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Photochemical α-cleavage reaction of benzoin and its derivatives

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Abstract

The quantum yields of α-cleavage type photodissociation (Φ_r) were determined for benzoin, α-phenylbenzoin and α-phenylbenzoin methyl ether by measuring the transient absorbance of the product radicals using a nanosecond laser flash photolysis technique. The dissociation yields are 0.25–0.35, which are close to the α-cleavage yields of other aryl and alkyl ketones in the nπ* excited state. The lowest excited singlet and the low-lying triplet states are assigned to the nπ* type electronic states according to the absorption and phosphorescence measurements. The assignment agrees with the fact that the dissociation yields of these benzoins are relatively high.

Keywords: Benzoin; α-Cleavage reaction; Quantum yield

1. Introduction

α-Photocleavage of carbonyl compounds is one of the most studied photoreactions and classified as Norrish type I reaction. Benzoins efficiently yield photoproducts through this type of reaction and are good photoinitiators for radical polymerization (for example, see Refs. [1,2]). Photochemical α-cleavage of benzoins has been studied by the conventional photochemical techniques [1–5], the CIDNP (chemically induced dynamic nuclear polarization) [6–9] and CIDEP (chemically induced dynamic electron polarization) measurements [10–13]. For example, photolysis of α-phenylbenzoin yields two important radicals, benzophenone ketyl (BPK) and benzoyl radicals [1–4]. Baumann et al. [4] studied the N_2 laser photolysis of α-phenylbenzoin and reported homolytic cleavage producing BPK. The assignment of the product BPK was carried out based on the fluorescence spectrum measured. Time resolved ESR experiment also supports the formation of BPK and benzoyl in the photodissociation of α-phenylbenzoin [13]. These α-cleavage reactions have been used as a radical source to generate BPK in the recent studies on BPK-amine complex formation [13], jet spectroscopy of BPK [14], the photodissociation of BPK [15] and so on. Though the photodissociation reaction has been applied for many studies, the excited states of benzoins have not been well characterized except for benzoin [11] and the dissociation quantum yield (Φ_r) have not been directly measured yet. The dissociation quantum yields reported [3] were estimated on the basis of the final product yields.

In the present study, we determined the Φ_r values of benzoin, α-phenylbenzoin and α-phenylbenzoin methyl ether by the direct measurements of the transient species utilizing the laser flash photolysis technique. The Φ_r values measured in the present study were 0.25–0.35 for these three benzoins. The benzoins used as a good photoinitiator have been confirmed to give relatively high Φ_r values. To understand the dissociation mechanism, we measured absorption and phosphorescence spectra and phosphorescence lifetime. The results of the measurements indicate that the S_1 state is of nπ* type and that the ^{3}nπ* state lies near the bottom of triplet manifold. The relation between the dissociation yield and electronic state character is discussed for these benzoins.

2. Experimental

2.1. Transient absorption

Details of a transient absorption detection system were already described elsewhere [16]. A XeCl excimer laser (Lambda Physik LPX, 308 nm, 20 ns duration time) was used as an excitation light source with the repetition rate of 1 Hz. A Xe flash lamp (Ushio UXL 150 DS, 150 W) was

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synchronously fired with excimer laser pulse to monitor the transient species produced by the photolysis laser. A Xe flash lamp was operated with a pulse duration time of about 200 μs. The monitoring light was detected with a monochromator (Nikon P-250)/photomultiplier tube (Hamamatsu Photonics R-928) combination system which had a spectral resolution of 2 nm. The transient absorption signals were digitized by a digital memory (Iwatsu DM-901) and analyzed by a personal computer. In all cases, the transient signals were accumulated over 30 times to improve *S*/*N* ratio.

2.2. Absorption and phosphorescence measurements

Absorption and phosphorescence spectra were measured by a UV/VIS spectrometer (Shimadzu UV-220) and a spectrofluorophotometer (Shimadzu RF-5300PC), respectively. For phosphorescence lifetime measurements, a N_2 laser (Molectron UV-24, 337 nm, 20 ns duration time) was used as an excitation light source and phosphorescence was monitored at 430 nm by the photomultipliertube through the monochromator. Phosphorescence spectra and lifetimes were measured at 77 K by using a quartz Dewer.

2.3. Samples

Benzophenone (Tokyo Kasei; GR grade) was purified by recrystallization a few times from ethanol and then from *n*-hexane. α-Phenylbenzoin was synthesized by the Grignard reaction of phenylmagnesiumbromide with benzil in tetrahydrofurane at 245 K and recrystallized from *n*-hexane. α-Phenylbenzoin methyl ether was prepared by the reaction of α-phenylbenzoin with NaOH and methyl trifluoromethanesulfonate. Benzoin and benzoin methyl ether (Kanto Chemical; GR grade) were used as received. All solvents purchased from Kanto Chemical (GR grade) were used as received. All samples were deareated by bubbling Ar gas saturated with solvent. For transient absorption measurements, sample solutions were flowed through a quartz cell with the flow rate of about 20 ml/min.

3. Results and discussion

3.1. Transient absorption spectra

Fig. 1 shows transient absorption spectrum obtained in the laser flash photolysis of α-phenylbenzoin in benzene. Characteristic absorption of BPK [17] is seen in the spectrum obtained at 7 μs, which shows a broad band with a peak around 540 nm and with a shoulder around 510 nm. The product BPK is rather stable and its lifetime under the present condition is longer than 50 μs. Fig. 2 shows transient spectra obtained in the laser flash photolysis of benzoin in benzene at room temperature. The broad bands was observed around 300 and 490 nm at 0.25–0.75 μs with decay rate of about 6×10^5 s^{-1}. This might be the triplet–triplet absorption of benzoin, but no clear evidence was found yet on this assignment. The spectrum obtained at 35–50 μs shows a broad band starting at around 450 nm and a peak at around 320 nm. This spectrum is similar to an absorption spectrum of α-hydroxybenzyl (αHB) measured in the photolysis of benzaldehyde in acetonitrile [18] where self-quenching reaction of benzaldehyde produces αHB and benzoyl radical. Therefore, we attributed this broad spectrum obtained at 35–50 μs to an absorption spectrum of αHB.

In the photolysis of benzoins, the product ketyl radicals appear within a few microseconds after laser excitation. The transient observation of ketyl radicals clearly suggests that

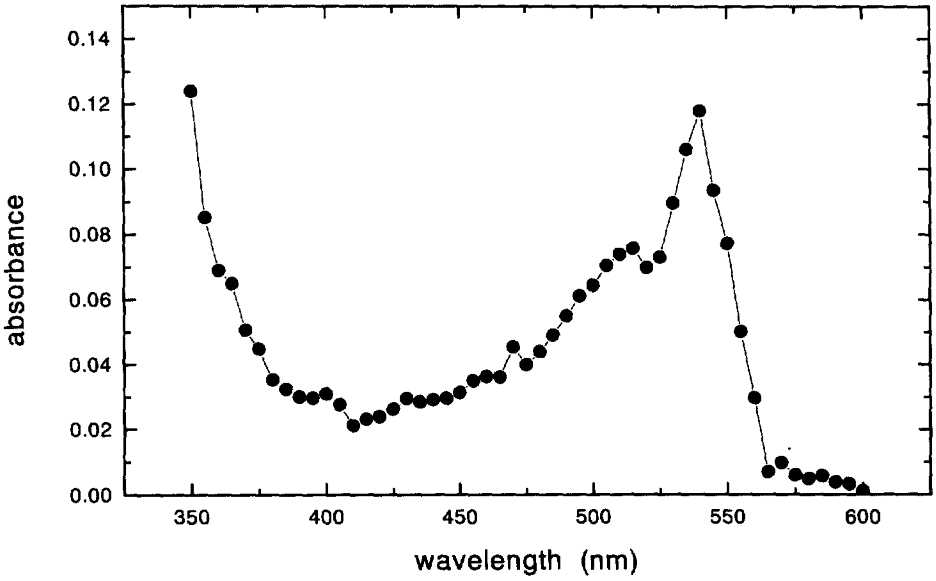

Fig. 1. Transient absorption spectrum measured in the laser flash photolysis of α-phenybenzoin in benzene at 7.0 μs after 308 nm laser pulse at room temperatur

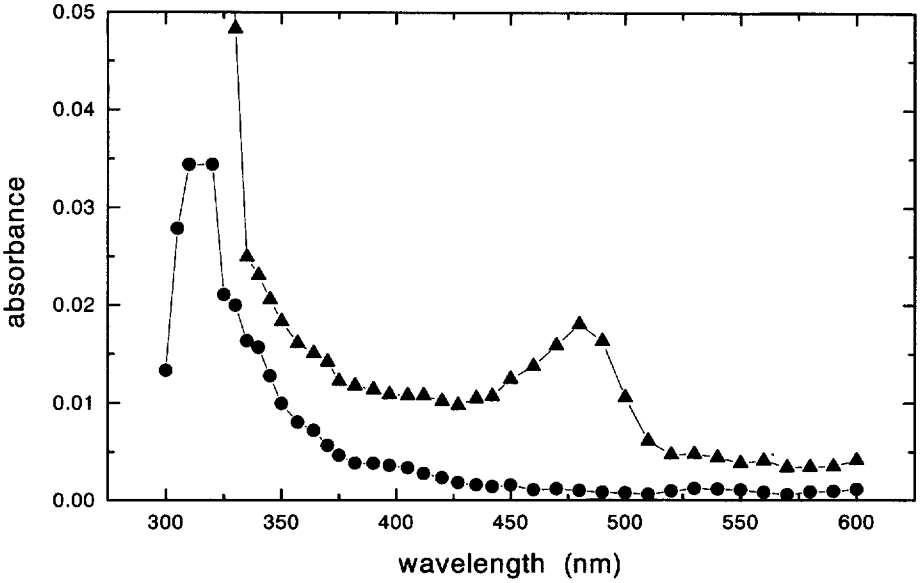

Fig. 2. Transient absorption spectra measured in the laser flash photolysis of benzoin in benzene at room temperature. The spectra were measured at 0.25–0.75 (triangle) and 35–50 (circle) μs after 308 nm laser pulse. An absorption band of α-hydroxybenzyl (αHB) appears in the region of 300 to 450 nm.

α-cleavage occurs by the photoexcitation of benzoins. Benzoyl radical, which is a counterpart radical of BPK and αHB, is not recognized in the spectra because the extinction coefficient is quite low in this spectral region [19]. The formation of BPK and αHB was detected by time resolved ESR spectroscopy in the laser photolysis of these benzoins [10–13]. The present results are consistent with these previous reports.

3.2. Dissociation quantum yield

It is generally difficult to determine the exact number of photons absorbed by molecules, which makes it difficult to determine an absolute quantum yield of any photochemical process. In the present study, we measured the laser power dependence of absorbance of ketyl radical formed by the laser excitation of benzoins as well as that of triplet benzophenone as a reference which gives the apparatus factor. Product radicals are generated by the 308 nm excitation of benzoins. The absorbance of product radical, A, is given by,

$$A=\varepsilon_K(1-10^{-a_{Bz}})\Phi_r kI \qquad (1)$$

where I [mJ] is laser intensity, k [M cm mJ^{-1}] is an apparatus factor, a_{Bz} is the absorbance of benzoins at 308 nm, and ε_K [M^{-1} cm^{-1}] is molar absorption coefficient of the product. The absorbance of the radicals was measured and plotted against laser power. Similar procedure was carried out for the triplet benzophenone as a reference, in which the extinction coefficient of the triplet–triplet absorption of benzophenone is known. The results for BPK are shown in Fig. 3 together with that for triplet benzophenone. The plots clearly indicate that the yields of BPK and triplet benzophenone linearly depend on the laser power, which means that these intermediates are formed through one photon processes. The same results were obtained for other benzoins, which indicate that the dissociation also occurs through one photon process. In this experiment, we attenuated the laser power as weak as possible, because intense laser pulse produced high concentration of radicals and made the decay complicated due to bimolecular reactions among radicals. Under our experimental conditions, the lifetimes of the product radicals were longer than 50 μs. From the ratio of the two slopes, m_i (= the slope for BPK/that for triplet benzophenone), the dissociation quantum yield is given as follows

$$\Phi_r=\frac{m_i\varepsilon_{3BP*}(1-10^{-a_{BP}})}{\varepsilon_K(1-10^{-a_{Bz}})} \qquad (2)$$

where, a_{BP} is absorbance of benzophenone at 308 nm and ε_{3BP*} is extinction coefficient of triplet benzophenone.

To determine Φ_r, it is necessary to know the extinction coefficients of intermediates. The molar absorption coefficients of triplet benzophenone and benzophenone ketyl rad-

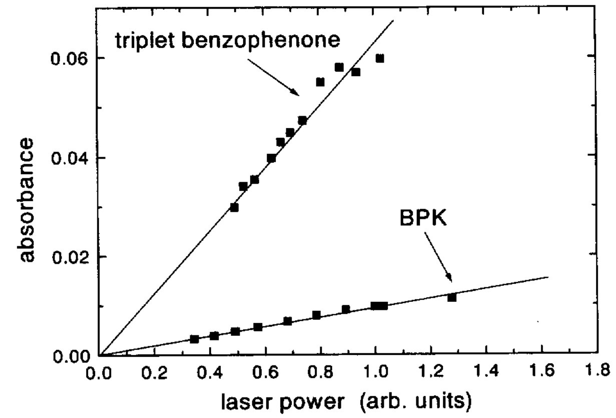

Fig. 3. Laser power dependence of the absorbance of BPK at 545 nm and benzophenone triplet–triplet absorption at 450 nm. Straight line fittings were carried out for both plots.

ical were reported as 6500 M^{-1} cm^{-1} at 525 nm and 4600 M^{-1} cm^{-1} at 545 nm [20], respectively. The molar absorption coefficients of αHB and diphenylmethoxymethyl (DPMM) have not been reported yet and we determined them as follows.

Fig. 4 shows transient absorption spectra obtained in the laser photolysis of benzophenone in (a) 1-butanol and (b) benzylalcohol. Photoreaction intermediates must be BPK + 1-butanol radical in (a) and BPK + αHB in (b). Thus, the transient absorption spectrum of (b) in Fig. 4 should include both BPK and αHB with the same concentration while only BPK should be observed in the spectrum (a) because no strong absorption band of 1-butanol radical exists in the region of 350–600 nm. As is clearly seen in Fig. 4, two absorption spectra do not coincide with each other and the spectrum (b) has higher extinction coefficient than spectrum (a) in 350–470 nm region. This is due to the absorption of αHB. The molar absorption coefficient of BPK in cyclohexane was reported to be 4600 M^{-1} cm^{-1} at a peak at 545 nm. Though the peak is slightly red-shifted to 547 nm in Fig. 4, the molar absorption coefficient is thought to be identical in both solvents. The spectra in Fig. 4 are depicted by assuming the molar absorption coefficient at the peak as 4600 M^{-1} cm^{-1}. The lifetimes of both radicals are longer than 50 μs,

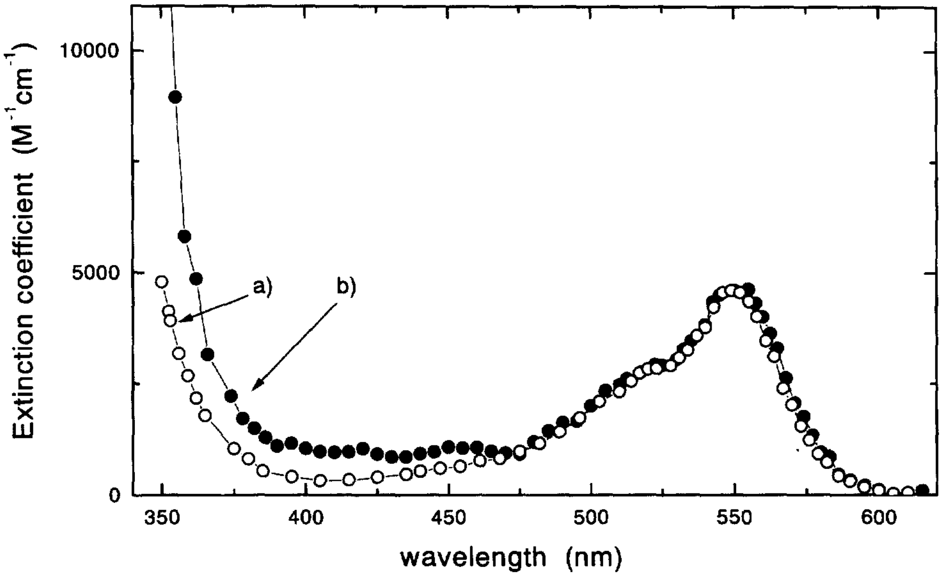

Fig. 4. Transient absorption spectra measured in the laser flash photolysis of benzophenone (a) in 1-butanol and (b) in benzylalcohol at room temperature.

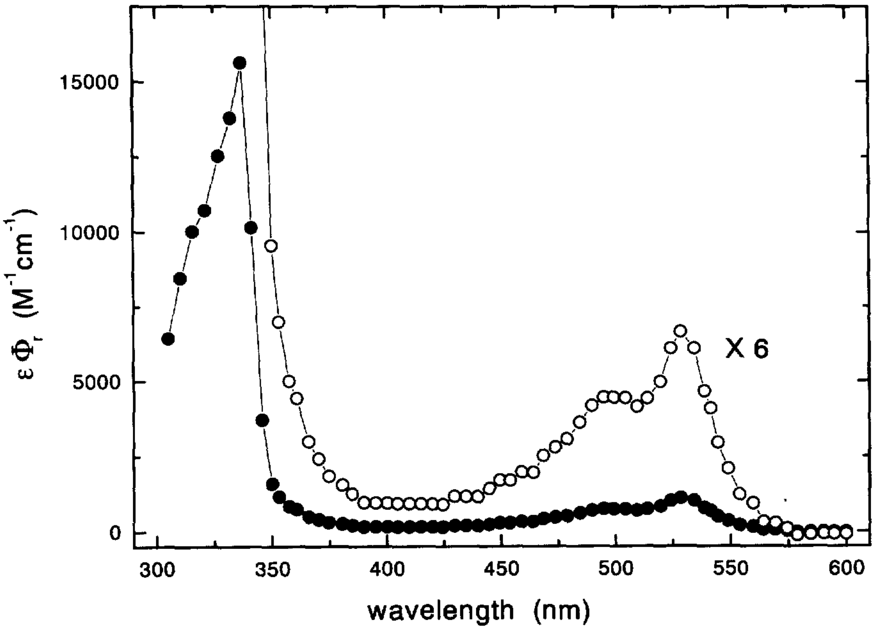

Fig. 5. Transient absorption spectrum of diphenylmethoxymethyl radical measured in the 308 nm laser flash photolysis of α-phenylbenzoin methyl ether in cyclohexane at room temperature. Φ_r and ε are the mean dissociation quantum yield of α-phenylbenzoin methyl ether and extinction coefficient of diphenylmethoxymethyl, respectively.

Table 1
Molar absorption coefficient of transient species

Transient species	Wavelength (nm)	ε ($M^{-1} cm^{-1}$)
Benzophenone ketyl radical (BPK)	545	4600
Triplet benzophenone	525	6500
Diphenyl methoxymethyl radical (DPMM)	530	4600
α-Hydroxybenzyl radical (αHB)	375	1045

Table 2
Photodissociation quantum yields of benzoins [a]

Samples	Φ_r
α-Phenylbenzoin	0.25 ($\pm$0.02) 0.33 [b]
α-Phenylbenzoin methyl ether	0.26 ($\pm$0.04)
Benzoin	0.35 ($\pm$0.05)

[a] In benzene
[b] In acetonitrile.

and the concentrations of BPK and αHB should be the same at the gate time (1 μs) of the spectrum (b). Therefore, we can determine the molar absorption coefficient of αHB as 1045 M^{-1} cm^{-1} at 375 nm from Fig. 4. In the present study, we determined the molar absorption coefficient at 375 nm because (1) parent benzoin has no absorption, (2) unknown absorption shown in Fig. 2 is relatively small and (3) absorption of αHB is practically high enough to measure absorbance under the present condition.

Fig. 5 shows transient absorption spectrum of DPMM, which is quite similar to that of BPK. The absorption band of BPK around 545 nm is slightly blue-shifted in DPMM, which is reasonable for methoxy substitution effect on ππ* type electronic transition. The extinction coefficient of DPMM at 530 nm (absorption maximum in the D_1–D_0 transition band) is assumed to be equal to that of BPK at λ_{max} (545 nm) of 4600 M^{-1} cm^{-1}.

All the extinction coefficients of transient species necessary in this work are summarized in Table 1. From the extinction coefficients and the slope ratios, m_i's, the Φ_r values are estimated using Eq. (2). The resultant values are listed in Table 2.

3.3. Absorption and phosphorescence spectra

3.3.1. Absorption spectra

Fig. 6a shows the absorption spectra of benzoin in 2-propanol and in benzene. One can recognize a weak and broad band in 380–310 nm region, which is followed by the absorption appearing in the spectral region shorter than 310 nm. This feature is quite similar to the absorption spectra of aromatic ketones. Therefore, these weak and strong bands are assigned to the $S_1(n\pi^*)$–S_0 and $S_2(\pi\pi^*)$–S_0 transitions, respectively. There are two remarkable features concerning the $S_1(n\pi^*)$–S_0 transition: (1) it does not show any obvious progression due to carbonyl stretching mode even in non-polar solvent, and (2) the band is slightly red-shifted in polar solvent. A very similar feature was also found for α-phenylbenzoin. These features are different from that of normal nπ* absorption. We suppose that the hydroxy group on β-carbon atom makes an intramolecular hydrogen bond with the carbonyl group in non-polar solvent, which vanishes the faint structure of carbonyl stretching. The red-shift in polar solvent suggests that the n-orbital is more stabilized by the intramolecular hydrogen bond formation than by the intermolecular hydrogen bond formation in 2-propanol. These unusual features disappear in benzoin methyl ether which shows normal blue-shift and remarkable progression due to carbonyl stretching mode as shown in Fig. 6b. Since no hydrogen bond is expected between methoxy and carbonyl groups in benzoin methyl ether, this result supports our assumption that benzoin and α-phenylbenzoin form the intramolecular hydrogen bond between OH and CO groups.

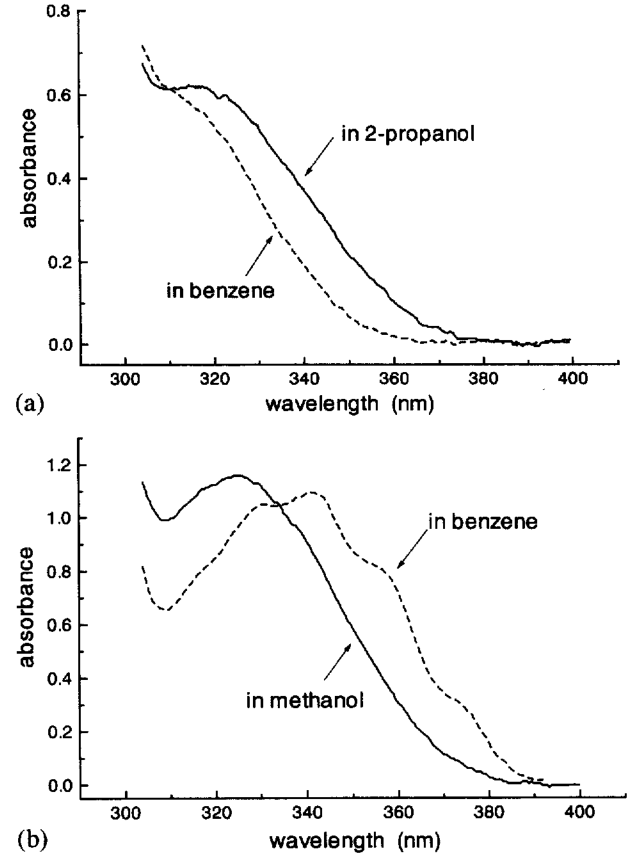

Fig. 6. Absorption spectra of (a) benzoin and (b) benzoin methylether in polar and non-polar solvents.

3.3.2. Phosphorescence spectra

The phosphorescence spectra of α-phenylbenzoin and benzoin were measured in toluene glass at 77 K. Fig. 7 shows the phosphorescence spectrum of α-phenylbenzoin. Similar spectrum was obtained for benzoin, though the intensity was low and the Franck–Condon pattern was different. As mentioned by Rehak et al. [5], the phosphorescence spectrum of

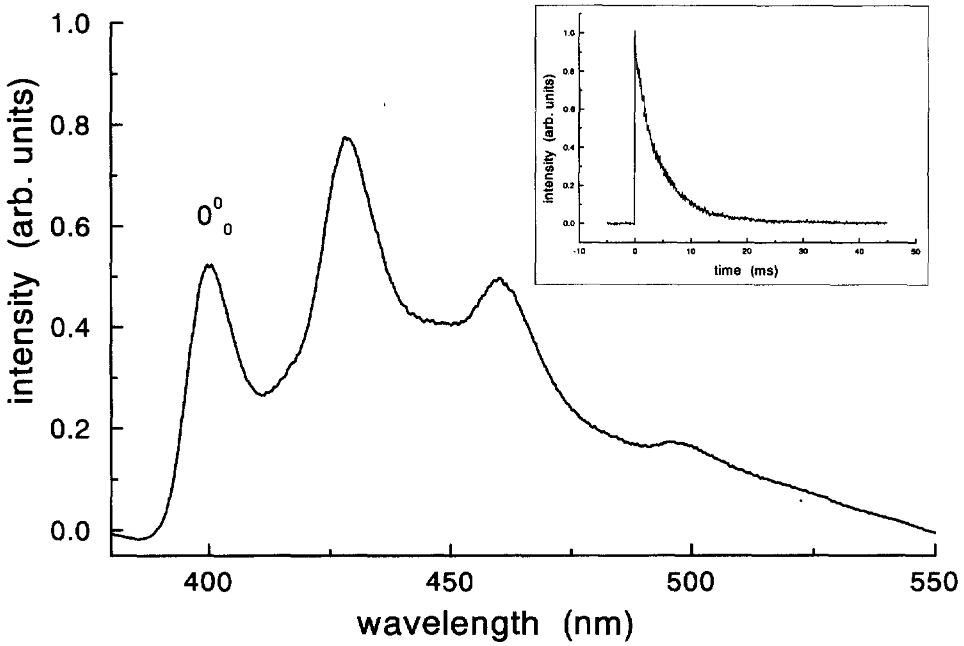

Fig. 7. Phosphorescence spectrum of α-phenylbenzoin in toluene glass matrix measured at 77 K. Inset shows phosphorescence decay profile monitored at 430 nm.

α-phenylbenzoin is similar to that of benzophenone. The phosphorescence spreads over the 400–550 nm region with remarkable vibronic structures. Though photoexcitation of benzoins is known to yield ketyl radicals, we did not detect their fluorescence. The cage effect in the matrix enhances recombination reaction, which suppresses the apparent ketyl radical yield. Four vibronic bands starting at 400 nm are seen in Fig. 7, and no emission was observed in other wavelength region. We assign the peak at 400 nm to the origin band of the phosphorescence. Energy separations between the successive peaks are 1640, 1557 and 1636 cm^{-1} from the short wavelength side, which are quite close to those of carbonyl stretching mode of aromatic ketones such as benzaldehyde [21]. Therefore, we attribute these peaks to a progression of carbonyl stretching mode. The time profiles of the phosphorescence of benzoins were measured and found to follow the single exponential decay as shown in the inset of Fig. 7 for α-phenylbenzoin. We performed a least squares fitting of the time profile and obtained the phosphorescence lifetime of 4.65 ms at 77 K. The T_1 energies and the phosphorescence lifetimes are summarized in Table 3.

The phosphorescence lifetime of the orders of millisecond is a quite typical value for the phosphorescence lifetime of the $n\pi^*$ triplet state of aromatic ketones. Furthermore, the carbonyl stretching mode is active in the $T_1 \rightarrow S_0$ transition, which might be another evidence that the phosphorescence is due to the $n\pi^*$ type transition. There are many reports [21,22] that the $^3n\pi^*$ and $^3\pi\pi^*$ states of aromatic ketones such as benzaldehyde, acetophenone, and so on, are located closely in the lowest energy region of the triplet manifold. These molecules show $n\pi^*$ type phosphorescence since the phosphorescence transition moment of $n\pi^*$ type is larger than that of $\pi\pi^*$ type. For benzoins, we conclude that the T_1 states are of $n\pi^*$ type in the electronic state or the reactive $n\pi^*$ state locates at almost the bottom of triplet manifold.

Table 3
Properties of triplet benzoins

Samples	Triplet (T_1) lifetime [a] (ms)	Triplet (T_1) energy (kcal mol^{-1})
α-Phenylbenzoin	4.65	71.5
Benzoin	1.94	72.2

[a] At 77 K in toluene.

4. Discussion

We measured the relatively high dissociation quantum yields for benzoin, α-phenylbenzoin, and α-phenylbenzoin methyl ether by using nanosecond laser flash photolysis. The S_1 states were assigned to $n\pi^*$ for these benzoins from the absorption spectra and the existence of the low-lying $^3n\pi^*$ state was indicated from the phosphorescence measurement. The $n\pi^*$ state is very reactive for α-cleavage compared to the $\pi\pi^*$ type electronic state according to a number of studies on alkyl ketons and arylalkyl ketons [23]. This is due to direct coupling of the $n\pi^*$ electronic state with the highly dissociative $n\sigma^*$ electronic state, while the $\pi\pi^*$ state cannot couple with it [23]. The present observation indicates that the three benzoins with $n\pi^*$ type excited state show relatively high quantum yield of dissociation, which is in good agreement with the previous studies on various ketones. The electronic excitation in the $S_1(n\pi^*)$ and $^3n\pi^*$ states is mainly localized in the benzoyl group and one cannot expect any remarkable differences in the σ type C–C bond strength between the CO group and α-carbon among these benzoins. This may be the reason why the dissociation yields are almost the same for these benzoins.

The measurements of absorption spectra of these benzoins suggest that there is an intramolecular hydrogen bond between CO and OH groups. Thus, the $n\pi^*$ state of these benzoins may slightly be different from normal arylketones. If the character of the hydrogen bond of carbonyl group in benzoins depends on the solvent, one can expect that excited state relaxation processes and the dissociation yield might be different. The present results show slightly different dissociation yield in benzene and acetonitrile for α-phenylbenzoin. If the hydrogen bond plays an important role in the dissociation, the intramolecular hydrogen bond might enhance the intramolecular relaxation process of the excited state, which suppresses the dissociation yield. To reveal the role of hydrogen bond in dissociation, it may be quite important to measure the dissociation yields in various solvent.

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