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A new-type photoreaction of a carbonyl compound
Part 2. Photoinduced ω-bond dissociation in *p*-halomethylbenzophenone studied by time-resolved EPR technique and laser flash photolysis

Minoru Yamaji[a,*], Ai Suzuki[a], Fuyuki Ito[b], Shozo Tero-Kubota[b],
Seiji Tobita[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, Poznan 60-780, Poland*

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Abstract

Photodissociation of the carbon-X (X = Br and Cl) bonds in *p*-bromo- and *p*-chloromethylbenzophenone (BMBP and CMBP) in solution were investigated by time-resolved EPR and laser flash photolysis techniques. BMBP and CMBP were found to undergo ω-bond cleavage to yield the *p*-benzoylbenzyl radical (BBR) at 295 K, and the quantum yields (Φ_{BBR}) were determined. The CIDEP signal originated from BBR formed upon decomposition of CMBP was obtained while that for BMBP was absent. By using triplet sensitization of acetone, the efficiencies (α_{BBR}) of the C─X bond fission in the triplet states of BMBP and CMBP were determined. The agreement between the Φ_{BBR} and α_{BBR} values for CMBP indicates that the C─Cl bond dissociation occurs only in the triplet state. In contrast to CMBP, the cleavage of the C─Br bond in BMBP upon direct excitation was concluded to be the event only in the excited singlet state without triplet formation, whereas the triplet state was also reactive for ω-bond dissociation. The rate of C─Br bond dissociation seemed to be greater than that of intersystem crossing from the S_1 to the T_1 state. Schematic energy diagrams of the excited states of BMBP and CMBP were shown, and the reaction profiles were discussed from the viewpoint of the C─X bond enthalpies.

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

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1. Introduction

Photoinduced bond cleavage of aromatic ketones has been well documented. Norrish types I and II reactions are typical events of carbon–carbon bond fission occurring at the α- and at β-positions of the carbonyl groups, respectively [1,2]. In a previous paper, by means of CIDEP and laser photolysis techniques, we found a new-type reaction of photoinduced homolytic bond cleavage, which occurs neither at α- nor β-position of a carbonyl group, i.e., ω-bond dissociation in *p*-mercaptomethylbenzophenone (MMBP) [3]. Photophysical processes of benzophenone have been well unveiled that the lowest triplet state (T_1) of n, π^* character is produced within 10 ps after photoexcitation due to a fast intersystem crossing [4–6]. ω-Bond cleavage in MMBP was shown to occur with an efficiency of 0.5 only in the triplet manifold because of the fast intersystem crossing and the C─S bond energy (60.9 kcal mol^{-1}) smaller than the triplet energy (68.5 kcal mol^{-1}) of MMBP [3]. In general, for occurrence of bond dissociation in the excited states of compounds, it is required that the bond enthalpy of the corresponding chemical bond should be smaller than the excited energy of the reactive state. Mean energies for a C─X single bond are listed in

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[*] Corresponding author. Tel.: +81 277 301212; fax: +81 277 301212.
[**] Co-corresponding author.
E-mail addresses: yamaji@chem.gunma-u.ac.jp (M. Yamaji), marcinia@amu.edu.pl (B. Marciniak).

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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
Si	69.3
Br	66.0
S	61.9

[a] [19].

Table 1. Between the carbon–halogen atom bonds, a C—Br bond is a candidate for ω-bond fission in the corresponding triplet benzophenone derivatives whose triplet energies may be close to that of benzophenone (69 kcal mol^{-1} [7]), while a C—Cl bond seems to be difficult to cleave in the triplet state. In the previous work, the C—Br bond cleavage was confirmed from transient measurements, though the reactive state is not yet definite.

In the present work, we investigate the reaction profiles of photoinduced ω-bond dissociation in *p*-halomethylbenzophenones in comparison with that of MMBP by means of laser photolysis technique and CIDEP measurement.

2. Experimentals

p-Chloromethylbenzophenone (CMBP) was synthesized according to the literature [8]. *p*-Bromomethylbenzophenone (BMBP) was purchased from Aldrich. Halomethylbenzophenones (HMBP; BMBP and CMBP) were purified by repeated recrystallizations from hexane. Acetone (Ac), 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, while 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 matrices at 77 K. Absorption and emission spectrum 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 [9]. Third harmonics (355 nm) of a Nd:YAG laser (Continuum Minilite, 6 mJ, 15 Hz) was used as a pulsed light source. Sample solutions for the CIDEP measurements were constantly deoxygenated by argon gas bubbling and flowed into a quartz cell in the EPR resonator.

All 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 HMBP 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 at 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 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 [10]. 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

Absorption spectra of BMBP and CMBP in ACN shown in Fig. 1 are similar to that of benzophenone. In a glass matrix of a mixture of methanol and ethanol (1:1, v/v) at 77 K, CMBP shows phosphorescence with vibrational structures, which resemble those of benzophenone (Fig. 1). It was confirmed that the phosphorescence excitation spectrum of CMBP agreed well with the corresponding absorption spectrum. Emission from BMBP was absent at 77 K. The energy level of the lowest triplet (T_1) state of CMBP was determined to be 68.4 kcal mol^{-1} from the phosphorescence origin. From the similarity in the phosphorescence spectrum of CMBP with that of benzophenone, it is inferred that the electronic character of the lowest excited triplet state of CMBP is of n, π^*.

Fig. 2(a) and (b) shows transient absorption spectra observed at 100 ns after 266 nm laser pulsing in the degassed ACN solutions of BMBP and CMBP at 295 K, respectively. Both the transient absorption spectra with the absorption peak at 320 nm are similar in shape, although that for BMBP seems to be somewhat broadened, to that of

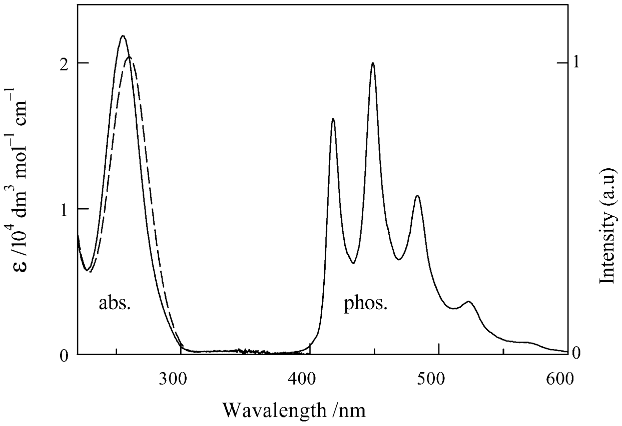


Fig. 1. Absorption spectra of CMBP (solid) and BMBP (dashed) in ACN at 295 K and a phosphorescence spectrum of CMBP in a mixture of methanol and ethanol (1:1, v/v) at 77 K. Phosphorescence from BMBP was absent at 77 K.

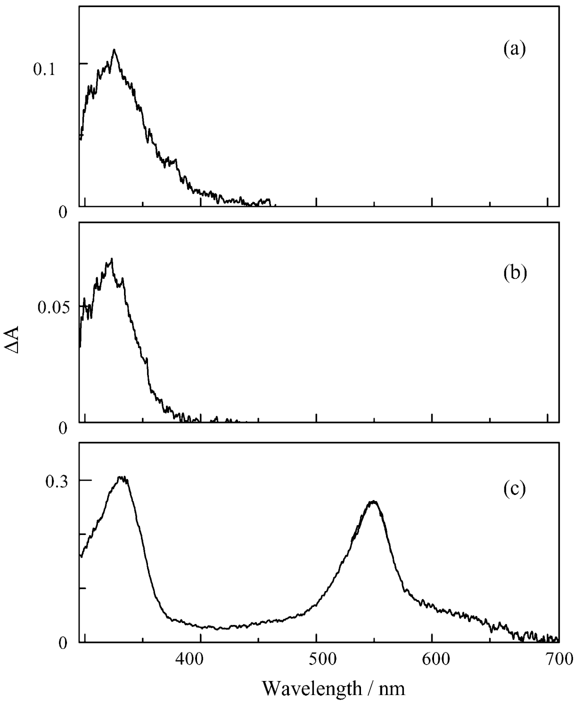


Fig. 2. Transient absorption spectra observed at 100 ns after 266 nm laser pulsing in the ACN solutions of BMBP (a) and CMBP (b) at 295 K, and in EPA glass of CMBP at 77 K (c).

the *p*-benzoylbenzyl radical (BBR) having a molar absorption coefficient of 7600 ± 400 $dm^3\ mol^{-1}\ cm^{-1}$ at 320 nm reported in a previous work [3], indicating that BMBP and CMBP undergo ω-bond dissociation upon photoirradiation at room temperature.

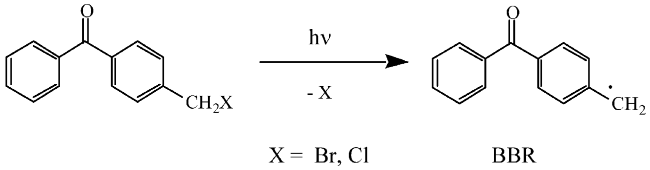


Fig. 2(c) displays a transient absorption spectrum obtained at 100 ns after 266 nm laser photolysis of CMBP in EPA glass at 77 K. Since the transient absorption spectrum obtained is similar to that of triplet benzophenone, the obtained absorption spectrum is attributed to triplet CMBP. This observation indicates that dissociation of the C–Cl bond in CMBP does not occur in a rigid matrix. On the other hand, we were unable to observe any transient absorption spectra after 266 nm laser photolysis of BMBP in EPA glass at 77 K. From the absence of the transient absorption for BMBP, it is inferred that even in rigid media, the C–Br bond of BMBP would dissociate in the excited singlet state to produce a singlet radical pair of the BBR and Br radicals, which readily undergo geminate recombination.

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

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

where $\Delta\varepsilon_{320}$ and I_{abs} are, respectively, the molar absorption coefficient change of BBR at 320 nm (7500 ± 400 $dm^3\ mol^{-1}\ cm^{-1}$ [3]) 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 [11].

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

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 $dm^3\ mol^{-1}\ cm^{-1}$ [12]) and triplet yield of benzophenone (1.0 [7]). By using Eqs. (1) and (2), the Φ_{BBR} value was determined to be 0.41 ± 0.03 for BMBP and 0.51 ± 0.03 for CMBP. In order to investigate the spin-multiplicity of the reactive excited state for generating the free radicals, CIDEP measurement was carried out for HMBP.

Fig. 3 shows a time-resolved EPR spectrum observed at a delay time of 700 ns after 355 nm laser excitation of CMBP (0.01 mol dm^3) in butyronitrile at 223 K. The CIDEP spectrum with the triplets of triplet was well reproduced by the computer simulation with splitting constants of 1.52, 0.50 and 0.175 mT and a *g*-value of 2.0029 (see Plate 1). The EPR parameters determined are appreciably close to those of the BBR ($a^H(CH_2)$ = 1.61, $a^H(o\text{-}H)$ = 0.508, $a^H(m$-

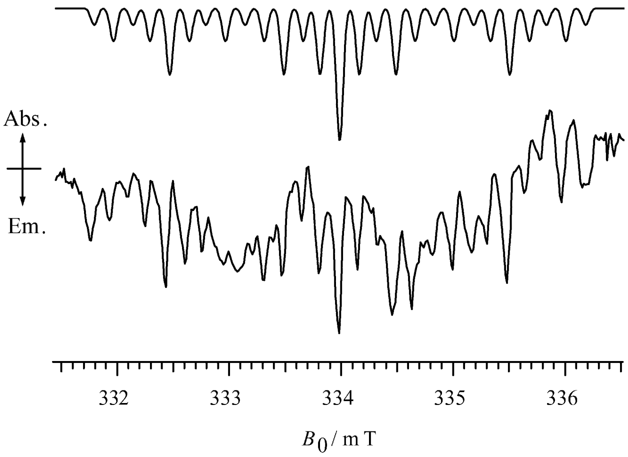


Fig. 3. A time-resolved EPR spectrum obtained at 700 ns after 355 nm laser pulsing in a butyronitrile solution of CMBP (1×10^{-2} mol dm^{-3}) at 223 K (lower) and the simulated one with the splitting constants shown in Plate 1 (upper).

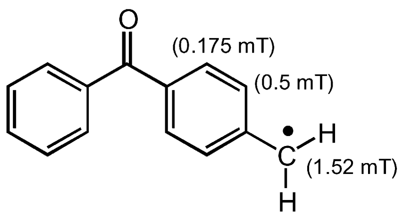


Plate 1.

H) = 0.195 mT; g = 2.0025) reported previously [3]. CIDEP signal of the chlorine atom was hard to detect in fluid solution because of broadening due to the spin-orbit interaction. The net-emissive polarization due to the triplet mechanism strongly indicates that the photoinduced C–Cl bond occurs in the triplet state of CMBP. Strong and broad signals superposed on that of BBR were also seen. The intensity of the signals increased with decreasing the flow rate of the sample solution. Therefore, they are, presumably, due to the secondary reactions of BBR and/or Cl atom produced.

On the other hand, CIDEP signal was absent upon photolysis of BMBP, whereas the formation of BBR was found through transient absorption measurements. These facts suggest that the C–Br bond in BMBP cleaves in the excited singlet state to provide a singlet radical pair in the solvent cage, $^1(\mathrm{BBR} + \mathrm{Br})_{\mathrm{cage}}$. The large spin-orbit coupling interaction of the Br atom eliminates the electron spin polarization due to the radical pair mechanism, even if the spin polarization is created during the interaction between the pair radicals in the solvent cage [13]. In order to investigate photochemical profiles in the triplet state of BMBP and CMBP, triplet sensitization was carried out by transient absorption measurements.

Triplet sensitization of acetone (Ac; 1.0 mol dm^{-3}) by using a XeCl excimer laser (308 nm) was performed in ACN solutions of BMBP and CMBP. The triplet energy of acetone (79.4 kcal mol^{-1} [7]) is larger than that of CMBP (68.4 kcal mol^{-1}). A time profile of a transient absorption at 320 nm for an Ac–CMBP system is shown in Fig. 4. The intensity of absorbance at 320 nm increases with the time evolution. The rate for the increase of the absorption intensity at 320 nm is obtained to be $2.3 \times 10^6\ \mathrm{s}^{-1}$. The same behavior of the absorption at 320 nm for an Ac–BMBP system after 308 nm laser photolysis was found. The transient absorption spectra obtained at the time of the maximum absorbance at 320 nm for the Ac–BMBP and –CMBP systems were similar to that of BBR. In other words, BBR is generated via the triplet states of BMBP and CMBP upon sensitization. The observed rates (k_{obsd}) for the formation of BBR from triplet HMBP are plotted as a function of the concentration of HMBP, [HMBP] in Fig. 5. Since the plots give straight lines, the k_{obsd} can be formulated by:

$$k_{\mathrm{obsd}} = k_0 + k_{\mathrm{q}}[\mathrm{HMBP}] \tag{3}$$

where k_0 and k_{q}, respectively, represent the decay rate of triplet acetone in the absence of HMBP and the rate constant for quenching of triplet Ac by HMBP. From the intercept and slope of the line, the values of k_0 and k_{q} were determined to be $8.0 \times 10^5\ \mathrm{s}^{-1}$ and $2.9 \times 10^9\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$ for BMBP and $8.0 \times 10^5\ \mathrm{s}^{-1}$ and $3.7 \times 10^9\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$ for CMBP.

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

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

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} [3]). The value of I_{abs} at 308 nm was determined by Eq. (2). The obtained values of $\Phi_{\mathrm{BBR}}^{\mathrm{sens}}$ for the Ac–CMBP system are plotted as a function of [CMBP] in Fig. 6. The $\Phi_{\mathrm{BBR}}^{\mathrm{sens}}$ value increases non-linearly with increasing [CMBP]. On the other hand, the $\Phi_{\mathrm{BBR}}^{\mathrm{sens}}$ value is related with the kinetic parameters, k_0 and k_{q}, by:

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

where α_{BBR}, α_{TET} and $\Phi_{\mathrm{ISC}}^{\mathrm{Ac}}$ are the efficiencies for the radical formation in the triplet state of HMBP and triplet energy transfer from triplet Ac to HMBP, and the triplet yield of Ac (1.0 [7]), respectively. By best-fitting Eq. (5) to the experimental values of $\Phi_{\mathrm{BBR}}^{\mathrm{sens}}$ with the use of the k_0 and k_{q} values obtained above, the product value of α_{BBR} and α_{TET} was obtained to be 0.37 ± 0.02 for CMBP and 0.39 ± 0.02 for BMBP. It was impossible to determine the definite value of α_{TET} for the Ac–HMBP system. By adopting the α_{TET} value for triplet energy transfer from triplet Ac to benzophenone in ACN (0.73 [3]) to the Ac–HMBP systems, the α_{BBR} values

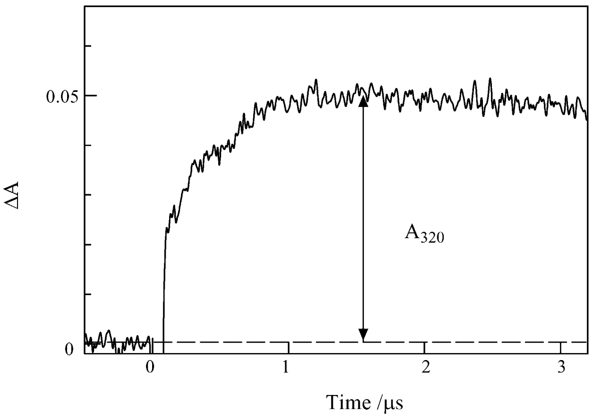


Fig. 4. A temporal absorbance change at 320 nm observed after 308 nm laser photolysis in an Ac (1.0 M)–CMBP (4.0×10^{-4} mol dm^{-3}) system in ACN at 295 K.

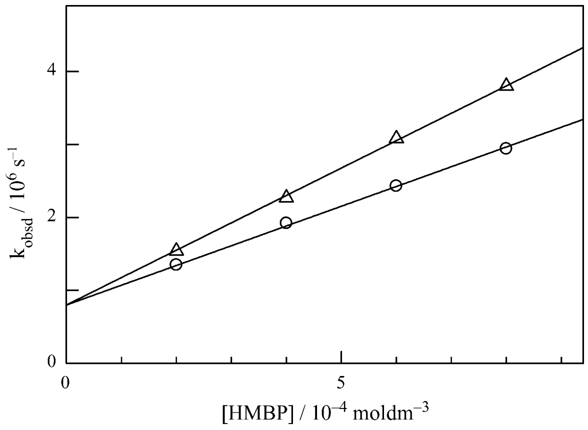


Fig. 5. Plots of the rate (k_{obsd}) for the formation of the *p*-benzoylbenzyl radical (BBR) obtained upon 308 nm laser photolysis in Ac (1.0 mol dm^{-3})–BMBP (○) and –CMBP (△) systems in ACN at 295 K.

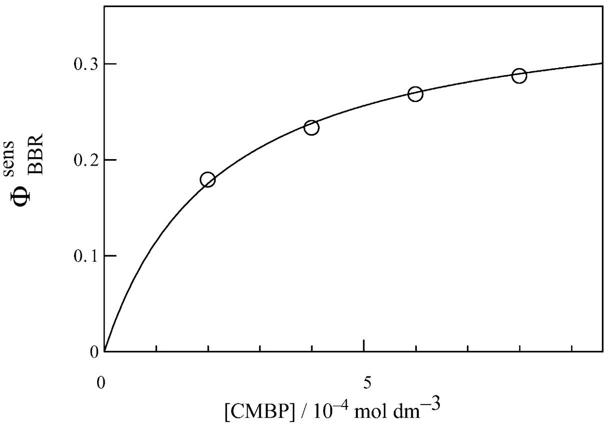


Fig. 6. Plots of the radical yield (Φ^{sens}_{BBR}) vs. [CMBP]. The solid curve was calculated by Eq. (5).

for the Ac–BMBP and –CMBP system are determined to be 0.53 ± 0.03 and 0.51 ± 0.03, respectively.

The enthalpy of the C–X bond of MMBP, D(C–X) was obtained on the basis of the heat of formation ($\Delta_f H$) for BMBP and CMBP, BBR and halogen atoms (X = Br and Cl) computed by using a semi-empirical PM3 program contained in MOPAC '97, being $\Delta_f H$ (BMBP) = 15.8 kcal mol^{-1}, $\Delta_f H$ (CMBP) = 5.5 kcal mol^{-1}, $\Delta_f H$ (BBR) = 42.1 kcal mol^{-1}, $\Delta_f H$ (Br$^\bullet$) = 26.7 kcal mol^{-1} and $\Delta_f H$ (Cl$^\bullet$) = 29.0 kcal mol^{-1} The D(C–X) value is calculated to be 53.0 kcal mol^{-1} for BMBP and 65.6 kcal mol^{-1} for CMBP by using Eq. (6).

$$\Delta_f H(\mathrm{HMBP}) = \Delta_f H(\mathrm{BBR}) + \Delta_f H(\mathrm{X}^\bullet) - D(\mathrm{C-X}) \quad (6)$$

The obtained values for D(C–X), which are close to those reported for $C_6H_5CH_2$–X being 55.0 kcal mol^{-1} for X = Br and 69.1 kcal mol^{-1} for X = Cl [7], are smaller than the triplet energy (ca. 68 kcal mol^{-1}) of HMBP. The C–X bonds of HMBP are, thus, fated to cleave in the triplet state of CMBP once the triplet state is produced.

When the C–X bond dissociates in the triplet state of HMBP, a triplet radical pair, $^3(\mathrm{BBR} + {}^\bullet\mathrm{X})_{cage}$ of BBR and Br or Cl radical 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 the spin-multiplicity being singlet by intersystem crossing, resulting in efficient formation of free radicals, BBR and X, 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_{BBR} value can be interpreted to be equal to that of the efficiency for the bond cleavage in the triplet state of HMBP. As for CMBP, the quantum yield (Φ_{BBR}) of the BBR formation has been determined to be 0.49 ± 0.03 upon direct excitation. Furthermore, from the CIDEP measurements, it is found that the free radical formation upon direct excitation of CMBP proceeds in the triplet state. The agreement of the α_{BBR} value (0.51 ± 0.03) with that of Φ_{BBR} within experimental errors indicates that upon direct excitation of CMBP, the cleavage of the C–Cl bond occurs only in the triplet state of CMBP, which may be produced by intersystem crossing having the quantum yield of unity.

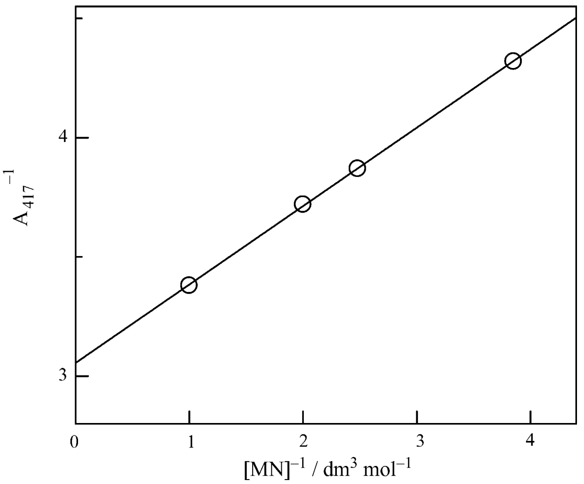


Fig. 7. Plots according to Eq. (8) for the quenching of triplet CMBP by 1-methylnaphthalene (MN).

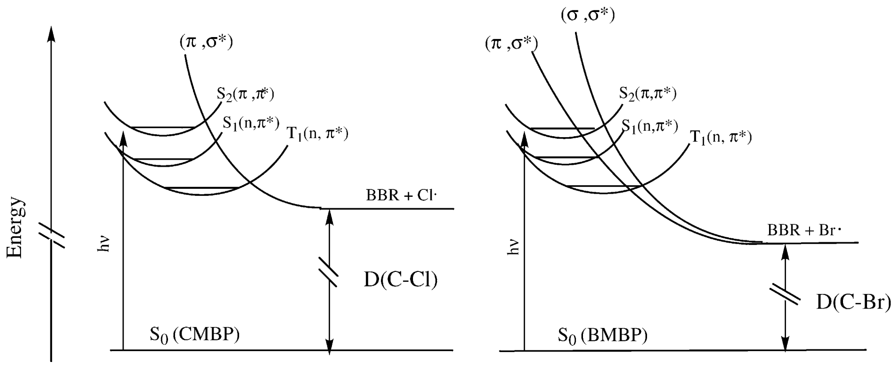
The lifetime of triplet CMBP at 295 K was estimated by means of a Stern-Volmer type analysis, employing 1-methylnaphthalene (MN) as a triplet quencher for 355 nm laser photolysis of CMBP in ACN. This technique has been widely used to determine lifetimes of short-lived triplet states [14,15]. The transient 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 CMBP according to Eq. (7).

$$^3\mathrm{CMBP}^* + \mathrm{MN} \xrightarrow{k_q} \mathrm{CMBP} + {}^3\mathrm{MN}^* \quad (7)$$

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. (8).

$$\Delta A_{417}{}^{-1} = \kappa + \frac{\kappa}{k_q \tau_T}[\mathrm{MN}]^{-1} \quad (8)$$

where k_q, τ_T and κ are, respectively, the quenching rate constant for Eq. (8), 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 CMBP (1.0 × 10^{-2} mol dm^3)–MN system as a function of [MN]$^{-1}$. The plots give a straight line, giving an intercept of 3.05 and a slope of 0.33 mol dm^{-3}. Thus, the Stern-Volmer constant ($k_q \tau_T$) is determined to be 9.27 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} [16]), the τ_T value is determined to be 1.1 ns, which is close to that of p-mercaptomethylbenzophenone (MMBP, 1.8 ns) whose triplet state is reactive for ω-bond dissociation at room temperature [3]. It seems that the photochemical profiles of CMBP for ω-cleavage are very similar to those of MMBP. We have determined the quantum yield of the C–Cl bond dissocia-



Scheme 1.

tion via the T_1 state of CMBP to be 0.51 at 295 K. Thus, the rate, k_{dis} for the C–Cl bond cleavage leading to the radical formation is estimated to be $4.6 \times 10^8\,\mathrm{s}^{-1}$ by using Eq. (9).

$$k_{\mathrm{dis}} = \Phi_{\mathrm{dis}} \tau_{\mathrm{T}}^{-1} \tag{9}$$

The residual rate, k_{nr} ($= \tau_{\mathrm{T}}^{-1} - k_{\mathrm{dis}}$) is considered to be due to a non-radiative process from the T_1 state to the ground state (S_0). On the other hand, upon 355 nm laser pulsing in the ACN solution of BMBP in the presence of MN (1.0 mol dm^3), formation of triplet MN was absent in the transient absorption. This observation indicates that the triplet state is not formed via intersystem crossing due to chemical reactions in the excited singlet states. This interpretation does not make discrepancy with the facts that: (1) phosphorescence from BMBP is absent at 77 K; (2) the CIDEP signal is silent; and (3) the Φ_{BBR} value (0.41) is smaller than the α_{BBR} (0.53), presumably, due to geminate recombination of the singlet biradical. Therefore, we conclude that the deactivation pathway of the excited single state of BMBP is governed by the C–Br bond rupture, resulting in the absence of the triplet state formation upon direct excitation.

Based on the results obtained hereinbefore, schematic energy diagrams of photoexcited HMBP are depicted in Scheme 1. Since the absorption spectra of HMBP and phosphorescence spectrum of CMBP are similar to those of benzophenone, the electronic character, ordering and energy level of HMBP may resemble those of benzophenone. The energy level of the S_1 (n, π^*) state is very close to that of the T_2 (π, π^*) state [1], which provides a fast intersystem crossing according to the El-Sayed rule to produce the T_1(n, π^*) within 10 ps [17]. The potential energy surface for the studied C–Cl bond cleavage can be interpreted as being a thermally activated crossing from the T_1(n, π^*) to a dissociative ^{3}(π, σ^*) state which leads to the formation of the π-(BBR) and σ-(Cl$^\bullet$) radicals on the analogy of the dissociation mechanism for *p*-mercaptomethylbenzophenone [3]. The S_1 state of CMBP is shown to be inefficient for ω-cleavage. The (π, σ^*) potential surface of CMBP may not interact with that of the S_1 state which is predominated by a fast intersystem crossing, resulting the absence of C–Cl dissociation in the S_1 state. In contrast to decomposition of CMBP, BMBP is concluded to undergo ω-bond cleavage in the excited singlet state upon direct excitation. The bond enthalpy of C–Br in BMBP was estimated to be smaller than that of C–Cl of CMBP. The potential surfaces of (σ, σ^*) and (π, σ^*) states of BMBP might be lowered in energy compared with those of CMBP. Therefore, the predissociation of BMBP may occur at a vibronic level of the S_1 state crossing predominantly with a dissociative ^{1}(σ, σ^*) state, leading to formation of a singlet σ–radical pair which readily undergoes geminate recombination. After some of the radical pairs escape from the solvent cages, the electronic configuration converts to π, σ of the BBR and Br$^\bullet$, thanks to the stabilization energy accrued from π-delocalization in BBR [18]. The predissociation rate of BMBP must be much greater than that of intersystem crossing from the S_1 to the T_2 state ($\sim 10^{11}\,\mathrm{s}^{-1}$).

The D(C–Br) of BMBP is estimated to be 53.0 kcal mol^{-1}, which is unambiguously smaller than those of D(C–Cl) of CMBP (65.6 kcal mol^{-1}), D(C–S) of MMBP (60.9 kcal mol^{-1} [3]) and D(C–O) (73.7 kcal mol^{-1}) of *p*-hydroxymethyl benzophenone where ω-dissociation is absent [3]. The reactive excited states for photoinduced ω-fission of benzophenone derivatives can be classified in terms of the D(C–X) value as follows: (1) For occurrence of photoinduced ω-bond dissociation, the D(C–X) value should be smaller than the triplet energy (E_{T} = ca. 68 kcal mol^{-1}). (2) When the D(C–X) value is smaller than E_{T}, the triplet state is dissociative by nature. (3) The threshold of the D(C–X) for the excited singlet state being reactive may be located at 55 ∼ 60 kcal mol^{-1}. The third statement is going to be examined in the following papers.

4. Conclusion

By means of time-resolved EPR and laser flash photolysis techniques, BMBP and CMBP are found to undergo ω-bond cleavage. Through transient absorption measurements, the Φ_{BBR} values of the BBR formation upon direct excitation are determined to be 0.41 ± 0.03 for BMBP and 0.51 ± 0.03 for CMBP at 295 K. The CIDEP signal originated from BBR formation is obtained for CMBP, while that for BMBP is absent. Upon sensitization of triplet acetone, the α_{BBR} values of the C–X bond fission in the triplet states of BMBP and CMBP are determined to be 0.53 ± 0.03 and 0.51 ± 0.03, respectively. As for CMBP, from the agreement between the Φ_{BBR} and α_{BBR} values, the C–Cl bond cleavage is concluded to occur only in the triplet state, which is produced with a triplet yield of unity due the rapid intersystem crossing. On the other hand, the cleavage of the C–Br bond in BMBP upon direct excitation is the event only in the excited singlet state without intersystem crossing, while the triplet state is also reactive for ω-bond dissociation. The C–Br bond dissociation in the S_1 state of BMBP is faster than intersystem crossing from the S_1 to the T_1 state. The schematic reaction profiles of BMBP and CMBP in the excited states are depicted in Scheme 1. The spin multiplicity of the reactive states for ω-bond cleavage seems to be classified by the *D*(C–X) value.

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