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Participation of the Lowest Excited Singlet States of 9-Bromoanthracene and 9,10-Dibromoanthracene for Their Photochemical Debrominations by Amine (Triethylamine or N,N-Dimethylaniline) in Acetonitrile

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From measurements of fluorescence and triplet-triplet absorption spectra of bromoanthracenes in acetonitrile-amines, it is concluded that bromoanthracene radical anions produced by a reaction of the lowest singlet states of bromoanthracenes with amines are the intermediates for the debrominations.

Since the photochemical debrominations of 9,10-dibromoanthracene (DBA) in acetonitrile-amine [triethylamine (TEA) or N,N-dimethyaniline (DMA)] were found to proceed via the consecutive reactions [DBA→9-bromoanthracene (BA) →anthracene], we concluded that the reaction intermediates were the bromoanthracene radical anions ($DBA^{\cdot-}$,$BA^{\cdot-}$) produced by a diffusion-controlled reaction of the lowest excited singlet (S_1) states of bromoanthracenes with amines (TEA,DMA).1) Recently, however, Soloveichik et al.2) observed that the dechlorination of 9,10-dichloroanthracene (DCA) in acetonitrile-DMA was strongly retarded upon addition of ferrocene or azulene, while the triplet yield of DCA increased with increasing DMA concentration. Based on these results, they refuted our conclusion and proposed that the haloanthracene radical anions produced via the singlet exciplexes of haloanthracenes with amines did not participate in the dehalogenations but the triplet exciplexes of haloanthracenes with amines were the reaction intermediates. Thus, the present paper deals with the reinvestigation concerning the debrominations of BA and DBA in acetonitrile containing TEA or DMA.

BA and DBA from Aldrich were recrystallized from ethanol, and BA was further purified by vacuum sublimation. GR-grade TEA and DMA from Wako were refluxed over calcium hydride and distilled under a nitrogen atmosphere. Spectral-grade acetonitrile (Dojin) was used as the solvent which was dried using molecular sieves 3A. All experiments were performed at room temperature and the sample solutions were degassed by several freeze-pump-thaw cycles. The fluorescence spectra were recorded using a Hitachi MPF-4 spectrofluorometer and the time-resolved triplet-triplet ($T' \leftarrow T_1$) absorption spectra due to the lowest excited triplet (T_1) states of bromoanthracenes were recorded using the second harmonic (347.2 nm, pulse width=20 ns) from a Q-switched ruby laser photolysis system.[3)]

Figure 1 shows the fluorescence spectra of BA and DBA recorded in the absence and presence of amines [TEA (a,c) and DMA (b,d)]. Clearly, the spectral intensities decrease with increasing amine concentration. From these spectra, the average intensities of two strong emission peaks in the absence (I_0^F) and presence (I_A^F) of amines are calculated, and plots of I_0^F/I_A^F against amine concentration give the straight lines as shown in Fig. 2. Choice of fluorescence lifetimes in the absence of amine, i.e. 0.16 ns for BA and 1.27 ns for DBA,[4)] gives the rate constants (k_q) on an order of 10^{10} $M^{-1}s^{-1}$ indicating that the S_1 states of bromoanthracenes react with amines by a diffusion-controlled reaction (1 M=1 mol dm^{-3}).

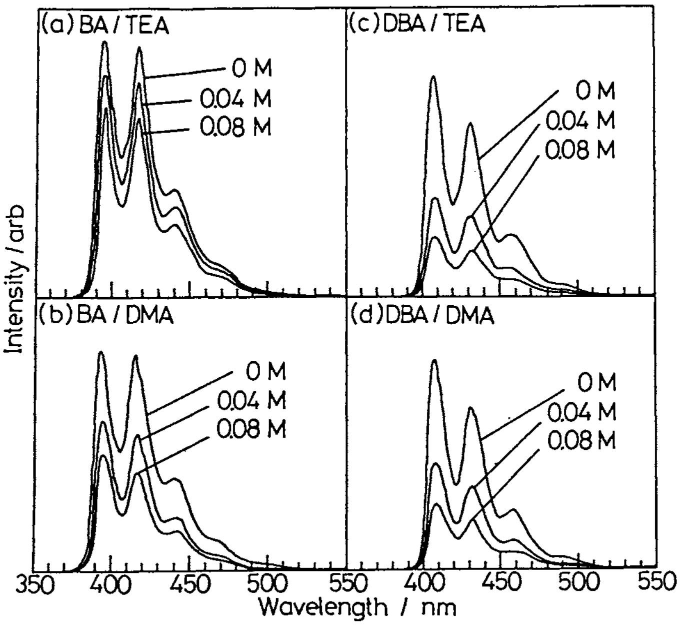

Fig. 1. Intensity decreases of fluorescence spectra of BA and DBA in acetonitrile caused upon addition of TEA (a,c) and DMA (b,d).

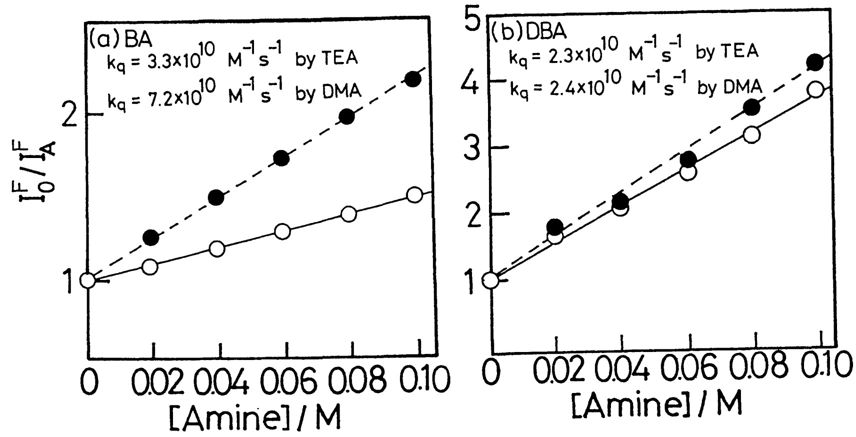

Fig. 2. Plots of I_0^F/I_A^F against amine concentaration in acetonitrile. ○, for TEA; ●, for DMA

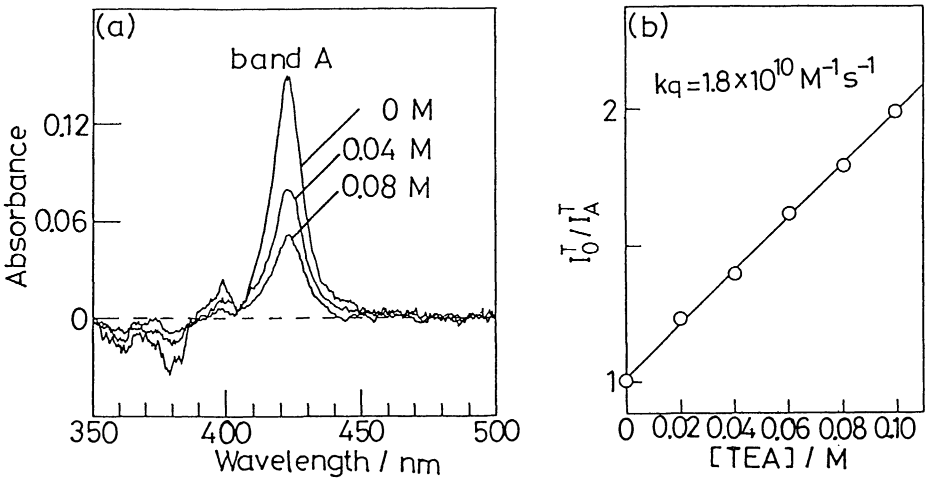

Fig. 3. Intensity decrease of the $T' \leftarrow T_1$ absorption spectra of DBA caused upon addition of TEA (a) and plot of I_0^T/I_A^T against TEA concentration (b) in acetonitrile.

When the time-resolved $T' \leftarrow T_1$ absorption spectra of bromoanthracenes are recorded at a delay time of 70 ns and a gate time of 20 ns, the spectral intensities also decrease with increasing amine concentration. A typical example for DBA-TEA is shown in Fig. 3(a). Since it has been confirmed that the T_1 states of bromoanthracenes decay in the microsecond time regime even in the presence of amines, the spectral decrease shown in Fig. 3(a) reflects the decrement in the yield of the S_1 state of DBA caused upon addition of TEA. Thus, the intensities of $T' \leftarrow T_1$ absorption spectra in the absence (I_0^T) and presence (I_A^T) of TEA are calculated by the integration of band A over the absorption wavenumbers, and a plot of I_0^T/I_A^T against TEA concentration gives a straight line with a S_1 quenching rate constant (1.8×10^{10} $M^{-1}s^{-1}$) which is nearly equal to that (2.3×10^{10} $M^{-1}s^{-1}$) obtained from the decrease of fluorescence intensity upon addition of TEA.

We have also obtained the following results:5) (1) Ferrocene quenches the T_1 states of bromoanthracenes by a diffusion-controlled reaction, but the rates of reactant decreases (or product increases) during steady-state photolysis in acetonitrile-amines are not affected upon addition of ferrocene; neither addition of azulene causes the change in the debromination rates. (2) The bromoanthracene radical anions are produced within the duration of nanosecond pulse excitation in acetonitrile-amines (1 M), while the T_1 states of bromoanthracenes are quenched by amines in the microsecond time regime accompanied with no formation of the radical anions of BA and DBA.

All the results obtained so far support our previous conclusion that the bromoanthracene radical anions produced by a diffusion-controlled reaction of the S_1 states of bromoanthracenes with amines are the reaction inte mediates for the debrominations.1) Since a similar result has also been obtained for DCA,6) the participation of the triplet exciplex of DCA with DMA in the dechlorination as proposed by Soloveichik et al.2) is doubtful.

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