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Reactive states for β-bond dissociation of α-phenoxylacetophenones studied by laser flash triplet sensitization techniques

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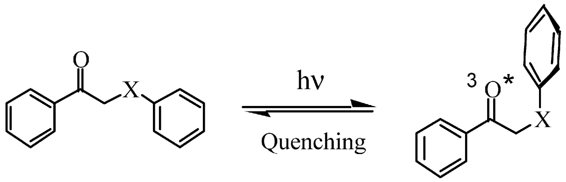
Abstract

Photoinduced β-bond dissociation of α-phenoxylacetophenones (PAs) substituted in the phenoxyl moiety has been investigated in polar media by means of laser flash photolysis and triplet sensitization techniques to clarify the spin multiplicity of the reactive states, excited lowest singlet (S_1) or triplet (T_1) state. The electronic character of the T_1 state of PAs was found to be of π,π^* from transient absorption spectra at 77 K. Any photochemical intermediates were absent in transient absorption upon direct photolysis and triplet xanthone sensitization of PAs having electron withdrawing substituent groups at 295 K. Hydroxy-PAs and methoxy-PAs undergo β-cleavage upon both direct excitation and triplet sensitization, providing the corresponding phenoxyl radicals. From disagreement between the quantum yields of the radical formation upon direct excitation and the efficiency of β-cleavage in the triplet state determined by triplet sensitization, it was concluded that the S_1 and T_1 states are both reactive for β-bond dissociation in PAs. The non-radiative deactivation process of triplet PAs was suggested to be due to efficient quenching of the $T_2(n,\pi^*)$ state by the β-phenyl ring. The deactivation profiles of excited PAs are discussed.

Keywords: Laser flash photolysis; β-Cleavage; Phenoxylacetophenone; Triplet sensitization

1. Introduction

Photochemistry of carbonyl compounds having β-phenyl ring has been paid attention from the viewpoint of the deactivation mechanisms of the triplet state [1–10]. It has been established that the efficient quenching of the carbonyl n,π^* triplet by through-space intramolecular interactions with β-phenyl ring shortens the lifetimes of the triplet states of such as β-phenylpropiophenones and α-phenoxylacetophenones compared with those of corresponding molecules without β-phenyl ring. For occurrence of this quenching, a *gauche* conformation is required where the π-system of the β-phenyl ring is allowed to overlap with the n-orbital of the carbonyl group [4].



X = CH_2; β-Phenylpropiophenone
O ; α-Phenoxylacetophenone

Based on the relationship between the Hammett constants of the substituent group and the triplet lifetimes, charge-transfer interaction was concluded to be involved in the quenching [8,10]. As with α-phenoxylacetophenones, it is reported that this quenching occurs in competition with fragmentation due to β-cleavage of the C–O bond in the triplet state, providing free radicals [9,10]. The quantum yields of β-cleavage depend on the substituent groups on the β-phenyl ring, varying from 10^{-3} to 0.14 determined by product analysis techniques in benzene [10]. The reactive state for the β-cleavage of

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α-phenoxylacetophenones upon photoexcitation was regarded as being only the triplet state. One of the best techniques to examine the photochemical reactivity in triplet states is suggested to be triplet sensitization using triplet energy transfer [11].

In this context, to verify the triplet reactivity, we have carried out laser flash photolysis of α-phenoxylacetophenones using xanthone as a sensitizer in acetonitrile. Based on the quantum yields of the formation of the radicals initially formed due to β-bond dissociation, the mechanism of the β-cleavage in α-phenoxylacetophenones as well as the reactive state is discussed.

2. Experimentals

2.1. Materials

α-Phenoxylacetophenone (PA) and its *p*-substituted derivatives, X-PA (X = MeO, OH, Ph, CN and NO_2) were synthesized from α-bromoacetophenone and corresponding phenols. Into an acetone solution of α-bromoacetophenone in the presence of KOH, a phenol derivative was added and the solution was stirred at room temperature for 2 h. After the solvent was evaporated, the benzene solution of the mixture was washed with water. The crude product was separated by passing it through a silica gel column with a mixture of benzene and ethyl acetate (10:1, v/v), and purified by recrystallization from ethanol. Xanthone (XT) was repeatedly recrystallized from ethanol. Acetonitirile (ACN) was purified by distillation and used as the solvent. A mixture of methanol and ethanol (1:1, v/v) and EPA (a mixture of diethyl ether, isopenetane and ethanol (5:5:3, v/v/v)) were used as the solvent for phosphorescence and transient absorption measurement at 77 K, respectively.

2.2. Apparatus

Emission spectra were recorded on a Hitachi F-4010 fluorescence spectrophotometer. Third (355 nm) and fourth harmonics (266 nm) of a Nd:YAG laser (JK Lasers HY-500; pulse width 8 ns; 1 Hz repetition) were used for an excitation light source. The details of the detection system for the time profiles of the transient absorption have been reported elsewhere [12]. The transient data obtained by laser flash photolysis were 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.

2.3. Samples

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 PAs for 266 nm laser photolysis was adjusted to achieve the optical density at 266 nm being ca. 0.7 in ACN ($\sim 10^{-4}$ mol dm^{-3}). Usual measurements were carried out at 295 K. The number of the repetition of laser pulsing in the sample was less than four pulses to avoid excess exposure. Several measurements were repeated using the same concentration systems to attain experimental errors less than ±5%.

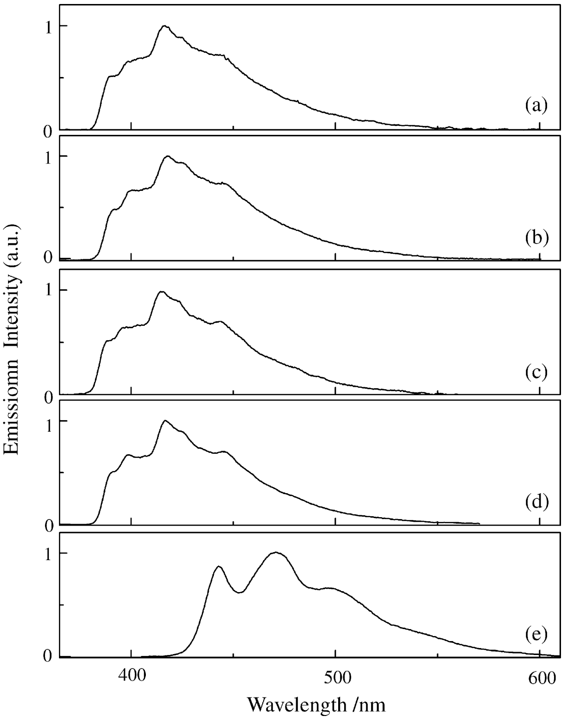

Fig. 1. Phosphorescence spectra of PAP (a), OH-PAP (b), MeO-PA (c), CN-PA (d) and Ph-PA (e) in a mixture of MeOH and EtOH at 77 K.

3. Results and discussion

Fig. 1 shows phosphorescence spectra of α-phenoxylacetophenones obtained in a mixture of methanol and ethanol (1:1, v/v) at 77 K. The shape of the obtained spectra having vibrational structures are similar to each other except for that of Ph-PA. The appearance of vibrations in phosphorescence spectra reveals a strong vibronic coupling between the $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ configurations. The phosphorescence spectrum of Ph-PA resembles those of biphenyl compounds [11], indicating that triplet exciton in Ph-PA is localized on the biphenyl moiety. Emission from NO_2-PA was absent. It was confirmed that the excitation spectra for the obtained phosphorescence agreed well with the corresponding absorption spectra. From the phosphorescence origins, the triplet energies (E_T) of emissive PAs were determined to be ca. 73.5 or 64.6 kcal mol^{-1} for Ph-PA. The E_T values determined are listed in Table 1.

Fig. 2 shows the transient absorption spectra observed at 500 ns after 266 nm laser pulsing in the studied PAs in EPA glass matrix at 77 K. The absorption peaks at 335 nm are seen for PA and X = MeO, OH and CN derivatives. It is known that the shapes of triplet absorption spectra of acetophenone derivatives are useful criteria determining the lowest triplet (T_1) nature, $^3(n,\pi^*)$ or $^3(\pi,\pi^*)$, both of which readily undergo inversion of the lowest state with changes of solvent polarity and substituent groups [13,14]. Since the absorption spectra obtained for PA and X = MeO, OH and CN derivatives resemble that of π,π^* triplet acetophenone [13,14], the electronic character of their T_1 states in polar media is of a π,π^* type in nature. The transient absorption spectrum of Ph-PA at 395 nm is similar to that of triplet biphenyl derivatives [11], which agrees with the result

Table 1
Triplet energies (E_T), quantum yields (Φ_{rad}) and efficiencies (α_{rad}) of radicals upon direct excitation and sensitization, quenching rate constants (k_q), Hammett constants (σ_p^+) for PAs, enthalpies for formation of X-PA and X-PR ($\Delta_f H$(X-PA) and $\Delta_f H$(X-PR)) and the C—O bond (D(C—O))

X	E_T[a] (kcal mol^{-1})	Φ_{rad}[b]	α_{rad}	k_q (10^9 dm^3 mol^{-1} s^{-1})	σ_p^{+}[c]	$\Delta_f H$(X-PA) (kcal mol^{-1})	$\Delta_f H$(X-PR) (kcal mol^{-1})	D(C—O)[d] (kcal mol^{-1})
NO_2	n.d.	0	0	10.0	0.79	189.2	227.3	57.9
CN	73.5	0 (0.0039)	0	4.0	0.66	17.2	49.4	52.0
H	73.5	0 (0.014)	0	4.3	0	−17.6	13.5	50.9
Ph	64.5	0.10	0	9.1	−0.13	6.7	36.6	49.7
MeO	73.9	0.22 (0.14)	≥0.27	7.6	−0.78	−55.0	−27.7	47.1
OH	73.2	0.18 (0.14)	≥0.24	5.1	−0.92	−61.7	−34.9	46.6

n.d., not determined.

[a] Determined from the 0–0 origin of the phosphorescence spectrum in a mixture of methanol and ethanol (1:1, v/v) at 77 K.

[b] Data in parentheses were obtained by product analysis in benzene [10].

[c] Data from ref. [19].

[d] Obtained by Eq. (6). See text for details.

from phosphorescence measurement that triplet energy in Ph-PA is localized on the biphenyl moiety of a π,π^* type. Transient absorption for NO_2-PA was absent. The observations of phosphorescence and transient absorption spectra at 77 K indicate that the employed PAs efficiently give the triplet states without any photochemical reactions at 77 K.

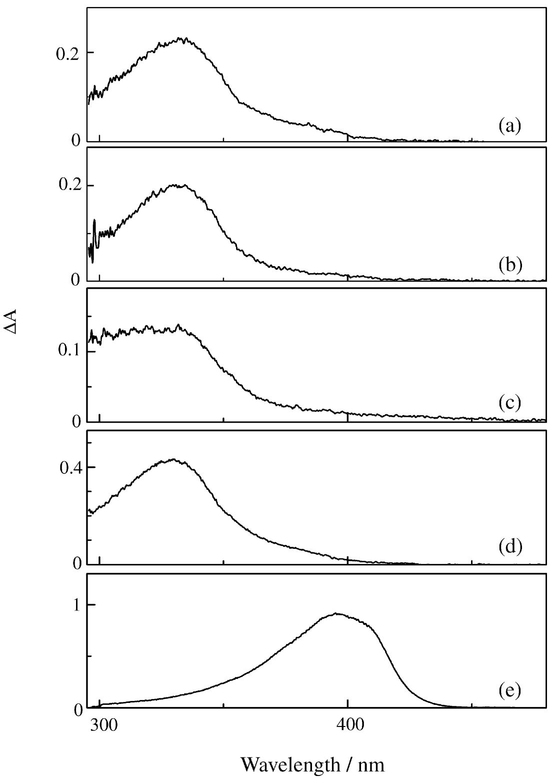

Fig. 2. The transient absorption spectra observed at 500 ns after 266 nm laser pulsing in EPA glass of PA (a), OH-PA (b), MeO-PA (c), CN-PA (d) and Ph-PA (e) at 77 K.

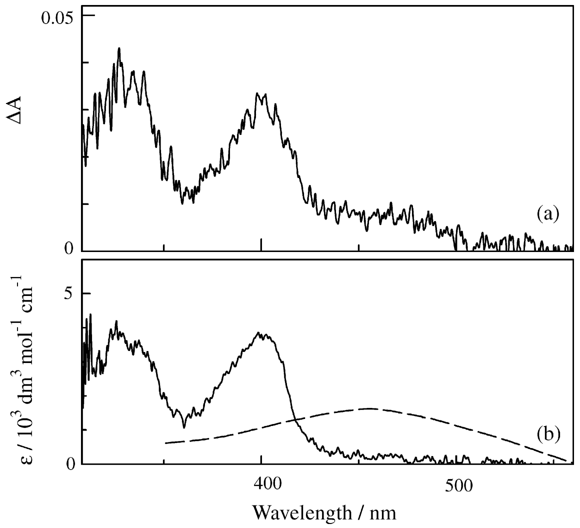

Fig. 3. (a) A transient absorption spectrum obtained at 100 ns after 266 nm laser pulsing in an ACN solution of MeO-PA. (b) Reference absorption spectra of the p-methoxyphenoxyl radical (MPR, solid) and benzoylmethyl radical (BMR, dash).

Laser flash photolysis at 295 K was carried out to investigate the initial photoreactions of PAs in ACN in a nanosecond time region. Fig. 3a shows a transient absorption spectrum obtained at 100 ns after 266 nm laser pulsing in an ACN solution of MeO-PA. Absorption peaks at 330 and 400 nm and a broad absorption band at 450 nm are seen. The former peaks are similar to those of the p-methoxyphenoxyl radical (MPR) while the latter is due to the benzoyl methyl radical (BMR) having the molar absorption coefficient, $\varepsilon = 1700$ dm^3 mol^{-1} cm^{-1} at 450 nm [15]. The ε value of MPR was determined to be 3800 dm^3 mol^{-1} cm^{-1} at 400 nm by comparing with that of the benzophenone ketyl radical ($\varepsilon = 3700$ dm^3 mol^{-1} cm^{-1} at 545 nm [16]) produced by H-atom abstraction of triplet benzophenone (BP) from p-methoxyphenol (MeOPhOH) upon 355 nm laser photoysis of a BP/MeOPhOH system in ACN. The reference absorption spectra of MPR and BMR are shown in Fig. 3b.[1]

The absorption spectrum obtained by laser photolysis can be reproduced by superposing those of MPR and BMR. The

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[1] The absorption spectrum of MPR was obtained by hydrogen atom abstraction of $tert$-butoxyl radical from MeOPhOH generated upon 308 nm laser pulsing in a di-$tert$-butyl peroxide (8.7×10^{-2} mol dm^{-3})/MeOPhOH (4.0×10^{-3} mol dm^{-3}) system in ACN at 295 K.

reproducibility in the transient absorption spectrum indicates that the decomposition of MeO-PA occurs upon photoexcitation to provide MPR and BMR.

The quantum yield (Φ_{rad}) of the radical formation upon 266 nm laser photolysis of MeO-PA was determined with the use of Eq. (1) based on the absorption change (ΔA_{400}) at 400 nm due to formation of MPR and BMR.

$$\Phi_{\mathrm{rad}} = \Delta A_{400}(\varepsilon_{400}^{\mathrm{MPR}} + \varepsilon_{400}^{\mathrm{BMR}})^{-1} I_{\mathrm{abs}}^{-1} \qquad (1)$$

where $\varepsilon_{400}^{\mathrm{MPR}}$, $\varepsilon_{400}^{\mathrm{BMR}}$ and I_{abs} are, respectively, the molar absorption coefficients of MPR at 400 nm (3800 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$) and of BMR at 400 nm (1300 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ [15]) and the number of the photon flux of a laser pulse absorbed by MeO-PA. The quantity of I_{abs} is determined by using the absorption of triplet benzophenone in ACN as an actinometer [17].

$$\Delta A_{\mathrm{T}}^{\mathrm{BP}} = \varepsilon_{\mathrm{T}}^{\mathrm{BP}} \Phi_{\mathrm{ISC}}^{\mathrm{BP}} I_{\mathrm{abs}} \qquad (2)$$

where $\Delta A_{\mathrm{T}}^{\mathrm{BP}}$, $\varepsilon_{\mathrm{T}}^{\mathrm{BP}}$ and $\Phi_{\mathrm{ISC}}^{\mathrm{BP}}$ 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 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ [18]) and triplet yield of benzophenone (1.0 [19]). By using Eqs. (1) and (2), the Φ_{rad} value was determined to be 0.18 ± 0.01. Upon 266 nm laser photolysis of HO-PA and Ph-PA in ACN, transient absorption due to BMR and *p*-hydroxyphenoxyl radical (HPR, $\varepsilon = 4500\ \mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ at 400 nm)[2] or *p*-phenylphenoxyl radical (PPR, $\varepsilon = 2700\ \mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ at 500 nm [20]) was obtained, respectively.

The Φ_{rad} values for OH-PA and Ph-PA were determined to be 0.18 ± 0.01 and 0.10 ± 0.005, respectively. With $\mathrm{NO_2}$-PA, CN-PA and PA, any perceptible transient absorption spectra were quite absent upon 266 nm laser photolysis at 295 K although triplet–triplet absorption spectra due to CN-PA and PA were seen at 77 K. From these observations, it is inferred that the triplet states of CN-PA and PA deactivate at room temperature immediately after being produced via intersystem crossing from the excited singlet states. As with $\mathrm{NO_2}$-PA, the excited singlet state may be governed by the internal conversion to the ground state without intersystem crossing and any chemical reactions. The Φ_{rad} values determined upon direct excitation are listed in Table 1.

The triplet energy (74.0 $\mathrm{kcal\,mol^{-1}}$ [19]) of xanthone is larger than that of PAs (ca. 73.5 $\mathrm{kcal\,mol^{-1}}$). Although the difference in triplet energy between XT and PAs is 0.5 $\mathrm{kcal\,mol^{-1}}$, efficient triplet energy transfer possibly occurs [21]. Triplet sensitization of XT by using third harmonics from a Nd:YAG laser (355 nm) was performed in ACN solutions of PAs. A time profile of the transient absorption at 625 nm for the XT/MeO-PA system is shown in Fig. 4. A decay rate of the absorption intensity at 625 nm due to triplet XT was obtained to be $6.0 \times 10^6\ \mathrm{s^{-1}}$. After triplet XT completely deactivated, a transient absorption spectrum with absorption bands at 400 and around 450 nm appeared (see inset in Fig. 4). The observed spectrum is similar to that obtained upon direct excitation of MeO-PA (Fig. 3a). The formation of the radicals, MPR and BMR indicates that the C–O bond of MeO-PA dissociates via the triplet state produced by triplet sensitization of XT. The observed rates (k_{obsd}) for the decay of triplet XT are plotted as a function of the concentration of MeO-PA [MeO-PA] in Fig. 5a. Since the plots give a straight line, the k_{obsd} can be formulated by:

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

where k_0 and k_{q}, respectively, represent the decay rate of triplet XT in the absence of MeO-PA and the rate constant for quenching of triplet XT by MeO-PA. From the intercept and slope of the line, the values of k_0 and k_{q} are determined to be $1.0 \times 10^6\ \mathrm{s^{-1}}$ and $7.6 \times 10^9\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$, respectively. The k_{q} values for other PAs obtained by the above method are listed in Table 1.

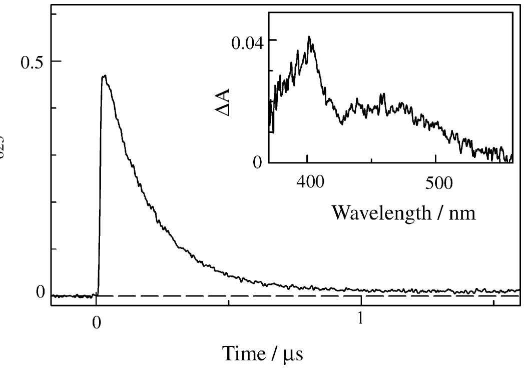

Fig. 4. The temporal absorbance change at 625 nm observed after 355 nm laser photolysis in a XT ($3.0 \times 10^{-3}\ \mathrm{mol\,dm^{-3}}$)/MeO-PA ($6.0 \times 10^{-4}\ \mathrm{mol\,dm^{-3}}$) system in ACN at 295 K. *Inset*: A transient absorption spectrum obtained at 1.2 μs for the system studied.

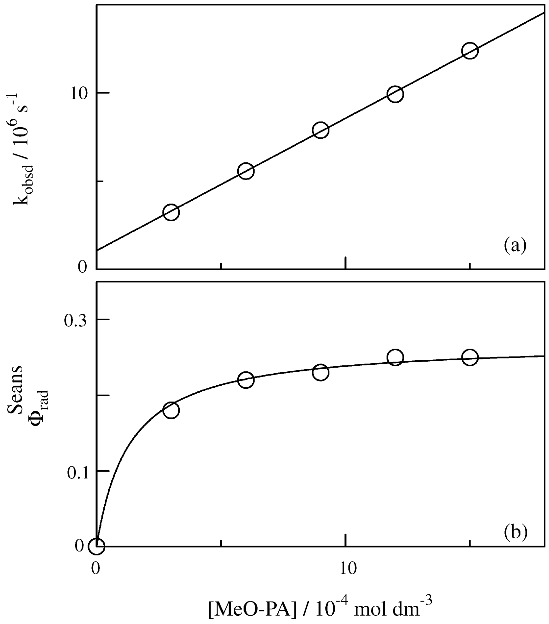

Fig. 5. The decay rate (k_{obsd}) of triplet XT (a) and the quantum yields ($\Phi_{\mathrm{rad}}^{\mathrm{sens}}$) for radical formation upon triplet sensitization (b) plotted as a function of the concentration of MeO-PA. The solid curve in (b) was calculated by Eq. (5).

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[2] Determined by the same procedure as the ε value of MPR with a BP/*p*-hydroxyphenol system in ACN.

XT sensitization of OH-PA provided appearance of the corresponding radicals whereas any transient absorption for X = H, CN, Ph and NO_2 was not perceptible after depletion of triplet XT. From the result that the magnitude of k_q is in the same order of 10^9 dm^3 mol^{-1} s^{-1}, it is inferred that triplet energy transfer does occur from triplet XT to PAs to produce triplet PAs that may deactivate so fast to the ground state through specific conformational quenching or undergo β-cleavage in the triplet states of MeO-PA and OH-PA.

The quantum yield ($\Phi_{\rm rad}^{\rm sens}$) for the formation of MPR and BMR upon triplet sensitization was determined by:

$$\Phi_{\rm rad}^{\rm sens} = \Delta A_{400}(\varepsilon_{400}^{\rm MPR} + \varepsilon_{400}^{\rm BMR})^{-1}(I_{\rm abs}^{\rm XT})^{-1} \tag{4}$$

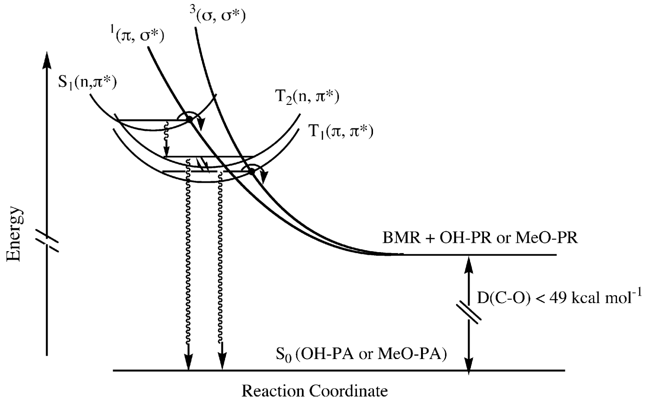
$\varepsilon_{400}^{\rm MPR}$, $\varepsilon_{400}^{\rm BMR}$ and $I_{\rm abs}^{\rm XT}$ are, respectively, the molar absorption coefficients of MPR at 400 nm (3800 dm^3 mol^{-1} cm^{-1}) and of BMR at 400 nm (1300 dm^3 mol^{-1} cm^{-1}) and the number of the photon flux of a laser pulse absorbed by XT. The value of $I_{\rm abs}^{\rm XT}$ at 355 nm was determined by using the triplet–triplet absorption of BP as an actinometer by adjusting absorbance at 355 nm (see Eq. (2)). The obtained values of $\Phi_{\rm rad}^{\rm sens}$ are plotted as a function of [MeO-PA] in Fig. 5b. The $\Phi_{\rm rad}^{\rm sens}$ value increases non-linearly with increasing [MeO-PA]. The $\Phi_{\rm rad}^{\rm sens}$ value is also formulated with the kinetic parameters, k_0 and k_q by:

$$\Phi_{\rm rad}^{\rm sens} = k_{\rm q}[\text{MeO-PA}]\alpha_{\rm rad}\alpha_{\rm TET}\Phi_{\rm ISC}^{\rm XT}(k_0 + k_{\rm q}[\text{MeO-PA}])^{-1} \tag{5}$$

where $\alpha_{\rm rad}$, $\alpha_{\rm TET}$ and $\Phi_{\rm ISC}^{\rm XT}$ are the efficiency for the radical formation in the triplet state of MeO-PA and triplet energy transfer from triplet XT to MeO-PA and the triplet yield of XT (1.0 [19]), respectively. By best-fitting Eq. (5) to the experimental values of $\Phi_{\rm rad}^{\rm sens}$ with the use of the k_0 and k_q values obtained above, the product value of $\alpha_{\rm rad}$ and $\alpha_{\rm TET}$ was obtained to be 0.27 ± 0.01. Since the value of $\alpha_{\rm TET}$ is not larger than unity, that of $\alpha_{\rm rad}$ for MeO-PA is not smaller than 0.27. As with OH-PA upon triplet sensitization, the product value of $\alpha_{\rm rad}$ and $\alpha_{\rm TET}$ was determined to be 0.24 ± 0.01 by the same manner to a XT/MeO-PA system. According to the spin conservation rule, a triplet radical pair, ^{3}(BMR + X-PR)$_{\rm cage}$ of BMR and the phenoxyl radical derivative, X-PR (X = MeO or OH) is initially produced in a solvent cage upon the C–O bond cleavage in triplet MeO- or OH-PA. The triplet radical pair is allowed to escape from the solvent cage without geminate recombination, resulting in efficient formation of free radicals, BMR and X-PR. Thus, the $\alpha_{\rm rad}$ value can be interpreted to be equal to that of the efficiency for the bond cleavage in the triplet state of X-PR. It is noteworthy that the $\Phi_{\rm rad}$ values for MeO-PA and OH-PA (0.22 and 0.18) is smaller than those of $\alpha_{\rm rad}$ ($\geq$0.27 and $\geq$0.24). From these disagreements, it is concluded that the reactive states for β-cleavage upon direct excitation of MeO-PA and OH-PA are not only the triplet states but also the excited singlet states. In an early study, the quantum yields for intersystem crossing of PAs were assumed to be unity [10]. However, the finding of the dual dissociative states of MeO-PA and OH-PA indicates that their quantum yields, $\Phi_{\rm isc}$ of intersystem crossing are not unity. In the present work, it was impossible to estimate definite $\Phi_{\rm isc}$ values and quantum yields for β-cleavage presumably in the S_1 state. Recently, excited singlet states of aromatic carbonyl compounds are found to undergo bond dissociation as well as the triplet state (ω-bond cleavage) [22–24].

Since occurrence of the β-cleavage in the S_1 state of OH-PA and MeO-PA is probably competitive with intersystem crossing, the rate of β-cleavage in the S_1 states may be as large as those of intersystem crossing. In the present work, the electronic character of the T_1 states of PAs except for Ph-PA and NO_2-PA were shown to be of a π,π* type from the triplet absorption at 77 K. The excited state ordering of the studied PAs except Ph-PA and NO_2-PA is considered to be $S_1(n,\pi^*) > T_2(n,\pi^*) > T_1(\pi,\pi^*)$. From the El-Sayed's selection rule, it is inferred that the intersystem crossing of PAs proceeds from the $S_1(n,\pi^*)$ to the $T_2(n,\pi^*)$ state, whose rate is relatively smaller than that of intersystem crossing from $S_1(n,\pi^*)$ to π,π* triplet, e.g., 1×10^{11} s^{-1} of benzophenone [25]. Once the $T_1(\pi,\pi^*)$ states of X-PAs except for Ph-PA and NO_2-PA are formed by internal conversion from the $T_1(\pi,\pi^*)$ states via the $T_2(n,\pi^*)$ state upon direct excitation or by triplet sensitization, we propose that irrespective of occurrence of β-cleavage, the $T_1(\pi,\pi^*)$ state undergoes a fast deactivation to the ground state via the $T_2(n,\pi^*)$ state interacted with the β-phenyl ring. The quenching rates of triplet XT by PAs obtained were all in the magnitude of 10^9 dm^3 mol^{-1} s^{-1}, indicating that triplet energy transfer undoubtedly proceeds to produce triplet states of PAs. However, any triplet absorption spectra of PAs were not observed at 295 K. Therefore, we consider that the absence of absorption of triplet PAs must be due to their shortened lifetimes of triplets by a fast non-radiative deactivation process. The most probable pathway is quenching of the n,π* triplet carbonyl moiety by the β-phenyl ring [4]. For the present case of PAs, the deactivation of triplet PAs should proceed by through-space interaction between the β-phenyl ring and the $T_2(n,\pi^*)$ state coupled with the $T_1(\pi,\pi^*)$ state by either vibronic mixing or a thermal population at 295 K. For the case of β-dissociative X-PA (X = MeO and OH), it must be considered that residual efficiencies ($1 - \alpha_{\rm rad}$) upon deactivation of these triplet states in fluid media are for quenching induced by β-phenyl ring.

Based on the obtained results and consideration of quenching of the $T_2(n,\pi^*)$ state by β-phenyl ring, a schematic energy diagram for photoexcited X-PA (X = OH and MeO) is depicted in Scheme 1 including the C–O bond cleavage processes. Dissociation profiles in the excited states of the X-PAs can be interpreted to be a thermally activated crossing to dissociative potential surfaces leading to free radicals. The plausible 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 [26]. With respect to X-PA, the $S_1(n,\pi^*)$ interacts with a singlet π,σ* dissociative potential for the C–O anti-bonding, competing intersystem crossing to the $T_1(\pi,\pi^*)$ state while the $T_1(\pi,\pi^*)$ correlates with a triplet σ,σ* surface, leading to formation of a singlet σ-radical pair in a solvent cage. After some of the σ-radical pairs of BMR and X-PA escape from the solvent cages, the electronic configuration of σ-radical in BMR



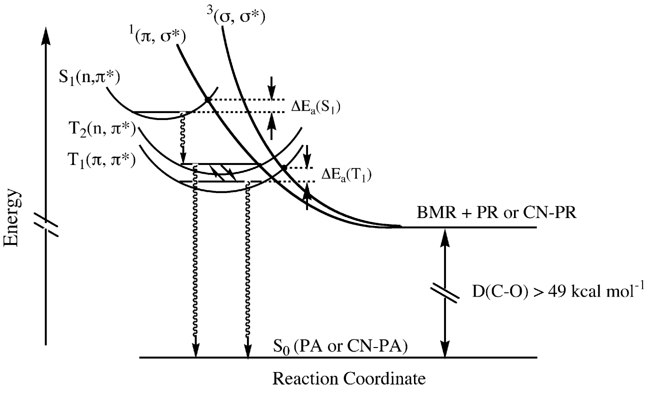
Scheme 1. An energy diagram for deactivation processes of excited OH-PA or MeO-PA including the β-bond decomposition process.

converts to that of π-radical due to stabilization energy accrued from π-delocalization [26]. The enthalpy of the C–O bond of PAs, D(C–O) was obtained on the basis of the heat of formation ($\Delta_f H$) for X-PA, BMR and X-PR computed by using a semi-empirical PM3 program contained in *MOPAC*'97 by Eq. (6).

$$\Delta_f H(\text{X-PA}) = \Delta_f H(\text{BMR}) + \Delta_f H(\text{X-PR}) - D(\text{C–O}) \qquad (6)$$

where $\Delta_f H$ (BMR) was 19.8 kcal mol^{-1} for all the cases. The calculated values of $\Delta_f H$ (X-PA), $\Delta_f H$ (X-PR) and D(C–O) are listed in Table 1. Both MeO-PA and OH-PA having D(C–O) values of ca. 47 kcal mol^{-1}, which is definitely smaller than the triplet energy of X-PA (ca. 73 kcal mol^{-1} for X = OH and MeO), are shown to dissociate in the triplet state. It seems that the threshold of bond enthalpies for cleaving the C–O bond in triplet PAs lies at ca. 49 kcal mol^{-1}.

On the other hand, any radical formations were not seen upon photolysis and sensitization of X-PAs (X = H, CN and NO_2). An energy diagram for X-PAs where radical formation is absent is drawn in Scheme 2. The absence of bond dissociation in excited states is interpreted in terms of a large energy barrier, ΔE_a from an excited state to a dissociative potential surface [24,27–29]. Since the C–O bond enthalpies of X-PAs where radical formation was not seen are larger than those of OH-PA and MeO-PA, the energy level of the crossing point between the excited state and the dissociative potential surface becomes higher than those for OH-PA or MeO-PA. Triplet X-PAs (X = H, CN and NO_2) are fated to deactivate to the ground state via the $T_2(n,\pi^*)$ state quenched of the β-phenyl ring.



Scheme 2. An energy diagram for deactivation processes of excited PA or CN-PA.

Fast quenching of triplet Ph-PA, where triplet exciton is shown to be localized on the biphenyl moiety of π,π^* from the phosphorescence spectrum, was seen upon XT sensitization. A fast deactivation mechanism of Ph-PA must differ from those of other PAs since triplet n,π^* character is absent in the biphenyl moiety. The triplet quenching mechanism for Ph-PA may be originated from charge-transfer interaction between triplet biphenyl and the carbonyl moiety, forming likely an intramolecular triplet exciplex. A similar intermolecular quenching mechanism is shown for deactivation of triplet aromatic compounds by ground state ketones via a triplet exciplex having weak charge-transfer character and sandwich-like structure [30].

4. Conclusion

Based on transient absorption measurements upon direct photolysis and triplet sensitization techniques, photoreactions of PAs were investigated in a nanosecond time-domain. Upon direct photoexcitation of hydroxy-PAs and methoxy-PAs, β-bond dissociation was confirmed from formation of corresponding phenoxyl radicals with quantum yield of ca. 0.2. These radicals were found to be produced from both the excited singlet and lowest triplet states since the α_{rad} values were evidently larger than the Φ_{rad} ones. These dual reactive states indicate that the intersystem crossing yields of those PAs are not unity. The fragmentation of OH-PA and MeO-PA can be understood by considering the smaller C–O bond enthalpies than those of undissociative X-PAs. The obtained value of D(C–O) decreases with a change of the Hammett constant, σ_p^+ of the substituent group from positive to negative values. Unfortunately, due to lacking of triplet lifetime data for PAs in ACN and the absence of bond dissociation in triplet PAs with positive σ_p^+ values, it is difficult to discuss the triplet quenching mechanism based on Hammett constants in the present study. The fast decay of X-PA should be due to through-space interactions of the β-phenyl ring with the $T_2(n,\pi^*)$ state coupled with the $T_1(\pi,\pi^*)$ state arising from either vibronic mixing or thermal population. As a triplet deactivation mechanism of Ph-PA, it was suggested that quenching of the triplet biphenyl moiety by the phenacyl moiety proceeds like a triplet exciplex reported previously [30].

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References

[1] D.G. Whitten, W.E. Punch, Mol. Photochem. 2 (1970) 77.
[2] P.J. Wagner, P.A. Kelso, A.E. Kemppainen, Mol. Photochem. 2 (1970) 81.
[3] F.R. Stermitz, D.E. Nicodem, V.P. Muralidharan, C.M. O'Donnell, Mol. Photochem. 2 (1970) 87.

[4] J.C. Scaiano, M.J. Perkins, J.W. Sheppard, M.S. Platz, R.L. Barcus, J. Photochem. 21 (1983) 137.

[5] T. Wismontski-Kinittel, T. Kilp, J. Phys. Chem. 88 (1984) 110.

[6] J.C. Netto-Ferreira, W.L. Leigh, J.C. Scaiano, J. Am. Chem. Soc. 107 (1985) 2617.

[7] R. Boch, C. Bohne, J.C. Netto-Ferreira, J.C. Scaiano, Can. J. Chem. 69 (1991) 2053.

[8] W.J. Leigh, J.-A.H. Banisch, M.S. Workentin, J. Chem. Soc. Chem. Commun. (1993) 988.

[9] J.C. Scaiano, J.C. Netto-Ferreira, J. Photochem. 32 (1986) 253.

[10] J.C. Netto-Ferreira, I.G.J. Avellar, J.C. Scaiano, J. Org. Chem. 55 (1990) 89.

[11] M. Yamaji, J. Kobayashi, S. Tobita, Photochem. Photobiol. Sci. 4 (2005) 294.

[12] M. Yamaji, Y. Aihara, T. Itoh, S. Tobita, H. Shizuka, J. Phys. Chem. 98 (1994) 7014.

[13] H. Lutz, E. Bréhéret, L. Lindqvist, J. Phys. Chem. 77 (1973) 1758.

[14] N.J. Turro, Modern Molecular Photochemistry, Benjamin/Cummings, Menlo Park, CA, 1978.

[15] H. Hayashi, Y. Sakaguchi, M. Tsunooka, H. Yanagi, M. Tanaka, Chem. Phys. Lett. 136 (1987) 436.

[16] K. Okada, M. Yamaji, H. Shizuka, J. Chem. Soc., Faraday Trans. 94 (1998) 861.

[17] M. Yamaji, T. Sekiguchi, M. Hoshino, H. Shizuka, J. Phys. Chem. 96 (1992) 9353.

[18] R.V. Bensasson, J.C. Gramain, J. Chem. Soc., Faraday Trans. 76 (1980) 1801.

[19] S.L. Murov, I. Carmicael, G. Hug, Handbook of Photochemistry, second ed., Mercel Dekker, New York, 1993 (revised and expanded).

[20] T. Yoshihara, M. Yamaji, T. Itoh, H. Shizuka, T. Shimokage, S. Tero-Kubota, Phys. Chem. Chem. Phys. 2 (2000) 993.

[21] M. Yamaji, S. Wakabayashi, S. Ueda, H. Shizuka, S. Tobita, Chem. Phys. Lett. 368 (2003) 41.

[22] M. Yamaji, A. Suzuki, F. Ito, S. Tero-Kubota, S. Tobita, B. Marciniak, J. Photochem. Photobiol. A: Chem. 170 (2005) 253.

[23] M. Yamaji, S. Inomata, S. Nakajima, K. Akiyama, S. Tobita, B. Marciniak, J. Phys. Chem. A 109 (2005) 3843.

[24] M. Yamaji, S. Inomata, S. Nakajima, K. Akiyama, S. Tero-Kubota, S. Tobita, B. Marciniak, Chem. Phys. Lett. 417 (2006) 211.

[25] P. Arouris, W.M. Gelbart, M.A. El-Sayed, Chem. Rev. 77 (1977) 793.

[26] W.G. Dauben, L. Salem, N.J. Turro, Acc. Chem. Res. 8 (1975) 41.

[27] X. Cai, M. Sakamoto, M. Hara, S. Tojo, A. Ouchi, A. Sugimoto, K. Kawai, M. Endo, M. Fujitsuka, T. Majima, J. Phys. Chem. A 109 (2005) 3797.

[28] X. Cai, M. Sakamoto, M. Hara, S. Inomata, M. Yamaji, S. Tojo, K. Kawai, M. Endo, M. Fujitsuka, T. Majima, Chem. Phys. Lett. 407 (2005) 402.

[29] X. Cai, M. Sakamoto, M. Yamaji, M. Fujitsuka, T. Majima, J. Phys. Chem. A 109 (2005) 5989.

[30] H. Shizuka, M. Yamaji, Bull. Chem. Soc. Jpn. 73 (2000) 267.