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Photochemistry of quinoxaline derivatives and mechanism of the triplet state quenching by electron-poor alkenes

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Abstract

The properties of the lowest excited triplet states of quinoxaline derivatives 2,3-dimethylquinoxaline (DMQ) and 2,3,6,7-tetramethylquinoxaline (TMQ) in acetonitrile have been investigated by using time-resolved laser flash photolysis at 266 nm. The transient absorption spectra and the self-quenching rate constants (k_{sq}) of the excited sensitizers have been obtained. The excited triplet states of DMQ and TMQ are efficiently quenched by some electron-poor alkenes, such as fumaronitrile (FN), dimethyl fumarate (DMF), diethyl fumarate (DEF), α-acetoxyacrylonitrile (AAN), acrylonitrile (AN) and crotononitrile (CrN). Obtained k_q values decrease significantly from FN ($2.50 \times 10^9\ M^{-1}\ s^{-1}$) to CrN ($1.70 \times 10^5\ M^{-1}\ s^{-1}$) with DMQ and from FN ($1.77 \times 10^9\ M^{-1}\ s^{-1}$) to CrN ($1.20 \times 10^5\ M^{-1}\ s^{-1}$) with TMQ, which are in accordance with the reduction potential (E_{red}) and electron cloud density of these electron-poor alkenes. Plots of log k_q versus free energy change ΔG_{ct} for different alkenes are linear and yield slopes $-2.75\ eV^{-1}$ for DMQ, $-2.69\ eV^{-1}$ for TMQ and $-2.99\ eV^{-1}$ for DMN in the endergonic region ($\Delta G_{ct} > 0$). These shallower slopes indicate processes involving only partial charge transfer. The failure to detect the ion radicals also supports that triplet exciplex is formed during the processes. In addition, the electronic effects of ortho-substituents are estimated according to the good linear relation between log k_q and Hammett σ constant.

Keywords: Laser flash photolysis; Quinoxaline; Electron-poor alkene; Charge transfer; Exciplex

1. Introduction

Photoinduced electron transfer plays an important role in light-driven chemical, physical and biological processes. Electron transfer reactions are generally studied in some polar solvents such as acetonitrile, in which ion pair of the electron transfer are stabilized by the strong solvation. Unfortunately, only partial charge transfer occurs between donor and acceptor in many acceptor/donor systems, especially the driving force (ΔG_{et}) is positive. In such circumstance there are no radical pair could be detected while a kind of transient species called exciplex could be produced instead. More and more researches have been focused on this transient in the last few decades. Eisenthal studied the intermolecular charge transfer dynamics of exciplex formation between anthracene and dialkylaniline in detail and obtained some useful indication [1]. Shizuka and co-workers employed triplet benzophenone with a variety of ground state molecules in acetonitrile and a mixture of acetonitrile/water on the basis of rate constant as well as efficiencies and concluded that triplet benzophenone would deactivate via triplet exciplex [2,3]. Aizawa et al. investigated the acetophenone/*N*, *N*, *N′*, *N′*-tetramethylbenzidine system and determined the pressure dependence of the formation and decay process between the two neutral species [4]. Grzeskowiak et al. measured the exciplex dipole moments of cyanoanthracene derivatives and determined the structures of exciplexes [5]. Further investigations showed that the triplet exciplexes had loose sandwich-like structures and weak charge transfer character [6].

The photophysics and photochemistry of aza-derivatives of 1,2-diaryl-ethylenes have received much attention because their (n, π^*) states introduced by nitrogen atoms have a significant effect on the photochemistry and photophysics of

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these compounds [7–9]. As a sort of typical aza-derivatives, quinoxalines are very important naturally occurring heterocycles and are usually found to have biological and pharmaceutical activity [10–13]. Furthermore, the quinoxaline analogues could give rise to interesting results in the excited states, i.e. high triplet yields on excitation at room temperature because quinoxalines have high intersystem crossing yields [7]. In recent years, numerous reports of the photochemistry and thermodynamics of various quinoxalines have been well documented [7,12,14], while there are few investigations with regard to the kinetic research of these compounds, especially about the time-resolved kinetics.

Photochemical reactions of quinoxaline derivatives with several acyclic and cyclic alkenes have been initially investigated by our group [15,16]. This work is an in-depth study. Here nanosecond laser flash photolysis was used to investigate various parameters related to the excited triplet states of two quinoxaline derivatives DMQ and TMQ. Mainly, we report the quenching rate constants for the reaction of a number of electron-poor alkenes with triplet DMQ and TMQ. Additionally, 2,3-dimethylnaphthalene (DMN) that bears the similar molecular configuration to DMQ was also introduced to make comparison. The dependence of ΔG_{ct}, E_{red} and σ values of alkenes on the k_q is examined to determine a triplet exciplex mechanism.

2. Experimental details

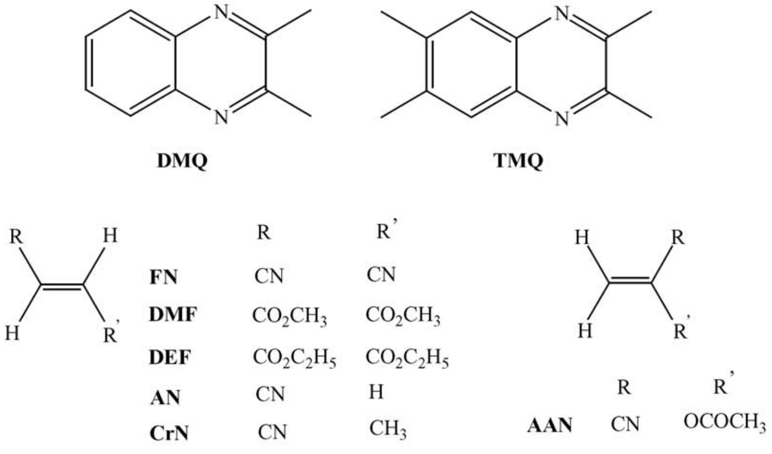
The samples of DMQ and TMQ were prepared and purified according to the given procedures reported elsewhere [12,17]. Their structures (Scheme 1) and purity were confirmed by satisfactory spectral data. DMN obtained from Fluka was used as received. fumaronitrile (FN), dimethyl fumarate (DMF), diethyl fumarate (DEF), α-acetoxyacrylonitrile (AAN), acrylonitrile (AN) and crotononitrile (CrN) were used as supplied from Aldrich. The resulting solutions were bubbled with high-purity nitrogen (99.99%) for 20 min before the spectroscopic measurements. Acetonitrile (MeCN) used as the solvent was spectrophotometric grade. All the spectra were recorded at ambient temperature.

Fluorescence emission spectra were recorded with a Shimadzu RF-5301PC spectrophotometer. Low-temperature phosphorescence spectra were determined in frozen matrix state at 77 K with a Perkin-Elmer LS55 luminescence spectrometer.

^{1}H NMR spectra were recorded at 400 MHz (AVANCE AV 400), the chemical shifts were reported in parts per million (δ) relative to $CDCl_3$ ($\delta = 7.25$ for a proton) or tetramethylsilane as the internal standard. Coupling constants were reported in hertz (Hz).

The oxidation potential (E_{ox}) of DMQ and TMQ versus SCE were measured in acetonitrile with 0.1 M TBAP as the supporting electrolyte. The scanning speed was maintained at 200 mV/s. Solution was bubbled with nitrogen prior to the measurement. The measured E_{ox} values are 1.23 V for DMQ and 1.59 V for TMQ, respectively.

The instrumentation and experimental procedures used for laser flash photolysis were reported previously [18]. The excitation light was the fourth harmonic (266 nm) of a Nd:YAG laser (Spectra Physics, GCR-170, repetition rate of 10 Hz) with a duration of 8 ns. The analyzing light was from a 500 W Xenon lamp. The laser and analyzing light beams perpendicularly passed through a quartz cell with an optical path length of 10 mm. A monochromator (MC-30N, Ritsu Oyo Kogaku) equipped with a GDB 59 photomultiplier at the rear of the exit slit was used to analyze the absorption. The signals from the photomultiplier were displayed and recorded as a function of time on a Tektronix TDS 380 oscilloscope. Each datum point was obtained by a 256-time average to improve the signal-to-noise ratio. The transient absorption spectra were obtained from a series of oscilloscope traces measured with the same solution in a point-by-point manner with respect to the wavelength.



Scheme 1. Chemical structures of sensitizers and quenchers.

3. Results and discussions

3.1. Laser flash photolysis

Irradiation of 0.65 mM Ar-purged solutions of DMQ in MeCN by 266 nm laser pulses of a nanosecond laser flash photolysis system produced its transient absorption spectra, as shown in Fig. 1. The spectrum exhibits two distinct absorption bands centered at 365 and 430 nm after laser pulse. Fig. 2 presents the decay curves of the transient species and logarithmic plots of absorbance versus time for the decay curves at 365 and 430 nm. Though the o.d. of excited states differ significantly at each wavelength in Fig. 2a, the absorbance at 365 and 430 nm are nearly the same after deducting the ground state absorption intensity as shown in Fig. 1. The first-order decay with the similar rate about $2.0 \times 10^5\ s^{-1}$ measured at these two bands is independent of λ, indicating the presence of only one transient species. The two transient absorptions are assigned to the triplet states of DMQ. Support for this assignment is given by the fact that the absorption bands at λ, 365 and 430 nm are quenched intensively in the presence of dissolved oxygen, see Fig. 3. In order to further confirm this hypothesis, β-carotene was used in our experiment according to its lower triplet energy (E_T = 20.2 kcal/mol) than that of DMQ (E_T = 61.1 kcal/mol) and TMQ (E_T = 67.6 kcal/mol) [19]. Fig. 4 shows the transient absorption spectra observed after laser photolysis in the DMQ (0.67 mM)/β-carotene (0.12 mM) system in MeCN. Concomitant with the decay of the absorption bands at 365 and 430 nm, a transient at 520 nm is observed which is at-

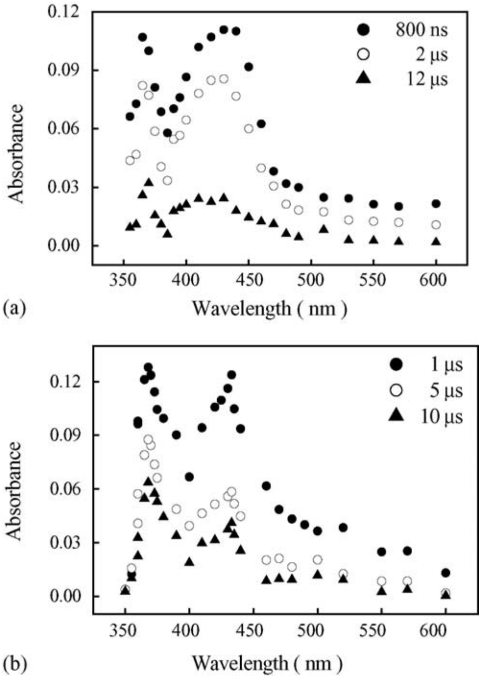


Fig. 1. Transient absorption spectra of two different quinoxaline derivatives in acetonitrile at different delayed time (**λ_{ex}** = 266 nm and a, b represents DMQ and TMQ, respectively).

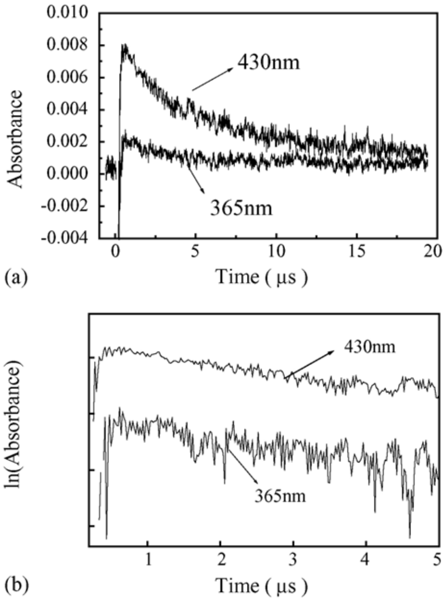


Fig. 2. (a) Time-resolved decay curves of triplet state of DMQ at 365 and 430 nm in acetonitrile after laser pulse. (b) Logarithmic plots of absorbance vs. time obtained of 0.65 mM DMQ.

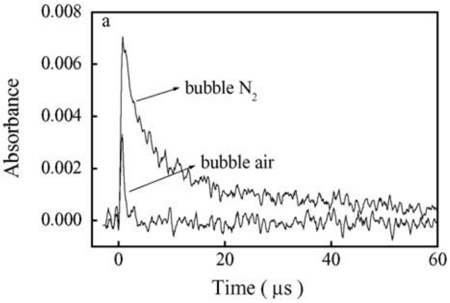


Fig. 3. Kinetic decay curves of the transient absorption at 430 nm for DMQ acetonitrile solution which has been purged with air or nitrogen for 20 min ([DMQ] = 0.57 mM).

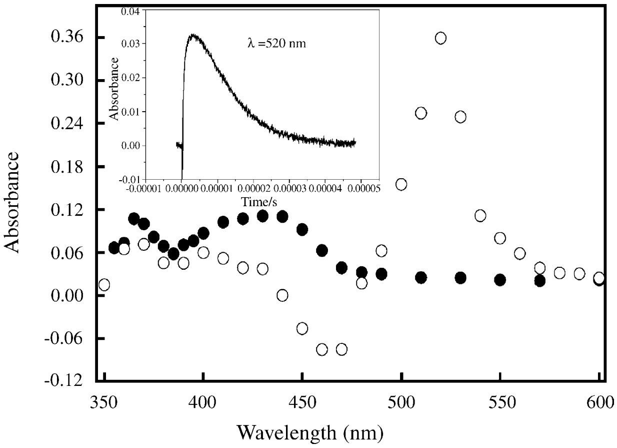


Fig. 4. Transient absorption spectra of 0.57 mM DMQ with 0.12 mM β-carotene (○) and without β-carotene(●) at 800 ns after laser pulse. Inset: growth of triplet state of β-carotene recorded at 520 nm.

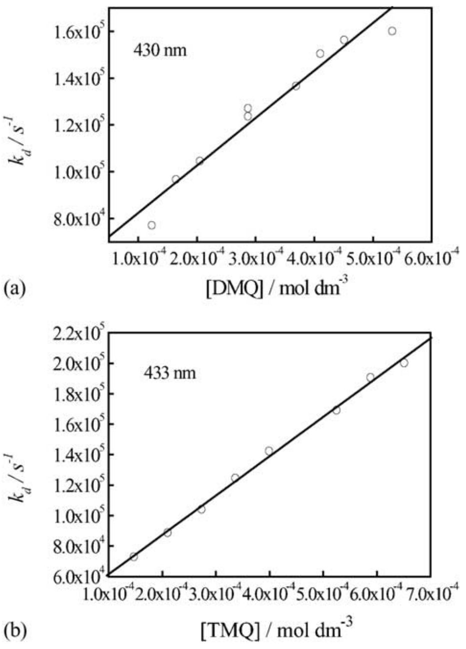


Fig. 5. Plot of apparent decay rate constants of DMQ (a) and TMQ (b) triplet state vs. the concentration of their ground states.

tributed to the triplet absorption of β-carotene [19]. The inset of Fig. 4 shows the concomitant growth of triplet state of β-carotene. Thus we conclude that the spectrum shown in Fig. 1 is mainly due to triplet DMQ. The first-order rate constants (k_{obs}) obtained for the decay of ^{3}DMQ* are plotted as a function of the concentration of its ground state (Fig. 5). The plots give a straight line, which is expressed by,

$$k_{obs} = k_0 + k_{sq}[\mathrm{DMQ}] \qquad (1)$$

where k_0 and k_{sq} represent the decay rate of ^{3}DMQ* at the infinitely diluted concentration and the self-quenching rate constant of ^{3}DMQ*, respectively. The k_{sq} value of DMQ is determined to be $2.03 \times 10^8\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ while the triplet lifetime τ_0 ($\tau_0 = 1/k_0$) is 16.1 μs.

In another experiment performed with TMQ at the same concentration of DMQ, the transient absorption of TMQ shown in Fig. 1b owns two similar peaks, which centered around 368 and 433 nm, were also attributed to the triplet states of the molecule identified by O_2 and β-carotene quenching. The k_{sq} value and triplet lifetime of ^{3}TMQ* are determined to be $2.58 \times 10^8\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and 28.0 μs, respectively. Other detailed kinetic parameters of ^{3}DMQ* and ^{3}TMQ* are listed in Table 1.

Table 1
Laser photolysis and other parameters of DMQ and TMQ

	λ_T (nm)	E_T (kcal/mol)	k_0 (10^4 s^{-1})	k_{sq} (10^8 M^{-1} s^{-1})	τ_0 (μs)
DMQ	365, 430	61.1	6.22 (430 nm)	2.03	16.1
TMQ	368, 433	67.6	3.58 (433 nm)	2.58	28.0

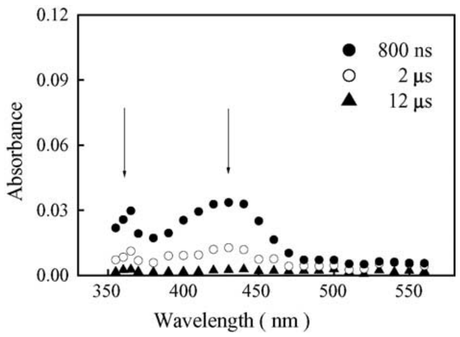


Fig. 6. Transient absorption spectra of DMQ in the presence of FN in N_2-purged acetonitrile at different delay time ([DMQ] = 0.5 mM, [FN] = 0.23 mM).

3.2. Quenching of ^{3}DMQ* (^{3}TMQ*) by electron-poor alkenes

Solutions containing both the sensitizer and electron-poor alkenes are subjected to pulsed laser irradiation at 266 nm where the sensitizer has strong absorption, but the alkenes do not absorb. In the presence of added electron-poor alkenes the lifetimes of ^{3}DMQ* and ^{3}TMQ* are shortened and the absorption still obeys pseudo-first-order kinetics while no new transient is detected between 350 and 750 nm. Fig. 6 displays the considerable decrease of absorption for DMQ in the presence of FN. Bimolecular rate constants k_q for the reactions of ^{3}DMQ* and ^{3}TMQ* with a variety of electron-poor alkenes are obtained according to

$$k_d = k_0 + k_{sq}[\mathrm{DMQ}] + k_q[\mathrm{alkene}] \qquad (2)$$

where k_d denote the decay rates of ^{3}DMQ* in the presence of different quenchers. All the k_q values range from FN ($2.50 \times 10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for DMQ and $1.77 \times 10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for TMQ) to CrN ($1.70 \times 10^5\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for DMQ and $1.20 \times 10^5\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for TMQ), as listed in Table 2. It is observed that all the k_q values of DMQ are always larger than those of TMQ.

In order to make a comparison, DMN was used as the third sensitizer. A similar phenomenon was detected from the quenching reactions between DMN and these alkenes. Six k_q values are also listed in Table 2 and they are successively from $3.63 \times 10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ (FN) to $1.30 \times 10^5\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ (CrN) according to the order from large to small. A marked difference is that the k_q values acquired from DMN are a little larger than the values of DMQ and TMQ (except for CrN, maybe caused by experimental error in very low rate constant).

The most likely explanation for above behavior is due to the displacement of two carbon atoms of benzene-like ring by nitrogen in quinoxaline molecules. As we all know that nitrogen atom is more electronegative than carbon atom. Though the whole benzene-like ring of each quinoxaline derivative is still conjugated, the electron cloud density of the whole ring in DMQ or TMQ is more dispersed than in DMN, which

Table 2
Quenching rate constants and free energy change for trilplet-alkene interactions

Substrate	DMN		DMQ		TMQ	
	k_q (M^{-1} s^{-1})	ΔG_{ct} (eV)[a]	k_q (M^{-1} s^{-1})	ΔG_{ct} (eV)	k_q (M^{-1} s^{-1})	ΔG_{ct} (eV)
Fumaronitrile	3.63×10^9	0.065	2.50×10^9	−0.155	1.77×10^9	−0.075
Dimethyl fumarate	2.83×10^8	0.295	9.64×10^7	0.075	5.38×10^7	0.155
Diethyl fumarate	2.14×10^8	0.345	7.57×10^7	0.215	4.62×10^7	0.205
α-Acetoxyacrylonitrile	3.32×10^7	(0.633)[b]	3.0×10^6	(0.746)[b]	2.10×10^6	(0.771)[b]
Acrylonitrile	1.48×10^6	0.915	7.05×10^5	0.785	4.22×10^5	0.775
Crotononitrile	1.30×10^5	1.545	1.70×10^5	1.325	1.20×10^5	1.405

[a] ΔG_{ct} for DMN was calculated from $\Delta G_{ct} = 23.06\,[E_{ox} - E_{red} - (q^2/\epsilon r)] - E_T$, where E_T of DMN is 58.8 kcal/mol (2.55 eV) [41] and E_{ox} of DMN is 1.35V vs. SCE [42].

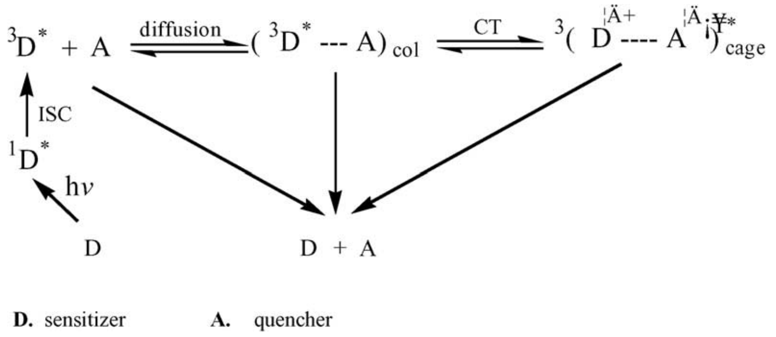
[b] ΔG_{ct} values in brackets for α-acetoxyacrylonitrile with three sensitizers were estimated from the plots in Fig. 9.

is disadvantageous to the formation of exciplex. The direct results of nitrogen atom-substitution for DMQ and TMQ are the slower k_q values obtained in quenching reactions. As to TMQ, the lower k_q values than that for DMQ is induced by two more methyl substituents that increase the steric hinderance.

It is well known that a collision complex (^{3}DMQ*-alkene)$_{col}$ could be formed right after the encounter of ^{3}DMQ* with alkene in the solvent. In general, this kind of collision complex would be produced to triplet ion pair ^{3}(DMQ$^{\bullet -}$-alkene$^{\bullet +}$)$_{cage}$ immediately after electron transfer in appropriate conditions. This electron transfer in the triplet state can efficiently produce the solvent-separated radical ion pair which can be easily detected in transient absorption spectrum [20]. Unfortunately, no new transient species are detected in the range from 350 to 800 nm, and NMR product studies show that irradiation of the mixture of DMQ (TMQ) and electron-poor alkenes formed no new chemical products. So we consider a triplet exciplex with weak charge-transfer (CT) character is created during the process. Iwata et al. have reported partial CT may intensify intersystem crossing (ISC) from the excited singlet to the triplet state [21], so CT character in the triplet state will enhance ISC from triplet to singlet without chemical reaction [22], resulting in the ground state of DMQ and alkene, as depicted in Scheme 2. Shizuka and co-workers have pointed out that in the collision complex of donor-acceptor pairs, charge-transfer interaction occurs to form an exciplex with weak CT character in the solvent cage [20]. In addition, thermodynamic results that will be discussed in detail in the next part also support this hypothesis.

Recent researches of exciplexes involving cyanoanthracenes and methylated bezenes have demonstrated a correlation between the magnitude of charge separation and redox potential of donor/acceptor molecules [23,24]. It is said that the percentage of charge transfer in the formation of exciplex increases with an increase in reduction potential of the acceptor [5]. In this study, the correlation between k_q values and reduction potential is absolute. We find that the quenching rate constant of FN is greater than other alkenes, which is consistent with its stronger ability to get electron ($E_{red} = -1.32$ V versus SCE). For other alkenes, owing to their lower k_q values, they should have weaker charge transfer ability than FN, especially for CrN ($E_{red} = -2.8$ V versus SCE). Fig. 7 shows a plot of quenching rate constants obtained from the reaction of ^{3}DMQ* and ^{3}TMQ* with alkenes. Good linear correlation between the two sets of data indicates the quenching mechanisms for these two sensitizers are the same [25].

The measured triplet energy of DMQ is 61.1 kcal/mol, which is a little larger than E_T values of FN (>59 kcal/mol) and AN (58 kcal/mol). As α,β-unsaturated nitriles, CrN and AAN have never been observed to phosphoresce, but their triplet energies are estimated from sensitization data to be 60–70 kcal/mol [26], so triplet-trilplet energy transfer (TET) process will be denied [27]. This is in accordance with the fact that we can't find any new absorption peaks in the transient spectra. The same phenomena were found for DMQ with DMF and DEF. As to TMQ, T–T energy transfer may



Scheme 2.

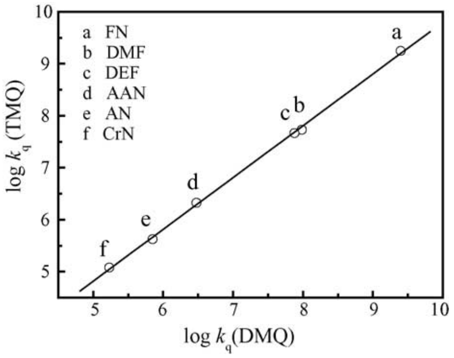


Fig. 7. Plot of correlation between quenching rate constants for triplet DMQ and TMQ by different alkenes.

be a possible deactivation process which would lead to triplet quenching. However, T–T absorption for these alkenes followed by energy transfer from triplet DMQ/TMQ are not observable under our experimental conditions. In addition, as the obtained quenching rate constants depend on the reduction potential of alkenes distinctively, the quenching of the excited molecules must be governed by CT interaction and triplet energy transfer is not a main process for the quenching.

3.3. Quenching rate constants: dependence on ΔG

In order to prove partial charge transfer mechanism for the reactions of quinoxaline derivatives and alkenes, we have determined k_q as a function of the free energy change ΔG_{ct}. The value of ΔG_{ct} (in kcal/mol) can be depicted [28]:

$$\Delta G_{ct} = 23.06[E_{ox} - E_{red} - (q^2/\epsilon r)] - E_T \qquad (3)$$

where E_{ox} (in V) and E_{red} (in V) are the oxidation potential of the donor and the reduction potential of the acceptor and E_T (in kcal/mol) is the triplet energy of the sensitizer. In our experiment, E_T values were determined to be 61.1 kcal/mol (2.65 eV) for DMQ and 67.6 kcal/mol (2.93 eV) for TMQ, respectively. The term $q^2/\epsilon r$ is the work term, which accounts for the coulombic energy of the product ions at the encounter distance ($q^2/\epsilon r = 0.055$ eV in acetonitrile). With the redox potential of alkenes, we can estimate the thermodynamic driving force easily. Generally speaking, photochemical electron transfer (ET) reactions occur only when the charge transfer step is either exergonic or <5 kcal/mol endergonic [29]. All of the free energy changes in Table 2 are positive (except for FN) which indicate that electron transfer is impossible according to Relm–Weller theory. Kikuchi et al. have shown that the deactivation mechanism for the photoexcited donor-acceptor pairs with positive ΔG_{ct} values in MeCN contains exciplex formation [30]. These thermodynamic results also support our exciplex formation conclusion. The ΔG_{ct} values with brackets in Table 2 merit attention. Because there was no available E_{red} value of AAN, the ΔG_{ct} of AAN cannot be calculated from Eq. (3). In fact, these values were estimated from the plots in Fig. 9 by using measured k_q data for all sensitizers. Then average E_{red} value for AAN was calculated according to Eq. (3) to be −2.09 V as listed in Table 3.

Table 3
Reduction potential, Hammet constants (σ) of electron poor-alkenes in acetonitrile

Substrate	E_{red} (V) vs. SCE	σ
Fumaronitrile	−1.32[a]	0.66 × 2
Dimethyl fumarate	−1.55[b]	0.45 × 2
Diethyl fumarate	−1.60[b]	0.45 × 2
α-Acetoxyacrylonitrile	(−2.09)[c]	(0.71)[e]
Acrylonitrile	−2.17[b]	0.66
Crotononitrile	−2.80[d]	0.66–0.17

[a] Ref. [43].
[b] Ref. [44].
[c] Approximation obtained from Eq. (3) as illustrated in text.
[d] Ref. [45].
[e] Approximation in brackets was obtained from the plots in Fig. 9.

It has been predicted that the k_q of ET shows a bell-shaped dependence on ΔG_{et} [31,32]. Relm and Weller denoted the log k_q should reach a plateau value corresponding to the diffusion rate constant (2×10^{10} M^{-1} s^{-1}) in the exergonic region while decreases sharply with a slope equal to 1/(2.3RT) in the endergonic region [33]. By introducing Marcus relationship, the slop of log k_q versus ΔG_{et} exhibits a unique inverted region in the highly exergonic region [31,32]. There is much controversy about the existence of such region [34]. The absence of Marcus inverted region in most photoinduced electron transfer reactions in solution may be due to several reasons (e.g. the existence of low-energy excited states of radical cations or others) that have been discussed for many years [35–37]. Fig. 8 demonstrates the correlation between k_q values (for DMQ) and ΔG_{ct}. The plot is reasonably linear with a slope of −2.75 eV^{-1} (r = 0.97) in the endergonic region. Similar results were determined to be −2.69 eV^{-1} (r = 0.95) for TMQ and −2.99 eV^{-1} (r = 0.98) for DMN. Generally speaking, a quenching process which involves essentially a full charge transfer display linear log k_q versus ΔG_{ct} with slope approaching −17 eV^{-1}, whereas processes involving only partial CT show shallower slopes [38,39]. Therefore, the slope of the line in Fig. 8 corresponds to only a small percentage of charge transfer in the quenching processes, which indicates a partial charge transfer complex formation.

In addition, we can also observe that k_q values obtained from reactions are in accordance with the electron cloud density (ECD) on the ethylene double bond. As to these alkenes, ECD is determined by those substituents which bind to two ends of ethylene. Hammett constants σ is often used to represent the electron withdrawing or releasing properties of various substituents. The electron-releasing substituents will have negative σ's and the electron-withdrawing substituents will have positive ones [19]. The σ's have been found to be very position dependent and para-value is compiled as σ_p. For example, σ_p for CN, CO_2CH_3 and $CO_2C_2H_5$ are 0.66, 0.45 and 0.45, respectively, and σ_p for H is 0.00, while CH_3 has a negative value −0.17 due to its electron-releasing property. According to these values in Table 3, FN has the largest σ

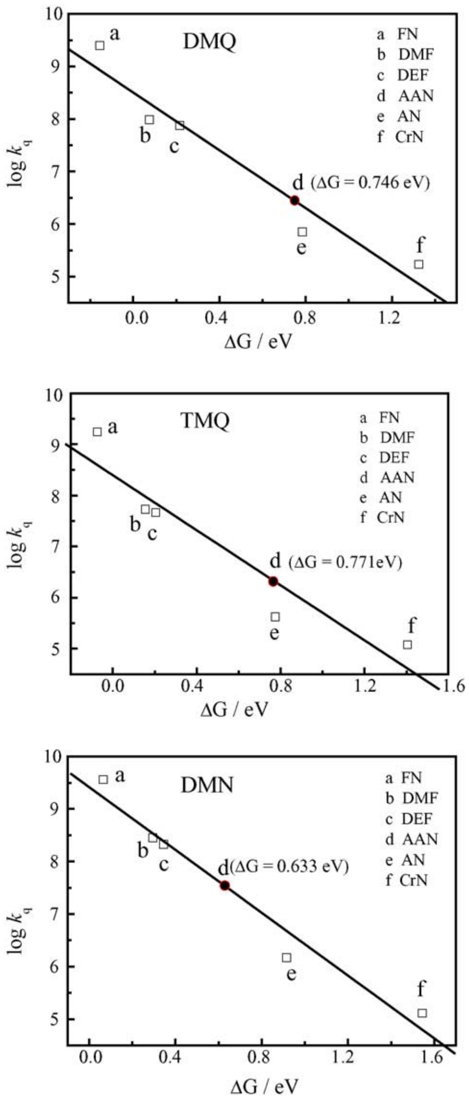


Fig. 8. Relm-Weller correlation plot of log k_q vs. ΔG for different alkenes.

value (0.66 + 0.66) and most rare ECD. So the k_q value of FN is also the largest one that is consistent with its reactivity. It is pointed out that there is a linear relation between σ and rate constant [19,40]. Indeed, Fig. 9 shows a good linear relation of measured log k_q with σ value in Table 2.

AAN is an exceptional case in our six quenchers. Two substitutes, CN and CO_2CH_3 are on the same carbon atom of ethylene double bond as shown in Scheme 1. Electronic effects of ortho-substituents are often swamped by steric hindrance and no available data for σ_0 can be used. Using measured k_q, the approximate σ value for AAN can be estimated from Fig. 9. Fortunately, the same σ value 0.71 was obtained from two systems of Fig. 9. If CN and CO_2CH_3 are in para position σ value should be 1.11(0.66 + 0.45), but due to the steric hindrance the σ value of AAN is decreased to 0.71. This value can be used as a reference.

At last, we can conclude from above that all the ΔG_{ct} and k_q values eventually depend only on electronic effects resulting from substitution on the alkenes. And no other than the substitution effect changes the exciplex-formation ability of these alkenes.

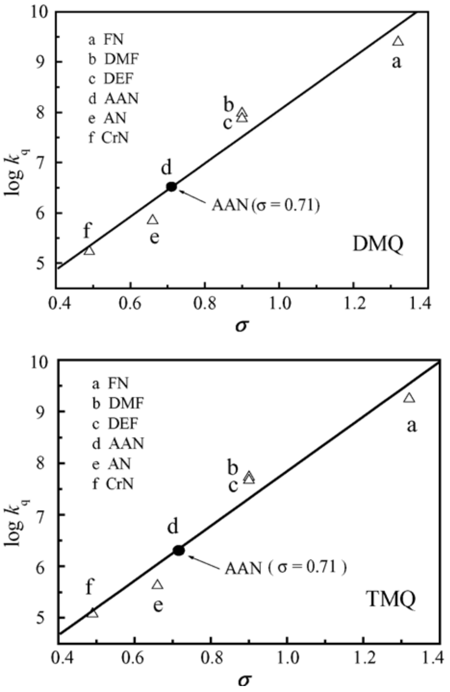


Fig. 9. Plot of log k_q vs. Hammett constants of each alkene (●) AAN.

4. Conclusion

In conclusion, the triplet states of two quinoxaline derivatives are generated and studied by laser flash photolysis. The quenching rate constants of the triplet DMQ and TMQ by electron-poor alkenes are measured. DMN is also introduced as a sensitizer for comparison. It is found that k_q values are controlled by reduction potential and ECD of these alkenes. The plots of log k_q versus the free energy change for some alkenes employed are linear with slopes of -2.75, -2.69 and $-2.99\,\mathrm{eV}^{-1}$ for DMQ, TMQ and DMN, respectively. The σ value 0.71 with ortho-substituents for AAN is estimated. The mechanism involving a triplet exciplex intermediate formation is determined for DMQ and TMQ with alkenes.

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