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# Photoreduction of Anthraquinone by Triethylamine in Ethanol and Toluene Studied by Steady-State Photolysis and Laser Photolysis

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Photoreduction of anthraquinone (AQ) by triethylamine (TEA) in toluene and ethanol was studied by means of steady-state photolysis and laser photolysis. In toluene, addition of TEA enhanced the quantum yield of photoreduction of AQ, and the reaction was found to originate via the formation of an exciplex between ground-state TEA and the lowest triplet state of AQ: This exciplex changed to a contact ion pair followed by proton transfer, generating anthrasemiquinone radical and triethylamine radical, and 9,10-anthracenediol was obtained as the final photoproduct. Although the mechanism of the photoreduction of AQ in ethanol/TEA was essentially the same as that in toluene/TEA and the final products in ethanol/TEA were 9,10-anthracenediol and its anion, the quantum yield of photoreduction decreased with increase in TEA concentration. It was proposed that the exciplex in ethanol was quenched by ground-state TEA via the formation of a triplex of a radical anion of AQ and a radical cation of TEA dimer bonded by the three $\sigma$-electrons on two nitrogen atoms, based on the suggestion made by Hub et al. (*J. Am. Chem. Soc.*, **106**, 701 (1984); **106**, 708 (1984)).

Photoinduced electron transfer is one of the most important primary processes in a number of photochemical reactions, and the photoreductions of aromatic carbonyls in amine solutions have been investigated extensively.[1-6] Although intermediacy of a radical anion of ketones or a complex (an exciplex, a charge-transfer complex or an ion pair) of triplet ketones with ground-state amines has been proposed, the mechanism for the formation of these ionic species and the interconversion among them are generally dependent on the combination of the donor and the acceptor as well as the nature of the solvent. Moreover, the absorption spectra of these various species are generally very similar to each other. Therefore, it is very important to know the difference in the absorption spectra of the ionic species for full understanding of their formation.

Since we have observed that the quantum yields of photoreduction of anthraquinone (AQ) and haloanthraquinones (the chloro and bromo compounds) are increased by the addition of triethylamine (TEA), it is expected that ionic species mentioned above are also produced upon photolysis of anthraquinones/TEA in solution. As an extension of our study on the photophysics and photochemistry of anthraquinones,[7-12] this paper deals with the details of the photoreduction of AQ by TEA in ethanol and toluene, studied by means of steady-state photolysis and laser photolysis. Preliminary results have already been published elsewhere.[13]

## Experimental

**Chemicals.** The details of the methods of preparation of AQ have been given in our previous paper.[7] GR-grade TEA (Wako) was refluxed over calcium hydride and distilled under nitrogen. Spectral-grade ethanol (Nakarai), and scintillation-grade benzene (Dojin) and toluene (Dojin) as the solvents were used without further purification. Unless otherwise stated, the sample solutions were degassed by several freeze-pump-thaw cycles.

**Steady-State Photolysis.** Photolysis of AQ/TEA in solution was carried out at room temperature using an USH-500D super-high pressure mercury lamp. Light of 313-nm monochromatic wavelength was selected by the 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). Absorption spectra were taken on a Hitachi 200-20 spectrophotometer. The quantum yields of photoreduction were determined by the Hatchard-Parker's tris(oxalato)ferrate(III) actinometry method.[14]

For the identification of absorption spectra of a radical anion (AQ$^{\cdot-}$) of AQ and monoanion (AQH$^-$) of 9,10-anthracenediol (AQH$_2$), photolyses of AQ and AQH$_2$ in alkaline ethanol were performed using 366- and 404-nm lights, respectively, where light of 366-nm monochromatic wavelength was selected by the combination of two Toshiba color glass filters (UV-35, UV-D35) and a filter solution ($CuSO_4 \cdot 5H_2O$, 100 g dm$^{-3}$, path length 3 cm) and 404-nm light was selected by the combination of a Toshiba color glass filter (UV-39) and a filter solution (loc. cit.).

**Laser Flash Photolysis.** All transient absorption spectra were taken at room temperature. Unless otherwise stated, picosecond laser photolysis was performed using the second harmonic (347.2 nm) of a picosecond mode-locked ruby laser. The details of this laser photolysis system with a 30 ps instrumental time constant have been given elsewhere.[15] A double-beam optical arrangement was adopted and an absorption spectrum over a range of 200-nm wavelengths was obtained by two measurements: First, reference and probe light intensities without firing the exciting laser pulse, i.e., $I_O^A(\lambda)$ and $I_O^B(\lambda)$, respectively, were measured. Next, reference and probe light intensities with firing the exciting laser pulse, i.e., $I_E^A(\lambda)$ and $I_E^B(\lambda)$, respectively, were measured. Then, the absorbance $D(\lambda)$ at a given delay time was calculated by a microcomputer using the following equation;

$$D(\lambda) = \log[I_E^A(\lambda)/I_E^B(\lambda)] - \log[I_O^A(\lambda)/I_O^B(\lambda)] \qquad (1)$$

where $\lambda$ is the wavelength. The sample solutions in a cell of 2-mm path length were not deaerated.

To confirm a weak triplet-triplet ($T' \leftarrow T_1$) absorption of AQ at 500—600 nm, picosecond laser photolysis was also performed using the third harmonic (355 nm), with a pulse width of ≈25 ps, from a mode-locked $Nd^{3+}$: YAG laser of Osaka University, where the sample solutions in a cell of 10-mm path length were deaerated. The details of this laser photolysis system have been given elsewhere by Miyasaka et al.[16] The time-resolved absorption spectrum over a range of 400-nm wavelengths was calculated by

$$D(\lambda)=\log[\Sigma I_E^A(\lambda)/\Sigma I_E^B(\lambda)]-\log[\Sigma I_0^A(\lambda)/\Sigma I_0^B(\lambda)] \quad (2)$$

where spectral averaging was made five times.

The details of the Q-switched ruby laser photolysis system have also been given elsewhere.[10,17] The half-peak duration of the second harmonic (347.2 nm) was 20 ns, and the decay of the transient absorption was recorded by a combination of an HTV R666 photomultiplier with an Iwatsu TS-8123 storage oscilloscope: Time-resolved absorption spectra at delay times longer than 2 μs were recorded by the "ISD" system,[18] that is, a combination of a nanosecond ruby laser with an image sensor detector and a microcomputer, where a pulsed xenon flash lamp with a 1.7-μs full width at half-maximum intensity was used as a probe-light source. The time-resolved absorption spectrum over a range of 400-nm wavelengths was calculated by

$$D(\lambda)=\log[\Sigma I_0(\lambda)-\Sigma I_b(\lambda)]-\log[\Sigma I_E(\lambda)-\Sigma I_d(\lambda)] \quad (3)$$

where $I_b(\lambda)$ is the dark current spectrum of the detector system, and $I_d(\lambda)$ is the emission intensity due to the excited species, as measured without the probe light upon firing of the laser pulse. (Also, spectral averaging was made five times.) The sample solutions in a cell of 10-mm path length were deaerated.

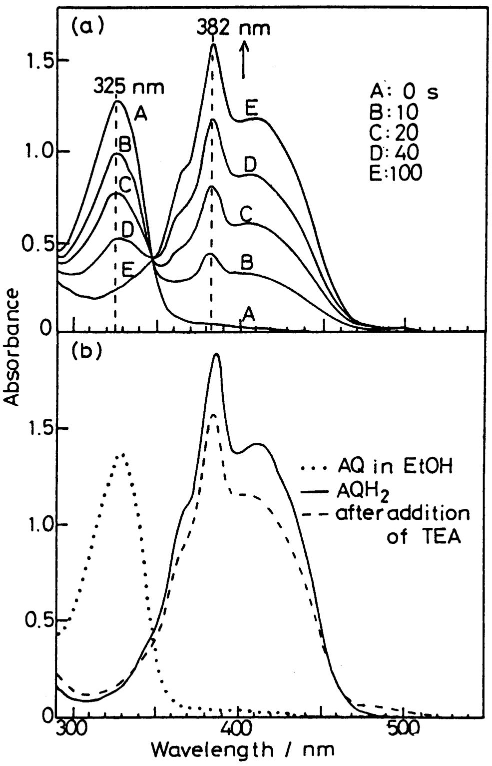


Fig. 1. Absorption spectral change of AQ/TEA (0.2 M) in ethanol upon irradiation with 313-nm light at room temperature (a), and change of the absorption spectrum of $AQH_2$ upon addition of TEA (b).

## Results

**Steady-State Photolysis.** The absorption spectral change of AQ/TEA (0.2 M; 1 M=1 mol dm$^{-3}$) in ethanol at room temperature is shown in Fig. 1a: Upon irradiation with 313-nm light, the absorption band of AQ with $\lambda_{max}$=325 nm decreased and a new band of the photoproduct with $\lambda_{max}$=382 nm built up, accompanied by an isosbestic point at 346 nm. This reaction is essentially the same as that of AQ in the absence of TEA.[8] Thus, one can safely conclude that the absorption band with $\lambda_{max}$=382 nm is due to $AQH_2$. In Fig. 1a, however, one can observe a weak tail at 470—530 nm. Such an absorption was not observed in the absence of TEA. We interpret this weak tail as the absorption due to $AQH^-$, based on the following reasons: (1) We have already reported that the forms of 10-cyano-9-anthrol (or its anion) and 10-benzoyl-9-anthrol (or its anion) in a solution containing TEA was dependent on the basicity, polarity and rigidity of medium as well as temperature.[19] The absorption bands of the base forms were observed at longer wavelengths than those of the acid forms. (2) As shown in Fig. 1b, 313-nm photolysis of AQ in ethanol without TEA yielded $AQH_2$. Subsequent addition of TEA in vacuo gave rise to the same absorption spectrum as that observed in Fig. 1a. (3) Upon addition of 0.2-ml aqueous solution of NaOH (0.01 M) to 4-ml ethanol solution of $AQH_2$ in vacuo, spectrum A of $AQH_2$ changed to spectrum B as shown in Fig. 2a; the concentration of NaOH in this alkaline ethanol is $4.8 \times 10^{-4}$ M. (Inserted spectrum is the absorption spectrum of $AQH^-$ reported by Carlson and Hercules.[20]) Upon photolysis with 404-nm light, the absorption bands at 393, ca. 484, ca. 773 and ca. 860 nm increased (cf. spectra C, D, and E).

AQ in alkaline ethanol is known to be photoreduced readily to form $AQ^{\bar{\cdot}}$. Figure 2b shows the absorption spectrum of $AQ^{\bar{\cdot}}$, prepared by 366-nm photolysis of AQ in alkaline ethanol (loc. cit.). The spectrum thus obtained is essentially identical with that reported by Carlson and Hercules[20] (cf. Inserted spectrum). Comparison of the absorption spectra in Fig. 2a with those in Fig. 2b suggests that photolyses of $AQH_2$, $AQH^-$, and AQ in alkaline ethanol give rise to the formation of $AQ^{\bar{\cdot}}$ as a final product. These results differ somewhat from that of Carlson and Hercules;[20] they reported that photolysis of $AQ^{\bar{\cdot}}$ in alkaline ethanol with 350-nm light gave rise to quantitative formation of $AQH^-$.

Anyway, it is reasonable to conclude that $AQH_2$ ionizes partly to the base form in TEA/ethanol solution. Thus, the quantum yields ($\Phi$) of photoreduction of AQ in several TEA/ethanol solutions were deter-

Table 1. Quantum Yields ($\phi$) of Photoreduction of AQ and Decay Constants of Exciplex ($k_1$) and Ion Pair ($k_2$)

| Solvent | | Concentration of TEA/M | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 0 | 0.02 | 0.05 | 0.1 | 0.2 | 0.4 | 1 |
| Ethanol | $\phi$ | 1.0 | 0.93 | — | 0.81 | 0.77 | 0.71 | 0.60 |
| | $k_1/10^6\,s^{-1}$ | — | 1.07 | 1.32 | 1.67 | 1.65 | 2.33 | 4.24 |
| | $k_2/10\,s^{-1}$ | — | 1.2 | 1.2 | 1.3 | 1.3 | 1.3 | 1.3 |
| Toluene | $\phi$ | 0.3 | 0.63 | 0.68 | 0.66 | 0.62 | 0.60 | 0.62 |
| | $k_1/10^6\,s^{-1}$ | — | 3.5 | 3.4 | 3.3 | 3.4 | 3.7 | 3.6 |
| | $k_2/10^5\,s^{-1}$ | — | 1.9 | 1.9 | 2.0 | 1.9 | 1.9 | 2.1 |

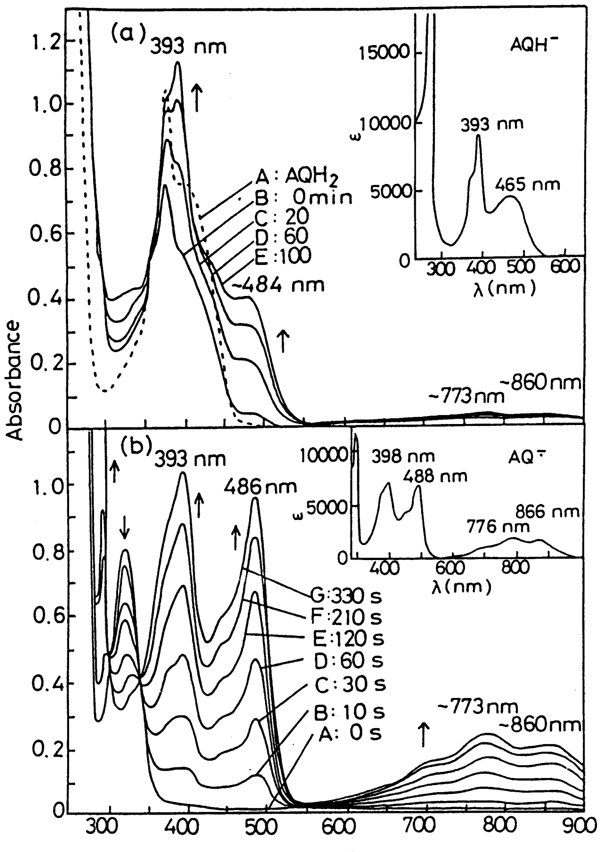


Fig. 2. Absorption spectral change of $AQH_2$ in alkaline ethanol (NaOH=$4.8\times10^{-4}$ M) upon irradiation with 404-nm light at room temperature (a), and absorption spectrum of $AQ^{\overline{\cdot}}$ prepared by 366-nm photolysis of AQ in alkaline ethanol at room temperature (b). Inserted spectra in (a) and (b) are the absorption spectra of $AQH^-$ and $AQ^{\overline{\cdot}}$, respectively, reported by Carlson and Hercules.[20]

mined by measuring the decrease in the absorbance of AQ, and the results obtained are listed in Table 1. For comparison, we also show the value of $\Phi$ obtained in ethanol without TEA.

Photolysis of AQ/TEA (0.2 M) in toluene gave the same result as that in toluene without TEA and the final photoproduct was $AQH_2$ (cf. Fig. 3). No formation of $AQH^-$ was observed. This is consistent with our previous observation[19] that the acid-base equilibrium of 10-cyano-9-anthrol and its base form (and 10-benzoyl-9-anthrol and its base form) depends on the dielectric constant of the solvent even in the presence of TEA. Thus, the values of $\Phi$ in several TEA/toluene solutions were determined by measuring the increase in the absorbance due to $AQH_2$, and the values obtained are also listed in Table 1 together with that in toluene without TEA.[21]

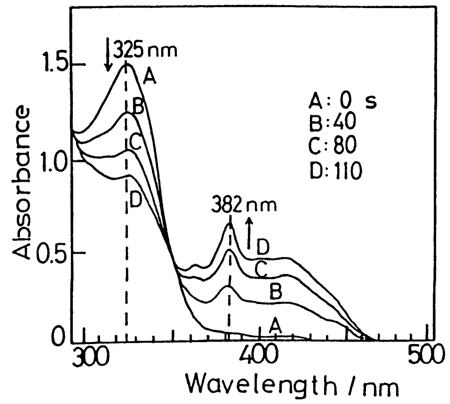


Fig. 3. Absorption spectral change of AQ/TEA (0.2 M) in toluene upon irradiation with 313-nm light at room temperature.

**Laser Flash Photolysis.** Figure 4 shows the transient absorption spectra obtained at room temperature upon picosecond laser photolyses of AQ/TEA (1 M) in ethanol (a) and toluene (b), respectively. The absorption spectra at a delay time of 40 ps in both solvents are nearly identical with the $T'\leftarrow T_1$ absorption spectrum of the lowest triplet state ($T_1$) of AQ, recorded at 77 K in EPA (ether/isopentane/ethanol=5 : 5 : 2 in volume ratio) without TEA (cf. Fig. 4c).[7,18]

Although the $T'\leftarrow T_1$ absorption spectra at room temperature are very weak, Manring and Peters[22] observed a strong $T'\leftarrow T_1$ absorption spectrum with a maximum absorbances at $\lambda_{max}$=623 and 677 nm, and a shoulder at 582 nm in deaerated benzene (cf. dotted line in Fig. 5b). Since this spectrum is obtained from the accumulation of at least 200 laser shots and the hydrogen-atom abstraction of triplet AQ from the solvent molecule gives rise to the formation of anthrasemiquinone radical ($AQH\cdot$),[10,11,20] the transient absorption spectrum observed by Manring and Peters might contain absorption due to $AQH\cdot$. In fact, Carlson and Hercules[20] have reported that $AQH\cdot$ has

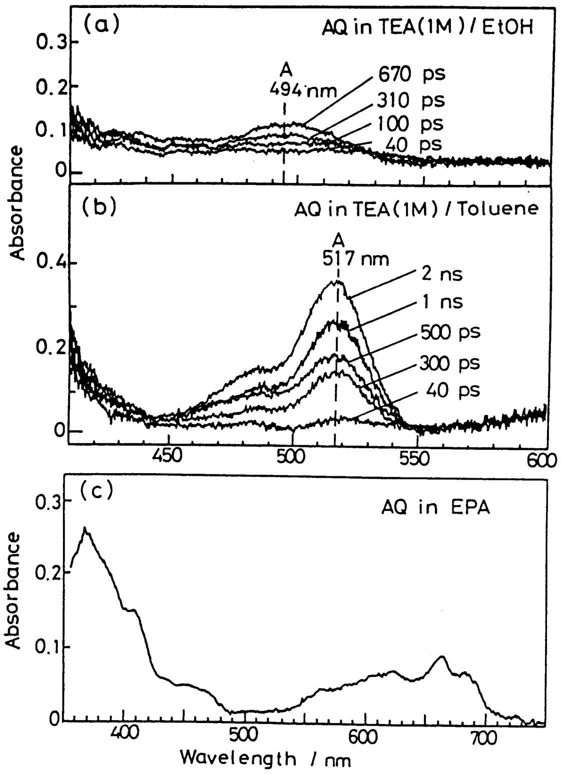


Fig. 4. Transient absorption spectra of AQ/TEA (1 M) in ethanol (a) and toluene (b) obtained by picosecond ruby laser photolysis at room temperature. The spectrum in (c) is the T′←T₁ absorption spectrum of AQ at 77 K in EPA, obtained by nanosecond ruby laser photolysis.

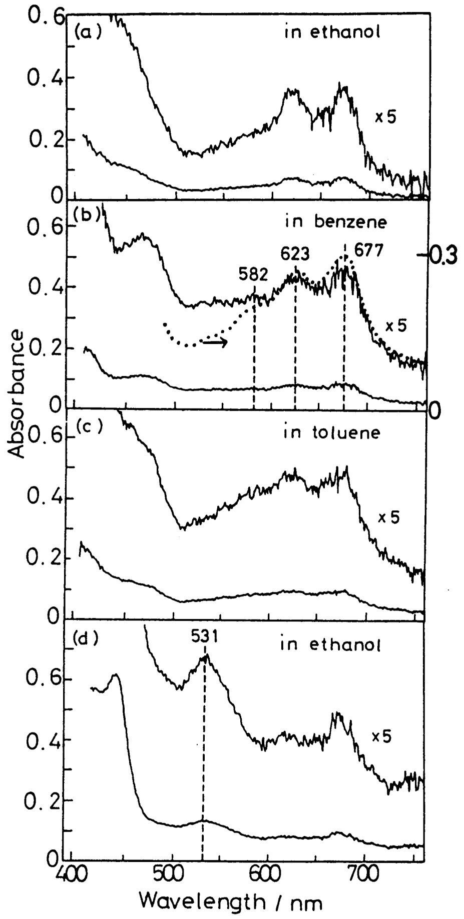


Fig. 5. The T′←T₁ absorption spectra of AQ at room temperature in ethanol (a), benzene (b), and toluene (c), obtained by picosecond $Nd^{3+}$:YAG laser photolysis at a delay time of 100 ps. The spectra in (d) were obtained for the sample which was illuminated by 175 laser shots before the spectral measurement, and the T′←T₁ absorption spectrum reported by Manring and Peters[22] is shown by a dotted line in (b).

three absorption bands at 678, 631, and 575 nm in ethanol. Thus, we have also performed picosecond laser photolyses of AQ in deaerated ethanol, benzene, and toluene using a picosecond $Nd^{3+}$: YAG laser of Osaka University.[16] Obviously, the spectra obtained by us (cf. Figs. 5a—c) are very weak compared with that obtained by Manring and Peters, being due to the fact that our transient spectra are not essentially accumulated as can be seen in Eq. 2. However, five times expansion of the transient spectra clearly indicates that they are identical with that obtained by Manring and Peters, even in ethanol solution in which the quantum yield of photoreduction is unity. We have also measured the transient spectra of the sample solutions which were illuminated by 175 laser shots before the spectral measurements. The spectra obtained in benzene and toluene were identical with those shown in Figs. 5b and c, although that in ethanol had an additional band at 531 nm (cf. Fig. 5d). This band is different from those of AQH• and $AQH_2$. (At present, we cannot assign this band.) All the results obtained so far indicate that the weak absorptions at 500—700 nm are not due to AQH• but due to triplet AQ, based on the following reasons: (1) The dominant feature of the absorption spectrum of AQH• is the existence of peaks of nearly equal intensity at 631 and 678 nm in ethanol.[20] (2) The absorption spectrum of AQH• is observed on a microsecond time scale after the excitation of AQ.[10,11,20] (3) The value of $\Phi$ is unity in ethanol, while that in toluene is smaller than 0.5 as can be seen in Table 1. However, the spectral intensities in Figs. 5a—c are almost identical.

In Fig. 4, a comparison of the T′←T₁ absorption spectrum at 40 ps delay with those at delay times longer than 100 ps suggests that a new intermediate (Band A) is produced after the buildup of the T₁ state of AQ, because the time constant for the buildup of the T′←T₁ absorption of AQ is less than 70 ps.[23] Upon picosecond laser photolyses of 1,8-dichloroanthraquinone (DCAQ)/TEA (1 M) in ethanol and toluene,[24] we observed that the transient absorption spectra at delay times shorter than 100 ps were identical with those observed in the absence of TEA.[12] A new intermediate ($\lambda_{max}$=540 nm in TEA/ethanol and 566 nm in TEA/toluene) similar to those in Fig. 4 built up at the expense of the $T_1$ state:[24] Recently, we have confirmed that addition of 2 M TEA in toluene quenches both the second triplet ($T_2$) and $T_1$ states of DCAQ.[25]

Figure 6a shows the results of nanosecond laser photolysis of AQ/TEA (0.2 M) in ethanol: The transient absorption at 490 nm appeared within the duration of the nanosecond laser pulse and increased up to 4 μs delay, and the maximum absorbance persisted beyond 200 μs with no measurable decay. In accordance with this, the transient absorption spectrum taken immediately after the nanosecond laser pulse is identical with that observed upon picosecond laser photolysis, while those (Band B) taken at delay times longer than 2 μs are shifted to the blue by ca. 8 nm as can be seen in Fig. 6b. (The spectrum shown by open circles was obtained by separate measurements of the absorbances at a number of desired wavelengths,[13] each following a single laser shot, that is, by point-to-point observation.) On a much longer time scale, Band B decayed accompanied by the appearance of a new absorption (Band E) as shown in Fig. 6c. Band E is identical with the absorption band of $AQH_2$ (cf. Fig. 1a). Moreover, the rise and decay of Band B could be fitted by first-order reaction kinetics as shown in Fig. 7. In ethanol, the rate constants for the buildup of Band B increased with increasing concentration of TEA (cf. closed circles in Fig. 8). On the other hand, no concentration effect of TEA on the decay of Band B was observed. (For comparison, we also show the variation of $1/\Phi$ with the concentration of TEA by open circles.)

Similar results were also obtained in toluene as shown in Fig. 9. The transient absorption of Band A ($\lambda_{max}$=517 nm) observed upon picosecond laser photolysis also appeared within the duration of the nanosecond laser pulse (cf. dotted line in Fig. 9a). And the

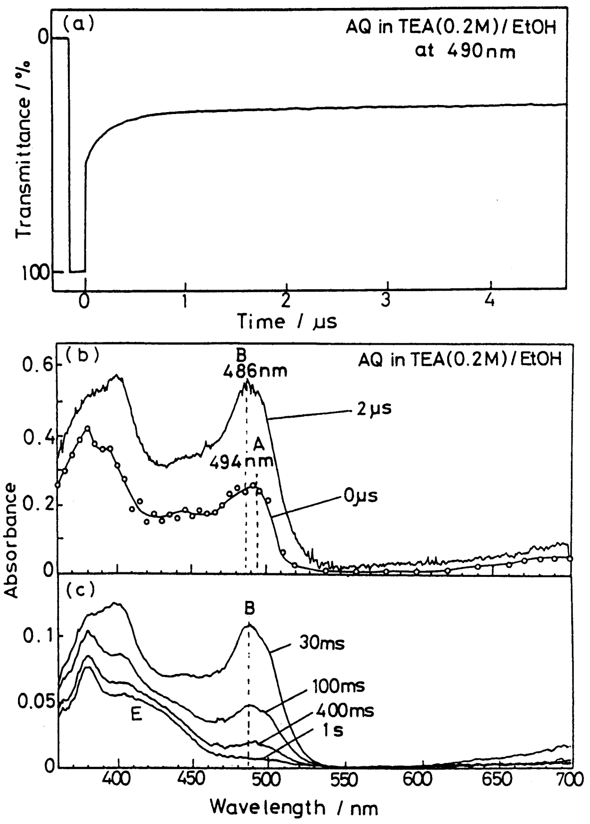


Fig. 6. Time-variation of the transient absorption at 490 nm (a) and change of the transient absorption spectra (b, c) of AQ/TEA (0.2 M) in ethanol, obtained by nanosecond ruby laser photolysis at room temperature.

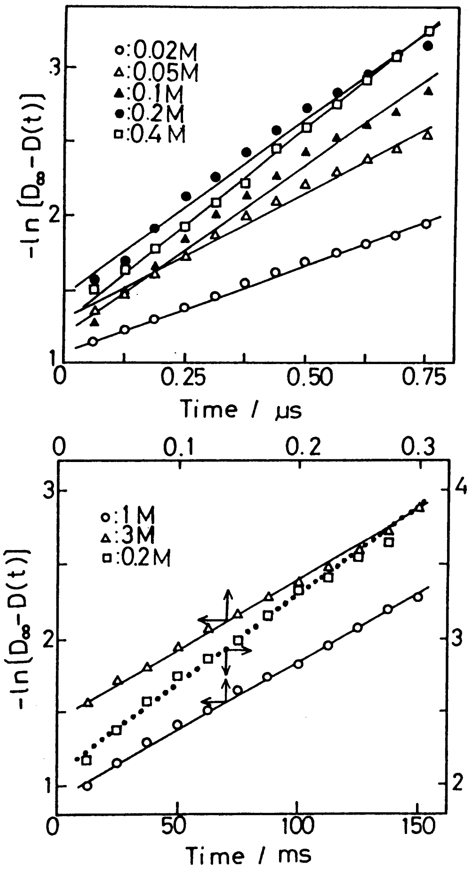


Fig. 7. First-order plots for the rise (full lines) and the decay (dotted line) of Band B in ethanol. Numbers in figures are the concentrations of TEA.

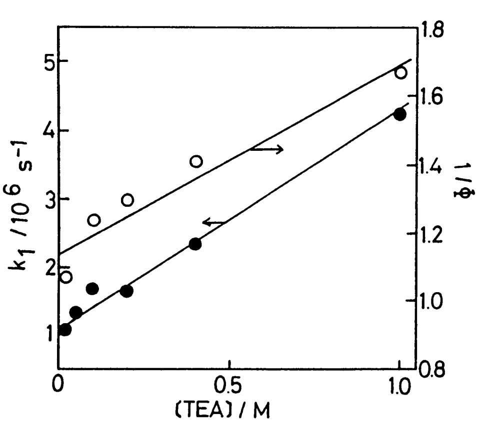


Fig. 8. Plots of $k_1$ (closed circles) and $1/\Phi$ (open circles) against the concentration of TEA in ethanol.

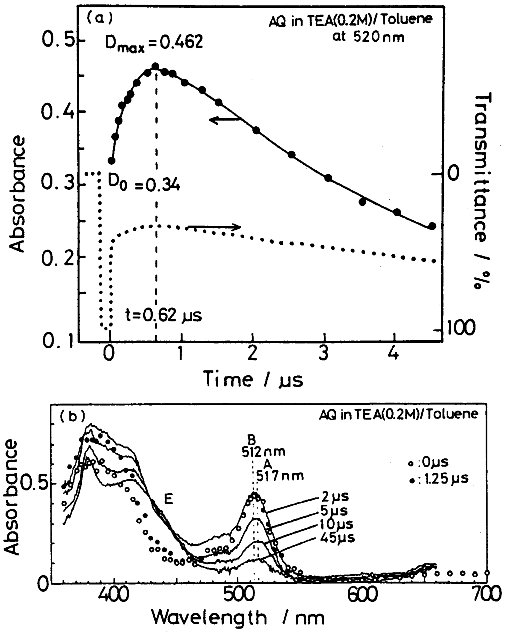


Fig. 9. Time-variation of the transient absorption at 520 nm (a, dotted line) and change of the transient absorption spectra (b) of AQ/TEA (0.2 M) in toluene, obtained by nanosecond ruby laser photolysis at room temperature. Closed circles and a full line in (a) are the absorbances and the best-fit theoretical curve, respectively.

transient absorption increased initially, followed by the spectral shift by ca. 5 nm to Band B (cf. Fig. 9b). (The spectra shown by open and closed circles were recorded by point-to-point measurement.[13]) Thus, one may say that the small spectral shift of ca. 5 nm is within the experimental error. However, the spectra recorded by the ISD system (full lines) are essentially identical with those obtained by point-to-point method. The decay of Band B was accompanied by the buildup of the new absorption due to $AQH_2$ (Band E at ca. 440 nm), and one can clearly observe the existence of two isosbestic points at 430 and 450 nm. The effects of the concentration of TEA on the buildup and decay of Band B were negligible.

## Discussion

The results of steady-state photolysis of AQ/TEA with 313-nm light indicate the existence of a clear isosbestic point which support quantitative conversion of AQ to $AQH_2$ (and its anion). Exposure to oxygen caused quantitative oxidation of $AQH_2$ back to AQ. These results are just the same as the photoreductions of AQ and haloanthraquinones in the absence of TEA.[8,9]

Table 1 shows that the values of $\Phi$ in TEA/toluene solutions are clearly greater than 0.5, while that in toluene without TEA is 0.3. This enhancement of the photoreduction of AQ by TEA is very similar to that of benzophenone (BP) by several amines,[1-6] and the generally accepted mechanism is that an electron is transferred from amines to triplet BP, forming a radical anion of BP or a complex (an exciplex, a charge-transfer complex or an ion pair) of triplet BP with ground-state amines. It is also thought that the complex is quenched either by proton transfer, generating a benzhydrol radical and an amine radical, or by spin inversion followed by back electron transfer, yielding ground-state BP and amine. In ethanol, the quantum yields of photoreduction of AQ decreased with increase in TEA concentration. This problem will be discussed later.

Except for Band E, the transient absorption spectra in Figs. 4b, 6b—c, and 9b are very similar to those of $AQ^{\overline{\cdot}}$ which were produced upon photolysis of AQ in alkaline ethanol (cf. Fig. 2b) or γ-radiolysis of AQ in 2-methyltetrahydrofuran at 77 K.[26] Although no transient photocurrent was detected in toluene, it was observed in ethanol. However, the rise and decay of this photocurrent were different from those of Bands A and B. Moreover, the intensity of the initial photocurrent increased after repeated measurements, indicating that the photocurrent is due to some ionic species produced electrochemically.

We conclude that Bands A and B are different from the $T' \leftarrow T_1$ absorption of AQ observed by us (cf. Fig. 5) and Manring and Peters,[22] based on the following reasons: The $T' \leftarrow T_1$ absorptions in Fig. 4 are very weak compared with Bands A and B. Moreover, their spectral profile and the positions of the absorption maxima are essentially different from those of the $T' \leftarrow T_1$ absorptions.

Based on the above discussion and those for the absorption spectra of the radical anions,[27] it is reasonable to make the following conclusions: (1) The intermediate (Band A) observed by picosecond laser photolysis is identical with that produced within the duration of the nanosecond laser pulse. This intermediate may be assigned to a triplet exciplex between ground-state TEA and the $T_1$ state of AQ. (2) In ethanol, the exciplex generates a contact ion pair (Band B) between $AQ^{\overline{\cdot}}$ and the radical cation ($TEA^{\dot{+}}$) of TEA. The contact ion pair may be relatively stable in a polar solvent such as ethanol, because no decay of the contact ion pair was observed up to 200 µs delay. Since $AQH_2$ was produced upon steady-state photolysis of AQ/TEA in ethanol as shown in Fig. 1a, the contact ion pair may finally disappear by proton transfer from $TEA^{\dot{+}}$ to $AQ^{\overline{\cdot}}$, generating neutral $AQH\cdot$ and triethylamine radical ($TEA\cdot$). Actually the decay of Band B was accompanied by the appearance of the absorption due to $AQH_2$ (cf. Fig. 6c). (3) In toluene, the exciplex also generates the contact ion pair, however, it is subsequently quenched by proton transfer on a microsecond time scale.

If the mechanism mentioned above is correct, the photoreduction of AQ by TEA in ethanol and toluene may be interpreted in terms of the following consecutive reactions based on the results of photoreduction of several anthraquinones without TEA[8-11] and BP/amines;[1-6] Triplet AQ+TEA→Exciplex→Contact ion pair→AQH·+TEA·; TEA·+AQ→AQH·; 2AQH·→AQ+$AQH_2$ (and its base form). AQH· may also be produced via the hydrogen-atom abstraction by ground-state AQ from TEA·, because the value of $\Phi$ in the presence of TEA are greater than 0.5 as shown in Table 1. In toluene without TEA, the value of $\Phi$ is smaller than 0.5, indicating that no AQH· is produced via the hydrogen-atom abstraction by ground-state AQ from a benzyl radical. In ethanol without TEA, the value of $\Phi$ was unity, while in TEA/ethanol solutions, $\Phi$'s were between 0.93 ([TEA]=0.02 M) and 0.60 ([TEA]=1 M). This may be due to the back electron transfer in the exciplex or ion pair. Also, quenching of the exciplex by ground-state TEA is expected to occur as will be discussed later.

From the buildup time of the exciplex of AQ/TEA, the rate constant for electron transfer from ground-state TEA to triplet AQ was estimated to be $\approx 2.5\times10^9$ $M^{-1}\,s^{-1}$ in ethanol. This value is nearly equal to those for BP/TEA in benzene ($3\times10^9$ $M^{-1}\,s^{-1}$)[2] and BP/1,4-diazabicyclo[2.2.2]octane (DABCO) in ethanol ($2.3\times10^9\,M^{-1}\,s^{-1}$).[5] Since the transient absorption at 490 nm did not decay up to 200 μs in ethanol, the buildup of the absorbance $D(t)$ at time $t$ can be given by

$$D(t)=D_0(1-\alpha\beta)\exp(-k_1t)+D_0\alpha\beta \tag{4}$$

where $D_0$ is the absorbance of the exciplex at $t$=0, $\alpha$ is the ratio of the extinction coefficient of the contact ion pair (Band B) to that of the exciplex (Band A), $\beta$ is the efficiency of formation of the contact ion pair from the exciplex and $k_1$ is the decay constant of the exciplex. We determined $D_\infty = D_0\alpha\beta$ from the absorbance at 4 μs delay in Fig. 6a, and the plots of $-\ln[D_\infty - D(t)]$ against time gave the straight lines as shown by full lines in Fig. 7. Band B decayed on a much longer time scale and the decay constant ($k_2$) could be obtained by the first-order plot of $-\ln[D(t)-D'_\infty]$ vs. $t$, where $D'_\infty$ is the absorbance due to the final product (cf. dotted line in Fig. 7). In Table 1, the decay constants of the exciplex and ion pair obtained so far are also listed.

In toluene, $D(t)$ may be expressed by

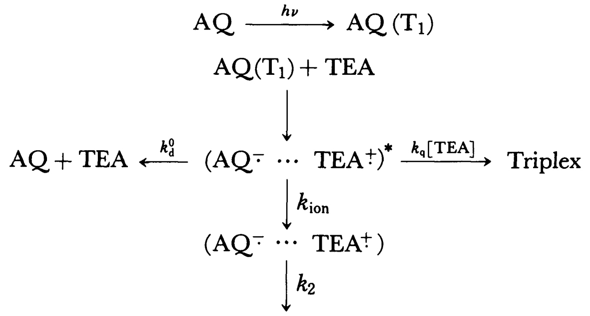
$$D(t)=D_0\left(1-\frac{\alpha\beta k_1}{k_1-k_2}\right)\exp(-k_1t)+\frac{D_0\alpha\beta k_1}{k_1-k_2}\exp(-k_2t). \tag{5}$$

We determined $\alpha\beta$ from the value of $D_{\max}$ as a function of $k_1$ and $k_2$ (cf. Fig. 9a), and the rate constants can be determined by a best fit of the theoretical curve of $D(t)$ to the experimental values. A typical curve of $D(t)$ is also shown in Fig. 9a (full line), and the best-fit values obtained so far are also listed in Table 1. (The value of $\alpha\beta$ was nearly constant, i.e., 1.53.)

Although we have proposed that triplet AQ produces exciplexes with ground-state TEA both in ethanol and toluene and there are many papers to infer the existence of triplet exciplexes,[28] direct observation of their phosphorescences is extremely rare. This may be due to the fact that the phosphorescences are generally observable only in rigid media at low temperature where diffusion is extremely slow. Since the phosphorescences can be studied only with the complexes which are present in the ground state already, and since the exciplexes mean the nonexistence of the ground-state complexes, observation of the exciplex phosphorescences may be difficult even at 77 K.

It is well known that the lifetimes of the singlet exciplexs or ion pairs are in general of the order of a few nanoseconds.[29] However, we believe that our data in Table 1 are reasonable based on the following considerations: (1) Decay constants even for singlet exciplexes are sometimes small:[29] benzene/tetracyanobenzene (TCNB), $k_1=6.8\times10^6\,s^{-1}$; toluene/TCNB, $k_1=8.2\times10^6\,s^{-1}$; pyrene/*N,N*-dimethylaniline, $k_1=5.3\times10^6\,s^{-1}$. (2) The phosphorescence lifetimes ($\tau_p$) of exciplexes at 77 K are shorter than those of the electron donors or electron acceptors.[29] For example, $\tau_p$ of TCNB complexes with benzene, toluene, mesitylene, durene, and hexamethylbenzene are 3.0, 2.4, 2.3, 1.7, and 0.76 s, respectively, and all shorter than that of TCNB itself, 3.2 s. This is consistent with our result at room temperature; the lifetime of triplet AQ in toluene is 15.3 μs, while that of AQ/TEA exciplex can be calculated from Table 1 to be ca. 0.29 μs. (3) In liquid solutions at room temperature, the triplet exciplexes with decay constants of $10^4$—$10^6\,s^{-1}$ are also known.[2,30,31]

Hub et al.[32] observed that an exciplex of singlet *trans*-stilbene (TS) with several amines was quenched by ground-state amines at their higher concentrations: They interpreted this quenching in terms of the interaction of amine radical cation with neutral amine, forming a triplex of a radical anion of TS and a radical cation of amine dimer bonded by the three σ-electrons on two nitrogen atoms. Thus, it is expected that the triplet exciplex of AQ/TEA may also be quenched by the formation of a triplet triplex of $AQ^{\overline{\cdot}}/TEA_2^{\dagger}$. In fact, the values of $\Phi$ in ethanol decreased with increase in the concentration of TEA, indicating exciplex quenching by ground-state TEA (cf. Table 1). If exciplex formation is assumed to occur irreversibly, one can give the following approximate kinetic scheme (Scheme 1).



Scheme 1.

Under these conditions, the decay constant of the exciplex can be given by

$$k_1 = k_d^0 + k_{ion} + k_q[TEA]. \tag{6}$$

A plot of $k_1$ against the concentration of TEA ([TEA]) gave a straight line with the quenching rate constant of $3.1\times10^6$ M$^{-1}$ s$^{-1}$ in ethanol (cf. Fig. 8). This value is about two orders of magnitude smaller than that obtained for the singlet exciplex of TS/TEA, i.e., $3\times10^8$ M$^{-1}$ s$^{-1}$, but may be nearly equal to that obtained for TS/diisopropylamine, i.e., $\ll 1.0\times10^7$ M$^{-1}$ s$^{-1}$ by Hub et al.[32] (In toluene, the value of $k_q$ was negligibly small compared with that in ethanol.)

The approximate values of $k_d^0$ and $k_{ion}$ for the exciplex of AQ/TEA in ethanol can be obtained from the dependence of $1/\Phi$ on [TEA] using the following equation;

$$\frac{1}{\Phi} = \left(\frac{k_d^0 + k_{ion}}{k_{ion}} + \frac{k_q[TEA]}{k_{ion}}\right)\cdot\frac{1}{\gamma} \tag{7}$$

where $\gamma$ is the efficiency of formation of AQH· from the contact ion pair. Since a plot of $1/\Phi$ against [TEA] gave a straight line (cf. open circles in Fig. 8), the values of $k_d^0$ and $k_{ion}$ were determined to be $8.4\times10^5$ s$^{-1}$ and $5.6\times10^6$ s$^{-1}$, respectively, on the assumption that $\gamma$ is unity. In toluene, the value of $\Phi$ is independent of [TEA] as can be seen in Table 1, indicating that the value of $k_d^0+k_{ion}$ is much greater than that of $k_q$ [TEA].

The formation of exciplexes with ground-state TEA was also observed for triplet α-haloanthraquinones both in ethanol and toluene.[13,24,26] However, our results are a little different from those of BP/amine (amine=TEA, *N*,*N*-diethylaniline, *N*,*N*-dimethylaniline, DABCO), reported by Peters et al.: In their first two papers,[4,5] they proposed that an electron was transferred from amine to triplet BP forming an exciplex. Later they changed the assignment of the exciplex to that of a solvent-separated ion pair,[6] but no explanation has been given. Presumably their assignment to the solvent-separated ion pair may be based on their finding that picosecond laser photolysis of BP/amine in acetonitrile gave rise to a new intermediate with $\lambda_{max}$ of 715 nm. Since this intermediate changed to another intermediate with $\lambda_{max}$ of 690 nm on a picosecond time scale, they concluded that the photoreduction proceeded via rapid electron transfer from amine to triplet BP forming the solvent-separated ion pair followed by the formation of a contact ion pair. In ethanol, the absorption maximum shifted to blue from 690 to 625 nm, and this spectral shift was attributed to the formation of a hydrogen-bonded solvent-separated ion pair from an initially formed contact ion pair.

In our present study both in ethanol and toluene, however, no spectral shift was observed on a picosecond time scale, nor in 2-methyltetrahydrofuran, acetone and dimethylsulfoxide. On a few microsecond time scale, the transient absorption shifted to blue by ca. 8 nm in ethanol and ca. 5 nm in toluene, and the shifted bands decayed following a single exponential function. Thus, we suggest that the exciplex is produced initially in both ethanol and toluene.

The spectral shifts observed by Peters et al. might be due to a special solvent effect of acetonitrile. This explanation is based on the following facts:[33] (1) Picosecond laser photolysis of AQ/TEA (1 M) in acetonitrile gave rise to the spectral change similar to those observed by Peters et al. Namely, an absorption band (Band X) with $\lambda_{max}$=540 nm built up during the first 500 ps delay and this band did not decay up to 2 ns. On the other hand, an absorption band (Band Y) with $\lambda_{max}$=515 nm increased up to 2 ns and the overall spectral profile at 2 ns delay looked like a superposition of Bands X and Y. (2) Nanosecond laser photolysis of AQ/TEA (0.2 M) in acetonitrile revealed that the absorption spectrum taken immediately after the laser pulse was similar to that observed upon picosecond laser photolysis at 2 ns delay, while those taken at delay times longer than 0.05 μs had no absorption due to Band Y. This indicates that Band Y shifted to red by ca. 25 nm: The transient absorption at 540 nm appeared within the duration of the nanosecond laser pulse, and it increased up to 1 μs delay. The maximum absorbance persisted beyond 50 μs and decayed on a much longer time scale, following second order reaction kinetics. (3) A transient photocurrent was detected in acetonitrile, and its buildup curve was identical with that of the transient absorption. (4) Nanosecond pulse radiolysis of AQ in acetonitrile without TEA gave rise to the appearance of a new absorption band similar to Band X: The rate constant for the buildup of this new absorption band was equal to that for the decay of the absorptions due to anionic species such as a solvated electron, monomeric and/or dimeric radical anion of acetonitrile.[34]

Thus, we proposed that Bands X and Y were due to a free $AQ^{\cdot-}$ and an exciplex, respectively. Since the transient absorption spectrum obtained by picosecond laser photolysis exhibited the time-dependent spectral change, the free $AQ^{\cdot-}$ and the exciplex may be produced independently from the different encounter collisional complexes between ground-state TEA and triplet AQ.[3,30] We suggested that the free $AQ^{\cdot-}$ and the exciplex in acetonitrile were produced via the $T_2$ and $T_1$ states of AQ, respectively, based on the following facts: The time constants for the internal conversion from the $T_2$ to $T_1$ states were estimated to be less than 70 ps for AQ and 1-chloroanthraquinone (1-CAQ),[23] while that for DCAQ was 0.70—0.75 ns.[12] In accordance with this, the ratio of the intensity of Band Y to that of Band X for DCAQ[35] was smaller than those for AQ[33] and 1-CAQ.[35]

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