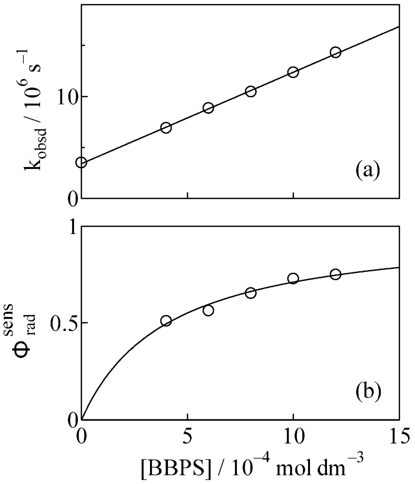


Figure 5. (a) Rate (k_{obsd}) for the decay of triplet XT plotted against [BBPS] upon 355 nm laser photolysis in XT (0.01 mol dm^{-3})/BBPS systems in ACN at 295 K. (b) Plots of the quantum yields (Φ_{rad}^{sens}) for radical formation vs [BBPS] upon 355 nm laser photolysis in XT (0.01 mol dm^{-3})/BBPS systems in ACN at 295 K. The solid curve was calculated by eq 5.

where k_0 and k_q respectively represent the decay rate of triplet XT in the absence of BBPS and the rate constant for quenching of triplet XT by BBPS. From the intercept and slope of the line, the values of k_0 and k_q were determined to be 3.5 × 10^6 s^{-1} and 8.6 × 10^9 dm^3 mol^{-1} s^{-1}.

The quantum yield (Φ_{rad}^{sens}) for the formation of BBR and PTR from BBPS upon triplet sensitization was determined by

$$\Phi_{rad}^{sens} = \Delta A_{450}\epsilon_{450}{}^{-1}I_{abs}{}^{-1} \qquad (4)$$

where ΔA_{450} and ϵ_{450} are the maximum absorption change due to the formation of PTR at 450 nm and the molar absorption coefficient change of PTR at 450 nm (2000 dm^3 mol^{-1} cm^{-1}).[29] The value of I_{abs} at 355 nm was determined by eq 2. The obtained values of Φ_{rad}^{sens} for the XT-BBPS system are plotted as a function of [BBPS] in Figure 5b. The Φ_{rad}^{sens} value increases nonlinearly with increasing [BBPS]. On the other hand, the Φ_{rad}^{sens} value is related with the kinetic parameters, k_0 and k_q by

$$\Phi_{rad}^{sens} = k_q[\mathrm{BBPS}]\alpha_{rad}\alpha_{TET}\,\Phi_{ISC}^{XT}(k_0 + k_q[\mathrm{BBPS}])^{-1} \quad (5)$$

where α_{BBR}, α_{TET}, and Φ_{ISC}^{XT} are the efficiencies for the radical formation in the triplet state of BBPS and triplet energy transfer from triplet XT to BBPS, and the triplet yield of XT (1.0),[28] respectively. By best-fitting eq 5 to the experimental values of Φ_{rad}^{sens} with the use of the k_0 and k_q values obtained above, the product value of α_{rad} and α_{TET} was obtained to be 1.0 ± 0.05. This value indicates that those of α_{rad} and α_{TET} are both close to unity. The quantum yield ($\Phi_{rad}(S_1)$) of radical formation upon 355 nm laser photolysis has been determined to be unity. The agreement of the determined α_{rad} value with that of $\Phi_{rad}(S_1)$ indicates that the cleavage of the C−S bond upon the S$_1$ band excitation of BBPS proceeds in the T$_1$ state produced by an efficient intersystem crossing from the S$_1$ state having a quantum yield (Φ_{ISC}) of unity.

The lifetime of triplet BBPS at 295 K was estimated by means of a Stern−Volmer type analysis, employing 1-methylnaphthalene (MN) as a triplet quencher for 355 nm laser photolysis of BBPS in ACN. This method has been widely used for characterizing short-lived triplet states.[14d,14e,15] The transient absorption having the maximum absorption at 417 nm due to triplet MN can be readily detected as a consequence of triplet energy transfer from triplet BBPS according to eq 6

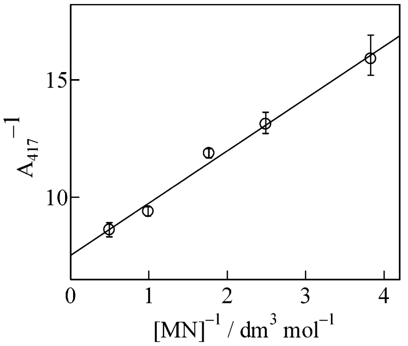


Figure 6. Plots according to eq 7 for quenching of triplet BBPS by 1-methylnaphthalene (MN).

$$^3\mathrm{BBPS}^* + \mathrm{MN} \xrightarrow{k_q} \mathrm{BBPS} + {}^3\mathrm{MN}^* \qquad (6)$$

The absorbance at 417 nm (ΔA_{417}) of triplet MN produced by triplet energy transfer is related to the Stern−Volmer constant according to eq 7

$$\Delta A_{417}{}^{-1} = \kappa + \frac{\kappa}{k_q\tau_T}[\mathrm{MN}]^{-1} \qquad (7)$$

where k_q, τ_T, and κ are respectively the quenching rate constant of triplet BBPS by MN, the lifetime of triplet BBPS, and a constant incorporating experimental factors as well as the molar absorption coefficient of triplet MN. Figure 6 shows the plots of the reciprocal of ΔA_{417} obtained by 355 nm laser photolysis of a BBPS (6.1 × 10^{-3} mol dm^3)/MN system as a function of [MN]$^{-1}$.

The plots give a straight line, giving an intercept of 7.52 and a slope of 2.23 mol dm^{-3}. Thus, the Stern−Volmer constant ($k_q\tau_T$) is determined to be 3.37 dm^3 mol^{-1}. By using the k_q value obtained for the quenching of triplet benzophenone by MN in ACN (8.4 × 10^9 dm^3 mol^{-1} s^{-1}),[33] the τ_T value is determined to be 400 ps, which is shorter than those of *p*-mercaptomethylbenzophenone (1.8 ns)[24] and *p*-chloromethylbenzophenone (1.1 ns),[25] whose triplet states are both reactive for ω-bond dissociation at room temperature. We have determined the quantum yield of the C−S bond dissociation via the T$_1$ state of BBPS to be 1.0 at 295 K. Thus, the rate, $k_{dis}(T_1)$, for the C−S bond cleavage leading to the radical formation is estimated to be 2.5 × 10^9 s^{-1} by using eq 8

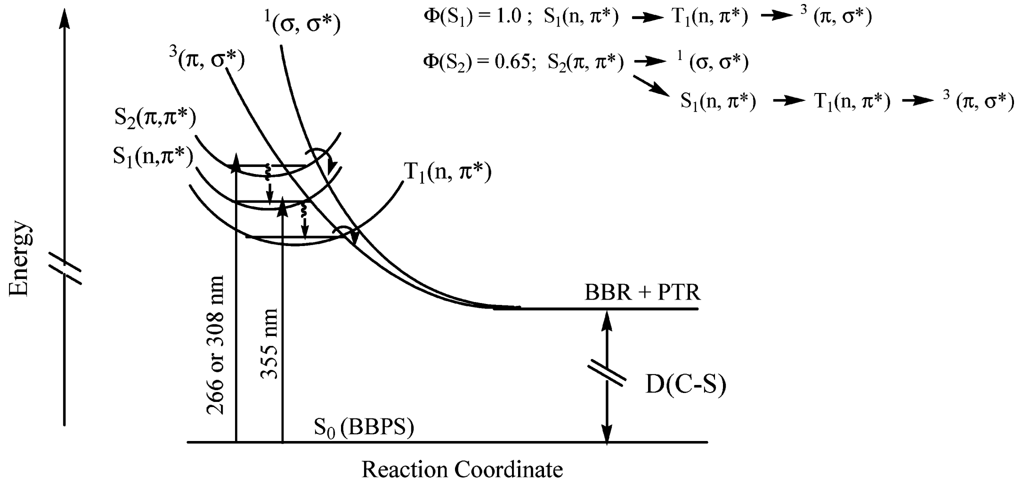
$$k_{dis}(T_1) = \Phi_{dis}\tau_T{}^{-1} \qquad (8)$$

The enthalpy of the C−S bond of BBPS, D(C−S), was obtained on the basis of the heat of formation ($\Delta_f H$) for BBPS, BBR, and PTR computed by using a semiempirical PM3 program contained in *MOPAC '97*, being $\Delta_f H$(BBPS) = 45.9 kcal mol^{-1}, $\Delta_f H$(BBR) = 42.1 kcal mol^{-1}, and $\Delta_f H$(PTR) = 56.1 kcal mol^{-1} The D(C−S) value is calculated to be 52.7 kcal mol^{-1} by using eq 9

$$\Delta_f H(\mathrm{BBPS}) = \Delta_f H(\mathrm{BBR}) + \Delta_f H(\mathrm{PTR}) - D(\mathrm{C{-}S}) \quad (9)$$

The obtained value of D(C−S) is substantially smaller than that (60.9 kcal mol^{-1}) of *p*-mercaptomethylbenzophenone (MMBP).[24] This may be due to the stabilization energy enhanced from π delocalization in PTR. The efficiency (α_{rad}) for ω dissociation of triplet MMBP was reported to be ca. 0.5,[24] which is half

SCHEME 1: Energy Diagram of Photoexcited BBPS Including the C−S Bond Cleavage Processes.



smaller than that for triplet BBPS. From the relationship between D(C−S) and α_{rad}, it is inferred that the ω-cleavage efficiency increases with a decrease of the bond energy. In contrast to MMBP, although the bond enthalpy (D(C−Br) = 53.0 cal mol^{-1})[25] for ω fission of the C−Br bond in *p*-bromomethylbenzophenone (BMBP) is close to D(C−S) for BBPS, the α_{rad} (0.53)[25] for BMBP is half as large as that for BBPS. It is noteworthy that the ω-dissociation efficiency in the triplet state seems to depend on not only the bond energy but also the leaving groups.

Based on the obtained results, a schematic energy diagram of photoexcited BBPS is depicted in Scheme 1 including the C−S bond cleavage processes.

Since the absorption and phosphorescence spectra of BBPS are similar to those of benzophenone, electronic character, ordering, and energy levels of excited states of BBPS seem to be similar of those of benzophenone. The dissociation profile in the excited states of BBPS can be interpreted to be a thermally activated crossing with dissociative potential surfaces leading to free radicals.[34] The electronic configurations of the pertinent dissociative potentials are of π,σ^* and π,π^*, and the energy level of the former would be located lower than that of the latter at a reaction coordinate. According to a crossing rule, excited states of π,π^* would correlate with a σ,σ^* state which leads to a pair of σ radicals, whereas those of n,π^* would interact with a π,σ^* state.[35] With respect to BBPS, the $T_1(n,\pi^*)$ interacts with a triplet π,σ^* potential for the C−S antibonding without an apparent activation energy since $\Phi_{rad}(S_1)$ was found to be independent of the ambient temperature. When the C−S bond dissociates in the triplet state of BBPS, a triplet π,σ radical pair, $^3(\text{BBR} + \text{PTR})_{cage}$, of BBR and PTR may be initially produced in a solvent cage according to the spin conservation rule. The triplet radical pair escapes from the solvent cage without geminate recombination which requires that the spin-multiplicity of the radical pair is changed from triplet to singlet via intersystem crossing, resulting in efficient formation of free radicals, BBR and PTR, since the rate of escaping from the solvent cage is considered to be much larger than that of intersystem crossing at 295 K. From the agreement between α_{rad} and $\Phi_{rad}(S_1)$ being unity, the quantum yield for intersystem crossing from the S_1 to the T_1 must be unity. This photophysical property of BBPS is similar to that of benzophenone.[1] Thus, the lifetime of $S_1(n,\pi^*)$ of BBPS would be as short as that of benzophenone (10 ps).[4] The $S_1(n,\pi^*)$ state of BBPS is found to be inefficient for ω cleavage. Due to the fast intersystem crossing of $S_1(n,\pi^*)$ in BBPS (~10^{11} s^{-1}), any singlet π,σ^* potential surfaces for BBPS decomposition would not interact with that of the S_1 state, resulting in the absence of C−S dissociation in the S_1 state.

The Φ_{rad} value for decomposition of BBPS was found to depend on excitation wavelength based on the fact that the $\Phi_{rad}(S_2)$ (= 0.65) was smaller than the $\Phi_{rad}(S_1)$ (= 1.0). The CIDEP signal patterns obtained upon excitation of the S_2 and S_1 bands indicate that the free radicals obtained in the nanosecond time domain were produced by cleavage of the C−S bond in the T_1 state which must be formed via the S_1 state. If the quantum yield of internal conversion from the S_2 to the S_1 state is unity, the $\Phi_{rad}(S_2)$ would have the identical value with that of $\Phi_{rad}(S_1)$. The residual yield ($1 - \Phi_{rad}(S_2)$) should be due to deactivating channels which compete with the internal conversion from the S_2 to the S_1 state. We propose that a plausible process is the C−S bond dissociation in the $S_2(\pi,\pi^*)$ state readily correlated with a dissociative singlet σ,σ^* potential without thermal activation, which leads to the formation of singlet σ radical pairs in solvent cages, $^1(\text{BBR} + \text{PTR})_{cage}$. The singlet pair readily undergoes geminate recombination forming the parent molecule. The half-lifetime of geminate recombination, e.g., for PTR, was reported to be ca. 10~40 ps in solution.[36] Therefore, the geminate recombination between BBR and PTR would be an event during the laser pulse duration (~8 ns) in the present system. The residual yield ($1 - \Phi_{rad}(S_2)$) of 0.35 would be responsible for ω dissociation in the S_2 state followed by the geminate recombination. The dissociation rate ($k_{dis}(S_2)$) in the S_2 state would be as large as that of internal conversion from the S_2 state to the T_1 state being in the magnitude of 10^{12} s^{-1}. It is noteworthy that the $k_{dis}(S_2)$ is substantially larger than that ($k_{dis}(T_1) = 2.5 \times 10^9$ s^{-1}) in the T_1 state. The difference in these cleavage rates may be attributed to that of electronic character and spin multiplicity of the crossing potential surfaces.

Conclusion

By means of time-resolved EPR and laser flash photolysis techniques, BBPS was shown to undergo ω-bond cleavage to yield BBR and PTR at room temperature in solution. The Φ_{rad} value was found to depend on the excitation wavelength. CIDEP signals originated from BBR formation via the triplet state were obtained upon both the S_2 and S_1 bands excitation. By using triplet sensitization of xanthone, the efficiency, α_{rad}, of the C−S bond fission in the T_1 state of BBPS was determined to be unity. The agreement between $\Phi_{rad}(S_1)$ and α_{rad} values indicates that the C−S bond dissociation occurs in the T_1 state via the S_1

state due to a fast intersystem crossing from the S_1 to the T_1 state. In contrast, the cleavage of the C−S bond upon excitation to the S_2 state was concluded to be competition with internal conversion from the S_2 to the S_1 state. The excitation wavelength dependence of the reaction yields upon photoexcitation of BBPS is unusual in the photochemistry of organic compounds in solution which should obey the Kasha's rule. The rate of ω cleavage and free radical yields seem to depend on the electronic character and spin multiplicity of the excited state and correlating dissociative potential surfaces. The smaller bond energy at the ω position than the triplet energy is indeed necessary for occurrence of ω dissociation, but the radical yields via the triplet state seem to be dependent not only on the bond energy value but also on the kind of leaving groups. By knowing these photochemical properties, we may be able to design a benzophenone derivative having a useful leaving group at the ω position in the role of a good photoinduced radical generator.

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Supporting Information Available: Absorption spectra of BBPS, *p*-methylbenzophenone, and thioanisol. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publishing Co.: Menlo Park, CA, 1978. (b) Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*, forwarded by Wagner, P. J.; Blackwell Scientific Publications: Oxford, U.K., 1991.

(2) Hoshino, M.; Shizuka, H. *Photoinduced Electron Transfer*; Fox, M. A., Chanon, N., Eds.; Elsevier: Amsterdam, 1988; part C, p 313, and references therein.

(3) Hoshino, M.; Shizuka, H. *New Aspects of Radiation Curing in Polymer Science and Technology*; Foussier, J. P., Rabek, J. F., Eds.; Elsevier: London, 1993; Vol. 2, p 638, and references therein.

(4) (a) Anderson, R. W., Jr.; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. *J. Chem. Phys.* **1974**, *61*, 2500. (b) Anderson, R. W., Jr.; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. *Chem. Phys. Lett.* **1978**, *28*, 153. (c) Damschen, D. E.; Merritt, C. D.; Perry, D. L.; Scott, G. W.; Telly, L. D. *J. Phys. Chem.* **1978**, *82*, 2268.

(5) Arouris, P.; Gelbart, W. M.; El-Sayed, M. A. *Chem. Rev.* **1977**, *77*, 793.

(6) Shizuka, H.; Yamaji, M. *Bull. Chem. Soc. Jpn. (Acc.)* **2000**, *73*, 267 and references therein.

(7) Bobrowski, K.; Marciniak, B.; Hug, G. L. *J. Photochem. Photobiol. A: Chem.* **1994**, *81*, 159.

(8) Hug, G. L.; Bobrowski, K.; Kozubek, H.; Marciniak, B. *Photochem. Photobiol.* **2000**, *72*, 1.

(9) (a) Shizuka, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2343. (b) Shizuka, H.; Tanaka, I. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 52.

(10) (a) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168. (b) Wagner, P. J.; Lindstrom, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 3062.

(11) Grunwell, J. R.; Marron, N. A.; Hanhan, S. *J. Org. Chem.* **1973**, *38*, 1559.

(12) Lewis, F. D.; Hoyle, C. H.; Magyar, J. G. *J. Org. Chem.* **1975**, *40*, 488.

(13) Brunton, G.; McBay, H. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1977**, *99*, 4447.

(14) (a) Scaiano, J. C.; Perkins, M. J.; Sheppard, J. W.; Platz, M. S.; Barcus, R. L. *J. Photochem.* **1983**, *21*, 137. (b) Netto-Ferreira, J. C.; Leigh, W. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 2617. (c) Scaiano, J. C.; Netto-Ferreira, J. C. *J. Photochem.* **1986**, *32*, 253. (d) McGimpsey, W. G.; Scaiano, J. C. *Can. J. Chem.* **1988**, *66*, 1474. (e) Netto-Ferreira, J. C.; Avellar, I. G. J.; Scaiano, J. C. *J. Org. Chem.* **1990**, *55*, 89. (f) Scaiano, J. C., Netto-Ferreira, J. C.; Wintgens, V. *J. Photochem. Photobiol. A: Chem.* **1991**, *59*, 265.

(15) Leigh, W. J.; Banisch, J.-A. H.; Workentin, M. S. *J. Chem. Soc., Chem. Commun.* **1993**, 988.

(16) Hall, M.; Chen, L.; Pandit, C. R., McGimpsey, W. G. *J. Photochem. Photobiol. A: Chem.* **1997**, *111*, 27.

(17) Kaneko, Y.; Hu, S.; Neckers, D. C. *J. Photochem. Photobiol. A: Chem.* **1998**, *114*, 173.

(18) Jockusch, S.; Landis, M. S.; Beat, F.; Turro, N. J. *Macromolecules* **2001**, *34*, 1619.

(19) (a) Suzuki, T.; Kaneko, Y.; Maeda, K.; Arai, T.; Akiyama, K.; Tero-Kubota, S. *Mol. Phys.* **2002**, *100*, 1469. (b) Suzuki, T.; Kaneko, Y.; Ikegami, M.; Arai, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 801.

(20) (a) Allonas, X.; Lalevée, J.; Fouassier, J.-P. *J. Photochem. Photobiol. A: Chem.* **2003**, *159*, 127. (b) Allonas, X.; Lalevée, J.; Fouassier, J.-P. *J. Photopolym. Sci. Technol.* **2004**, *17*, 29.

(21) (a) Wagner, P. J.; Sedon, J.; Waite, C.; Gudmundsdottir, A. *J. Am. Chem. Soc.* **1994**, *116* 10284. (b) Wagner, P. J.; Waite, C. I. *J. Am. Chem. Soc.* **1995**, *117*, 7388. (c) Wagner, P. J.; Sedon, J. H.; Gudmundsdottir, A. *J. Am. Chem. Soc.* **1996**, *118*, 746.

(22) Shah, B. K.; Neckers, D. C. *J. Am. Chem. Soc.* **2004**, *126*, 1830.

(23) (a) Cai, X.; Sakamoto, M.; Hara, M.; Toji, S.; Yamaji, M.; Kawai, K.; Endo, M.; Fujitsuka, M.; Majima, T. submitted for publication. (b) Cai, X.; Sakamoto, M.; Hara, M.; Iomata, S.; Yamaji, M.; Toji, S.; Kawai, K.; Endo, M.; Fujitsuka, M.; Majima, T. *Chem. Phys. Lett.*, in press.

(24) Yamaji, M.; Yoshihara, T.; Tachikawa, T.; Tero-Kubota, S.; Tobita, S.; Shizuka, H.; Marciniak, B. *J. Photochem. Photobiol. A: Chem.* **2004**, *162*, 513.

(25) Yamaji, M.; Suzuki, A.; Ito, F.; Tero-Kubota, S.; Tobita, S.; Shizuka, H.; Marciniak, B. *J. Photochem. Photobiol. A: Chem.* in press.

(26) Tero-Kubota, S.; Akiyama, K.; Ikoma, T.; Ikegami, Y. *J. Phys. Chem.* **1991**, *95*, 766.

(27) Yamaji, M.; Aihara, Y.; Itoh, T.; Tobita, S.; Shizuka, H. *J. Phys. Chem.* **1994**, *98*, 7014.

(28) Murov, S. L.; Carmichael, I.; Hug, G. *Handbook of Photochemistry*, 2nd ed.; Mercel Dekker: New York, 1993.

(29) Yamaji, M.; Wakabayashi, S.; Ueda, S.; Shizuka, H,; Tobita, S. *Chem. Phys. Lett.* **2003**, *368*, 41.

(30) Yamaji, M.; Sekiguchi, T.; Hoshino, M.; Shizuka, H. *J. Phys. Chem.* **1992**, *96*, 9353.

(31) Bensasson, R. V.; Gramain, J. C. *J. Chem. Soc., Faraday Trans.* **1980**, *76*, 1801.

(32) Okamoto, H.; Yamaji, M.; Satake, K.; Tobita, S.; Kimura, M. *J. Org. Chem.* **2004**, *39*, 7860.

(33) Tanaka, T. Ph.D. Thesis, Gunma University: Gunma, Japan, 1997.

(34) (a) Grimme, S. *Chem. Phys.* **1992**, *163*, 313. (b) Pohlers, G.; Dreeskamp, H.; Grimme, S. *J. Photochem. Photobiol. A: Chem.* **1996**, *95*, 41.

(35) Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41.

(36) (a) Scott, T. W.; Liu, S. N. *J. Phys. Chem.* **1989**, *93*, 1393. (b) Hirata, Y.; Niga, Y.; Ohta, M.; Takizawa, M.; Okada, T. *Res. Chem. Intermed.* **1995**, *21*, 823.