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ARTICLES

Photoinduced Bond Dissociation of 4-Methylcoumarin Derivatives in Solution Studied by Laser Flash Photolysis and DFT Calculations

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Photochemical properties of 4-coumarinylmethyl derivatives (CM−X, X = Br, Cl, OH, OPh, SH, and SPh) in solution were studied by laser flash photolysis and DFT calculations. It was found that CM−Br and CM−SPh undergo photoinduced bond dissociation in the lowest excited singlet state, yielding the 4-coumarinylmethyl radical (CMR) and the corresponding radical with quantum yields of ∼0.25. Laser flash photolysis of CM−Cl, OH, OPh, and SH provided no or very little transient absorption of the corresponding triplet state. Upon triplet sensitization of CM−X using benzophenone (BP) as a triplet sensitizer, efficient formation of triplet CM−OH and −OPh was seen, whereas CM−SH and −SPh underwent the C−S bond cleavage in the lowest triplet (T_1) state, resulting in production of CMR and the corresponding radicals with efficiencies (α_{rad}) of ≥0.66. CM−Br and −Cl efficiently quenched triplet BP without formation of appreciable intermediates. On the basis of the results of laser flash photolysis and DFT calculations, photochemical features of triplet CM−X were discussed in detail.

Introduction

There are a large number of photochemical studies of bond dissociation taking place from aromatic carbonyl compounds in the excited states. Norrish type I and II reactions and carbon−heteroatom bond cleavage occurring at the α- and β-positions of aromatic carbonyl compounds have been widely studied by means of product analysis and time-resolved transient measurements.[1−4] The mechanisms of these photochemical reactions are closely related to the spin multiplicity and electronic structures of the corresponding reactive excited states. For instance, it is well-known that C−C bond dissociation upon type II photoelimination is initiated by biradical formation due to intramolecular H-abstraction of triplet n,π* carbonyls. Recently, we have been studying photoinduced bond dissociation occurring at positions other than α- and β-bonds in aromatic carbonyls (ω-bond cleavage).[5−10] The reactive excited state of the ω-bond has been characterized to be mainly the lowest

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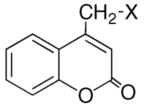
SCHEME 1: Structures of CM−X Used in the Present Study



CM-X ; X = Br, Cl, OH, OPh, SH and SPh

excited triplet (T_1) state, irrespective of the electronic character, n,π* or π,π*. The absence of bond cleavage in the excited singlet (S_1) states is interpreted in terms of the short lifetimes of the S_1 state due to the efficient intersystem crossing to the T_1 state according to the relationship between the n,π and π,π* character of excited singlet and triplet states (El-Sayed rule).

Coumarin and its derivatives have been subjected to photochemical and photophysical studies because of a wide range of applications, such as laser dyes and fluorescent labels as well as the molecular systems that constitute an important photosensitizer for both in vitro and in vivo systems.[11−13] A number of photophysical properties of coumarin and its derivatives have been studied by emission and EPR measurements.[14−21] It is established that the electronic configuration of the S_1 state of coumarin is of an n,π* type.[20] Because the energy of the S_2(π,π*) state is closely located in the vicinity of that of the S_1(n,π*) state, photoexcited coumarin is efficiently deactivated from the S_1 to the ground state via internal conversion induced by the proximity effect.[22,23] In fact, the triplet yield of coumarin is as small as 0.05 in acetonitrile solution.[24] (See also Supporting Information.) By adding substitution groups to the coumarin moiety, the electronic character of the S_1 state alters from n,π* to π,π*, resulting in the observation of fluorescence in the blue−green region that has been used as laser dyes[25] or fluorescent probes under various conditions.[26] It seems that the formation of triplet coumarins is not efficient. On the other hand, the [2+2]photodimerization reaction of coumarin and its derivatives has been extensively studied mainly by photoproduct analysis.[27−41] The reactive states for photodimerization were shown to be both excited singlet and triplet states, although they are readily affected by the various substituent group, substituent positions, and the environmental polarity of the media.[40] Conversely, in these two decades, several research groups have paid attention to photoinduced bond dissociation of coumarin derivatives, that is, 4-coumarinylmethyl ester derivatives.[42−62] These coumarins are promising caged compounds for photolabile protecting bioactivities as a result of photochemical reactions associated with the C−O bond dissociation. On the basis of fluorescence measurements of these coumarin derivatives, it is concluded that the C−O bond dissociates in the S_1 state due to the heterolytic cleavage of the C−O bond.[53,54,60,61] However, bond dissociation in the triplet state is still less convincing because of the small triplet yield.[44] The triplet sensitization technique using triplet energy transfer has been extensively used to study photophysical and photochemical properties of various triplet molecules when the molecules have low quantum yields of triplet formation. Acetone, acetophenone, or benzophenone (BP), whose triplet excitation energies (E_T) are ∼76, 74, or 69 kcal mol^{-1}, respectively, are typical triplet sensitizers.[63] Since the energy level of triplet coumarin is located at ∼62 kcal mol^{-1},[63] it is possible to efficiently produce triplet states of coumarins by using these triplet sensitizers, which allows investigation of the photochemical behaviors of triplet coumarins. To our best knowledge, there are no photochemical investigations of photoinduced bond cleavage in triplet coumarin derivatives. In the present study, we investigate photochemical properties of coumarin and 4-coumarinyl methyl derivatives (CM−X; see Scheme 1) in solution by using laser photolysis techniques and DFT calculations. Homolytic bond cleavage in the S_1 and T_1 states of some CM−X's is found, and the quantum yields are determined. The features of bond dissociation in the triplet state are discussed.

Experimental Section

Coumarin (CM) was purchased from Kishida. 4-Chloromethylcoumarin (CM−Cl) was synthesized according to the literature.[64] 4-Phenoxymethylcoumarin (CM−OPh) and 4-coumarinylmethyl phenyl sulfide (CM−SPh) were synthesized by the reaction of CM−Cl with phenol or thiophenol in the presence of K_2CO_3 in acetone, respectively. 4-Bromomethylcoumarin (CM−Br) was prepared by refluxing a benzene solution of CM−Cl in the presence of KBr. 4-Hydroxymethylcoumarin (CM−OH) was synthesized by refluxing a mixture of ethanol and hydrochloric acid (1:1, v/v) of 4-acetoxymethylcoumarin prepared by refluxing acetic anhydrous solution of CM−Cl in the presence of KBr and sodium acetate.[54] 4-Mercaptomethylcoumarin (CM−SH) was prepared by using ion-exchange resin IRA-400 from Aldrich in methanol with NaSH and CM−Cl.[65] Crude coumarin derivatives (CM−X) were passed through a silica gel column with a mixture of benzene and dichloromethane (5:1 v/v) and recrystallized from hexane for purification. The yields of the synthesized compounds were more than 10%. Acetonitrile (ACN) and ethanol were distilled for purification. Diethyl ether (spectroscopy grade, Kanto) and isopentane (spectroscopy grade, Fluka) were used as supplied. ACN was used as the solvent at 295 K, while a mixture of diethyl ether−isopentane−ethanol (EPA, 5:5:2 v/v/v) or ethanol was used as the matrix at 77 K. Absorption and emission spectra were recorded on a U-best 50 spectrophotometer (JASCO) and a Hitachi F-4010 fluorescence spectrophotometer, respectively. All of the samples for transient absorption measurements were prepared in the dark and degassed in a quartz cell with a 1 cm path length by several freeze−pump−thaw cycles on a high-vacuum line. The concentrations of coumarin and CM−X for direct laser photolysis were adjusted to achieve the optical density at the excitation wavelength (266 or 308 nm), being less than 1.0 in ACN. Transient absorption measurements were carried out at 295 K unless noted. A XeCl excimer laser (308 nm; Lambda Physik, Lextra 50) and the third (355 nm) and fourth harmonics (266 nm) of a Nd^{3+}:YAG laser (JK Lasers HY-500; pulse width 8 ns) were used as light sources for transient absorption. Less than five repeated pulses were used to avoid excess exposure. The details of the detection system for the time profiles of the transient absorption have been reported elsewhere.[66] The transient data obtained by laser flash photolysis were analyzed by using the least-squares best-fitting method. The transient absorption spectra were taken with a USP-554 system from Unisoku, with which one can provide a transient absorption spectrum with one laser pulse.

Time-resolved EPR measurements were carried out by using an X-band EPR spectrometer (Varian E-109E) without magnetic field modulation, as reported previously.[67] A XeCl excimer laser (Lambda Physik COMPex 102, 308 nm, 20 Hz) was used as a pulsed light source. Sample solutions for the CIDEP measurements were constantly deoxygenated by argon gas bubbling and flowed into a quartz cell in the EPR resonator.

Relaxed ground-state geometries for calculations of vertical excitation energies were optimized at the (u)B3LYP/6-31G* level, with single-point energies calculated at the (u)B3LYP/6-311++G** level. Calculations for triplet-state energies, electronic-state energy, and geometries were performed using density functional theory (DFT) and time-dependent DFT (TDDFT) with a Becke's style three-parameter hybrid exchange functional and Lee−Yang−Parr correlation functional (B3LYP).[68−70] Polarized valence triple-ζ basis

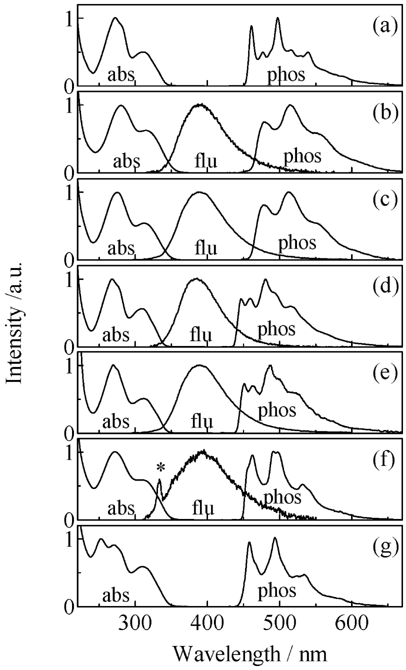


Figure 1. Absorption and fluorescence spectra in ACN at 295 K and phosphorescence spectra in ethanol at 77 K of coumarin (a), CM−Br (b), CM−Cl (c), CM−OH (d), CM−OPh (e), CM−SH (f), and CM−SPh (g). The asterisked fluorescence peak in (f) is due to the Raman scattering of the excitation light.

sets, 6-311G(d), were employed for the calculations. In calculation of the potential energy curves of the C−X bond cleavage, constrained geometry optimizations for the lowest triplet (T_1) states were performed at an unrestricted DFT level with a triplet spin multiplicity using the GAUSSIAN 03 program package.[71] All quantum chemical calculations were carried out on a lab-developed PC cluster system consisting of 32 Pentium IV CPUs (3.0∼3.4 GHz) or Itanium processors (Altix, SGI, 16 Itanium 1.8 GHz).

Results and Discussion

Absorption and Emission Measurements. Figure 1 shows absorption and fluorescence spectra of coumarin and CM−X in ACN at 295 K and phosphorescence spectra in a glass matrix of ethanol at 77 K.

It was confirmed that the emission excitation spectra agreed well with the corresponding absorption spectra. The shapes of the absorption spectra are similar to each other except for that of CM−SPh. It is reported that the electronic configuration of the lowest excited singlet (S_1) state of coumarin is n,π^*,[20] which results in the absence of fluorescence. On the other hand, very weak fluorescence ($\Phi_f < 10^{-3}$) was observed from all CM−X's except CM−SPh. These observations indicate that the electronic character of the S_1 state of CM−X is π,π^*. The shapes of the phosphorescence spectra are similar to each other. The electronic character of the lowest excited triplet (T_1) state of coumarin is shown to be π,π^* in nature.[14] From the similarity of the phosphorescence spectra, it is inferred that the electronic character of triplet CM−X's is also π,π^*. The energy levels, E_T of the triplet manifold of coumarin and CM−X were determined to be ∼60−63 kcal mol^{-1} from the phosphorescence origins. The determined E_T values are listed in Table 1.

Absorption and emission profiles were examined from the viewpoint of DFT calculations. Vertical excitation energies were calculated at the PBE1PBE/6-311++G** level from the computed relaxed ground states obtained at the B3LYP/3-31G* level. The results are supplied in Supporting Information. It is found that the computed electronic transitions are in very good agreement with the experimental ones. The error in energy is less than 5% for most of the compounds. Knowing that the experimental spectra were recorded in polar solvent, these results give confidence to the computational method. As with computed S_0−T_1 transitions energies, it can be seen that there is an excellent agreement between computed wavelengths and experimental maxima of phosphorescence, especially for CM−Br and −Cl. In the cases of CM−OH, −OPh, −SH, and −SPh, the experimental energy is higher than the computed one by about 2% only. From this agreement, it is inferred that the PBE1PBE function is reliable for computation of electronic energies of organic molecules. Therefore, there would be no

TABLE 1: Triplet Energies (E_T), Quantum Yields (Φ_{rad}) of the Radical Formation, Quenching Rate Constant (k_q) of Triplet BP, Efficiencies (α_{rad}) for Radical Formation in the Triplet State, Calculated Bond Dissociation Energies (BDE) of the C−X Bonds of CM−X, and Calculated Activation Energies (ΔE_a^{cal}) for C−X Bond Cleavage in the Triplet State Obtained in the Present Work[a]

X	E_T[b]/kcal mol^{-1}	Φ_{rad}	k_q/10^9 dm^3 mol^{-1} s^{-1}	α_{rad}	BDE(C−X)[c]/ kcal mol^{-1}	ΔE_a^{cal}/ kcal mol^{-1}
OH	64.0	∼0	6.3	∼0	81.6	*d*
Cl	59.8	∼0	7.6	*e*	62.7	*d*
SH	62.9	∼0	3.9	≥0.66	56.5	3.8
Br	59.7	0.24[f]	5.9	*e*	50.2	∼0
OPh	63.4	∼0	6.9	∼0	50.2	10.7
SPh	62.4	0.25[f]	6.5	≥0.67	43.9	1.9

[a] The E_T and k_q values of coumarin were, respectively, determined to be 62.0 kcal mol^{-1} and 8.6 × 10^9 dm^3 mol^{-1} s^{-1}. [b] Determined from the 0−0 origin of the phosphorescence spectra in ethanol at 77 K. [c] Estimated using eq 7. [d] Not calculated. [e] Not determined because the triplet states were not formed by triplet energy transfer. [f] Errors ± 0.04. See text for detail.

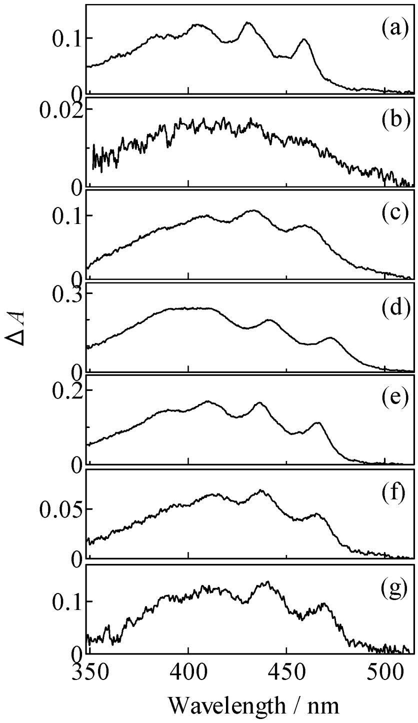


Figure 2. Transient absorption spectra obtained at 500 ns after 266 nm laser pulsing in EPA glass of coumarin (a), CM−Br (b), CM−Cl (c), CM−OH (d), CM−OPh (e), CM−SH (f), and CM−SPh (g) at 77 K.

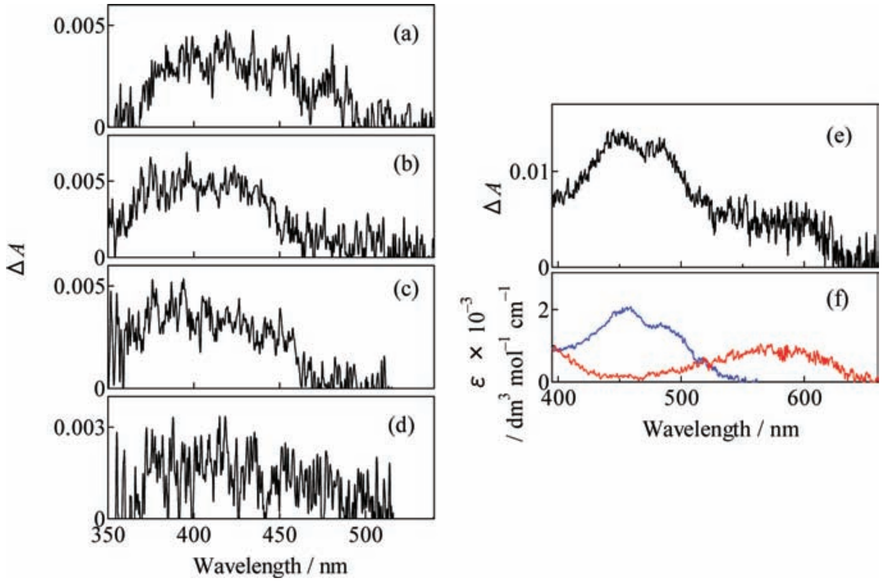


Figure 3. Transient absorption spectra obtained at 500 ns upon 308 nm laser pulsing in a degassed ACN solution of coumarin (a), CM−OPh (b), CM−OH (c), CM−Cl (d), and CM−SPh (e) at 295 K (solid). (f) Reference absorption spectra of the phenylthiyl radical (PTR, blue color) and 4-coumanylmethyl radical (CMR, red color).

important distortion of the molecule between the S_0-T_1 transition and the T_1-S_0 one. Inspection of the molecular orbital involved in each electronic transition allows the determination of the nature of the different electronic states. From the calculation results (data deposited in Supporting Information), it can be said that both the S_0-S_1 and S_0-T_1 transitions are of π,π^* nature for all CM−X's.

Photochemical Profiles of Coumarin and CM−X upon Direct Excitation. Figure 2 shows transient absorption spectra observed at 500 ns after 266 nm laser pulsing in EPA glass of coumarin and CM−X's at 77 K.

The transient absorption spectrum of coumarin, which is shown to be the triplet−triplet absorption,[24,72−74] is similar to those of the others. Therefore, the obtained absorption spectra for CM−X are due to the corresponding triplets. After depletion of the triplet absorption, no appreciable absorbance was seen in the wavelength region studied, 350−720 nm. From these observations, it is obvious that intersystem crossing in coumarin and CM−X is efficient in glass matrixes, and no photochemical reactions seem to occur at 77 K.

Figure 3a−d shows transient absorption spectra obtained upon 308 nm laser pulsing in an ACN solution of coumarin, CM−OPh, −OH, and −Cl at 295 K.

They can be assigned to be due to triplet coumarin and corresponding CM−X triplets. The intensities of the obtained absorption spectra of the triplet states are very weak, presumably because of the small triplet yields at room temperature (for instance, 0.048 and 0.091 for coumarin and CM−OPh in ACN, respectively; see Supporting Information). With CM−SH, no appreciable absorption spectra were seen in the transient absorption. The transient profile upon photolysis of CM−SH is provided in Supporting Information. It seems that internal conversion from the S_1 state to the ground state is predominant after photoexcitation of CM−SH. However, laser flash photolysis of CM−SPh in ACN provided an absorption spectrum having peaks around 450 and 580 nm, as shown in Figure 3e. This absorption spectrum can be reproduced using those of the phenylthiyl radical (PTR), having a molar absorption coefficient of $\varepsilon = 2000$ dm^3 mol^{-1} cm^{-1} at 450 nm,[75] and the 4-coumarinylmethyl radical (CMR; $\varepsilon = 900$ dm^3 mol^{-1} cm^{-1} at 580 nm determined in the present work) shown in Figure 3f. The successful reproduction of the transient absorption spectrum indicates that CM−SPh undergoes photoinduced C−S bond dissociation.

The quantum yield (Φ_{rad}) of the radical formation upon laser pulsing of CM−SPh was determined with the use of eq 1.

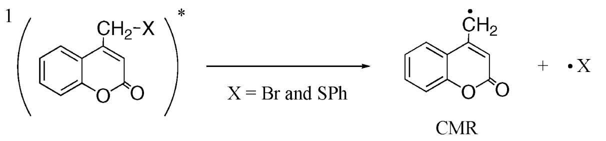
$$\Phi_{\text{rad}} = \Delta A_{450}\varepsilon_{450}{}^{-1}I_{\text{abs}}{}^{-1} \qquad (1)$$

where ΔA_{450}, ε_{450} and I_{abs} are, respectively, the absorption change at 450 nm due to radical formation at 100 ns after laser pulsing, the sum of the molar absorption coefficients of PTR and CMR at 450 nm (2100 dm^3 mol^{-1} cm^{-1}),[75] and the number of the photon flux of an incident laser pulse at the excitation wavelength. The quantity of I_{abs} was determined by using the absorption of triplet benzophenone (BP) in ACN as an actinometer.[76]

$$\Delta A_{\text{T}}^{\text{BP}} = \varepsilon_{\text{T}}^{\text{BP}}\Phi_{\text{ISC}}^{\text{BP}}I_{\text{abs}} \qquad (2)$$

where $\Delta A_{\text{T}}^{\text{BP}}$, $\varepsilon_{\text{T}}^{\text{BP}}$, and $\Phi_{\text{ISC}}^{\text{BP}}$ are, respectively, the initial absorbance at 520 nm for the formation of triplet benzophenone obtained immediately after laser pulsing, the molar absorption coefficient of triplet BP at 520 nm in ACN (6500 dm^3 mol^{-1} cm^{-1}),[77] and the triplet yield of BP (1.0).[63] By using eqs 1 and 2, the Φ_{rad} values were determined to be 0.26 ± 0.03 and 0.24 ± 0.02 upon 266 and 308 nm laser photolyses, respectively. This agreement in the Φ_{rad} values, within the errors, indicates that the C−S bond in CM−SPh cleaves in the lowest excited singlet or triplet manifold. With CM−Br, formation of CMR was observed, and the values of Φ_{rad} were determined to be 0.26 ± 0.03 and 0.24 ± 0.02 upon 266 and 308 nm laser photolyses, respectively, based on the absorbance at 580 nm for CMR formation and the molar absorption coefficient of CMR at 580 nm, $\varepsilon_{580} = 900$ dm^3 mol^{-1} cm^{-1}. The Φ_{rad} values for CM−SPh and −Br were not affected in the presence of the dissolved oxygen; the triplet state may not be involved in the bond dissociation upon direct excitation.

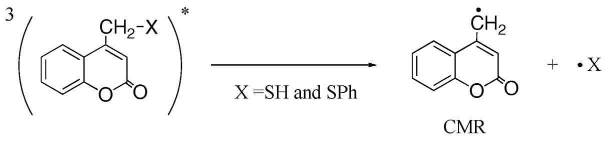
CIDEP measurements of photolytic CM−SPh provide further information on spin multiplicities of the dissociative state. The CIDEP signal was absent upon 308 nm laser photolysis of



CM−SPh in butyronitrile at room temperature. It is recognized from transient absorption measurements that PTR and CMR are generated upon photolysis of CM−SPh. We have reported that photolysis of *p*-benzoylbenzyl phenyl sulfide shows net emissive CIDEP signals because the C−S bond cleaves in the triplet state.[5] The absence of CIDEP signal from photoexcited CM−SPh suggests that the triplet manifold of CM−SPh is inefficient to the radical formation upon direct excitation. Considering that the $\Phi_{\rm rad}$ values are independent of the presence of the dissolved oxygen, it is plausible that the C−S bond dissociates in the $S_1(\pi,\pi^*)$ state of CM−SPh. The deactivation processes of the S_1 state of CM−SPh are governed by the efficient C−S bond rupture, which may hamper intersystem crossing from the S_1 to the triplet state at room temperature.

Laser Flash Triplet Sensitization of Coumarin and CM−X. In order to investigate photochemical profiles in the triplet states of coumarin and CM−X, triplet sensitization by using benzophenone (BP) was carried out by transient absorption measurements. Triplet energy transfer from triplet BP (E_T = 69.1 kcal mol^{-1})[63] to coumarin and CM−X (E_T = ~60−63 kcal mol^{-1}) possibly occurs. Figure 4 shows transient absorption spectra obtained upon 355 nm laser pulsing in BP/coumarin or BP/CM−X (X = OPh, SPh, and SH) systems in ACN.

With BP/coumarin and BP/CM−OPh systems, the intensity of transient absorption at 520 nm due to triplet BP decreases according to first kinetics with rates ($k_{\rm obsd}$) of 5.3 × 10^6 and 6.4 × 10^6 s^{-1} (see insets in Figure 4a and b, respectively). After depletion of triplet BP, absorption spectra of triplet coumarin and triplet CM−OPh were obtained. It was observed that the intensity of absorbance at 395 nm for triplet coumarin and triplet CM−OPh increases with the same rates of the corresponding decay of triplet BP. The formation of triplet coumarin and triplet CM−OPh upon BP sensitization indicates that triplet energy transfer from triplet BP efficiently produces triplet states of coumarin and CM−OPh. With a BP/CM−OH system, absorption of triplet CM−OH was also formed via triplet energy transfer from triplet BP (see Supporting Information). The absorption spectra of triplet CM−OPh and −OH disappeared in the microsecond time domain, giving no residual absorption in the studied wavelength region. On the other hand, after depletion of triplet BP, transient absorption spectra of PTR plus CMR for the BP/CM−SPh system and CMR for the BP/CM−SH system are obtained in the transient absorption (see Figure 4c and d, respectively). From the observations of the radical formation, it is obvious that CM−SPh and −SH undergo homolytic dissociation of the C−S bonds in the triplet manifold. With BP/CM−Br and −Cl systems, no appreciable intermediates were seen in transient absorption in the wavelength range of 370−680 nm, although quenching of triplet BP was unambiguously recognized, as mentioned later. (The transient profiles are provided in Supporting Information.)



The rates ($k_{\rm obsd}$) for the decay of triplet BP obtained in the studied systems are plotted as a function of the concentration, [Q], of coumarin or CM−X (X = OPh, SPh, and SH) as quenchers of triplet BP in Figure 5a.

Since plots give straight lines, the $k_{\rm obsd}$ can be formulated by

$$k_{\rm obsd} = k_0 + k_q[Q] \qquad (3)$$

where k_0 and k_q, respectively, represent the decay rate of triplet BP in the absence of Q and the rate constant for quenching of triplet BP by Q. From the intercept and the slope of the line, the values of k_0 (=2.0 × 10^5 s^{-1}) and k_q were determined. The k_q values are listed in Table 1 along with those of other CM−X (Cl, Br, and OH) determined by the same procedure.

Quantum yields ($\Phi_{\rm rad}^{\rm sens}$) of the radical formation upon triplet sensitization of CM−SPh and −SH were determined by eq 4.

$$\Phi_{\rm rad}^{\rm sens} = \Delta A_\lambda \varepsilon_\lambda^{-1} I_{\rm abs}^{\rm BP-1} \qquad (4)$$

where ΔA_λ, ε_λ and $I_{\rm abs}^{\rm BP}$ are, respectively, the maximum absorption change due to the formation of PTR plus CMR at 450 nm for the BP/CM−SPh system or of CMR at 580 m for the BP/CM−SH system, molar absorption coefficients of PTR plus CMR at 450 nm (2100 dm^3 mol^{-1} cm^{-1}) or of CMR at 580 nm (900 dm^3 mol^{-1} cm^{-1}), and the number of photon flux of an incident 355 nm laser pulse absorbed by BP. The value of $I_{\rm abs}^{\rm BP}$ at 355 nm was determined by using triplet−triplet absorption of benzophenone as an actinometer (see eq 2). The obtained values of $\Phi_{\rm rad}^{\rm sens}$ for the BP/CM−SPh and −SH systems are plotted as a function of [Q] in Figure 5b as well as the maximum absorbance, $\Delta A_{395}^{\max}$, of triplet coumarin or CM−OPh formed by triplet sensitization. On the other hand, $\Delta A_{395}^{\max}$ and $\Phi_{\rm rad}^{\rm sens}$ are related to the kinetic parameters, k_0 and k_q, by eqs 5 and 6.[5−10]

$$\Delta A_{395}^{\max} = \alpha_{\rm TET}\varepsilon_{395}^{\rm T-T}\Phi_{\rm ISC}^{\rm BP} I_{\rm abs}^{\rm BP} k_q[Q](k_0 + k_q[Q])^{-1} \qquad \text{Q for coumarin and CM−OPh} \qquad (5)$$

$$\Phi_{\rm rad}^{\rm sens} = \alpha_{\rm rad}\alpha_{\rm TET}\Phi_{\rm ISC}^{\rm BP} k_q[Q](k_0 + k_q[Q])^{-1} \qquad \text{Q for CM−SPh and CM−SH} \qquad (6)$$

where $\alpha_{\rm TET}$, $\alpha_{\rm rad}$, and $\Phi_{\rm ISC}^{\rm BP}$ are efficiencies for triplet energy transfer from triplet BP to Q, that for the radical formation in the triplet state of CM−SPh or −SH, and the triplet yield of BP (1.0),[63] respectively. By best-fitting eqs 5 and 6 to the experimental values of $\Delta A_{395}^{\max}$ and $\Phi_{\rm rad}^{\rm sens}$, respectively, with the use of the k_0 and k_q values obtained above, product values of $\alpha_{\rm TET}\varepsilon_{395}^{\rm T-T}$ for coumarin and CM−OPh were found to be 4600 ± 200 and 4400 ± 200 dm^3 mol^{-1} cm^{-1}, respectively, whereas those of $\alpha_{\rm rad}\alpha_{\rm TET}$ for CM−SPh and −SH were 0.67 ± 0.04 and 0.66 ± 0.04 dm^3 mol^{-1} cm^{-1}, respectively. Assuming that the $\alpha_{\rm TET}$ value is the same among coumarin and CM−X, the $\alpha_{\rm rad}$ values of CM−SPh and −SH are estimated to be ≥0.67 and ≥0.66, respectively, since the $\alpha_{\rm TET}$ value does not exceed unity. Conversely, since the $\alpha_{\rm rad}$ value does not exceed unity, the $\alpha_{\rm TET}$ value is not less than 0.67. From this consideration, it is inferred that the $\varepsilon_{395}^{\rm T-T}$ value of coumarin is estimated to be ≤6600 dm^3 mol^{-1} cm^{-1}. The estimated value of $\varepsilon_{395}^{\rm T-T}$ for coumarin is smaller than that reported previously (10000 dm^3 mol^{-1} cm^{-1}).[24]

On the basis of the obtained k_q values, quenching of triplet BP by CM−Br and −Cl was shown to proceed in a diffusion process, although sensitized intermediates were not observed in the transient absorption. Such a quenching process can be seen upon triplet sensitization of halomethyl compounds.[78] Because of the heavy atom effect, the triplet sensitizers may be deactivated to the ground state without transferring the triplet energy to the quenchers.

Dissociation Profiles of Triplet CM−X Based on DFT Calculations of the State Energy. Bond dissociation energies, BDE(C−X) of the C−X bonds in CM−X were obtained by eq

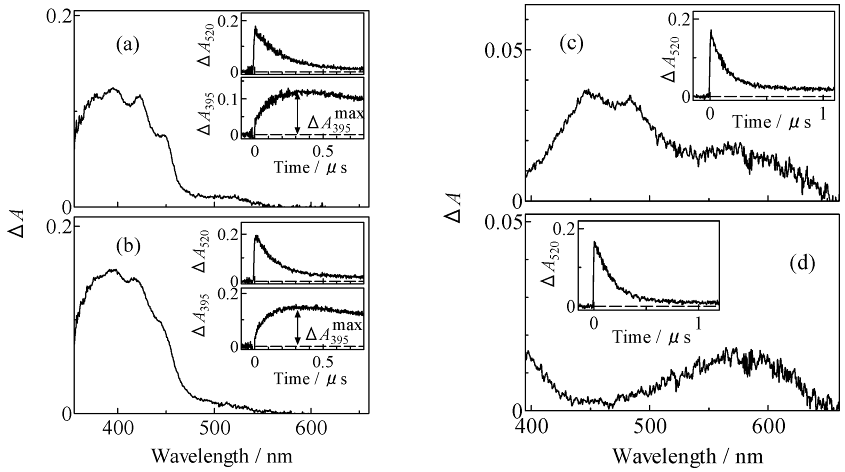


Figure 4. (a) A transient absorption spectrum obtained at 500 ns upon 355 nm laser photolysis of a BP (0.01 mol dm^{-3})/coumarin (6.0 × 10^{-4} mol dm^{-3}) system in ACN. Insets: temporal absorbance changes at 520 nm for triplet BP (upper) and that at 395 nm for triplet coumarin (lower). (b) A transient absorption spectrum obtained at 500 ms upon 355 nm laser photolysis of a BP (0.01 mol dm^{-3})/CM−OPh (9.0 × 10^{-4} mol dm^{-3}) system in ACN. Insets: temporal absorbance changes at 520 nm for triplet BP (upper) and that at 395 nm for triplet CM−OPh (lower). (c) A transient absorption spectrum obtained at 800 ns upon 355 nm laser photolysis of a BP (0.01 mol dm^{-3})/CM−SPh (9.5 × 10^{-4} mol dm^{-3}) system in ACN. Inset: a temporal absorbance change at 520 nm for triplet BP. (d) A transient absorption spectrum obtained at 800 ns upon 355 nm laser photolysis of a BP (0.01 mol dm^{-3})/CM−SH (14.4 × 10^{-4} mol dm^{-3}) system in ACN. Inset: a temporal absorbance change at 520 nm for triplet BP.

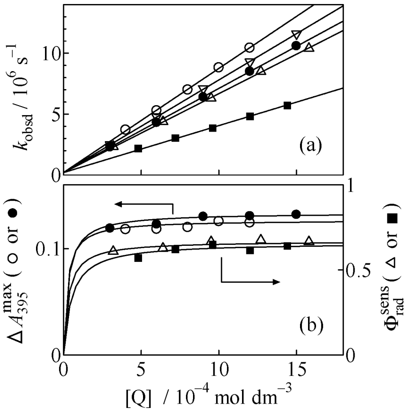


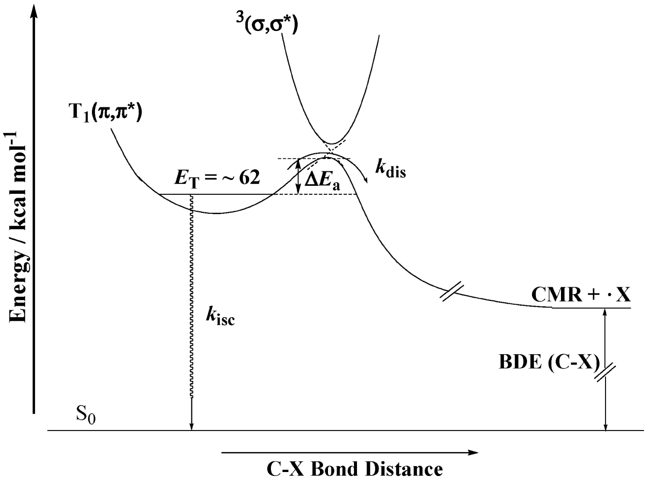
Figure 5. (a) Rates (k_{obsd}) for the decay of triplet BP plotted as a function of [Q] upon 355 nm laser photolysis in BP (7.0 × 10^{-3} mol dm^{-3})/coumarin (○), CM−OPh (●), CM−SPh (△), CM−SH (■), and CM−Cl (▽) systems in ACN at 295 K. (b) The maximum absorbance, ΔA_{395}^{max} at 395 nm due to formation of triplet CM (○) and CM−OPh (●) plotted as a function of [Q] obtained upon 355 nm laser photolysis in BP (0.01 mol dm^{-3})/CM and CM−OPh systems in ACN at 295 K, respectively, and quantum yields (Φ_{rad}^{sens}) for radical formation plotted as a function of [Q] obtained upon 355 nm laser photolysis in BP (0.01 mol dm^{-3})/CM−SPh (△) and CM−SH (■) systems in ACN at 295 K. The solid curves were calculated by eq 5 for ΔA_{395}^{max} and by eq 6 for Φ_{rad}^{sens}.

7 on the basis of the heat of formation ($\Delta_f H$) for CM−X, CMR, and X radical calculated at the DFT level.

$$\Delta_f H(\mathrm{CM{-}X}) = \Delta_f H(\mathrm{CMR}) + \Delta_f H(\mathrm{X}) - \mathrm{BDE(C{-}X)} \qquad (7)$$

The estimated BDE(C−X) values are listed in Table 1, while data of $\Delta_f H$ are shown in Supporting Information. Generally, for occurrence of bond dissociation in excited states, the state energy of the dissociative state is required to be equivalent or greater than the corresponding BDE. With CM−X's used in the present work, CM−OH and −Cl have larger BDEs than the corresponding triplet energies. In fact, we have found that dissociation of the C−OPh bond is absent in triplet CM−OPh although that of the C−Cl bond in triplet CM−Cl, unfortunately, could not be elucidated. In contrast, the other CM−X's (X = SH, Br, OPh, and SPh) definitely have the BDE values smaller than the corresponding E_T values (~62 kcal mol^{-1}). For this case, the dissociation mechanism of excited molecules is interpreted by considering a thermally activated crossing of the reactive excited state with dissociative potential curves that lead to free radicals (avoided crossing).[79] A schematic energy diagram for triplet CM−X is depicted in Scheme 2, including the C−X bond cleavage processes.

SCHEME 2: A Schematic Energy Diagram of Triplet CM−X Including the C−X Bond Cleavage Processes



It was originally suggested that radical cleavages of excited states proceed by avoided crossings between the states of the same overall symmetry. The potential dissociative surfaces for the present system are triplet π,σ* and σ,σ*. According to the avoided crossing rule, the electronic configuration of the dissociative potentials, which strongly interacts with the T$_1$(π,π*) state of CM−X, is σ,σ*. There would be an energy barrier, ΔE_a between the T$_1$(π,π*) and ^{3}(σ,σ*) potentials, and the C−X bond cleavage would proceed with a rate k_{dis} for the dissociation process. When the C−X bond dissociates in the triplet state of CM−X, a triplet σ-radical pair, ^{3}(CMR + X•)$_{cage}$ of CMR and X radical may be initially produced in a solvent cage according to the spin conservation rule. The triplet radical pair would escape from the solvent cage without geminate recombination

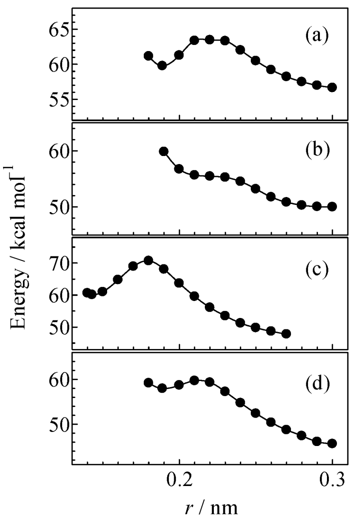


Figure 6. Potential energy curves of the triplet states of CM−SH (a), −Br (b), −OPh (c) and −SPh (d) calculated at the B3LYP/6-311G(d) level as a function of the distance r of the C−X bond.

since a rate of the intersystem crossing from triplet to singlet in the radical pair may be smaller than the rate of escaping. The electronic configuration of the σ-radical in CMR immediately after bond dissociation may convert to that of the π-radical due to stabilization accrued from π-delocalization in CMR. Consequently, the α_{rad} value should correspond to the intrinsic efficiency of the C−X bond rupture in the triplet manifold. The residual efficiency, $1 - \alpha_{\mathrm{rad}}$, should be due to intersystem crossing from the T_1 to the ground state with a rate of k_{isc}. Therefore, the efficiency α_{rad} for C−X bond cleavage is expressed by eq 8 with the use of k_{dis} and k_{isc}.

$$\alpha_{\mathrm{rad}} = k_{\mathrm{dis}}(k_{\mathrm{dis}} + k_{\mathrm{isc}})^{-1} \qquad (8)$$

On the basis of the results that triplet-sensitized CM−OPh, where no C−O bond cleavage is found, deactivates in the microsecond time domain, the magnitude of k_{isc} would be as large as 10^5 s^{-1}. We have estimated the α_{rad} values for CM−SH and −SPh to be larger than ~0.66. Therefore, the corresponding k_{dis} values can be equivalent to ~10^5 s^{-1} or more than 10^5 s^{-1}. Considering that triplet CM−SH undergoes the bond cleavage although the BDE of CM−SH (56.5 kcal mol^{-1}) is larger than that (50.2 kcal mol^{-1}) of CM−OPh, where no bond dissociation occurs, it seems that the BDE value is not closely related to the reactivity toward the C−X bond dissociation in triplet CM−X, whose BDE value is smaller than the corresponding triplet energy.

To examine the relationship between the reactivity of bond dissociation in triplet CM−X and the ΔE_{a} value, we performed DFT calculations of the state energy of triplet CM−X's. Figure 6 shows the states energies of triplet PB−X's estimated by DFT calculations plotted as a function of the bond distance r between carbon and the X atom of the C−X bond.

The activation energy $\Delta E_{\mathrm{a}}^{\mathrm{cal}}$ for homolytic dissociation of the C−X bond in the triplet state was obtained from the difference between the calculated maximum state energy, $E_{\mathrm{T\,max}}^{\mathrm{cal}}$, of the triplet and the calculated triplet energy, $E_{\mathrm{T}}^{\mathrm{cal}}$.

$$\Delta E_{\mathrm{a}}^{\mathrm{cal}} = E_{\mathrm{T\,max}}^{\mathrm{cal}} - E_{\mathrm{T}}^{\mathrm{cal}} \qquad (9)$$

The estimated $\Delta E_{\mathrm{a}}^{\mathrm{cal}}$ values are listed in Table 1, whereas the $E_{\mathrm{T\,max}}^{\mathrm{cal}}$ and $E_{\mathrm{T}}^{\mathrm{cal}}$ are noted in Supporting Information. With CM−SH and −SPh, where the C−S bond is cleavable in the triplet manifold, there seems to be a correlation between the BDE(C−S) and the $\Delta E_{\mathrm{a}}^{\mathrm{cal}}$ values. That is, with a decrease of the BDE(C−S), the $\Delta E_{\mathrm{a}}^{\mathrm{cal}}$ decreases. In contrast, the $\Delta E_{\mathrm{a}}^{\mathrm{cal}}$ value of CM−OPh, having no fragmentation in the triplet state, is 3−5 times greater than those of CM−SH and −SPh. The threshold value of $\Delta E_{\mathrm{a}}^{\mathrm{cal}}$ for the C−X bond cleavage in triplet CM−X would be located between 4 and 10 kcal mol^{-1}. As for the calculations for the state energy of triplet CM−Br, the triplet energy was not definite and decreased with an increase of the C−Br distance. From this result, it is inferred that the C−Br bond in triplet CM−Br is dissociative in nature, although it was impossible to rationalize this feature experimentally.

Conclusion

Photophysical and photochemical profiles of CM−X's were investigated by means of emission measurements, laser photolysis techniques, and DFT calculations. The electronic character of the S_1 state of CM−X is of a π,π^* type, and the intersystem crossing to the T_1 state is not efficient at room temperature (for example, $\Phi_{\mathrm{isc}} = 0.09$ for CM−OPh). However, phosphorescence spectra and the triplet−triplet absorption spectra of CM−X are clearly seen in a rigid matrix at 77 K. Laser flash photolysis of CM−X at room temperature reveals that (1) CM−SPh and −Br undergo photoinduced homolytic cleavage of the corresponding C−X bond with the quantum yields of ~0.25 in the S_1 state, (2) no transient signals is observed for CM−SH, and (3) triplet absorption with very weak intensity is seen for other CM−X's. It is difficult to elucidate the photochemical reactions of these triplet states formed via the S_1 state upon direct photoexcitation of CM−X. Triplet sensitization using benzophenone (BP) as a sensitizer is an efficient procedure to form triplet CM−X's. With coumarin, CM−OPh, and CM−OH, absorption spectra of the corresponding triplet state were obtained. The molar absorption coefficient of triplet coumarin was estimated to be ≤6600 dm^3 mol^{-1} cm^{-1} at 395 nm, which is smaller than the value reported previously.[24] No photochemical reactions from the triplet states of CM−OH and −OPh were found. Conversely, a photochemical process of homolytic bond cleavage in triplet states of coumarin derivatives was found in the present work for the first time. With CM−SH and −SPh, the formation of the corresponding radicals due to the C−S bond rupture was observed. The efficiency of the C−S bond dissociation was estimated to be more than ~0.66. Unfortunately, the formation of triplet CM−Br and −Cl by triplet sensitization was unsuccessful because the triplet sensitizer was efficiently quenched by the 4-halomethylcoumarines. On the basis of DFT calculations of the triplet-state energy of CM−X's, it can be said that for occurrence of the C−X bond cleavage in the triplet state of CM−X, the corresponding BDE smaller than the triplet energy is necessary, but not sufficient, and that the chemical reactivity toward the C−X bond dissociation in the triplet state of CM−X depends on the E_{a} values rather than the BDE(C−X).

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Supporting Information Available: The absorption spectrum of CM−SPh, data of optoacoustic measurements for determining the Φ_{isc} values, transient profiles upon direct excitation of CM−OH, −SH, and −Br and upon triplet sensitization of CM−Br and −Cl, and DFT calculation results. This material is available free of charge via the Internet at http://pubs.acs.org.

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