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ARTICLES

Properties and Reactivity of Xanthyl Radical in the Excited State

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The properties and reactivity of the 9-xanthyl radical ($X^\bullet$) in the doublet excited state ($X^\bullet(D_1)$) were investigated using nanosecond−picosecond two-color two-laser flash photolysis. The absorption and fluorescence spectra of $X^\bullet(D_1)$ were observed for the first time. The reactivity of $X^\bullet(D_1)$ toward a series of halogen donors and electron acceptors in acetonitrile and 1,2-dichloroethane (DCE) was investigated. It is confirmed that $X^\bullet(D_1)$ has a halogen abstraction ability from a series of halogen donors. On the basis of the solvent effect on the quenching rate constants of $X^\bullet(D_1)$, an electron transfer from $X^\bullet(D_1)$ to CCl_4 was indicated.

Introduction

Free radicals are some of the important intermediates in an array of chemical and biological reactions. Nowadays, it is known that free radicals play important roles in a variety of biological and industrial processes. Since the reactivity of radicals is an attractive subject from the photophysical, photochemical, and photobiological points of view, the reactivity of excited radicals is also important. Since excited radicals show different reactivities from that in the ground state,[1,2] the investigation of the reactivity of excited radicals would help to develop new kind of chemistry using excited radicals. For example, we reported the efficient fabrication method of gold nanoparticle using the excited benzophenone ketyl radical with high reducing ability than that in the ground state.[3]

The 9-xanthyl radical ($X^\bullet$) is one of the well-investigated free radicals.[4−6] The interesting property of xanthene is its chemical transformation induced by a one-electron oxidation. The 9-xanthyl radical cation ($X^{\bullet+}$) undergoes a fast deprotonation to form $X^\bullet$, which transfers an electron to the molecular oxygen to form the closed shell cation. Similar stepwise oxidation processes have also been revealed for the NADH analogues.[7] Therefore, xanthene has been investigated as the model compound of NADH.[8] In addition, radicals of xanthene and xanthene dye can be applied as an initiator for several polymerizations.[9]

Although the properties and reactivity of $X^\bullet$in the ground state ($X^\bullet(D_0)$) were well-investigated, the study of those of $X^\bullet$ in the doublet excited state ($X^\bullet(D_1)$) was limited. To the best of our knowledge, there is only one report about $X^\bullet(D_1)$. The halogen abstraction of $X^\bullet(D_1)$ from CCl_4 has been reported based on the bleaching of the $X^\bullet(D_0)$ absorption in 1,2-dichloroethane (DCE) during the pulse radiolysis-laser-two-step-excitation method.[10] However, no absorption and fluorescence of $X^\bullet(D_1)$ was observed in their study due to the poor time-resolution of the instruments and short lifetime of $X^\bullet(D_1)$. Moreover, the halogen abstraction rate constant was not determined. A method with a high time resolution is necessary to investigate the properties and reactivity of $X^\bullet(D_1)$ in detail.

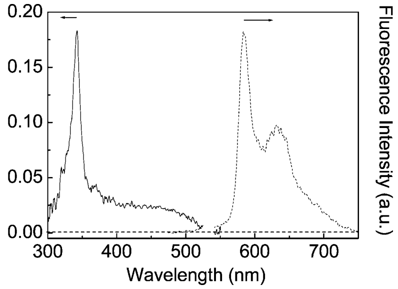

Figure 1. Absorption (solid line) and fluorescence (dotted line) spectra of the $X^\bullet$ in Ar-saturated acetonitrile at room temperature. The absorption spectrum was obtained during the 266 nm laser flash photolysis, while the fluorescence spectrum was obtained during the 266 and 532 nm two-color two-laser flash photolysis of X (5.0×10^{-3} M). The blank around 532 nm in the spectrum is due to the residual SHG of the Nd^{3+}:YAG laser.

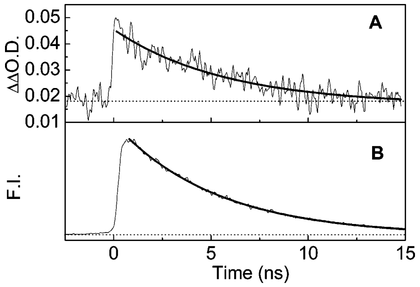

Figure 2. Kinetic traces of ΔΔO. D. at 480 nm (A) and fluorescence intensity (F.I.) at 630 nm (B) of $X^\bullet$ during the two-color two-laser photolysis in Ar-saturated acetonitrile. The solid lines are the best fits based on the first-order kinetics.

Recent advance in short pulse laser instrumentation has revealed a variety of dynamic processes of the short-lived

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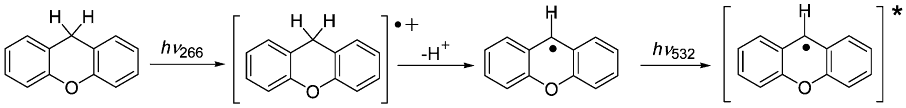
SCHEME 1



excited states of various molecules. The $D_1 \rightarrow D_0$ fluorescence of excited radicals is detectable in the condensed phase at room temperature. In our previous study, we successfully observed the fluorescence and transient absorption spectra of several ketyl radicals in the excited state with a short lifetime using nanosecond−picosecond two-color two-laser flash photolysis.[11]

In the present study, the properties and reactivity of $X^{\bullet}(D_1)$ were investigated using nanosecond−picosecond two-color two-laser flash photolysis. The absorption and fluorescence spectra of $X^{\bullet}(D_1)$ were observed for the first time. The solvent effect on the photophysical properties of $X^{\bullet}(D_1)$ was examined. The reactivity of $X^{\bullet}(D_1)$ toward a series of halogen donors and electron acceptors (1,1,2-trichloroethane, dichloromethane, chloroform, chloroacetonitrile, 1,1-dichloroacetonitrile, 1,1,1-trichloroacetonitrile, CCl_4, and CBr_4) was investigated using the fluorescence quenching method in acetonitrile and DCE. It was revealed that $X^{\bullet}(D_1)$ has a high reactivity and shows a variety of reactions.

Results and Discussion

Generation of 9-Xanthenyl Radical ($X^{\bullet}$). $X^{\bullet}$ was generated by the deprotonation of $X^{\bullet+}$, which was generated from the photoionization of xanthene upon the first 266 nm nanosecond-laser (266 nm, 80 mJ pulse^{-1}, 5 ns fwhm) irradiation in acetonitrile (Scheme 1). It is reported that $X^{\bullet}$ was oxidized by molecular oxygen to form the xanthyl cation (X^+) through a one-electron-transfer mechanism.[4] To suppress the generation of X^+, the sample solutions were deoxygenated by bubbling with Ar gas for 30 min before irradiation. The spectrum of $X^{\bullet}$ with a strong peak at 345 nm and a weak shoulder tailing to 580 nm agrees with the reported one (Figure 1).[5]

Fluorescence Spectrum and Lifetime of $X^{\bullet}$ in the Excited State ($X^{\bullet}(D_1)$). The generated $X^{\bullet}$ was excited at the visible absorption shoulder using the second laser (532 nm, 20 mJ pulse^{-1}, 30 ps fwhm) with a delay time of 1 μs after the first laser. Upon excitation, $X^{\bullet}$ showed a fluorescence with a peak (λ_f) at 589 nm (Figure 1), which is quite separated from the absorption peak of $X^{\bullet}$ ($\Delta\lambda = 244$ nm). An analogous large red shift in fluorescence has been reported for radicals such as the benzyl and other arylmethyl radicals.[1] The apparent large red shift is due to the low oscillator strength for the $D_0 \rightarrow D_1$ transition. Thus, the observed absorption peak at 345 nm is the $D_0 \rightarrow D_n$ ($n > 1$) transition. From the fluorescence maximum, the energy gap between the D_1 and D_0 states of $X^{\bullet}$ ($\Delta E(D_1-D_0)$) was estimated to be 2.20 eV.

The fluorescence lifetime (τ_f) of $X^{\bullet}(D_1)$ was measured at the peak position of the fluorescence spectrum. The fluorescence decay curve was fitted well with the single-exponential decay function (Figure 2). The τ_f value of $X^{\bullet}(D_1)$ was estimated to be 5.2 ± 0.2 ns. Essentially, the same fluorescence spectrum and lifetime were observed in DCE (Table 1).

Transient Absorption Spectra of $X^{\bullet}(D_1)$. Immediately after the second laser irradiation, a broad absorption band was observed at around 370 nm (Figure 3). Since the lifetime of the broad band (τ) was 5.0 ± 0.2 ns, which is essentially the same as the τ_f, this broad band can be attributed to $X^{\bullet}(D_1)$ (Figure 2). Unfortunately, since the absorption of $X^{\bullet}(D_1)$ overlapped with the bleaching of $X^{\bullet}(D_0)$ (i.e., the ground-state absorption of $X^{\bullet}$), the absorption spectrum of $X^{\bullet}(D_1)$ in the 300−350 nm region was unclear.

TABLE 1: Spectroscopic Data for $X^{\bullet}(D_1)$ in Ar-Saturated Acetonitrile and DCE Giving Fluorescence Peak Wavelength (λ_f) and Lifetimes of Fluorescence (τ_f) and Absorption (τ)

compound	solvent	λ_f (nm)	τ_f (ns)	τ (ns)
$X^{\bullet}(D_1)$	acetonitrile	589	5.2 ± 0.2	5.0 ± 0.2
	DCE	585	5.0 ± 0.2	4.9 ± 0.2

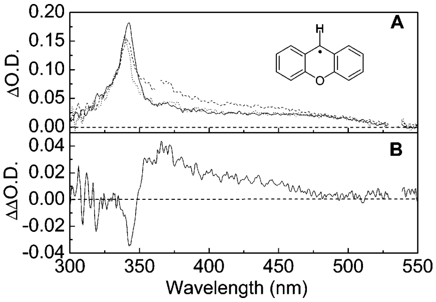


Figure 3. Transient absorption spectra observed 1 μs after the 5 ns laser pulse during the one-laser photolysis (266 nm, solid line (a)) and at 0.5 ns (dashed line (b))and 15 ns (dotted line) after the 30 ps second laser pulse during the two-color two-laser photolysis (266- and 532 nm) of X (1.0×10^{-4} M) in Ar-saturated acetonitrile (A). The second laser was irradiated 1 μs after the first laser pulse. The transient absorption spectrum of $X^{\bullet}(D_1)$ (B) was obtained 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.

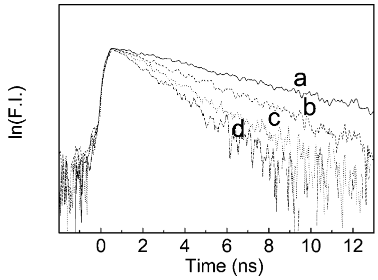
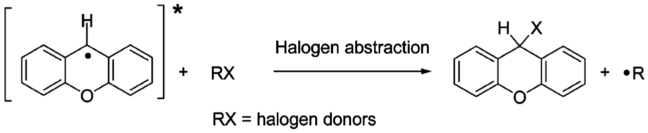


Figure 4. Plots of ln(F.I.) vs time (ns) of $X^{\bullet}(D_1)$ in Ar-saturated acetonitrile in the absence (a) and presence of CCl_4 with 0.013 (b), 0.026 (c), and 0.039 (d) M.

SCHEME 2



Reaction of $X^{\bullet}(D_1)$ with Quenchers. It is reported that $X^{\bullet}(D_1)$ is reactive toward compounds with abstractable halogen atoms (Scheme 2).[10] Several halogen donors (1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, dichloromethane, chloroform, chloroacetonitrile, 1,1-dichloroacetonitrile, 1,1,1-trichloroacetonitrile, CCl_4, and CBr_4) were selected to investigate the reactivity of $X^{\bullet}(D_1)$ in acetonitrile and DCE. In the presence of chloroacetonitrile, 1,1-dichloroacetonitrile, 1,1,1-trichloroacetonitrile,

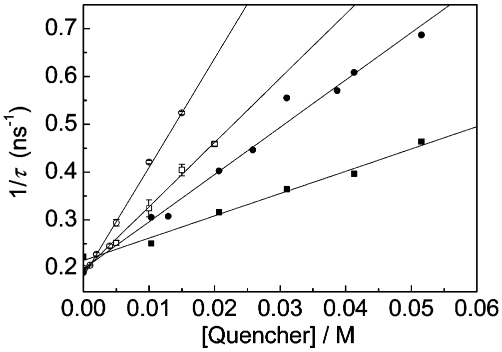


Figure 5. Plots of $1/\tau$ versus concentration of the quenchers ([Quencher]) ((●) CCl_4 and (○) CBr_4 in Ar-saturated acetonitrile and (■) CCl_4 and (□) CBr_4 in Ar-saturated DCE).

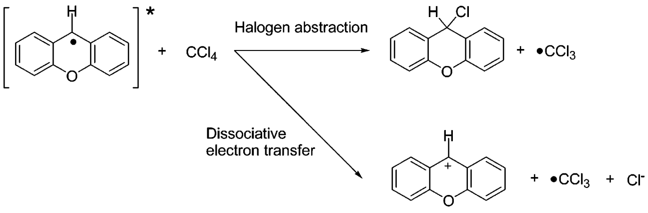
CCl_4, and CBr_4, the bleaching of $X^\bullet(D_0)$ and a decrease in τ_f were observed upon the second laser irradiation in acetonitrile and DCE (Figure 4). On the other hand, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, dichloromethane, and chloroform were all inert toward $X^\bullet(D_1)$.

To determine the fluorescence quenching rate, the τ_f value was measured as a function of the concentration of the halogen donor. The reaction between $X^\bullet(D_1)$ and the halogen donor leads to a shorter τ_f value of $X^\bullet(D_1)$ with the increasing concentration of the halogen donor ([Q]). From the plots of the reciprocal τ_f vs [Q] (Figure 5), the quenching rate constant (k_q) was determined according to eq 1,

$$\frac{1}{\tau_f} = \frac{1}{\tau_{f0}} + k_q[Q] \qquad (1)$$

where τ_{f0} is the fluorescence lifetime of $X^\bullet(D_1)$ in the absence of quenchers. The k_q values of $X^\bullet(D_1)$ for several halogen donors in DCE were estimated and summarized in Table 2. Although halogen donors are also good electron acceptors, the electron transfer process is unfavorable in nonpolar solvents such as DCE. Therefore, we concluded that only halogen abstraction occurred between $X^\bullet(D_1)$ and the halogen donors in DCE. Furthermore, the k_q values in DCE increased with the decreasing value of the substrate bond dissociation energy (D_R) of the halogen donors. This tendency also supports the quenching process due to halogen abstraction. Although $X^\bullet(D_1)$ was quenched by chloroacetonitrile, 1,1-dichloroacetonitrile, 1,1,1-trichloroacetonitrile, CCl_4, and CBr_4, no quenching of $X^\bullet(D_1)$ by 1,1,2,2-tetrachloroethane, dichloromethane, chloroform was observed. It is suggested that the threshold of the D_R value of the halogen donors, which can be abstracted by $X^\bullet(D_1)$, was 3.2−3.0 eV. The k_q values for CBr_4 and 1,1,1-trichloroacetonitrile were similar to the diffusion-controlled rate constant in DCE ((0.98−1.1) × 10^{10} M^{-1} s^{-1}).[12] Although the D_R value of chloroacetonitrile is lower than that of CCl_4, the k_q value of $X^\bullet(D_1)$ by chloroacetonitrile was lower than that by CCl_4. The difference in the k_q value would be caused by the difference in the hard sphere radius (a_R) of the halogen donors. The reaction distance between two molecules can be expressed by the sum of the a_R value of $X^\bullet(D_1)$ and the halogen donors. Since a_R of CCl_4 (3.37 Å) is greater than that of chloroacetonitrile (2.93 Å),[15] CCl_4 is favorable for the bimolecular quenching process (Table 2). It is suggested that the bimolecular reaction would be enhanced due to the increase in the reaction distance between $X^\bullet(D_1)$ and the halogen donors.

SCHEME 3



The k_q values of $X^\bullet(D_1)$ for several halogen donors in acetonitrile were also estimated using eq 1 and summarized in Table 2. The k_q values in acetonitrile also increased with the decreasing D_R and increasing reduction potential of the halogen donors. In the case of 1,1,1-trichloroacetonitrile and CBr_4, the k_q values were similar to the diffusion-controlled rate constant in acetonitrile ((2.0−2.3) × 10^{10} M^{-1} s^{-1}).[12]

It is noteworthy that the k_q value of CCl_4 in acetonitrile is approximately two times greater than that in DCE. Although the electron-transfer process was suppressed in nonpolar solvents such as DCE, both the dissociative electron transfer and the halogen abstraction between $X^\bullet(D_1)$ and the halogen donors were expected in acetonitrile (Scheme 3). Thus, it is suggested that the dissociative electron transfer from $X^\bullet(D_1)$ to CCl_4 occurs in acetonitrile, leading to the increased k_q value. Unfortunately, detection of the X^+ upon the second laser irradiation was quite difficult because the absorption of X^+ (380 nm) was hidden by the absorption of $X^\bullet(D_1)$ and the bleaching of $X^\bullet(D_0)$. For 1,1-dichloroacetonitrile and chloroacetonitrile, the reaction rate constants in acetonitrile and DCE were similar within the estimation error. It is suggested that the electron-transfer process from $X^\bullet(D_1)$ to 1,1-dichloroacetonitrile or chloroacetonitrile in acetonitrile was not favorable and the halogen abstraction process is the dominant reaction.

The rate of electron transfer depends on the driving force ($-\Delta G_{ELT}$).[15−18] Thus, we estimated the ΔG_{ELT} of the electron transfer from $X^\bullet(D_1)$ to the halogen donors. Halogen donors undergo the C−Cl bond cleavage following the one-electron reduction.[15−17] According to the "sticky" dissociative electron transfer theory,[15,16] ΔG_{ELT} is represented by eq 2

TABLE 2: Quenching Rate Constant (k_q) of $X^\bullet(D_1)$ by Quenchers in Ar-Saturated Acetonitrile and DCE, the Substrate Bond Dissociation Energy (D_R), Reduction Potential ($E_{RCl/R^\bullet+Cl^-}$) of the Quenchers, Hard Sphere Radius (a_R), and Driving Force for the Electron Transfer from $X^\bullet(D_1)$ to the Quenchers ($-\Delta G_{ELT}$)

quencher	k_q (× 10^{10} M^{-1} s^{-1}) in acetonitrile	k_q (× 10^{10} M^{-1} s^{-1}) in DCE	D_R (eV)	$E_{RCl/R^\bullet+Cl^-}$ (V vs SCE)	a_R (Å)	$-\Delta G_{ELT}$ (eV) in acetonitrile
CBr_4	2.2 ± 0.1	1.3	2.4[b]	−0.37[b]	*d*	1.8
CCl_4	0.97	0.46	2.985 ± 0.03[c]	−0.825[c]	3.37[c]	1.3
$CHCl_3$	*a*	*a*	3.24 ± 0.03[c]	−1.090[c]	3.14[c]	1.1
CH_2Cl_2	*a*	*a*	3.47 ± 0.05[c]	−1.325[c]	2.94[c]	0.84
$Cl_2CH-CHCl_2$	*a*	*a*	3.28 ± 0.03[c]	−1.105[c]	3.13[c]	1.1
$NCCCl_3$	2.4 ± 0.1	1.9 ± 0.1	2.48 ± 0.03[c]	−0.325[c]	3.42[c]	1.8
$NCCHCl_2$	0.26 ± 0.01	0.24 ± 0.01	2.69 ± 0.03[c]	−0.550[c]	3.17[c]	1.6
$NCCH_2Cl$	0.003 ± 0.01	0.014 ± 0.05	2.88 ± 0.03[c]	−0.755[c]	2.93[c]	1.4

[a] Quenching was not observed. [b] Reference 2. [c] Reference 15. [d] The value was not reported.

$$\Delta G_{\mathrm{ELT}} = E_{\mathrm{OX}} - E_{\mathrm{RCl/R^{\bullet}+Cl^{-}}} - w_{\mathrm{p}} - \Delta E(\mathrm{D}_1-\mathrm{D}_0) \qquad (2)$$

where E_{OX} is the oxidation potential of $\mathrm{X}^{\bullet}$ (for $\mathrm{X}^{\bullet}$, $E_{\mathrm{OX}} = -0.002$ V vs SCE),[19] $E_{\mathrm{RCl/R^{\bullet}+Cl^{-}}}$ is the reduction potential of the $\mathrm{RCl/R^{\bullet}} + \mathrm{Cl^{-}}$ couple,[15] and w_{p} is the Coulombic energy in acetonitrile (0.06 eV). The $-\Delta G_{\mathrm{ELT}}$ values of the electron transfer from $\mathrm{X}^{\bullet}(\mathrm{D}_1)$ to CCl_4 is estimated to be 1.3 eV. Thus, the electron transfer from $\mathrm{X}^{\bullet}(\mathrm{D}_1)$ to CCl_4 is exothermic and favorable. The estimated $-\Delta G_{\mathrm{ELT}}$ values in acetonitrile are summarized in Table 2.

Although the $-\Delta G_{\mathrm{ELT}}$ values of the electron transfer from $\mathrm{X}^{\bullet}(\mathrm{D}_1)$ to 1,1-dichloroacetonitrile or chloroacetonitrile were greater than that of the electron transfer to CCl_4, no electron transfer from $\mathrm{X}^{\bullet}(\mathrm{D}_1)$ to 1,1-dichloroacetonitrile or chloroacetonitrile was observed. Therefore, other factors should be considered to explain this confliction.

The electron transfer becomes the fastest when the reorganization energy is similar to the $-\Delta G_{\mathrm{ELT}}$ values. That is, the reorganization energy also influences the electron-transfer rate. Especially, in the present cases, the influence of the reorganization energy on the electron transfer cannot be negligible due to the bond cleavage of the halogen donors following the electron transfer. Since the electron transfer to halogen donors undergoes a carbon−halogen bond cleavage following the one-electron reduction, the reorganization energy of the electron transfer is affected by the bond breaking of the carbon−halogen bond.[15−17] It is reported that the solvent reorganization energy of 1,1-dichloroacetonitrile (1.145 eV) and chloroacetonitrile (1.192 eV) at the transition state was greater than that of CCl_4 (1.078 eV).[15] Thus, it is suggested that the electron transfer to 1,1-dichloroacetonitrile or chloroacetonitrile was unfavorable due to the large reorganization energy compared to that involving CCl_4.

Conclusions

Summary, the properties and reactivity of $\mathrm{X}^{\bullet}(\mathrm{D}_1)$ were revealed using nanosecond−picosecond two-color two-laser flash photolysis. The absorption and fluorescence spectra of $\mathrm{X}^{\bullet}(\mathrm{D}_1)$ were observed for the first time. The k_{q} values of $\mathrm{X}^{\bullet}(\mathrm{D}_1)$ by several halogen donors were estimated using the fluorescence quenching method. It was confirmed that $\mathrm{X}^{\bullet}(\mathrm{D}_1)$ abstracts the halogen radical from a series of halogen donors. The threshold of the D_{R} value of the halogen donors, which can be abstracted by $\mathrm{X}^{\bullet}(\mathrm{D}_1)$, was estimated to be 3.2−3.0 eV. The electron-transfer process from $\mathrm{X}^{\bullet}(\mathrm{D}_1)$ to CCl_4 was indicated by the solvent effect on the k_{q} value. It was revealed that $\mathrm{X}^{\bullet}(\mathrm{D}_1)$ has a high reactivity and shows a variety of reactions.

Experimental Section

The two-color two-laser flash photolysis experiment was carried out using the fourth harmonic oscillation (266 nm) of a nanosecond $\mathrm{Nd^{3+}}$:YAG laser (Quantel, Brilliant; 5 ns fwhm) as the first laser, and the second harmonic oscillation (532 nm) of a picosecond $\mathrm{Nd^{3+}}$:YAG laser (Continuum, RGA69−10; 30 ps fwhm, 10 Hz) as the second laser. The delay time of the two laser flashes was adjusted to 1 μs using four channel digital delay/pulse generators (Stanford Research Systems, model DG 535). The breakdown of the Xe gas generated by the fundamental pulse of the picosecond $\mathrm{Nd^{3+}}$:YAG laser was used as a probe light. The transient absorption 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 allowed to flow into a transparent rectangular quartz cell (1.0 × 0.5 × 2.0 cm). For the measurements of both the fluorescence spectra and decay profiles, the streak camera was used as the detector.

Xanthene was purchased from Aldrich and used without further purification. The sample solutions were prepared in acetonitrile or DCE and deoxygenated by bubbling with Ar gas for 30 min before the irradiation. All experiments were carried out at room temperature.

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(12) According to the Smoluchowski equation, the diffusion-controlled rate constant (k_{diff}) is expressed by eq 3,[13]

$$k_{\mathrm{diff}} = 4\pi D_{\mathrm{DA}} d_{\mathrm{cc}} \qquad (3)$$

where D_{DA} denotes the sum of the diffusion constant between $\mathrm{X}^{\bullet}(\mathrm{D}_1)$ and the halogen-donating molecules and d_{cc} is the reaction distance assumed to be 5.5 Å. The diffusion constant (D) was estimated from the Stokes−Einstein relation (eq 4),[13]

$$\mathrm{D} = \frac{k_{\mathrm{B}} T}{6\pi r_{\mathrm{A}} \eta'} \qquad (4)$$

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.[13,14]

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