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Journal of Photochemistry and Photobiology A: Chemistry 162 (2004) 513–520

Journal of Photochemistry and Photobiology A:Chemistry

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A new-type photoreaction of a carbonyl compound
Part 1. Photoinduced ω-bond dissociation in *p*-mercaptomethylbenzophenone studied by time-resolved EPR technique, steady-state and laser flash photolyses in solution

Minoru Yamaji [a,1], Toshitada Yoshihara [a], Takashi Tachikawa [b], Shozo Tero-Kubota [b], Seiji Tobita [a], Haruo Shizuka [a], Bronislaw Marciniak [c,*]

[a] *Department of Chemistry, Gunma University, Kiryu 376-8515, Japan*
[b] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan*
[c] *Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6 Street, Poznan 60-780, Poland*

Received 3 June 2003; received in revised form 3 June 2003; accepted 23 September 2003

Abstract

Photodissociation of the carbon–sulfur bond in *p*-mercaptomethylbenzophenone (MMBP) in acetonitrile has been investigated by means of steady-state photolysis, time-resolved EPR and laser photolysis techniques. MMBP undergoes photodecomposition to yield *p*-methylbenzophenone in acetonitrile at 295 K. The initial intermediate due to the photodecomposition of MMBP is revealed to be the *p*-benzoylbenzyl radical (BBR) from the transient absorption and CIDEP measurements. Based on the molar absorption coefficient of BBR, the quantum yield (Φ_{rad}) of the BBR formation upon direct photoexcitation was determined to be 0.49 ± 0.03. Triplet sensitization of MMBP by acetone is performed to study the C–S bond dissociation in the triplet state of MMBP. Based on the quantum yields and rates of the BBR formation upon sensitization of MMBP, the efficiency (α_{dis}) of the C–S bond fission in the triplet state is determined to be 0.51 ± 0.03. The agreement between the Φ_{rad} and α_{dis} values indicates that the C–S bond dissociation occurs only in the triplet state which is produced with a triplet yield of unity due the rapid intersystem crossing from the lowest singlet state to the triplet state. The lifetime of triplet MMBP at 295 K was determined to be 1.8 ns by using triplet energy transfer from triplet MMBP to 1-methylnaphthalene. The apparent activation energy for the photodecomposition of MMBP was determined to be 0.4 kcal mol^{-1} whereas the enthalpy of the C–S bond of MMBP was estimated to be 60.9 kcal mol^{-1} that is smaller than the triplet energy (68.5 kcal mol^{-1}) of MMBP. The energy diagram of the excited states of MMBP is shown including the thermodynamic mechanism for the C–S bond dissociation of MMBP.

Keywords: Laser flash photolysis; CIDEP; Bond cleavage; *p*-Mercaptomethylbenzophenone

1. Introduction

Benzophenone and acetophenone have been widely subjected 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. The photophysical processes of benzophenone are well understood through pico- and nano-second time-resolved measurements [1–4]. The lowest triplet state (T_1) of *n*, π* character is produced within 10 ps after photoexcitation. Therefore, the T_1 state whose triplet energy is 69.2 kcal mol^{-1} [5] is usually reactive in bimolecular reactions via a diffusion process in solution. A large number of studies on bimolecular reactions of triplet benzophenones in solution have been performed [1,6–10]. On the other hand, as to unimolecular photoreactions of ketones, photoinduced bond cleavage has been well documented [1]. Norrish Type I is a typical photoreaction of carbon–carbon bond scission occurring at the α-position of the carbonyl groups. With a homolytic bond dissociation between carbon and heteroatom, it is reported that acetoanilide undergoes C–N bond cleavage in the excited singlet state [11] while triplet phenacyl sulfides give the phenacyl radical as the initial intermediate by β-cleavage [12]. It is crucial for

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[*] Corresponding authors. Tel.: +48-61-8291327; fax: +48-61-8658008.
E-mail addresses: yamaji@chem.gunma-u.ac.jp (M. Yamaji), marcinia@amu.edu.pl (B. Marciniak).

[1] Co-corresponding author.

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doi:10.1016/S1010-6030(03)00396-4

Table 1
Mean enthalpies D(C–X) for C–X bond[a]

X	D(C–X) (kcal mol^{-1})
O	83.9
C	83.2
Cl	78.4
N	69.7
Br	66.0
S	61.9

[a] Data from [29].

understanding the mechanism of photoinduced bond scission to reveal the spin-multiplicity and electronic character of the reactive state and to consider the relation between the excited energy and the bond enthalpy. For occurrence of the bond scissions in the excited states of carbonyls, it is required that the bond enthalpy of the corresponding chemical bond should be smaller than the excited energy of the reactive state. Single-bond energies for C–X are listed in Table 1. From the viewpoint of the energy relation, C–S and C–Br bonds are potential to cleave in the triplet state of benzophenone derivatives having the triplet state energies close to 69 kcal mol^{-1}. To our knowledge, little photochemical investigation on homolytic bond dissociation in benzophenone derivatives has been performed [13–16].

In the present paper, we report a new-type reaction of photoinduced chemical bond cleavage which occurs at neither α- nor β-position of a carbonyl group in *p*-mercaptomethylbenzophenone. By means of laser photolysis and time-resolved EPR techniques, the thermodynamic profiles and reactive state for the bond dissociation are investigated in details.

2. Experimental

2.1. Materials

The compounds used in the present study were synthesized as follows.

2.1.1. p-Hydroxymethylbenzophenone (HMBP)

p-Benzoylbenzoic acid (25 g, 0.11 mol) was refluxed in benzene (300 ml) with ethylene glycol (250 ml, 4.5 mol) and *p*-toluenesulfonic acid monohydrate (5 g, 0.026 mol) for 48 h. After the ketalized product was obtained by evaporation, it was refluxed in dry THF for 12 h in the presence of $LiAlH_4$ (6.5 g, 0.17 mol). The product was washed with 10% HCl (100 ml) to give HMBP. Yield 60%. HMBP was purified by recrystallization from hexane.

2.1.2. p-Bromomethylbenzophenone (BMBP)

The solution of dry toluene (200 ml) with PBr_3 (6.2 ml, 0.066 mol) and HMBP (14 g, 0.066 mol) was stirred at room temperature for 3 h. After evaporation of the solution, BMBP was obtained. Yield 90%. BMBP was recrystallized from hexane for purification.

2.1.3. p-Mercaptomethylbenzophenone (MMBP)

The ethanol solution (200 ml) of BMBP (16.3 g, 0.059 mol) and thiourea (4.9 g, 0.059 mol) was refluxed for 6 h. The solution was cooled with ice to give precipitate. After an aqueous solution of 2 N NaOH was added, the solution was heated under N_2 atmosphere at 80–90 °C for 3 h, and acidified with H_2SO_4 to give crude MMBP. MMBP was purified by passing it through a silica gel column with benzene, and recrystallized from hexane. Yield 30%.

Acetonitirile (ACN) and butyronitrile were used as the solvents. Acetone (Ac), ACN and butyronitrile were distilled for purification.

2.2. Instruments

Absorption and emission spectra were measured with a U-best 50 spectrophotometer (JASCO) and a Hitachi F-4010 fluorescence, respectively.

2.3. Steady-state photolysis

The ACN solution of MMBP was deoxygenated by bubbling with highly pure argon. The light source was a low-pressured mercury lamp at 254 nm. The intensity of the incident light was determined to be 3.8×10^{-6} Einstein $\mathrm{dm}^{-3}\,\mathrm{s}^{-1}$ by using uranyl oxylate actinometry [5]. Steady-state photolysis was carried out at 295 K. The photoproducts of MMBP were analyzed with HPLC (Waters 600E) with a mixture of ACN and H_2O (1:4) as a developing solvent.

2.4. CIDEP measurements

The time-resolved EPR measurements were carried out by using an X-band EPR spectrometer (Varian E-109E) without magnetic field modulation as reported previously [17]. Third harmonics (355 nm) of a Nd:YAG laser (Continuum Minilite, 6 mJ, 15 Hz) was used as a pulsed light source. The sample solutions for the CIDEP measurements were constantly deoxygenated by argon gas bubbling and flowed into a quartz cell in the EPR resonator.

2.5. Laser flash photolysis

All the samples in a quartz cell with a 1 cm path length were degassed by several freeze-pump-thaw cycles on a high vacuum line. The concentration of the benzophenone derivatives for 266 nm laser photolysis was adjusted to achieve the optical density at 266 nm being ca. 0.7 in ACN. Transient absorption measurements were carried out in the temperature range from −43 to 45 °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. Usual measurements were carried out at room temperature (295 K). Fourth harmonics (266 nm) of a Nd^{3+}:YAG laser (JK Lasers HY-500; pulse width 8 ns) and a XeCl excimer laser (308 nm; Lambda Physik, Lextra 50) at 308 nm were used for flash photolysis. The number of the repetition of laser pulsing in the 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 [18]. 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.

3. Results and discussion

3.1. Steady-state photolysis and emission measurements

Fig. 1 shows the absorption spectral changes of MMBP in degassed ACN upon irradiation at 254 nm light. The intensity of the absorption band at 257 nm decreases with an increase of irradiation time, showing an isosbestic point at 296 nm. The quantum yield for disappearance of MMBP was determined to be 0.37 ± 0.03. One of the photoproducts was isolated and identified to be *p*-methylbenzophenone. The quantum yield of its formation was determined to be 0.02 ± 0.01. The initial photoreaction of MMBP is considered to be the bond dissociation between the carbon and sulfur atoms in the mercaptomethyl group.

In a glass matrix of a mixture of methanol/ethanol (1:1, v/v) at 77 K, HMBP and MMBP show phosphorescence with vibrational structures, which resemble those of benzophenone. It was confirmed that the phosphorescence excitation spectra of HMBP and MMBP agreed well with the corresponding absorption spectra. The emission from BMBP was absent at 77 K. The energy levels of the lowest triplet state of HMBP and MMBP were determined to be 68.8 and 68.5 kcal mol^{-1}, respectively, from the phosphorescence origins. From the similarity in the absorption and phosphorescence spectra of MMBP with those of benzophenone, it is inferred that the electronic character and ordering of the excited singlet and triplet states of MMBP at 77 K are the same as those of benzophenone.

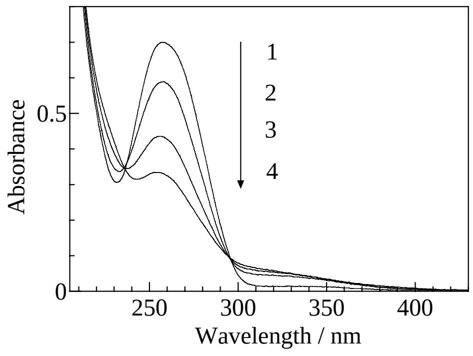


Fig. 1. Absorption spectral changes of MMBP in ACN upon 254 nm UV irradiation at (1) 0 min, (2) 3 min, (3) 6 min and (4) 10 min at 295 K.

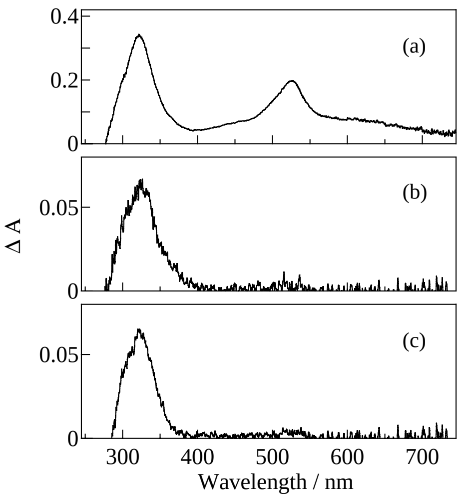
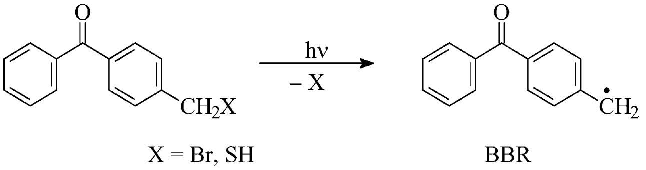


Fig. 2. The transient absorption spectra observed at 100 ns after 266 nm laser pulsing in the ACN solutions of (a) HMBP, (b) BMBP and (c) MMBP at 295 K.

3.2. Laser flash photolysis at 266 nm

In order to detect the initial intermediate produced upon photolysis of MMBP, laser flash photolysis was carried out. Fig. 2 shows the transient absorption spectra observed at 100 ns after 266 nm laser pulsing in the degassed ACN solutions of HMBP, BMBP and MMBP at 295 K. The intensity of the transient absorption spectrum for HMBP, which is similar to that of triplet benzophenone, was accelerated to decrease by the dissolved oxygen. Thus, the transient absorption spectrum obtained for HMBP is safely attributed to that of triplet HMBP. Both the transient absorption spectra obtained for BMBP and MMBP with the absorption peak at 320 nm are similar to each other, but the absorption band at 540 nm, which is seen for HMBP, is absent. We, therefore, attribute the transient absorption spectrum obtained for BMBP and MMBP to that of the *p*-benzoylbenzyl radical (BBR) generated by the cleavage of the C–Br and C–S bonds, respectively.



The transient absorption spectrum of MMBP in EPA (a mixture of diethyl ether, isopentane and ethanol, 5:5:3 (v/v/v)) at 77 K observed at 100 ns after 266 nm laser pulsing resembled that of triplet HMBP. From the similarity of the spectrum shape, that absorption spectrum is assigned to that of the triplet MMBP. Since no absorption spectrum of BBR was observed after depletion of triplet MMBP at 77 K, it seems that dissociation of the C–S bond in MMBP does not occur in a rigid matrix.

The quantum yield (Φ_{rad}) of the radical formation upon 266 nm laser photolysis of MMBP was determined with the use of Eq. (1) based on the absorption change (ΔA_{320}) at 320 nm due to formation of BBR.

$$\Delta A_{320} = \Delta\varepsilon_{320}\Phi_{rad}I_{abs} \quad (1)$$

where $\Delta\varepsilon_{320}$ and I_{abs} are, respectively, the molar absorption coefficient change of BBR at 320 nm (7500 ± 400 $dm^3\,mol^{-1}\,cm^{-1}$)[2] and the number of the photon flux of a laser pulse at the excitation wavelength.

The quantity of I_{abs} is determined by using the absorption of triplet benzophenone (BP) in ACN as an actinometer [20].

$$\Delta A_T^{BP} = \varepsilon_T^{BP}\Phi_{ISC}^{BP}I_{abs} \quad (2)$$

where ΔA_T^{BP}, ε_T^{BP} and Φ_{ISC}^{BP} are, respectively, the initial absorbance at 520 nm for the formation of triplet benzophenone obtained immediately after laser pulsing, the molar absorption coefficient of triplet BP at 520 nm in ACN (6500 $dm^3\,mol^{-1}\,cm^{-1}$ [21]) and triplet yield of benzophenone (1.0 [5]). By using Eqs. (1) and (2), the Φ_{rad} value was determined to be 0.49 ± 0.03. The candidates for the reactive state of the C–S bond cleavage are the excited singlet and/or triplet states of MMBP. In order to investigate the spin-multiplicity of the reactive excited state for generating the free radicals, CIDEP measurement was carried out for MMBP.

3.3. CIDEP measurements

Fig. 3 shows the time-resolved EPR spectrum obtained at 500 ns after laser pulsing in a butyronitrile solution of MMBP (5×10^{-3} mol dm^{-3}) at 230 K and simulated one. The CIDEP spectrum with the triplets of triplet was well reproduced by the computer simulation with a g-value of 2.0029 and the splitting constants of 1.52, 0.50, and 0.175 mT for BBR (see Scheme 1). The EPR parameters determined are close to those of the benzyl radical ($a^H(CH_2) = 1.61$, $a^H(o\text{-}H) = 0.508$, $a^H(m\text{-}H) = 0.195$ mT, and $g = 2.0025$ [22]). Therefore, the hyperfine structure is interpreted as arising from BBR. The counter radical of $HS^\bullet$ is hard to detect in fluid solutions, presumably, the spectrum of the $HS^\bullet$ radical may show remarkable broadening due to the spin–orbit interaction. The net-emissive CIDEP spectrum observed due to the triplet mechanism clearly suggests that the free radicals obtained in the transient absorption upon laser photolysis of MMBP are generated in the triplet state of MMBP. Still remains a possibility that the C–S bond dissociation might occur also in the excited singlet state of MMBP to produce a singlet radical pair, $^1(BBR + {}^\bullet SH)_{cage}$ encapsulated in a solvent cage according to the spin-conservation rule. The singlet radical pair is ready to undergo geminate recombination in the solvent cage to produce the parent molecule. For such a case, it is hard to detect the free radicals escaped from the solvent cage by CIDEP techniques. We, thus, carried out triplet sensitization of MMBP by acetone at room temperature in order to survey the reactivity of the triplet state of MMBP only.

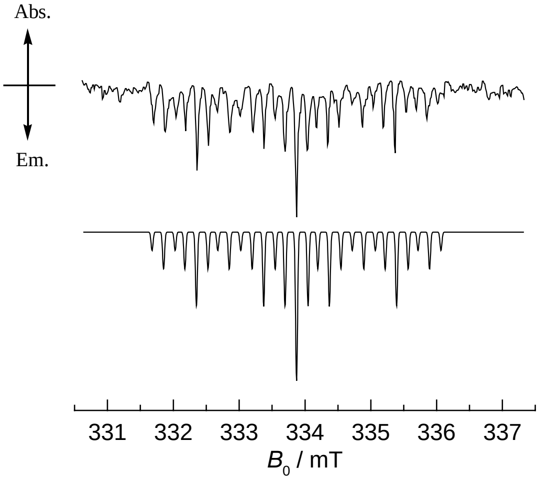
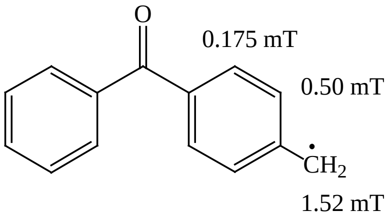


Fig. 3. The time-resolved EPR spectrum obtained at 500 ns after laser pulsing in the butyronitrile solution of MMBP (5×10^{-3} mol dm^{-3}) at 230 K (upper) and the simulated one with the splitting constants shown in Scheme 1 (lower).

3.4. Triplet sensitization of MMBP by acetone

The triplet energy of acetone (79.4 kcal mol^{-1} [5]) is larger than that of MMBP (68.5 kcal mol^{-1}). Triplet sensitization of acetone (Ac, 0.7 mol d m^{-3}) by using a XeCl excimer laser (308 nm) was performed in ACN solutions of HMBP, BMBP and MMBP. A time profile of the transient absorption at 320 nm for the Ac–MMBP system is shown in Fig. 4. The rate for the increase of the absorption intensity at 320 nm is obtained to be $1.4 \times 10^6\,s^{-1}$. The transient absorption spectra with the absorption maximum at 320 nm obtained for HMBP, BMBP and MMBP are all similar to those of the corresponding compounds obtained upon direct excitation (Fig. 2). Briefly, triplet HMBP is



Scheme 1.

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[2] The molar absorption coefficient of BBR was determined by comparing with that (2000 $dm^3\,mol^{-1}\,cm^{-1}$ at 450 nm [19]) of the phenylthiyl radical produced upon 266 nm laser photolysis of p-benzoylbenzyl phenyl sulfide in degassed ACN.

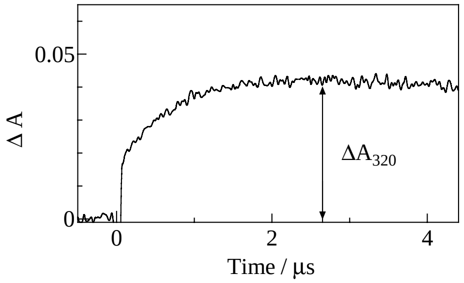


Fig. 4. The temporal absorbance change at 320 nm observed after 308 nm laser photolysis in the Ac (0.7 mol dm^{-3})–MMBP (4.0×10^{-4} mol dm^{-3}) system in ACN at 295 K.

produced by triplet sensitization while BBR is generated for BMBP and MMBP. For BMBP and MMBP, the C–Br and C–S bonds seem to dissociate in the triplet manifold of BMBP and MMBP. The observed rates (k_{obsd}) for the formation of BBR from MMBP are plotted as a function of the concentration of MMBP, [MMBP] in Fig. 5. Since the plots give a straight line, the k_{obsd} can be formulated by:

$$k_{\mathrm{obsd}} = k_0 + k[\mathrm{MMBP}] \tag{3}$$

where k_0 and k_q, respectively, represent the decay rate of triplet acetone in the absence of MMBP and the rate constant for quenching of triplet Ac by MMBP. From the intercept and slope of the line, the values of k_0 and k_q are determined to be 5.2×10^5 s^{-1} and 2.2×10^9 dm^3 mol^{-1} s^{-1}, respectively.

The quantum yield ($\Phi_{\mathrm{rad}}^{\mathrm{sens}}$) for the formation of BBR from MMBP upon triplet sensitization was determined by:

$$\Phi_{\mathrm{rad}}^{\mathrm{sens}} = \Delta A_{320} \Delta\varepsilon_{320}^{-1} I_{\mathrm{abs}}^{-1} \tag{4}$$

where ΔA_{320} and $\Delta\varepsilon_{320}$ are the maximum absorption change due to the formation of BBR at 320 nm (see Fig. 4) and the molar absorption coefficient change of BBR at 320 nm (7500 dm^3 mol^{-1} cm^{-1}). The value of I_{abs} at 308 nm was determined by Eq. (2). The obtained values of ($\Phi_{\mathrm{rad}}^{\mathrm{sens}}$) are plotted as a function of [MMBP] in Fig. 6. On the other hand, the ($\Phi_{\mathrm{rad}}^{\mathrm{sens}}$) value increases non-linearly with increasing [MMBP]. The ($\Phi_{\mathrm{rad}}^{\mathrm{sens}}$) value is also related with the kinetic parameters, k_0 and k_q by:

$$\Phi_{\mathrm{rad}}^{\mathrm{sens}} = k_\mathrm{q}[Q]\alpha_{\mathrm{rad}}\alpha_{\mathrm{TET}}\Phi_{\mathrm{ISC}}^{\mathrm{Ac}}(k_0 + k_\mathrm{q}[Q])^{-1} \tag{5}$$

where α_{rad}, α_{TET} and $\Phi_{\mathrm{ISC}}^{\mathrm{Ac}}$ are the efficiencies for the radical formation in the triplet state of MMBP and triplet energy transfer from triplet Ac to MMBP, and the triplet yield of Ac (1.0 [5]), respectively. By best-fitting Eq. (5) to the experimental values of Φ_{rad} 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 0.37 ± 0.02. It was impossible to determine the definite value of α_{TET} for the Ac–MMBP system. By adopting the α_{TET} value for triplet energy transfer from triplet Ac to benzophenone in ACN (0.73) [28] to the Ac–MMBP system, the α_{rad} value for the Ac–MMBP system is determined to be 0.51 ± 0.03.

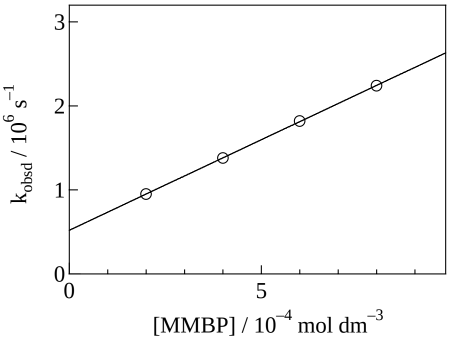


Fig. 5. Plots of the rate (k_{obsd}) for the formation of the *p*-benzoylbenzyl radical (BBR) obtained upon 308 nm laser photolysis in the Ac (0.7 mol dm^{-3})–MMBP system in ACN at 295 K.

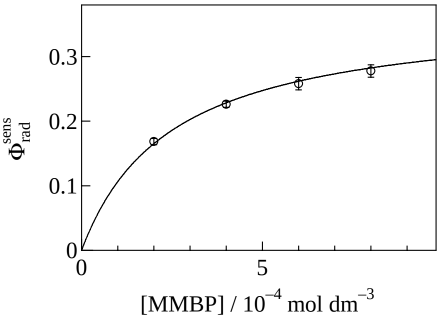
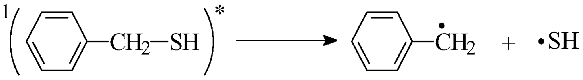


Fig. 6. Plots of the radical yield $\Phi_{\mathrm{rad}}^{\mathrm{sens}}$ vs. [MMBP]. The solid curve was calculated using Eq. (5).

According to the spin-conservation rule, the triplet radical pair, $^3(\mathrm{BBR} + {}^\bullet\mathrm{SH})_{\mathrm{cage}}$ of BBR and the SH radical is initially produced in a solvent cage when the C–S bond dissociates in the triplet state of MMBP. The triplet radical pair escapes from the solvent cage without geminate recombination which requires the spin-multiplicity being singlet by intersystem crossing, resulting in efficient formation of free radicals, BBR and HS$^\bullet$, since the rate of escaping from the solvent cage is considered to be much larger than that of intersystem crossing at 295 K. Thus, the α_{rad} value can be interpreted to be equal to that of the efficiency for the bond cleavage in the triplet state of MMBP. On the other hand, we have determined the quantum yield ($\Phi_{\mathrm{rad}} = 0.49 \pm 0.03$) of the radical formation at 295 K upon direct excitation in ACN. Furthermore, from the CIDEP measurements, it is found that the free radical formation upon direct excitation of MMBP proceeds in the triplet state of MMBP. The agreement of the α_{rad} value (0.51 ± 0.03) with that of Φ_{rad} within experimental errors indicates that upon direct excitation of MMBP, the cleavage of the C–S bond in MMBP occurs only in the triplet state of MMBP, which may be produced by intersystem crossing of a quantum yield (Φ_{isc}) of unity.

It is noteworthy to compare the subjected reaction with photodecomposition of benzylmercaptan (BzM) in solution. The reactive state and quantum yield for the benzyl radical formation of BzM upon photoexcitation were found to be the excited singlet state and 0.2 ± 0.01 in ACN (unpublished data).



From the viewpoint of molecular structures, MMBP is attached with the benzoyl group to BzM. By substituting with the benzoyl group in BzM, one can alter the reactive state for bond dissociation from the excited singlet state to the triplet state where geminate recombination is free, resulting in increasing the radical yield. This modification can be applied to molecular designing for precursors that provide free radicals as initiators in polymerization in bulk.

3.5. Lifetime of the triplet state

The lifetime of triplet MMBP at 295 K was estimated by means of a Stern–Volmer type analysis, employing 1-methylnaphthalene (MN) as a triplet quencher. This technique has been widely used in the characterization of short-lived triplet states [23–25]. 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 ketones according to Eq. (6).

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

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 for Eq. (6), the lifetime of triplet MMBP and a constant incorporating experimental factors as well as the molar absorption coefficient of triplet MN. Fig. 7 shows the plots of the reciprocal of ΔA_{417} obtained by 355 nm laser photolysis of a MMBP (5.6×10^{-3} mol dm^{-3})–MN system as a function of $[\mathrm{MN}]^{-1}$. The plots give a straight line, giving an intercept of 2.27 and a slope of 0.18 mol dm^{-3}. Thus, the Stern–Volmer constant ($k_q\tau_T$) is determined to be 15.1 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} [26]), the τ_T value is determined to be 1.8 ns.

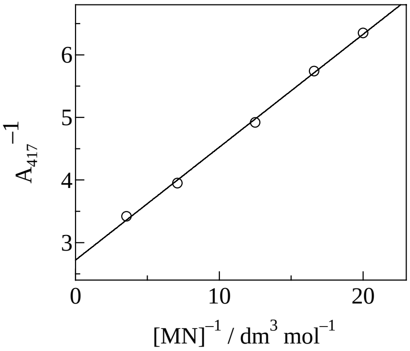


Fig. 7. Plots according to Eq. (7) for the quenching of triplet MMBP by 1-methylnaphthalene.

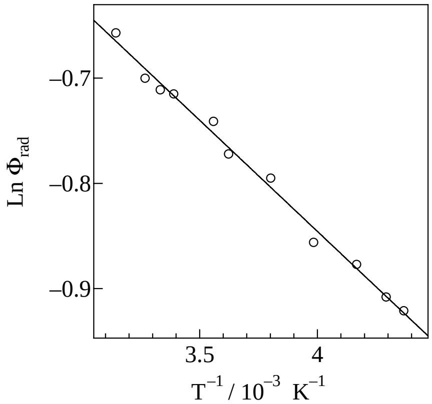


Fig. 8. Natural logarithmic plots of the quantum yield (Φ_{rad}) for the formation of *p*-benzoylbenzyl radical (BBR) obtained upon 266 nm laser photolysis of MMBP as a function of the reciprocal of the temperature, *T*.

3.6. Temperature dependence of the radical yield

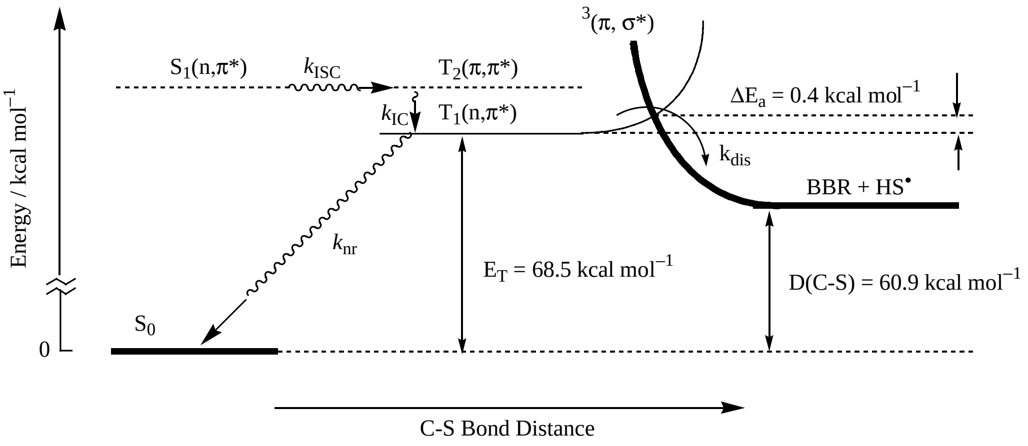
The temperature dependence of the quantum yield (Φ_{rad}) of the free radical formation from triplet MMBP was studied in the temperature range, 230–318 K. Fig. 8 shows the natural logarithmic plots of Φ_{rad} obtained upon 266 nm laser pulsing in the ACN solution of MMBP as a function of the reciprocal of the temperature, *T*. The plots give a straight line having a slope of 210, indicating that the apparent activation energy, ΔE_a for the formation of BBR is 0.42 kcal mol^{-1}. Therefore, on the basis of the Φ_{rad} value (0.49) at 295 K, Φ_{rad} (*T*) is expressed by:

$$\Phi_{rad}(T) = (1.0 \pm 0.05)\exp(-210T^{-1}) \qquad (8)$$

The ultimate photodecomposition yield of MMBP in ACN is thus estimate to be nearly equal to unity.

3.7. Energy diagram of photoexcited MMBP

Based on the results obtained hereinbefore, the energy diagram of photoexcited MMBP in ACN can be depicted in Scheme 2 including the BBR formation process. Since the absorption and phosphorescence spectra of MMBP are similar to those of benzophenone, it seems that the electronic character, ordering and energy level of MMBP resemble those of benzophenone. After the $S_1(n, \pi^*)$ state of MMBP is produced upon direct excitation, the $T_1(n, \pi^*)$ having a triplet energy of 68.5 kcal mol^{-1} would be produced within 10 ps via a fast intersystem crossing with a rate, k_{ISC} through the $T_2(\pi, \pi^*)$ state, according to the El-Sayed rule [27]. The potential energy surfaces for the



Scheme 2.

studied C–S bond cleavage can be interpreted as being a thermally activated crossing, where the activation energy is determined to be 0.4 kcal mol^{-1}, from the $T_1(n, \pi^*)$ to a dissociative $^3(\pi, \sigma^*)$ state which leads to the formation of the π (BBR) and σ ($^\bullet$SH) radicals. The lifetime, τ_T of the T_1 state of MMBP is found to be 1.8 ns at 295 K whereas the quantum yield of the C–S bond dissociation via the T_1 state of MMBP is determined to be 0.51 at 295 K. Thus, the rate, k_{dis} for the C–S bond cleavage leading to the radical formation is estimated to be 2.8×10^8 s^{-1} by using Eq. (9).

$$k_{dis} = \Phi_{dis}\tau_T^{-1} \quad (9)$$

The residual rate, k_{nr} $(= \tau_T^{-1} - k_{dis})$ is considered to be due to a non-radiative process from the T_1 state to the ground state (S_0).

The enthalpy of the C–S bond of MMBP, D(C–S) was obtained on the basis of the heat of formation ($\Delta_f H$) for MMBP, BBR and hydrothiyl radical ($^\bullet$SH) computed by using a semi-empirical PM3 program contained in MOPAC '97, being $\Delta_f H$ (MMBP) = 18.8 kcal mol^{-1}, $\Delta_f H$ (BBR) = 42.1 kcal mol^{-1} and $\Delta_f H$ (HS$^\bullet$) = 37.6 kcal mol^{-1}. The D(C–S) value is calculated to be 60.9 kcal mol^{-1} by using Eq. (10).

$$\Delta_f H(\mathrm{MMBP}) = \Delta_f H(\mathrm{BBR}) + \Delta_f H(\mathrm{HS}^\bullet) - D(\mathrm{C–S}) \quad (10)$$

The obtained value for D(C–S) of MMBP is smaller than the triplet energy (68.5 kcal mol^{-1}) of MMBP. The C–S bond is, thus, fated to cleave in the triplet state of MMBP once the triplet state is produced. On the other hand, upon laser photolysis of HMBP, the triplet formation was found in the transient absorption measurements, and after the depletion of the triplet state, no formation of BBR was observed, indication that the C–O bond does not cleave in the triplet state. By using the $\Delta_f H$ values for HMBP and the hydroxy radical ($^\bullet$OH) being −28.8 and 2.8 kcal mol^{-1}, respectively, the enthalpy of the C–O bond in HMBP, D(C–O) was obtained to be 73.7 kcal mol^{-1}, which is larger than the triplet energy of HMBP (68.8 kcal mol^{-1}) by 5 kcal mol^{-1}. These energetic considerations demonstrate that it is required for the bond fission in the triplet state that the energy level of the reactive triplet state should be, at least, greater than the bond energy. The dissociation of BMBP occurs in the excited singlet state upon direct excitation. The details of photoreactions of BMBP as well as *p*-chloromethybenzophenone in comparison with those of MMBP will be reported in the following paper.

4. Conclusion

Photolysis of *p*-mercaptomethylbenzophenone (MMBP) in acetonitrile leads to dissociation of the C–S bond. Based on the transient absorption and CIDEP measurements, the initial intermediate was found to be the *p*-benzoylbenzyl radical (BBR). The quantum yield (Φ_{rad}) of the BBR formation upon direct excitation was determined to be 0.49 ± 0.03. By using triplet sensitization of acetone, the efficiency (α_{dis}) of the C–S bond fission in the triplet state of MMBP was determined to be 0.51 ± 0.03. The agreement between the Φ_{rad} and α_{dis} values indicates that the C–S bond dissociation occurs only in the triplet state, which is produced with a triplet yield of unity due to the rapid intersystem crossing. The lifetime of triplet MMBP at 295 K was determined to be 1.8 ns by using triplet energy transfer from triplet MMBP to 1-methylnaphthalene. The apparent activation energy for the photodecomposition of MMBP was found to be 0.4 kcal mol^{-1}, and the enthalpy of the C–S bond of MMBP was estimated to be 60.9 kcal mol^{-1} that is smaller than the triplet energy (68.5 kcal mol^{-1}) of MMBP.

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