November, 1992] Bull. Chem. Soc. Jpn., 65, 3141—3148 (1992)

Solvent Effects on the Formation and Decay of Ionic Intermediates for the Photoreduction of Anthraquinone by Triethylamine in Ethanol, Toluene, and Acetonitrile at Room Temperature

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(Received June 29, 1992)

In toluene and ethanol containing triethylamine (TEA), a reaction of the lowest excited triplet state [$^3AQ(T_1)$] of anthraquinone (AQ) with ground-state TEA gave rise to the formation of an exciplex [$^3(AQ\text{–}TEA)^*$] which converted into a contact ion pair between the AQ radical anion ($AQ^{\cdot-}$) and the TEA radical cation ($TEA^{\cdot+}$). By an intramolecular proton transfer, this contact ion pair yielded anthrasemiquinone radical followed by the formation of 9,10-anthracenediol (AQH_2); in ethanol, the monoanion (AQH^-) of AQH_2 was also produced. In ethanol/TEA, moreover, not only the decay rate constant of $^3(AQ\text{–}TEA)^*$ but also the quantum yield for the photoreduction of AQ were affected by the change of TEA concentration. This was interpreted in terms of the existence of a rapid interconversion between $^3(AQ\text{–}TEA)^*$ and a triplex [$^3(AQ\text{–}TEA_2)^*$] of $^3AQ(T_1)$ with ground-state TEA. In contrast to the exciplex formation in ethanol and toluene, free $AQ^{\cdot-}$ (and $TEA^{\cdot+}$) and $^3(AQ\text{–}TEA)^*$ [or a contact (or solvent-separated) ion pair between $AQ^{\cdot-}$ and $TEA^{\cdot+}$] were produced in acetonitrile via the second and lowest excited triplet states of AQ, respectively: In the submicrosecond time regime, $^3(AQ\text{–}TEA)^*$ or the contact (or solvent-separated) ion pair dissociated into the radical ions ($AQ^{\cdot-}$ and $TEA^{\cdot+}$) followed by their second-order reaction yielding finally AQH_2 and AQH^-.

In previous papers,[1,2] we reported that the primary process for the photoreduction of anthraquinone (AQ) by triethylamine (TEA) in ethanol or toluene was originated by the formation of an exciplex [$^3(AQ\text{–}TEA)^*$] of the lowest triplet state [$^3AQ(T_1)$] of AQ with ground-state TEA, which converted into a contact ion pair [$^3(AQ^{\cdot-}\text{-}TEA^{\cdot+})$] between the AQ radical anion ($AQ^{\cdot-}$) and the TEA radical cation ($TEA^{\cdot+}$); by an intramolecular proton transfer from $TEA^{\cdot+}$ to $AQ^{\cdot-}$, $^3(AQ^{\cdot-}\text{–}TEA^{\cdot+})$ generated the anthrasemiquinone radical ($AQH\cdot$) finally yielding 9,10-anthracenediol (AQH_2) in toluene [or AQH_2 and its monoanion (AQH^-) in ethanol].

In toluene, not only the decay rate constant (k_E) of $^3(AQ\text{–}TEA)^*$ but also the quantum yield (Φ) for the photoreduction of AQ were not affected by the change of TEA concentration. In ethanol, however, k_E and $1/\Phi$ increased linearly with increasing TEA concentration; the decay rate constant of $^3(AQ^{\cdot-}\text{–}TEA^{\cdot+})$ was independent of TEA concentration in both ethanol and toluene. We thus proposed that $^3(AQ\text{–}TEA)^*$ in ethanol was quenched by ground-state TEA via the formation of a triplex [$^3(AQ\text{–}TEA_2)^*$] of $^3AQ(T_1)$ with ground-state TEA.

For chloroanthraquinones such as the 1-chloro, 2-chloro, and 1,5-dichloro compounds in both ethanol and toluene,[3] however, we recently observed that the increment of exciplex decay rate constants with increasing TEA concentration was not linear but the decay rate constants of the contact ion pairs were still independent of TEA concentration: For 1,8-dichloro compound in toluene, not only the decay rate constant of the exciplex but also that of the contact ion pair decreased non-linearly with increasing TEA concentration; in ethanol, the exciplex decay rate constant increased non-linearly with increasing TEA concentration but the decay rate constant of the contact ion pair was also independent of TEA concentration. These results cannot be interpreted in terms of only the linear quenching of exciplex by increasing TEA concentration. Since our previous determination of rate constants for the AQ–TEA system is performed by recording the trace of the electrical waveform (the change of transmittance) on the screen of an oscilloscope and by a hand-drawn point-to-point first-order plot of the calculated absorbance against time, some inaccuracy and arbitrariness are unavoidable. Thus, the present paper deals with the reinvestigation regarding the effect of TEA concentration on the decay rate constants of $^3(AQ\text{–}TEA)^*$ and $^3(AQ^{\cdot-}\text{–}TEA^{\cdot+})$ as well as that on the quantum yield for the photoreduction of AQ in ethanol and toluene.

Although the photoreduction of several aromatic ketones by amine is generally interpreted in terms of electron transfer from ground-state amine to triplet ketones,[4—10] the mechanism for the formation of ionic species (exciplexes, radical ions and their ion pairs) and the interconversion among these ionic species are dependent on the nature of the solvents and the excited-state behavior of triplet ketones. We thus also deals with the photoreduction of AQ by TEA in acetonitrile. A preliminary result has been published elsewhere.[11]

Experimental

CP-grade AQ (Wako) was purified by recrystallization from toluene, followed by column chromatography on 200-mesh alumina (2 cm i.d.×30 cm) using toluene as the developer, vacuum sublimation and subsequent recrystallization from ethanol. GR-grade TEA (Wako) was refluxed over calcium hydride and distilled under a nitrogen atmosphere. The solvents used were spectral-grade acetonitrile (Dojin) and ethanol (Nacarai), and scintillation-grade toluene (Dojin), which were dried over molecular sieves 3A (Wako) preheated in a crucible over a Bunsen burner and cooled in vacuo.

All experiments were perfomed at room temperature and picosecond laser photolysis was carried out using the second harmonic (347.2 nm) from a mode-locked ruby laser with a pulse width of 30 ps at half-maximum intensity (FWHM); the sample solution in a cell of 2-mm path length was not degassed. The details of this laser photolysis system have been given elsewhere.[12] For nanosecond laser photolysis, the sample solution in a cell of 10-mm path length was degassed by several freeze-pump-thaw cycles and the sample excitation was performed by the second harmonic (347.2 nm) from a Q-switched ruby laser with a pulse duration of 20 ns (FWHM):[13] The transient absorption spectrum over a wavelength range of 200 nm was recorded using a multichannel analyzer composed of a polychromator (Unisoku M200), an image intensifier (Hamamatsu V3347U) and a linear position-sensitive detector (Unisoku USP501) controlled by a personal computer (NEC 9801RA); operating the image intensifier in gated or continuous mode, the transient absorption spectrum in the nanosecond-millisecond time regime could be recorded very easily from one excitation laser shot. The decay of transient absorption was analyzed by means of a combination of a photomultiplier (Hamamatsu R666 or RCA 8575) with a storage oscilloscope (Iwatsu TS-8123) controlled by the personal computer. For the measurement of transient photocurrent, the sample cell with two plane-parallel platinum electrodes (8 mm×8 mm) separated by 10 mm and a fast preamplifier was constructed, and an electrode bias of 450 V was supplied by dry batteries: The voltage signal across the 50-Ω load registor was fed into the first preamplifier and displayed on the storage oscilloscope; the rise time of this preamplifier-oscilloscope system was ca. 10 ns.

For steady-state photolysis of AQ, excitation of the degassed sample solution in a cell of 10-mm path length was carried out using 313-nm monochromatic light selected from an USH-500D super-high pressure mercury lamp by a combination of two Toshiba color glass filters (UV-29 and UV-D33S) and a filter solution ($Ni_2SO_4 \cdot 6H_2O$, 50 g dm^{-3}, path length 2 cm). The change of absorption spectrum upon photolysis was recorded using a Hitachi 200-20 spectrophotometer, and the quantum yield for the photoreduction of AQ was determined by measuring the decrement of reactant absorption following the Hatchard–Parker's tris(oxalato)ferrate(III) actinometry method.[14]

Results

As reported in previous papers,[1,2] picosecond laser photolysis of AQ in ethanol and toluene containing TEA reveals no time-dependent change of the transient absorption spectrum with Band A which is the absorption of ^{3}(AQ–TEA)*: Although the spectrum (with Band A) obtained at the end of nanosecond pulse excitation (40-ns delay) is almost identical with that obtained by picosecond laser photolysis, the spectrum [with Band B which is the absorption of $^3(AQ^{\cdot-}\text{–}TEA^{\cdot+})$] obtained at 2-μs delay is shifted to a shorter wavelength by 8 nm in ethanol or 5 nm in toluene; at a much longer delay time, Band B decreases accompanied by the appearance of absorption band due to AQH_2 in toluene (or those due to AQH_2 and AQH^- in ethanol). In accordance with this time-dependent spectral change, the transient absorption (appeared within the duration of nanosecond pulse excitation) in ethanol/TEA (0.2 M; 1 M=1 mol dm^{-3}) increases slowly up to 4-μs delay as shown in Fig. 1a. Although the maximum absorption persists beyond 200-μs delay with no measurable decrease, it decays in the millisecond time regime (cf. full

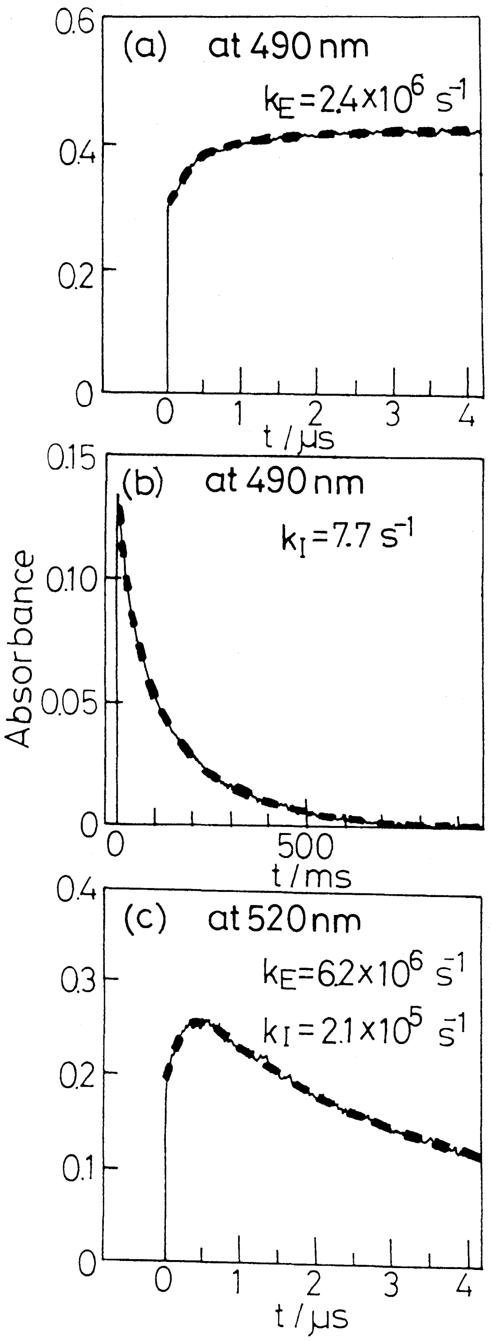


Fig. 1. Rise (a) and decay (b) of transient absorption with time obtained by nanosecond laser photolysis of AQ in ethanol–TEA (0.2 M), and those (c) in toluene–TEA (0.2 M) (full lines). The dashed lines are the simulated single-exponential (a, b) and bi-exponential (c) functions with the rate constants indicated.

line in Fig. 1b), and both the rise and decay curves can be analyzed by first-order reaction kinetics with rate constants of k_E=2.4×10^6 s^{-1} and k_I=7.7 s^{-1}, respectively (cf. dashed lines). In toluene/TEA (0.2 M), however, both the rise and decay of transient absorption are seen in the microsecond time regime as shown by the full line in Fig. 1c, and the change of transient absorption with time can be analyzed by the following bi-exponential function,

$$\Delta D(t) = D_1\exp(-k_E t) + D_2\exp(-k_I t) \qquad (1)$$

where D_1 and D_2 are the experimental constants, and k_E and k_I are 6.2×10^6 and 2.1×10^5 s^{-1}, respectively (cf. dashed line).

In Fig. 2, the values of k_E (a) and k_I (b) obtained at various TEA concentration in ethanol (open circles) and toluene (closed circles) are plotted against TEA concentration ([TEA]=0.02—1 M). Clearly, only k_E in ethanol increases with increasing TEA concentration, but k_E in toluene and k_I in both ethanol and toluene are almost independent of TEA concentration. For comparison, we have also determined the quantum yields (Φ) for the photoreduction of AQ in the presence of TEA, and have found that Φ in ethanol decreases with increasing TEA concentration but Φ in toluene is independent of TEA concentration as shown in Fig. 2c.

Figure 3 shows the transient absorption spectra obtained by picosecond laser photolysis of AQ in acetonitrile/TEA (1 M). Clearly, a new absorption (Band X with λ_{max}=540 nm) grows in at first and then another absorption (Band Y with λ_{max}=510 nm) increases gradually up to 2-ns delay, and the overall spectral profile at this delay time looks like a superposition of Bands X and Y. Although this result suggests that an intermediate with Band X and that with Band Y are produced independently, this circumstance has already been confirmed from the result obtained for 1,8-dichloroanthraquinone in acetonitrile/TEA (1 M), which has two characteristic triplet–triplet absorption bands (Band C with λ_{max}=539 nm and Band D with λ_{max}=508 nm) due to the second excited triplet state and the lowest excited triplet state, respectively:[15] At a delay time of 40 ps, only Bands C and D identical with those obtained in the absence of TEA[16] are observed; at 100-ps delay, however, no Band C can be seen but a new absorption (Band X with λ_{max}=590 nm) is observed; at delay times longer than 100 ps, Band D decreases and another new absorption (Band Y with λ_{max}=550 nm) increases accompanied by a clear isosbestic point at ca. 539 nm.

In Fig. 4a, we show the transient absorption spectra (full lines) obtained by nanosecond laser photolysis of AQ in acetonitrile/TEA (0.2 M). As shown by the dashed line, a normalization of the spectrum at the end of pulse excitation (40-ns delay) to that at 1-μs delay clearly reveals that the intensity ratio of Band X to Band Y at 1-μs delay is greater than that at 40-ns delay. This indicates that the intermediate with Band Y changes to that with Band X in the submicrosecond time regime. In accordance with this result, the transient absorption (appeared within a duration of nanosecond pulse excitation) increases slowly up to 1-μs delay with accompanying rise of transient photocurrent (cf. full lines in Figs. 4b and 4c). On the assumption that the excitation pulse profile (cf. dotted lines in Figs. 4b and 4c) is the Gaussian with a pulse width of 20 ns (FWHM), the rises of transient absorption and photocurrent can be analyzed by first-order reaction kinetics as shown by the dashed lines, and the rate constant (k_1=1.1×10^7 s^{-1}) obtained from the rise of transient absorption is almost equal to that (k_2=1.2×10^7 s^{-1}) obtained from the rise of transient photocurrent.[17]

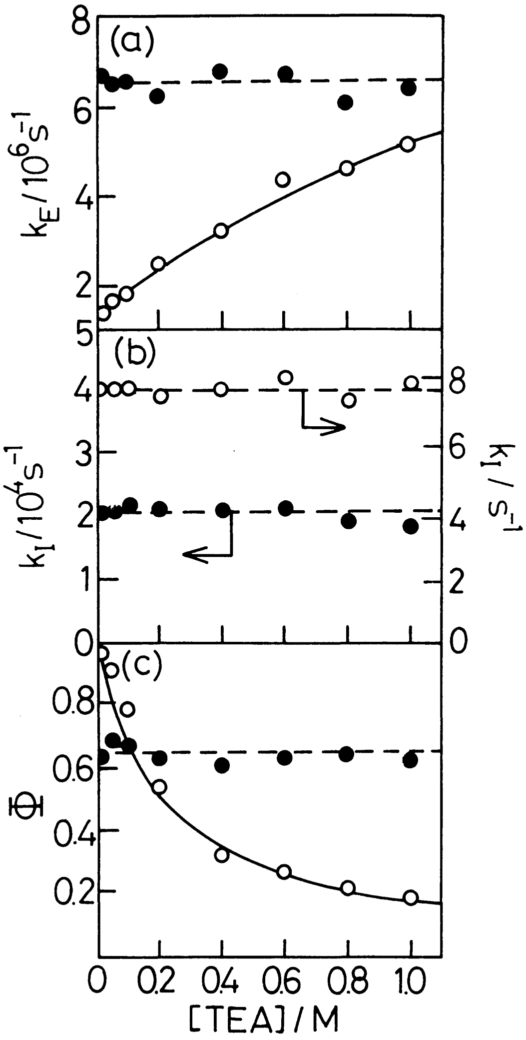


Fig. 2. Plots of k_E (a), k_I (b), and Φ (c) against TEA concentration in ethanol (○) and toluene (●). In (a) and (c), the self-consistent and best-fit curves calculated by Eqs. 1 and 3, respectively, are shown by the full lines.

In the millisecond time regime, as shown in Fig. 5, the decrease of Band X is accompanied by the appearance of new absorption (Bands P and Q); as shown in the inset,

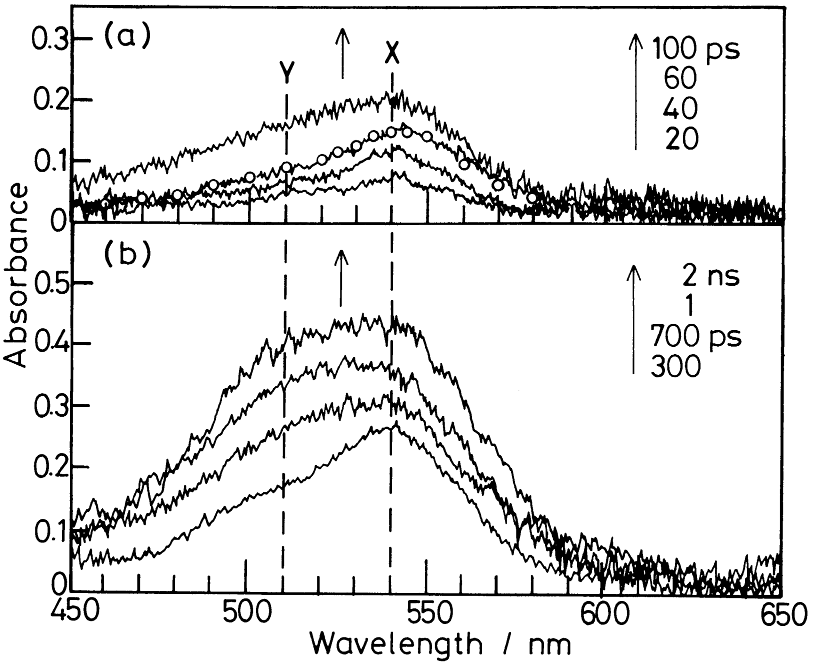


Fig. 3. Transient absorption spectra obtained by picosecond laser photolysis of AQ in acetonitrile–TEA (1 M). The spectrum shown by open circles in (a) is the normalized absorption spectrum of free AQ$^{\cdot-}$ produced upon nanosecond pulse radiolysis of AQ in acetonitrile without TEA.[19]

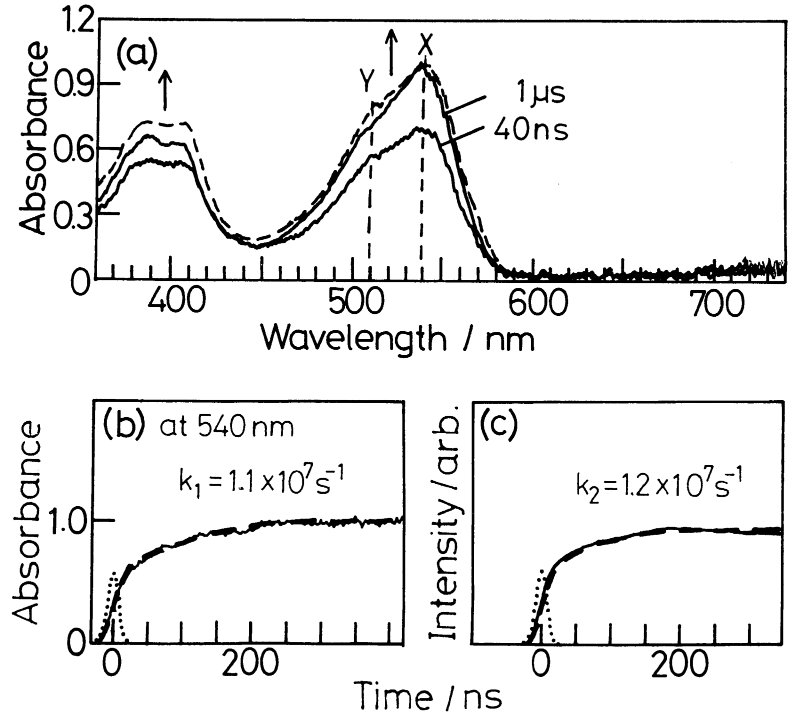


Fig. 4. Transient absorption spectra (a), and rises of transient absorption (b), and photocurrent (c) with time obtained by nanosecond laser photolysis of AQ in acetonitrile–TEA (0.2 M) (full lines). The dashed line in (a) is the normalized spectrum obtained at 40-ns delay, and those in (b) and (c) are simulated by first-order reaction kinetics (with the rate constants indicated) on the assumption that the excitation pulse profile (dotted lines) is the Gaussian with a pulse width of 20 ns (FWHM).

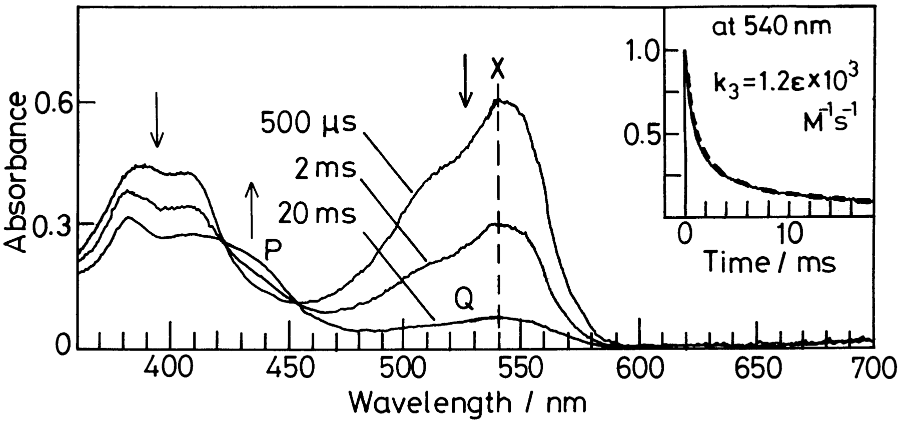


Fig. 5. Change of transient absorption spectra in the millisecond time regime obtained by nanosecond laser photolysis of AQ in acetonitrile–TEA (0.2 M). In the inset, the full line is the decay curve of transient absorption with time and the dashed line is the simulated second-order decay curve with the rate constant indicated, where ε is the molar absorption coefficient of $AQ^{\cdot-}$.

the decay curve (full line) of transient absorption can be analyzed by second-order reaction kinetics with a rate constant of $k_3=1.2\varepsilon\times10^3$ M^{-1} s^{-1} (cf. dashed line), where ε is the molar absorption coefficient of the transient species, i.e., free $AQ^{\cdot-}$ as will be discussed later. We conclude that Bands P and Q are the absorptions of AQH_2 and AQH^-, respectively, based on the following facts: (1) As shown in Fig. 6a, steady-state photolysis of AQ in acetonitrile/TEA (0.2 M) causes the decrement of reactant absorption (Band R) and the increment of product absorptions (Bands P and Q, and absorptions at <300 nm) accompanied by two isosbestic points at 293 and 346 nm. (2) In the absence of TEA, no Band Q can be seen as shown by the full lines in Fig. 6b and the photoproduct (with Band P and weak absorptions at <300 nm) has been identified to be AQH_2 in accordance with the result obtained in ethanol without TEA;[2] addition of TEA (0.2 M) in vacuo after photolysis gives rise to the appearance of Band Q (the absorption of AQH^-) and the increment of absorptions at <300 nm (cf. dashed line).

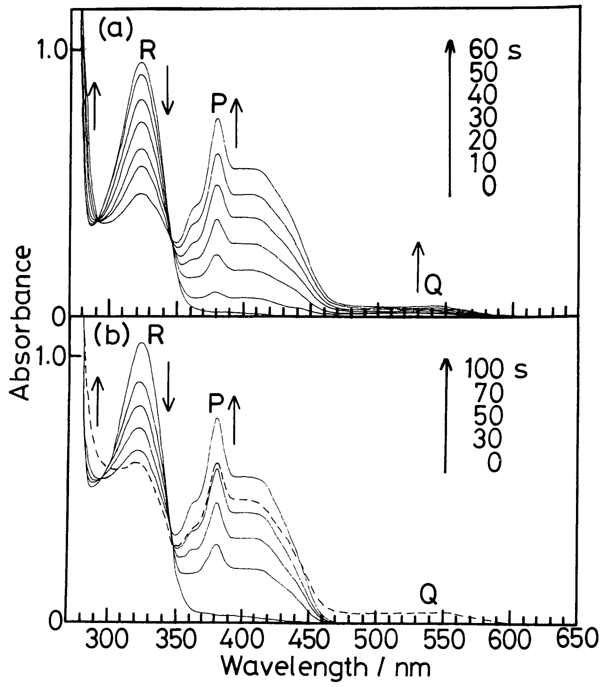
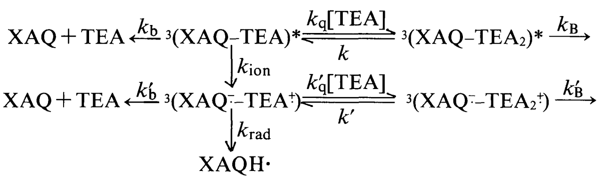


Fig. 6. Changes of absorption spectra upon 313-nm steady-state photolysis of AQ in acetonitrile in the presence (a) and absence (b) of TEA (0.2 M). In (b), the spectrum shown by the dashed line is obtained upon addition of TEA (0.2 M) in vacuo after photolysis.

Discussion

1. Photoreduction of AQ by TEA in Ethanol and Toluene. Figure 2a clearly reveals that the increment of k_E in ethanol is not strictly linear with increasing TEA concentration. We thus conclude that the linear increment of k_E with increasing TEA concentration reported in the previous paper[2] is incomplete, although the previous observation that there are no effects of TEA concentration on k_E (in toluene) and k_I (in both ethanol and toluene) is correct. Based on the conclusion obtained from the results for several chloroanthraquinones (XAQ),[3] we thus again propose the following generalized kinetic scheme (Scheme 1),



Scheme 1.

where the experimental decay rate constants of the exciplex (k_E) and the contact ion pair (k_I) are expressed by,

$$k_E = \frac{k_A + k_B K[\mathrm{TEA}]}{1 + K[\mathrm{TEA}]}, \tag{1}$$

$$k_I = \frac{k_A' + k_B' K'[\mathrm{TEA}]}{1 + K'[\mathrm{TEA}]}, \tag{2}$$

and $k_{ion}+k_b$ and $k_{rad}+k_b'$ are denoted by k_A and k_A', and $K(=k_q/k)$ and $K'(=k_q'/k')$ are ratio of the rate constants for interconversion between ^{3}(XAQ–TEA)* and ^{3}(XAQ–TEA$_2$)* and that of the rate constants for interconversion between ^{3}(XAQ$^{-\cdot}$–TEA$^{+\cdot}$) and ^{3}(XAQ$^{-\cdot}$–TEA$_2^{+\cdot}$), respectively. In the present case, however, k_E in toluene is almost independent of TEA concentration, indicating that TEA does not quench ^{3}(AQ–TEA)* or that k_A is equal to k_B, resulting in no evaluation of $K(=k_q/k)$; in either case, however, k_E becomes equal to $k_A=k_{ion}+k_b$. No effect of TEA concentration on k_I in both ethanol and toluene also indicates no evaluation of $K'(=k_q'/k')$, and thus k_I is equal to $k_A'=k_{rad}+k_b'$. Assuming that the efficiency (γ) for the formation of AQH$_2$ from AQH· is independent of TEA concentration, the quantum yield for the photoreduction of AQ in ethanol is given by

$$\Phi = \frac{\gamma k_{ion} k_{rad}}{k_I}\left(\frac{k_A + k_B K[\mathrm{TEA}]}{1 + K[\mathrm{TEA}]}\right)^{-1} \times\left[1 + K[\mathrm{TEA}]\left(1 + \frac{k_A - k_B}{k_q[\mathrm{TEA}] + k}\right)\right]^{-1} \tag{3}$$

The self-consistent and best-fit curves for k_E (calculated by Eq. 1) and Φ (calculated by Eq. 3) in ethanol are shown by the full lines in Figs. 2a and 2c, respectively, where k_I is taken to be 7.7 s^{-1} and the best-fit values are $k_A=k_{ion}+k_b=1.3\times10^6$ s^{-1}, $k_B=1.3\times10^7$ s^{-1}, $K(=k_q/k)=0.5$ M^{-1} and $\gamma k_{ion}k_{rad}=1.0\times10^7$ s^{-2}. In comparison with the values obtained for chloroanthraquinones (XAQ) in ethanol,[3] k_B for AQ is much greater than those (1.2—5.1$\times10^6$ s^{-1}) for XAQ but all the other values for AQ are nearly equal to those for XAQ. Since k is found to be greater than 1×10^8 s^{-1}, the value of $K=0.5$ M^{-1} indicates that k_q should be greater than 5×10^7 M^{-1} s^{-1} in accordance with those ($k_q>1.4\times10^7$—2.1×10^8 M^{-1} s^{-1}) estimated for XAQ.

2. Photoreduction of AQ by TEA in Acetonitrile. It is well known that the photoreduction of several aromatic ketones by amine is initiated via the formation of complexes (exciplexes or excited charge-transfer complexes between triplet ketones and ground-state amine), radical ions (the radical anions of ketones and the radical cation of amine) and their ion pairs.[4–10] Since the quantum yield (0.82) for the photoreduction of AQ in acetonitrile/TEA (0.2 M) is found to be greater than that (0.40) in acetonitrile without TEA (indicating that the photoreduction of AQ is accelerated upon addition of TEA), the intermediate with Band X can be safely ascribed to an ionic species. The time-dependent change of the transient absorption spectrum with Bands X and Y (observed in acetonitrile) is, however, different from that of the transient absorption spectrum with Bands A and B (observed in ethanol or toluene)[1,2] as follows: (1) The intensity of Band A due to the absorption of ^{3}(AQ–TEA)* produced via the lowest excited triplet state of AQ [^{3}AQ(T$_1$)] is very weak at 40 ps delay and no time-dependent spectral change of the transient absorption spectrum can be seen in the picosecond to a few nanosecond time regime; on the other hand, Band X can clearly be seen even at 20 ps delay where the concentration of ^{3}AQ(T$_1$) is negligibly small owing to a long internal conversion time ($\leqq$70 ps)[18] from the second excited triplet (T$_2$) state to the lowest excited triplet (T$_1$) state of AQ, and after then Band Y increases gradually resulting in the time-dependent change of the transient absorption spectrum as shown in Fig. 3. (2) In a few microsecond time regime, Band A shifts to Band B due to the absorption of ^{3}(AQ$^{-\cdot}$–TEA$^{+\cdot}$), i.e., the blue-shift by 8 nm in ethanol and 5 nm in toluene, accompanied by no transient photocurrent; in contrast, Band Y shifts to Band X (the red-shift by 30 nm) in the submicrosecond time regime accompanied by the rate-matching increase of transient photocurrent as shown in Fig. 4. (3) Band B decays following first-order reaction kinetics accompanied by the appearance of absorption of AQH$_2$ in toluene (or those of AQH$_2$ and AQH$^-$ in ethanol), while the decay of Band X (accompained by the formation of AQH$_2$ and AQH$^-$) can be analyzed by second-order reaction kinetics as shown in the inset of Fig. 5a. (4) Band X (λ_{max}=540 nm) has an absorption maximum at a wavelength longer than those for Band A (λ_{max}=494 nm in ethanol and 517 nm in toluene) and Band B (λ_{max}=486 nm in ethanol and 512 nm in toluene), while Band Y (λ_{max}=510 nm) has an absorption maximum at a wavelength between 486 and 517 nm; although Bands A and B in ethanol are greatly shifted to the blue compared with those in toluene, this may be due to the stabilization of ^{3}(AQ–TEA)* and ^{3}(AQ$^{-\cdot}$–TEA$^{+\cdot}$) caused by their hydrogen bonding with ethanol.

Based on the above discussion, we propose that Band X is the absorption of free AQ$^{-\cdot}$ produced by the direct electron transfer from ground-state TEA to the T$_2$ state of AQ and Band Y is the absorption of ^{3}(AQ–TEA)* or a contact (or solvent-separated) ion pair between AQ$^{-\cdot}$ and TEA$^{+\cdot}$ produced by a reaction of ^{3}AQ(T$_1$) with ground-state TEA. In fact, as shown in Fig. 3a, the spectrum with Band X at 60 ps delay is very similar to the absorption spectrum (open circles) of free $AQ^{\bar{\cdot}}$ produced by nanosecond pulse radiolysis of AQ in acetonitrile without TEA.[19] Although the appearance of Band X at 20 ps delay is somewhat inconsistent with the time constant for a diffusion-controlled reaction of $^3AQ(T_2)$ with TEA (1 M), we believe that the electron transfer from ground-state TEA to $^3AQ(T_2)$ may occur in a long-range distance, i.e., the diffusion-controlled reaction is unnecessary. Moreover, the assignment of Band X to free $AQ^{\bar{\cdot}}$ produced by a rapid decomposition of an excited charge-transfer complex which is the excited state of a ground-state complex of AQ with TEA can be ruled out based on the following facts: (1) No formation of the ground-state complex is observed. (2) If the direct excitation of the ground-state complex occurs, Band X should grow in within a duration (30 ps at FWHM) of the excitation light pulse and its intensity should be constant at a delay time longer than 60 ps. (3) For anthraquinones (XAQ; AQ and 1,8-dichloroanthraquinone),[20] we have really observed the formation of ground-state complexes of XAQ with 2,5-dimethylhexa-2,4-diene; upon excitation of these complexes, the excited singlet charge-transfer complexes are produced, and their absorption bands grow in within a duration of the excitation light pulse and decay following a single-exponential function with a lifetime of 100 ps. (3) Miyasaka et al.[10] have also reported that the lifetimes of the singlet ion pairs produced immediately after excitation of the ground-state complexes of benzophenone with *N,N*-dimethylaniline (and with *N,N*-diethylaniline) are 85 and 93 ps, respectively.

The result obtained for AQ in acetonitrile/TEA is very similar to those obtained for haloanthraquinones such as the 1-chloro (1-CAQ), 2-chloro (2-CAQ), 1,5-dichloro (1,5-DCAQ), 1,8-dichloro (1,8-DCAQ) and 1,8-dibromo (1,8-DBAQ) compounds,[15] where the intensity ratios (I_X/I_Y) of Band X to Band Y calculated for the spectra at 2 ns delay are 1.01 (2-CAQ), 1.05 (1-CAQ), 1.08 (1,5-DCAQ), 1.27 (1,8-DBAQ), and 1.54 (1,8-DCAQ). Since I_X/I_Y for AQ is 1.04 (cf. Fig. 3b) and since the $T_2 \rightarrow T_1$ internal conversion times are ≦70 (AQ, 1-CAQ, 2-CAQ, 1,5-DCAQ),[18] 70—110 (1,8-DBAQ),[21] and 700—750 (1,8-DCAQ)[16] ps, one can safely conclude that I_X/I_Y increases with increasing $T_2 \rightarrow T_1$ internal conversion time, supporting our proposal that free $AQ^{\bar{\cdot}}$ (and $TEA^{\dot{+}}$) and $^3(AQ\text{–}TEA)^*$ [or the contact (or solvent-separated) ion pair between $AQ^{\bar{\cdot}}$ and $TEA^{\dot{+}}$] are produced via the T_2 and T_1 states of AQ, respectively. Since the T_1 states of AQ and 2-CAQ are of $n\pi^*$ character and those of the α-halo compounds are of mixed $n\pi^*$–$\pi\pi^*$ (1-CAQ, 1,5-DCAQ) or $\pi\pi^*$ (1,8-DBAQ, 1,8-DCAQ) character,[22,23] the electronic configurations for the T_2 states of AQ and 2-CAQ are certainly different from those of the α-halo compounds.[16,21] In spite of this circumstance, the electron transfer mechanism obtained for AQ and 2-CAQ is identical with that obtained for the α-halo compounds. Hence, the difference in the electron-transfer mechanism observed for the T_2 and T_1 states of anthraquinones in acetonitrile can not be interpreted in terms of the difference in the electronic configuration. Since the direct electron transfer from ground-state TEA to the T_2 states of anthraquinones yielding their free radical anions is observed only in acetonitrile, its special solvent effect might affect the electron transfer mechanism. In order to discuss this problem, however, more detailed experiments using various solvents may be necessary. Of course, the conversion of the exciplexes into the contact ion pairs in ethanol (and toluene) and the dissociation of the exciplexes (or the contact or solvent-separated ion pairs) into the free radical ions in acetonitrile may be interpreted in terms of the difference in the polarities (or the dielectric constants) of solvents.

Conclusion

We have shown that the mechanism of photoinduced electron transfer obtained for the TEA–AQ system is identical with that obtained for the TEA–XAQ system,[3,15] however, the electron-transfer mechanism and the behavior of ionic intermediates in ethanol (and toluene) are remarkably different from those in acetonitrile. In this sense, one has to keep in mind that an electron-transfer mechanism proposed for a given system cannot be considered as a general rule applicable to other systems. Especially when one wants to understand the experimental results in terms of an electron-transfer rate theory, the great care must be taken regarding the nature of the solvent and the excited-state behavior of the donor or the acceptor.

This work was financed by a Grant-in-Aid for Scientific Research Nos. 04303001 and 04640444 from the Ministry of Education, Science and Culture. One of us (K. H.) also gratefully acknowledges the generous financial support of Chisso Co., Ltd.

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