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Laser photolysis studies of electron transfer between triplet naphthoquinones and amines

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Abstract

Electron transfer between triplet naphthoquinones (^{3}Nap*; 1,4-naphthoquinone, 2-methyl-1,4-naphthoquinone and 2,3-dimethyl-1,4-naphthoquinone in the triplet state) and *N,N*-dimethylaniline (DMA) or triethylamine (TEA) in acetonitrile (MeCN) and a mixture of MeCN and H_2O (4:1, v/v) was studied by laser photolysis techniques at 295 K. By analysis of the transient absorption spectrum observed after the completion of electron transfer, the absorption spectra and coefficients of the naphthoquinone anion radicals (Nap$^{\bullet-}$) were determined on the basis of those of the DMA cation radical (DMA$^{\bullet+}$) in MeCN and MeCN–H_2O (4:1, v/v). The values of the rate constants (k_{et}) for electron transfer between ^{3}Nap* and DMA were found to be close to those for diffusion-controlled processes as predicted by the Rehm–Weller theory on electron transfer. Using the determined molar absorption coefficients of Nap$^{\bullet-}$, the efficiencies (Γ_{rad}) for the formation of Nap$^{\bullet-}$ and DMA$^{\bullet+}$ were shown to be unity since the radical ion pair produced (^{3}[Nap$^{\bullet-}$ + DMA$^{\bullet+}$]) readily dissociates into Nap$^{\bullet-}$ and DMA$^{\bullet+}$ due to the triplet spin multiplicity.

Keywords: Laser photolysis; Electron transfer; Triplet naphthoquinones; Amines

1. Introduction

Quinone compounds have been used as triplet electron acceptors in order to mimic and elucidate the mechanism of electron transfer in photosynthesis [1–11]. Bimolecular electron transfer between photoexcited benzoquinone, anthraquinone and their derivatives and amines has been investigated by laser flash photolysis [12,13]. Information on the absorption spectra and molar absorption coefficients of the anion radicals has enabled quantitative analysis to be performed in organic solvents. The absorption spectra and molar absorption coefficients of naphthoquinone anion radicals, produced unimolecularly by pulse radiolysis in aqueous solution, have been reported [14–17]. However, little research on the bimolecular electron transfer of triplet naphthoquinones in organic solvents has been reported using laser flash photolysis because of a lack of information on the absorption spectra and coefficients of naphthoquinone anion radicals in solvents such as acetonitrile or carbon tetrachloride, which are inert with regard to hydrogen atom abstraction of triplet naphthoquinones (see Ref. [18]).

In this work, laser flash photolysis studies of electron transfer in the naphthoquinone–amine system were carried out to determine the absorption spectra and coefficients of naphthoquinone anion radicals in acetonitrile and a mixture of acetonitrile and water. The mechanism of electron transfer in the above system is discussed in detail in terms of the quantum yields of formation of the corresponding anion and cation radicals.

2. Experimental details

1,4-Naphthoquinone (NQ) (Wako), 2-methyl-1,4-naphthoquinone (MNQ) (Wako) and 2,3-dimethyl-1,4-naphthoquinone (DMNQ) (Eisai Chemical Co., Ltd.) were purified by passing through a silica gel column with benzene. Triethylamine (TEA) and *N,N*-dimethylaniline (DMA) were purified by distillation in vacuo. Benzophenone was sublimated in vacuo. Acetonitrile (MeCN) and deionized water were purified by distillation. MeCN and its mixture with water (MeCN–H_2O (4:1, v/v)) were used as solvents.

All samples were degassed by freeze–pump–thaw cycles on a high vacuum system in a quartz cell (path length, 10 mm). The transient spectral data were obtained at 295 K.

A nanosecond Nd^{3+}:YAG laser system at 355 nm (JK Lasers HY-500; pulse width, 8 ns; laser power, 40 mJ per pulse at 355 nm) was employed for sample excitation. The

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Table 1
Quantum yields of intersystem crossing (Φ_{isc}), triplet energies (E_T) and reduction potentials (E_{red}) of NQ, MNQ and DMNQ

Naphthoquinone	Φ_{isc} [a]	E_T (kcal mol^{-1}) [b]	E_{red} (V) [c]
NQ	0.74 [d]	57.3	−0.71 [e]
MNQ	0.86 [f]	57.2	−0.77 [e]
DMNQ	0.98 [d]	50.8	−0.82 [g]

[a] Determined in MeCN by the thermal lensing method at 295 K [20]. Error, ±2%.

[b] Determined from the 0–0 band of the phosphorescence spectrum in methanol–ethanol (1:1, v/v) glass at 77 K.

[c] Vs. saturated calomel electrode (SCE) in MeCN.

[d] From Ref. [20].

[e] From Ref. [21]

[f] From Ref. [22].

[g] Corrected data from Ref. [15].

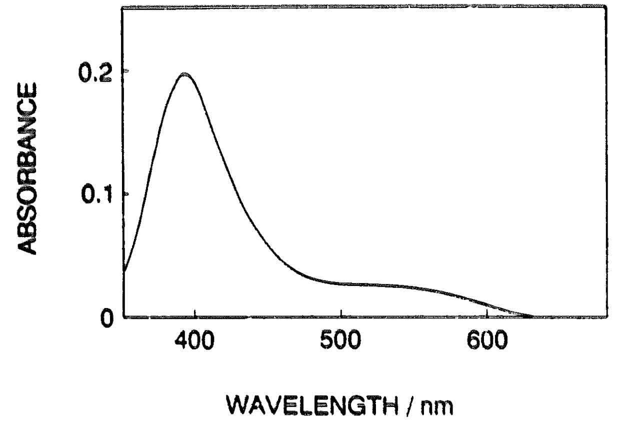

Fig. 1. Transient absorption spectrum obtained 120 ns after the 355 nm laser pulse in the system containing NQ (6.0×10^{-4} M) and TEA (5.0×10^{-3} M) in MeCN–H_2O (4:1, v/v).

detection system for the time profiles of transient absorption has been described elsewhere [19]. The transient absorption spectra were taken using a UPS-600 system (Unisoku), which afforded a transient spectrum with a one-shot laser pulse.

The quantum yields of intersystem crossing (Φ_{isc}), triplet energies (E_T) and reduction potentials (E_{red}) of the naphthoquinones used are listed in Table 1.

3. Results and discussion

3.1. Determination of the absorption spectra and coefficients of naphthoquinone anion radicals in MeCN and MeCN–H_2O (4:1, v/v)

It has been reported by the chemically induced dynamic electron polarization (CIDEP) method that triplet NQ ($^3NQ^*$) is reactive for electron transfer with TEA to produce the naphthoquinone anion radical ($NQ^{\bullet -}$) [23]. However, transient observations for this system have not been performed. Therefore the transient absorption spectrum for the NQ–TEA system was elucidated by nanosecond laser photolysis.

Previously [20], it has been reported that the triplet–triplet (T–T) absorption of NQ with a peak at 365 nm appears after nanosecond laser photolysis in MeCN solution. When 355 nm laser photolysis was carried out in the system containing NQ (6.0×10^{-4} M) and TEA (5.0×10^{-3} M) in MeCN–H_2O (4:1, v/v), a transient absorption spectrum with a peak at 393 nm (Fig. 1) was obtained after depletion of $^3NQ^*$ at 120 ns. As mentioned above, the reaction between $^3NQ^*$ and TEA involves electron transfer. Therefore the absorption spectrum in Fig. 1 can be assigned to $NQ^{\bullet -}$ since no absorbance of the TEA cation radical is observed in the long-wavelength region ($\lambda > 350$ nm). The absorption spectrum of $NQ^{\bullet -}$, obtained by electron transfer in MeCN–H_2O (4:1, v/v), resembles those reported previously by pulse radiolysis (absorption maxima at 390 nm in aqueous solutions [15,16] and 380 nm in methanol [17]).

In order to determine the molar absorption coefficient of $NQ^{\bullet -}$, DMA was employed as electron donor since the absorption spectrum of its cation radical is well known [24]. Fig. 2(a) shows the time-resolved transient absorption spectra obtained by 355 nm laser photolysis of the system containing NQ (6.0×10^{-4} M) and DMA (3.0×10^{-4} M) in MeCN–H_2O (4:1, v/v). The absorption spectrum at 50 ns with a peak at 365 nm can be assigned to $^3NQ^*$ [20]. With time, the T–T absorption spectrum of NQ decays with a first-order rate constant (7.5×10^{6} s^{-1}) with an isosbestic point at 370 nm, and a new absorption spectrum with peaks at approximately 390 and 465 nm appears with the same first-order rate as that for the decay of $^3NQ^*$. The absorption

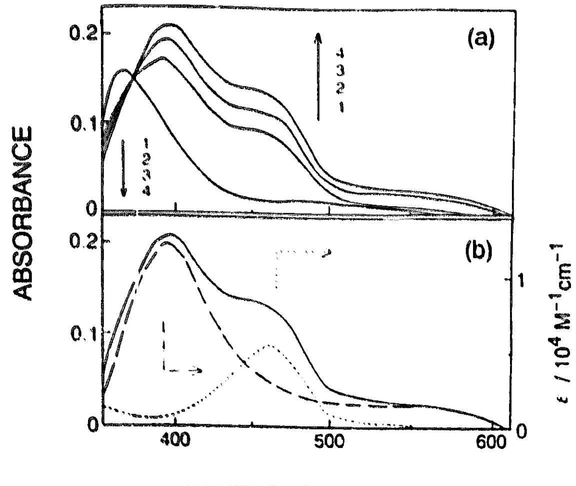

Fig. 2. (a) Time-resolved transient absorption spectra obtained at (1) 50, (2) 120, (3) 250 and (4) 450 ns after 355 nm laser photolysis in the system containing NQ (6.0×10^{-4} M) and DMA (3.0×10^{-4} M) in MeCN–H_2O (4:1, v/v). (b) The transient absorption spectrum obtained 450 ns after the 355 nm laser pulse in the system containing NQ (6.0×10^{-4} M) and DMA (3.0×10^{-4} M) in MeCN–H_2O (4:1, v/v) (full line); analysed absorption spectra of $NQ^{\bullet -}$ (broken line) and $DMA^{\bullet +}$ (dotted line) in MeCN–H_2O (4:1, v/v).

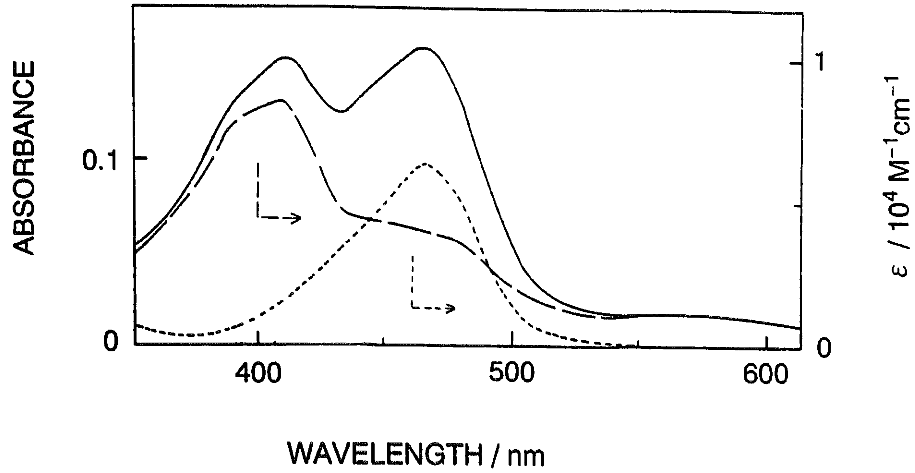

Fig. 3. Transient absorption spectrum obtained 360 ns after 355 nm laser photolysis in the system containing NQ (6.0×10^{-4} M) and DMA (3.0×10^{-4} M) in MeCN (full line); analysed absorption spectra of $NQ^{\bullet-}$ (broken line) and $DMA^{\bullet+}$ (dotted line) in MeCN.

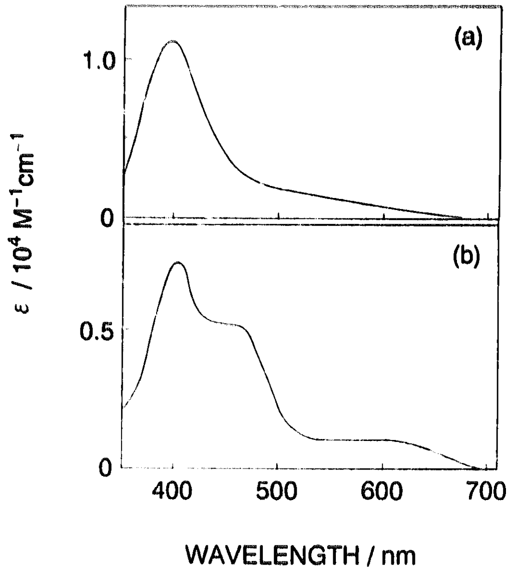

Fig. 4. Absorption spectra of $MNQ^{\bullet-}$ obtained by laser photolysis in the system containing MNQ (7.0×10^{-4} M) and DMA (1.2×10^{-3} M): (a) at 160 ns in MeCN–H_2O (4:1, v/v); (b) at 110 ns in MeCN (see text for details.

spectrum at 450 ns is shown in Fig. 2(b). This absorption spectrum can be reproduced by those of $NQ^{\bullet-}$ and the DMA cation radical ($DMA^{\bullet+}$) (shown in Fig. 2(b)) with a concentration ratio of 1:1. Therefore the spectral changes in Fig. 2(a) can be attributed to electron transfer from DMA to $^3NQ^*$ to form $NQ^{\bullet-}$ and $DMA^{\bullet+}$. On the basis of the molar absorption coefficient (ϵ) of $DMA^{\bullet+}$ (5500 M^{-1} cm^{-1} at 465 nm in MeCN–H_2O (4:1, v/v) [25]), the ϵ value of $NQ^{\bullet-}$ in MeCN–H_2O (4:1, v/v) was determined to be 12 200 ± 400 M^{-1} cm^{-1} at 393 nm, which is consistent with that reported previously (12 500 M^{-1} cm^{-1} at 390 nm) in aqueous solution [15,16].

The absorption spectrum and ϵ value of $NQ^{\bullet-}$ in neat MeCN are different from those in MeCN–H_2O (4:1, v/v). Fig. 3 shows the transient absorption spectrum obtained by 355 nm laser photolysis of the system containing NQ (6.0×10^{-4} M) and DMA (3.0×10^{-4} M) in MeCN at 360 ns after $^3NQ^*$ has been completely quenched by electron transfer. This spectrum was also reproduced by those of $DMA^{\bullet+}$ and $NQ^{\bullet-}$ in MeCN with a concentration ratio of 1:1. Separately, the absorption spectrum of $NQ^{\bullet-}$ in MeCN was obtained by laser photolysis of the NQ–TEA system in MeCN. On the basis of the ϵ value of $DMA^{\bullet+}$ (6300 M^{-1} cm^{-1} at 465 nm in MeCN [25]), that of $NQ^{\bullet-}$ in MeCN was determined to be 8500 ± 200 M^{-1} cm^{-1} at 408 nm. The same method was applied to MNQ and DMNQ for the determination of the absorption spectra and coefficients of the corresponding naphthoquinone anion radicals in MeCN–H_2O (4:1, v/v) and MeCN. The data obtained are shown in Figs. 4 and 5 and listed in Table 2. The absorption spectra of the

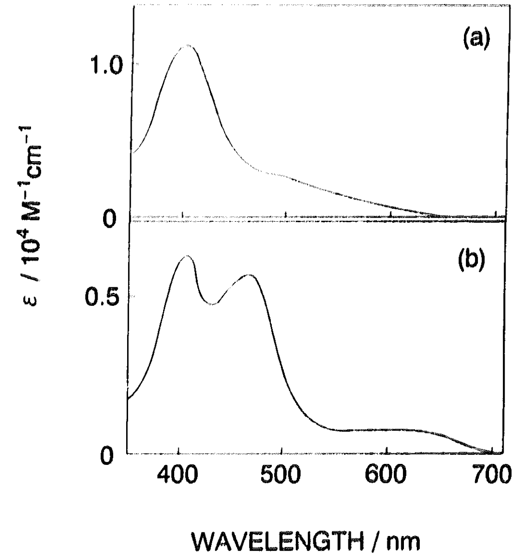

Fig. 5. Absorption spectra of $DMNQ^{\bullet-}$ obtained by laser photolysis in the system containing DMNQ (7.0×10^{-4} M) and DMA (1.5×10^{-3} M): (a) at 220 ns in MeCN–H_2O (4:1, v/v); (b) at 200 ns in MeCN (see text for details).

Table 2
Molar absorption coefficients of the naphthoquinone anion radicals at the absorption peaks [a,b]

Solvent	$NQ^{\cdot -}$	$MNQ^{\cdot -}$	$DMNQ^{\cdot -}$
MeCN–H_2O (4:1, v/v)	12200 (393 nm)	12800 (398 nm)	12200 (400 nm)
MeCN	8500 (408 nm)	7500 (403 nm)	6200 (405 nm)

[a] Error, ±5%. Unit, M^{-1} cm^{-1}.
[b] See text for details.

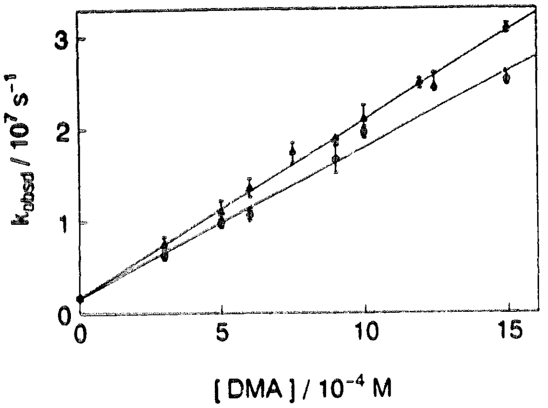

Fig. 6. Plots of the decay rate (k_{obsd}) of $^3NQ^*$ observed after 355 nm laser photolysis in the system containing NQ (6.0×10^{-4} M) and DMA in MeCN–H_2O (4:1, v/v) (○) and MeCN (▵) as a function of [DMA].

naphthoquinone anion radicals ($Nap^{\cdot -}$) determined in MeCN–H_2O (4:1, v/v) are different from those in neat MeCN, where all anion radicals have absorption shoulders around 480 nm. Since the absorption spectrum of $NQ^{\cdot -}$ in MeCN–H_2O (4:1, v/v) resembles those in methanol and aqueous solution [15–17], the different absorption spectrum of $Nap^{\cdot -}$ in neat MeCN may originate from solvation by hydrogen bonding of the solvent molecules to $Nap^{\cdot -}$. In solvents with a hydroxyl group, the absorption spectrum of $Nap^{\cdot -}$ gives only one peak around 400 nm. The absorption spectrum of $Nap^{\cdot -}$ depends on the solvent properties.

3.2. Mechanism and efficiency of formation of naphthoquinone anion radicals

In order to determine the quenching mechanism of triplet naphthoquinones ($^3Nap^*$) by DMA, the decay rate (k_{obsd}) of $^3Nap^*$ and the quantum yields (Φ_{rad}) of formation of $Nap^{\cdot -}$ and $DMA^{\cdot +}$ were measured as a function of [DMA].

Fig. 6 shows plots of k_{obsd} vs. [DMA] obtained for the system containing NQ (6.0×10^{-4} M) and DMA in MeCN–H_2O (4:1, v/v) and MeCN. Since both plots show a straight line, k_{obsd} can be expressed by

$$k_{obsd} = k_0 + k_q[DMA] \qquad (1)$$

where k_0 and k_q are the decay rate constant of $^3NQ^*$ in the absence of DMA and the quenching rate constant of $^3NQ^*$ by DMA. From the slope and intercept of the line, the values of k_0 and k_q were determined to be 1.7×10^6 s^{-1} and 1.9×10^{10} M^{-1} s^{-1} in MeCN and 1.7×10^6 s^{-1} and 1.6×10^{10} M^{-1} s^{-1} in MeCN–H_2O (4:1, v/v) respectively. For MNQ–DMA and DMNQ–DMA systems in MeCN and MeCN–H_2O (4:1, v/v), the k_q values were determined by the same method and the results are listed in Table 3. Since the k_q values obtained are close to the diffusion limit (1.9×10^{10} M^{-1} s^{-1} in MeCN at 25 °C [26]), the quenching of $^3Nap^*$ by DMA occurs by a diffusion process.

The quantum yields (Φ_{rad}) for the formation of $Nap^{\cdot -}$ and $DMA^{\cdot +}$ were obtained as follows. The Φ_{rad} values can be defined by Eq. (2) since $Nap^{\cdot -}$ and $DMA^{\cdot +}$ were found to be formed in a concentration ratio of 1:1

$$\Phi_{rad} = [Nap^{\cdot -}]I_{abs}^{-1} = [DMA^{\cdot +}]I_{abs}^{-1} \qquad (2)$$

I_{abs} represents the photon flux absorbed from the incident laser pulse by the naphthoquinones in the ground state. I_{abs} was determined using the T–T absorption of benzophenone in MeCN as an actinometer [27]. The concentrations of $Nap^{\cdot -}$ and $DMA^{\cdot +}$ were determined using Eq. (3) by measuring the maximum absorbance at the peak wavelength λ

$$[Nap^{\cdot -}] = [DMA^{\cdot +}] = OD_\lambda(\epsilon_\lambda^{-} + \epsilon_\lambda^{+})^{-1} \qquad (3)$$

where OD_λ is the absorbance at λ after depletion of $^3Nap^*$ and ϵ_λ^- and ϵ_λ^+ are the molar absorption coefficients of $Nap^{\cdot -}$ and $DMA^{\cdot +}$ at λ respectively. These values can be read from Figs. 2(b), 3, 4 and 5. Typical time traces for obtaining OD_λ are shown in Fig. 7 for the NQ–DMA system in MeCN–H_2O (4:1, v/v). For this case, ϵ_λ^- and ϵ_λ^+ are 12 200 and 500 M^{-1} cm^{-1} at 393 nm and 2600 and 5500

Table 3
Rate constants of decay of $^3Nap^*$ in the absence of DMA (k_0) and quenching by DMA (k_q), efficiencies (Γ_{rad}) and rate constants (k_{et}) of electron transfer of triplet naphthoquinones [a]

Naphthoquinone	MeCN–H_2O (4:1, v/v)				MeCN			
	k_0 [b] (10_5 s^{-1})	k_q [c] (10^{10} M^{-1} s^{-1})	Γ_{rad}	k_{et} [d] (10^{10} M^{-1} s^{-1})	k_0 [b] (10^5 s^{-1})	k_q [c] (10^{10} M^{-1} s^{-1})	Γ_{rad}	k_{et} [d] (10^{10} M^{-1} s^{-1})
NQ	17	1.6	1.0	1.6	17	1.9	1.0	1.9
MNQ	26	1.4	1.0	1.4	20	1.7	1.0	1.7
DMNQ	0.63	1.5	1.0	1.5	0.90	1.8	1.0	1.8

[a] Errors within ±5%.
[b] Determined from the intercept of the plots of k_{obsd} vs. [DMA] (see text for details).
[c] Determined from the slope of the plots of k_{obsd} vs. [DMA] (see text for details).
[d] Determined by Eq. (5) (see text for details).

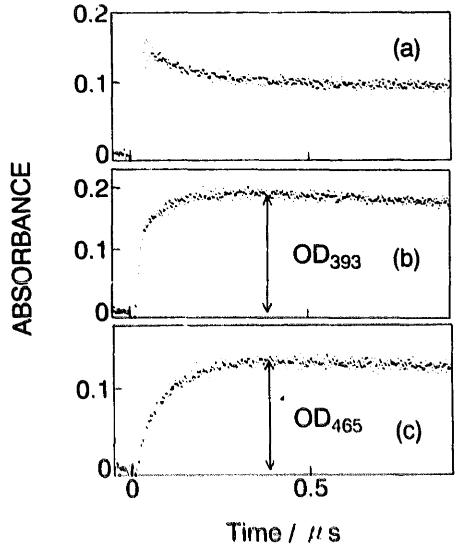

Fig. 7. Time profiles of the absorbance change observed after 355 nm laser photolysis of the system containing NQ (6.0×10^{-4} M) and DMA (5.0×10^{-4} M) in MeCN–H_2O (4:1, v/v) at (a) 365, (b) 393 and (c) 465 nm.

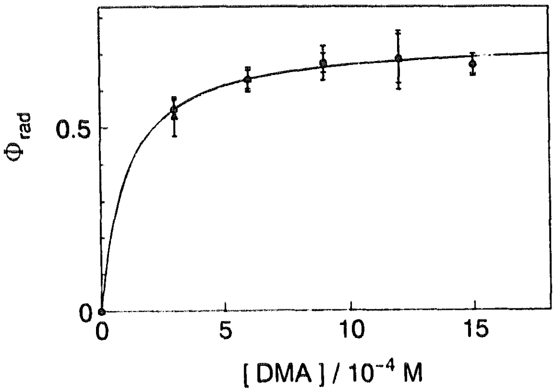

Fig. 8. Plots of the quantum yield (Φ_{rad}) of formation of $NQ^{\bullet -}$ and $DMA^{\bullet +}$ obtained at 393 nm (O) and 465 nm (△) for the system containing NQ (6.0×10^{-4} M) and DMA in MeCN – H_2O (4:1, v/v). The full curve was calculated using Eq. (4). See text for details.

M^{-1} cm^{-1} at 465 nm. Using Eqs. (2) and (3), the Φ_{rad} values were obtained experimentally. For example, Fig. 8 shows plots of Φ_{rad} vs. [DMA] for the NQ–DMA system in MeCN–H_2O (4:1, v/v). At each [DMA] value, the Φ_{rad} value obtained at 393 nm is in agreement with that at 465 nm within experimental error, and with increasing [DMA], they show a non-linear increase. On the basis of the Φ_{rad} values obtained experimentally, the efficiencies (Γ_{rad}) for the formation of $Nap^{\bullet -}$ and $DMA^{\bullet +}$ by electron transfer between $^3Nap^*$ and DMA can be calculated according to

$$\Phi_{rad} = k_q[DMA]\Gamma_{rad}\Phi_{isc}(k_0 + k_q[DMA])^{-1} \qquad (4)$$

where Φ_{isc} is the quantum yield of naphthoquinone intersystem crossing (Table 1). By best fitting of Eq. (4) to the experimental Φ_{rad} values, for example for the NQ–DMA system in MeCN–H_2O (4:1, v/v), using k_0 (1.7×10^6 s^{-1}), k_q (1.6×10^{10} M^{-1} s^{-1}) and Φ_{isc} (0.74), the Γ_{rad} value was determined to be unity. The full curve in Fig. 8 was calculated using Eq. (4) with $\Gamma_{rad} = 1$. For the MNQ–DMA and DMNQ–DMA systems in MeCN and MeCN–H_2O (4:1, v/v), the value of Γ_{rad} was unity as listed in Table 3. The reason for such a large efficiency can be explained by the spin multiplicity. As stated above, $^3Nap^*$ is quenched by DMA via collisions during which electron transfer takes place. Immediately after the completion of electron transfer from DMA to $^3Nap^*$, a triplet radical ion pair ($^3[Nap^{\bullet -} + DMA^{\bullet +}]$) is formed within a solvent cage according to the spin conversion rule. However, since back electron transfer is difficult due to the triplet spin multiplicity, the triplet radical ion pair readily dissociates into $Nap^{\bullet -}$ and $DMA^{\bullet +}$ by solvation, resulting in a high efficiency.

The rate constant for electron transfer (k_{et}) from DMA to $^3Nap^*$ to form the radical ions $Nap^{\bullet -}$ and $DMA^{\bullet +}$ is related to k_q and Γ_{rad} by

$$k_{et} = \Gamma_{rad}k_q \qquad (5)$$

Since the Γ_{rad} value is unity for all cases in the present work, the k_{et} values are equal to those of k_q. From these results, it can be concluded that the quenching process of $^3Nap^*$ by DMA occurs solely by electron transfer. These large values of k_{et} may be interpreted in terms of the Rehm–Weller behaviour of photoinduced intermolecular electron transfer reactions [28,29]. The free energy change (ΔG_{et} in kcal mol^{-1}) for electron transfer of the present system can be given by

$$\Delta G_{et} = 23.06(E_{ox} - E_{red}) - E_T - E_c \qquad (6)$$

where E_{ox} and E_{red} are the oxidation potential of DMA (0.81 V vs. SCE in MeCN [30]) and the reduction potentials of the naphthoquinones (see Table 1) respectively and E_T and E_c are the triplet energies of the naphthoquinones and the coulombic potentials in MeCN (1.4 kcal mol^{-1} [31]) and MeCN–H_2O (4:1, v/v) respectively. Using Eq. (6), the ΔG_{et} values were calculated to be sufficiently negative (−23.6, −22.2 and −14.6 kcal mol^{-1} for NQ, MNQ and DMNQ in MeCN respectively) to give $k_{et} = 10^{10}$ M^{-1} s^{-1} according to the Rehm–Weller behaviour [28]. It seems that, for the present case, the observed photoinduced electron transfer reactions do not follow Marcus behaviour [29,32], since the calculated ΔG_{et} values are located in the so-called inverted region where k_{et} is predicted to be less than 10^{10} M^{-1} s^{-1} according to Marcus theory [32].

4. Conclusions

The following results have been obtained from laser photolysis studies of the electron transfer from DMA or TEA to $^3Nap^*$: (1) the absorption spectra and coefficients of $Nap^{\bullet -}$ have been determined in MeCN–H_2O (4:1, v/v) and MeCN (Figs. 2(b), 3, 4 and 5; Table 2); (2) the k_{et} values listed in Table 3 are close to the diffusion limit; (3) the Γ_{rad} values are unity due to the triplet spin multiplicity.

Acknowledgements

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