Photoreduction of Aminoanthraquinones by an Electron Transfer *via* the Upper Excited nπ* Triplet State

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The photoreduction of 2-piperidinoanthraquinone (**1**) by an electron transfer from hydroxide ion in aqueous 2-propanol was reinvestigated. The reaction proceeded actively on irradiation at 365 nm, but very weakly on irradiation at 420 nm. The fluorescence of **1** was not affected by hydroxide ion. 1,3-Cyclohexadiene as a triplet quencher retarded the photoreduction. All results revealed that the reactive state of **1** in the photoreduction is not the intramolecular excited CT state, but the upper excited nπ* triplet state. Kinetic studies indicated that the rate of deactivation from the $T_2(^3n\pi^*)$ level of **1** is unusually slow ($k_d = 1.7\times10^8$ s^{-1}). The photoreduction *via* the upper excited $T_2(^3n\pi^*)$ level was also observed in 1-amino- and 1-piperidinoanthraquinone, while 2-aminoanthraquinone did not exhibit any reactivity. Wavelength-dependencies (313 nm, 365 nm, and >420 nm irradiations) of the photoreductions were also observed.

Anthraquinone derivatives have four $\pi\pi^*$ absorption bands in the wavelength range between 220 nm and 350 nm, and also an nπ* band at longer wavelength near 400 nm. When electron donating substituents such as hydroxyl, amino, and methylamino groups are introduced into the nucleus, a new $\pi\pi^*$ absorption band, an intramolecular charge transfer band, appears in the visible region.[1] In the photochemistry of anthraquinone derivatives, it has long been emphasized that the excited triplet nπ* state is very reactive, while the intramolecular CT state has little reactivity.[2] Recently we have found a new photosubstitution reaction of aminohaloanthraquinones with amines under irradiation with visible light and demonstrated that the intramolecular CT state is reactive in the reaction.[3] A. K. Davies *et al.* also postulated that the intramolecular CT state is reactive in the photoreduction of 2-piperidinoanthraquinone (**1**) by an electron transfer from hydroxide ion or alkoxide ion on irradiation with the light of $\lambda=365$ nm.[4] However, an ambiguity remains in their conclusion about the reactive state; another possibility of the photoreduction *via* the upper excited $T_2(^3n\pi^*)$ level can not be excluded. The results of our reinvestigation of this photoreduction of **1** by hydroxide ion showed that the reaction proceeds not *via* the intramolecular CT state but *via* the upper excited $T_2(^3n\pi^*)$ state, contrary to Davies' conclusion. We also examined the photoreduction *via* the upper excited nπ* level of other anthraquinones (1-aminoanthraquinone (**2**), 2-aminoanthraquinone (**3**), 1-piperidinoanthraquinone (**4**) and we observed dramatic wavelength dependencies (313 nm, 365 nm, and >420 nm irradiations) on the photoreduction in these anthraquinones including 2-SO_3Na (**5**) and 1-SO_3Na (**6**) derivatives.

Experimental

Materials. *2-Piperidinoanthraquinone (1)*: 2-Chloroanthraquinone (10 g) and piperidine (150 ml) were heated to reflux for 8 h. The excess piperidine was evaporated from the reaction mixture and the residual red crystals of **1** were washed thoroughly with water and dried. The yield was 12.3 g. The crude **1** was purified by repeated recrystallizations from ethanol–benzene mixture (4 : 1 v/v); mp 164—165 °C; Found: C, 78.18%; H, 5.71%; N, 4.63%. Calcd for $C_{19}H_{17}NO_2$: C, 78.31%; H, 5.89%; N, 4.80%. 1-Aminoanthraquinone (**2**) (Sumitomo Chemical Co.) was purified by column chromatography (Al_2O_3/toluene) and repeated recrystallizations from benzene; mp 252—253 °C; Found: C, 75.31%; H, 3.86%; N, 6.44%. Calcd for $C_{14}H_9NO_2$: C, 75.32%; H, 4.06%; N, 6.27%. 2-Aminoanthraquinone (**3**) (Sumitomo Chemical Co.) was purified by the procedures recommended by Maki[5] using 82% aqueous sulfuric acid; mp 302 °C; Found: C, 75.24%; H, 3.78%; N, 6.02%. Calcd for $C_{14}H_9NO_2$: C, 75.32%; H, 4.06%; N, 6.27%. 1-Piperidinoanthraquinone (**4**): 1-Chloroanthraquinone (15 g) and piperidine (225 ml) were refluxed for 2.5 h. After evaporating off the excess piperidine, the red crystals of **4** were washed thoroughly with water and dried. The yield was 17.3 g. The crude **4** was passed through a silica-gel column (hexane–acetone, 3 : 1 v/v) and recrystallized repeatedly from ethanol; mp 124 °C; Found: C, 78.24%; H, 5.88%; N, 4.67%. Calcd for $C_{19}H_{17}NO_2$: C, 78.31%; H, 5.89%; N, 4.80%. Both sodium anthraquinone-2-sulfonate (**5**) and sodium anthraquinone-1-sulfonate (**6**) (Sumitomo Chemical Co.) were purified by respective salting-outs and repeated recrystallizations from water until molar absorption coefficients in their UV spectra became constant. 2-Propanol and methanol were purified as reported previously.[3] 1,3-Cyclohexadiene (Tokyo Kasei, GR) was further purified by fractional distillation before use.

Procedure. Each sample (4 ml) was degassed in a quartz cell by repeated freeze and thaw procedures and was irradiated with a high pressure mercury lamp (Toshiba H-400P or USHIO USH-500D) through the following filter systems; Toshiba UV-D25 glass filter and aqueous solution of K_2CrO_4 (0.27 g/dm^3) Na_2CO_3 (1.0 g/dm^3) (optical length: 1 cm) for the irradiation by monochromatic light of 313 nm; Toshiba UV-DIA glass filter and naphthalene (5.0×10^{-2} mol/dm^3) in 2-propanol (optical length: 1 cm) for irradiation at 365 nm. The visible and UV absorption spectra of the irradiated reaction mixtures were recorded by a Shimadzu UV-200 spectrophotometer. The number of photons absorbed by each sample was determined by the use of a chemical actinometer of potassium tris(oxalato)ferrate(III).[6] In a typical case, the numbers of photons of the incident light of 313 nm and 365 nm were 3.2×10^{15} quanta/s and 1.6×10^{16} quanta/s, respectively.

Results

Photoreduction of 2-Piperidinoanthraquinone (1) in Alkaline

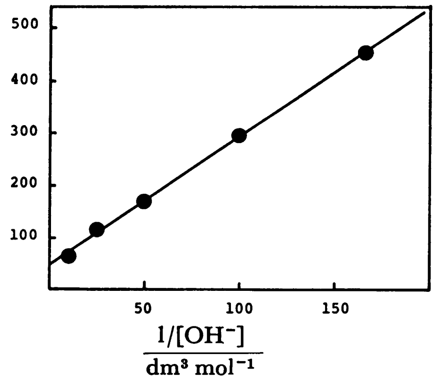
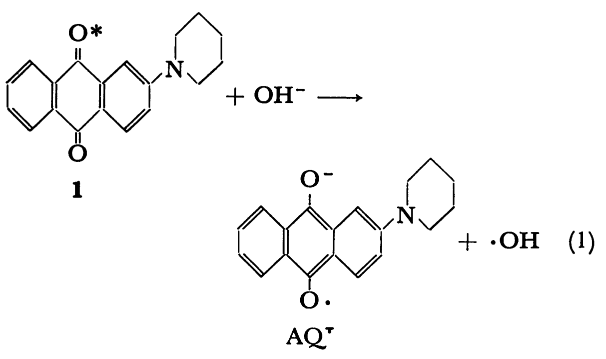


Fig. 1. Effect of the concentration of hydroxide ion on the quantum yield of the photoreduction of **1**; [**1**]: 1.00×10^{-4} mol/dm³ in 4 : 1 2-propanol–water mixture under nitrogen atmosphere; irradiation light: $\lambda=365$ nm.

Aqueous 2-Propanol. When **1** (1.00×10^{-4} mol/dm³) and sodium hydroxide (5.00×10^{-2} mol/dm³) in 4 : 1 2-propanol–water mixture was irradiated with monochromatic light of $\lambda=365$ nm under nitrogen atmosphere, the absorption bands at $\lambda=402$, 476, and >650 nm, assigned to the radical anion of **1**, increased. Isosbestic points were observed at $\lambda=377$, 498, and 570 nm. Introduction of air to the irradiated reaction mixture caused rapid disappearance of the radical anion of **1**, and **1** was recovered unchanged. A similar effective photoreduction was also observed in aqueous acetonitrile which is considered to have little reactivity toward a conventional hydrogen atom abstraction (Φ(in 4 : 1 acetonitrile–water)/Φ(in 4 : 1 2-propanol–water)$=0.56$ when $[\mathrm{NaOH}]=5\times10^{-2}$ mol/dm³). As shown in Fig. 1, the reciprocal of the quantum yield for the production of the radical anion of **1** was found to be linear with the reciprocal of the total amount of hydroxide ion added to the reaction system. These results suggest that the radical anion of **1** is produced not by a conventional hydrogen abstraction by the excited **1** from the solvent followed by a deprotonation (Eqs. 2 and 3), but by a direct electron transfer from the hydroxide ion (Eq. 1).



(1)

$$\mathrm{AQ^* + H\text{-}\overset{|}{\underset{|}{C}}\text{-} \longrightarrow AQH\cdot + \cdot\overset{|}{\underset{|}{C}}\text{-}} \qquad (2)$$

$$\mathrm{AQH\cdot + OH^- \longrightarrow AQ^{\cdot-} + H_2O} \qquad (3)$$

Table 1. Effect of the wavelength of irradiating light on the photoreduction of **1**

Wavelength of irradiation/nm	Relative quantum yield
313	1.0
365	1.0
>420	0.003

The radical anion of **1** was stable in the reaction system for more than 1d. Hence it was supposed that most of the hydroxyl radical, a powerful oxidizing agent, produced in the reaction system along with the radical anion of **1** (Eq. 1) would abstract a hydrogen atom from 2-propanol to produce water and acetone (Eq. 4). In the irradiated reaction mixture acetone was really detected by GLC analysis (column/PEG-20M; 40 °C).

$$\mathrm{OH\cdot + (CH_3)_2CHOH \longrightarrow H_2O + (CH_3)_2\dot{C}OH} \qquad (4)$$

$$\mathrm{(CH_3)_2\dot{C}OH + AQ \longrightarrow (CH_3)_2C{=}O + AQH\cdot} \qquad (5)$$

The radical anion of **1** is also produced by a deprotonation of the semiquinone radical (AQH·) generated in Eq. 5. If the photoreduction of **1** by hydroxide ion proceeds *via* the ¹CT level as proposed by Davies *et al.*,[4] **1** should be photoreduced on irradiation with light of $\lambda>420$ nm which excites **1** exclusively to its ¹CT level. The fluorescence of **1** should be quenched by the addition of hydroxide ion to an extent predicted from the linear plot of Fig. 1. However, as shown in Table 1, the radical anion of **1** was only very weakly produced on irradiation with light of $\lambda>420$ nm, and the fluorescence intensity of **1** was not affected by the presence of hy-

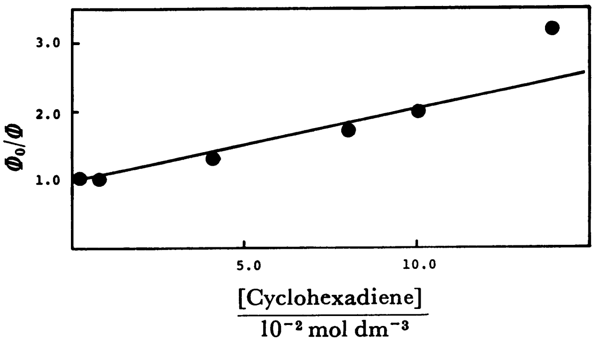


Fig. 2. Stern-Volmer plot for the quenching effect of 1,3-cyclohexadiene on the photoreduction of **1**; [**1**]: 1.00×10^{-4} mol/dm³ in 4 : 1 2-propanol-water mixture under nitrogen atmosphere; [OH⁻]: 0.1 mol/dm³; irradiation light: $\lambda=365$ nm.

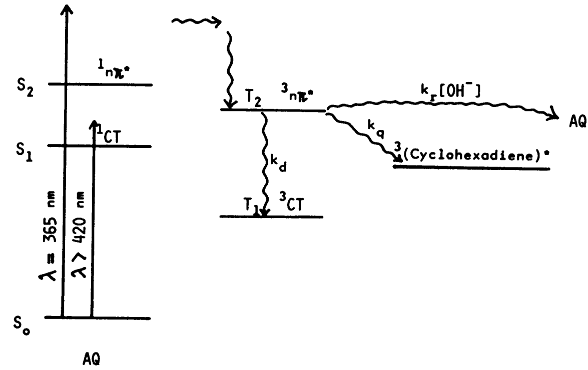


Fig. 3. Energy state diagram of **1** and the reaction scheme of the photoreduction by hydroxide ion.

droxide ion (1×10^{-3}—1×10^{-1} mol/dm^3). These results clearly indicate that the photoreduction of **1** does not proceed *via* the ^{1}CT level, but *via* the upper excited level. Moreover, the photoreduction was retarded by the addition of 1,3-cyclohexadiene as a triplet quencher[22] and a linear Stern-Volmer plot was obtained with the Stern-Volmer constant, $k_q\cdot\tau=20$ dm^3/mol (Fig. 2). Since the triplet level of 1,3-cyclohexadiene ($E_T=217$ kJ/mol) is higher than the $T_1(^3CT)$ of **1** and lower than the $T_2(^3n\pi^*)$,[7] 1,3-cyclohexadiene can be considered to quench the $T_2(^3n\pi^*)$ level of **1**. It is concluded that the photoreduction of **1** by an electron transfer from hydroxide ion proceeds *via* the $T_2(^3n\pi^*)$ level of **1**. These conclusions are schematized in Fig. 3. The quantum yield (Φ) for the production of the radical anion of **1** can be written as

$$\Phi = 2\Phi_T\,(365\text{ nm})\frac{k_r[OH^-]}{k_d+k_r[OH^-]}, \tag{6}$$

and the Stren-Volmer equation is

$$\Phi_0/\Phi = 1+\frac{k_q[CHD]}{k_d+k_r[OH^-]}, \tag{7}$$

where Φ_T(365 nm) denotes the triplet yield upon the irradiation of the light of $\lambda=365$ nm, k_i [i=r, d, and q] represents each rate constant in Fig. 3, and CHD refers to 1,3-cyclohexadiene. Equation 6 and the ratio of the slope to the intercept in the plot of Equation 1 indicate $k_d/k_r=5.0\times10^{-2}$ mol/dm^3. Equation 7 indicates that the Stern-Volmer cons tant in the plot of Fig. 2 is $k_q/(k_d+k_r[OH^-])=20$ dm^3/mol ($[OH^-]=0.1$ mol/dm^3). Supposing that the quenching rate constant k_q by 1,3-cyclohexadiene is diffusion controlled (10^{10} dm^3 mol^{-1} s^{-1}), the rate constants of $k_r=3.3\times10^9$ dm^3 mol^{-1} s^{-1} and $k_d=1.7\times10^8$ s^{-1} are obtained.[23] From the intercept in the linear plot of Fig. 1, Φ_T(365 nm) is found to be 1.0×10^{-2}.

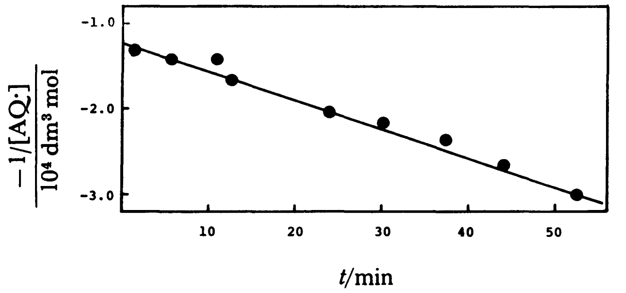


Fig. 4. Decay of the radical anion ($AQ^{\overline{\cdot}}$) of **2** generated in the photoreduction by hydroxide ion; [**2**]: 1.00×10^{-4} mol/dm^3 in 4 : 1 2-propanol–water mixture under nitrogen atmosphere; [OH$^-$]: 5.0×10^{-2} mol/dm^3; irradiation light: $\lambda>300$ nm.

Photoreduction of other Anthraquinones in Alkaline Aqueous Alcohol. Such ready photoreduction of **1** by hydroxide ion *via* the upper excited $T_2(^3n\pi^*)$ level prompted our investigation of other anthraquinones such as **2**, **3**, **4**, **5**, and **6**. The results are summarized in Table 2. **2** (1.00×10^{-4} mol/dm^3) and sodium hydroxide (5.00×10^{-2} mol/dm^3) in 4 : 1 2-propanol–water mixture was irradiated with the light of $\lambda>300$ nm under nitrogen atmosphere. The corresponding radical anion of **2** ($\lambda_{max}=389$, 482 nm) was also readily produced with the irradiation, having isosbestic points

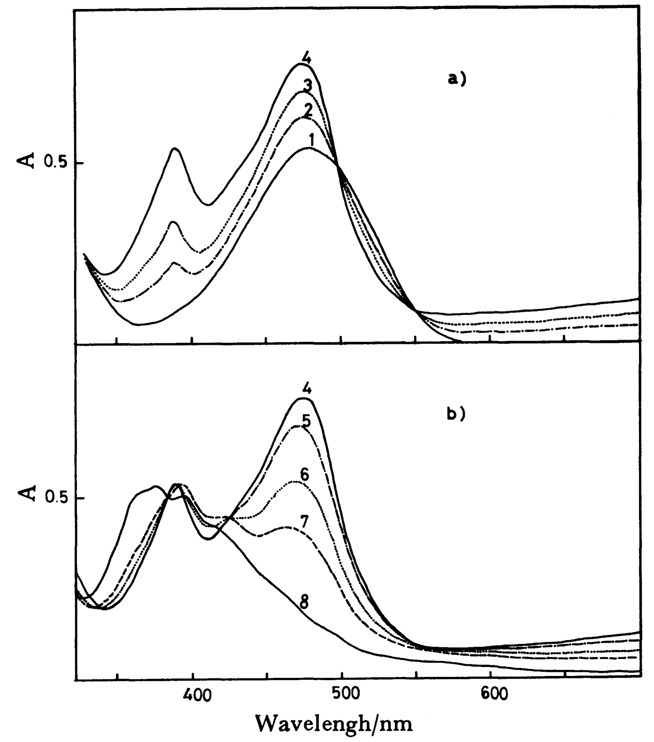


Fig. 5. Visible absorption spectra of the photoreduction of **2** by hydroxide ion in 1 : 1 methanol–water mixture under nitrogen atmosphere; [**2**]: 1.00×10^{-4} mol/dm^3; [OH$^-$]: 8.71×10^{-2} mol/dm^3; a) irradiation light: $\lambda>300$ nm; **1** (——): 0 min; **2** (-·-·-): 70 min; **3** (······): 210 min; **4** (——): 400 min; b) irradiation light: 280 nm$<\lambda<$400 nm; **5** (-·-·-): 8 min after **4**; **6** (······): 35 min after **4**; **7** (------): 60 min after **4**; **8** (——): 21 min irradiation without a glass filter after **7**.

Table 2. Photoreduction of aminoanthraquinones *via* the upper excited nπ^* triplet states

Anthraquiones	2-Piperidino (**1**)[a]	1-NH$_2$ (**2**)[b]	2-NH$_2$ (**3**)[b]	1-Piperidino (**4**)[a]	2-SO$_3$Na (**5**)[b]	1-SO$_3$Na (**6**)[b]
λ_{max}/nm	477,352	479,309	448,298	522,322	329	328
Φ365 nm/Φ313 nm	1.0	0.0	—	0.0	1.0	0.91
Φ>420 nm/Φ313 nm	0.0	0.0	—	0.0	—	—
Φ_T(313 nm)/%	1.0	0.5	—	—	100	9.4
Φ_T(365 nm)/%	1.0	0.0	—	0.0	100	8.5
$[k_d/k_r]$/mol dm^{-3}	5.0×10^{-2}	1.5×10^{-2}	—	—	—	7.6×10^{-2}
Product	$AQ^{\overline{\cdot}}$	$AQ^{\overline{\cdot}}$	—	AQ^{2-}	$AQ^{\overline{\cdot}}$	$AQ^{\overline{\cdot}}$
Type of reaction	E.T,[c]	E.T.	—	H.A.[d], E.T.	H.A., E.T.	E.T.

a) In 4 : 1 2-propanol–water. b) In 1 : 1 methanol–water. c) E.T.: Electron transfer. d) H.A.: Hydrogen abstraction.

at $\lambda=320$, 510, 551 nm. Introduction of air to the irradiated reaction mixture also caused rapid disappearance of the radical anion of **2** and **2** was recovered unchanged. However the radical anion of **2** was unstable in 2-propanol–water and gradually disappeared with a second order decay constant of $k=2.8$ dm^3 mol^{-1} s^{-1} as shown in Fig. 4. This may be due to the following second order decay process of dismutation (Eq. 8). Of

$$\mathrm{AQ}^{\overline{\cdot}} + \mathrm{AQ}^{\overline{\cdot}} \xrightarrow{k} \mathrm{AQ}^{2-} + \mathrm{AQ} \qquad (8)$$

the solvent compositions examined (aqueous solutions of methanol, ethanol, and 2-propanol), 1 : 1 methanol–water mixture was found to stabilize the radical anion for several hours. The visible absorption spectra of the reaction system in 1 : 1 methanol–water mixture are shown in Fig. 5. The corresponding radical anion of **2** alone was produced during the first 400 minutes of irradiation through a soda glass filter which only transmitted radiation of $\lambda>300$ nm (Fig. 5(a)). On prolonged irradiation the absorption intensities at $\lambda=389$ nm, 475 nm, and >650 nm gradually decreased and then, upon the irradiation through UVD-33S glass filter which transmitted radiation of 280 nm$<\lambda<$400 nm, the radical anion disappeared rapidly with the production of the dianion of **2** ($\lambda_{\max}=395$ nm) having new isosbestic points at $\lambda=388$, 392, and 425 nm (Fig. 5(b)). Further irradiation of the reaction system by a 500 W high pressure mercury lamp without a glass filter also caused a disappearance of the dianion with an increment of the absorption intensity near 370 nm which might be characterized by the production of aminoanthrone derivative[8] (line(8) in Fig. 5(b)). As summarized in Eq. 9, the photochemical reduction of **2** proceeded *via* three steps. At an early stage of the photoreaction the radical anion of **2** is produced from **2** (Process I; Fig. 5(a)) and after the complete conversion of **2** into the radical anion, the dianion of **2** is produced from the radical anion (Process II; Fig. 5(b)). Finally, an end product which may be aminoanthrone is produced from the dianion of **2** (Process III). The

$$\mathrm{AQ} \xrightarrow{h\nu} \mathrm{AQ}^{\overline{\cdot}} \xrightarrow{h\nu} \mathrm{AQ}^{2-} \xrightarrow{h\nu} \text{aminoanthrone} \qquad (9)$$

spectra in Fig. 5(a) indicate that the absorption coefficients of the radical anion of **2** at the $\lambda_{\max}$ of 389 and 475 nm in 1 : 1 methanol–water mixture are 53200 and 76000 dm^2/mol respectively. As is shown in Fig. 6, a plot of the reciprocal of the quantum yield of the photoreduction of process I versus the reciprocal of the concentration of hydroxide ion added to the reaction system gave a fairly straight line. The ratio of the slope to the intercept in the plot was found to be 1.5×10^{-2} mol/dm^3. Hence the radical anion of **2** is also supposed to be produced by a direct electron transfer from hydroxide ion to the excited **2** in a manner similar to the case of **1**. As mentioned above, irradiation with light of 313 nm was effective for the photoreduction of **2**. On the other hand, neither visible light irradiation (>420 nm), which excited **2** to ^{1}CT level, nor irradiation with light of 365 nm which excited **2** to $^1n\pi^*$ level induced photoreduction of **2**. Moreover the fluorescence intensity of **2** was hardly affected by hydroxide ion; the Stern-Volmer constant of the fluorescence quenching by hydroxide ion was smaller than 4 dm^3/mol. These results clearly indicate that the photoreduction of **2** by an electron transfer from hydroxide ion proceeds through the upper excited state which can be populated by 313 nm excitation. Though the quenching experiments by appropriate triplet quenchers could not be carried out because of their insolubilities in 1 : 1 methanol–water mixture, by analogy with the case of **1**, it is well supposed that the upper excited triplet $n\pi^*$ (T_2) level of **2** is responsible for the photoreduction. The value of the intercept in the plot of Fig. 6 indicates the triplet yield upon irradiation of the light of 313 nm, Φ_T(313 nm), to be 0.5×10^{-2}. A mixture of **3** (1.0×10^{-4} mol/dm^3) and sodium hydroxide (5.0×10^{-2} mol/dm^3) in 1 : 1 methanol–water mixture was irradiated with light of $\lambda=313$ nm, 365 nm and $\lambda>420$ nm under nitrogen atmosphere, respectively. Contrary to our expectation, in every case **3** did not react at all, even with prolonged irradiation at 313 nm. This unexpected result seems very interesting and will be discussed later.

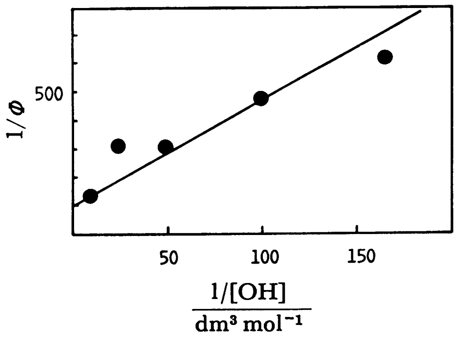


Fig. 6. Effect of the concentration of hydroxide ion on the quantum yield of the photoreduction of **2**; [**2**]: 1.00×10^{-4} mol/dm^3 in 1 : 1 methanol–water mixture under nitrogen atmosphere; irradiation light: $\lambda=313$ nm.

The photoreduction of **4** (1.0×10^{-4} mol/dm^3) in 4 : 1 2-propanol–water mixture in the presence of hydroxide ion (5.0×10^{-2} mol/dm^3) gave its dianion ($\lambda_{\max}=408$ and 493 nm) alone. Both quantum yields in the presence and the absence of hydroxide ion were almost the same to each other; in the latter case 1-piperidino-9,10-anthracenediol was produced. These results were in accord with those reported by Davies *et al.*[4] Since the production of 1-piperidino-9,10-anthracenediol from **4** at neutral conditions is believed to be due to hydrogen abstraction from 2-propanol, the dianion formation at alkaline conditions is also considered to be caused by hydrogen abstraction by the excited **4** in its triplet $n\pi^*$ state, followed by a deprotonation (Eqs. 2 and 3) in contrast to the reactions of **1** and **2**. The dianion of **4**, however, was produced effectively even in alkaline aqueous acetonitrile solution. This indicates that the electron transfer mechanism from hydroxide ion was also operating in the photoreduction of **4** along with the hydrogen abstraction mechanism. The dependency of the photoreduction of **4** on the wavelength of irradiation was similar to that of **2**: The reaction was only induced with irradiation of light of $\lambda=313$ nm and **4** did not react at all upon irradiation of the light of $\lambda=365$ nm and λ>420 nm, respectively. Hence the upper excited triplet nπ^* state (T_2), which can be populated by 313 nm excitation is probably responsible for the photoreduction of **4**. Compound **5** is a good sensitizer for the photosensitized oxidation and its photochemistry has been most intensively studied.[2] The triplet (^{3}nπ^*) yield of **5** is known to be unity and the quantum yield for the formation of 9,10-dihydroxy-2-anthracenesulfonate from **5** by a hydrogen abstraction is also unity at neutral condition.[9] In alkaline solution or in the presence of an appropriate electron donor, photoreduction by an electron transfer mechanism is also significant.[10] Irradiation of **5** (1.0×10^{-4} mol/dm^3) in the presence of sodium hydroxide (5.0×10^{-2} mol/dm^3) in 1 : 1 methanol–water mixture with the light of λ>300 nm induced an effective formation of the radical anion of **5** ($\lambda_{\max}$=400 and 502 nm) as a sole end product. The quantum yield for the formation of the radical anion of **5** was not affected by the concentration of hydroxide ion (0.1—6×10^{-3} mol/dm^3) and by the wavelength of irradiation (λ=313 and 365 nm). Compound **6** has been classified as a poor sensitizer.[11] When **6** (1.0×10^{-4} mol/dm^3) and sodium hydroxide (5.0×10^{-2} mol/dm^3) in 1 : 1 methanol–water mixture was irradiated with light of λ>300 nm, the radical anion of **6** ($\lambda_{\max}$=400 and 497 nm) was produced at an early stage of the reaction. The radical anion produced was stable in the dark for several hours in 1 : 1 methanol–water. On prolonged irradiation, the dianion of **6** was further produced from the radical anion after the complete conversion of **6** into the radical anion. The spectral changes were similar to those of the reaction of **2**. The absorption coefficient of the radical anion of **6** at 497 nm in 1 : 1 methanol–water was estimated to be 45100 dm^2/mol. Studzinskii *et al.* reported that the quantum yield for the production of the radical anion was independent of the wavelength of irradiation in alkaline aqueous alcohols.[12] However, careful investigation revealed a slight wavelength dependency; Φ365 nm/Φ313 nm=0.91±0.05. A plot of the reciprocal of the quantum yield versus the reciprocal of the concentration of hydroxide ion added to the reaction system gave a fairly straight line with a value of 7.6×10^{-2} mol/dm^3 for the ratio of the slope to the intercept. This suggests that the radical anion formation in alkaline aqueous methanol is mainly induced by an electron transfer from hydroxide ion. The values of the intercept in the plot also indicate the triplet (^{3}nπ^*) yield upon irradiation with light of 313 and 365 nm, Φ_T(313 nm) and Φ_T(365 nm) to be 9.4×10^{-2} and 8.5×10^{-2}, respectively. It is easily understood that the low reactivity of **6** (classified as a poor sensitizer) is mainly ascribable to such a low intersystem-crossing efficiency of ^{1}nπ^* states.

Discussion

The energy state diagram of anthraquinone derivatives (**1**—**4**), having an electron-donating group, is depicted in Fig. 7.[2,13] The first absorption band in the visible region for each derivative corresponds to the lowest excited singlet state (S_1 : ^{1}CT) and the absorption band near λ=300 nm to the $\pi\pi^*$ singlet state overlying the nπ^* state. On the other hand the energy state diagram of **5** and **6** have no intramolecular CT level.[2,13] In the case of anthraquinone the nπ^* (^{1}U) and the higher $\pi\pi^*$ (^1L_b) levels have the energy of 24000 and 30000 cm^{-1}, respectively.[14] Taking account of both mechanisms of electron transfer from hydroxide ion and hydrogen abstraction from the solvent *via* the nπ^* level, the quantum yield of the photoreduction is given by Eq. 10.

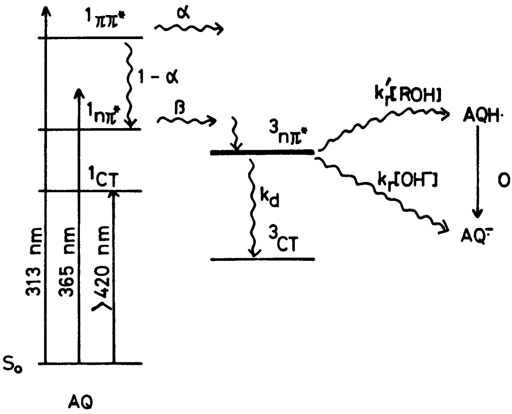


Fig. 7. Energy state diagram of the anthraquinone derivatives having electron donating substituents.

$$\Phi \propto \Phi_T\left(\frac{k_r[\mathrm{OH^-}]+k_r'[\mathrm{ROH}]}{k_d+k_r[\mathrm{OH^-}]+k_r'[\mathrm{ROH}]}\right), \tag{10}$$

where Φ_T denotes the nπ^* triplet yield upon the irradiation of the light of appropriate wavelength, k_d the rate constant of the deactivation of the ^{3}nπ^*, k_r the rate constant of electron transfer, and k_r' the rate constant of hydrogen abstraction. From Fig. 7 the triplet yields upon the irradiation of the light of λ=313 nm are expressed by Eqs. 11 and 12, respectively,

$$\Phi_T\,(313\text{ nm}) = \alpha + (1-\alpha)\beta, \tag{11}$$

$$\Phi_T\,(365\text{ nm}) = \beta, \tag{12}$$

where α and β denote the apparent individual intersystem crossing efficiencies of the higher $^1\pi\pi^*$ and ^{1}nπ^* states respectively. By solving equations 11 and 12 the values of α and β can be estimated from the triplet yields summarized in Table 2. The values of α and β for **2** are 5×10^{-3} and zero, while those for **6** are 9.8×10^{-3} and 8.5×10^{-2}. High efficiency of the intersystem crossing of ^{1}nπ^* $\rightsquigarrow$ ^{3}nπ^* of **5** (β=1.0) renders it impossible to estimate the value of the intersystem crossing, α, from the higher level. The absence of the wavelength dependency between 313 and 365 nm in the case of **1** with low Φ_T value (Φ_T=1.0%) apparently indicates the absence of the intersystem crossing from the higher $^1\pi\pi^*$ state. However, as indicated in Table 2, the second absorption band ($\lambda_{\max}$=352 nm) of **1** is largely red-shifted as compared with other derivatives. Hence the respective irradiation of the light of 313 and 365 nm may excite **1** to the same level of the higher $^1\pi\pi^*$ overlying the ^{1}nπ^*. More precise investigation on the wavelength dependency of the photoreduction of **1** may be required. The value of k_d of **1** indicates the lifetime of the T_2(^{3}nπ^*) state to be 5.9×10^{-9} s in 4 : 1 2-propanol–water mixture. The lifetime of the T_2(^{3}nπ^*)

of **2** in 1 : 1 methanol–water is also estimated to be longer than 6.7×10^{-9} s from the value of $k_d/k_r=1.5\times10^{-2}$ mol/dm^3, supposing k_r to be diffusion controlled (10^{10} dm^3/mol s) as a maximum limit. These values are longer as compared with those of T_2 of anthracenes (2—5×10^{-10} s),[15] naphthalene (1.7×10^{-11} s).[16] In the study of the photoreduction of 1-dimethylaminoanthraquinone by hydrogen abstraction, Davies *et al.* pointed out that anthraquinone derivatives might have a lifetime long enough to photoreact in their upper excited $T_2(^3n\pi^*)$ level.[17] 1-Amino-2,4-dibromoanthraquinone is also known to have a long-lived $T_2(^3n\pi^*)$ state in benzene.[18] These long lifetimes of $T_2(^3n\pi^*)$ in spite of upper excited levels are considered to be characteristic of aminoanthraquinones. The rate of internal conversion from T_2 with 0 vibrational level to T_1 with n isoenergetic vibrational levels, $k_{ic}(T_2\rightarrow T_1)$, which nearly equals the rate of deactivation, k_d, is theoretically given by Eq. 13.[19]

$$k_{ic}(T_2\rightarrow T_1)\propto\langle\psi_{T_2}|\boldsymbol{J}|\psi_{T_1}\rangle^2\cdot|\textstyle\sum_n\langle\chi_{T_2 0}|\chi_{T_1 n}\rangle|^2, \qquad (13)$$

where ψ_{T_2} and ψ_{T_1} are the electronic wave functions of T_2 and T_1, $\boldsymbol{J}$ is the nuclear kinetic energy operator, and $x_{T_2 0}$ and $x_{T_1 n}$ are the nuclear wave functions of the corresponding states. The orthogonality between the $T_2(^3n\pi^*)$ and $T_1(^3CT)$ states can cause a poor electronic term in Eq. 13. The second term of Eq. 13 is the well known Franck-Condon factor and is largely affected by the energy gap between the two states.[20] Since the $T_2(^3n\pi^*)$ levels of aminoanthraquinones have been considered to have similar energies to that of the $^3n\pi^*$ of anthraquinone (259 kJ/mol)[2] and the $T_1(^3CT)$ levels were reported to lie in the range of 236—201 kJ/mol (**3**), 197—176 kJ/mol (**1** and **2**), and <123 kJ/mol (**4**),[7] the energy gaps between the T_2 and T_1 of these aminoanthraquinones are estimated to have larger values than 62 kJ/mol (**1** and **2**) and 136 kJ/mol (**4**), while that of **3** is in the range of 23—58 kJ/mol. These rather large energy gaps (except that of **3**) may also cause a poor Franck-Condon factor resulting in the long life of the $T_2(^3n\pi^*)$ levels. The lifetime of the $T_2(^3n\pi^*)$ of each derivative may be in the order of **4**>**1**≈**2**>**3** in accord with the order of the energy gap. The lifetime of the $T_2(^3n\pi^*)$ of **3** may be too short for any reactions to be observed. While the $T_2(^3n\pi^*)$ of **1** and **2** may have moderate lifetimes to permit only rapid process of electron transfer to compete, the $T_2(^3n\pi^*)$ of **4** may have sufficient long one even for rather slow reaction of hydrogen abstraction[21] to proceed.

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21) The rate of hydrogen abstraction from alcohols by the excited antraquinone in its $^3n\pi^*$ state has been reported to be in the range of *ca.* 10^6—10^7 dm^3/mol s.[2]

22) The fluorescence of **1** in 4 : 1 2-propanol–water mixture was not quenched by 1,3-cyclohexadiene (1×10^{-3}—0.5 mol/dm^3).

23) The observed rate constant ($k_r=3.3\times10^9$ dm^3 mol^{-1} s^{-1}) of the electron transfer from hydroxide ion to **1** coincides reasonably with the calculated value (1.2×10^9 dm^3 mol^{-1} s^{-1}) with the aid of the Rehm and Weller's equation when the oxidation and reduction potentials of hydroxide ion and **1** are taken to be 2.0 and −0.80 V *vs.* NHE, respectively. (D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).