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Primary process for the photochemistry of 9,10-dibromoanthracene yielding 9-bromoanthracene in cyclohexane–amine (triethylamine or *N*,*N*-dimethylaniline) studied by picosecond laser photolysis

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Abstract

Picosecond laser photolysis of 9,10-dibromoanthracene (DBA) in cyclohexane–amine (triethylamine or *N*,*N*-dimethylaniline) leads to the formation of a DBA–amine exciplex between the lowest excited singlet state of DBA and ground state amine. However, during the decrease in the exciplex absorption with time, no accompanying appearance of an absorption band attributable to the DBA radical anion ($DBA^{\cdot -}$) can be seen. Nanosecond laser photolysis of DBA in cyclohexane–amine also reveals no existence of an absorption band attributable to $DBA^{\cdot -}$, but its absorption band is clearly seen in acetonitrile–amine (cf. K. Hamanoue, S. Tai, T. Hidaka, T. Nakayama, M. Kimoto and H. Teranishi, *J. Phys. Chem.*, *88* (1984) 4380, K. Hamanoue, T. Nakayama, K. Ikenaga, K. Ibuki and A. Otani, *J. Photochem. Photobiol. A: Chem.*, *69* (1993) 305). In accordance with this, the rate of DBA → 9-bromoanthracene debromination on steady state photolysis in cyclohexane–amine is extremely slow compared with that in acetonitrile–amine. On the basis of these results, it can be concluded that the intermediate in the amine-assisted DBA → 9-bromoanthracene debromination is $DBA^{\cdot -}$, but the decomposition of the DBA–amine exciplex into $DBA^{\cdot -}$ and the amine radical cation is strongly affected by the dielectric constant of the pure solvent. © 1997 Elsevier Science S.A.

Keywords: 9-Bromoanthracene; Cyclohexane–amine; 9,10-Dibromoanthracene; Picosecond laser photolysis

1. Introduction

In previous papers [1–3], we reported the results obtained by nanosecond laser photolysis of *meso*-substituted haloanthracenes (9-chloro, 9,10-dichloro, 9-bromo and 9,10-dibromo compounds) in acetonitrile–amine (triethylamine or *N*,*N*-dimethylaniline); the generation of haloanthracene radical anions was observed within the duration of pulse excitation. From an examination of the effects of the amine concentration on the intensities of the fluorescence and triplet–triplet absorption spectra of the haloanthracenes, as well as the effect of the solvent on the rate of amine-assisted dehalogenation (yielding 9-haloanthracenes or anthracene) caused by steady state photolysis, we proposed that the intermediate for dehalogenation was the haloanthracene radical anion generated by the decomposition of the exciplex formed by a diffusion-controlled reaction between the lowest excited singlet state of the haloanthracene and ground state amine. However, no absorption bands attributable to the lowest excited singlet state of the haloanthracene and the haloanthracene–amine exciplex were detected by nanosecond laser photolysis.

In this paper, we study picosecond laser photolysis of 9,10-dibromoanthracene (DBA) in cyclohexane–amine; we investigate the excited state dynamics of the lowest excited singlet state of DBA forming an exciplex with ground state amine. Since steady state photolysis indicates that the rate of DBA → 9-bromoanthracene debromination in cyclohexane–amine is extremely slow compared with that in acetonitrile–amine, we conclude that the intermediate for amine-assisted DBA → 9-bromoanthracene debromination is the DBA radical anion, but the generation of this radical anion from the DBA–amine exciplex is strongly affected by the dielectric constant of the pure solvent. Preliminary results have been published elsewhere [4].

2. Experimental details

DBA from Aldrich was recrystallized three times from ethanol, and GR grade triethylamine (TEA) and *N*,*N*-dime-

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thylaniline (DMA) from Wako were refluxed over calcium hydride and distilled under a nitrogen atmosphere. Spectral grade cyclohexane (CH) from Dojin was used as a solvent without further purification, and the sample solution was degassed by several freeze–pump–thaw cycles or deoxygenated by bubbling of Ar gas.

All experiments were performed at room temperature. The transient absorption spectra were measured by a pump–probe method using a picosecond Nd:glass laser photolysis system [5]; the third harmonic light pulse (351 nm) with a full width at half-maximum (FWHM) of 7 ps was used for sample excitation and the probing light pulse was generated by focusing the fundamental light pulse (1054 nm) into D_2O. The emission spectra were recorded using a Hitachi MPF-4 spectrofluorometer and the changes in the emission intensities with time were measured by a single-photon counting method using the second harmonic light pulse (400 nm) from a picosecond Ti:sapphire laser [6].

In order to determine the rate of amine-assisted DBA → 9-bromoanthracene debromination, steady state photolysis was carried out in the presence of 0.04 mol dm^{-3} amine (TEA or DMA) using 404.6 nm monochromatic light from a USH-500D super-high-pressure mercury lamp; the absorbance decrease of DBA at 402 nm was measured using a Hitachi 200-20 spectrophotometer.

3. Results and discussion

Fig. 1(a) and (b) show the fluorescence spectra (originating from the lowest excited singlet state ($^1DBA^*$) of DBA) recorded in the absence and presence of amine (TEA or DMA). Since the addition of amine causes a spectral decrease, the fluorescence intensities in the absence (I_0) and presence (I_A) of amine were calculated by spectral integration over wavenumbers. As shown in Fig. 1(c) and (d), plots of I_0/I_A (open circles) against amine concentration give straight lines up to 0.1 mol dm^{-3} amine concentration; the slopes of the straight lines are $s' = 11.2$ dm^3 mol^{-1} (Fig. 1(c)) and 23.8 dm^3 mol^{-1} (Fig. 1(d)).

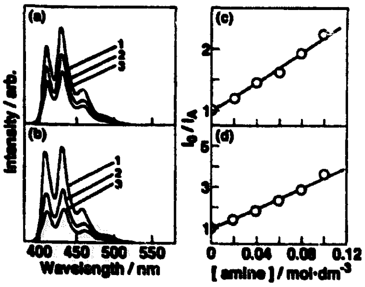


Fig. 1. Spectral decrease in DBA fluorescence (monomer emission) observed in CH containing TEA (a) and DMA (b), and plots of I_0/I_A (O) against TEA (c) and DMA (d) concentration in CH. The concentrations of amine in (a) and (b) are 0 (1), 0.04 (2) and 0.08 (3) mol dm^{-3}, and the slopes of the straight lines drawn for I_0/I_A are $s' = 11.2$ (c) and 23.8 (d) dm^3 mol^{-1}.

At a high amine concentration (0.5–2 mol dm^{-3}), the fluorescence band attributed to monomer emission originating from $^1DBA^*$ and a broad emission band are observed as shown in Fig. 2(a) and (b). In the absence of amine, no broad emission band can be seen, and the decay curve of the monomer emission band with time can be analysed by a single-exponential function with a decay rate constant of $k_f = 6.7 \times 10^8$ s^{-1}. In the presence of amine, the intensity ($I_M(t)$) of the monomer emission band decreases continuously, but the intensity ($I_E(t)$) of the broad emission band increases at first and then decreases with time. Typical examples obtained in the presence of 1 mol dm^{-3} TEA are shown by the broken lines in Fig. 2(c) and (d). The full lines (with rate constants $k_1 = 1.3 \times 10^{10}$ s^{-1} and $k_2 = 3.8 \times 10^9$ s^{-1}) are the best-fit emission intensities calculated by taking into account the excitation pulse profile (Exc) and using the biexponential concentration functions of the transient species responsible for the monomer emission band ($C_M(t)$) and the broad emission band ($C_E(t)$) given by Eqs. (1) and (2) respectively

$$C_M(t) = c_1 \exp(-k_1 t) + c_2 \exp(-k_2 t) \quad (1)$$

$$C_E(t) = c_3[-\exp(-k_1 t) + \exp(-k_2 t)] \quad (2)$$

where c_1, c_2 and c_3 are the positive experimental constants; in the presence of 1 mol dm^{-3} DMA, the rate constants are found to be $k_1 = 4.8 \times 10^{10}$ s^{-1} and $k_2 = 1.4 \times 10^9$ s^{-1}. $I_M(t)$ and $I_E(t)$ at various amine concentrations were also measured, and a plot of $k_1 + k_2$ against the concentration of TEA (open circles) or DMA (filled circles) gives a straight line as shown in Fig. 3.

Fig. 4 shows the transient absorption spectra obtained by picosecond laser photolysis of DBA in the presence of 1 mol dm^{-3} amine (TEA or DMA). Clearly, an absorption band (B_M) with an absorption maximum at $\lambda_{max} = 620$ nm

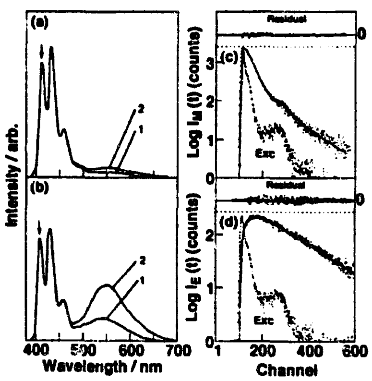


Fig. 2. Monomer and exciplex emission bands observed for DBA in CH containing 1 (1) or 2 (2) mol dm^{-3} TEA (a) and 0.5 (1) or 1 (2) mol dm^{-3} DMA (b), and $I_M(t)$ at 440 nm (c) and $I_E(t)$ at 600 nm (d) obtained in CH containing 1 mol dm^{-3} TEA (· · ·); 100 channel = 264.2 ps. The spectral intensities in (a) and (b) are normalized at the emission peaks indicated by the arrows, and the full curves in (c) and (d) are the best-fit emission intensities calculated by taking into account the excitation pulse profile (Exc) and using the biexponential concentration functions given by Eqs. (1) and (2) respectively; the rate constants are $k_1 = 1.3 \times 10^{10}$ s^{-1} and $k_2 = 3.8 \times 10^9$ s^{-1}.

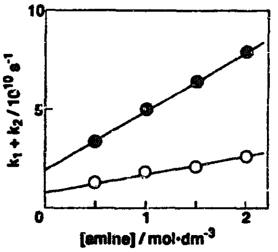


Fig. 3. Plot of $k_1 + k_2$ against TEA (○) or DMA (●) concentration in CH.

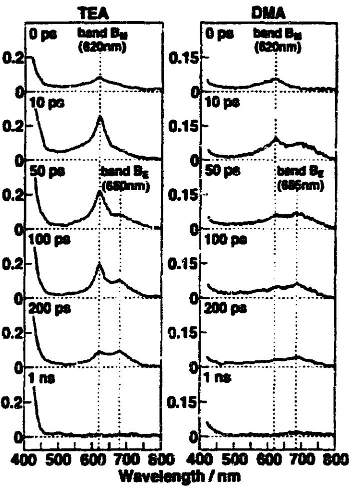


Fig. 4. Transient absorption spectra obtained by picosecond laser photolysis of DBA in CH containing 1 mol dm^{-3} TEA or DMA.

decreases with time accompanied by the increase and then decrease of another absorption band (B_E) with an absorption maximum at $\lambda_{max} = 680$ or 685 nm. In the absence of amine, no band B_E can be seen and band B_M decreases with time following a single-exponential function with a decay rate constant (6.7×10^8 s^{-1}) equal to the fluorescence decay rate constant (k_f) obtained previously. Hence band B_M shown in Fig. 4 can safely be assigned to the singlet–singlet ($S' \leftarrow S_1$) absorption originating from ^{1}DBA*.[1] In fact, with regard to the spectral profile and the position of the absorption maximum, band B_M is very similar to the $S' \leftarrow S_1$ absorption bands reported for anthracene and its several derivatives [7]. In the presence of 1 mol dm^{-3} amine, as shown in Fig. 5, the time-dependent absorbance changes of bands B_M ($D_M(t)/D_M(\text{max})$, open circles) and B_E ($D_E(t)/D_E(\text{max})$, filled circles) can be reproduced by the full and broken curves respectively, which were calculated assuming a gaussian intensity function (FWHM = 7 ps) for both the excitation and probing light pulses and using Eqs. (1) and (2) for the concentrations of transient species responsible for bands B_M and B_E respectively. Naturally, the rate constants (k_1 and k_2) thus obtained are found to be equal to those obtained for $I_M(t)$ and $I_E(t)$.

The broad emission band shown in Fig. 2(a) or (b) is very similar to that of the 9,10-dichloroanthracene–DMA exciplex in *n*-heptane reported by Soloveichik et al. [8]. Although they observed no exciplex emission for DBA in *n*-heptane–DMA, we have observed a broad emission band (similar to that shown in Fig. 2(a) or (b)) and an absorption band (similar to band B_E shown in Fig. 4) for DBA in *n*-heptane–amine (TEA or DMA) [9]. Hence all the results obtained so far can be interpreted in terms of the formation of an exciplex (^{1}(DBA–amine)*) by reaction of ^{1}DBA* with ground state amine (cf. Scheme 1[2]) [11], i.e. both the broad emission band (shown in Fig. 2(a) or Fig. 2(b)) and the absorption band (B_E shown in Fig. 4) are responsible for ^{1}(DBA–amine)*. Putting $k = k_q$[amine] and $k_E = k_G + k_{ion} + k'_{isc}$, the rate constants ($k_1$ and k_2) obtained previously can be expressed by

$$k_{1,2} = \tfrac{1}{2}[k + k' + k_E + k_f \pm \{(k + k_f - k' - k_E)^2 + 4kk'\}^{1/2}] \tag{3}$$

where $k_f = k'_G + k_{isc}$ is the fluorescence decay rate constant (6.7×10^8 s^{-1}) obtained in the absence of amine. Since

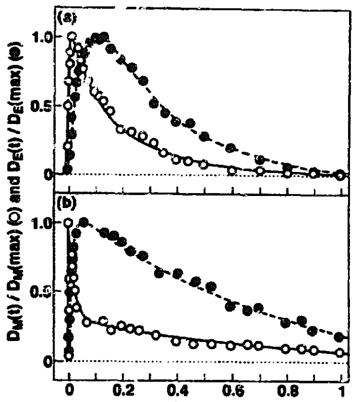
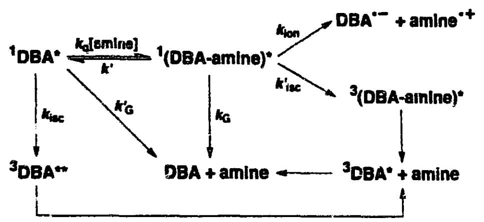


Fig. 5. $D_M(t)/D_M(\text{max})$ at 620 nm (○) (a, b) and $D_E(t)/D_E(\text{max})$ at 680 (a) or 685 (b) nm (●) obtained in CH containing 1 mol dm^{-3} TEA (a) or DMA (b). The full and broken curves are the best-fit absorbances calculated assuming a gaussian intensity function (FWHM = 7 ps) for both the excitation and probing light pulses and using the biexponential concentration functions given by Eqs. (1) and (2) respectively; the rate constants are $k_1 = 1.3 \times 10^{10}$ s^{-1} and $k_2 = 3.8 \times 10^9$ s^{-1} (a) or $k_1 = 4.8 \times 10^{10}$ s^{-1} and $k_2 = 1.4 \times 10^9$ s^{-1} (b).



Scheme 1.

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[1] The absorption band at wavelengths shorter than approximately 450 nm is due to the triplet–triplet absorption originating from the lowest excited triplet state of DBA [1,3].

[2] In the absence of amine, the formation of the lowest excited triplet state (^{3}DBA*) is ascribed to the indirect ^{1}DBA* → ^{3}DBA** → ^{3}DBA* intersystem crossing through an adjacent higher excited triplet state (^{3}DBA**) [10]. Also, the amine-assisted formation of ^{3}DBA* observed in acetonitrile, ethanol and *n*-heptane [1,3,9] is interpreted in terms of intersystem crossing from ^{1}(DBA–amine)* to its triplet exciplex (^{3}(DBA–amine)*) followed by rapid decomposition into ^{3}DBA* and ground state amine.

Scheme 1 indicates that $k'_E = k' + k_E = k' + k_G + k_{ion} + k'_{isc}$ is the overall decay rate constant of ^{1}(DBA–amine)*, Eq. (3) gives the following relation

$$k_1 + k_2 = k_q[\text{amine}] + k'_E + k_f \qquad (4)$$

The slopes and intercepts of the straight lines shown in Fig. 3 therefore give the following rate constants: $k_q = 8.9 \times 10^9$ dm^3 mol^{-1} s^{-1} and $k'_E = 7.7 \times 10^9$ s^{-1} in the presence of TEA, and $k_q = 2.9 \times 10^{10}$ dm^3 mol^{-1} s^{-1} and $k'_E = 2.0 \times 10^{10}$ s^{-1} in the presence of DMA. The quenching rate constant ($k_q = 8.9 \times 10^9$ dm^3 mol^{-1} s^{-1}) of ^{1}DBA* by ground state TEA is nearly equal to that ($k_D = 7.4 \times 10^9$ dm^3 mol^{-1} s^{-1}) estimated for a diffusion-controlled reaction using the Debye–Smoluchowski equation ($k_D = 8RT/3000\eta$) and the viscosity ($\eta = 0.898$ cP [12]) of CH at 25 °C. Although $k_q = 2.9 \times 10^{10}$ dm^3 mol^{-1} s^{-1} obtained in the presence of DMA is somewhat greater than $k_D = 7.4 \times 10^9$ dm^3 mol^{-1} s^{-1}, no reason for this discrepancy has yet been found.

Denoting the efficiency for the repopulation of ^{1}DBA* from ^{1}(DBA–amine)* to be $\gamma = k'/(k' + k_E)$ (cf. Scheme 1), the relative intensity of the monomer emission band (I_0/I_A) at a given amine concentration can be expressed by

$$\begin{aligned} I_0/I_A &= k_1 k_2 / k_f(k' + k_E) \\ &= 1 + k_q[\text{amine}](1 - \gamma)/k_f = 1 + s'[\text{amine}] \qquad (5) \end{aligned}$$

Since $s' = k_q(1 - \gamma)/k_f$ is the slope of the straight line shown in Fig. 1(c) or Fig. 1(d), a choice of k_q and k_f gives the value of $\gamma = k'/(k' + k_E)$. Using the value of $k'_E = k' + k_E$ obtained previously, the decay rate constants (k' and k_E) of ^{1}(DBA–amine)* can thus be calculated as follows: for $\gamma = 0.14$ and $k'_E = 7.7 \times 10^9$ s^{-1} in the presence of TEA, $k' = 1.1 \times 10^9$ s^{-1} and $k_E = 6.6 \times 10^9$ s^{-1}; for $\gamma = 0.44$ and $k'_E = 2.0 \times 10^{10}$ s^{-1} in the presence of DMA, $k' = 8.5 \times 10^9$ s^{-1} and $k_E = 1.1 \times 10^{10}$ s^{-1}.[3]

Fig. 6(a) and (b) show the absorption spectral changes on steady state photolysis of DBA in CH containing 0.04 mol dm^{-3} amine (TEA or DMA). Clearly, the decrease in reactant absorptions (peaks R$_1$, R$_2$ and R$_3$) is accompanied by the increase in product absorptions (peaks P$_1$, P$_2$ and P$_3$, which are identical with the absorption peaks of 9-bromoanthracene). Although steady state photolysis of DBA in acetonitrile (CH_3CN) containing 0.04 mol dm^{-3} amine also gives rise to the formation of 9-bromoanthracene, no broad absorption band (at wavelengths longer than approximately 410 nm), as observed in Fig. 6(a) and (b), can be seen [9]. Since the maximum photolysis times are 4 min in CH_3CN–TEA and 80 s in CH_3CN–DMA, the broad absorption band observed in CH–amine can be ascribed to an absorption band of a byproduct obtained on prolonged photolysis. Measuring the 402 nm absorbances of DBA at photolysis times of zero (D_0) and t (D_t), their ratio (D_t/D_0) is plotted against the photolysis time as shown in Fig. 6(c) and (d). Dividing the initial slope by that obtained in CH_3CN–TEA (or CH_3CN–DMA) [9], the rate of DBA → 9-bromoanthracene debromination in CH–TEA (or CH–DMA) is found to be 1.5×10^{-2} times (or 5.9×10^{-4} times) slower than that in CH_3CN–TEA (or CH_3CN–DMA). We thus suppose that the faster rate of debromination in CH_3CN–amine than in CH–amine indicates that the decomposition of ^{1}(DBA–amine)* into the DBA radical anion (DBA$^{\cdot -}$) and the amine radical cation (amine$^{\cdot +}$) in CH_3CN–amine is much more effective compared with that in CH–amine, i.e. DBA$^{\cdot -}$ is an intermediate in the amine-assisted DBA → 9-bromoanthracene debromination.

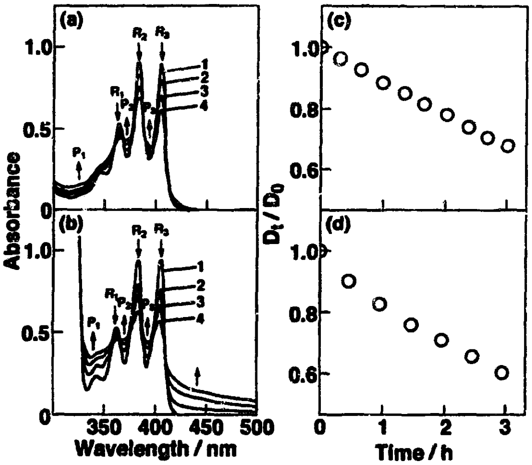

Fig. 6. Absorption spectral change on steady state photolysis of DBA (a, b) and a plot of D_t/D_0 against the photolysis time (c, d) obtained in CH containing 0.04 mol dm^{-3} TEA (a, c) or DMA (b, d). In (a) and (b), the photolysis times are 0 (1), 1 (2), 2 (3) and 3 (4) h.

Soloveichik et al. [13] have reported that the photochemical dechlorination of 9,10-dichloroanthracene by DMA in CH_3CN is strongly retarded on addition of azulene (and ferrocene), and that the increase in the triplet decay rate constant with increasing DMA concentration is not linear. On the basis of these results, they have proposed that the haloanthracene radical anions produced via the exciplexes of singlet haloanthracenes with ground state amine do not participate in the dehalogenation, but the exciplexes of triplet haloanthracenes with ground state amine are the reaction intermediates. However, our previous studies have revealed the participation of the lowest excited singlet states of haloanthracenes in the dehalogenation by amine, and no evidence supporting the triplet exciplex mechanism has been obtained [1–3]. Our conclusion that the intermediates of the dehalogenation of haloanthracenes are the radical anions is supported by the following facts.

1. In photochemistry, the radical anions produced via several singlet exciplexes are generally believed to be the intermediates for the dehalogenation of aromatic halides by amine [14–18].
2. In radiation chemistry, organic halides are frequently used as effective electron scavengers, where an electron easily

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[3] $s = k_q/k_f$ reported for 9-chloroanthracene, 9,10-dichloroanthracene, 9-bromoanthracene and 9,10-dibromoanthracene in CH_3CN–DMA [1–3] should read $s' = k_q(1 - \gamma)/k_f$, because the exciplex absorptions and emissions can be clearly seen [9]; also, $\beta = k'_{isc}/(k_G + k_{ion} + k'_{isc})$ reported previously should read $\beta' = k'_{isc}/(k' + k_G + k_{ion} + k'_{isc})$.

attaches to the organic halides giving rise to dissociation of the radical anions into the neutral radicals and the halogen anions by a so-called dissociative electron attachment reaction [19–21].

3. For DBA and 9-bromoanthracene at room temperature in CH_3CN without amine, pulse radiolysis generates the bromoanthracene radical anions and γ-radiolysis causes debromination identical with that caused by photolysis in CH_3CN–amine [22]; for 9,10-dichloroanthracene and 9-chloroanthracene in the absence of amine, γ-radiolysis causes dechlorination (at room temperature in CH_3CN) or generates the radical anions (at 77 K in 2-methyltetrahydrofuran) [2].

In spite of these circumstances, nanosecond laser photolysis of DBA reveals the existence of an absorption band responsible for $DBA^{\cdot -}$ only in CH_3CN–amine [1]; no such an absorption band can be seen in CH–amine. Furthermore, as shown in Figs. 4 and 5, picosecond laser photolysis of DBA in CH–amine reveals that band B_E, due to the absorption of ^{1}(DBA–amine)*, decreases with time to zero absorbance and no accompanying appearance of the absorption band responsible for $DBA^{\cdot -}$ can be seen during the decrease in band B_E. Since the rate of DBA → 9-bromoanthracene debromination in CH_3CN–amine is very rapid compared with that in CH–amine, and since the dielectric constant (37.5) of CH_3CN is much greater than that (2.02) of CH [23], it can be concluded that the generation of $DBA^{\cdot -}$ in a polar solvent such as CH_3CN–amine is essential for the effective amine-assisted debromination of DBA, i.e. the decomposition of ^{1}(DBA–amine)* into $DBA^{\cdot -}$ and amine$^{\cdot +}$ is affected by the dielectric constant of the pure solvent. This conclusion is consistent with the results obtained in ethanol and *n*-heptane containing amine [9].

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