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Steady-state and laser flash photolysis studies on photochemical formation of 4-*tert*-butyl-4'-methoxydibenzoylmethane from its derivative *via* the Norrish Type II reaction in solution

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ABSTRACT

A photochemical formation process of avobenzone (AB; 4-*tert*-butyl-4'-methoxydibenzoylmethane) from 1,1-(4-*tert*-butybenzoyl)(4'-methoxybenzoyl)butane (PrAB) is studied by steady-state and laser flash photolysis in solution. The quantum yield of the formation via the triplet state of PrAB is determined to be 0.23 in degassed acetonitrile at 295 K. The Arrhenius plots of the decay rate of triplet PrAB show that photoelimination proceeds with an activation energy of 6.0 kcal mol⁻¹ and the frequency factor of $4.6 \times 10^{10} \text{ s}^{-1}$.

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1. Introduction

It is well known that B-diketones undergo keto-enol tautomerization in solution [1–3]. 1.3-Dibenzovlmethane (DBM) is a typical representative of the B-dicarbonyl compounds. A number of photochemical studies of DBM derivatives have been carried out to reveal the processes of keto-enol tautomerization [4-8]. Because of intramolecular H-bonding in DBM derivatives, the "chelated" enol form is largely favored in the ground state although the keto-enol tautomer ratio depends on the α -substituted groups, the nature of solvent, temperature and other surrounding conditions. The chelated enol form of DBMs shows strong absorption bands in the UVA region (315–380 nm) due to the π - π ^{*} transition of the chelated quasi-aromatic π -electron system. However, most of DBMs are non-fluorescent in solution, indicating the presence of efficient non-radiative processes from the excited singlet states. This process has been revealed to involve the formation of transient enol isomers (rotamers). The isomer, thus formed, is recovered to the chelated enol form in the dark. Therefore, DBMs are potential compounds for sunscreen agents. The tau-

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E-mail addresses: yamaji@chem-bio.gunma-u.ac.jp (M. Yamaji), mmiranda@qim.upv.es (M.Á. Miranda). tomerization and isomerization processes of DBMs are noted in Scheme 1.

The most widely used UVA sunscreen is 4-*tert*-butyl-4'methoxydibenzoylmethane (trade names, Avobenzone, Parsol 1789, etc., here abbreviated as AB). There is an amount of reports for understanding and utilizing photochemical and photophysical properties of AB [2,4,8–23]. AB has such a large absorbance at 350 nm that the molecular structure in the ground state is in the enol form. Photochemical behavior of AB is almost the same as that of DBM (Scheme 1) whereas AB is shown to photodecompose via the Norrish Type I mechanism [10,11].

In a previous paper, we prepared a methylated AB (1,1-(4-*tert*butylbenzoyl)(4'-methoxybenzoyl)ethane; MeAB) which shows large absorption in the UVC region (200–280 nm), concluding that the methyl group hinders a keto form of DBM moiety tautomerizing to an enol form in the ground state [23]. Laser photolysis investigations of MeAB revealed an efficient formation of the triplet state due to a fast intersystem crossing from the excited singlet state of the keto-formed MeAB. This photophysical feature is similar to that of carbonyl aromatic compounds, such as benzophenone whose electronic character of the triplet state is of an n,π^* type. Indeed, it is reported that 1,1-(4-*tert*-butylbenzoyl)(4'methoxybenzoyl)decane (C10-AB) has large absorption in the UVC domain, and that C10-AB undergoes the Norrish Type II reaction, resulting in formation of AB with a quantum yield of 10^{-3} [17].

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Scheme 1. .

Occurrence of photoelimination indicates that the electronic character of triplet C10-AB is of an n,π^* type. Consequently, introduction of substituent groups to the AB skeleton allows the formation of n,π^* triplets. To our best knowledge, there are very few investigations on photochemical formation of DBM derivatives via triplet states of the parent molecules.

In the present study, we prepare an AB derivative having the propyl group on the β -carbon of the DBM skeleton (1,1-(4-*tert*-butylbenzoyl)(4'-methoxybenzoyl)butane; PrAB) for the purpose of understanding the photoelimination process in solution. By using steady-state and laser photolysis techniques, the photochemical features of PrAB are investigated in detail.



2. Experimental

Avobenzone (AB; 4-tert-butyl-4'-methoxydibenzoylmethane) >99% purity was purchased from Fluka, and purified by recrystallizations from methanol before the use. Methylavobenzone (1,1-(4-tert-butylbenzoyl)(4'-methoxybenzoyl)ethane; MeAB) was prepared and purified according to the procedure reported previously [23]. Propylavobenzone (1,1-(4-tert-butylbenzoyl)(4'methoxybenzoyl)butane; PrAB) was prepared as followed. Avobenzone (0.5 g, 1.6 mmol) was dissolved in 25 mL of acetone and led to react overnight with an excess of 1-chloropropane from Sigma-Aldrich and K₂CO₃ (0.45 g, 3.2 mmol) at 60-70 °C under inert atmosphere. The crude was filtered and the organic phase was reserved. The solvent was evaporated under reduced pressure. The product was isolated by silica-gel column chromatography using a mixture of hexane-ethyl acetate (70:30, v/v) as an eluent. Propylavobenzone was isolated with c.a. 50% yield, and characterized by NMR spectrometry.

¹H NMR (300 MHz, CDCl₃). δ [ppm] = 8.05 (d, *J* = 9.0 Hz, 2*H*, ArH); 7.95 (d, *J* = 8.9 Hz, 2*H*, ArH); 7.45 (d, *J* = 8.9 Hz, 2*H*, ArH); 6.95 (d, *J* = 9.0 Hz, 2*H*, ArH); 5.12 (t, *J* = 6.6 Hz, 1*H*, CH); 3.87 (s, 3*H*, OCH₃); 2.10 (m, 2*H*, CH₂); 1.45 (m, 2*H*, CH₂); 1.33 (s, 9*H*, CH₃,); 0.98 (t, *J* = 7.35 Hz, 3*H*, CH₃).

¹³C NMR (75 MHz, CDCl₃). δ [ppm] = 195.9 (CO), 194.8 (CO), 163.7 (C), 157.1 (C), 133.6 (C), 130.9 (CH,), 129.2 (C), 128.6 (CH), 125.8 (CH), 114.0 (CH), 57.2 (CH), 55.5 (OCH₃), 35.1 (C), 31.0 (CH₃), 21.6 (CH₂), 14.1 (CH₃).

N-Methyldiphenylamine (MDPA) from Tokyo Kasei (TCI) was distilled under reduced pressure for purification before the use. Acetonitrile (ACN) was distilled for purification. Methylcyclohexane (MCH, Spectrosol) from Dojin and isopentane (IP, for UV-spectroscopy) from Fluka were used without further purifica-

Table 1

Absorption properties and triplet energies of AB derivatives used in the present work.

Compound	$\lambda_{max}{}^a/nm$ ($\epsilon/dm^3 mol^{-1} cm^{-1}$)	$E_{\rm T}$ ^b /kcal mol ⁻¹
AB	356 (32,400)	58.4
MeAB	260 (21,000)	70.7
PrAB	269 (26,900)	70.7
d In acotonitrilo		

In acetonitrile.

 $^{\rm b}$ Determined from the 0–0 origin of the corresponding phosphorescence spectrum in ethanol at 77 K.

tion. ACN and MCH were used as the solvent while a mixture (MP) of MCH and IP (1:1, v/v) was used as a matrix at 77 K.

Absorption spectra were recorded on a U-best 50 (JASCO) or a Cary 300 spectrophotometer while emission spectra were on a Hitachi F-4010 fluorescence spectrophotometer. All the samples for transient absorption measurements were prepared in the dark, and Ar-purged or degassed in a quartz cell with a 1 cm path length by several freeze-pump-thaw cycles on a high vacuum line. Fourth harmonics (266 nm) of a Nd³⁺:YAG laser (JK Lasers HY-500; pulse width 8 ns) was used as the excitation laser light source. The details of the detection system for the time profiles of the transient absorption have been reported elsewhere [24]. 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 can provide a transient absorption spectrum with one laser pulse. Steady-state photolysis was carried out by using a low-pressured mercury lamp (254 nm). The photon flux at 254 nm was determined by using N-methyldiphenylamine in aerated methylcyclohexane as a chemical actinometer. The quantum yield for the formation of N-methylcarbazole from N-methyldiphenylamine has been established as 0.42 [25].

All the samples were prepared in a quartz cell with a 1 cm path length in the dark. They were degassed by Ar-bubbling or several freeze-pump-thaw cycles on a high vacuum line when necessary. The concentration of PrAB for 266-nm laser photolysis was adjusted to achieve the optical density at 266 nm being less than 2.0 in ACN. Steady-state photolysis was carried out at 295 K whereas the ambient temperature of the samples in a quartz cell for laser flash photolysis was kept at 295 K or varied between -33 and 22 °C in a quartz dewar with a mixture of methanol and liquid nitrogen with a precision of ± 0.5 °C. The number of the repetition of laser pulsing in the sample was less than four pulses to avoid excess exposure. Several transient data obtained at the same concentration systems were averaged within $\pm 5\%$ errors.

3. Results and discussion

3.1. Absorption and emission measurements

Fig. 1 shows absorption spectra of AB, MeAB and PrAB in ACN at 295 K and phosphorescence spectra in ethanol at 77 K.



Fig. 1. Absorption and fluorescence spectra in ACN at 295 K and phosphorescence spectra in ethanol at 77 K for AB (a), MeAB (b) and PrAB (c). Fluorescence from MeAB and PrAB was not observed.

Fluorescence at 295 K was absent from MeAB and Pr AB in ACN whereas weak fluorescence from AB was observed. The absorption band of AB is located at 356 nm (ε = 32,400 dm³ mol⁻¹ cm⁻¹) indicating that AB takes the enol form in the ground state [12] while those of MeAB and PrAB are at 260 nm. Based on the result that the absorption band of MeAB at 260 nm is due to the keto form [23], it can be said that PrAB also takes the keto form in the ground state. Very weak fluorescence from AB was recorded at 295 K while that from MeAB and PrAB in ACN was not observed under the same conditions. From these observations, it is inferred that the electronic character of lowest excited singlet, S₁ state of MeAB and PrAB is of n, π^* . The phosphorescence spectra obtained in the present study show vibrational structures due to the carbonyl progression. It was confirmed that the excitation spectra of the emission obtained from AB, MeAB and PrAB agrees well with the corresponding absorption spectra. The energy level of



Fig. 2. Absorption spectra at 0, 5, 10, 15, 20, 30, 45 and 90 s upon 254-nm light photolysis of PrAB in degassed (a) and aerated ACN solution (b) of PrAB at 295 K.

avobenzone derivatives obtained in present work are listed in Table 1.

3.2. Steady-state photolysis of PrAB

Fig. 2 shows absorption spectrum changes of PrAB in ACN upon 254-nm light irradiation. As time increased, the intensity of the absorption band at 260 nm decreased having isosbestic points while that at 356 nm increased. The new absorption band at 356 nm is very similar to that of AB, indicating that AB is the photoproduct of PrAB. This was confirmed by recording the NMR of a photolyzed mixture, which was shown to contain AB as the only product, together with some unreacted PrAB. In the presence of dissolved oxygen in the ACN solution, the decomposition of PrAB and the formation of AB were suppressed. From these observations, it is inferred that the photochemical formation of AB from PrAB proceeds via the Norrish Type II reaction that mainly occurs in n,π^* triplet states of carbonyl compounds. Although propene was also expected as the photoproduct, it was not optically detected in the present work.



the lowest triplet (T_1) state was determined to be 58.4 kcal mol⁻¹ for AB and 70.7 kcal mol⁻¹ for MeAB and PrAB from the 0–0 origins of the phosphorescence spectra. The spectroscopic data of

Based on the quantum yield of photoconversion of *N*-methyldiphenylamine (MDPA) to *N*-methylcarbazole in aerated methylcyclohexane (0.42 [25]), quantum yields, Φ_{dec} and Φ_{AB} of the decomposition of PrAB and the formation of AB upon 254-nm

Table 2

Photochemical data for PrAB in acetonitrile obtained in the present work.

$\Phi_{ m dec}{}^{ m a}$	$\Phi_{AB}{}^{a}$	$arPsi_{AB}^{deg}$ a	$\Phi_{ m AB}^{ m aer \ b}$	$k_d^{c,d}/s^{-1}$	$k_{\rm q}{}^{ m c,d}/{ m dm^3}{ m mol^{-1}}{ m s^{-1}}$	$\Delta E_{\rm a}{}^{\rm c}/{\rm kcal}{\rm mol}^{-1}$	A^{c}/s^{-1}
0.21	0.23	0.23	0.04	1.6×10^6	4.6×10^9	6.0	4.6×10^{10}

^a Errors \pm 0.02. ^b Errors \pm 0.01.

^c Errors \pm 5%.

^d At 295 K.



Fig. 3. Transient absorption spectra at 100 ns (blue color) and $4 \mu s$ (red color) upon 266-nm laser pulsing in PrAB in ACN at 295 K. Insets; temporal absorbance changes at 386 nm (upper) and 356 nm (lower). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.).

steady-state photolysis were determined to be 0.21 ± 0.02 and 0.23 ± 0.02 , respectively in degassed ACN at 295 K (Table 2). The procedure to determine these yields was the same as that described in the literature [26].

266-nm Laser photolysis was carried out to survey the primary intermediates upon photolysis of PrAB. Fig. 3 shows transient absorption spectra obtained upon 266-nm laser pulsing in a degassed ACN solution of PrAB. The shape of the transient absorption spectrum at 100 ns resembles that of triplet methylavobenzone in a keto form reported previously [23]. Thus, the obtained transient absorption spectrum can be due to triplet PrAB. The intensity of the triplet absorption decreased with a rate, k_d of $1.6 \times 10^6 \text{ s}^{-1}$, providing an absorption spectrum having the maximum at 356 nm at 4 μ s. The absorption spectrum at 4 μ s can be ascribed to AB. Considering the photochemical profiles upon steady-state photolysis of PrAB, the obtained absorption spectral change demonstrates formation of AB from triplet PrAB via the Norrish Type II reaction. These facts show that the electronic character of triplet PrAB is of n, π^* type.

When the ACN solution of PrAB was aerated $([O_2] = 1.9 \times 10^{-3} \text{ mol dm}^{-3} [27])$, the decay rate, k_{aer} of triplet PrAB was determined to be $10.3 \times 10^6 \text{ s}^{-1}$. From this value, the quenching rate constant, k_q of triplet PrAB by the dissolved oxygen is estimated to be $4.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ by Eq. (1).

$$k_{\text{aer}} = k_{\text{d}} + k_{\text{q}}[O_2] \tag{1}$$

where k_d represents the decay rate $(1.6 \times 10^6 \text{ s}^{-1})$ of triplet PrAB in the absence of the dissolved oxygen. The obtained k_q value is smaller than the diffusion limit $(2.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ at } 20 \circ \text{C} [27])$ of ACN, indicating that the quenching of triplet PrAB by the dissolved oxygen proceeds in a diffusion process.

Quantum yields, Φ_{AB} for the formation of AB upon 266-nm laser photolysis of PrAB in ACN were determined by using MDPA in aerated MCH as a chemical actinometer. Based on the absorbance change, ΔA_{356}^{AB} for the formation of AB seen in the transient absorption at 356 nm (see inset in Fig. 3), Φ_{AB} is formulated by Eq. (2).

$$\Phi_{\rm AB} = \Delta A_{356}^{\rm AB} \varepsilon_{356}^{\rm AB-1} l^{-1} (1 - 10^{-A_{266}^{\rm PrAB}})^{-1} I_0^{-1}$$
(2)

where ε_{356}^{AB} *l*, A_{266}^{PrAB} and I_0 are, respectively, the molar absorption coefficient of AB at 356 nm (32,400 dm³ mol⁻¹ cm⁻¹), the optical path length (1 cm), the absorbance of PrAB at 266 nm and fluence of the incident laser pulse. The quantity of I_0 can be determined



Fig. 4. Absorbance changes, ΔA_{λ} at λ nm obtained upon 266-nm laser photolysis of PrAB in degassed ACN (\odot ; $\lambda = 356$ nm), MDPA in aerated MCH (\bigcirc ; $\lambda = 343$ nm) and PrAB in aerated ACN (\Box ; $\lambda = 356$ nm) plotted as a function of the term, $1 - 10^{-A_{266}}$.

by using Eq. (3) based on the quantum yield of photoconversion from MDPA to *N*-methylcarbazole (MC) in MCH (0.42 [25]) and the absorbance change due to the formation of MC.

$$I_0 = \Delta A_{343}^{\rm MC} \varepsilon_{343}^{\rm MC-1} l^{-1} (1 - 10^{-A_{266}^{\rm MDPA}})^{-1} \Phi_{\rm MC}^{-1}$$
(3)

Here, ΔA_{343}^{MC} , ε_{343}^{MC} , l and A_{266}^{MDPA} are, respectively, the absorbance change at 343 nm due to the formation of MC, the molar absorption coefficient of MC at 343 nm (5800 dm³ mol⁻¹ cm⁻¹ [25]), the optical path length (1 cm) and the absorbance of MDPA at 266 nm.

Fig. 4 shows absorbance changes, ΔA_{λ} due to the formed species ($\lambda = 356$ nm for AB and $\lambda = 343$ nm for MC) obtained upon 266-nm laser photolysis of PrAB and MDPA plotted as a function of the term, $1 - 10^{-A_{266}}$. These plots show straight lines. By using the slopes of these lines and Eqs. (2) and (3), the values of Φ_{AB} were determined to be 0.23 ± 0.02 and 0.04 ± 0.01 in degassed and aerated ACN at 295 K, respectively. The Φ_{AB} value obtained for the degassed ACN solution is in a good agreement with that (0.23) obtained upon stead-state photolysis of PrAB.

On the other hand, the quantum yield of AB formation in degassed ACN, Φ_{AB}^{deg} is correlated with that in aerated ACN, Φ_{AB}^{aer} by the Stern-Volmer relationship expressed with Eq. (5).

$$\Phi_{AB}^{deg} \Phi_{AB}^{aer-1} = 1 + k_q k_d^{-1} [O_2]$$
(5)

When the obtained values of Φ_{AB}^{deg} (=0.23), k_q (=4.6 × 10⁹ dm³ mol⁻¹ s⁻¹) and k_d (=1.6 × 10⁶ s⁻¹) are applied in Eq. 5 with $[O_2] = 1.9 \times 10^{-3}$ mol dm⁻³ [27], the value of Φ_{AB}^{aer} was estimated to be 0.04, which is the same as the value obtained upon 266-nm laser photolysis of PrAB in aerated ACN. This agreement indicates that the photoelimination of PrAB forming AB proceeds only in the triplet state of PrAB. In other words, photochemical processes are absent in the excited singlet states of PrAB, presumably due to the fast intersystem crossing from the lowest excited singlet state, S₁(n, π^*).

The rate, $k_{\rm eli}$ of the elimination reaction of triplet PrAB is, thus, estimated to be $3.7 \times 10^5 \, {\rm s}^{-1}$ by using Eq. (6).

$$k_{\rm eli} = \Phi_{\rm AB}^{\rm deg} k_{\rm d} \tag{6}$$

According to the established mechanism for photoelimination of triplet n,π^* carbonyl compounds, the initial chemical process of triplet PrAB should be intramolecular γ -H-atom abstraction producing a triplet biradical, BR which leads to β -cleavage of the C–C bond.



Fig. 5. Arrhenius plots of k_d for the decay of triplet PrAB in ACN.



An absorption spectrum of the corresponding triplet biradical was not seen in the transient absorption spectrum change from triplet PrAB to AB, indicating that the lifetime of the biradical is very short compared to that of triplet PrAB, presumably, due to a large rate of the successive β -bond cleavage of the C–C bond. Therefore, the determined rate, $k_{\rm eli}$ may be responsible for the intramolecular H-atom abstraction of triplet PrAB. The residual quantum yield, $1 - \Phi_{AB}^{deg}$ (0.77) and the rate, $k_{\rm d} - k_{\rm eli}$ (1.2 × 10⁶ s⁻¹) are of the intersystem crossing from the T₁ state to the ground state of PrAB in ACN at 295 K.

3.3. Temperature dependence of photoelimimation of PrAB

Temperature dependence of the decay rate, k_d of triplet PrAB was elucidated in the temperature range from 240 to 295 K. Fig. 5 shows Arrhenius plots of k_d in ACN. The plots show a straight line, indicating that the decay rate, k_d is expressed by the Arrhenius expression with the apparent activation energy, ΔE_a and the frequency factor, A.

$$Lnk_d = LnA - \Delta E_a R^{-1} T^{-1} \tag{7}$$

From the slope, $\Delta E_a R^{-1}$ (= 3.0 × 10³ K) and the intercept, Ln *A* (= 24.56) of the line, the values of ΔE_a and *A* were, respectively, determined to be 6.0 (±0.3) kcal mol⁻¹ and 4.6 (±0.3) × 10¹⁰ s⁻¹. The magnitude of the ΔE_a and *A* values of PrAB determined here indicates that the photoelimination reaction of PrAB is a typical adiabatic process. Activation energies and corresponding frequency factors for photoelimination reactions of valerophenone and isocaprophenone derivatives are reported [28]. These activation energies vary from 2.7 to 6.9 kcal mol⁻¹ depending on the substituent group whereas they are not much different from the value (6.0 kcal mol⁻¹) determined for PrAB. With the frequency factors, those reported in the literature are in the magnitude of $10^{10}-10^{11} s^{-1}$, which are close to that for PrAB obtained in the present work.

4. Conclusion

Photochemical and photophysical features of PrAB in solution were studied by steady-state and laser flash photolysis. From the maximum wavelength of the absorption spectrum of PrAB, it was inferred that PrAB in the ground state is in a keto form. Based on the phosphorescence spectrum of PrAB, the triplet energy was determined to be 70.7 kcal mol⁻¹. Steady-state and laser flash photolyses of PrAB revealed that triplet PrAB undergoes the Norrish Type II reaction, forming AB with a quantum yield of 0.23 in degassed ACN. Occurrence of H-atom abstraction of triplet PrAB indicates that the electronic character of the T₁ state is of n,π^* The activation energy and the frequency factor for photoelimination of triplet PrAB were, respectively, determined to be 6.0 kcal mol⁻¹ and 4.6×10^{10} s⁻¹ by the Arrhenius-type analysis of decay kinetics of triplet PrAB. These thermodynamic parameters indicate that the photoelimination reaction of triplet PrAB is an adiabatic process.



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