J. Phys. Chem. A **2005,** *109,* 5989−5994

C−O Bond Cleavage of Benzophenone Substituted by 4-CH_2OR (R= C_6H_5 and CH_3) with Stepwise Two-Photon Excitation

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Received: April 4, 2005

The C−O bond cleavage from benzophenone substituted with 4-CH_2OR (*p*-$BPCH_2OR$, **1**−**3**), such as *p*-phenoxymethylbenzophenone (**1**, R= C_6H_5) and *p*-methoxymethylbenzophenone (**2**, R= CH_3), occurred by a stepwise two-photon excitation during two-color, two-laser flash photolysis. On the other hand, no C−O bond cleavage occurred from *p*-hydroxymethylbenzophenone (**3**, R = H). The first 355-nm laser excitation of **1**−**3** generates *p*-$BPCH_2OR$ in the lowest triplet excited state (T_1) which has an absorption at 532 nm. When *p*-$BPCH_2OR(T_1)$ is excited with the second 532-nm laser to *p*-$BPCH_2OR$ in the higher triplet excited state (T_n), the C−O bond cleavage occurred within the laser flash duration of 5 ns. The quantum yields of the C−O bond cleavage during the second 532-nm laser irradiation were found to be 0.015 ± 0.007 and 0.007 ± 0.003 for **1** and **2**, respectively. Although these values are low, the diminishing **1**(T_1) or **2**(T_1) was found to convert, in almost 100% yield, to phenoxyl ($C_6H_5O^\bullet$) and *p*-benzoylbenzyl ($BPCH_2^\bullet$) radicals or methoxyl ($CH_3O^\bullet$) and $BPCH_2^\bullet$ radicals, respectively. The T_n excitation energy, the energy barrier along the potential surface between the T_n states and product radicals, and delocalization of the T_n state molecular orbital including BP and CH_2OR (R = C_6H_5, CH_3, H) moieties are important factors for the occurrence of the C−O bond cleavage. It is found that the C−O bond cleavage and production of free radicals, such as $BPCH_2^\bullet$, $C_6H_5O^\bullet$, and $CH_3O^\bullet$, can be performed by a stepwise two-photon excitation. The present study is an example in which the chemical reactions can be selectively initiated from the T_n state but not from the S_1 and T_1 states.

Introduction

Benzophenone (BP) and its derivatives in the lowest triplet excited states (T_1), generated through an intersystem crossing from the singlet excited states (S_1) in 100% yield during irradiation, are some of the most important excited states and reactive intermediates in photochemistry.[1,2] The properties of $BP(T_1)$ and its derivatives(T_1) are well known.[2] For example, the transient absorption of $BP(T_1)$ with a peak at 525 nm is widely used as the reference of the T_1 state. Because the $BP(T_1)$ state energy (E_{T_1} = 286 kJ mol^{-1}) is relatively high, $BP(T_1)$ is widely used as a triplet sensitizer to generate other molecules in the T_1 state from the triplet−triplet energy-transfer reactions.[3] In addition, BP ($E_{1/2}^{red}$ (standard calomel electrode, SCE) = −1.83 V)[2] is also used as the electron acceptor to oxidize molecules,[4,5] and bimolecular reactions of $BP(T_1)$, such as hydrogen abstraction and $2\pi + 2\pi$ cycloaddition are well known.[3,6−8] It is concluded that $BP(T_1)$ is reactive with various molecules.

On the other hand, no unimolecular reaction of $BP(T_1)$ has been observed.[1−3] However, the C−S bond cleavage of BP substituted with 4-CH_2SH in the T_1 state ($BPCH_2SH(T_1)$) has been recently reported.[9] The O−O bond cleavage in *tert*-butyl-4-(4′-methylbenzoyl)perbenzoate and C−X (X = Cl and Br) bond cleavage in 4-(halomethyl)benzophenone were also found when the BP chromophore was excited to the T_1 state.[10,11] The C−S, O−O, and C−X bond cleavages occur for the $BP(T_1)$ excitation energies (E_{T1}) higher than the bond-dissociation energies (E_{BDE}) of the C−S, O−O, and C−X bonds. On the other hand, the C−O bond cleavage does not occur in BP substituted with 4-CH_2OH in the T_1 state ($BPCH_2OH(T_1)$), because E_{BDE} of the C−O bond (308 kJ mol^{-1})[9,12] is higher than E_{T_1} of $BPCH_2OH(T_1)$ (286 kJ mol^{-1}). Since the carbon- and oxygen-centered radicals are important in organic chemistry, for example, they can be practically used as radical initiators for polymerization;[13] controlling the C−O bond cleavage is a very attractive subject.

We have reported that the fast C−O bond cleavage occurs to produce naphthylmethyl radicals from naphthalene substituted by 1- or 2-CH_2OR, 1,4-$(CH_2OR)_2$, or 1,8-$(CH_2OR)_2$ (R = C_6H_5 and $C_6H_4CO\ C_6H_5$) in the T_n states.[14,15] The T_n state excitation energy of the naphthalene derivatives is higher than the E_{BDE} of the C−O bond and was efficiently delocalized in the naphthalene chromophore and C−O bond due to the interaction of the naphthalene $\pi\pi^*$ and oxygen p orbital, while the T_1 state excitation energy is lower than the E_{BDE} and localized in the naphthalene chromophore. Therefore, the C−O bond cleavage occurs in the T_n state and not in the T_1 state. Along with this finding, it is interesting to examine whether such a delocalization occurs in the T_n excitation energy for $n\pi^*$ and the oxygen p orbital. For example, does benzophenone $n\pi^*$ interact with the oxygen p orbital in $BPCH_2OR(T_n)$? Does the C−O bond dissociation occur from $BPCH_2OR(T_n)$?

We now report the occurrence of the C−O bond cleavage of $BPCH_2OR(T_n)$ (R = C_6H_5, CH_3, H) during the two-color two-laser flash photolysis. It was found that not only the T_n state excitation energy but also the characteristics of the R group

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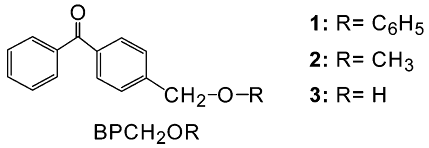
10.1021/jp051703b CCC: $30.25

SCHEME 1: Structures of the Benzophenone Derivatives (1−3) Used in the Present Study



have significant effects on the occurrence of the C−O bond cleavage. The three $BPCH_2OR$ derivatives, i.e., *p*-phenoxymethylbenzophenone (**1**, R = C_6H_5), *p*-methoxymethylbenzophenone (**2**, R = CH_3), and *p*-hydroxymethylbenzophenone (**3**, R = H), used in this study are shown in Scheme 1.

Experimental Section

Materials. *p*-Phenoxymethylbenzophenone, *p*-methoxymethylbenzophenone, and *p*-hydroxymethylbenzophenone were synthesized according to the literature.[16] Acetonitrile (spectral grade) was purchased from Nacalai Tesque, Inc. Sample solutions were freshly prepared and deoxygenated by bubbling with Ar. All experiments were carried out at room temperature.

Two-Color Two-Laser Flash Photolysis. Two nanosecond Nd:YAG laser systems (Continuum, Surelite II-10; 5-ns full width at half maximum (fwhm), 10 Hz, and Brilliant, Quantel; 5-ns fwhm, 10 Hz) were employed for laser flash photolyses at 355 and 532 nm, which are similar to the former reports.[17,18] Two laser flashes were synchronized by a pulse generator with a delay time of 10 ns−10 μs and overlapped through the sample. The probe light was obtained from a 450-W Xe lamp (Osram XBO-450). The probe beam was passed through an iris with a diameter of 0.3 cm and sent into the sample with a perpendicular intersection of the laser beams. The probe beam was then focused on a monochromator (Nikon G250). The output of the monochromator was monitored using a photomultiplier tube (PMT) (PMT, Hamamatsu Photonics R928). The signal from the PMT was recorded on a transient digitizer (TDS 580D four-channel digital phosphor oscilloscope, 1 GHz, Tektronix). A Hamamatsu Photonics multichannel analyzer (C5967) system was used for measurement of the transient absorption spectra. The total system was controlled with a personal computer via GP−IB interface. To avoid any damage of the sample solution by the probe light, a suitable cutoff filter was used in front of the sample.

Results and Discussion

***p*-BPCH₂OR(T₁) with One-Laser Flash Photolysis.** The transient absorption spectra of **1**−**3** in the lowest triplet excited state (T_1) were observed during the 355-nm laser (3 mJ $pulse^{-1}$) irradiation of **1-3** in an Ar-saturated acetonitrile solution at room temperature (Figure 1).

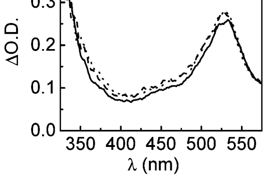


Figure 1. Transient absorption spectra obtained at 100 ns after the 355-nm laser irradiation during the laser flash photolysis of **1** (dotted line), **2** (broken line), and **3** (solid line) in Ar-saturated acetonitrile solution at room temperature.

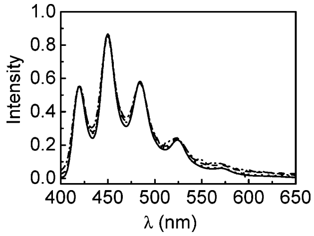


Figure 2. Phosphorescence spectra of BP (solid line), **1** (dotted line), **2** (dashed line), and **3** (broken line) in MeOH−EtOH (1:1 v/v) rigid matrix at 77 K. The phosphorescence spectra of BP, **1**, **2**, and **3** are normalized at 418 nm.

Since the transient absorption spectra of **1**(T_1)−**3**(T_1) are very similar to that of BP(T_1) and no emissions from **1**(S_1)−**3**(S_1) were observed, the extinction coefficients and intersystem crossing quantum yields from the S_1 to T_1 state of **1**−**3** are expected to be similar to those of BP(T_1) ($\epsilon_{525} = 6250$ M^{-1} cm^{-1} and $\Phi_{ISC} = 1.0$, respectively).[1,2] The transient absorption peak of **1**(T_1)−**3**(T_1) was observed at 525 nm, indicating that the phenyl, methyl, and hydroxyl substituents have no effect on the T−T absorption, i.e., the energy gap between T_1 and T_n ($\Delta E_{T_1-T_n}$) is equivalent. The triplet excitation energy is localized at the BP moiety in **1**(T_1)−**3**(T_1). The phosphorescence spectra of **1**−**3** were the same as that of BP with a 0−0 peak at 418 nm in the MeOH−EtOH (1:1 v/v) rigid matrix at 77 K (Figure 2), indicating that nπ* character of **1**(T_1)−**3**(T_1) is similar to that of BP(T_1) and that the E_{T_1} values of **1**−**3** are the same as that of BP(T_1) ($E_{T_1} = 286$ kJ mol^{-1}).

No new peak was observed during the decay of **1**(T_1)−**3**(T_1), suggesting that no C−O bond cleavage occurred from the **1**(T_1)−**3**(T_1) (eqs 1−3).

$$BPCH_2OR(S_0) \xrightarrow{h\nu_{355}} BPCH_2OR(S_1) \tag{1}$$

$$BPCH_2OR(S_1) \xrightarrow{\text{ISC } 100\%} BPCH_2OR(T_1) \tag{2}$$

$$BPCH_2OR(T_1) \xrightarrow{\text{ISC } 100\%} BPCH_2OR(S_0) \tag{3}$$

C−O Bond Cleavage from *p*-BPCH₂OR(T*ₙ*) during Two-Color Two-Laser Flash Photolysis. When **1**(T_1) was excited with the second 532-nm laser flash, the bleaching of **1**(T_1) at 525 nm ($\Delta\Delta O.D._{525}$) and generation of a new absorption band in the region of 375−420 nm with peaks at 383 and 398 nm ($\Delta\Delta O.D._{398}$) were observed (Figure 3). $\Delta\Delta O.D._{525}$ and $\Delta\Delta O.D._{398}$ linearly increased with the increasing second 532-nm laser power (Figure 4).

Because **1**(S_0) has no absorption at 532 nm, only **1**(T_1) was excited to produce **1**(T_n) during the second 532-nm laser irradiation. The bleaching of **1**(T_1) at 525 nm is attributed to the occurrence of some reactions from **1**(T_n) without the reproduction of **1**(T_1). Two new absorption peaks were observed at 383 and 398 nm, while the transient absorption indicated little change in the region of 320−370 nm as shown in Figure 3d. The new absorption band in the region of 320−420 nm is composed of a broad band at 320 nm and two peaks at 383 and 398 nm as shown in Figure 3e, which are assigned to the characteristic absorption of the *p*-benzoylbenzyl radical ($BPCH_2^\bullet$) and phenoxyl radical ($C_6H_5O^\bullet$) respectively.[9,19,20] The reduced bleaching of the absorption of **1**(T_1) in the region of 320−370 nm than that at 525 nm during the 355- and 532-nm two-laser irradiation, Figure 3b, confirmed the formation of $BPCH_2^\bullet$ in this region. On the other hand, based on the ϵ value of $C_6H_5O^\bullet$ at 398 nm ($\epsilon_{398} = 2200 \pm 200$ M^{-1} cm^{-1})[19,20] and ϵ value of $BPCH_2^\bullet$ at 320 nm ($\epsilon_{320} = 7500 \pm 400$ M^{-1} cm^{-1}),[9] the

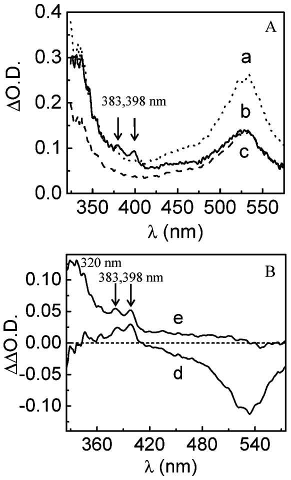


Figure 3. (A) Transient absorption spectra obtained at 200 ns after the 355-nm laser (a, dotted line) and 100 ns after the 355- and 532-nm two lasers (b, solid line) irradiation during the laser flash photolysis of **1** in Ar-saturated acetonitrile solution at room temperature. The broken line (c) shows the spectrum with the bleaching of **1**(T_1) but no formation of new absorption band. The delay time of the second 532-nm laser after the first 355-nm laser was 100 ns. (B) The transient absorption spectral changes of **1**(T_1) after the second 532-nm laser irradiation were obtained by subtraction of a from b (d) and subtraction of c from b (**e**), respectively.

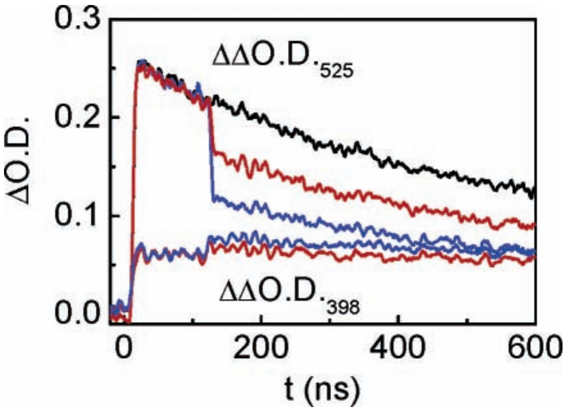


Figure 4. Time profiles show the ΔO.D. changes of **1**(T_1) at 525 and 398 nm, during the 355- and 532-nm two-laser irradiation with 532-nm laser powers of 50 (red line) and 100 mJ pulse^{-1} (blue line) during the laser flash photolysis of **1** in Ar-saturated acetonitrile solution at room temperature.

concentration of **1**(T_1) disappeared ([**1**(T_1)] = ($\Delta\Delta$O.D.$_{525}$ = 0.11)/(ϵ_{525} = 6250 M^{-1} cm^{-1}) = 1.76 × 10^{-5} M) was almost equal to those of the formed $C_6H_5O^\bullet$ and $BPCH_2^\bullet$ ([$C_6H_5O^\bullet$] = ($\Delta\Delta$O.D.$_{398}$ = 0.04)/(ϵ_{398} = 2200 ± 200 M^{-1} cm^{-1}) = 1.82 ± 0.16 × 10^{-5} M and [$BPCH_2^\bullet$] = ($\Delta\Delta$O.D.$_{320}$ = 0.12)/(ϵ_{320} = 7500 ± 400 M^{-1} cm^{-1}) = 1.60 ± 0.12 × 10^{-5} M) within the second-laser duration, where $\Delta\Delta$O.D.$_{525}$, $\Delta\Delta$O.D.$_{398}$, and $\Delta\Delta$O.D.$_{320}$ were the decrease, increase, and increase of the transient absorptions at 525, 398, and 320 nm, assigned to **1**(T_1), $C_6H_5O^\bullet$ radical, and $BPCH_2$. radical, respectively. Therefore, the C−O bond cleavage occurred from **1**(T_n) during the second 532-nm laser irradiation of **1**(T_1), and almost 100% of the disappearing **1**(T_1) was converted to $C_6H_5O^\bullet$ and $BPCH_2^\bullet$ radicals upon the second 532-nm laser excitation of **1**(T_1) (eqs 4 and 5).

$$BPCH_2OC_6H_5(T_1) \xrightarrow{h\nu_{532}} BPCH_2OC_6H_5(T_n) \quad (4)$$

$$BPCH_2OC_6H_5(T_n) \xrightarrow{\text{C−O cleavage}} BPCH_2^\bullet + {}^\bullet OC_6H_5 \quad (5)$$

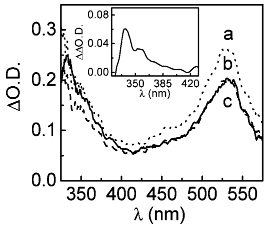


Figure 5. Transient absorption spectra obtained at 200 ns after irradiation with the 355-nm laser (a, dotted line) and 100 ns after the 355- and 532-nm two lasers (b, solid line) during the laser flash photolysis of **2** in Ar-saturated acetonitrile solution at room temperature. The delay time of the second 532-nm laser after the first 355-nm laser was 100 ns. The broken line (c) shows the spectrum with the bleaching of **2**(T_1) but no formation of any new absorption band. The delay time of the second 532-nm laser after the first 355-nm laser was 100 ns. The inset shows the formation of the new absorption band in the region of 310−425 nm, obtained by subtraction of c from b.

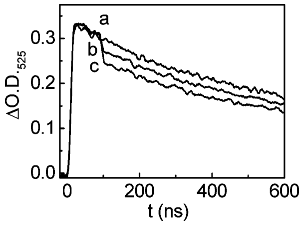


Figure 6. Time profiles show the ΔO.D. changes of **2**(T_1) at 525 during the one 355-nm laser (a) and 355- and 532-nm two-laser irradiation with 532-nm laser powers of 50 (b) and 80 mJ pulse^{-1} (c) during the laser flash photolysis of **2** in Ar-saturated acetonitrile solution at room temperature.

Similar results to those for **1** were observed for **2** (Figures 5 and 6).

The bleaching of **2**(T_1) at 525 nm increased by increasing the second 532-nm laser power. The lower bleaching during the absorption of **2**(T_1) in the region of 320−370 nm than that of at 525 nm during the 355- and 532-nm two lasers irradiation also suggests the formation of $BPCH_2^\bullet$ in this region. Because the methoxyl radical ($CH_3O^\bullet$) has no absorption in the region of 300−600 nm or a very weak one,[20] no new absorption peak was observed during the second 532-nm laser irradiation. Similarly, according to the ϵ value of $BPCH_2^\bullet$ at 320 nm, the concentration of **2**(T_1) that disappeared ([**2**(T_1)] = ($\Delta\Delta$O.D.$_{525}$ = 0.05)/(ϵ_{525} = 6250 M^{-1} cm^{-1}) = 8.0 × 10^{-6} M) was almost equal to that of the $BPCH_2^\bullet$ formed ([$BPCH_2^\bullet$] = ($\Delta\Delta$O.D.$_{320}$ = 0.06)/(ϵ_{320} = 7500 ± 400 M^{-1} cm^{-1}) = 8.0 ± 0.45 × 10^{-6} M), where $\Delta\Delta$O.D.$_{525}$ and $\Delta\Delta$O.D.$_{320}$ decreased and increased in the transient absorption at 525 and 320 nm, assigned to **2**(T_1) and $BPCH_2^\bullet$, respectively. Therefore, the C−O bond cleavage also occurred from **2**(T_n) during the second 532-nm laser irradiation of **2**(T_1), and almost 100% of the disappeared **2**(T_1) was converted to $CH_3O^\bullet$ and $BPCH_2$. radicals upon the second 532-nm laser excitation of **2**(T_1) (eqs 6 and 7).

$$BPCH_2OCH_3(T_1) \xrightarrow{h\nu_{532}} BPCH_2OCH_3(T_n) \quad (6)$$

$$BPCH_2OCH_3(T_n) \xrightarrow{\text{C−O cleavage}} BPCH_2^\bullet + {}^\bullet OCH_3 \quad (7)$$

However, an entirely different result was observed for **3** during the two-color two-laser flash photolysis. No bleaching of **3**(T_1) at 525 nm was observed (Figure 7), indicating that no reaction occurred from **3**(T_n) or reaction occurred from **3**(T_n)

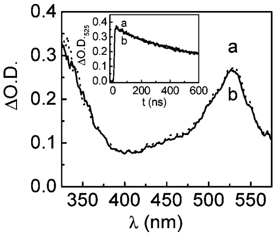


Figure 7. Transient absorption spectra obtained at 200 ns after the 355-nm laser (a, dotted line) and 100 ns after the 355- and 532-nm two-laser (b, solid line) irradiation during the laser flash photolysis of **3** in Ar-saturated acetonitrile solution at room temperature. The delay time of the second 532-nm laser after the first 355-nm laser was 100 ns. The dotted and solid lines are overlapped. The inset shows the time profiles obtained at 525 nm with the 355-nm laser (a) and the 355- and 532-nm two-laser irradiation with the 532-nm laser power of 100 mJ pulse^{-1} (b).

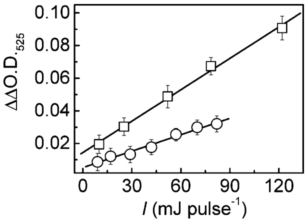


Figure 8. Plots of ΔΔO.D.$_{525}$ of **1**(T_1) (square) and ΔΔO.D.$_{525}$ of **2**(T_1) (circle) vs 532-nm laser power.

and reproduced **3**(T_1) again within the second 532-nm laser pulse duration (5 ns) (eqs 8−10).

$$\mathrm{BPCH_2OH(T_1)} \xrightarrow{h\nu_{532}} \mathrm{BPCH_2OH(T_n)} \qquad (8)$$

$$\mathrm{BPCH_2OH(T_n)} \xrightarrow[\times]{\text{C-O cleavage}} \mathrm{BPCH_2\bullet + \bullet OH} \qquad (9)$$

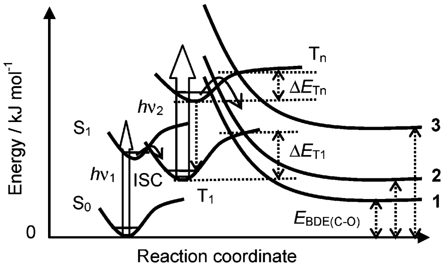
$$\mathrm{BPCH_2OH(T_n)} \longrightarrow \mathrm{BPCH_2OH(T_1)} \qquad (10)$$

Linear lines were obtained when ΔΔOD.$_{525}$ of **1**(T_1) and ΔΔO.D.$_{525}$ of **2**(T_1) were plotted vs the second 532-nm laser power (I mJ pulse^{-1}) (Figure 8).

The quantum yield (Φ) of the C−O bond cleavage was calculated to be 0.015 ± 0.007 for **1** and 0.007 ± 0.003 for **2**, respectively, from ΔΔO.D.$_{525}$ and the number of the second 532-nm laser photons absorbed by the T_1 state using an actinometry of the T−T absorption of zinc tetraphenylporphyrin at 470 nm in cyclohexane ($\epsilon_T\Phi_T$ = 50000 M^{-1} cm^{-1} at 470 nm).[21] It was found that the Φ(**1**) value was almost two times greater than Φ(**2**). The difference in Φ(**1**) and Φ(**2**) is a result of the substituent effect on BPs(T_n).

Mechanism of the C−O Bond Cleavage from *p*-BPCH$_2$OR(T$_n$). The $E_{\mathrm{BDE(C-O)}}$ value of **3** was reported to be 308 kJ mol^{-1} based on the heat formation (ΔH_f) for **3**, BPCH$_2^\bullet$, and $^\bullet$OH using a semiempirical PM3 program contained in MOPAC97.[9] Similarly, the $E_{\mathrm{BDE(C-O)}}$ values of **1** and **2** were roughly calculated to be 184 and 241 kJ mol^{-1} for **1** and **2** based on the ΔH_f values for **1**, BPCH$_2^\bullet$, and C$_6$H$_5$O$^\bullet$, and for **2**, BPCH$_2^\bullet$, and CH$_3$O$^\bullet$, respectively. It was found that the $E_{\mathrm{BDE(C-O)}}$ values of **1** and **2** were less than the E_{T_1} values of **1**(T_1) and **2**(T_1). However, no C−O bond cleavage was observed from **1**(T_1) and **2**(T_1). This result showed that the occurrence of the C−O bond cleavage is not simply related to the E_{T_1} value. A large energy barrier exists along the potential surface between the T_1 states and product radicals (ΔE_{T_1}), or there is no crossing point at all between the two potential surfaces of the T_1 states and product radicals in the cases of **1** and **2**. Therefore, no C−O bond cleavage occurred from **1**(T_1) and **2**(T_1) even when the E_{T_1} values are greater than the $E_{\mathrm{BDE(C-O)}}$ values. On the other hand, based on the absorption edge of **1**(T_1)−**3**(T_1) and the E_{T_1} values, the T_n state energies (E_{T_n}) of **1**(T_n)−**3**(T_n) are estimated to be higher than 450 kJ mol^{-1}, suggesting the possible occurrence of the C−O bond cleavage from **1**(T_n)−**3**(T_n). The remarkable difference between Φ(**1**) and Φ(**2**) and no bleaching of **3**(T_n) during the second 532-nm laser irradiation also indicated that the occurrence of the C−O bond cleavage depends not only on the E_{T_n} value but also on the character of the substituent. On the basis of the $E_{\mathrm{BDE(C-O)}}$ values of **1**−**3**, the potential surface of the BPCH$_2^\bullet$ and C$_6$H$_5$O$^\bullet$ radicals is expect to be the lowest, that of BPCH$_2^\bullet$ and $^\bullet$OH is the highest one, and that of BPCH$_2^\bullet$ and CH$_3$O$^\bullet$ is expected to be in the middle among **1**−**3**. The order of the energy barrier along the potential surface between the T_n states and the product radicals (ΔE_{T_n}) is $\Delta E_{\mathbf{1}(T_n)} < \Delta E_{\mathbf{2}(T_n)} \ll \Delta E_{\mathbf{3}(T_n)}$. Therefore, the ΔE_{T_n} value is one factor determining the bond cleavage yield. Since the E_{T_n} values with the 532-nm excitation are much higher than the $E_{\mathrm{BDE(C-O)}}$ values for **1**−**3**, the C−O bond cleavage for all of **1**(T_n)−**3**(T_n) would occur. However, no cleavage occurred in **3**(T_n). Therefore, the delocalization of the T_n state including the C−O bond is also important for the occurrence. A theoretical calculation of the T_n state potential surface may support the present experimental results, although it is a subject not related to the present study. Since the ω bond cleavage has been interpreted as being a thermally activated crossing to a dissociative potential surface leading to the C−O bond dissociation according to a selection rule for bond cleavage (avoided crossing),[9,22] a schematic energy diagram of the photoexcited **1**−**3** upon stepwise laser photolysis is shown in Scheme 2.

SCHEME 2: Energy Diagram during the C−O Bond Cleavage of 1−3 with Stepwise Two-Photon Excitation Using Two Lasers[a]



[a] $h\nu_1$, first 355-nm laser excitation; $h\nu_2$, second 532-nm laser excitation; ISC, intersystem crossing; ΔE_{T_1} and ΔE_{T_n}, energy barrier between the potential surfaces of the T_1 or T_n states and product radicals.

Because the E_T values of **1**(T_1)−**3**(T_1) are same as that of BP(T_1), the 4-CH$_2$OR (R = C$_6$H$_5$, CH$_3$, H) group has no interaction with the BP chromophore. When **1**(T_1)−**3**(T_1) was excited to **1**(T_n)−**3**(T_n), an electronic delocalization exists between the BP chromophore and 4-CH$_2$OR group in **1**(T_n)−**3**(T_n), showing the difference in the electronic characters between **1**(T_n)−**3**(T_n) and **1**(T_1)−**3**(T_1). The T_n molecular orbital must be dispersed over the entire molecule, since the C−O bond cleavage requires the delocalization of the antibonding character in the C−O bond of **1**(T_n)−**3**(T_n). The C$_6$H$_5$ group has π electrons, and the O atom of OR has nonbonding electrons. The size of R is in the order C$_6$H$_5$ > CH$_3$ > H. Therefore, the electronic delocalization of the T_n state is expected to be in the order **1**(T_n) > **2**(T_n) > **3**(T_n). In other words, the phenyl group with π electrons is bonded to the oxygen atom in **1**, and the excitation energy in **1**(T_n) is delocalized more significantly in the moiety including the C−O bond than that in **2**(T_n) in which the methyl group having no π electrons is bonded to the oxygen atom in **2**. Such a delocalization in the T_n state can explain the larger Φ(**1**) and

Φ(**2**) values. The delocalization of the T_n molecular orbital in **3**(T_n) including the BP and CH_2OH moieties is impossible, because a hydrogen atom is bonded to the oxygen atom in **3**. Therefore, no occurrence of the C−O bond cleavage was observed despite much higher E_{T_n} than $E_{BDE(C-O)}$ for **3**.

Comparison of Properties between BP(T_1) and BP(T_n) and between *p*-BPCH$_2$OR(T_1) and *p*-BPCH$_2$OR(T_n). Because the properties of BP(T_1) are very important in photochemistry, those of BP and its derivatives in the T_n states are also important. However, in contrast to BP(T_1), a few studies have been reported on the properties of BP(T_n).[18,23−26] Obi and co-workers found that the hydrogen abstraction reaction of BP(T_n) from solvent molecules occurred.[23] Later they found that the dissociation of BP(T_n) strongly depends on the method to generate BP(T_n). Fast dissociation of BP(T_n) occurred during the 308-nm laser irradiation of BP(T_1), while no dissociation occurred during the 532-nm laser irradiation.[25,27] McGimpsey and Scaiano found that bleaching of the transient absorption of BP(T_1) occurred during the 517-nm dye laser irradiation of BP(T_1) in benzene.[24] They assumed that the excitation of BP(T_1) to BP(T_n) results in the repopulation of BP in the ground state (S_0) by energy transfer from BP(T_n) to benzene, producing benzene(T_1) which decays to benzene(S_0) without the triplet energy transfer to BP. Recently, we found that the transient behavior of the quencher (Q) of BP(T_n) depends on the quencher structure. After energy transfer from BP(T_n) to Q to give Q(T_1), the sequential triplet energy transfer from Q(T_1) to BP occurred in 100% for *p*-dichlorobenzene and *tert*-butylbenzene as Q but not for benzene, chlorobenzene, and *o*-dichlorobenzene as Q.[18] On the other hand, the reactions sensitized by BP(T_n) were studied using the two-color two-laser excitation technique.[17] Fast internal conversion of BP(T_n) to BP(T_1) occurs within a nanosecond laser flash duration, while the triplet energy transfer proceeds from BP(T_n) to the appropriate Q. The lifetimes of BP(T_n) and several BP derivatives in the T_n state (BPs(T_n)) have been estimated to be 110−450 ps from the dependence of the quenching efficiency on the Q concentration.[18] It is clear that BP(T_n) and BPs(T_n) have much shorter lifetimes than those of BP(T_1) and BPs(T_1). For example, the lifetime of BP(T_n) is 450 ps, while that of BP(T_1) is 7 μs. Therefore, the BP(T_n) and BPs(T_n) decay to BP(T_1) and BPs(T_1) in almost 100% yield with no unimolecular reactions. Moreover, the bimolecular reactions of BP(T_n) and BPs(T_n) can occur only in the presence of high concentrations of reactant molecules because of the short lifetimes.

For the *p*-BPCH$_2$OR, the properties of *p*-BPCH$_2$OR(T_1) are very similar to those of BP(T_1) as described above, and the lifetimes of *p*-BPCH$_2$OR(T_n) are also expected to be very short, similar to that of BP(T_n). However, the C−O bond cleavage occurred in *p*-BPCH$_2$OR(T_n). It is suggested that the T_n state energy delocalization including the C−O bond occurs in *p*-BPCH$_2$OR(T_n) although the T_1 state energy localized in the BP moiety of *p*-BPCH$_2$OR(T_1) has an nπ* character. Although the Φ values of the C−O bond cleavage from the T_n state, 0.015 ± 0.007 for **1** and 0.007 ± 0.003 for **2**, are much smaller than those of the C−S ($\Phi = 0.51$),[9] O−O ($\Phi = 0.82$),[10] and C−X ($\Phi = 0.61$ for X = Cl and $\Phi = 0.37$ for X = Br)[10] bond cleavage from the T_1 state, the diminishing *p*-BPCH$_2$OR(T_1) was converted in 100% yield to the free radicals. It is suggested that the C−O bond cleavage and production of the two radical fragments, such as $BPCH_2^•$, $C_6H_5O^•$, and $CH_3O^•$, can be generated not from the T_1 state but from the T_n state using the two-color, two-laser flash photolysis technique. The two-color two-laser flash photolysis technique will be a powerful tool for initiating some chemical reactions from the T_n state, although no reaction occurs from the S_1 and T_1 states. The present study is an example in which the chemical reactions can be initiated from the T_n state even when such reactions cannot proceed in the S_1 and T_1 states.

Conclusions

The C−O bond cleavage from **1**(T_n) and **2**(T_n) was observed during the two-color two-laser photolysis. The diminishing **1**(T_1) or **2**(T_1) was converted, in almost 100% yield, to $C_6H_5O^•$ and $BPCH_2^•$ radicals or $CH_3O^•$ and $BPCH_2^•$ radicals, respectively, through the C−O bond cleavage within the laser flash duration of 5 ns. The quantum yield of the C−O bond cleavage was calculated to be 0.015 ± 0.007, 0.007 ± 0.003, and 0 for **1**, **2**, and **3**, respectively, indicating that **1**(T_n) and **2**(T_n) undergo the C−O bond cleavage in a minor yield and mainly decay to **1**(T_1) and **2**(T_1), respectively, through internal conversion, and that **3**(T_n) completely decays to **3**(T_1) within 5 ns. It is suggested that E_{T_n}, ΔE_{T_n}, and delocalization of the T_n molecular orbital including BP and the CH_2OR moieties are important factors for the occurrence of the C−O bond cleavage. It is also found that the delocalization of the T_n molecular orbital occurs not only in the molecules with the $\pi\pi$* T_1 state, such as the substituted naphthalenes, but also in the molecules with the nπ* T_1 state, such as *p*-BPCH$_2$OR. The T_n state photochemistry provides an attractive new research field. We would like to emphasize that the occurrence of these chemical reactions can be initiated from the T_n state, even when such chemical reactions cannot proceed in the S_1 and T_1 states. Because the T_1 state can be selectively excited to give the T_n state, one can control the occurrence of the reactions in the T_n state using the two-color, two-laser flash photolysis technique.

Acknowledgment. This work has been partly supported by a Grant-in-Aid for Scientific Research on Priority Area (417), 21st Century COE Research, and others from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japanese Government. The authors also thank to JSPS for a fellowship for X.C.

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