

## Excited-state dynamics for interpretation of the solvent-dependent photochemistry of 9,10-dichloroanthracene in the presence of 2,5-dimethylhexa-2,4-diene

Toshihiro Nakayama\*, Tetsuhiko Nagahara, Sadao Miki, Kumao Hamanoue<sup>1</sup>

Department of Chemistry, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

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### Abstract

In connection with quenching of the lowest excited singlet state of 9,10-dichloroanthracene (DCA) by ground-state 2,5-dimethylhexa-2,4-diene (DMHD), measurements of the fluorescence spectra reveal formation of an exciplex ((DCA–DMHD)<sup>\*</sup>) irrespective of the dielectric constant ( $\epsilon$ ) of a solvent. By means of subpicosecond and nanosecond laser photolysis as well as steady-state photolysis, however, the following results are obtained: (a) in acetonitrile, methanol or acetone, decomposition of (DCA–DMHD)<sup>\*</sup> generates the DCA radical anion (DCA<sup>•-</sup>) as an intermediate for the formation of 9-chloroanthracene (CA), but its rate ( $v$ ) decreases in the order of  $v(\text{acetonitrile}, \epsilon=37.5) > v(\text{acetone}, \epsilon=20.7) > v(\text{methanol}, \epsilon=32.7)$ ; (b) in 1-octanol ( $\epsilon=10.3$ ), diethyl ether ( $\epsilon=4.34$ ) or heptane ( $\epsilon=1.92$ ), decomposition of (DCA–DMHD)<sup>\*</sup> generates an open-form transient (OFT, i.e. a ground-state singlet biradical or its zwitterionic form (ZIF)) as an intermediate for formation of the [4+2] adduct; (c) in ethanol ( $\epsilon=24.6$ ) or 2-propanol ( $\epsilon=19.9$ ), not only OFT (major) but also DCA<sup>•-</sup> (minor) are generated from (DCA–DMHD)<sup>\*</sup> and formation of two compounds (the [4+2] adduct and CA) in ethanol (or only the former compound in 2-propanol) can be seen. We thus conclude that not only the dielectric constant of a solvent but also its hydrogen-bonding ability affects the photochemistry of DCA originating from (DCA–DMHD)<sup>\*</sup>. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Excited state; 9,10-Dichloroanthracene; 2,5-Dimethylhexa-2,4-diene

### 1. Introduction

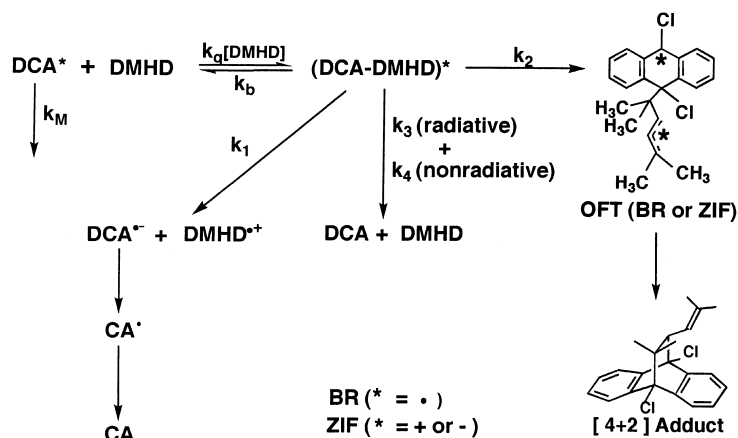
For photoinduced and amine-assisted dehalogenation of aromatic halocompounds, their radical anions (generated by decomposition of the exciplexes formed between the lowest excited singlet states of halocompounds and ground-state amine) were generally proposed to be the intermediates [1–10]. For 9,10-dichloroanthracene (DCA) in the presence of amine (*N,N*-dimethylaniline), however, Soloveichik et al. [11] reported that not the DCA radical anion (generated by decomposition of the singlet DCA–amine exciplex) but the triplet DCA–amine exciplex participated in DCA→9-chloroanthracene (CA) dechlorination. In order to contest this conclusion, we performed picosecond and nanosecond laser photolysis as well as steady-state photolysis of *meso*-substituted haloanthracenes (the 9-chloro, 9,10-dichloro, 9-bromo and 9,10-dibromo compounds) in several solvents containing amine (triethyl-

amine or *N,N*-dimethylaniline) [12–15]. Our conclusion was that quenching of the lowest excited singlet states of haloanthracenes by ground-state amine gave rise to formation of the exciplexes or the encounter complexes (or the ion pairs) depending on the nature of solvents, but decomposition of these unstable complexes really generated the haloanthracene radical anions as the intermediates for dehalogenation of haloanthracenes yielding 9-haloanthracenes (or anthracene).

As an extension of our study on the photoinduced molecular association [12–19], the present paper deals with the excited-state dynamics for interpretation of the solvent-dependent photochemistry of DCA in the presence of 2,5-dimethylhexa-2,4-diene (DMHD). Although quenching of the lowest excited singlet state of DCA by ground-state DMHD gives rise to formation of a DCA–DMHD exciplex irrespective of the dielectric constant of a solvent, decomposition of a DCA–DMHD exciplex generating the DCA radical anion or an open-form transient (OFT) (a ground-state singlet biradical or its zwitterionic form (ZIF)) as an intermediate for formation of CA or the

\* Corresponding author.

<sup>1</sup> Co-corresponding author.



Scheme 1.

[4+2] adduct, respectively, is dependent on a choice of the solvent (cf. Scheme 1), i.e. not only the dielectric constant of a solvent but also its hydrogen-bonding ability affects the photochemistry of DCA originating from a DCA–DMHD exciplex. For DCA in acetonitrile–DMHD, Saltiel et al. [20,21] reported formation of a DCA–DMHD exciplex (by direct excitation of a ground-state DCA–DMHD complex) or a DCA–DMHD triplex (by reaction of a DCA–DMHD exciplex with DMHD) as well as protonation of the DCA radical anion by the DMHD radical cation yielding CA finally. No such things, however, have been found in the present study.

## 2. Experimental details

DCA (Aldrich) was recrystallized three times from ethanol and DMHD (Aldrich) was distilled immediately before use. The solvents used were spectral-grade ones (acetonitrile (Dojin), acetone (Dojin), methanol (Dojin), ethanol (Nacalai), 2-propanol (Dojin) and heptane (Dojin)), diethyl ether (Merck) and distilled GR-grade 1-octanol (Wako); although heptane and diethyl ether were used without further purification, all the other solvents were dried using molecular sieves 4A (Wako). All experiments were performed at room temperature and the sample solutions used for subpicosecond laser photolysis in a flow cell of 2 mm path length were deoxygenated by bubbling of Ar gas, while those used for nanosecond laser photolysis and steady-state photolysis in a cell of 10 mm path length were degassed by several freeze-pump-thaw cycles.

The fluorescence spectra were recorded using a Hitachi MPF-4 spectrofluorometer, and only in the absence of DMHD, the fluorescence lifetimes were determined by a single-photon-counting method using the second harmonic (400 nm) from a picosecond Ti:sapphire laser [22]. For subpicosecond laser photolysis, the second harmonic (400 nm) from a femtosecond Ti:sapphire oscillator (Tsunami, model 3960) equipped with a regenerative amplifier (model

TSA-50) was used for sample excitation and the transient absorption spectra were recorded by a pump-probe method using the probing (and reference) light pulses generated by focusing the fundamental (800 nm) into water [23]. The former light pulse (after passing through the sample cell) and the latter light pulse were imaged separately onto the entrance slits of the corresponding polychromator-image sensor detector systems. After then, the 30-times accumulated intensity spectra of the probing and reference light pulses were recorded at various delay-line settings for calculation of the transient absorption spectra corrected for the group velocity dispersion of the probing light pulse. By 620 nm absorbance measurements of the singlet–singlet absorptions due to the lowest excited singlet state of 9,10-dibromoanthracene (DBA) in cyclohexane at various delay-line settings, the time-zero point and the instrumental time constant (0.25 ps) were determined, i.e. a Gaussian function with a full width at the half-maximum intensity (FWHM) of 0.25 ps was assumed for both the excitation and probing light pulses.

Nanosecond laser photolysis was carried out using a Nd<sup>3+</sup>:YAG laser (Continuum Surelight I). The excitation light pulse was the third harmonic (355 nm) with FWHM=5 ns and the transient absorption spectra were recorded using a multichannel analyzer [24]. The decay curves of transient absorptions were analyzed by means of a combination of a photomultiplier (Hamamatsu R636-10) with a storage oscilloscope (Iwatsu TS-8123), and the transient photocurrents were measured by the method reported previously [18].

In order to find out the overall solvent-dependent photochemistry of DCA in the presence of DMHD, steady-state photolysis was performed using the 404.6 nm monochromatic light selected from a USH-500D super-high-pressure mercury lamp and the absorption spectral change during photolysis was recorded using a Hitachi 200-20 spectrophotometer. The photoproduct that was different from CA was separated by thin-layer chromatography using a silica gel plate (Merck) and a mixed solvent

(hexane/dichloromethane=4:1 in volume ratio) as a developer, and then analyzed using a GE QE-300  $^1\text{H-NMR}$  spectrometer and Wako NMR-grade  $^2\text{H}$ -chloroform as the solvent.

### 3. Results and discussion

#### 3.1. Solvent-dependent generation of the DCA radical anion or an OFT (a ground-state singlet biradical or its ZIF) as an intermediate for formation of CA or the [4+2] adduct, respectively

Fig. 1 shows the transient absorption spectra (the solid lines) obtained immediately after nanosecond pulse excitation of DCA in acetonitrile ( $\epsilon=37.5$ ), acetone ( $\epsilon=20.7$ ) and methanol ( $\epsilon=32.7$ ) containing 1 M DMHD, i.e. the delay time is 10 ns and  $\epsilon$  is the dielectric constant of a solvent [25]; hereafter, unless otherwise stated, all the solvents contain 1 M DMHD. In comparison with the normalized absorption spectrum of the DCA radical anion ( $\text{DCA}^{\bullet-}$ ) obtained by nanosecond laser photolysis of DCA in acetonitrile containing triethylamine, i.e. the dotted line shown in Fig. 1(a) [12], it is expected that  $\text{DCA}^{\bullet-}$  is also generated in the presence of DMHD. In fact, in acetonitrile and acetone, the lifetime ( $\tau_t$ ) obtained by the single-exponential decrease in transient absorption (cf. Fig. 2(a) or (b)) is equal to that ( $\tau_p$ ) obtained by the single-exponential decrease in transient photocurrent (cf. Fig. 2(a') or (b')). Interestingly,  $\epsilon$  of methanol is greater than that of acetone, but the absorption spectrum

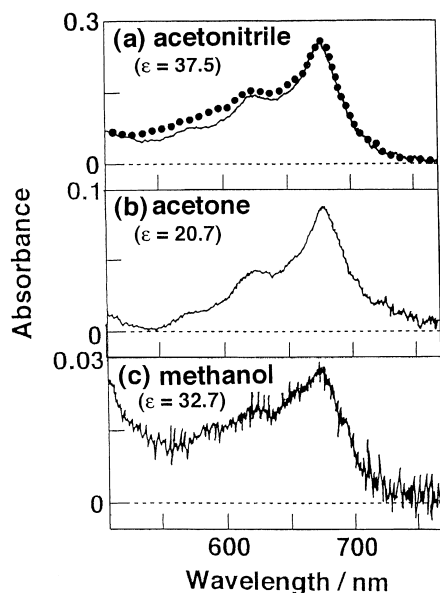


Fig. 1. Transient absorption spectra at 10 ns delay (—) obtained by nanosecond laser photolysis of DCA in acetonitrile, acetone and methanol containing 1 M DMHD. In (a), the dotted line is the normalized absorption spectrum of  $\text{DCA}^{\bullet-}$  obtained by nanosecond laser photolysis of DCA in acetonitrile–triethylamine [12].

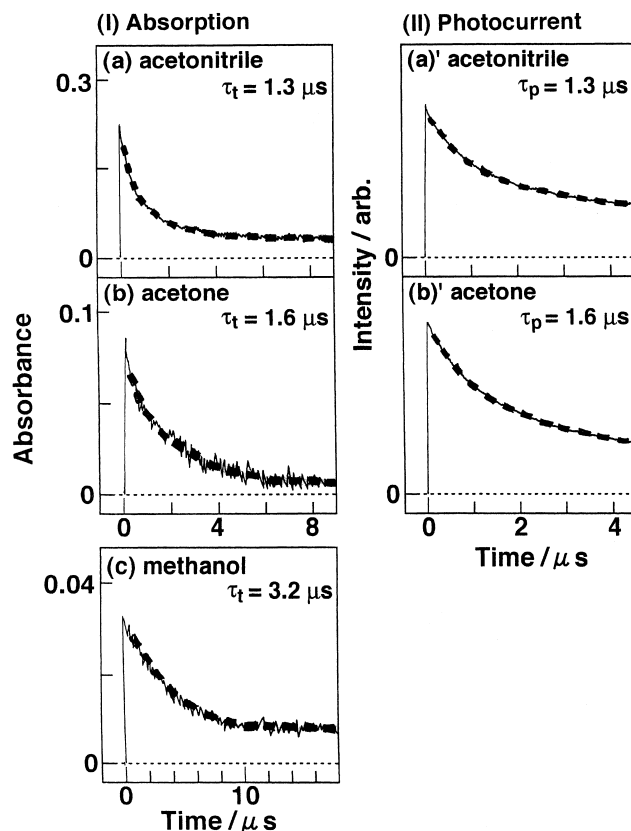


Fig. 2. (a)–(c) Decay curves of transient absorptions monitored at 670 nm; (a') and (b') those of photocurrents (—) obtained by nanosecond laser photolysis of DCA in acetonitrile, acetone and methanol containing 1 M DMHD. The dashed curves are the best-fit single-exponential functions with lifetimes ( $\tau_t$  or  $\tau_p$ ) indicated.

of  $\text{DCA}^{\bullet-}$  obtained in the former solvent (cf. Fig. 1(c)) is very weak compared to that obtained in the latter solvent (cf. Fig. 1(b)). In accordance with this, the transient photocurrent in methanol is too weak to measure its decay curve but determination of  $\tau_t$  is possible as shown in Fig. 2(c).

For DCA in all the solvents stated above, the absorption spectral changes caused by steady-state photolysis reflect formation of CA. A typical example obtained in acetonitrile is shown in Fig. 3(a) and it is clear that the decrement of reactant absorptions (peaks  $R_1$ ,  $R_2$  and  $R_3$ ) is accompanied by the increment of product absorptions (peaks  $P_1$ ,  $P_2$  and  $P_3$ ) identical to those of CA. The rate ( $v$ ) of CA formation, however, is found to decrease in the order of  $v(\text{acetonitrile}, \epsilon=37.5) > v(\text{acetone}, \epsilon=20.7) > v(\text{methanol}, \epsilon=32.7)$ . Since this result is consistent with those obtained by nanosecond laser photolysis (cf. Figs. 1 and 2), we conclude that an intermediate for photoinduced and DMHD-assisted  $\text{DCA} \rightarrow \text{CA}$  dechlorination is really  $\text{DCA}^{\bullet-}$ . For this radical anion in acetonitrile, Saltiel et al. [21] proposed that protonation by the DMHD radical cation ( $\text{DMHD}^{\bullet+}$ ) followed by chlorine-atom elimination gave rise to formation of CA. As stated previously, however, not the second-order but the first-order disappearance of  $\text{DCA}^{\bullet-}$  can clearly be

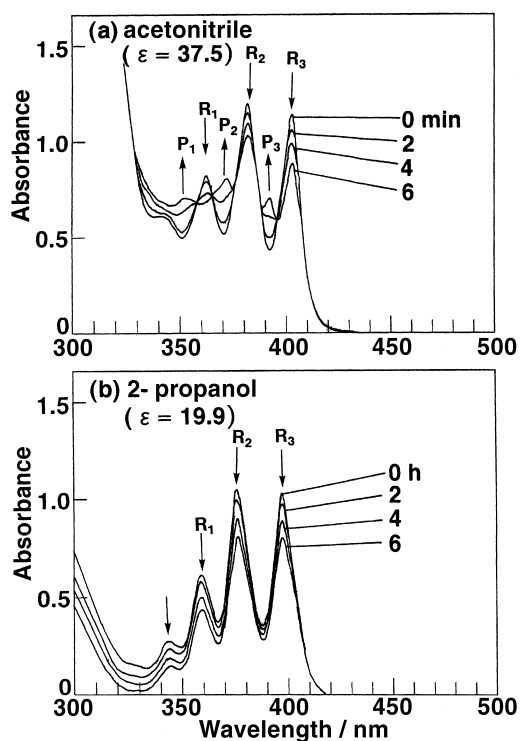


Fig. 3. Absorption spectral changes upon steady-state photolysis of DCA in acetonitrile and 2-propanol containing 1 M DMHD.

seen. This indicates that dissociation of  $\text{DCA}^{\bullet-}$  into the chlorine anion ( $\text{Cl}^-$ ) and the CA radical ( $\text{CA}^\bullet$ ) followed by its hydrogen-atom abstraction from the solvents and/or DMHD (or  $\text{DMHD}^{\bullet+}$ ) gives rise to formation of CA.

For haloanthracenes (the 9-chloro, 9,10-dichloro, 9-bromo and 9,10-dibromo compounds) in acetonitrile, ethanol, cyclohexane and heptane containing amine (triethylamine or *N,N*-dimethylaniline) [10,12–15], we observed their photoinduced dehalogenation yielding 9-haloanthracenes or anthracene. In the presence of DMHD, however, Fig. 3(b) indicates that steady-state photolysis of DCA in 2-propanol ( $\epsilon=19.9$ ) causes the absorption spectral change different from that shown in Fig. 3(a). No clear  $\text{DCA} \rightarrow \text{CA}$  dechlorination can be seen and the decrement of reactant absorptions upon photolysis is extremely slow compared to that shown in Fig. 3(a). Similar results are obtained in 1-octanol ( $\epsilon=10.3$ ), diethyl ether ( $\epsilon=4.34$ ) and heptane ( $\epsilon=1.92$ ), and  $^1\text{H-NMR}$  analysis reveals the final product to be the [4+2] adduct (cf. a dibenzobicyclo[2.2.2]octadiene-type compound shown in Scheme 1), i.e. 0.65 ppm (s, 3H, one methyl at the bridge carbon), 0.85 ppm (s, 3H, the other methyl at the bridge carbon), 1.58 ppm (s, 3H, one methyl at the vinyl carbon), 1.68 ppm (s, 3H, the other methyl at the vinyl carbon), 2.73 ppm (d, 1H,  $J=10.8$  Hz, proton at the bridge carbon), 4.41 ppm (d, 1H,  $J=10.8$  Hz, vinyl proton), 7.24–7.28 ppm (m, 4H, aromatic), 7.62–7.65 ppm (m, 1H, aromatic) and 7.69–7.78 ppm (m, 3H, aromatic); this assignment is consistent with that reported by Saltiel et al. [26].

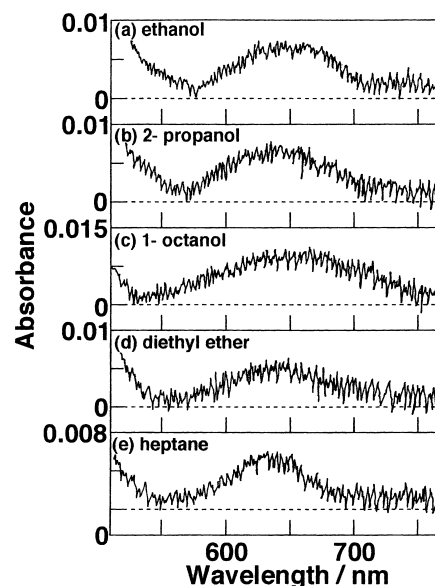


Fig. 4. Transient absorption spectra at 10 ns delay obtained by nanosecond laser photolysis of DCA in ethanol, 2-propanol, 1-octanol, diethyl ether and heptane containing 1 M DMHD.

In ethanol ( $\epsilon=24.6$ ), the absorption spectral change caused by steady-state photolysis reveals formation of not only CA but also the [4+2] adduct; however, the rate of  $\text{DCA} \rightarrow \text{CA}$  dechlorination is very slow compared to that in methanol ( $\epsilon=32.7$ ). Owing to an extremely weak transient photocurrent, determination of its lifetime by nanosecond laser photolysis is impossible and a transient absorption spectrum thus obtained (cf. Fig. 4(a)) is somewhat different from the absorption spectrum of  $\text{DCA}^{\bullet-}$  (cf. Fig. 1). As shown in Fig. 5(a), furthermore, the decay curve of transient absorption (the solid curve) can be reproduced by a single-exponential function (the dashed curve) with a lifetime of  $\tau_1=0.41$   $\mu\text{s}$ . In 2-propanol ( $\epsilon=19.9$ ), 1-octanol ( $\epsilon=10.3$ ), diethyl ether ( $\epsilon=4.34$ ) and heptane ( $\epsilon=1.92$ ), no transient photocurrents are detectable, but the transient absorption spectra shown in Fig. 4(b)–(e) and their decay curves shown in Fig. 5(b)–(e) are similar to those obtained in ethanol ( $\epsilon=24.6$ ). On the basis of formation of the [4+2] adduct upon steady-state photolysis of DCA in benzene, Saltiel et al. [26] proposed that an exciplex formed between the lowest excited singlet state ( $\text{DCA}^*$ ) of DCA and ground-state DMHD was the precursor for generation of a ground-state singlet biradical as an intermediate (cf. BR shown in Scheme 1).

If the transient absorption spectra shown in Fig. 4 are due to the absorption of BR, then, the lifetimes ( $\tau_1$ ) of transient absorptions indicated in Fig. 5 correspond to the time constants for conversion of BR to the [4+2] adduct. For photo-induced formation of the [4+2] adduct between 9-cyanoanthracene and DMHD, however, Okada et al. [27] proposed equilibrium population of a singlet exciplex and a ground-state singlet biradical with a lifetime of 520–575 ps.

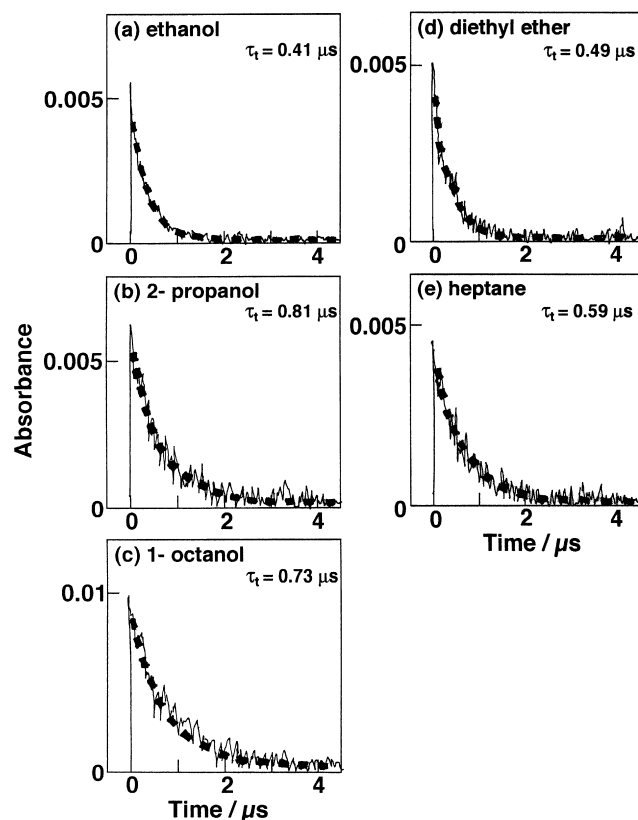


Fig. 5. Decay curves of transient absorptions (—) obtained by nanosecond laser photolysis of DCA in ethanol, 2-propanol, 1-octanol, diethyl ether and heptane containing 1 M DMHD. The monitoring wavelength is 650 nm and the dashed curves are the best-fit single-exponential functions with lifetimes ( $\tau_1$ ) indicated.

This lifetime is very short compared to those obtained by us and conversion of BR to its ZIF followed by formation of the [4+2] adduct can not be ruled out (cf. Scheme 1). If this mechanism is true, the transient absorption spectra shown in Fig. 4 can be assigned to the absorptions of ZIF. We thus believe that the intermediate responsible for the transient absorption spectra shown in Fig. 4 is an OFT, i.e. BR or ZIF.

### 3.2. Solvent-dependent decomposition of a singlet DCA–DMHD exciplex generating $DCA^{\bullet-}$ or OFT

Fig. 6 shows the fluorescence spectra obtained for DCA in the absence (the dashed lines) and the presence (the dotted or solid lines) of DMHD. Irrespective of  $\epsilon$  of a solvent, addition of DMHD gives rise to the appearance of a broad emission band at wavelengths longer than those for the structured emission band. Undoubtedly, the former band is due to the exciplex emission originating from a singlet DCA–DMHD exciplex and the latter band is due to the monomer emission originating from  $DCA^*$ . Up to the DMHD concentration of 0.08 M, it is confirmed that no exciplex emissions are contained in the monomer emission peaks indicated by arrows. Their intensities in the absence ( $I_0$ ) and the presence ( $I_D$ )

of DMHD are thus measured, and plots of  $I_0/I_D$  against the concentration of DMHD are found to give the straight lines with slopes ( $S$ ) listed in Table 1. By hand-made drawing, furthermore, estimation of the pure exciplex emission bands and then their integration over wavenumbers are performed at the DMHD concentration of 1 M, and the relative yields of exciplex emissions ( $\Phi_T$ ) thus obtained are also listed in Table 1.

In comparison with the exciplex emission band in a solvent with  $\epsilon \geq 19.9$ , that in a solvent with  $\epsilon \leq 10.3$  shifts greatly to shorter wavelengths and significant overlap of the exciplex and monomer emission bands can be seen in heptane<sup>2</sup>. A similar result is also obtained for an exciplex formed between the lowest excited singlet state ( $DBA^*$ ) of DBA and ground-state DMHD [19]. For an exciplex formed between  $DBA^*$  and amine (triethylamine or *N,N*-dimethylaniline) [14,15], however, shift of the exciplex emission band to shorter wavelengths with decreasing  $\epsilon$  of a solvent is not so very large, and no partial overlap of the exciplex and monomer emission bands can be seen. For haloanthracenes (the 9-chloro, 9,10-dichloro, 9-bromo and 9,10-dibromo compounds) in acetonitrile, ethanol, cyclohexane and heptane containing amine (triethylamine or *N,N*-dimethylaniline) [12–15], furthermore, only dehalogenation (yielding 9-haloanthracenes or anthracene via the haloanthracene radical anions) could be observable irrespective of  $\epsilon$  of a solvent as well as its hydrogen-bonding ability and the rate of debromination decreased with decreasing  $\epsilon$ . In contrast, the photochemistry of DCA in the presence of DMHD is solvent-dependent as discussed previously, i.e. CA and/or the [4+2] adduct are formed depending on the nature of a solvent.

In order to find out the detailed mechanism for solvent-dependent decomposition of a singlet DCA–DMHD exciplex, therefore, subpicosecond laser photolysis is performed and Fig. 7(a) shows the transient absorption spectra (the solid lines) thus obtained in acetonitrile ( $\epsilon=37.5$ ). In the absence of DMHD, the normalized spectrum (the dotted line with only band A) is obtained and the spectral profile as well as the position of absorption maximum are very similar to those of the singlet–singlet ( $S' \leftarrow S_1$ ) absorption spectra reported for the lowest excited singlet states of anthracene and its several derivatives [14,15,19,29]. In the presence of DMHD, therefore, it looks like the decrement of band A (due to the  $S' \leftarrow S_1$  absorption of  $DCA^*$ ) with time is accompanied by the increment and then the decrement of band B (due to the absorption of another transient species); band B' is confirmed to be due to the absorption of  $DCA^{\bullet-}$  and band B'' is very similar to the absorption of  $DMHD^{\bullet+}$  [27,30]. In fact, as shown in Fig. 8(a), the time-dependent absorbance changes ( $D_t/D_{max}$ ) of bands A (the open circles) and B (the closed circles) can well

<sup>2</sup> Owing to this, no observation of the exciplex emission band in heptane reported previously [28] can be ascribed to the lack of our careful spectral check.

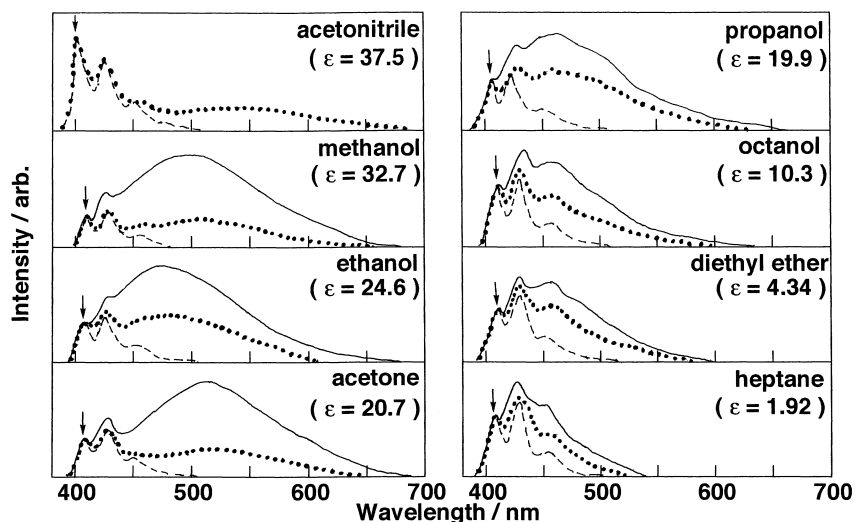


Fig. 6. Fluorescence spectra obtained for DCA in various solvents containing 0 M (---), 1 M (●●●) and 2 M (—) DMHD. The excitation wavelength is 380 nm and the spectral intensity is normalized at the emission peak indicated by the arrow.

be reproduced by the smooth curves which are calculated assuming a Gaussian intensity function (FWHM=0.25 ps) for both the excitation (and probing) light pulses and using the biexponential functions (with time constants  $\tau_1$  and  $\tau_2$ ) given by Eqs. (1) and (2), respectively:

$$\frac{D_t}{D_{\max}} = a_1 \exp\left(-\frac{t}{\tau_1}\right) + a_2 \exp\left(-\frac{t}{\tau_2}\right) + a_3 \quad (1)$$

$$\frac{D_t}{D_{\max}} = -b_1 \exp\left(-\frac{t}{\tau_1}\right) + b_2 \exp\left(-\frac{t}{\tau_2}\right) + b_3 \quad (2)$$

where  $a_{1-3}$  as well as  $b_{1-3}$  are the positive experimental constants and  $b_1$  is found to be equal to  $b_2$ .

Band B shown in Fig. 7(a) is very similar to the absorption bands of exciplexes formed between DBA\* and amine (triethylamine or *N,N*-dimethylaniline) in several solvents [14,15]. We thus believe that band B is due to the absorption of an exciplex ((DCA–DMHD)\*) formed between DCA\* and DMHD. Since the mechanism for formation and decay of an exciplex as shown in Scheme 1 is well known [31],

the concentrations of DCA\* and (DCA–DMHD)\* at time  $t$  can be calculated using Eqs. (3) and (4), respectively, which have two time constants ( $\lambda_{1,2}$ ) given by Eq. (5), where  $k_E$  is the sum of rate constants  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$ , and [DMHD] is the concentration of DMHD; since intersystem crossing from a singlet DCA–DMHD [26] (or DCA–amine [12]) exciplex to the corresponding triplet exciplex followed by its rapid decomposition gives rise to population of the lowest excited triplet state of DCA,  $k_4$  is the sum of rate constants for intersystem crossing to a triplet DCA–DMHD exciplex and nonradiative decomposition into DCA+DMHD:

$$[\text{DCA}^*] \propto \frac{1}{\lambda_1 - \lambda_2} \{ (k_q[\text{DMHD}] + k_M - \lambda_2) \exp(-\lambda_1 t) + (\lambda_1 - k_q[\text{DMHD}] - k_M) \exp(-\lambda_2 t) \} \quad (3)$$

$$[(\text{DCA-DMHD})^*] \propto \frac{1}{\lambda_1 - \lambda_2} \{ -\exp(-\lambda_1 t) + \exp(-\lambda_2 t) \} \quad (4)$$

Table 1

Slopes ( $S$ ) for plots of  $I_0/I_D$  against [DMHD], relative yields of exciplex emissions ( $\Phi_r$ ) at [DMHD]=1 M, rate constants ( $k_q$ ,  $k_b$ ,  $k_E$ ) for (DCA–DMHD)\* and intermediates (INT) obtained in various solvents<sup>a</sup>

Solvent	$S$ ( $\text{M}^{-1}$ )	$\Phi_r$	$k_q$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$k_b$ ( $\text{s}^{-1}$ )	$k_E$ ( $\text{s}^{-1}$ )	INT
Acetonitrile ( $\epsilon=37.5$ )	69.1	1.0	$1.3 \times 10^{10}$	$2.5 \times 10^9$	$4.8 \times 10^9$	DCA• <sup>-</sup>
Methanol ( $\epsilon=32.7$ )	78.3	2.9	$1.1 \times 10^{10}$	$3.3 \times 10^7$	$2.2 \times 10^8$	DCA• <sup>-</sup>
Ethanol ( $\epsilon=24.6$ )	56.5	6.6	$1.1 \times 10^{10}$	$1.5 \times 10^8$	$2.6 \times 10^8$	OFT $\gg$ DCA• <sup>-</sup>
Acetone ( $\epsilon=20.7$ )	70.1	2.5	$1.8 \times 10^{10}$	$1.9 \times 10^9$	$1.6 \times 10^9$	DCA• <sup>-</sup>
2-Propanol ( $\epsilon=19.9$ )	30.2	9.9	$2.3 \times 10^{10}$	$2.2 \times 10^9$	$4.1 \times 10^8$	OFT $\gg$ DCA• <sup>-</sup>
1-Octanol ( $\epsilon=10.3$ )	12.1	15.2	$5.4 \times 10^{10}$	$2.6 \times 10^{10}$	$7.2 \times 10^8$	OFT
Diethyl ether ( $\epsilon=4.34$ )	18.6	24.2	$3.8 \times 10^{10}$	$2.0 \times 10^{10}$	$1.2 \times 10^9$	OFT
Heptane ( $\epsilon=1.92$ )	5.8	30.4	$9.0 \times 10^{10}$	$1.9 \times 10^{10}$	$1.4 \times 10^8$	OFT

<sup>a</sup>  $\epsilon$  is the dielectric constant of a pure solvent [25], and OFT is the ground-state singlet biradical (BR) or its zwitterionic form (ZIF).

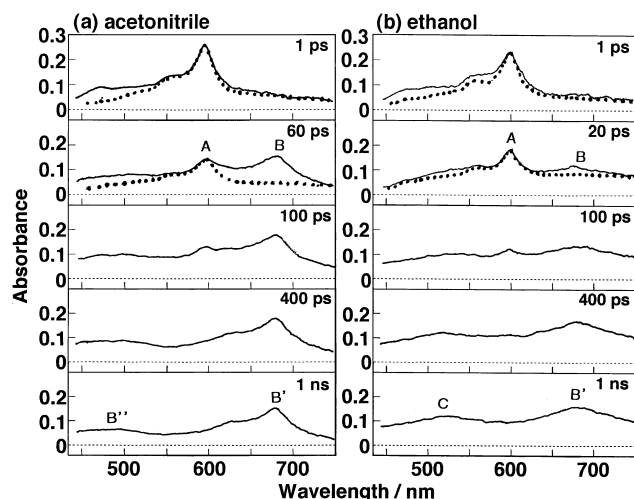


Fig. 7. Transient absorption spectra (—) obtained by subpicosecond laser photolysis of DCA in acetonitrile and ethanol containing 1 M DMHD. The dotted lines are the normalized  $S' \leftarrow S_1$  absorption spectra obtained for DCA in the absence of DMHD.

$$\lambda_{1,2} = \frac{1}{2} \{k_q[\text{DMHD}] + k_b + k_E + k_M \pm \sqrt{(k_q[\text{DMHD}] + k_M - k_b - k_E)^2 + 4k_b k_q[\text{DMHD}]} \} \quad (5)$$

except for the residual absorbances (constants  $a_3$  and  $b_3$  corresponding to the absorbances of  $\text{DCA}^{*-}$ ), therefore, Eqs. (1) and (2) (with  $b_1=b_2$ ) are consistent with Eqs. (3) and (4), respectively.

By measurements of the fluorescence spectra and their life-times in acetonitrile, Saltiel et al. [20,21] concluded that  $(\text{DCA-DMHD})^*$  was formed not only by a reac-

tion of  $\text{DCA}^*$  with DMHD but also by direct excitation of a ground-state  $\text{DCA-DMHD}$  complex. If this were to be correct, the transient absorption responsible for  $(\text{DCA-DMHD})^*$  should build up within a duration of the excitation light pulse. In contrast, Fig. 8(a) indicates that band B never grows in within a duration of subpicosecond pulse excitation. Furthermore, examination of the absorption spectral change responsible for DCA upon addition of DMHD in acetonitrile reflects no formation of a ground-state  $\text{DCA-DMHD}$  complex. For benzophenone in acetonitrile and anthraquinones (anthraquinone and haloanthraquinones) in toluene [32–35], we really observed formation of the ground-state ketone–DMHD complexes, i.e. addition of DMHD caused the intensity increment (and broadening to a longer wavelength) of absorption spectra responsible for ground-state aromatic ketones and picosecond laser photolysis revealed that direct excitation of the ground-state ketone–DMHD complexes gave rise to a population of the excited singlet charge-transfer complexes (or the singlet ion pairs) within a duration of pulse excitation. In acetonitrile, formation of a triplex between  $(\text{DCA-DMHD})^*$  and DMHD was also reported by Saltiel et al. [20,21]. In the present study, however, no such an evidence is obtained and the results obtained can well be explained by Scheme 1, i.e. irrespective of the monitoring wavelength, the time-dependent absorbance changes of bands A and B shown in Fig. 8(a) can well be reproduced by the biexponential functions given by Eqs. (1) and (2), respectively.

Almost identical results are obtained by subpicosecond laser photolysis of DCA in methanol ( $\epsilon=32.7$ ) and acetone ( $\epsilon=20.7$ ). In comparison with the transient absorption spectra obtained in acetonitrile (cf. Fig. 7(a)), however, those obtained in ethanol ( $\epsilon=24.6$ ) indicate the very weak intensity

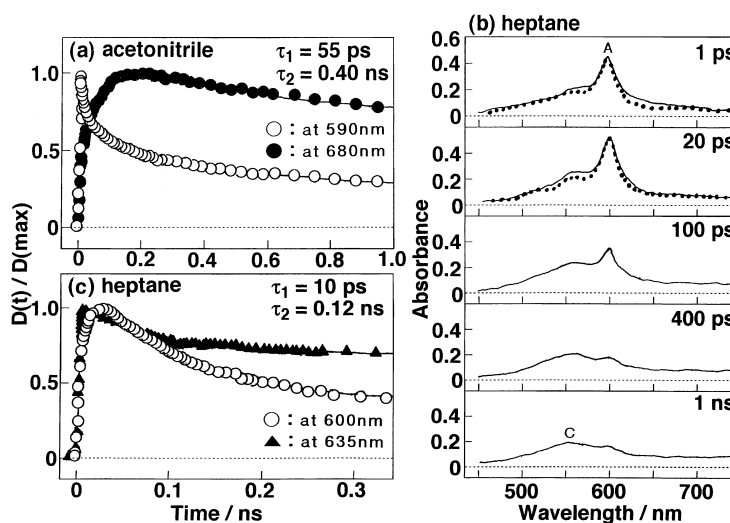


Fig. 8. (a) and (c) Time-dependent absorbance changes ( $D_i/D_{\text{max}}$ ) of bands A (○, ▲) and B (●) in acetonitrile and heptane containing 1 M DMHD; (b) transient absorption spectra (—) in heptane–DMHD (1 M) obtained by subpicosecond laser photolysis of DCA. Assuming a Gaussian intensity function (FWHM=0.25 ps) for both the excitation and probing light pulses, the best-fit absorbances (—) in (a) are calculated using the biexponential functions given by Eq. (1) (○) and 2 (●,  $b_1=b_2$ ); in (c), however, the best-fit absorbances (—) for band A are calculated using the biexponential functions given by Eq. (1) (▲) and 2 (○,  $b_1 \neq b_2$ ). The dotted lines in (b) are the normalized  $S' \leftarrow S_1$  absorption spectra obtained for DCA in the absence of DMHD.

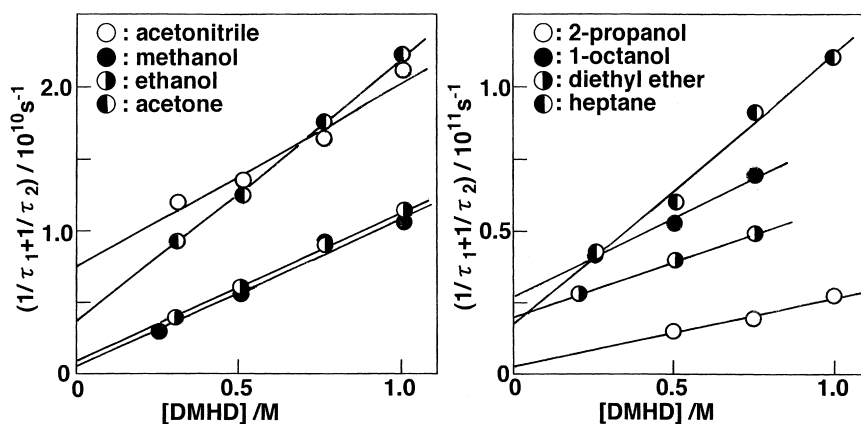


Fig. 9. Plots of  $1/\tau_1 + 1/\tau_2$  against [DMHD] in various solvents.

of band B and the existence of not only band B' but also band C as the residual absorption bands (cf. Fig. 7(b)), i.e. band C is somewhat different from band B'' obtained in acetonitrile. Although a similar result is also obtained in 2-propanol ( $\epsilon=19.9$ ), the intensities of bands B and B' are very weak compared to those in ethanol. In 1-octanol ( $\epsilon=10.3$ ), diethyl ether ( $\epsilon=4.34$ ) or heptane ( $\epsilon=1.92$ ), furthermore, no bands B and B' can be seen, i.e. only bands A and C are observable. A typical example obtained in heptane is shown in Fig. 8(b) and it looks like that DCA\* responsible for band A is the precursor for generation of a residual species responsible for band C. As shown in Fig. 8(c), however, the absorbance of band A monitored at 600 nm increases and then decreases to a constant absorbance following a biexponential function given by Eq. (2) with  $b_1 \neq b_2$  (cf. the open circles), while that monitored at 635 nm decreases to a constant absorbance following a biexponential function given by Eq. (1) (cf. the closed triangles)<sup>3</sup>; at 535 nm, the absorbance of band C is constant up to  $\sim 100$  ps delay and then it decreases somewhat to a constant absorbance following a single-exponential function with a lifetime ( $\tau_2$ ) equal to that obtained for band A. These results indicate the existence of partial overlap among bands A, C and that of (DCA-DMHD)\*. Hence, in a solvent with  $\epsilon \leq 10.3$ , superposition of absorptions due to DCA\* and (DCA-DMHD)\* is consistent with significant blue-shift of the exciplex emission with decreasing  $\epsilon$  of a solvent (cf. Fig. 6). Since the residual absorption spectrum with band C (cf. Fig. 8(b)) is clearly different from the absorption spectrum of OFT (BR or ZIF) shown in Fig. 4(e), constants  $a_3$  and  $b_3$  (given in Eqs. (1) and (2), respectively) can be ascribed to the absorbances of BR if OFT is ZIF. This is consistent with the assignment of a 520 nm band to the absorption of a ground-state singlet biradical (generated from a singlet 9-cyanoanthracene-DMHD exciplex) by

<sup>3</sup> In heptane, the single-exponential decay of band A with time and no observation of band C reported previously [28] are found to be owing to no flow of the sample solution.

Okada et al. [27]. A possibility that OFT is BR, however, can not be ruled out absolutely, and thus, the constants ( $a_3$  and  $b_3$ ) might be ascribed to the absorbances due to the excited singlet state of BR.

Irrespective of solvent-dependent decomposition of (DCA-DMHD)\* stated so far, Eq. (5) indicates that the sum of rate constants  $\lambda_1 = 1/\tau_1$  and  $\lambda_2 = 1/\tau_2$  should be expressed by Eq. (6):

$$\frac{1}{\tau_1} + \frac{1}{\tau_2} = k_q[\text{DMHD}] + k_b + k_E + k_M \quad (6)$$

where  $1/k_M$  is the fluorescence lifetime obtained for DCA\* in the absence of DMHD; since these lifetimes obtained in acetonitrile (8.6 ns), ethanol (8.5 ns) and heptane (8.7 ns) are found to be nearly equal, those in the other solvents are assumed to be 8.6 ns. The rate constants  $k_q$  and  $k_I = k_b + k_E$  can thus be obtained from the slope and the intercept of Eq. (6), respectively. By measurements of the time-dependent absorbance changes of bands A and B at various DMHD concentrations in all the solvents studied here, the rate constants ( $1/\tau_1$  and  $1/\tau_2$ ) are determined and plots of  $1/\tau_1 + 1/\tau_2$  against the concentration of DMHD give the straight lines shown in Fig. 9. The efficiency for repopulation of DCA\* from (DCA-DMHD)\* can be defined by  $\gamma = k_b/k_I$  (cf. Scheme 1), and thus, the intensity ratio ( $I_0/I_D$ ) of monomer emissions measured previously in the absence ( $I_0$ ) and the presence ( $I_D$ ) of DMHD is given by Eq. (7):

$$\frac{I_0}{I_D} = \frac{\lambda_1 \lambda_2}{k_I k_M} = 1 + \frac{(1-\gamma)k_q[\text{DMHD}]}{k_M} \quad (7)$$

Since the slope ( $S = (1-\gamma)k_q/k_M$ ) of this equation is listed in Table 1,  $\gamma$  can be calculated by a choice of  $k_q$  and  $k_M$ . A combination of  $\gamma$  thus obtained with  $k_I = k_b + k_E$ , furthermore, gives the decay rate constants ( $k_b$ ,  $k_E$ ) of (DCA-DMHD)\*. All the rate constants thus obtained are listed in Table 1. In acetonitrile or acetone,  $k_b = (2.5-1.9) \times 10^9 \text{ s}^{-1}$  and  $k_E = (4.8-1.6) \times 10^9 \text{ s}^{-1}$  obtained for (DCA-DMHD)\* are comparable with those



( $k_b=1.4\times 10^9\text{ s}^{-1}$  and  $k_E=3.1\times 10^9\text{ s}^{-1}$ ) obtained for an exciplex ((DBA–DMHD)<sup>\*</sup>) formed between DBA<sup>\*</sup> and DMHD [19] as well as those ( $k_b=2.7\times 10^9\text{ s}^{-1}$  and  $k_E=4.8\times 10^9\text{ s}^{-1}$ ) obtained for an exciplex formed between DBA<sup>\*</sup> and *N,N*-dimethylaniline [14].  $k_b=1.5\times 10^8\text{ s}^{-1}$  and  $k_E=2.6\times 10^8\text{ s}^{-1}$  obtained in ethanol, however, are one order of magnitude smaller than those obtained in acetonitrile and acetone; although  $k_E=2.2\times 10^8\text{ s}^{-1}$  obtained in methanol is almost equal to that obtained in ethanol,  $k_b=3.3\times 10^7\text{ s}^{-1}$  obtained in the former solvent is one order of magnitude smaller than that obtained in the latter solvent.

A qualitative interpretation of solvent-dependent generation of an intermediate (DCA<sup>•−</sup> or OFT) summarized in Table 1 is that the relatively small and large values of  $\Phi_r$  and  $S$ , respectively, reflect enhanced generation of DCA<sup>•−</sup> (and thus suppressed generation of OFT). In acetonitrile ( $\varepsilon=37.5$ ), acetone ( $\varepsilon=20.7$ ) or methanol ( $\varepsilon=32.7$ ), the order of  $k_q$  ( $10^{10}\text{ M}^{-1}\text{ s}^{-1}$ ) is greater than those of  $k_M$  ( $10^8\text{ s}^{-1}$ ),  $k_b$  ( $10^9\text{--}10^7\text{ s}^{-1}$ ) and  $k_E\approx k_1+k_3+k_4$  ( $10^9\text{--}10^8\text{ s}^{-1}$ ). This indicates that the quantum yield of exciplex emission given by  $k_3k_q[\text{DMHD}]/(k_Mk_b+k_Mk_E+k_Ek_q[\text{DMHD}])$  is nearly equal to  $k_3/k_E$  at  $[\text{DMHD}]=1\text{ M}$ . If there is no solvent effect on the rate constant ( $k_3$ ) for exciplex emission, then, it looks like  $k_E(\text{acetonitrile})/k_E(\text{acetone})=3.0$  is nearly equal to  $\Phi_r=2.5$  in acetone, but  $k_E(\text{acetonitrile})/k_E(\text{methanol})=21.8$  is 7.5 times greater than  $\Phi_r=2.9$  in methanol. This might suggest that only the rate constant ( $k_1$ ) for generation of DCA<sup>•−</sup> from (DCA–DMHD)<sup>\*</sup> is reduced by decreasing  $\varepsilon$  of a solvent, but its hydrogen-bonding ability reduces all the rate constants ( $k_1$ ,  $k_3$  and  $k_4$ ). In ethanol ( $\varepsilon=24.6$ ) or 2-propanol ( $\varepsilon=19.9$ ) where  $k_E$  should be equal to  $k_1+k_2+k_3+k_4$ , however, no linear correlation can be found between  $\Phi_r$  and  $1/k_E$ . In solvents with  $\varepsilon\leq 10.3$ , the order of  $k_q$  ( $10^{10}\text{ M}^{-1}\text{ s}^{-1}$ ) is equal to that of  $k_b$ , and thus,  $\Phi_r$  should be proportional to  $k_2k_q[\text{DMHD}]/(k_Mk_b+k_Mk_E+k_Ek_q[\text{DMHD}])$  at  $[\text{DMHD}]=1\text{ M}$ ; in this case,  $k_E$  is nearly equal to  $k_2+k_3+k_4$ . The value of  $\Phi_r$  in a given solvent relative to that in heptane ( $\varepsilon=1.92$ ) is 0.80 in diethyl ether ( $\varepsilon=4.34$ ) or 0.50 in 1-octanol ( $\varepsilon=10.3$ ), while the corresponding value of  $k_r=k_q[\text{DMHD}]/(k_Mk_b+k_Mk_E+k_Ek_q[\text{DMHD}])$  at  $[\text{DMHD}]=1\text{ M}$  is 0.13 or 0.21, respectively. For the linear correlation between  $\Phi_r$  and  $k_r$ , even a qualitative explanation can thus not be given; however, both the values of  $\Phi_r$  and  $k_r$  in heptane ( $\varepsilon=1.92$ ) are greater than the corresponding values in a solvent with  $\varepsilon=4.34\text{--}10.3$ .

#### 4. Conclusion

The solvent-dependent photochemistry of DCA in the presence of DMHD can be interpreted as follows (cf. Scheme 1): (1) in acetonitrile ( $\varepsilon=37.5$ ), methanol ( $\varepsilon=32.7$ ) or acetone ( $\varepsilon=20.7$ ), DCA<sup>•−</sup> generated from (DCA–DMHD)<sup>\*</sup> is an intermediate for formation of CA, i.e. dissociation of DCA<sup>•−</sup> into Cl<sup>−</sup> and CA<sup>•</sup> followed by its hydrogen-atom abstraction from the solvent and/or DMHD

(or DMHD<sup>•+</sup>) yields CA; (2) in 1-octanol ( $\varepsilon=10.3$ ), diethyl ether ( $\varepsilon=4.34$ ) or heptane ( $\varepsilon=1.92$ ), OFT (BR or ZIF) generated from (DCA–DMHD)<sup>\*</sup> is an intermediate for formation of the [4+2] adduct; owing to forbidden [4+2] addition between DCA<sup>\*</sup> and DMHD [36], formation of the [4+2] adduct from (DCA–DMHD)<sup>\*</sup> via the stepwise processes is reasonable; (3) in ethanol ( $\varepsilon=24.6$ ) or 2-propanol ( $\varepsilon=19.9$ ), decomposition of (DCA–DMHD)<sup>\*</sup> generates not only OFT (major) but also DCA<sup>•−</sup> (minor); although two compounds (the [4+2] adduct and CA) are formed in ethanol, only the former compound is formed in 2-propanol.

In the presence of DMHD, the solvent-dependent photochemistry of DCA is similar to that reported for DBA [19]<sup>4</sup>. The differences between them, however, are as follows: (i) the order of dechlorination rate is  $v(\text{acetonitrile}, \varepsilon=37.5)>v(\text{acetone}, \varepsilon=20.7)>v(\text{methanol}, \varepsilon=32.7)>v(\text{ethanol}, \varepsilon=24.6)$ , but that of debromination rate is  $v(\text{acetonitrile}, \varepsilon=37.5)>v(\text{acetone}, \varepsilon=20.7)\gg v(\text{methanol}, \varepsilon=32.7)$  and no absorption spectral change reflecting debromination can be seen in ethanol; (ii) the coexistence of OFT (major) and DXA<sup>•−</sup> (minor) for DXA(=DCA) can clearly be seen in ethanol and 2-propanol, but that for DXA(=DBA) is observed only in methanol. We thus conclude that not only the dielectric constant of a solvent but also its hydrogen-bonding ability affects the photochemistry of DXA originating from an exciplex formed between the lowest excited singlet state (DXA<sup>\*</sup>) of DXA and ground-state DMHD.

Our present discussion is based on an assumption that both DXA<sup>•−</sup> and OFT are generated from an identical exciplex. For formation of an exciplex between DXA<sup>\*</sup> and DMHD, however, their reasonable interaction may be of either  $4\pi+4\pi$ - or  $4\pi+2\pi$ -type. Hence, an alternative interpretation of our results is that an exciplex formed by the former interaction generates DXA<sup>•−</sup> and another exciplex formed by the latter interaction generates OFT. If there exists rapid interconversion between these two exciplexes or if formation of one of them is predominant in a given solvent, then, the time-dependent absorbance changes of bands A and B can still be reproduced by the biexponential functions given by Eqs. (1) and (2), respectively.

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<sup>4</sup> On the basis of the present results, generation of BR by a diffusion-controlled reaction of DBA<sup>\*</sup> with DMHD proposed in the previous paper [19] is incorrect.

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