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Studies on Photochemical Processes of Xanthene Dyes by Means of the Transient Absorption Spectra in the Visible/Near-IR Regions

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The rate constants for quenching of the triplet states of eosin and erythrosin ($^3D^*$) with various substrates have been evaluated using nanosecond laser flash photolysis while observing the transient absorption bands in the visible/near-IR regions. Intense transient absorption bands due to $^3D^*$ were observed at about 1040 nm. An energy-transfer reaction from $^3D^*$ to anthracene-9-carboxylic acid was confirmed by the appearance of the absorption band of the triplet state of the acid at 425 nm. The ion radicals of electron donors and electron acceptors were also observed with the decay of $^3D^*$, indicating the occurrence of an electron-transfer reaction. High hydrogen-abstraction abilities of $^3D^*$ were also confirmed for substituted phenols and benzenethiols. The negative slopes of the Hammett plots indicate that the reaction center of $^3D^*$ has a highly electrophilic nature.

Xanthene dyes (D) are promising sensitizers for different types of photochemical reactions with quenchers in various solvents, including buffered aqueous solutions.[1—15] Particularly, heavy atom-substituted xanthenes, such as eosin and erythrosin, are notable for their favorable properties to high triplet quantum yields ($\Phi_T = 0.8$—1.0) and relatively long lived triplet states ($t_{1/2} = 0.1$—0.3 ms).[12] The triplet states of the dyes ($^3D^*$) participate in chemical reactions: i.e., electron-transfer, addition, and H-atom abstraction reactions.

The photochemistry of eosin under both reductive and oxidative conditions has been studied by Koizumi's group[1—4] as well as several other groups.[16—22] The photophysical and photochemical properties of the xanthene dyes are well established as sensitizers in photography,[23,24] single oxygen formation and the oxidation of biologically important molecules.[25]

The flash photolysis of eosin and erythrosin in the presence of amines has been performed by Kasche and Linsqvist,[26] by Rizzuto and Spikes,[19] and others.[27—29] Although the quenching of $^3D^*$ with oxidative or reductive processes was usually followed by the decay of the transient-absorption band in the visible region, the observation of the triplet–triplet (T–T) absorption bands in the visible region was restricted by strong absorption bands of these dyes in this region. It is, thus, preferable to observe the T–T absorption bands in the near-IR region. In the case of some xanthene dyes, it is reported that the T–T absorption bands were observed at ca. 1000 nm by conventional flash photolysis.[30,31]

In the present study we observed the transient absorption spectra of eosin and erythrosin in the near-IR region by nanosecond laser photolysis. From the decay of the T–T absorption bands, the quenching rate constants for photochemical processes were obtained. We found that the ion radicals of some quenchers also showed their characteristic absorption bands in the near-IR region. The elemental reaction processes can be confirmed by direct observation of the decay of $^3D^*$ and the rise of ion radicals or free radicals.

Experimental

Eosin Y and erythrosin B were obtained from Aldrich Co., Ltd. The quenchers are all commercially available. Most of the reagents were purified by recrystallization.

Solutions containing dye and quenchers were excited by 532 nm light from a Nd:YAG laser (6 ns fwhm) with 7—10 mJ power. For measurements of the transient-absorption spectra in the visible region, a photomultiplier was used as a detector for monitoring the transmitted light from a continuous Xe-monitor lamp (150 W). In the near-IR region, a Ge-APD detector and a pulsed xenon-monitor lamp were employed.[32,33] The steady-state UV/visible absorption spectra were measured with a JASCO/V-570 spectrophotometer. All of the measurements were performed at 23 °C. MO calculations were performed by the AM1 method in MOPAC'94.[34]

Results and Discussion

Steady-State UV/Visible Spectra. The steady state visible absorption spectra of eosin in aqueous solution and ethanol are shown in Fig. 1. The intense absorption peaks at 520—530 nm are appropriate to be excited by 532 nm laser light. The absorption peak at 520 nm in aqueous solution shifts to a longer wavelength up to 530 nm in ethanol, with decreasing the absorption intensity. Although similar absorption spectra were observed for erythrosin, the shift of the absorption peak at 530 nm was smaller than that of eosin. The same type of solvent dependency of the absorption spectra was observed for the hydroxyxanthenes, in which the shift in the absorption maximum is due to hydrogen bonding.[35]

Upon the addition of various quenchers, the absorption spectra of eosin and erythrosin did not change much, indicating no ground-state interaction, except for methylviologen (MV^{2+}). In both ethanol and aqueous solutions, complex formation between dyes and MV^{2+} slightly shifted the ab-

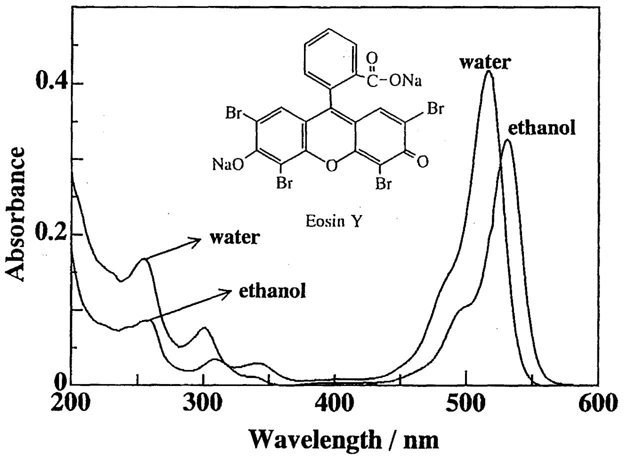


Fig. 1. Absorption spectra of eosin (0.02 mmol dm^{-3}) in ethanol and water (pH = 9.2) in 2 mm optical cell.

sorption maximum and appreciably decreased the absorption intensity of the dyes. The fluorescence intensity of the dyes also decreases along with the MV^{2+} concentration due to static quenching.[8,12)]

Transient Absorption Spectra. Figure 2 shows the transient-absorption spectra observed by the 532 nm-laser irradiation of eosin in ethanol in the region of 600—1350 nm. The absorption band with a peak at 1040 nm was attributed to the T–T absorption band due to its similarity with the reported T–T absorption.[30,31)] Immediately after a laser pulse, a negative absorbance was observed in the 600—700 nm region, which can be attributed to the emission of eosin.

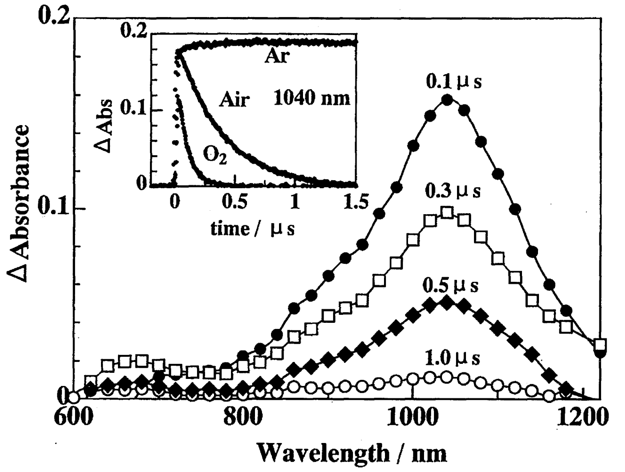


Fig. 2. Transient absorption spectra observed after laser photolysis (532 nm) of eosin (0.02 mmol dm^{-3}) in aerated ethanol. Insert: Decay profiles at 1040 nm.

For erythrosin, a similar transient absorption band due to the T–T transition was observed by the 532 nm-laser pulse. The absorption peak is almost the same as that of eosin.[31)] The same transient spectrum in water as in alcohol was observed. For both eosin and erythrosin, the transient absorption bands due to T–T absorption in aqueous solution were shifted to a longer wavelength compared with those in ethanol.

Quenching with O_2. Both the eosin and erythrosin triplet states are effectively quenched by O_2, depending on the O_2-concentration (Insert in Fig. 2). The first-order rate constant (k_{1st}) was obtained from the slope of the first-order plot of the $^3D^*$-decay, showing linearity. The slope of the pseudo-first order plot (k_{1st} vs. $[O_2]$) gives the second-order rate constant for the O_2-quenching reaction (k_{O2}), as listed in Table 1. As a O_2-quenching reaction, both energy transfer and electron transfer can be considered (Eqs. 1 and 2). It has been reported that the quantum yields of singlet oxygen ($^1O_2$) are 0.57 for eosin and 0.68 for erythrosin.[37,38)] Thus, energy transfer is predominant to the electron transfer producing $O_2^{-\bullet}$;

$$ {}^3D^* + O_2 \xrightarrow{k_{O_2}} D + {}^1O_2 \qquad (1) $$

$$ \qquad\qquad \longrightarrow D^{\bullet +} + O_2^{\bullet -} \qquad (2) $$

The observed rate constants were slightly smaller than the diffusion-controlled limit (5.5×10^9—6.4×10^9 mol^{-1} dm^3 s^{-1}),[39)] although the reaction is sufficiently exothermic according to the energy levels of the triplet states (Table 1).

Energy Transfer. The same transient-absorption band of ^{3}(eosin)* was observed in aqueous solution as shown in Fig. 3. In the presence of anthracene-9-carboxylic acid (9-AC), a rise in the absorption band of the triplet state of 9-AC was observed at 425 nm[40)] (Insert in Fig. 3) along with the decay of $^3D^*$, indicating an energy transfer. The quenching rate constants (k_q) for eosin in ethanol were found to be slower than in aqueous solution (Table 1), suggesting the association of 9-AC in ethanol. On assuming the quantum yield of energy transfer=1 in Fig. 3, the molar extinction coefficients of the T–T transition (ε_t) of $^3D^*$ at 1040 nm were evaluated

Table 1. Quenching Rate Constants with Triplet Quenchers (k_q)

Quencher	Solvent	k_q/mol^{-1} dm^3 s^{-1}		Comment[a)]
		Eosin	Erythrosin	$T_1 = 14800$ cm^{-1} (eosin) $T_1 = 14700$ cm^{-1} (erythrosin)
β-Carotene	Ethanol	6.9×10^8	3.3×10^8	$T_1 = 6785$ cm^{-1}
O_2	Ethanol	1.1×10^9	1.1×10^9	$T_1 = 8770$ cm^{-1}
9-AC	Ethanol	8.4×10^8	1.1×10^9	$T_1 = 14450$ cm^{-1}
	Aqueous	2.3×10^9	1.8×10^9	
Perylene	Ethanol	7.9×10^9	6.5×10^9	$T_1 = 12270$ cm^{-1}

a) T_1 values were cited from Refs. 36, 42, 43, 44, and 45. 9-AC: anthracene-9-carboxylic acid.

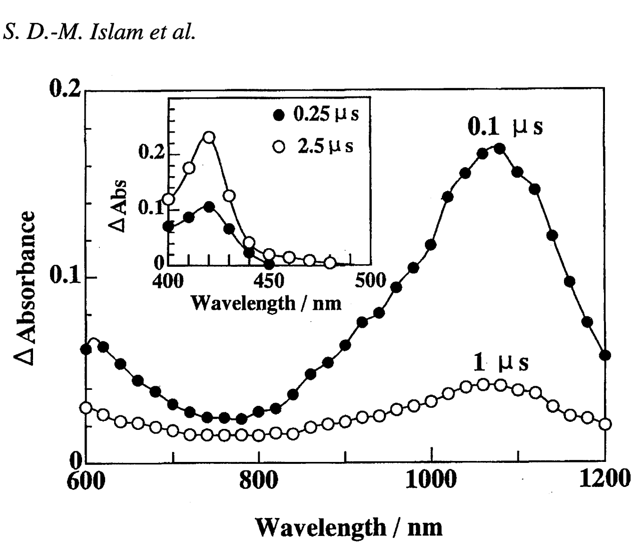


Fig. 3. Transient absorption spectra observed after laser photolysis (532 nm) of eosin (0.02 mmol dm^{-3}) in the presence of 9-AC (1.0 mmol dm^{-3}) in deaerated water (pH = 9.2; ionic strength = 0.08). Insert: Transient absorption spectra observed in the vis region.

to be 32000 and 39000 mol^{-1} dm^3 cm^{-1} for eosin and erythrosin, respectively, using $\varepsilon_t = 43000$ mol^{-1} dm^3 cm^{-1} for anthracene.[41)]

For β-carotene, the rate constants for eosin and erythrosin are smaller than the others in spite of its low triplet energy, which is in agreement with the reported value for rose bengal, suggesting some interactions between β-carotene and the triplet state of rose bengal.[46)]

Electron Transfer from Donors. Upon the addition of electron donors, such as amines, the quenching of ^{3}D* was observed. In the case of 3,3′,5,5′-tetramethylbenzidine (TMB), both the transient absorption bands of ^{3}D* and TMB$^{+\bullet}$ (λ_{max} = 880 nm) were observed immediately after the laser pulse, because these two absorption bands overlap.[33,47)] Then, ^{3}D* gradually decreases with an increase of TMB$^{+\bullet}$, as shown in Fig. 4. The time profile at 880 nm can be curve-resolved with the decay of ^{3}D* and the rise of TMB$^{+\bullet}$. From the ratio [TMB$^{+\bullet}$]$_{max}$/[^{3}D*]$_{int}$, which can be calculated using the observed absorbance and ε values (ε = 34000 mol^{-1} dm^3 cm^{-1} for TMB$^{+\bullet}$),[33)] the quantum yield of electron transfer is 0.5. The quenching rate constants were evaluated, as summarized in Table 2, with some oxidation potentials.[48—52)] The rate constants decrease with high values of the oxidation potentials; this follows the normal tendency for electron transfer (Eq. 3). For TMB, the rate constant for electron transfer (k_{elt}) was evaluated to be 0.5 $k_q = 1.2\times10^9$ mol^{-1} dm^3 s^{-1} in ethanol.

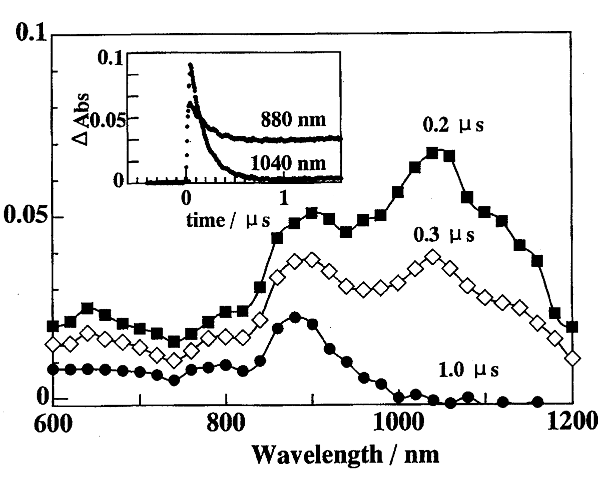
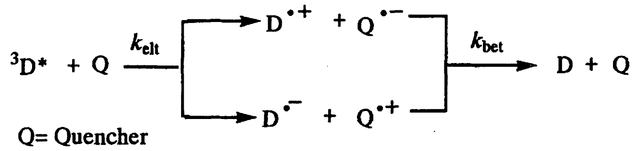


Fig. 4. Transient absorption spectra observed after laser photolysis (532 nm) of eosin (0.02 mmol dm^{-3}) in the presence of TMB (2.6 mmol dm^{-3}) in deaerated ethanol. Insert: Time profiles at 880 and 1040 nm.



(3)

For 1,4-diazabicyclo[2.2.2]octane (DABCO) and 2,2′,2″-nitrilotriethanol (triethanolamine, TEOA), the rate constants from DABCO and TEOA to ^{3}D* are faster in aqueous solution than in ethanol. This tendency is in a good agreement with the same type of solvent effect on a photoinduced electron-transfer reaction between the triplet state of safranine-T and aliphatic amines.[52)]

When erythrosin was excited by 532 nm light in the presence of 1,4-benzenedithiolate ($^-$SC$_6$H$_4$S$^-$) in a basic solution, transient bands appeared at 390 and 740 nm (Fig. 5), which are the characteristics absorption bands of $^-$SC$_6$H$_4$S$^\bullet$.[53,54)] The intensity of the transient absorption of ^{3}D* (Fig. 5) decreased with [$^-$SC$_6$H$_4$S$^-$] compared to others (Fig. 2), which is probably due to an interaction of ^{3}D* with $^-$SC$_6$H$_4$S$^-$. The phenolate anion also quenched ^{3}D* in an aqueous basic solution, suggesting a good electron donor.

Electron Transfer to Acceptors. In the presence of quinones, the transient absorption bands characteristic to the radical anions of quinones appeared at 450 nm[14,55)] with the decay of ^{3}D*, indicating electron transfer from ^{3}D* to quinones (Eq. 3). The transient absorbance due to half-oxidized eosin at 460 nm[56,57)] could not be observed, due to the absorbance of the quinone radical anion at this region.

Table 2. Quenching Rate Constants with Electron Donors (k_q)

Electron donors	Solvent	k_q/mol^{-1} dm^3 s^{-1}		Comment
		Eosin	Erythrosin	
TMB	Ethanol	2.4×10^9	2.3×10^9	E_{ox}= 0.48
TMPD[a)]	Ethanol	4.3×10^9	3.3×10^9	E_{ox}= 0.21
DPPD[b)]	Ethanol	2.6×10^9	2.2×10^9	—
DABCO	Aqueous	1.7×10^8	2.2×10^8	E_{ox}= 0.68
	Ethanol	6.9×10^6	3.7×10^6	
TEOA	Aqueous	7.3×10^7	2.4×10^7	—
	Ethanol	1.0×10^6	3.0×10^5	
$^-$SC$_6$H$_4$S$^-$	Aqueous	2.7×10^9	2.3×10^9	—
PhO$^-$	Aqueous	1.3×10^8	1.3×10^8	E_{ox}= 0.80

a) TMPD: tetramethyl-1,4-phenylenediamine. b) DPPD: *N,N′*-diphenyl-1,4-phenylenediamine. E_{ox} values are taken from Refs. 48, 49, 50, 51, and 52.

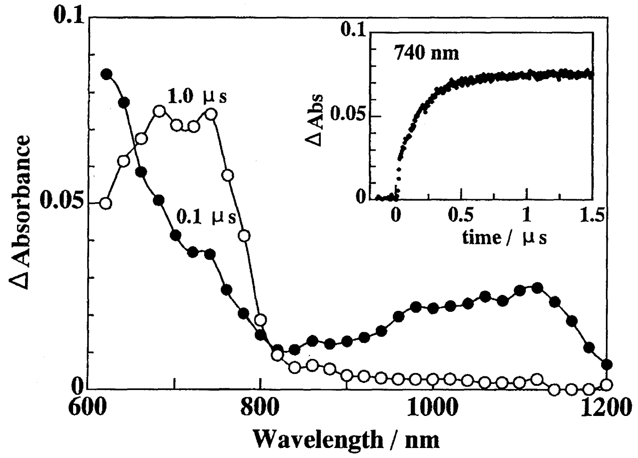


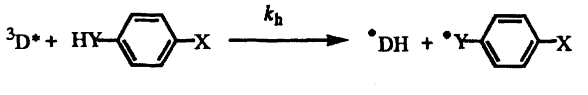
Fig. 5. Transient absorption spectra observed after laser photolysis (532 nm) of erythrosin (0.02 mmol dm^{-3}) in the presence of $^{-}SC_6H_4S^{-}$ (2.5 mmol dm^{-3}) in deaerated water (pH = 9.2; ionic strength = 0.08). Insert: Time profiles at 740 nm.

The rate constants with electron acceptors are summarized in Table 3 along with some reduction potentials.[14,58] It can be noticed that the rate constants decrease along with a decrease in the reduction potential of the quinones. Similar results were also observed for the electron-transfer reaction from the triplet states of rose bengal and safranine-T to 1,4-benzoquinone.[14,59] For chloranil with high electron acceptor ability, the rate constants are similar to those of 1,4-benzoquninone. For 2,5-di-*t*-butyl-1,4-benzoquinone, the bulky substituents decrease the rate constants due to an increase in the steric hindrance.

Electron transfer from $^3D^*$ to MV^{2+} is greatly influenced by the reaction media; the rate constants in aqueous solution are larger than that in ethanol, although the transient absorption band of ^{3}(erythrosin)* could not be observed in the presence of MV^{2+} in ethanol. This is probably due to the fact that ^{3}(erythrosin)* forms a relatively strong CT-complex with MV^{2+}. This is also assumed for ^{3}(eosin)*–MV^{2+}, because the initial intensity of the transient band of ^{3}(eosin)* decreases along with an increase in the concentrations of MV^{2+} in ethanol.

In the long time-scale, the decays of 1,4-benzosemiquinone anion at 455 nm obey second-order kinetics, suggesting that a back electron-transfer reaction occurs. From the slope of the second-order plot, k_{bet} for eosin was evaluated to be 5.0×10^8 mol^{-1} dm^3 s^{-1} using the reported ε value for 1,4-benzoquinone$^{-\bullet}$.[55]

H-Atom Abstraction. By the laser photolysis of dyes in the presence of 1,4-hydroquinone in ethanol, the absorption band appeared at 405 nm with the decay of $^3D^*$, as shown in Fig. 6. The 405 nm band is characteristic to the absorption band of $HOC_6H_4O^\bullet$,[60] suggesting the H-atom abstraction reaction of $^3D^*$ (Eq. 4).



X = H, -CH$_3$, -OCH$_3$, -OH, -NH$_2$, SH Y=O and S (4)

The quenching rate constants with typical H-atom donors are summarized in Table 4. The rate constants for 2,5-di-*t*-butyl-1,4-hydroquinone in ethanol, which are close to those reported in the FT-EPR study in 1-propanol,[61] are higher than

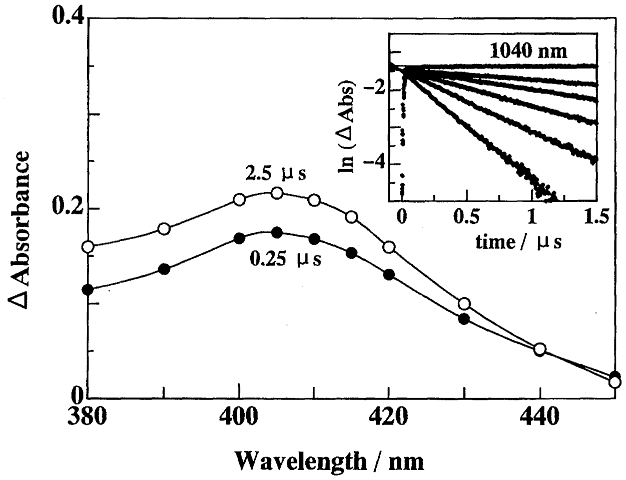


Fig. 6. Transient absorption spectra in visible region observed after laser photolysis (532 nm) of eosin (0.02 mmol dm^{-3}) in the presence of 1,4-hydroquinone (50 mmol dm^{-3}) in deaerated ethanol. Insert: First-order plots for decay at 1040 nm.

Table 3. Quenching Rate Constants with Electron Acceptors (k_q)

Electron acceptors	Solvent	k_q/mol^{-1} dm^3 s^{-1}		Comment[a]
		Eosin	Erythrosin	
1,4-Benzoquinone	Ethanol	4.1×10^9	4.5×10^9	E_{red}=−0.16
	Aqueous[b]	3.5×10^9	4.7×10^9	
Duroquinone	Ethanol	2.0×10^9	2.5×10^9	E_{red}=−1.05
DBBQ[c]	Ethanol	1.6×10^9	2.0×10^9	E_{red}=−1.24
Chloranil	Ethanol	3.6×10^9	4.8×10^9	E_{red}=−0.02
MV^{2+}	Aqueous	6.9×10^9	4.9×10^9	E_{red}=−0.69
MV^{2+}	Ethanol	3.5×10^9	—[d]	

a) E_{red} values were taken from Refs. 14 and 58. b) Acidic aqueous solution. c) DBBQ: 2,5-di-*t*-buty-1,4-benzoquinone. d) The transient absorption band at 1040 nm disappeared on addition of MV^{2+}.

Table 4. Quenching Rate Constants with H-atom Donors (k_q) in Ethanol

H-Atom donors	k_q [a]/mol^{-1} dm^3 s^{-1}	
	Eosin	Erythrosin
Phenol	8.2×10^4	6.0×10^4
1,4-Hydroquinone	8.0×10^7	8.0×10^7
DBHQ[b]	2.5×10^8	2.1×10^8
α-Tocopherol	3.7×10^8	2.9×10^8
Benzenethiol	1.1×10^6	1.1×10^6
1,4-Benzenedithiol	1.1×10^7	2.1×10^7

a) For other derivatives, the rate constants can be estimated from the plots in Fig. 7. b) DBHQ: 2,5-di-*t*-butyl-1,4-hydroquinone.

for 1,4-hydroquinone, due to the electronic factors, rather than the steric factor. Although the decay rate for phenol is slow, tocopherol is highly reactive to $^3D^*$; a similar tendency was also observed for the reaction of triplet rose bengal in acetonitrile.[14] 1,4-hydroquinone is more reactive than 1,4-benzenedithiol for $^3D^*$.

To investigate the substituent effect for the reactions of $^3D^*$ with 4-XC_6H_4OH or 4-XC_6H_4SH as H-atom donors, Hammett plots of $\log k_q$ against σ^+-constants according to Eq. 5 are shown in Fig. 7.

$$\Delta(\log k_q) = \rho^+\sigma^+. \qquad (5)$$

The H-abstraction reactivity of $^3D^*$ decreases with the electron-withdrawing substituent of both 4-XC_6H_4OH and 4-XC_6H_4SH. Similar substituents effect of phenol derivatives were observed for the reaction of safranine-T in methanol.[62] The negative slopes (ρ^+) of Hammett relation indicate the electrophilic nature of the reaction center of $^3D^*$ with respect to 4-XC_6H_4OH and 4-XC_6H_4SH.[63,64] The ρ^+ values were evaluated to be for 4-XC_6H_4OH [$\rho^+=-3.6$ for ^{3}(eosin)* and -3.7 for ^{3}(erythrosin)*] and 4-XC_6H_4SH [$\rho^+=-1.9$ for ^{3}(eosin)* and -1.8 for ^{3}(erythrosin)*]. For each hydrogen donor, similar ρ^+ value implies that the electrophilic ability of ^{3}(eosin)* is similar to that of ^{3}(erythrosin)*. Since the reaction center of $^3D^*$ for the H-atom abstraction reaction is considered to be $\rangle C{=}O$ of $^3D^*$, the electrophilic nature of $^3D^*$ suggests that the triplet state of $\rangle C{=}O$ behaves as $\rangle C^\bullet{-}O^\bullet$ in which O-atom is electron deficient. This speculation was supported by a MO calculation for a model compound of xanthene dyes (xanthone), indicating low electron densities of the carbonyl O-atom in the upper and lower SOMO of $^3D^*$. The ρ^+ values for 4-XC_6H_4OH is more negative than those of 4-XC_6H_4SH. This suggests that the polar nature of the transition state for the reaction with 4-XC_6H_4OH is higher than that of 4-XC_6H_4SH; i.e., the contribution of charge transfer taking place from H-atom donors to $^3D^*$ in the transition state is high for 4-XC_6H_4OH.

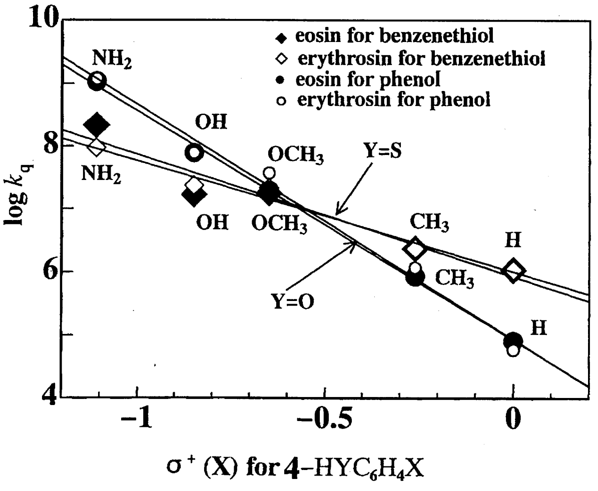


Fig. 7. Hammett plots for quenching rate constants of $^3D^*$ with 4-X-C_6H_4YH (Y = O and S).

Summary

The T–T absorptions of both eosin and erythrosin observed at about 1000 nm with high molar extinction coefficients were useful for following the various reactions of $^3D^*$, giving quite reliable quenching rate constants. The observation of the rise in the absorbance of the secondary species is also an advantage in measurements in the near-IR, because the fluorescence and depletion of D in the visible region do not disturb the observation. The electrophilicity of $^3D^*$ was confirmed from the Hammett relations for H-abstraction reactions of $^3D^*$ with phenols and benzenethiols.

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