Dechlorination of Meso-Substituted Chloroanthracenes (9,10-Dichloro and 9-Chloro Compounds) via Their Radical Anions Produced by a Diffusion-Controlled Reaction of the Lowest Excited Singlet States of Chloroanthracenes with Ground-State Amine (Triethylamine or N,N-Dimethylaniline) in Acetonitrile at Room Temperature

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Steady-state photolysis of XA (9,10-dichloroanthracene and 9-chloroanthracene) in acetonitrile-amine (triethylamine or N,N-dimethylaniline) causes the consecutive reactions (DCA \rightarrow CA \rightarrow anthracene), but the rate of dechlorination is not affected upon addition of azulene and ferrocene in spite of quenching of the lowest excited triplet states [${}^{3}XA(T_{1})$] of XA by these additives with quenching rate constants of the order for that of a diffusion-controlled reaction. Although not only the intensities of fluorescence spectra due to the lowest excited singlet states [${}^{1}XA(S_{1})$] of XA but also those of triplet-triplet absorption spectra due to ${}^{3}XA(T_{1})$ decrease with increasing amine concentration, the appearance of absorption spectra due to the chloroanthracene radical anions (XA⁻) within the duration of nanosecond pulse excitation has been attributed to the formation of singlet exciplexes [${}^{1}(XA-amine)^{*}$] by a diffusion-controlled reaction of ${}^{3}XA(S_{1})$ with ground-state amine followed by decomposition into XA⁺ and the amine radical cations. Since ${}^{3}XA(T_{1})$ are quenched by amine in the microsecond time regime and no evidence supporting the participation of the triplet exciplexes of chloroanthracenes with amine in the dechlorination as proposed by Soloveichik et al. is obtained (cf. ref 2), we have concluded that XA⁺⁻ produced via ${}^{1}(XA-amine)^{*}$ are the reaction intermediates for dechlorination of XA.

Introduction

For the photochemical debromination of meso-substituted bromoanthracenes (9,10-dibromo and 9-bromo compounds) by amine [triethylamine (TEA) or N,N-dimethylaniline (DMA)] in acetonitrile, we have proposed that the reaction intermediates are the bromoanthracene radical anions produced by a diffusioncontrolled reaction of the lowest excited singlet states of bromoanthracenes with ground-state amine yielding the singlet exciplexes followed by the decomposition into the bromoanthracene radical anions and the amine radical cation.¹ Meanwhile, Soloveichik et al.² have reported that the photochemical dechlorination of 9,10-dichloroanthracene by DMA in acetonitrile is strongly retarded upon addition of azulene (and ferrocene) and that the increment of triplet decay rate constant with increasing DMA concentration is not linear. Based on these results, they have refuted our conclusion and 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.

In photochemistry, however, the radical anions produced via the several singlet exciplexes are generally believed to be the intermediates for the dehalogenation of aromatic halides by amine.³⁻¹⁰ Moreover, our recent reinvestigation has still revealed the participation of the lowest excited singlet states of bromoanthracenes in their debromination by amine, and no evidence supporting the triplet exciplex mechanism is obtained.^{11,12} Thus, the present paper deals with the photochemical dechlorination of 9,10-dichloroanthracene (DCA) and 9-chloroanthracene (CA) by amine (TEA or DMA) studied by steady-state photolysis and laser photolysis in acetonitrile at room temperature. A preliminary result for DCA has been published elsewhere.¹³

Experimental Section

Zone-refined anthracene (Tokyo Kasei) was used without further purification, and DCA and CA from Aldrich were recrystallized from ethanol; CA was further purified by vacuum sublimation. GR-grade azulene (Aldrich) and ferrocene (Nacarai) were used without further purification, but GR-grade TEA and DMA from Wako were refluxed over calcium hydride and distilled under a nitrogen atmosphere. The solvents used were spectralgrade acetonitrile (CH₃CN) from Dojin and 2-methyltetrahydrofuran (MTHF) from Aldrich which were dried using 3A molecular sieves (Wako) preheated in a crucible over Bunsen burner and cooled in vacuo; dried MTHF was further distilled under nitrogen atmosphere and again dried using sodium metal. The sample solutions were degassed by several freeze-pump-thaw cycles.

Steady-state photolysis was performed using a USH-500D super-high-pressure mercury lamp for DCA and a UXL-500 D xenon lamp for CA, and the absorption spectral change was recorded using a Hitachi 200-20 spectrophotometer: For photolysis of DCA, the 404.6-nm monochromatic light was selected by a combination of two Toshiba color glass filters (UV-39 and V-V40) and a filter solution (CuSO₄·5H₂O, 50 g dm⁻³, path length 3 cm); for photolysis of CA, however, the light of wavelengths longer than 390 nm was selected by a combination of a Toshiba UV-39 color glass filter and the filter solution. For DCA in CH₃CN/amine (0.04 and 0.08 M), the quantum yields (Φ_R) of dechlorination yielding CA were determined by the Hatchard-Parker potassium ferrioxalate actinometry method¹⁴ measuring the decrement in the reactant absorption at 403 nm.

Static fluorescence spectra due to the lowest excited singlet states $[{}^{1}XA(S_{1})]$ of XA (DCA and CA) were recorded using a Hitachi MPF-4 spectrofluorometer with no correction of the sensitivity. On the other hand, the time-resolved fluorescence spectra due to ${}^{1}XA(S_{1})$, the triplet-triplet $(T' \leftarrow T_{1})$ absorption spectra due to the lowest excited triplet states $[{}^{3}XA(T_{1})]$ of XA, and the absorption spectra of the chloroanthracene radical anions (XA⁻⁻) were recorded by sample excitation using the second harmonic (347.2 nm, pulse width = 20 ns) from a Q-switched ruby laser equipped with a multichannel analyzer controlled by a personal computer (NEC PC-9801RA);¹⁵ the sensitivity of the multichannel analyzer was corrected by using a halogen lamp as a standard light source. By operating the multichannel analyzer in the gated mode and using a pulsed xenon flash lamp (Unisoku USP543S) as a probing-light source, the absorption spectra of XA⁻⁻ were recorded at 0-ns delay (a delay time where the excitation pulse intensity was maximum) and a gate time of 50 ns, while the $T' \leftarrow T_1$ absorption spectra of ${}^{3}XA(T_1)$ were recorded at a delay time of 70 ns and gate time of 20 ns in order to avoid the disturbance due to fluorescences; the quantum yields (Φ_T) of triplet formation for DCA in CH₃CN/amine (0.04 and 0.08 M) were determined from the integrated intensities of $T' \leftarrow T_1$ absorption spectra relative to that of anthracene with $\Phi_{\rm T}$ of 0.72.¹⁶ To detect the all fluorescing lights, however, the time-resolved fluorescence spectra of ${}^{1}XA(S_{1})$ were recorded by operating the multichannel analyzer in the continuous mode, and the gate of



Figure 1. Dechlorination of XA upon steady-state photolysis in CH₃CN/TEA (0.04 M) (a) and γ -radiolysis in CH₃CN (b) at room temperature.



Figure 2. Decrement in the relative absorbances (D_t/D_0) of XA during steady-state photolysis at room temperature in CH₃CN/TEA (0.04 M) without (O) and with 1×10^{-4} M azulene (\blacktriangle) [or ferrocene (\blacksquare)].

multichannel analyzer was opened before sample excitation; the fluorescence quantum yields (Φ_F) due to ${}^1XA(S_1)$ in CH₃CN without amine were determined from the integrated intensities of time-resolved fluorescence spectra relative to that of anthracene with Φ_F of 0.27.¹⁶ The decays of absorptions due to ${}^3XA(T_1)$ and XA⁻⁻ were analyzed by means of a combination of a photomultiplier (Hamamatsu R666) with a storage oscilloscope (Iwatsu TS-8123) controlled by the personal computer, while the fluorescence decays of ${}^1XA(S_1)$ were measured using a Horiba time-resolved photoluminescence and fluorescence spectrometer (NAES-700L) with an excitation light source of a N₂ laser (337 nm with pulse width of 0.7 ns).

In the absence of amine, γ -radiolysis of XA was performed at room temperature (in CH₃CN) and 77 K (in MTHF) using ⁶⁰Co γ -rays at an exposure-dose rate of ~76 Gy/min.

Results and Discussion

Figure 1a shows the change of absorption spectra upon steady-state photolysis of XA in CH₃CN/TEA (0.04 M) at room temperature; similar results are also obtained in CH₃CN/DMA (0.04 M). In comparison with absorption and fluorescence spectra of the authentic samples, we have concluded that the photoproducts from DCA and CA are CA and anthracene, respectively. Since these results are identical with those obtained for 9,10-dibromoanthracene and 9-bromoanthracene,¹ it can safely be con-

TABLE I: Quantum Yields of Dechlorination (Φ_R) and Triplet Formation (Φ_T) Obtained for DCA in CH₃CN/Amine

| amine/M | Φ _R | Φ _T | |
|----------|-------------------|-------------------|--|
| TEA 0.04 | 0.037 ± 0.007 | 0.121 ± 0.006 | |
| 0.08 | 0.064 ± 0.008 | 0.079 🛳 0.004 | |
| DMA 0.04 | 0.083 ± 0.018 | 0.086 🕿 0.004 | |
| 0.08 | 0.117 ± 0.014 | 0.073 ± 0.004 | |
| | | | |

TABLE II: Quenching Rate Constants (k_q) of ¹XA(S₁) by Amine, and the Best-Fit Values of $\alpha (=\beta k_q/k_{inc})$ and $\beta [=k'_{inc}/(k_G + k_{ion} + k'_{inc})]$ in CH₃CN/Amine

| | $\frac{1}{k_q/M^{-1} s^{-1}}$ | | α/M ⁻¹ | | β/10 ⁻² | |
|-----|-------------------------------|-----------------------|-------------------|-----|--------------------|-----|
| | TEA | DMA | TEA | DMA | TEA | DMA |
| DCA | 1.6 × 10 ^{10a} | | 24 | | 6.4 | |
| | 1.4×10^{10b} | 2.5×10^{10b} | 20 | 35 | 6.1 | 6.0 |
| | 1.4×10^{10c} | 2.7×10^{10c} | 20 | 39 | 6.1 | 5.9 |
| CA | 1.1×10^{10a} | | 3.6 | | 9.9 | |
| | 1.2×10^{10b} | 2.4×10^{10b} | 4.5 | 10 | 12 | 13 |
| | 1.1×10^{10c} | 2.4×10^{10c} | 3.6 | 10 | 9.9 | 13 |

^a From the increment of fluorescence decay rate constants by amine. ^b From the quenching of static fluorescence spectra by amine. ^c From the quenching of time-resolved fluorescence spectra by amine.



Figure 3. Fluorescence decay curves (full lines) of ${}^{1}XA(S_{1})$ in CH₃CN without amine at room temperature (a, b), and plots of fluorescence decay rate constants ($k_{\rm F}$) against TEA concentration (c). The dashed lines in (a) and (b) are simulated single-exponential functions with lifetimes (τ) indicated.

cluded that the dechlorination of DCA by amine proceeds by the consecutive reactions (DCA \rightarrow CA \rightarrow anthracene).

Figure 2 shows the effects of azulene and ferrocene on the decrement in the relative reactant absorbances (D_i/D_0) during steady-state photolysis of XA in CH₃CN/TEA (0.04 M). Since similar results are also obtained in CH₃CN/DMA (0.04 M), it can be safely concluded that addition of azulene or ferrocene (1 × 10⁻⁴ M) does not affect the decrement of XA, although Soloveichik et al.² have reported that the quantum yield for the dechlorination of DCA by DMA decreases remarkably upon addition of these additives. We thus have determined the quantum yields (Φ_R) of dechlorination for DCA yielding CA in CH₃CN/amine (0.04 and 0.08 M) upon no addition of azulene or ferrocene and the values of Φ_R are listed in Table I.

Figure 3a,b shows the single-exponential fluorescence decays of ${}^{1}XA(S_{1})$ in CH₃CN without amine at room temperature. Similar fluorescence decay curves are also obtained in CH₃CN/TEA, but the fluorescence decay constants $(k_{\rm F})$ increase linearly with increasing TEA concentration as shown in Figure 3c; the fluorescence quenching rate constants $(k_{\rm q})$ thus obtained are listed in Table II. In accordance with these results, the intensities of static fluorescence spectra due to ${}^{1}XA(S_{1})$ decrease with increasing amine concentration as shown in Figure 4a,b. From these spectra, the average intensities of two strong emission peaks (A and B) in the absence $(I_{\rm b}^{\rm F})$ and presence $(I_{\rm c}^{\rm F})$ of amine are calculated, and plots of $I_{\rm b}^{\rm F}/I_{\rm b}^{\rm F}$ against amine concentration give



Figure 4. Intensity decrement in the static fluorescence spectra of ${}^{1}XA(S_{1})$ upon addition of amine in CH₃CN at room temperature (a, b), and plots of I_{0}^{π}/I_{A}^{π} against amine concentration (c). The straight lines (-, --) correspond to eq 1.



Figure 5. Intensity decrement in the time-resolved fluorescence spectra of ${}^{1}XA(S_{1})$ upon addition of amine in CH₃CN at room temperature (a, b), and plots of I_{0}^{F}/I_{A}^{F} against amine concentration (c). The straight lines (-, ---) correspond to eq 1.

the straight lines (cf. Figure 4c). As shown in Figure 5a,b, the intensities of time-resolved fluorescence spectra due to ${}^{1}XA(S_{1})$ also decrease with increasing amine concentration; although the spectral profiles shown in Figure 5a,b are somewhat different from those shown in Figure 4a,b, this is due to the lack of sensitivity correction for a conventional (Hitachi MPF-4) spectrofluorometer. By the integration of time-resolved fluorescence spectra over emission wavenumbers, the intensities of fluorescence spectra are calculated and plots of I_0^F/I_A^F against amine concentration give the straight lines as shown in Figure 5c. Denoting the fluorescence lifetimes of ${}^{1}XA(S_1)$ in the absence of amine to be τ , I_0^F/I_A^F are given by

$$I_0^{\rm F}/I_{\rm A}^{\rm F} = 1 + k_{\rm e}\tau[\text{amine}] \tag{1}$$

and a choice of the values of τ (8.6 ns for DCA and 3.2 ns for



Figure 6. Intensity decrement in the $T' \leftarrow T_1$ absorption spectra of ${}^{3}XA(T_1)$ upon addition of amine in CH₃CN at room temperature.



Figure 7. Plots of I_0^T/I_A^T against amine concentration in CH₃CN at room temperature. The dashed lines correspond to eq 1, and the full lines are simulated by $I_0^T/I_A^T = (1 + k_q r[amine])/(1 + \alpha[amine])$ using the values of k_q obtained from the quenching of time-resolved fluorescence spectra by amine (cf. Table II).

CA indicated in Figure 3a,b) gives the quenching rate constants (k_q) of the order of 10^{10} M⁻¹ s⁻¹ as listed in Table II, indicating that the quenching of ${}^{1}XA(S_1)$ by amine is a diffusion-controlled reaction.

The intensities of $T' \leftarrow T_1$ absorption spectra due to ${}^{3}XA(T_1)$ also decrease with increasing amine concentration as shown in Figure 6; a normalization of the $T' \leftarrow T_1$ absorption spectra in the presence of amine to those in the absence of amine reveals no change in the spectral profile. Since these spectra are recorded at a delay time of 70 ns and a gate time of 20 ns and since the $T' \leftarrow T_1$ absorptions are found to decay in the microsecond time regime even in the presence of amine (cf. Figure 9), the intensity decrease of $T' \leftarrow T_1$ absorption spectra upon addition of amine can be ascribed to the decrement in the yields of ${}^{1}XA(S_{1})$. Calculating the intensities of $T' \leftarrow T_1$ absorption spectra in the absence (I_0^{T}) and presence $(I_{\mathrm{A}}^{\mathrm{T}})$ of amine by the integration of T' $- T_1$ absorption band (band C) over absorption wavenumbers from $\bar{\nu}_a$ to $\bar{\nu}_b$ indicated in Figure 6, the ratios of I_0^T/I_A^T are potted against amine concentration as shown by open circles in Figure 7. If ${}^{3}XA(T_{1})$ are produced only via the indirect ${}^{1}XA(S_{1}) \rightarrow {}^{3}XA(T_{n}) \rightarrow {}^{3}XA(T_{1})$ intersystem crossing through an adjacent higher excited triplet (T_{n}) state, ${}^{17-19}$ the ratio of I_{0}^{T}/I_{A}^{T} can also be given by

$$I_0^{\mathrm{T}}/I_{\mathrm{A}}^{\mathrm{T}} = 1 + k_{\mathrm{q}}\tau[\mathrm{amine}] \tag{2}$$

TABLE III: Quenching Rate Constants (k'_q) of ³XA(T₁) by Amine, Azulene, or Ferrocene in CH₃CN and the Decay Rate Constants $(k'_{XA^{-}})$ of XA⁻⁻ in CH₃CN/Amine (1 M)

| | | $k'_{q}/M^{-1} s^{-1}$ | | | | $k_{XA^{*-}}/s^{-1}$ | |
|-----------|--|--|--|--|--|--|--|
| | TEA | DMA | azulene | ferrocene | TEA | DMA | |
| DCA CA | 1.8×10^{5} 2.3×10^{5} | 5.0×10^4 2.2×10^5 | 6.0×10^{8} 7.1 × 10 ⁹ | 3.8×10^9 3.2×10^9 | 2.8×10^4 9.7 × 10 ⁴ | 3.9 × 10 ⁵ 9.5 × 10 ⁵ | |

SCHEME I



indicating that the values of k_q obtained from I_0^T/I_A^T should be equal to those obtained from I_0^T/I_A^T . In contrast, as shown in Figure 7, the values of I_0^T/I_A^T (open circles) deviate greatly from the dashed lines which are obtained by Stern-Volmer plots of I_0^T/I_A^T against amine concentration as shown in Figure 5c. The smaller values of I_0^T/I_A^T than those of I_0^T/I_A^T may reflect an additional formation of ${}^3XA(T_1)$ by amine.

This amine-assisted formation of ${}^{3}XA(T_{1})$ has also been observed for 9,10-dibromoanthracene and 9-bromoanthracene,¹² where we have proposed that the intersystem crossing from the singlet exciplexes $[1(XA-amine)^*]$ to the triplet exciplexes $[^{3}(XA-amine)^{*}]$ is followed by the decomposition into $^{3}XA(T_{1})$ and ground-state amine as shown by Scheme I. Hence, I_0^T/I_A^T should be equal to $(1 + k_q \tau [amine])/(1 + \alpha [amine])$, where α is given by $\beta k_q/k_{isc}$ and $\beta = k'_{isc}/(k_G + k_{ion} + k'_{isc})$ is the efficiency for the formation of ${}^{3}XA(T_1)$ via ${}^{1}(XA-amine)^{*}$. By a best fit of the calculated values $\{(1 + k_q \tau [amine])/(1 + \alpha [amine])\}$ to the experimental values, the change of I_0^T/I_A^T with amine concentration can well be reproduced as shown by the full lines in Figure 7, where the values of k_0 obtained from the quenching of time-resolved fluorescence spectra by amine are used. Since the fluorescence quantum yields (Φ_F) in CH₃CN without amine are found to be 0.64 for DCA and 0.02 for CA, the rate constants (k_{isc}) for the ¹XA(S₁) \rightarrow ³XA(T_n) intersystem crossing are calculated to be 4.2×10^7 s⁻¹ for DCA and 3.0×10^8 s⁻¹ for CA. In Table II, the best-fit values of α (determined using various values of k_{a} and those of β (calculated by $\beta = \alpha k_{isc}/k_{q}$) are listed.

Figure 8a,b shows the transient absorption spectra obtained by nanosecond laser photolysis of XA in CH₃CN/amine (1 M) at room temperature; the spectra are recorded at a delay time of 0 ns and a gate time of 50 ns. In the absence of amine, however, no absorption bands [F, G, and H (and E in the presence of DMA)] can be seen except for bands C and D which are the T' \leftarrow T₁ absorptions of ³XA(T₁). We have assigned bands F, G, and H to the absorptions of the chloroanthracene radical anions (XA^{-}) produced by a diffusion-controlled reaction of ${}^{1}XA(S_{1})$ with ground-state amine yielding 1(XA-amine)* followed by the decomposition into XA^{•-} and the amine radical cations (amine^{•+}) based on the following facts: (1) The spectra with bands F, G, and H shown in Figure 8a,b are identical with those shown in Figure 8c which are recorded after γ -radiolysis of XA at 77 K in MTHF; we believe that the spectra in Figure 8c are due to the absorptions of XA⁺, because their spectra are very similar to those of the bromoanthracene radical anions produced upon pulse radiolysis (at room temperature in CH₃CN) and γ -radiolysis (at 77 K in MTHF) of 9,10-dibromoanthracene and 9-bromoanthracene.²⁰ (2) ${}^{3}XA(T_{1})$ in CH₃CN decay following a single-exponential function irrespective of absence (a) and presence (b, c) of amine as shown in Figure 9, and the decay rate constants $(k_{\rm T})$ thus obtained increase linearly with increasing amine concentration as shown in Figure 10a,b: The quenching rate constants $(k'_q \approx 10^4 - 10^5 \text{ M}^{-1} \text{ s}^{-1})$ of ${}^3\text{XA}(\text{T}_1)$ by amine listed in Table III, however, are much smaller than those ($k_a \approx 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) obtained for the quenching of ${}^{1}XA(S_{1})$ by amine (cf. Table II), indicating that the spectra shown in Figure 8a,b cannot be attributed to a



Figure 8. Transient absorption spectra obtained by nanosecond laser photolysis of XA in CH₃CN/amine (1 M) at room temperature (a, b), and absorption spectra of XA⁺ obtained by γ -radiolysis (3 min) of XA in MTHF at 77 K (c).



Figure 9. Decays of $T' \leftarrow T_1$ absorptions (full lines monitored at 420 nm) due to ${}^{3}XA(T_1)$ in CH₃CN (a) and CH₃CN/amine (0.1 M TEA or 0.4 M DMA) (b, c) at room temperature. The dashed lines are simulated single-exponential functions with decay rate constants (k_T) indicated.

transient species produced by a reaction of ${}^{3}XA(T_{1})$ with amine. (3) Band E observed in the presence of DMA is very similar to that of the published absorption spectrum due to DMA^{*+};²¹⁻²³ no clear observation of the absorption band due to TEA^{*+} may be ascribed to its weak absorption.²²

As stated previously, the ${}^{1}XA(S_{1}) \rightarrow {}^{3}XA(T_{n})$ intersystem crossing rate constants (k_{isc}) are 4.2×10^{7} s⁻¹ for DCA and 3.0



Figure 10. Plots of triplet decay rate constants (k_T) against concentration of amine (a, b), azulene or ferrocene (c) in CH₃CN at room temperature.

× 10⁸ s⁻¹ for CA. Thus, the greater values of $k_q[\text{amine}] = (1.4-2.7) \times 10^{10} \text{ s}^{-1}$ for DCA [and $(1.1-2.4) \times 10^{10} \text{ s}^{-1}$ for CA] in CH₃CN/amine (1 M) compared with those of k_{isc} indicate that ¹(XA-amine)* are produced with a nearly unit efficiency and that almost all of ³XA(T₁) are produced via the indirect ¹(XA-amine)* \rightarrow ³(XA-amine)* \rightarrow ³XA(T₁) process shown in Scheme I. Since Figure 8a,b reveals that the intensities of absorption bands C due to ³XA(T₁) are 1.3-1.8 times greater than those of absorption bands H due to XA^{*-} and since the absorption coefficients [(4.2-5.1) × 10⁴ M⁻¹ cm⁻¹ at ~420 nm²⁴] of ³DCA(T₁) are 1.5-3.9 times greater than those of XA^{*-} (~2.8 × 10⁴ M⁻¹ cm⁻¹ for DCA⁻ at 675 nm and ~1.3 × 10⁴ M⁻¹ cm⁻¹ for CA^{*-} at 700 nm estimated from those of the radical anions of 9,10-dibromoand 9-bromoanthracenes¹), k_{ion} may be roughly equal to k'_{isc} . Hence, the small values [(5.9-13) × 10⁻²] of $\beta = k'_{\text{isc}}/(k_G + k_{\text{ion}} + k'_{\text{isc}})$ may reflect that k_G is 6-15 times greater than $k_{\text{ion}} \approx k'_{\text{isc}}$.

time following a single-exponential function and the decay rate constants (k_{XA}) obtained are of the order of 10^4-10^5 s⁻¹ as listed in Table III; typical decay carves obtained in CH₃CN/TEA (1 M) are shown in Figure 11. Although the decay of absorption due to DMA⁺⁺ can be analyzed by first-order reaction kinetics, the decay rate constant $(3.1 \times 10^5 \, \text{s}^{-1})$ obtained is smaller than those of XA⁻⁻ listed in Table III. The decays of absorptions due to XA^{•-}, moreover, can also be analyzed by second-order reaction kinetics, but the decay rate constants (~5 \times $10^{11}~M^{-1}~s^{-1}$ for DCA⁻⁻ and $\sim 3 \times 10^{11}$ M⁻¹ s⁻¹ for CA⁻⁻) obtained in the presence of 1 M DMA are 1 order of magnitude greater than that $(2.0 \times$ 10^{10} M⁻¹ s⁻¹)²⁵ estimated from the viscosity of CH₃CN using the Debye-Smoluchowski equation, and the half-lives of XA⁻⁻ are independent of the initial concentration of XA⁻⁻; an analysis of the decays of absorptions due to XA⁻⁻ by a combination of firstand second-order reaction kinetics, moreover, indicates that a decay rate constant smaller than $\sim 5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ does not affect the single-exponential decays of XA*-. We thus believe that the second-order reaction between XA*- and amine*+ can be ruled out and that the difference between the decay rate constants of XA⁺ in CH₃CN/TEA and those in CH₃CN/DMA is due to the effect of solvent property.

If ${}^{3}(XA-amine)^{*}$ as proposed by Soloveichik et al.² are produced by a reaction of ${}^{3}XA(T_{1})$ with ground-state amine and if these triplet exciplexes give rise to the formation of XA^{*-}, Table III



Figure 11. Decays of absorptions (full lines) due to XA⁻⁻ in CH₃CN/ TEA (1 M) at room temperature. The dashed lines are simulated single-exponential functions with decay rate constants (k_{XA} -) listed in Table III.

indicates that one cannot confirm the formation of XA⁻⁻ in CH₃CN/DMA (1 M) owing to the smaller values of k'_{q} [DMA] = 5.0 × 10⁴ (DCA)-2.2 × 10⁵ (CA) s⁻¹ compared with those of $k_{XA^{-1}}$ = 3.9 × 10⁵ (DCA)-9.5 × 10⁵ (CA) s⁻¹. In CH₃CN/TEA (1 M), however, the rises and decays of absorptions due to XA*should be detectable in the microsecond time regime, because k_{XA} -= 2.8×10^4 (DCA)- 9.7×10^4 (CA) s⁻¹ are smaller than k'_{0} [TEA] = 1.8×10^5 (DCA)-2.3 × 10^5 (CA) s⁻¹. In contrast, no such an evidence has been obtained. Even if the dechlorination does occur in ${}^{3}(XA-amine)^{*}$ produced by a reaction of ${}^{3}XA(T_{1})$ with ground-state amine and no XA*- are produced, the following results cannot support the triplet exciplex mechanism: (1) The decay rate constants (k_T) of ${}^{3}XA(T_1)$ in CH₃CN/amine increase linearly with increasing amine concentration as shown in Figure 10a,b, indicating no existence of such an equilibrium between ${}^{3}XA(T_{1})$ + amine and ${}^{3}(XA$ -amine)* as proposed by Soloveichik et al.,² during decrement of the $T' \leftarrow T_1$ absorption spectra of ${}^{3}XA(T_{1})$ with time in CH₃CN/amine (0.04 M), moreover, no change in the spectral profile can be seen. (2) Addition of azulene or ferrocene in CH₃CN accelerates the decays of ${}^{3}XA(T_{1})$ with quenching rate constants (k'_{a}) of the order of 10^{8} – 10^{9} M⁻¹ s⁻¹ (cf. Figure 10c and Table III), while Figure 2 reveals no effects of these additives on the decrement of reactant absorptions during steady-state photolysis in CH₃CN/TEA (0.04 M); similar results are also obtained in CH₃CN/DMA (0.04 M) as stated previously. (3) As listed in Table I, the quantum yields (Φ_R) for the dechlorination of DCA yielding CA in CH₃CN/amine (0.08 M) are greater than those in $CH_3CN/amine$ (0.04 M), while the quantum yields (Φ_T) for the formation of ${}^{3}XA(T_1)$ decrease with increasing amine concentration; in the presence of 0.08 M DMA; moreover, $\Phi_R = 0.117$ is greater than $\Phi_T = 0.073$.

All the results obtained so far are consistent with those obtained for bromoanthracenes.^{1,11,12} We thus again conclude that the haloanthracene radical anions produced by Scheme I are the intermediates for the dehalogenation, i.e., the exciplexes of triplet haloanthracenes with ground-state amine do not participate in the dehalogenation. Although Soloveichik et al.² have concluded that the haloanthracene radical anions do not participate in the dehalogenation, we would like to deny their conclusion on the basis of the following reasons. (1) As shown in Figure 1, γ -radiolysis of DCA and CA in CH₃CN without amine at room temperature causes the dechlorination essentially identical with that caused by photolysis in CH₃CN/TEA: The results obtained by photolysis in CH₃CN/TEA are identical with those obtained in CH₃CN/ DMA as stated previously; in comparison with the results obtained by photolysis (cf. a), the results obtained by γ -radiolysis (cf. b) reveals no clear formation of CA (from DCA) and AQ (from CA), probably being due to the further radiolysis of the products in accordance with the fact that the absorption increment around 300 nm caused by radiolysis is much greater than that caused by photolysis. (2) In CH₃CN without amine at room temperature, pulse radiolysis of bromoanthracenes yields the bromoanthracene radical anions and γ -radiolysis causes the debromination.²⁰

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Reaction of Hydrated Electrons with Guanine Nucleosides: Fast Protonation on Carbon of the Electron Adduct

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The reactions of hydrated electrons (e_{aq}) and hydrogen atoms (H[•]) with guanosine, 2'-deoxyguanosine, and 1-methylguanosine (G) were studied by pulse radiolysis with optical and conductometric detection. In neutral solution, the reaction of both e_{aq} and H[•] with these purines leads to the same neutral radical. This is suggested to be the H adduct to the C8 position $(G(C8H)^{\circ})$ formed by H[•] addition and by protonation at C8 of the electron adducts, via tautomerization $(k = 1.2 \times 10^6)$ s⁻¹ for the case of guanosine) following protonation of the radical anion at a hetero atom ($k \ge 10^7 \text{ s}^{-1}$). The C-protonated radical is only a weak reductant: It does not react $(k \le 10^7 \text{ M}^{-1} \text{ s}^{-1})$ with the oxidant methylviologen (E = -0.44 V/NHE), but with the stronger oxidant $Fe(CN)_6^{3-}$ (E = 0.36 V/NHE) there is some reactivity (k = 5.9 × 10⁸ M⁻¹ s⁻¹). In acidic solution $G(C8H)^{\circ}$ protonates at a heteroatom to give a radical cation ($pK_a = 5.4-5.5$). The same radical cation results also from the reaction of H* with G at pH 3. The C8 protonated electron adduct of 1-methylguanosine deprotonates (from the amino function at C2) with a pK_a of 13.3. C-protonated electron adducts of the purines have so far not been detected in irradiated DNA. Since the tendency for their formation (by protonation by the water of hydration of DNA) is probably very high, the failure to detect these radicals in DNA can be taken as indication that electron transfer from the purine radical anions to pyrimidines in their neighborhood is faster than their C protonation.

Introduction

According to the two-component model,³ the ESR spectrum of irradiated DNA in the solid phase⁴ at room temperature can be explained on the basis of only two radical species: the guanine radical cation and the C6-protonated thymine radical anion. This situation, as well as the results of various studies with model compounds,⁵ can be explained as resulting from electron and electron hole migration in DNA, by which the randomly distributed initial damage is concentrated at specific bases. These ideas have recently suffered some criticism,^{4a} arising especially from the realization that proton-transfer reactions may play an important role in the fixation of the radical sites.⁶⁻⁸ These proton-transfer reactions include reversible (de)protonation of heteroatoms but also irreversible protonations at carbon.⁹⁻¹¹ Ultimately, the electrons result in the formation of 5,6-dihydrothymin-5-yl radical.

An example of the importance of proton transfer in aqueous solution is the competition between deoxycytidine (C) and thymidine (T) for e_{sq}^{-} produced in ionizing events.¹² Whereas in the gas phase T is more electron affinic than C,¹³ in aqueous solution the higher basicity of the radical anion of C ($pK \ge 13$) relative to that of T (pK = 6.9) has a leveling effect, making the (aqueous solution) reduction potentials of C and T equal ($E_{8-9} = -1.1$ V/NHE).¹² In agreement with this concept, recent ESR ex-