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ARTICLES

Three-Color Three-Laser Photochemistry of Di(*p*-methoxyphenyl)methyl Chloride

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Three-color three-laser photochemistry of di(*p*-methoxyphenyl)methyl chloride ((p-$CH_3OC_6H_4)_2CHCl$ = An_2CHCl) was studied by three-step excitation using 308-, 355-, and 495-nm lasers with delay times of 100 ns to 3 μs. Di(*p*-methoxyphenyl)methyl radical ($An_2CH^•$) was produced together with $An_2CH^•$ in the excited state ($An_2CH^{•*}$) and di(*p*-methoxyphenyl)methyl cation (An_2CH^+) in quantum yields of 0.09, 0.12, and 0.12, respectively, after a laser flash during 308-nm laser (first laser) photolysis of An_2CHCl in acetonitrile. Excitation of $An_2CH^•$ with a 355-nm laser (second laser) resulted in formation of transient absorption of $An_2CH^{•*}$ and An_2CH^+ and fluorescence of $An_2CH^{•*}$ with a peak at 550 nm. The formation of An_2CH^+ from $An_2CH^•$ requires two-photon energy at 355 nm and proceeds by resonant two-photon ionization (RETPI) of $An_2CH^•$ through sequential excitation of $An_2CH^{•*}$. Excitation of An_2CH^+ with a 495-nm laser (third laser) produced fluorescence with a peak at 560 nm. Although the fluorescence of An_2CH^+ was also observed without the second laser excitation because of the initial formation of An_2CH^+ during the first 308-nm laser photolysis, the fluorescence intensity of An_2CH^+ increased approximately 1.2 times with the second 355-nm laser excitation of $An_2CH^•$. Therefore, the second laser excitation can perform the conversion of $An_2CH^•$ to An_2CH^+ through RETPI within the laser flash duration, and the fluorescence intensity of An_2CH^+ can be controlled by the second irradiation.

Introduction

Multilaser chemistry is defined as chemistry involving multiexcitation with more than two lasers, in which short-lived species such as excited molecules and reactive intermediates are generated by the first excitation of starting molecules, and used as starting molecules for the second excitation. Short-lived species generated by the second excitation are used as starting molecules for the third excitation. In other words, photochemistry of short-lived species can be investigated by the multistep excitation method using more than two lasers. Properties of lasers such as the monochromaticity, fine directivity, high intensity, and short-pulse duration are certainly used in the multilaser photochemistry in which selective excitation of a short-lived molecule, spatially selective excitation, time control of irradiation, and excitation at high laser fluence are carried out.

As the simplest multilaser chemistry, two-laser chemistry of short-lived species such as excited molecules and reactive intermediates in liquid phase has been extensively investigated by various groups. For example, Miranda et al. have reported that heterolytic cleavage of C−Cl bond proceeds to give α-chloroalkylbenzyl cation and chloride ion during the first 266-nm laser flash photolysis of dichlorodiphenylalkanes,[1,2] followed by dehydrochlorination of the cation to give α-*E*-allylbenzyl cation, and that the α-*E*-allylbenzyl cation isomerizes to the *Z*-isomer with the second laser excitation at 480 or 532 nm. Ouchi et al. have reported that two-step homolytic cleavages of two C−Br or C−Cl bonds proceed to give a biradical during two-color two-laser photolyses of 1,8-bis(bromomethyl)- and 1,8-bis(chloromethyl)naphthalenes using the first 193-, 248-, or 308-nm and second 351-nm excimer lasers.[3] It has been reported by Redmond et al. that hydrogen abstraction of a triplet ketone proceeds to give ketyl radical during the first 308-nm laser flash photolysis of substituted benzophenone, and that the ketyl radical is excited to give fluorescence during the second 337- or 532-nm laser flash photolysis.[4] It has been also reported by Goez et al. that photoinduced electron transfer (PET) between ketones such as 4-carboxybenzophenone and 1,5-anthraquinonedisulfonate and donor molecules occurs to give the radical anion and cation during the first 308-nm laser flash photolysis, and electron detachment from the radical anion proceeds to give the ketone and solvated electron during the second 387.5-nm laser flash photolysis.[5,6] Wang et al., Johnston et al., McGimpsey et al., and Goez et al. have reported that the excited singlet or triplet state molecules are generated during the first 266-, 308-, or 355-nm laser flash photolysis of anthracene, diphenylamine, (4′-(phenanthrene-9-carboxylate)methyl-4-methylnaphthoate)-biphenyl, and dimethylaminobenzonitrile and $Ru(bpy)_3{}^{2+}$, respectively, and that the radical cations are produced during the second 355-, 480-, 532-, or 590-nm laser flash photolysis of the excited-state molecules.[7−11] It has been reported by Wang et al. that resonant two-photon ionization (RETPI) of all-*trans*-1,6-diphenyl-1,3,5-hexatriene (*t*-DPH) proceeds to give the

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SCHEME 1: Three-Laser Photochemistry of A using the Three-Color Three-Laser Photolysis Method

$$\mathrm{A} \xrightarrow{h\nu_1} \mathrm{A^*} \longrightarrow \mathrm{B} \xrightarrow{h\nu_2} \mathrm{B^*} \longrightarrow \mathrm{C} \xrightarrow{h\nu_3} \mathrm{C^*} \longrightarrow \mathrm{Product}$$

t-DPH radical cation during the first 308- or 355-nm laser flash photolysis of *t*-DPH, and that *t*-DPH radical cation isomerizes to the cis-isomer radical cation during the second 590-nm laser flash photolysis.[12] It has been reported by Itoh et al., Brewer et al., and Fuket et al. that the ground-state tautomer is excited to give the equilibrated excited-state tautomers during the first 248-, 308-, or 355-nm laser flash photolysis of 3-hydroxyflavone,[13−15] 3-hydroxychromone,[13] 7-hydroxyquinoline,[16,17] 7-hydroxyisoflavone,[18] 7-hydroxy-1-indanone,[19] 7-azaindole dimer,[20] 2-(2-hydroxyphenyl)benzoxazole,[21,22] and 7-azaindole/1-azacarbazole,[23] and that fluorescence of two excited-state tautomers was observed during the second dye-laser flash photolysis.

In the two-step, two-laser flash photolysis, short-lived species such as excited molecules and reactive intermediates are generated in liquid phase from one-photon excitation, photolysis, PET, and RETPI during the first laser flash photolysis. Photochemistry such as isomerization and ionization of short-lived species occurs through the excited state during the second laser flash photolysis. Although the two-laser chemistry has been extensively investigated, three-color three-laser chemistry in liquid phase has never been reported. The first laser ($h\nu_1$) excitation of starting molecule (A) produces short-lived species (B) through A in the excited state (A*), the second laser ($h\nu_2$) excitation of B produces another short-lived species (C) through B in the exited state (B*), and the third laser ($h\nu_3$) excitation of C produces another short-lived species or causes photochemistry of C through C in the exited state (C*) (Scheme 1). The delay times of $h\nu_2$ and $h\nu_3$ from $h\nu_1$ and $h\nu_2$, respectively, depend on the formation rates and stabilities of B and C.

In the present work, three-step three-laser photochemistry of di(*p*-methoxyphenyl)methyl chloride ((p-$CH_3OC_6H_4)_2CHCl$ = An_2CHCl) has been investigated by three-color three-laser flash photolysis with delay times of 100 ns to 3 μs. Homolysis and heterolysis of the C−Cl bond within a laser flash duration (picosecond to nanosecond) are well-known in photochemistry of An_2CHCl in various solvents.[24,25] Both di(*p*-methoxyphenyl)methyl radical ($An_2CH^\bullet$) and di(*p*-methoxyphenyl)methyl cation (An_2CH^+) are generated during the first 308-nm laser irradiation. Then, $An_2CH^\bullet$ is irradiated by the second 355-nm laser to give An_2CH^+ through RETPI of $An_2CH^\bullet$, and then An_2CH^+ is irradiated by the third 495-nm laser to give the excited An_2CH^+.

Experimental Section

An_2CHCl was prepared by reactions of di(*p*-methoxyphenyl)methanol with HCl and methylene chloride (CH_2Cl_2) in the presence of anhydrous $CaCl_2$, according to the reported method,[24] and purified by fractional distillation. Acetonitrile (Wako) as a solvent for laser flash photolysis was dried over calcium hydride (CaH_2), and purified by distillation for several times.

Three-color three-laser flash photolysis experiment was carried out using 308-nm laser flash from a XeCl excimer laser (Lambda Physics, Compex102; pulse width of 25 ns fwhm) as the first laser, the third harmonic oscillation (355-nm) of an Nd^{3+}:YAG laser (Quantel Brilliant Q-switch laser; pulse width of 5 ns fwhm) as the second laser, and 495-nm flash from an OPO laser (Continuum Surelite) pumped by a Q-switched Nd^{3+}:YAG laser (Continuum Surelite) as the second or third laser. The monitor light source was a 450 W Xe lamp (Osram XBO-450) synchronized with the laser flash. The intensity of monitor light source was detected using a photomultiplier (Hamamatsu R928). The electric signal from the photomultiplier was digitalized by oscilloscope, and transported to a personal computer with the interface RS 232C. Transient absorption spectra were measured by a multichannel analyzer fitted with an image intensifier with 30 ns gate width (Hamamatsu C4500), and transported to a personal computer. The samples were prepared in a transparent rectangular cell made by quartz (1.0 × 1.0 × 4.0 cm, optical-path length of 1.0 cm) at room temperature, and were degassed with Ar for 15 min. The concentration (1.9×10^{-2} M) of An_2CHCl was chosen to have the absorbance of 1.0 at 308 nm of the excitation laser wavelength. The first laser beam passed through an aperture with a diameter of 1.0 cm which was the widest among three laser beams. The second laser diameter was wider than that of the third laser. The third laser irradiation spot was wider than the divergence of the monitor light.

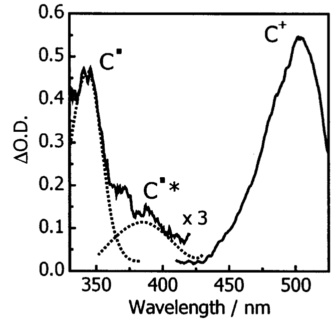

Figure 1. Transient absorption spectrum observed at 100 ns after a flash during 308-nm laser flash photolysis of An_2CHCl (1.9×10^{-2} M) in acetonitrile. This spectrum has been analyzed by three peaks at 348, 385, and 510 nm assigned to $An_2CH^\bullet$ ($\Delta O.D._{348} = 0.16$), $An_2CH^{\bullet *}$ ($\Delta O.D._{385} = 0.045$), and An_2CH^+ ($\Delta O.D._{510} = 0.49$), respectively.

γ-Radiolysis was carried out using a ^{60}Co γ source (dose, 2.6×10^2 to 1.0×10^3 Gy) at 77 K. Optical absorption spectra were taken at 77 K by a spectrophotometer and multichannel photodetector, while fluorescence spectra were measured at 77 K by a fluorescence spectrophotometer. The fluorescence lifetime measurement was carried out by single photon counting method.

Results

1. Transient Absorption Measurements. *One-Laser Photolysis*. The transient absorption spectrum with three peaks at 348, 385, and 510 nm was observed at 100 ns after a flash from a XeCl laser at 308 nm with 4.5×10^{-2} J pulse^{-1} during laser flash photolysis of An_2CHCl in acetonitrile (Figure 1). This spectrum has been analyzed by three peaks at 348, 385, and 510 nm assigned to $An_2CH^\bullet$ ($\Delta O.D._{348} = 0.16$), $An_2CH^{\bullet *}$ ($\Delta O.D._{385} = 0.045$), and An_2CH^+ ($\Delta O.D._{510} = 0.49$), respectively.[24,25] The time profiles of ΔO.D. at 348, 385, and 510 nm (Figures 2 (2) and 2 (3)) show the decay of $An_2CH^\bullet$ and formation of $An_2CH^{\bullet *}$ and An_2CH^+, respectively, during 308- and 355-nm laser flash photolyses of An_2CHCl. $\Delta O.D._{348} = 0.005$, $\Delta O.D._{385} = 0.0035$, and $\Delta O.D._{510} = 0.025$ in Figure 2 (3) were much smaller than those in Figure 2 (2), indicating that formation yields of $An_2CH^\bullet$, $An_2CH^{\bullet *}$, and An_2CH^+ with the 355-nm excitation were much lower than those with the 308-nm excitation. This is due to lower photon numbers absorbed by An_2CHCl with the 355-nm excitation compared with the 308-nm excitation, because the excitation wavelength at 355 nm was at the longer wavelength edge of the absorption

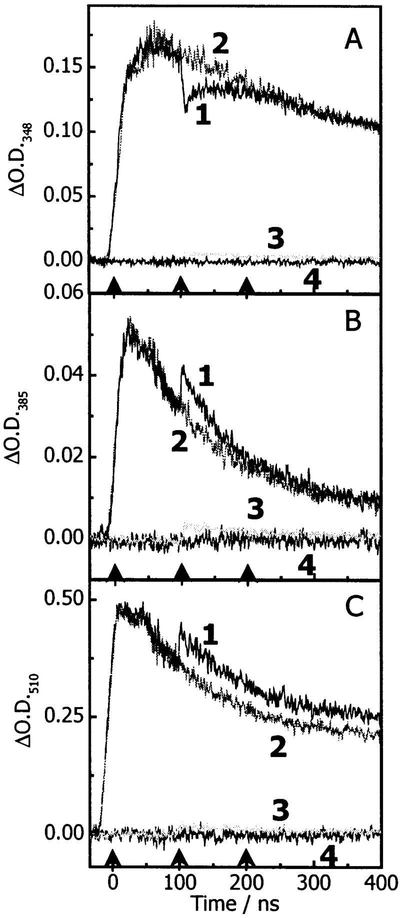

Figure 2. Time profiles of transient absorption at 348 (A), 385 (B), and 510 nm (C) assigned to $An_2CH^\bullet$, $An_2CH^{\bullet *}$, and An_2CH^+, respectively, during the three-color three-laser (first 308-, second 355-, and third 495-nm laser) photolysis of An_2CHCl (1), and one-laser photolysis at 308 nm (2), 355 nm (3), and 495 nm (4) in acetonitrile at room temperature. The delay times between the first and second lasers and between the second and third lasers were 100 ns. Three arrows show the timing of three laser flashes. No change was observed for the transient absorption with the third 495-nm laser excitation.

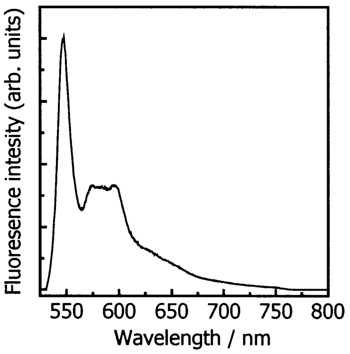

Figure 3. Transient fluorescence spectrum of $An_2CH^\bullet$ observed immediately after the second 355-nm laser flash and at 3 μs after the first 308-nm laser flash during the two-color two-laser photolysis of An_2CHCl in acetonitrile.

peak. No transient absorption was observed during 495-nm laser photolysis of An_2CHCl. Half-lifetimes of the decay of $An_2CH^\bullet$, $An_2CH^{\bullet *}$, and An_2CH^+ were 500, 110, and 260 ns, respectively. Although the decay rate constants of diphenylmethyl radical and cation have been reported by Bartl et al.,[24] no data are available for $An_2CH^\bullet$ and An_2CH^+. Only decay rate constant of $An_2CH^{\bullet *}$ has been found to be 5.8×10^6 s^{-1} from the transient absorption and fluorescence measurements of $An_2CH^{\bullet *}$,[26] which is in the same order of that calculated from the half-lifetime of 110 ns observed in the present study.

Two-Laser Photolysis. Figure 2 (A) (1) shows the time profile of $\Delta O.D._{348}$. The delay time of the second 355-nm laser flash was 100 ns after the first 308-nm laser irradiation. Formation of $An_2CH^\bullet$ occurred in the time scale shorter than a few tens of nanoseconds after the first 308-nm laser flash as described above. Bleaching of $An_2CH^\bullet$ ($\Delta\Delta O.\ D._{348} = 0.04$) and recovery of $An_2CH^\bullet$ were observed within a laser flash and in the time scale of 100 ns, respectively, after the second 355-nm laser excitation.

Figure 2 (B) (1) shows the time profile of $\Delta O.D._{385}$ assigned to $An_2CH^{\bullet *}$ which formed in the time scale shorter than a few tens of nanosecond after the first 308-nm laser irradiation. Formation of $An_2CH^{\bullet *}$ ($\Delta\Delta O.D._{385} = 0.009$) was also observed with excitation of the second 355-nm laser flash. After the formation of $\Delta O.D._{385}$ within the laser flash, $\Delta O.D._{385}$ decreased rapidly in the time scale of 100 ns and then decreased according to the time profile without the second 355-nm laser excitation. The rapid decay of $\Delta O.D._{385}$ was consistent with the recovery of $\Delta O.D._{348}$ (Figure 2 (A) (1)).

Figure 2 (C) (1) shows the time profile of $\Delta O.D._{510}$ assigned to An_2CH^+. Formation of $An_2CH^\bullet$ occurred in the time scale shorter than a few tens of nanoseconds after the first 308-nm laser flash, and formation of An_2CH^+ ($\Delta\Delta O.D._{510} = 0.061$) was observed with excitation of the second 355-nm laser flash. No change of the time profiles of ΔO.D. at 348, 380, and 510 nm was observed during the first 308- or 355-nm laser irradiation and the second 495-nm laser irradiation with the delay time of 200 or 100 ns, respectively.

These results were essentially similar to those reported by Faria and Steenken using the first 248-nm and second 308-nm lasers.[26] Since An_2CHCl in acetonitrile has the ground-state absorption at 308 nm and $An_2CH^\bullet$ has an absorption peak at 348 nm, both An_2CHCl and $An_2CH^\bullet$ can be excited with irradiation at 308 nm. Therefore, selective excitation of $An_2CH^\bullet$ can be performed with laser photolysis at 355 nm.

Three-Laser Photolysis. Figure 2 (1) shows the time profiles of ΔO.D. at 348, 380, and 510 nm. The delay times of the second 355-nm laser irradiation after the first 308-nm laser irradiation and of the third 495-nm laser irradiation after the second 355-nm laser irradiation were both 100 ns. The transient behaviors of $An_2CH^\bullet$, $An_2CH^{\bullet *}$, and An_2CH^+ were same as those during two-laser photochemistry with the first 308-nm and second 355-nm laser irradiation, since $An_2CH^\bullet$, $An_2CH^{\bullet *}$, and An_2CH^+ did not form during the third 495-nm laser irradiation.

2. Transient Fluorescence Measurements. Figure 3 shows the transient fluorescence spectrum with a peak at 550 nm and characteristic vibrational bands at the longer wavelength observed immediately after the second 355-nm laser flash and at 3 μs after the first 308-nm laser flash during the two-color two-laser photolysis of An_2CHCl in acetonitrile. The spectrum was assigned to the fluorescence of $An_2CH^{\bullet *}$.[27] Figure 4A shows the transient fluorescence spectra with a peak at 560 nm observed immediately after the third 495-nm laser irradiation, respectively, during the three-color three-laser photolysis of An_2CHCl in acetonitrile. The spectrum was assigned to the fluorescence of excited An_2CH^+ (An_2CH^{+*}) as described below. The lower intensity fluorescence spectrum drawn by dotted line (Figure 4A) was observed without the second 355-nm laser irradiation. The fluorescence intensity of An_2CH^+ increased approximately 1.2 times with the second 355-nm laser excitation

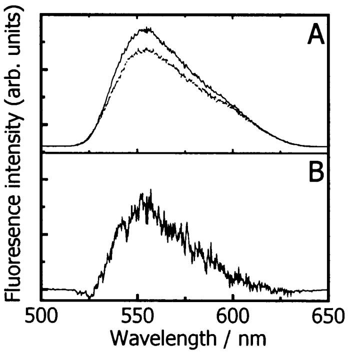

Figure 4. Transient fluorescence spectra for An_2CH^+ observed immediately after the third 495-nm laser flash during three-color three-laser photolysis of An_2CHCl in acetonitrile (solid line with higher intensity) (A). The dotted line with lower intensity was observed without the second 355-nm laser irradiation (A). The difference fluorescence spectrum (B) obtained from the solid line subtracted by the dotted line. The delay times between the first and second lasers and between the second and third lasers were both 3 μs.

of $An_2CH^{\bullet}$. Figure 4B shows a difference spectrum between two fluorescence spectra.

To assign the fluorescence of An_2CH^+, we examined γ-radiolysis of *n*-butyl chloride rigid matrix containing An_2CHCl at 5.0×10^{-3} M at 77 K where An_2CH^+ was generated from dissociation of chlorine atom from An_2CHCl radical cation. The absorption and fluorescence spectra of An_2CH^+ were observed with peaks at 510 and 530 nm, respectively, and were similar to those observed for An_2CH^+ in acetonitrile at room temperature in the present study. The fluorescence lifetime of An_2CH^{+*} in *n*-butyl chloride rigid matrix at 77 K was measured to be 4.2 ns by single photon counting method.

Discussion

It has been reported by Steenken et al. that homolytic and heterolytic cleavages of the C$-$Cl bond proceed to give $An_2CH^{\bullet}$ + chlorine atom ($Cl^{\bullet}$) and An_2CH^+ + chloride ion (Cl^-) during laser flash photolysis of An_2CHCl.[24] The formation of $An_2CH^{\bullet *}$ has been also found to occur through sequential excitation of $An_2CH^{\bullet}$ within a laser flash duration. We examined the 308-nm laser flash photolysis of An_2CHCl in acetonitrile and found essentially same results with formation of $An_2CH^{\bullet}$ ($[An_2CH^{\bullet}] = 3.4 \times 10^{-6}$ M, the absorption coefficient (ϵ) at 352 nm, $\epsilon_{352} = 4.7 \times 10^4\ M^{-1}\ cm^{-1}$),[24] $An_2CH^{\bullet *}$ ($[An_2CH^{\bullet *}] = 4.6 \times 10^{-6}$ M, $\epsilon_{385} = 3.2 \times 10^3\ M^{-1}\ cm^{-1}$) (see below), and An_2CH^+ ($[An_2CH^+] = 4.5 \times 10^{-6}$ M, $\epsilon_{507} = 1.1 \times 10^5\ M^{-1}\ cm^{-1}$)[24] in the ratio of 27:37:36 immediately after the 308-nm laser irradiation. The emission spectrum of $An_2CH^{\bullet *}$ with the characteristic structure around 550$-$700 nm was also observed during the laser photolysis. The numbers of 308-nm laser photons absorbed by An_2CHCl was calculated to be 3.7×10^{-5} Einstein L^{-1} from absorbance = 1.0 of the An_2CHCl solution at 308 nm with the path length of the laser beam (1.0 cm) in the sample solution using chemical actinometry of T$-$T absorption of the triplet benzophenone at 532 nm in benzene ($\epsilon_T = 6250\ M^{-1}\ cm^{-1}$).[28] Therefore, the formation quantum yields of $An_2CH^{\bullet}$, $An_2CH^{\bullet *}$, and An_2CH^+ were found to be 0.092, 0.12, and 0.12 from ΔO.D.$_{348}$, ΔO.D.$_{385}$, and ΔO. D.$_{510}$, respectively. Those values for $An_2CH^{\bullet}$ and An_2CH^+ have been reported by Steenken et al. to be 0.24 and 0.31, respectively, during 248-nm laser photolysis,[24] while that of $An_2CH^{\bullet *}$ has not been reported.

On the basis of the results, An_2CHCl is excited to An_2CHCl in the singlet excited state (An_2CHCl^*) with irradiation of a XeCl excimer laser at 308 nm ($h\nu_{308}$) (eq 1), An_2CHCl^* causes the homolytic and heterolytic cleavages of the C$-$Cl bond within a laser flash duration (30 ns) to give $An_2CH^{\bullet} + Cl^{\bullet}$ (eq 2) and $An_2CH^+ + Cl^-$ (eq 3), respectively, while $An_2CH^{\bullet *}$ forms subsequently from excitation of $An_2CH^{\bullet}$ within the laser flash duration (eq 4). From the formation quantum yields and formation of $An_2CH^{\bullet *}$ via two-photon excitation, An_2CHCl^* decomposes and deactivates in 45 and 55% yields, respectively. Generation of An_2CH^+ within the laser flash duration may be also explained by fast electron transfer between $An_2CH^{\bullet}$ and $Cl^{\bullet}$ in the contact radical pair (eq 5). We cannot distinguish two mechanisms of the formation of An_2CH^+, initial formation (eq 3) or stepwise formation (eqs 2 and 5), since the stepwise processes (eqs 2 and 5) must proceed within the laser flash duration of 30 ns. Direct and stepwise formation mechanisms of diphenylmethyl cations with or without substituents on the phenyl rings such as methyl, methoxyl, chloro, fluoro, and others have been discussed by Steenken et al. during 248-nm laser photolysis of the corresponding diphenylmethyl halides in several solvents.[24]

$$An_2CHCl + h\nu_{308} \rightarrow An_2CHCl^* \tag{1}$$

$$An_2CHCl^* \rightarrow An_2CH^{\bullet} + Cl^{\bullet} \tag{2}$$

$$An_2CHCl^* \rightarrow An_2CH^+ + Cl^- \tag{3}$$

$$An_2CH^{\bullet} + h\nu_{308} \rightarrow An_2CH^{\bullet *} \tag{4}$$

$$An_2CH^{\bullet}/Cl^{\bullet} \rightarrow An_2CH^+ + Cl^- \tag{5}$$

After the second 355-nm laser irradiation ($h\nu_{355}$), the transient absorption bands of $An_2CH^{\bullet *}$ and An_2CH^+ at 385 and 510 nm, respectively, increased, while the band of $An_2CH^{\bullet}$ at 348 nm was bleached. The increases of ΔO.D.$_{385}$ and ΔO.D.$_{510}$ and decrease of ΔO.D.$_{348}$ were found to be $\Delta\Delta$O.D.$_{385}$ = 0.0058, $\Delta\Delta$O.D.$_{510}$ = 0.046, and $\Delta\Delta$O.D.$_{348}$ = $-$0.045, respectively. The increase of An_2CH^+ concentration and decrease of $An_2CH^{\bullet}$ concentration were calculated to be $\Delta[An_2CH^+] = 4.0 \times 10^{-7}$ and $\Delta[An_2CH^{\bullet}] = -9.6 \times 10^{-7}$ M, respectively, using the ϵ values. The yield of An_2CH^+ was 42% from the excitation of $An_2CH^{\bullet}$ at 355 nm. Since formation of An_2CH^+ occurs through RETPI involving sequential two-step excitation as discussed later, it is reasonably assumed that $An_2CH^{\bullet *}$ is produced in the remaining 58% yield, $\Delta[An_2CH^{\bullet *}] = 5.6 \times 10^{-7}$ M. Thus, ϵ_{385} of $An_2CH^{\bullet *}$ was calculated to be $1.0 \times 10^4\ M^{-1}\ cm^{-1}$.

Since the increase of ΔO.D.$_{385}$ and bleach of ΔO.D.$_{348}$ occurred within a laser flash at 355 nm, $An_2CH^{\bullet}$ in the ground doublet state (D_0) is excited to $An_2CH^{\bullet *}$ in the excited doublet state (D_n, $n > 2$)[24,25,29] with the second 355-nm laser irradiation (eq 6). From the transient absorption peak at 385 nm and transient fluorescence peak at 550 nm assigned to $An_2CH^{\bullet *}$, the Stokes shift of $An_2CH^{\bullet}$ was found to be 165 nm. The $D_0 \rightarrow D_1$ absorption is a forbidden process similar to that for diphenylmethyl radical,[24,25,29] while the $D_0 \rightarrow D_n$ absorption and $D_0 \leftarrow D_1$ fluorescence are allowed processes with high transition probabilities. Therefore, the apparent large Stokes shift can be understood.

Thus, $An_2CH^{\bullet *}$ (D_n) decayed very fast to the lowest excited doublet state of $An_2CH^{\bullet *}$ (D_1) via nonradiative deactivation (eq 7) at the rate constant of approximately $10^{11}\ s^{-1}$ which was estimated from the energy gap of $An_2CH^{\bullet *}$ (D_n)-$An_2CH^{\bullet *}$ (D_1) according to the relationship between the energy gap of the singlet excited state (S_1) and ground state (S_0) and the rate constant of the internal conversion of $S_0 \leftarrow S_1$.[30,31] The recovery of the transient absorption of $An_2CH^\bullet$ (D_0) at 348 nm was consistent with the decay of $An_2CH^{\bullet}*$ (D_1) at 385 nm in the time scale of 100 ns. $An_2CH^{\bullet}*$ (D_1) decayed to $An_2CH^\bullet$ (D_0) with fluorescence (eq 8) or via nonradiative deactivation with a half-lifetime of 110 ns. $An_2CH^{\bullet}**$ ($D_{n'}$, $n' > 2$) was generated from excitation of $An_2CH^{\bullet}*$ (D_1) with the second 355-nm laser flash (eq 9). Since An_2CH^+ was generated during the second 355-nm laser irradiation, ionization of $An_2CH^{\bullet}**$ occurs to give An_2CH^+ (eq 10). The photon energy at 355 nm is 3.5 eV, and the oxidation potential of $Ph_2CH^\bullet$ is estimated to be 5.8 eV from ionization potential (I. P.) of 7.3 eV[32,33] and solvation energy of 1.5 eV for the solvated electron in acetonitrile. The oxidation potential of $An_2CH^\bullet$ must be lower than that for $Ph_2CH^\bullet$ because of the electron donating methoxyl groups. Therefore, RETPI of $An_2CH^\bullet$ with two-step excitation involving $An_2CH^{\bullet}*$ (D_1) and $An_2CH^{\bullet}**$ ($D_{n'}$) is energetically possible and occurs within a laser flash as shown in eq 10

$$An_2CH^\bullet\ (D_0) + h\nu_{355} \rightarrow An_2CH^{\bullet}*\ (D_n) \qquad (6)$$

$$An_2CH^{\bullet}*\ (D_n) \rightarrow An_2CH^{\bullet}*\ (D_1) \qquad (7)$$

$$An_2CH^{\bullet}*\ (D_1) \rightarrow An_2CH^\bullet\ (D_0) + h\nu_{f550} \qquad (8)$$

$$An_2CH^{\bullet}*\ (D_1) + h\nu_{355} \rightarrow An_2CH^{\bullet}**\ (D_{n'}) \qquad (9)$$

$$An_2CH^{\bullet}**\ (D_{n'}) \rightarrow An_2CH^+ + e_s^- \qquad (10)$$

The numbers of 355-nm laser photons absorbed by $An_2CH^\bullet$ was calculated to be 1.5×10^{-6} Einstein L^{-1} from $\Delta O.D._{355} = 0.16$ for $An_2CH^\bullet$ with the laser beam path (1.0 cm) using T−T absorption of triplet benzophenone.[34] Therefore, quantum yields of the bleaching of $An_2CH^\bullet$ (D_0) and formations of $An_2CH^{\bullet}*$ (D_1) and An_2CH^+ were found to be 0.62, 0.36, and 0.26 from $\Delta\Delta O.D._{348}$, $\Delta\Delta O.D._{385}$, and $\Delta\Delta O.D._{510}$, respectively. From the formation quantum yields and formation of An_2CH^+ via RETPI of $An_2CH^\bullet$, excitation of $An_2CH^\bullet$ generates $An_2CH^{\bullet}*$ and An_2CH^+ in 36 and 26% yields, respectively, and deactivates in 38% yield.

The concentrations of $An_2CH^\bullet$ (D_0), $An_2CH^{\bullet}*$ (D_1), and An_2CH^+ were 3.4×10^{-6}, 3.3×10^{-6}, and 3.4×10^{-6} M, respectively, with the ratio of 34:33:34 at 100 ns after 308-nm laser flash and just before the second 355-nm laser irradiation. The decreased concentration of $An_2CH^\bullet$ (D_0) and increased concentrations of $An_2CH^{\bullet}*$ (D_1) and An_2CH^+ were 9.6×10^{-7}, 5.6×10^{-7}, and 4.0×10^{-7} M in the ratio of 50:29:21, respectively, during the second 355-nm laser photolysis. Therefore, the concentrations of $An_2CH^\bullet$ (D_0), $An_2CH^{\bullet}*$ (D_1), and An_2CH^+ were 2.5×10^{-6}, 4.2×10^{-6}, and 3.9×10^{-6} M in the ratio of 24:40:37, respectively, immediately after the second 355-nm laser flash with the delay time of 100 ns after the first 308-nm laser flash. The ratio of concentrations of $An_2CH^\bullet$ (D_0): $An_2CH^{\bullet}*$ (D_1): An_2CH^+ changed from 34:33:34 to 24:40:37 during the second 355-nm laser flash photolysis. This indicates that excitation of $An_2CH^\bullet$ (D_0) gives $An_2CH^{\bullet}*$ (D_1) and An_2CH^+ in the ratio of 1.4:1.

The lifetime of $An_2CH^{\bullet}**$ ($D_{n'}$) has been reported to be in the femtosecond to picosecond range.[26] No change of the transient absorbance was observed during the third 495-nm laser photolysis ($h\nu_{495}$) of An_2CH^+ (eq 11), while the fluorescence of An_2CH^+ ($h\nu_{f560}$) was observed with a peak at 560 nm (eq 12). This result clearly demonstrates that $An_2CH^{+}*$ is generated with excitation of An_2CH^+ at 495 nm and that $An_2CH^{+}*$ emits fluorescence at 560 nm within a laser flash duration. This is consistent with the lifetime of 4.2 ns for $An_2CH^{+}*$ (see above).

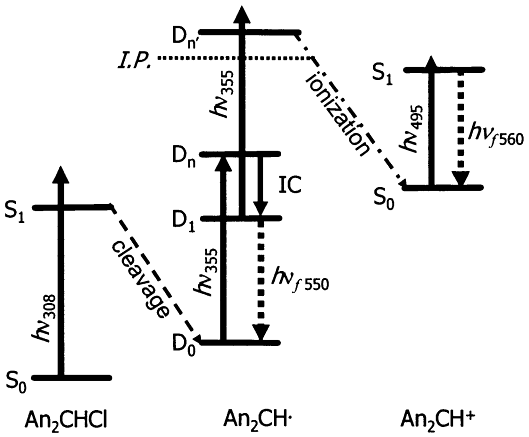

Figure 5. Energy diagram for three-color three-laser photochemistry of An_2CHCl in acetonitrile.

$$An_2CH^+ + h\nu_{495} \rightarrow An_2CH^{+}* \qquad (11)$$

$$An_2CH^{+}* \rightarrow An_2CH^+ + h\nu_{f560} \qquad (12)$$

On the basis of the experimental results, the energy diagram is suggested for the three-color three-laser photolysis of An_2CHCl (Figure 5). Since three intermediates of $An_2CH^\bullet$, $An_2CH^{\bullet}*$, and An_2CH^+ formed immediately after a laser flash, the homolytic and heterolytic cleavages to $An_2CH^\bullet + Cl^\bullet$ (eq 2) and $An_2CH^+ + Cl^-$ (eq 3), respectively, occurred together with sequential excitation of $An_2CH^\bullet$ to $An_2CH^{\bullet}*$. Electron transfer between $An_2CH^\bullet$ and $Cl^\bullet$ may be involved for the formation of An_2CH^+.

The concentration of An_2CH^+ was 3.4×10^{-6} M just before the second 355-nm laser flash, while that was 3.9×10^{-6} M immediately after the second 355-nm laser flash. Therefore, the ratio of the concentrations of An_2CH^+ before and after the second 355-nm laser flash was approximately 1:1.2.

The yield of An_2CH^+ from RETPI of $An_2CH^\bullet$ and fluorescence intensity of An_2CH^+ increased with the second 355-nm laser excitation of $An_2CH^\bullet$. The fluorescence intensity of An_2CH^+ increased approximately 1.2 times with the second 355-nm laser excitation of $An_2CH^\bullet$. Thus, fluorescence yield of An_2CH^+ was enhanced by the second 355-nm laser irradiation. The present study is the first example to control the intermediates and reaction pathways using the three-color three-laser photolysis in solution.

According to Scheme 1A−C, in the three-color three-laser photochemistry of An_2CHCl are An_2CHCl, $An_2CH^\bullet$, and An_2CH^+, respectively. The first laser ($h\nu_{308}$) excitation of An_2CHCl produces $An_2CH^\bullet$ through An_2CHCl*, the second laser ($h\nu_{355}$) excitation of $An_2CH^\bullet$ produces An_2CH^+ through RETPI of $An_2CH^\bullet$ involving $An_2CH^{\bullet}*$, and the third laser ($h\nu_{495}$) excitation of An_2CH^+ gives fluorescence of An_2CH^+. Control the intermediates and reaction pathways is accomplished in this reaction, although three intermediates of $An_2CH^\bullet$, $An_2CH^{\bullet}*$, and An_2CH^+ are generated during the first 308-nm laser excitation of An_2CHCl.

Characteristics of the multiccolor multilaser flash photolysis involving the three-color three-laser flash photolysis should be further discussed from the viewpoint of controlling the intermediates and reaction pathways. It is essentially impossible to activate selectively an intermediate and to cause a selective reaction of the intermediates in thermal chemistry and one-laser chemistry. However, selective activation of an intermediate can be easily accomplished by the molecule-selective and time-specific excitation during the multiccolor multilaser photolysis, as shown in the three-color three-laser photochemistry of An_2CHCl. We can point out possibilities of the multiccolor multilaser flash photolysis to generate new reactive intermediates, reactions, and chemical species at a given time during the reaction pathway, and to change a reaction pathway to other ones. In addition, spatial selectivity of lasers allows us to apply the multiccolor multilaser photolysis method to biological and material science and technology such as photodynamic therapy[35,36] and photopolymerization[37−39] which will be developed by time- and spatial-control of photochemical reactions with respect to the reactive intermediates.

Conclusions

The three-color three-laser chemistry in solution was demonstrated for the first time by the three-color three-laser flash photolysis of An_2CHCl in which the delay times of the second 355-nm laser irradiation after the first 308-nm laser irradiation and of the third 495-nm laser irradiation after the second 355-nm laser irradiation were both 100 ns. The first 308-nm laser excitation of An_2CHCl produced $An_2CH^\bullet$ through An_2CHCl^*, the second 355-nm laser excitation of $An_2CH^\bullet$ produced An_2CH^+ through RETPI of $An_2CH^\bullet$ involving $An_2CH^{\bullet *}$, and the third 495-nm laser excitation of An_2CH^+ gave fluorescence of An_2CH^+. The present work is the first example to control the intermediates and reaction pathways using the three-color three-laser photolysis method in solution.

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