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Remarkable Reactivities of the Xanthone Ketyl Radical in the Excited State Compared with That in the Ground State

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The properties and reactivities of the xanthone (Xn) ketyl radical (XnH•) in the doublet excited state (XnH•(D_1)) were examined by using two-color two-laser flash photolysis. The absorption and fluorescence of XnH•(D_1) were observed for the first time. Several factors governing the deactivation processes of XnH•(D_1) such as interaction and reaction with solvent molecules were discussed. The remarkable change of reactivity of XnH•(D_1) compared with that in the ground state (XnH•(D_0)) was indicated from the experimental results. The rapid halogen abstraction of XnH•(D_1) from some halogen donors such as carbon tetrachloride (CCl_4) was found to occur. The halogen abstraction occurred more efficiently in the polar solvents than in the nonpolar solvents. It is suggested that the polar solvents promote the spin distribution of XnH•(D_1) of the phenyl ring favorable to the halogen abstraction.

Introduction

Radicals play important roles in various processes from the viewpoints of physics, chemistry, and biology.[1−3] Reactions of radicals are of interest in a variety of practical applications such as thin-layer synthesis, radical polymerization, and photodynamic therapy.[3a,c−g] The reactivity of radicals in the excited state is also an interesting subject. When radicals in the ground state are excited with photoirradiation within the lifetimes, those in the excited state are generated. A considerable number of studies of the excited radicals have been carried out with absorption and fluorescence spectroscopic measurements to elucidate the electronic structures and chemical properties in the condensed phase.[2,4−10] It has been reported that the reactivities of radicals in the ground states are different from those in the excited state for a limited numbers of radicals.[2,5−10] For example, some arylmethyl and stable aryl-substituted allyl radicals in the excited state abstract a halogen atom from the halogen-donating molecules, while those in the ground state are inert toward halogen donor molecules.[8c,9e−g] Furthermore, unimolecular bond cleavage[5,6] and cyclization,[8] bimolecular electron transfer,[9] hydrogen abstraction,[8c,10] and cross-coupling reactions[7] occur for several radicals in the excited states, although only inefficient or no reaction occurs for those in the ground state. For the xanthone ketyl radical (XnH•), it has been predicted that the reactivity of XnH• in the lowest doublet excited state (XnH•(D_1)) is different from that of XnH• in the doublet ground state on the basis of the laser-jet experiments.[2,7] However, there is no report on the fluorescence and absorption properties of XnH•(D_1) due to its quite short lifetime. There is also no investigation for the unimolecular and bimolecular reactivity of XnH•(D_1) in the condensed phase.

Nanosecond−picosecond two-color two-laser flash photolysis is a powerful method for detecting short-lived transient species such as higher triplet excited states and excited radicals which can be generated by the excitation of the lowest triplet excited state and ground state radicals, respectively.[4i,11] In the previous work, we have successfully detected the absorption and fluorescence of a series of ketyl radicals of benzophenone derivatives in the excited state directly using nanosecond−picosecond two-color two-laser flash photolysis.[4i] The absorption spectra and lifetimes of benzophenone ketyl radicals in the excited state were significantly affected by the number and electronic character of substituents of the phenyl ring.

In the present work, we applied nanosecond−picosecond two-color two-laser flash photolysis to detect the time-resolved transient absorption and fluorescence spectra of XnH•(D_1) in various solvents. To the best of our knowledge, this is the first report on the transient absorption and fluorescence spectra of XnH•(D_1). It is revealed that the reactivities of XnH• were significantly changed between the D_1 and D_0 states. Several factors governing the deactivation processes of XnH•(D_1) such as interaction and reaction with solvent molecules will be discussed. Furthermore, it is clarified that XnH•(D_1) is reactive toward carbon tetrachloride (CCl_4) and 1,1,1-trichloroethane ($C_2H_3Cl_3$), resulting in halogen abstraction of XnH•(D_1) from CCl_4 and $C_2H_3Cl_3$.

Experimental Section

The two-color two-laser flash photolysis experiment was carried out using the fourth harmonic (266 nm) or third harmonic (355 nm) oscillation of a nanosecond Nd^{3+}:YAG laser (Quantel, Brilliant; 5 ns fwhm) as the first laser and the second harmonic (532 nm) oscillation of a picosecond Nd^{3+}:YAG laser (Continuum, RGA69-10 LD; 30 ps fwhm, 10 Hz) as the second laser. The delay time of the two laser flashes was adjusted to 1 μs by four channel digital delay/pulse generators (Stanford Research Systems, model DG 535). The breakdown of Xe gas generated by the fundamental pulse of the picosecond Nd^{3+}:YAG laser was used as a probe light. Transient absorption and fluorescence spectra and kinetic traces were measured using a streak camera (Hamamatsu Photonics, C7700) equipped with a CCD camera (Hamamatsu Photonics, C4742-98) and were stored on a PC. To avoid stray light and pyrolysis of the sample by the probe light, suitable filters were employed. The samples were flowed

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in a transparent rectangular quartz cell ($1.0 \times 0.5 \times 2.0$ cm^3) at room temperature.

Xn was recrystallized from ethanol before use. Sample solutions were deoxygenated by bubbling Ar gas for 30 min before irradiation.

Results and Discussion

Generation of XnH•(D$_0$). XnH• was generated by the photoreduction of Xn. Upon the first 266- or 355-nm nanosecond-laser irradiation, generated xanthone in the triplet excited state (Xn(T$_1$)) decayed through hydrogen abstraction from a hydrogen-donating solvent to produce XnH• in the doublet ground state (XnH•(D$_0$)) (eq 1).[12]

$$\mathrm{Xn} \xrightarrow[h\nu_{266\text{ or }355}]{} \mathrm{Xn(T_1)} \xrightarrow[\text{hydrogen abstraction}]{} \mathrm{XnH\bullet(D_0)} \qquad (1)$$

The absorption spectra of XnH•(D$_0$) in various solvents are shown in Figure 1. The spectrum of XnH•(D$_0$) in cyclohexane which has peaks at 344, 391, 484, 565, and 611 nm was well consistent with the reported one.[12b] The absorption spectrum of XnH•(D$_0$) changed significantly depending on the solvent. The peak positions of XnH•(D$_0$) (λ_a^{max}) are summarized in Table 1, together with the relative intensities (RIs) of the absorption peak around 610 nm for that at 480 nm in various solvents (RI $= \Delta OD_{610}/\Delta OD_{480}$). The RI values dramatically increased in polar solvents such as 2-propanol and acetonitrile (containing 1% cyclohexane). This apparent difference in absorption spectra is ascribed to the change of character of XnH•(D$_0$) depending on the solvent polarity.

Fluorescence Spectra and Lifetime of XnH•(D$_1$). The generated ketyl radical was excited at the visible absorption band using the second laser (532 nm, 15 mJ/pulse, 30 ps fwhm) with a delay time of 1 μs after the first laser (eq 2).

$$\mathrm{XnH\bullet(D_0)} \xrightarrow[h\nu_{532}]{} \mathrm{XnH\bullet(D_1)} \qquad (2)$$

Upon the excitation, XnH• showed the fluorescence corresponding to the D$_1$ → D$_0$ transition. The fluorescence spectrum of XnH•(D$_1$) was almost a mirror image of the absorption spectrum in each solvent (Figure 1). The fluorescence from XnH• in the excited state (XnH•(D$_1$)) in various solvents was observed for the first time. The fluorescence spectrum of XnH•(D$_1$) exhibited a red shift with an increase of the solvent polarity. In toluene and 2-propanol, XnH•(D$_1$) showed a larger Stokes shift (υ_{ss}) than others. The fluorescence maximum of XnH• (λ_f^{max}) and observed υ_{ss} values in various solvents are listed in Table 1. The change of fluorescence properties can be attributed to (1) dipole−dipole interaction between solvent and solute molecules or (2) specific solvent−solute interaction such as the formation of hydrogen bonding. To have a better understanding of XnH•(D$_1$) in the excited state, the observed υ_{ss} was plotted against the Dimroth $E_T(30)$ parameter.[13] However, υ_{ss} values of XnH• did not show a linear correlation with the $E_T(30)$ parameter.[13] Since the linearity of this plot suggests the dipole−dipole interaction between solvent and solute molecules, dipole−dipole interaction between solvent and XnH•(D$_1$) can be negligible. The larger υ_{ss} value of XnH• in toluene can be attributed to the π−π interaction with toluene, as suggested by Scaiano et al.[12a] For 2-propanol, its strong hydrogen-bonding ability should be responsible for the larger υ_{ss}.[13] Thus, the solvent-dependent υ_{ss} of XnH• can be attributed to the specific solvent−solute interactions, that is, π−π interaction with toluene and the formation of hydrogen bonding with 2-propanol.

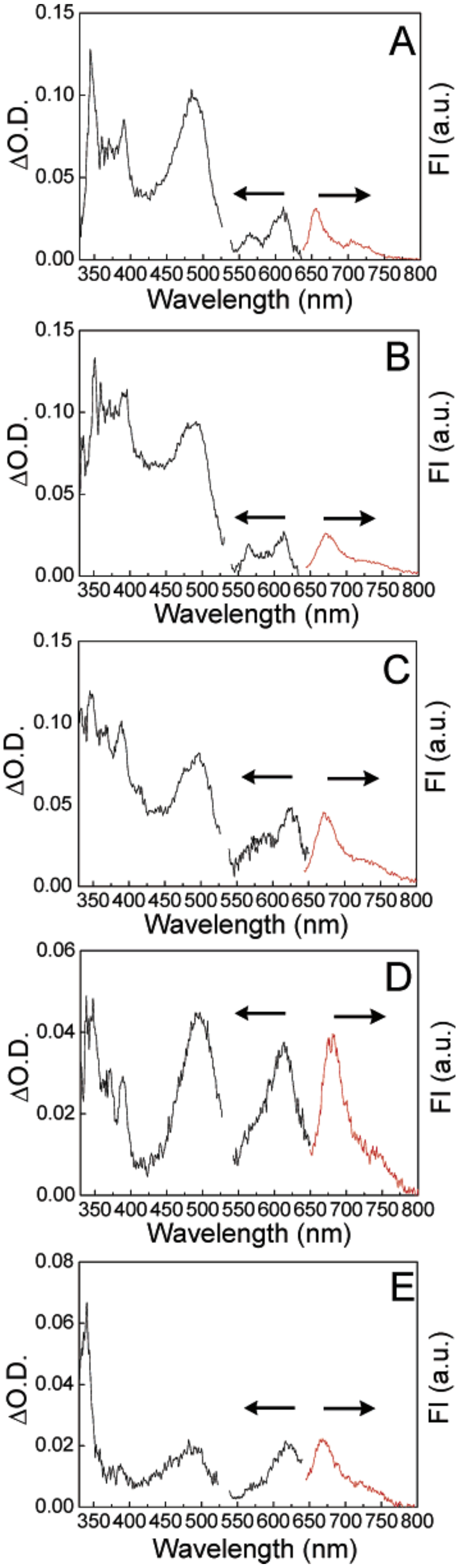


Figure 1. Absorption (black line) spectra of XnH• obtained following the first 266- (A, D, and E) or 355-nm (B and C) preparation pulse and fluorescence (red line) spectra obtained 0.1 ns after the second 532-nm excitation pulse two-color two-laser flash photolysis in Ar-saturated solvents at room temperature: (A) cyclohexane; (B) toluene; (C) 2-methyltetrahydrofurane; (D) 2-propanol; (E) acetonitrile (containing 1% cyclohexane). The blank around 532 nm in the spectra was due to the residual SHG of the Nd^{3+}:YAG laser.

The energy gaps between the D$_1$ and D$_0$ states of XnH• (ΔE(D$_1$ − D$_0$)) in various solvents were determined from the fluorescence maxima (Table 1). The ΔE(D$_1$ − D$_0$) values of

TABLE 1: Spectroscopic Data for XnH• in Various Solvents

compound	solvent	λ_a^{max} (nm)	RI[a]	λ_f^{max} (nm)	ν_{ss} (10^3 cm^{-1})
xanthone	cyclohexane	344, 391, 484, 565, 611	0.28	656	1.1
	toluene	351,[b] 396, 490, 564, 613	0.27	671	1.4
	MTHF	345,[b] 390, 497, 591, 627	0.59	671	1.0
	2-propanol	338, 389, 496, 613	0.87	681	1.6
	acetonitrile[c]	341, 387, 482, 617	1.2	668	1.2

[a] Relative intensity of the absorption peak around 610 nm for that at 480 nm. [b] The values were not clearly determined due to the interference of the ground state absorption. [c] Containing 1% cyclohexane.

TABLE 2: Dielectric Constants of the Solvents (ϵ), Lifetimes of Transient Absorption (τ_0) and Fluorescence (τ_r), Rate Constants of the Chemical Reaction (k_C), Rate Constants of Radiative (k_r) and Nonradiative (k_{nr}) Relaxation Processes, and Energy Gaps between XnH•(D$_0$) and XnH•(D$_1$)

solvent	ϵ	τ_0 (ns)	τ_r (ns)	k_C (10^8 s^{-1})	$k_r + k_{nr}$ (10^8 s^{-1})	ΔE(D$_1$ − D$_0$) (eV)
cyclohexane	2.0	0.36 ± 0.02	0.35 ± 0.02	0.72 ± 0.02	2.1 ± 0.1	1.88
toluene	2.4	0.29 ± 0.01	0.30 ± 0.01	2.0	1.4	1.85
MTHF	7.0	0.21 ± 0.02	0.25 ± 0.02	0.27 ± 0.01	3.7 ± 0.2	1.85
2-propanol	20	0.17 ± 0.03	0.18 ± 0.02	0.19 ± 0.01	5.4 ± 0.3	1.82
acetonitrile[a]	36	0.23 ± 0.02	0.26 ± 0.02	1.2 ± 0.1	2.6 ± 0.1	1.86

[a] Containing 1% cyclohexane.

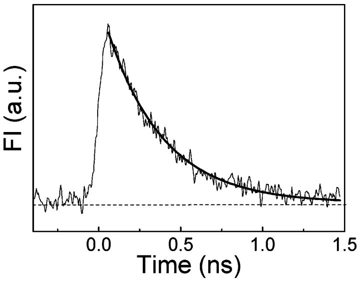


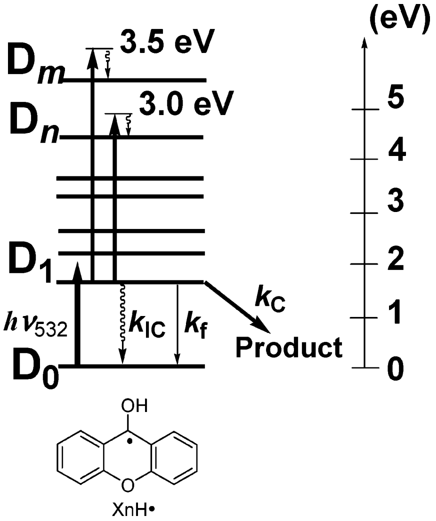
Figure 2. Kinetic trace of the fluorescence intensity of XnH• at 672 nm during the two-color two-laser photolysis. The solid line is the best fit obtained by the calculations based on the first-order kinetics.

XnH•(D$_1$) slightly decreased with increasing solvent polarity, indicating the stabilization of the D$_1$ state and/or destabilization of the D$_0$ state in polar solvents.

The fluorescence lifetimes (τ_r) of XnH•(D$_1$) in various solvents were measured at the peak position of the fluorescence spectrum. All fluorescence decay curves were fitted well with the single-exponential decay function (Figure 2). XnH•(D$_1$) showed the relatively longer τ_r in nonpolar solvents. The fluorescence properties of XnH•(D$_1$) such as lifetime and ΔE(D$_1$ − D$_0$) are summarized in Table 2. It is noteworthy that XnH•(D$_1$) showed shorter τ_r in 2-propanol than those in other solvents.

Absorption Spectrum and Lifetime of XnH•(D$_1$). Immediately after the second laser irradiation of XnH•(D$_0$), new transient absorption peaks appeared at around 350 and 430 nm (Figure 3A). The spectral shape of the new transient species was given by subtracting the spectrum observed during one-laser photolysis from that observed at 0.2 ns after the irradiation during the two-color two-laser photolysis (Figure 3B). The decay lifetimes (τ_0) at the two absorption peaks at 350 and 430 nm were similar to each other, suggesting that two absorption bands originated from a single transient species. The τ_0 value estimated from the absorption decay (Figure 3C) was essentially the same as the τ_r value estimated from the fluorescence decay. Thus, these transient absorption bands were attributed to the D$_n$ ← D$_1$ transition (Scheme 1). The transient absorption spectrum of XnH•(D$_1$) exhibited two absorption peaks, from which transition energies from the D$_1$ state to two higher doublet excited states (D$_m$ and D$_n$) were estimated to be 3.5 and 3.0 eV, respectively. The transient absorption spectrum of XnH•(D$_1$) was obtained in each solvent (Figure 4). The absorption peak of XnH•(D$_1$) in the visible region was red-shifted and broadened with increasing solvent polarity.

SCHEME 1: Energy Level Diagram of XnH• in the Ground and Excited States and Transient Processes in Cyclohexane



Upon excitation with the second laser, bleaching and recovery of XnH•(D$_0$) were observed (Figure 5). It is noteworthy that the ratio of bleaching and recovery of XnH•(D$_0$) was significantly affected by the solvent properties. The incomplete recovery of XnH•(D$_0$) after the second laser irradiation indicates that the irreversible processes, such as chemical reaction with the solvent molecule and unimolecular bond cleavage, occurred from XnH• in the excited doublet states. As an example of irreversible processes of XnH•(D$_1$), the head-to-tail cross-coupling reaction with 2-propanol (Scheme 2) has been reported from the results of the laser-jet experiment.[7] For the benzophenone ketyl radical in the excited state, the intermolecular reaction with the solvent molecules and the unimolecular cleavage of the O−H ketyl bond yielding benzophenone and a hydrogen atom have been reported.[6] Thus, the decay of XnH•(D$_1$) should include a chemical reaction, internal conversion, and radiative transition processes (Scheme 1). The τ_0 value can be expressed as shown in eq 3

$$\tau_0 = \frac{1}{k_C + k_r + k_{nr}} \tag{3}$$

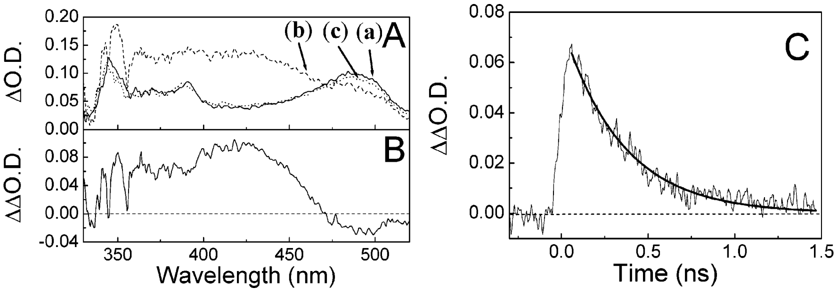
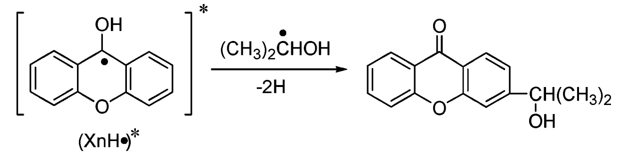


Figure 3. Transient absorption spectra obtained following the first preparation pulse (266 nm, solid line (a)) of Xn (4.0×10^{-4} M) and 0.2 (broken line (b)) and 5 ns (dotted line (c)) after the second excitation pulse (532 nm) in Ar-saturated cyclohexane. The second laser was irradiated at 1 μs after the first laser pulse. The transient absorption spectrum of XnH•(D_1) (B) was given by subtracting spectrum a from spectrum b. The blank around 532 nm in the spectra was due to the residual SHG of the Nd^{3+}:YAG laser. Kinetic trace of absorption at 430 nm of XnH• during the two-color two-laser photolysis (C). The solid line is the best fit obtained by the calculations based on the first-order kinetics.

SCHEME 2



where k_C, k_r, and k_{nr} are the rate constants of a chemical reaction, radiative relaxation, and nonradiative processes of XnH•(D_1), respectively. Because the chemical reaction does not regenerate XnH•(D_0), the sum of k_r and k_{nr} is given by eq 4

$$1 - \frac{\Delta\Delta OD(t = \infty)}{\Delta\Delta OD(t = 0)} = (k_r + k_{nr})\tau_0 \tag{4}$$

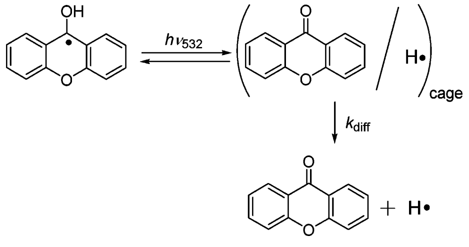
where $\Delta\Delta OD(t = 0)$ and $\Delta\Delta OD$ $(t = \infty)$ refer to $\Delta\Delta OD$ immediately after and sufficiently after the second laser irradiation, respectively, estimated from the curve fitting. On the other hand, k_C can be estimated from eq 5.

$$\frac{\Delta\Delta OD(t = \infty)}{\Delta\Delta OD(t = 0)} = k_C\tau_0 \tag{5}$$

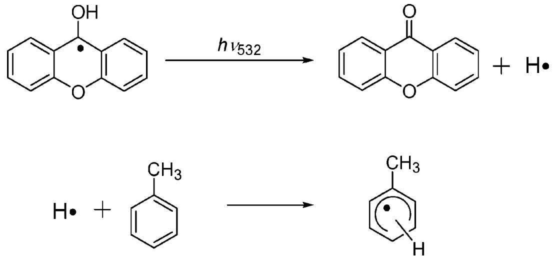
From these relations, the k_C and ($k_r + k_{nr}$) values for XnH• were estimated, as summarized in Table 2.

It is noteworthy that the k_C values of XnH•(D_1) in cyclohexane, toluene, and acetonitrile (containing 1% cyclohexane) were larger than those in 2-methytetrahydrofuran (MTHF) and 2-propanol (Table 2). Since recovery of XnH•(D_0) in 2-propanol was almost complete, the head-to-tail coupling reaction from XnH•(D_1) seems to be inefficient under our experimental conditions.[7] It is reported that the benzophenone ketyl radical in the D_1 state abstracts a hydrogen atom from cyclohexane. The spin density at the hydroxy-bearing carbon atom of the benzophenone ketyl radical is shifted substantially to the para position in the D_1 state.[7] The similar change of spin density between the D_0 and D_1 states was reported on XnH•.[7] Therefore, XnH•(D_1) could have the hydrogen abstraction ability from cyclohexane. Hydrogen abstraction of XnH•(D_1) is possible in cyclohexane and acetonitrile (containing 1% cyclohexane). In acetonitrile (containing 1% cyclohexane), the k_C value was faster than that in cyclohexane. Since the concentration of cyclohexane in acetonitrile (containing 1% cyclohexane) was 100 times smaller than that in neat cyclohexane, it seems that another reaction occurred concomitantly with the hydrogen abstraction in acetonitrile (containing 1% cyclohexane). The cleavage of the O−H ketyl bond generating Xn and a hydrogen atom will be the possible reaction pathway induced by the second laser irradiation. According to the Noyes model, the efficiency of escape from the solvent cage should vary linearly with the inverse of the bulk viscosity ($1/\eta$).[14a] Since the solvent viscosity of acetonitrile is much smaller than that of cyclohexane, the generated Xn and a hydrogen atom escape easily from the solvent cage, preventing the regeneration of XnH• in acetonitrile (containing 1% cyclohexane) (Scheme 3). The efficiency of OH bond cleavage depending on solvent viscosity has been reported by Agmon et al.[14b] It is noteworthy that XnH•(D_1) in toluene showed a small recovery and faster k_C value compared with those in other solvents. The unimolecular cleavage of the O−H ketyl bond of XnH•(D_1) seems to be efficient also in toluene, since the formation of a toluene-H-adduct is possible with the generated hydrogen radical (Scheme 4).[6]

SCHEME 3



SCHEME 4



The ($k_r + k_{nr}$) value of XnH•(D_1) was significantly affected by the solvent. The ($k_r + k_{nr}$) value of XnH•(D_1) was quite large in 2-propanol. It is known that the formation of hydrogen bonding between solute and solvent molecules promotes the nonradiative relaxation process.[15] Thus, it is suggested that the formation of a hydrogen bond between 2-propanol and ketyl radicals enhances the nonradiative relaxation process.

Intermolecular Reaction of XnH•(D_1) with a Halogen Atom Donor. The reactivity of XnH•(D_1) toward compounds with abstractable halogen atoms such as CCl_4, $CHCl_3$, CH_2Cl_2, and $C_2H_3Cl_3$ was examined. Although $CHCl_3$ and CH_2Cl_2 were inert for halogen abstraction, CCl_4 and $C_2H_3Cl_3$ showed reactivity with XnH•(D_1). In the presence of CCl_4, the irreversible component in the recovery of XnH•(D_0) increased dramatically. In all examined solvents, similar change was observed.

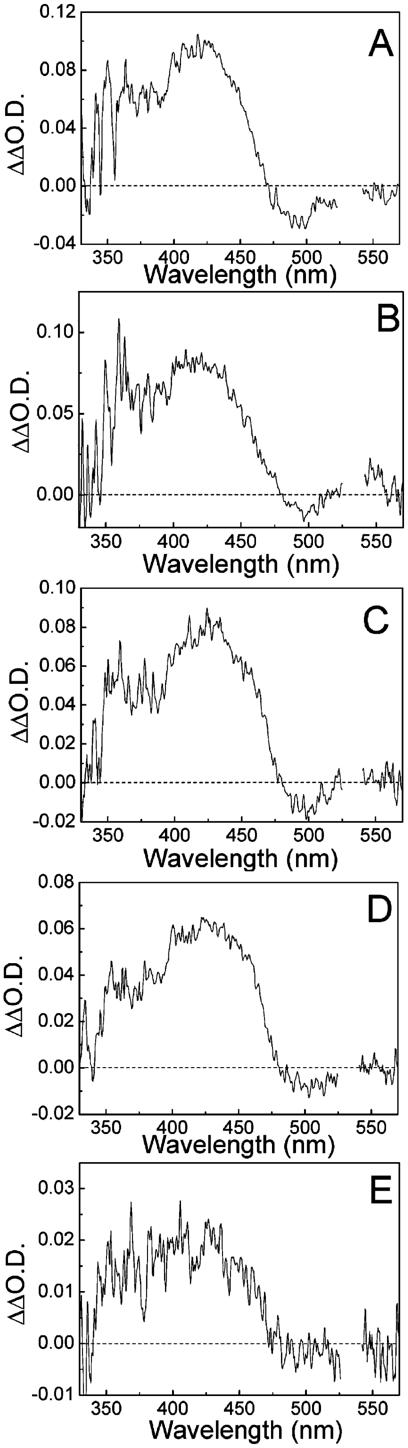


Figure 4. Transient absorption spectra of XnH•(D_1) obtained following the first 266-nm preparation pulse and 0.2 ns after the second 532-nm excitation pulse of Xn: (A) cyclohexane; (B) toluene; (C) 2-methyltetrahydrofurane; (D) 2-propanol; (E) acetonitrile (containing 1% cyclohexane) in various solvents. The blank around 532 nm in the spectra was due to the residual SHG of the Nd^{3+}:YAG laser.

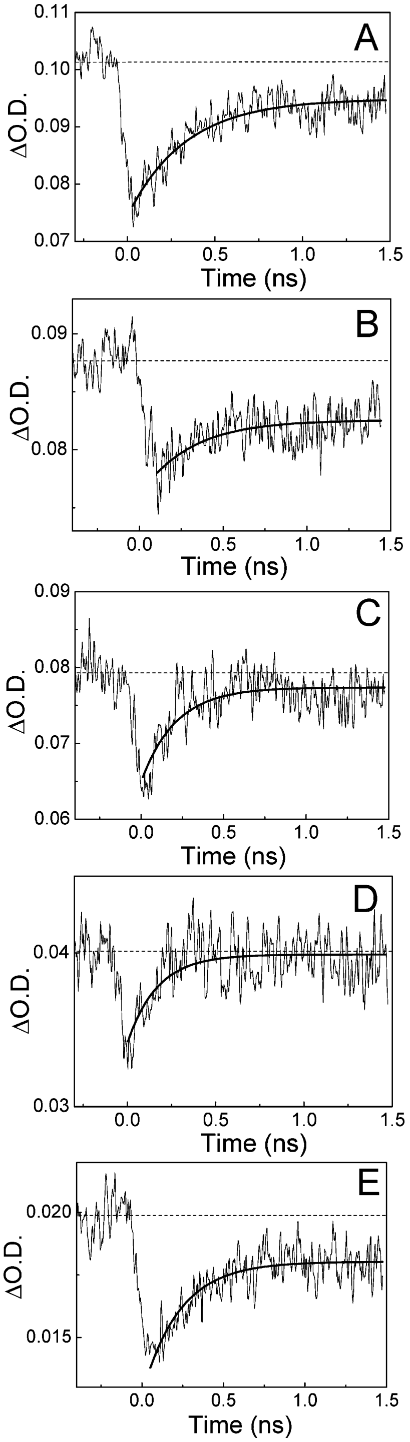


Figure 5. Second laser induced bleaching and recovery of the transient absorption of XnH•(D_0) at 490 nm: (A) cyclohexane; (B) toluene; (C) 2-methyltetrahydrofurane; (D) 2-propanol; (E) acetonitrile (containing 1% cyclohexane).

The proportion of the irreversible component increased with increasing concentration of CCl_4. Additionally, fluorescence quenching of XnH•(D_1) by CCl_4 was observed (Figure 6). Therefore, it is concluded that XnH•(D_1) was quenched by CCl_4. Since the formation of the xanthonenol cation which has a strong peak at 372 nm ($\epsilon = 3.8 \times 10^4$ M^{-1} cm^{-1})[16] was not observed after the second laser irradiation, dissociative electron transfer from XnH•(D_1) to CCl_4 should not occur. Since the triplet energy of CCl_4 has been reported to be between 3.1 and 3.8 eV, the energy transfer from XnH•(D_1) to CCl_4(S_1) or CCl_4(T_1) was not included.[17] Additionally, the formation a of complex between XnH•(D_1) and halogen donors can be ignored because the shape of the fluorescence spectra was not changed by adding a halogen donor (Figure 6). Therefore, it is suggested that chlorine atom abstraction from CCl_4 by XnH•(D_1) occurred (Scheme 5). Since XnH•(D_0) has little reactivity with the CCl_4 molecule, it should be noted that the reactivity of XnH• was dramatically enhanced in the excited state.[12b]

To determine the fluorescence quenching efficiency and solvent effect on the reactivity of halogen abstraction, the

TABLE 3: Diffusion Coefficients of XnH• ($D_{XnH•}$), Diffusion-Controlled Rate Constants (k_{diff}), and Quenching Rate Constants of XnH•(D_1) by CCl_4 and $C_2H_3Cl_3$ (k_q)

solvent	$D_{XnH•}$ (10^{-9} m^2 s^{-1})	k_{diff} (10^9 M^{-1} s^{-1})	XnH•(D_1)/CCl_4 k_q (10^9 M^{-1} s^{-1})	XnH•(D_1)/$C_2H_3Cl_3$ k_q (10^9 M^{-1} s^{-1})
cyclohexane	0.62[a]	8.2	6.1 ± 0.3	0.30 ± 0.04
toluene	0.89[b]	13	6.8 ± 0.4	0.048 ± 0.1
MTHF	1.0[c]	15	8.8 ± 1	0.23 ± 0.05
2-propanol	0.33[a]	3.8	12 ± 1	0.31 ± 0.07
acetonitrile[d]	1.07[a]	19	17 ± 1	0.39 ± 0.06

[a] Reference 20e. [b] The D value in benzene was employed, since benzene has similar solvent properties and size to toluene. [c] Estimated from the correlation between D and η.[20e,k] [d] Containing 1% cyclohexane.

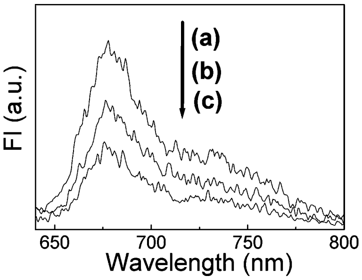


Figure 6. Fluorescence spectra of XnH•(D_1) containing CCl_4 (0.1 (a), 0.2 (b), and 0.35 M (c), respectively) obtained following the first 266-nm preparation pulse and 0.2 ns after the second 532-nm excitation pulse in MTHF.

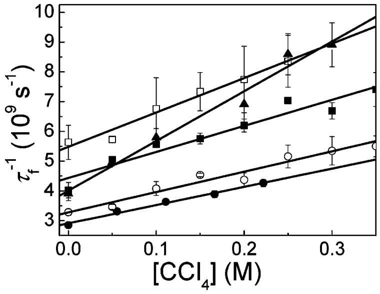
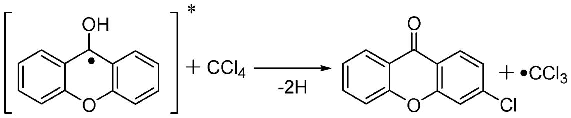


Figure 7. Stern−Volmer plots in various solvents: (●) cyclohexane; (○) toluene; (■) MTHF; (□) 2-propanol; (▲) acetonitrile (containing 1% cyclohexane).

SCHEME 5



fluorescence lifetime in a mixture (τ_r) was measured as a function of the CCl_4 concentration in various solvents. The halogen abstraction process leads to a reduced τ_r value of XnH• in the presence of CCl_4. From the plots of reciprocal τ_r versus CCl_4 concentration (Figure 7), the quenching rate constant (k_q) was determined on the basis of eq 6

$$\frac{1}{\tau_r} = \frac{1}{\tau_{r0}} + k_q[CCl_4] \tag{6}$$

where τ_{r0} denotes the fluorescence lifetime in the absence of CCl_4. The k_q values of $C_2H_3Cl_3$ were estimated by the same method. The k_q value of CCl_4 was 10 times larger than that of $C_2H_3Cl_3$. The determined k_q values were summarized in Table 3.

According to the Smoluchowski equation, the diffusion-controlled rate constant (k_{diff}) was expressed as shown in eq 7[18,19]

$$k_{diff} = 4\pi D_{DA} d_{cc} \tag{7}$$

where D_{DA} denotes the sum of the diffusion constant between XnH•(D_1) ($D_{XnH•}$) and halogen-donating molecules (D_H) and d_{cc} is the reaction distance 5.5 Å estimated from the results of PM3 calculations. D_H was estimated from the Stokes−Einstein relation (eq 8)[18,19]

$$D_{XnH•} = \frac{k_B T}{6\pi r_A \eta} \tag{8}$$

where k_B, r_A, η, and T denote the Boltzmann constant, the radius of the solute, the viscosity of the solvent, and the temperature, respectively.[18,19] As for $D_{XnH•}$, it is known that the diffusion of radicals was anomalously slow due to the strong interaction between the radical and the surrounding molecule.[18,20] Terazima et al. reported that the D value of the benzophenone ketyl radical generated by photoinduced hydrogen abstraction showed 2−3 times smaller D values than that of the parent molecule even though the ketyl radical and parent molecule possess nearly the same size and shape.[20d] Thus, we employed these D values of the benzophenone ketyl radical in ref 20e for $D_{XnH•}$, which was measured by the time-resolved transient grating method. The estimated k_{diff} values were shown in Table 3. C−Cl bond dissociation energies of CCl_4, $CHCl_3$, CH_2Cl_2, and $C_2H_3Cl_3$ are reported to be 70, 79, 83, and 74 kcal mol^{-1}, respectively.[8c,21] As shown in Table 3, the k_q values for CCl_4 in various solvents were similar to the k_{diff} values. Therefore, the halogen abstraction reaction of XnH•(D_1) with CCl_4 occurred at the diffusion-controlled rate constant because of the sufficient driving force. The estimated k_q values for $C_2H_3Cl_3$ were 10 times slower than the k_{diff} values. The k_q values for CH_2Cl_2 and $CHCl_3$ were much slower than those for $C_2H_3Cl_3$. Therefore, the k_q values reflect the bond dissociation energy.[21] This correlation supports the Cl abstraction reaction.[8c]

It is noteworthy that the k_q value for $C_2H_3Cl_3$ increased with increasing solvent polarity. The k_q value for $C_2H_3Cl_3$ may reflect the change of reactivity of XnH•(D_1) induced by the solvent properties. The halogen abstraction rate constant was correlated with π-electron density at the carbon to which the halogen is attached. It is reported qualitatively that excess electron density at the carbon retards the abstraction while deficient electron density enhances the rate.[22] Since the charge density of XnH•(D_1) should be delocalized in the polar solvents, the charge density at the para position of the phenyl ring may be lowered as favorable to the abstraction.

Conclusions

In the present work, we directly detected the absorption spectra and fluorescence of XnH•(D_1) in various solvents. The reactivities of XnH•(D_1) were significantly affected by the solvent properties. The dipole−dipole interaction between XnH•(D_1) and the solvent molecules was not observed. XnH•(D_1) showed the specific solvent−solute interactions with the toluene and 2-propanol. The solvent effect on the lifetime of XnH•(D_1) was examined. The interaction and reactivity of XnH•(D_1) with the solvent molecules govern the lifetime of XnH•(D_1). The halogen abstraction of XnH•(D_1) from CCl_4 and $C_2H_3Cl_3$ was also found. The k_q value of the halogen abstraction of XnH•(D_1) from CCl_4 showed correlation with the diffusion-controlled rate constant when the anomalously slow diffusion of radical was taken into account, while that with $C_2H_3Cl_3$ reflected the reactivity of XnH•(D_1) depending on the solvent polarity.

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References and Notes

(1) (a) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publishing Co.: Melco Park, CA, 1978. (b) Suppan, P. *Chemisrty and light*; The Royal Society of Chemistry: Cambridge, U.K., 1994.

(2) (a) Ramamurthy, V.; Schanze, K, S. *Molecular and supramolecular photochemistry*; Marcel Dekker: New York, 1994; Vol. 2. (b) Scaiano, J. C.; Johnston, L. J.; McGimpsey, W. G.; Weir, D. *Acc. Chem. Res.* **1988**, *21*, 22. (c) Melnikov, M. Y.; Smirnov, V. A. *Handbook of Photochemistry of Organic Radicals*; Begell house: New York, 1996.

(3) (a) Lazár, M.; Rychlý, J.; Klimo, W.; Pelikán, P.; Valko, L. *Free Radicals in Chemistry and Biology*; CRC press, Inc.: Boca Raton, Florida, 1987. (b) Pryor, W. A., Ed. *Free Radicals in Biology*; Academic: New York, 1976; Vols. 1−5. (c) Edmondson, S.; Osborne, V. L.; Huck, W. T. S. *Chem. Soc. Rev.* **2004**, *33*, 14. (d) Corrales, T.; Catalina, F.; Peinado, C.; Allen, N. S. *J. Photochem. Photobiol., A* **2003**, *159*, 103. (e) Davidson, R. S. *J. Photochem. Photobiol., A* **1993**, *73*, 81. (f) Monroe, B. M.; Weed, G. C. *Chem. Rev.* **1993**, *93*, 435. (g) Nyman, E. S.; Hynninen, P. H. *J. Photochem. Photobiol., B* **2004**, *73*, 1.

(4) (a) Hodgson, B. W.; Keene, J. P.; Land, E. J.; Swallow, A. J. *J. Chem. Phys.* **1975**, *63*, 3671. (b) Razi Naqvi, K.; Wild, U. P. *Chem. Phys. Lett.* **1976**, *41*, 570. (c) Topp, M. R. *Chem. Phys. Lett.* **1976**, *39*, 423. (d) Obi, K.; Yamaguchi, H. *Chem. Phys. Lett.* **1978**, *54*, 448. (e) Baumann, H.; Schumacher, K. P.; Timpe, H.-J.; Rehak, V. *Chem. Phys. Lett.* **1982**, *89*, 315. (f) Thurnauer, M. C.; Meisel, D. *Chem. Phys. Lett.* **1982**, *92*, 343. (g) Hiratsuka, H.; Yamazaki, T.; Maekawa, Y.; Hikida, T.; Mori, Y. *J. Phys. Chem.* **1986**, *90*, 774. (h) Tokumura, K.; Mizukami, N.; Udagawa, M.; Itoh, M. *J. Phys. Chem.* **1986**, *90*, 3873. (i) Sakamoto, M.; Cai, X.; Hara, M.; Tojo, S.; Fujitsuka, M.; Majima, T. *J. Phys. Chem. A* **2004**, *108*, 8147.

(5) (a) Gannon, T.; McGimpsey, W. G. *J. Org. Chem.* **1993**, *58*, 913. (b) Adam, W.; Denninger, U.; Finzel, R.; Kita, F.; Platsch, H.; Walker, H.; Zang, G. *J. Am. Chem. Soc.* **1992**, *114*, 5027. (c) Ouchi, A.; Koga, Y.; Adam, W. *J. Am. Chem. Soc.* **1997**, *119*, 592. (d) Haider, K.; Platz, M. S.; Despres, A.; Lejeune, V.; Migirdicyan, E.; Bally, T.; Haselbach, E. *J. Am. Chem. Soc.* **1988**, *110*, 2318. (e) Adam, W.; Schneider, K.; Stapper, M.; Steenken, S. *J. Am. Chem. Soc.* **1997**, *119*, 3285. (f) Jent, F.; Paul, H.; Fisher, H. *Chem. Phys. Lett.* **1988**, *146*, 315. (g) Banks, J. T.; Scaiano, J. C.; Adam, W.; Sculte Oestrich, R. *J. Am. Chem. Soc.* **1993**, *115*, 2473. (h) Cai, X.; Sakamoto, M.; Hara, M.; Tojo, S.; Ouchi, A.; Kawai, K.; Endo, M.; Fujitsuka, M.; Majima, T. *J. Am. Chem. Soc.* **2004**, *126*, 7432. (i) Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2877. (j) Netto-Ferreira, J. C.; Muphy, W. F.; Redmond, R. W.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 4472.

(6) (a) Johnston, L. J.; Lougnot, D. J.; Wintgens, V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 518. (b) Redmond, R. W.; Scaiano, J. C.; Johnston, L. J. *J. Am. Chem. Soc.* **1990**, *112*, 398. (c) Redmond, R. W.; Scaiano, J. C.; Johnston, L. J. *J. Am. Chem. Soc.* **1992**, *114*, 9768.

(7) (a) Adam, W.; Kita, F.; Oestrich, R. F. *J. Photochem. Photobiol., A* **1994**, *80*, 187. (b) Adam, W.; Kita, F. *J. Am. Chem. Soc.* **1994**, *116*, 3680.

(8) (a) Letsinger, R. L.; Collat, R.; Magnusson, M. *J. Am. Chem. Soc.* **1954**, *76*, 4185. (b) Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1985**, *107*, 83. (c) Breslin, D. T.; Fox, M. A. *J. Phys. Chem.* **1993**, *97*, 13341. (d) Ruberu, S. R.; Fox, M. A. *J. Phys. Chem.* **1993**, *97*, 143.

(9) (a) Baumann, H.; Merckel, C.; Timpe, H. J.; Graness, A.; Kleinschmidt, J.; Gould, I. R. Turro, N. J. *Chem. Phys. Lett.* **1984**, *103*, 497. (b) Weir, D. *J. Phys. Chem.* **1990**, *94*, 5870. (c) Adam, W.; Sculte Oestrich, R. *J. Am. Chem. Soc.* **1992**, *114*, 6031. (d) Arnold, B. R.; Scaiano, J. C.; McGimpsey, W. G. *J. Am. Chem. Soc.* **1992**, *114*, 9768. (e) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6368. (f) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396. (g) Weir, D.; Johnston, L. J.; Scaiano, J. C. *J. Phys. Chem.* **1988**, *92*, 1742.

(10) Nagarajan, V.; Fessenden, R. W. *Chem. Phys. Lett.* **1984**, *112*, 207.

(11) (a) Fujitsuka, M.; Oseki, Y.; Hara, M.; Cai, X.; Sugimoto, A.; Majima, T. *ChemPhysChem* **2004**, *5*, 1240. (b) Cai, X.; Sakamoto, M.; Hara, M.; Tojo, S.; Kawai, K.; Endo, M.; Fujitsuka, M.; Majima, T. *J. Phys. Chem. A* **2004**, *108*, 7147. (c) Oseki, Y.; Fujitsuka, M.; Hara, M.; Cai, X.; Sugimoto, A.; Majima, T. *J. Phys. Chem. B* **2004**, *108*, 16727.

(12) (a) Coenjarts, C.; Scaiano, J. C. *J. Am. Chem. Soc.* **2000**, *122*, 3635. (b) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747. (c) Sakaguchi, Y.; Hayashi, H.; Murai, H.; I'Haya, Y. J. C. *J. Am. Chem. Soc.* **1988**, *110*, 7479.

(13) Christian, R. *Chem. Rev.* **1994**, *94*, 2319.

(14) (a) Brennecke, J. F.; Chateauneuf, J. E. *Chem. Rev.* **1999**, *99*, 433. (b) Agmon, N.; Pines, E.; Huppert, D. *J. Chem. Phys.* **1988**, *89*, 1524.

(15) Biczók, L.; Bérces, T.; Linschitz, H. *J. Am. Chem. Soc.* **1997**, *119*, 11071. (b) Biczók, L.; Bérces, T.; Inoue, H. *J. Phys. Chem. A* **1999**, *103*, 3837.

(16) McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 2929.

(17) Sakamoto, M.; Cai, X.; Hara, M.; Tojo, S.; Fujitsuka, M.; Majima, T. *J. Am. Chem. Soc.* **2004**, *126*, 9709.

(18) Arita, T.; Kajimoto, O.; Terazima, M.; Kimura, Y. *J. Chem. Phys.* **2004**, *120*, 7071.

(19) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

(20) (a) Levison, S. A.; Noyes, R. M. *J. Am. Chem. Soc.* **1964**, *86*, 4525. (b) Burkhart, R. D.; Wong, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 7203. (c) Autrey, T.; Kandanarachchi, P.; Franz, J. A. *J. Phys. Chem. A* **2001**, *105*, 5948. (d) Terazima, M.; Hirota, N. *J. Chem. Phys.* **1993**, *98*, 6257. (e) Terazima, M.; Okamoto, K.; Hirota, N. *J. Phys. Chem.* **1993**, *97*, 13387. (f) Terazima, M.; Okazaki, T.; Hirota, N. *J. Photochem. Photobiol., A* **1995**, *92*, 7. (g) Okamoto, K.; Terazima, M.; Hirota, N. *J. Chem. Phys.* **1995**, *103*, 10445. (h) Terazima, M.; Okamoto, K.; Hirota, N. *J. Chem. Phys.* **1995**, *102*, 2506. (i) Donkers, R. L.; Leaist, D. G. *J. Phys. Chem. B* **1997**, *101*, 304. (j) Okamoto, K.; Hirota, N.; Terazima, M. *J. Phys. Chem. A* **1997**, *101*, 5269. (k) Terazima, M. *Acc. Chem. Res.* **2000**, *33*, 687.

(21) Zhijieliu, L.; Betterton, E. A.; Robert, G. A. *Environ. Sci. Technol.* **2000**, *34*, 804.

(22) (a) Danen, W. C.; Saunders, D. G. *J. Am. Chem. Soc.* **1969**, *91*, 5924. (b) Danen, W. C.; Saunders, D. G.; Rose, K. A. *J. Am. Chem. Soc.* **1974**, *96*, 4558.