

Homolytic cleavage of C–Si bond of *p*-trimethylsilylmethylacetophenone upon stepwise two-photon excitation using two-color two-laser flash photolysis

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Abstract

C–Si bond cleavage of *p*-trimethylsilylmethylacetophenone(**1**) occurred in a higher triplet excited state (T_n), giving mainly *p*-acetylbenzyl radical with the transient absorption in the region of 295–360 nm, with a quantum yield of 0.046 ± 0.008 using the two-color two-laser photolysis techniques. In contrast, the C–Si bond cleavage of *p*-trimethylsilylmethylbenzophenone(**2**) was absent in the T_n state whose energy is larger than the C–Si bond cleavage energy. The results can explain existence of a bond cleavage crossing between potential surfaces of the T_n state and a dissociative state of the C–Si bond for **1**, but not for **2**.

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1. Introduction

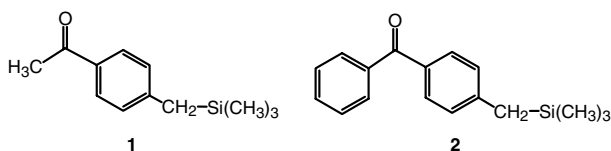
The higher excited states show the higher reactivities compared with the lowest excited state from the viewpoint of excitation energy [1]. Some reactions, which are still inert in the lowest excited state, could occur in higher excited states. Therefore, investigation of the properties of molecules in the higher excited singlet (S_n) and triplet (T_n) states is an attractive subject [2–5]. The formation of carbazolyl radical from carbazole in the S_n and T_n states has been reported based on the transient absorption measurements using the double excitation method [6,7]. We have recently reported that the C–O bond in 1- and 2-[(4-benzoylphenoxy)methyl]naphthalenes cleaves in the T_n state, but not in the lowest

triplet excited state (T_1) by using the two-color two-laser irradiation method [8]. The stepwise photocleavage of two C–O bonds in 4-benzoylphenoxy-methyl-substituted naphthalenes through the T_n state with three-step excitation by three-color three-laser irradiation method was also shown [9]. It seems that the reactivity of the T_n state is different from that of the T_1 state. It is well known that the C–Si bond is photochemically stable [10]. To our best knowledge, there are no reports on the C–Si bond cleavage under the direct light irradiation [10]. It is suggested that the C–Si bond will not dissociate in the S_1 and T_1 states due to the larger dissociation energy of the C–Si bond than the pertinent state energies. In contrast, in higher excited states, the C–Si bond may cleave due to much higher excitation energies than the dissociation energy of the C–Si bond.

Herein, we report, for the first time, occurrence of the C–Si bond cleavage of *p*-trimethylsilylmethylacetophenone (**1**) in the T_n state, but absence of decomposition

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Scheme 1. Structures of acetophenone and benzophenone derivatives (**1** and **2**) used in the present study.

of *p*-trimethylsilylmethylbenzophenone (**2**) in the T_n state. The structures of **1** and **2** are shown in Scheme 1. The occurrence of the C–Si bond fission depends not only on the T_n state energy but also on the crossing between the potential surfaces of the T_n and a dissociative state for the C–Si bond.

2. Experimental

2.1. Materials

p-Trimethylsilylmethylacetophenone and *p*-trimethylsilylmethylbenzophenone were synthesized according to the literature [11]. 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.

2.2. Two-color two-laser flash photolysis

Two nanosecond Nd:YAG laser systems (Continuum, Surelite II-10; 5-ns fwhm, 10 Hz, and Brilliant, Quantel; 5-ns fwhm, 10 Hz) were employed for laser flash photolyses at 266, 355, and 532 nm. The probe light was obtained from a 450 W Xe-lamp (Osram XBO-450). The probe beam was arranged to the entrance side of the laser beam. The probe beam was then focused on a monochromator (Nikon G250). The output of the monochromator was monitored using a photomultiplier tube (PMT) (photomultiplier tube, 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 multi-channel analyzer (C5967) system was used for measurement of the transient absorption spectra.

3. Results and discussion

Upon 266-nm laser photolysis of acetonitrile solution of **1**, a transient absorption spectrum with a peak at 380 nm was obtained (Fig. 1). The transient absorption with a lifetime of several microseconds was efficiently quenched by oxygen. These properties are similar to

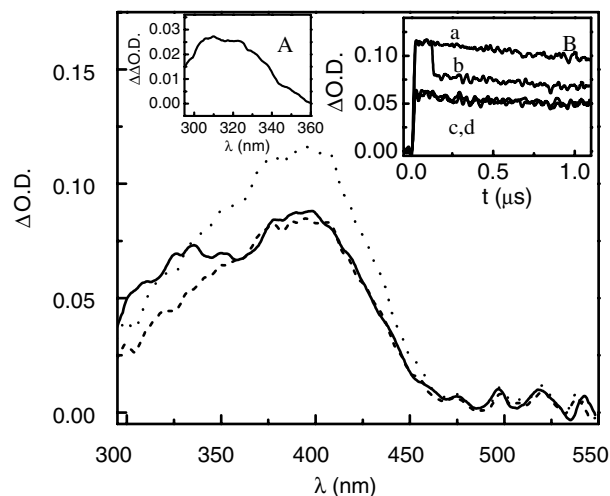


Fig. 1. Transient absorption spectra obtained at 200 ns after the first 266-nm laser flash (dotted line) and at 100 ns after the second 355-nm laser flash (solid line) during the two-color two-laser flash photolysis of **1**. The delay time of the second laser after the first laser was 100 ns. The broken spectrum shows the bleaching of **1**(T_1) without formation of any peak. The insets show the spectral change in the region of 295–360 nm, obtained by subtraction of the broken spectrum from the solid one (A), and time profiles of the transient absorption (B) at 380 nm using one 266-nm (6 mJ pulse^{-1}) laser (a), or 266- and 355-nm (60 mJ pulse^{-1}) two-laser (b), and at 317 nm using one 266-nm laser (c), or 266- and 355-nm two-laser (d) during the one- or two-laser flash photolysis. (c) and (d) are overlapped.

those of triplet acetophenone [12,13]. Therefore, the transient absorption spectrum with a peak at 380 nm is assigned to the T_1 state of **1** ($\mathbf{1}(T_1)$) formed with a formation quantum yield (Φ_T) of 1.0 [13]. The extinction coefficient of $\mathbf{1}(T_1)$ at 380 nm (ϵ_{380}) was calculated to be $8000 \pm 500 \text{ M}^{-1} \text{ cm}^{-1}$ based on $\epsilon_{330} = 7160 \text{ M}^{-1} \text{ cm}^{-1}$ of acetophenone(T_1) as the reference [13]. Upon 266 or 355 nm laser photolysis of acetonitrile solution of **2**, a transient absorption spectrum with a peak at 530 nm was also assigned to $\mathbf{2}(T_1)$ (Fig. 2) since it was similar to the absorption profiles of triplet benzophenone [12,13]. From the observation that no residual transient absorption was left after depletion of the absorption spectra of $\mathbf{1}(T_1)$ and $\mathbf{2}(T_1)$, it is inferred that the C–Si bond does not dissociate in $\mathbf{1}(T_1)$ and $\mathbf{2}(T_1)$.

When $\mathbf{1}(T_1)$ was excited by the second 355-nm laser pulsing, an immediate bleaching of the absorption of $\mathbf{1}(T_1)$ was observed, while almost no change was around 317 nm (Fig. 1, solid line). No recovery in $\Delta\text{O.D.}$ was observed after the bleaching for $\mathbf{1}(T_1)$ (Fig. 1, inset B,b). These results suggest that an absorption band appeared in the region of 295–360 nm as shown in Fig. 1, inset A is probably assigned to the *p*-acetylbenzyl radical, although the transient absorption spectrum of *p*-acetylbenzyl radical has not been reported. The transient absorption spectra of various *p*-substituted benzyl radicals (*p*-X-benzyl radical: X = F, Cl, Br, CH₃, OCH₃, CN, and NO₂) have been observed to have a peak in the region of 295–360 nm [14,15]. *p*-Acetylbenzyl radical

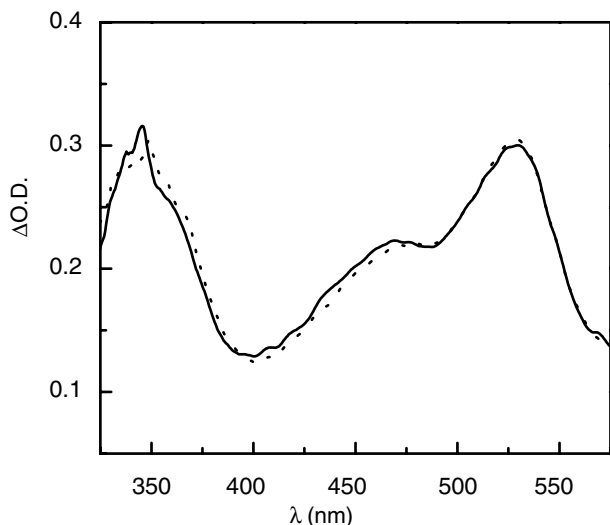


Fig. 2. Transient absorption spectra obtained at 200 ns after the first 355-nm laser flash (dotted line) and at 100 ns after the second 532-nm laser flash (solid line) during the two-color two-laser flash photolysis of **2**. The delay time of the second laser after the first laser was 100 ns.

is one of *p*-X-benzyl radicals and, therefore, it is assumed to have the similar absorption to those of various *p*-X-benzyl radicals. Because there is no report of ϵ value of *p*-acetylbenzyl radical, we assume that ϵ_{317} of *p*-acetylbenzyl radical is similar to that of benzyl radical ($\epsilon_{317} = 12000 \pm 1500 \text{ M}^{-1} \text{ cm}^{-1}$) [14,15]. The transient absorption spectrum of *p*-acetylbenzyl radical (ΔOD_{317} in Fig. 1, inset A) was overlapped with that of **1**(T_1) in the region of 295–360 nm, and obtained by subtraction of the broken spectrum (with the bleaching of **1**(T_1) but no formation of any peak) from the solid one. Therefore, the formation of *p*-acetylbenzyl radical can be calculated from ΔOD_{317} . The concentration of **1**(T_1) disappeared ($[\mathbf{1}(T_1)] = (\Delta\text{OD}_{380} = 0.022)/(\epsilon_{380} = 8000 \pm 500 \text{ M}^{-1} \text{ cm}^{-1}) = 3 \times 10^{-6} \text{ M}$) was similar to that of the *p*-acetylbenzyl radical formed ($[p\text{-acetylbenzyl radical}] = (\Delta\text{OD}_{317} = 0.031)/(\epsilon_{317} = 12000 \pm 1500 \text{ M}^{-1} \text{ cm}^{-1}) = 3 \times 10^{-6} \text{ M}$) within the second-laser duration, where ΔOD_{380} and ΔOD_{317} were the decrease and increase of the transient absorption at 380 and 317 nm, assigned to **1**(T_1) and *p*-acetylbenzyl radical, respectively. Therefore, it is suggested that the disappeared **1**(T_1) changes mainly to *p*-acetylbenzyl radical and trimethylsilyl radical through the C–Si bond cleavage within the second-laser duration. The formation of trimethylsilyl radical was not observed with the transient absorption measurements because of no absorption in the region of 300–600 nm [14].

The ΔOD_{380} value increased with increasing the second 355-nm laser. When ΔOD_{380} was plotted against the second 355-nm laser power, I (Fig. 3), a straight line was obtained. From the slope of the line, the quantum yield (Φ) of the C–Si bond cleavage from **1**(T_n) was estimated to be 0.046 ± 0.008 from ΔOD_{380} and the num-

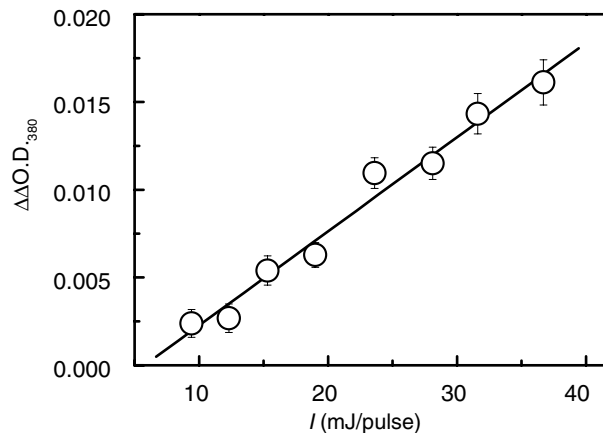


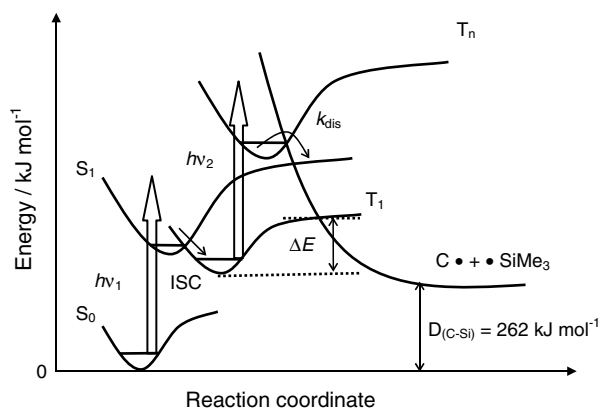
Fig. 3. Plots of $\Delta\Delta\text{OD}_{380}$ vs., 355-nm laser power, I .

ber of the second laser photons absorbed by **1**(T_1) using an actinometry of T–T absorption of benzophenone at 525 nm in benzene ($\epsilon_T = 6500 \text{ M}^{-1} \text{ cm}^{-1}$ at 525 nm) [12,13].

On the other hand, bleaching in the absorption spectrum of **2**(T_1) was not observed when **2**(T_1) was excited by the second 532-nm (Fig. 2) or 355-nm laser pulsing. These observations indicate that **2**(T_n) undergoes a non-radiative deactivation to the **2**(T_1) within the second laser-pulse duration.

The triplet energies of **1**(T_1) and **2**(T_1) ($E_{\mathbf{1}(T_1)} = 292 \text{ kJ mol}^{-1}$ and $E_{\mathbf{2}(T_1)} = 286 \text{ kJ mol}^{-1}$) determined from the origins of phosphorescence spectra of **1** and **2** obtained in a mixture of methanol and ethanol (1:1 v/v) at 77 K are larger than the C–Si bond dissociative energies ($D_{\text{C-Si}}$) estimated to be 262 kJ mol^{-1} for **1** and 234 kJ mol^{-1} for **2**, respectively, by using the semi-empirical PM3 calculations. For the bond cleavage, distribution of the excitation energy to the cleaving bond in the molecule is essential [10,16–18]. Hence, the absence of C–Si bond cleavage suggests that the excitation energy is not sufficiently distributed to the C–Si bond in **1**(T_1) and **2**(T_1), or, in other words, that a large energy barrier (E) may exist between the potential surfaces of the T_1 state and the C–Si bond dissociation.

From the obtained results, it is inferred that the occurrence of the C–Si bond cleavage in the T_n state is controlled by not only the energy but also the electronic delocalization of the molecule. The occurrence of the C–Si bond cleavage in **1**(T_n) and the absence of that in **2**(T_n) can be explained by electronic delocalization in the T_n state including the C–Si bond or the existence of a thermally activated crossing between potential surfaces of the T_n state and a π , σ^* or a σ , σ^* state leading to the C–Si bond dissociation according to a selection rule for bond cleavage (avoided crossing) [19]. A schematic energy diagram of photoexcited **1** upon stepwise laser photolysis is shown in Scheme 2.



Scheme 2. An energy diagram of photoexcited **1** by two-color two-laser photolysis techniques. $h\nu_1$: the first 266-nm laser excitation; $h\nu_2$: the second 355-nm laser excitation; ISC: intersystem crossing; k_{dis} : rate constant of the C–Si bond dissociation; ΔE : energy barrier between the potential surfaces; C•: *p*-acetylbenzyl radical; •SiMe₃: trimethylsilyl radical.

When the S_1 state of **1** is produced upon the first 266-nm laser irradiation, a very fast ($\sim 10^{11} \text{ s}^{-1}$) intersystem crossing (ISC) from the S_1 to the T_1 state proceeds [1]. No C–Si bond cleavage occurred from the S_1 and T_1 states although $E_{1(S_1)}$ and $E_{1(T_1)}$ are higher than $D_{(\text{C-Si})}$, suggesting that ΔE is too large for a bond cleavage crossing to proceed from the potential surfaces of the S_1 or T_1 states to that of the C–Si bond dissociation. On the other hand, the C–Si bond dissociated from **1**(T_n) generated upon excitation of **1**(T_1) by the second 355-nm laser photolysis. It seems that $E_{1(T_n)}$ is much higher than $D_{(\text{C-Si})}$, and that ΔE is small for the crossing between potential surfaces of the T_n state and the C–Si bond dissociation of **1**. Although Φ of the C–Si bond cleavage from **1**(T_n) was 0.046 ± 0.008 and the non-reactive process is the major route for relaxation of **1**(T_n), the disappeared **1**(T_1) changes mainly to *p*-acetylbenzyl and trimethylsilyl radicals through the C–Si bond cleavage. Because **1**(T_1) can be selectively excited to give **1**(T_n), one can control the occurrence of the C–Si bond cleavage from **1**(T_n) to give *p*-acetylbenzyl and trimethylsilyl radicals using the two-color two-laser flash photolysis technique. The occurrence of the chemical reactions can be initiated from the T_n state, even when such chemical reactions can not proceed in the T_1 state. The similar mechanism can be considered for **2**(T_1) and **2**(T_n) where the C–Si bond cleavage is absent. ΔE is still high for the crossing between potential surfaces of the T_n state and the C–Si bond dissociation of **2**. It is suggested that the T_n state energy is still localized on the benzophenone moiety in **2**(T_n). In other words, the excitation energy is not sufficiently dispersed from the benzophenone moiety to the C–Si bond even in **2**(T_n). The difference between **1** and **2** is only phenyl and methyl attached to the carbonyl group. The different experimental results for **1**(T_n) and **2**(T_n) indicate that the properties of

the T_n state are effected by the phenyl and methyl substituents.

4. Conclusions

The C–Si bond cleavage from **1**(T_n) with $\Phi = 0.046 \pm 0.008$ has been observed by using the two-color two-laser flash photolysis techniques for the first time. The disappeared **1**(T_1) changes mainly to *p*-acetylbenzyl and trimethylsilyl radicals through the C–Si bond cleavage. The occurrence of the C–Si bond cleavage depends on both excitation energy and crossing between potential surfaces of the T_n and the C–Si bond dissociation of **1**. On the other hand, C–Si bond cleavage does not occur from **2**(T_n). These results indicate that the photochemical properties of the T_n state are quite different from those of the T_1 state, and strongly depend on the molecules. The present study shows possibilities that new reactions may be found in the S_n and T_n states of various molecules by using the two-color two-laser flash photolysis technique.

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