

Photoreduction of Aminoanthraquinones by an Electron Transfer *via* the Upper Excited $n\pi^*$ Triplet State

Haruo INOUE,* Kiyoshi KAWABE, Noboru KITAMURA, and Mitsuhiro HIDA

Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University,
Fukazawa, Setagaya-ku, Tokyo 158

(Received July 8, 1981)

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 $n\pi^*$ triplet state. Kinetic studies indicated that the rate of deactivation from the $T_2(^3n\pi^*)$ level of **1** is unusually slow ($k_d = 1.7 \times 10^8 \text{ s}^{-1}$). 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 $>420 \text{ nm}$ 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 $n\pi^*$ 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 $n\pi^*$ 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 $\lambda = 365 \text{ nm}$.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 $n\pi^*$ level of other anthraquinones (1-aminoanthraquinone (**2**), 2-aminoanthraquinone (**3**), 1-piperidinoanthraquinone (**4**) and we observed dramatic wavelength dependencies (313 nm, 365 nm, and $>420 \text{ nm}$ 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 $\text{C}_{19}\text{H}_{17}\text{N}$:

NO_2 : C, 78.31%; H, 5.89%; N, 4.80%. 1-Aminoanthraquinone (**2**) (Sumitomo Chemical Co.) was purified by column chromatography ($\text{Al}_2\text{O}_3/\text{toluene}$) and repeated recrystallizations from benzene; mp 252–253 °C; Found: C, 75.31%; H, 3.86%; N, 6.44%. Calcd for $\text{C}_{14}\text{H}_9\text{NO}_2$: C, 75.32%; H, 4.06%; N, 6.27%. 2-Aminoanthraquinone (**3**) (Sumitomo Chemical Co.) was purified by the procedures recommended by Maki⁵⁾ using 82% aqueous sulfuric acid; mp 302 °C; Found: C, 75.24%; H, 3.78%; N, 6.02%. Calcd for $\text{C}_{14}\text{H}_9\text{NO}_2$: 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 $\text{C}_{19}\text{H}_{17}\text{NO}$: 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/dm³) Na_2CO_3 (1.0 g/dm³) (optical length: 1 cm) for the irradiation by monochromatic light of 313 nm; Toshiba UV-DIA glass filter and naphthalene ($5.0 \times 10^{-2} \text{ mol/dm}^3$) 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

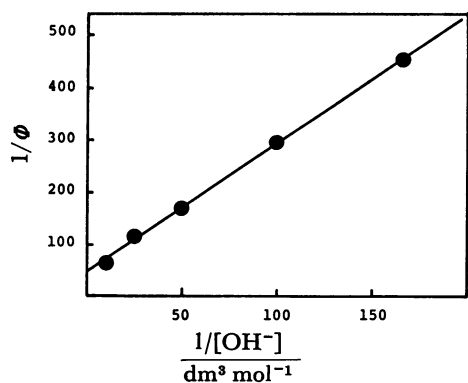
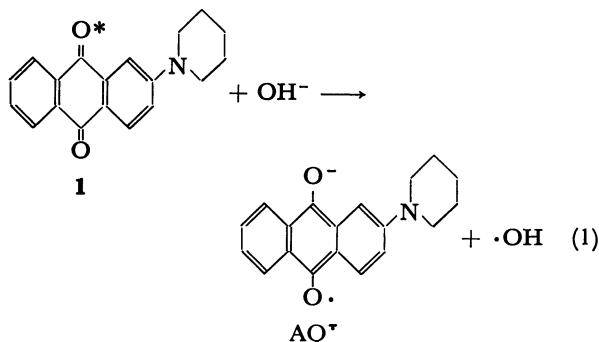


Fig. 1. Effect of the concentration of hydroxide ion on the quantum yield of the photoreduction of **1**; [**1**]: $1.00 \times 10^{-4} \text{ mol/dm}^3$ in 4 : 1 2-propanol–water mixture under nitrogen atmosphere; irradiation light: $\lambda = 365 \text{ nm}$.

Aqueous 2-Propanol. When **1** ($1.00 \times 10^{-4} \text{ mol/dm}^3$) and sodium hydroxide ($5.00 \times 10^{-2} \text{ mol/dm}^3$) in 4 : 1 2-propanol–water mixture was irradiated with monochromatic light of $\lambda = 365 \text{ nm}$ under nitrogen atmosphere, the absorption bands at $\lambda = 402, 476$, and $>650 \text{ nm}$, 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 $[\text{NaOH}] = 5 \times 10^{-2} \text{ mol/dm}^3$). 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).

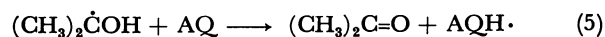
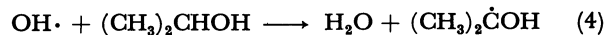


The radical anion of **1** was stable in the reaction system for more than 1 d. Hence it was supposed that most of the hydroxyl radical, a powerful oxidizing agent,

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

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).



The radical anion of **1** is also produced by a deprotonation of the semiquinone radical ($\text{AQH}\cdot$) 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 $\lambda > 420 \text{ nm}$ 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 $\lambda > 420 \text{ nm}$, and the fluorescence intensity of **1** was not affected by the presence of hy-

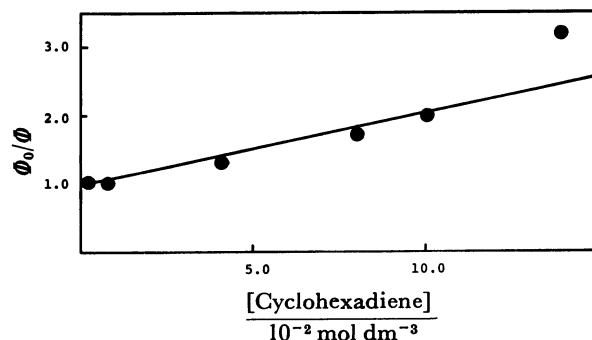


Fig. 2. Stern-Volmer plot for the quenching effect of 1,3-cyclohexadiene on the photoreduction of **1**; [**1**]: $1.00 \times 10^{-4} \text{ mol/dm}^3$ in 4 : 1 2-propanol–water mixture under nitrogen atmosphere; $[\text{OH}^-]$: 0.1 mol/dm^3 ; irradiation light: $\lambda = 365 \text{ nm}$.

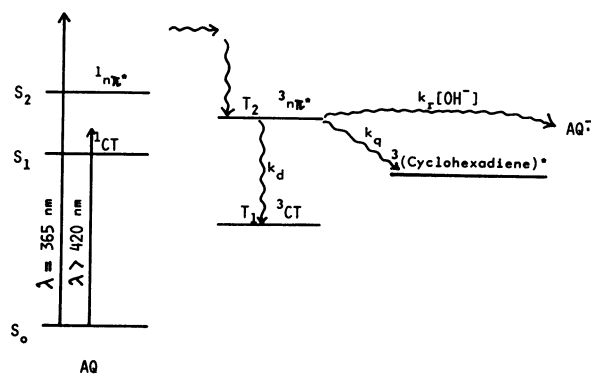


Fig. 3. Energy state diagram of **1** and the reaction scheme of the photoreduction by hydroxide ion.

dioxide ion (1×10^{-3} – 1×10^{-1} mol/dm³). These results clearly indicate that the photoreduction of **1** does not proceed *via* the ¹CT level, but *via* the upper excited level. Moreover, the photoreduction was retarded by the addition of 1,3-cyclohexadiene as a triplet quencher²²⁾ and a linear Stern-Volmer plot was obtained with the Stern-Volmer constant, $k_q \cdot \tau = 20$ dm³/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

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

and the Stern-Volmer equation is

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

where $\Phi_T(365 \text{ nm})$ denotes the triplet yield upon the irradiation of the light of $\lambda = 365 \text{ nm}$, 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 $k_d/k_r = 5.0 \times 10^{-2}$ mol/dm³. Equation 7 indicates that the Stern-Volmer constant in the plot of Fig. 2 is $k_q/(k_d + k_r[\text{OH}^-]) = 20$ dm³/mol ($[\text{OH}^-] = 0.1$ mol/dm³). Supposing that the quenching rate constant k_q by 1,3-cyclohexadiene is diffusion controlled (10^{10} dm³ mol⁻¹ s⁻¹), the rate constants of $k_r = 3.3 \times 10^9$ dm³ mol⁻¹ s⁻¹

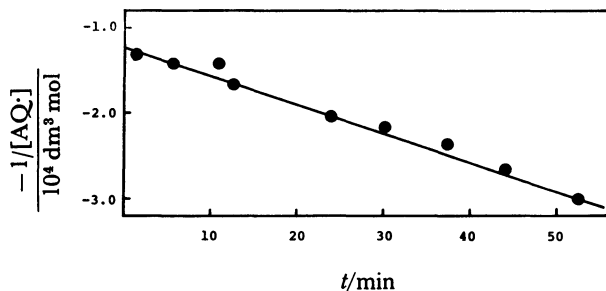


Fig. 4. Decay of the radical anion ($\text{AQ}^\bullet$) of **2** generated in the photoreduction by hydroxide ion; [**2**]: 1.00×10^{-4} mol/dm³ in 4 : 1 2-propanol–water mixture under nitrogen atmosphere; $[\text{OH}^-]$: 5.0×10^{-2} mol/dm³; irradiation light: $\lambda > 300 \text{ nm}$.

and $k_d = 1.7 \times 10^8 \text{ s}^{-1}$ are obtained.²³⁾ From the intercept in the linear plot of Fig. 1, $\Phi_T(365 \text{ nm})$ is found to be 1.0×10^{-2} .

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/dm³) and sodium hydroxide (5.00×10^{-2} mol/dm³) in 4 : 1 2-propanol–water mixture was irradiated with the light of $\lambda > 300 \text{ nm}$ under nitrogen atmosphere. The corresponding radical anion of **2** ($\lambda_{\text{max}} = 389, 482 \text{ nm}$) was also readily produced with the irradiation, having isosbestic points

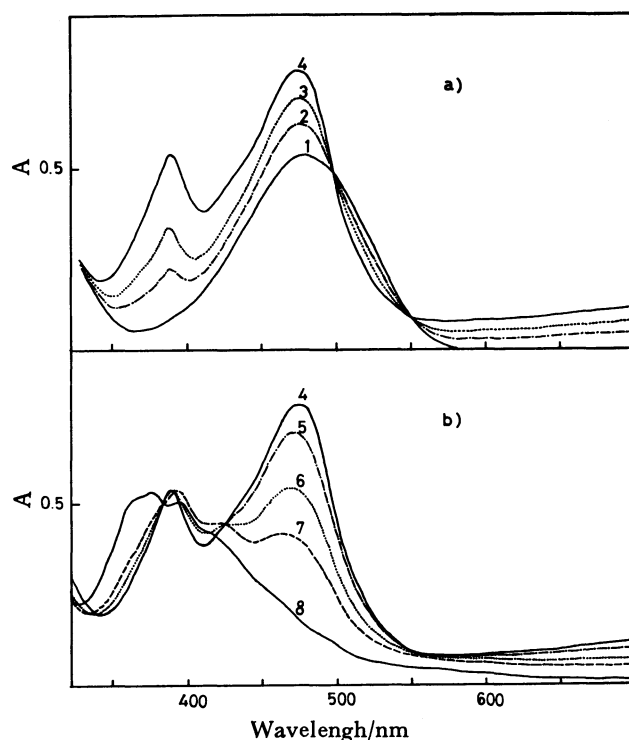


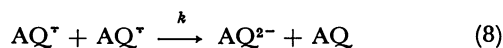
Fig. 5. Visible absorption spectra of the photoreduction of **2** by hydroxide ion in 1 : 1 methanol–water mixture under nitrogen atmosphere; [**2**]: 1.00×10^{-4} mol/dm³; $[\text{OH}^-]$: 8.71×10^{-2} mol/dm³; a) irradiation light: $\lambda > 300 \text{ nm}$; **1** (—): 0 min; **2** (---): 70 min; **3** (.....): 210 min; **4** (—): 400 min; b) irradiation light: $280 \text{ nm} < \lambda < 400 \text{ nm}$; **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 $n\pi^*$ TRIPLET STATES

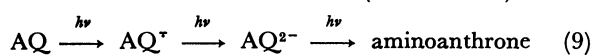
Anthraquinones	2-Piperidino (1) ^{a)}	1-NH ₂ (2) ^{b)}	2-NH ₂ (3) ^{b)}	1-Piperidino (4) ^{a)}	2-SO ₃ Na (5) ^{b)}	1-SO ₃ Na (6) ^{b)}
$\lambda_{\text{max}}/\text{nm}$	477,352	479,309	448,298	522,322	329	328
$\Phi_{365 \text{ nm}}/\Phi_{313 \text{ nm}}$	1.0	0.0	—	0.0	1.0	0.91
$\Phi_{>420 \text{ nm}}/\Phi_{313 \text{ nm}}$	0.0	0.0	—	0.0	—	—
$\Phi_T(313 \text{ nm})/\%$	1.0	0.5	—	—	100	9.4
$\Phi_T(365 \text{ nm})/\%$	1.0	0.0	—	0.0	100	8.5
$[k_d/k_r]/\text{mol dm}^{-3}$	5.0×10^{-2}	1.5×10^{-2}	—	—	—	7.6×10^{-2}
Product	$\text{AQ}^\bullet$	$\text{AQ}^\bullet$	—	AQ^{2-}	$\text{AQ}^\bullet$	$\text{AQ}^\bullet$
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 $k=2.8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ as shown in Fig. 4. This may be due to the following second order decay process of dismutation (Eq. 8). Of



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 $280 \text{ nm} < \lambda < 400$ nm, the radical anion disappeared rapidly with the production of the dianion of **2** ($\lambda_{\text{max}}=395$ 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 derivative⁹⁾ (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



spectra in Fig. 5(a) indicate that the absorption coefficients of the radical anion of **2** at the λ_{max} of 389 and

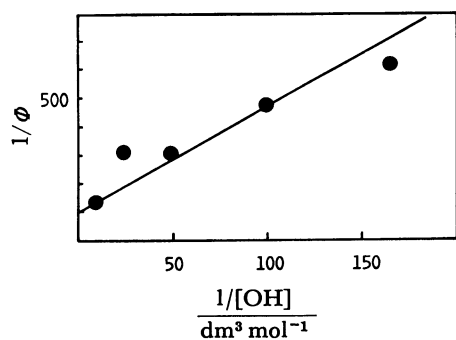


Fig. 6. Effect of the concentration of hydroxide ion on the quantum yield of the photoreduction of **2**; [**2**]: $1.00 \times 10^{-4} \text{ mol/dm}^3$ in 1 : 1 methanol–water mixture under nitrogen atmosphere; irradiation light: $\lambda=313$ nm.

475 nm in 1 : 1 methanol–water mixture are 53200 and $76000 \text{ dm}^2/\text{mol}$ 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 $1.5 \times 10^{-2} \text{ mol/dm}^3$. 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 ^1CT 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 $4 \text{ dm}^3/\text{mol}$. 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, $\Phi_T(313 \text{ nm})$, to be 0.5×10^{-2} . A mixture of **3** ($1.0 \times 10^{-4} \text{ mol/dm}^3$) and sodium hydroxide ($5.0 \times 10^{-2} \text{ mol/dm}^3$) 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.

The photoreduction of **4** ($1.0 \times 10^{-4} \text{ mol/dm}^3$) in 4 : 1 2-propanol–water mixture in the presence of hydroxide ion ($5.0 \times 10^{-2} \text{ mol/dm}^3$) gave its dianion ($\lambda_{\text{max}}=408$ 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 $\lambda > 420$ nm, respectively. Hence the upper excited triplet $n\pi^*$ 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 photo-sensitized oxidation and its photochemistry has been most intensively studied.²⁾ The triplet ($^3n\pi^*$) 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/dm³) in the presence of sodium hydroxide (5.0×10^{-2} mol/dm³) in 1 : 1 methanol–water mixture with the light of $\lambda > 300$ 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/dm³) and by the wavelength of irradiation ($\lambda = 313$ and 365 nm). Compound **6** has been classified as a poor sensitizer.¹¹⁾ When **6** (1.0×10^{-4} mol/dm³) and sodium hydroxide (5.0×10^{-2} mol/dm³) in 1 : 1 methanol–water mixture was irradiated with light of $\lambda > 300$ 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 dm²/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; $\Phi_{365 \text{ nm}}/\Phi_{313 \text{ nm}} = 0.91 \pm 0.05$. 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/dm³ 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 ($^3n\pi^*$) yield upon irradiation with light of 313 and 365 nm, $\Phi_T(313 \text{ nm})$ and $\Phi_T(365 \text{ nm})$ 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 $^1n\pi^*$ 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 ($S_1 : ^1CT$) and the absorption band near $\lambda = 300$ nm to the $\pi\pi^*$ singlet state overlying

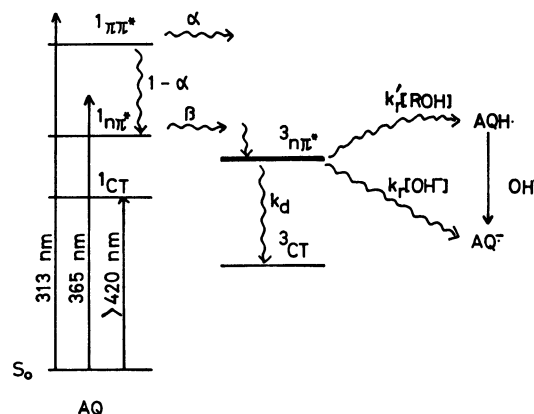


Fig. 7. Energy state diagram of the anthraquinone derivatives having electron donating substituents.

the $n\pi^*$ 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 $n\pi^*$ (1U) 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 $n\pi^*$ level, the quantum yield of the photoreduction is given by Eq. 10.

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

where Φ_T denotes the $n\pi^*$ triplet yield upon the irradiation of the light of appropriate wavelength, k_d the rate constant of the deactivation of the $^3n\pi^*$, 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 $\lambda = 313$ nm are expressed by Eqs. 11 and 12, respectively,

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

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

where α and β denote the apparent individual intersystem crossing efficiencies of the higher $^1\pi\pi^*$ and $^1n\pi^*$ 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 $^1n\pi^* \rightsquigarrow ^3n\pi^*$ of **5** ($\beta = 1.0$) 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 ($\Phi_T = 1.0\%$) 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 $^1n\pi^*$. 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 $T_2(^3n\pi^*)$ state to be 5.9×10^{-9} s in 4 : 1 2-propanol–water mixture. The lifetime of the $T_2(^3n\pi^*)$

of **2** in 1 : 1 methanol–water is also estimated to be longer than 6.7×10^{-9} s from the value of $k_d/k_r = 1.5 \times 10^{-2}$ mol/dm³, supposing k_r to be diffusion controlled (10^{10} dm³/mol s) as a maximum limit. These values are longer as compared with those of T₂ of anthracenes ($2-5 \times 10^{-10}$ 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 T₂(³nπ*) level.¹⁷⁾ 1-Amino-2,4-dibromoanthraquinone is also known to have a long-lived T₂(³nπ*) state in benzene.¹⁸⁾ These long lifetimes of T₂(³nπ*) in spite of upper excited levels are considered to be characteristic of aminoanthraquinones. The rate of internal conversion from T₂ with 0 vibrational level to T₁ 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⁾

$$k_{ic}(T_2 \rightarrow T_1) \propto \langle \phi_{T_1} | J | \phi_{T_2} \rangle^2 \cdot |\sum_n \langle \chi_{T_{10}} | \chi_{T_{1n}} \rangle|^2, \quad (13)$$

where ϕ_{T_2} and ϕ_{T_1} are the electronic wave functions of T₂ and T₁, *J* is the nuclear kinetic energy operator, and $\chi_{T_{20}}$ and $\chi_{T_{1n}}$ are the nuclear wave functions of the corresponding states. The orthogonality between the T₂(³nπ*) and T₁(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 T₂(³nπ*) levels of aminoanthraquinones have been considered to have similar energies to that of the ³nπ* of anthraquinone (259 kJ/mol)²⁾ and the T₁(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 T₂ and T₁ 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 T₂(³nπ*) levels. The lifetime of the T₂(³nπ*) 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 T₂(³nπ*) of **3** may be too short for any reactions to be observed. While the T₂(³nπ*) of **1** and **2** may have moderate lifetimes to permit only rapid process of electron transfer to compete, the T₂(³nπ*) of **4** may have sufficient long one even for rather slow reaction of hydrogen abstraction²¹⁾ to proceed.

References

- 1) R. A. Morton and W. T. Earlsman, *J. Chem. Soc.*, **1941**, 159; Z. Yoshida and F. Takabayashi, *Tetrahedron*, **24**, 933 (1968); H. Inoue, T. Hoshi, J. Yoshino, and Y. Tanizaki, *Bull. Chem. Soc. Jpn.*, **45**, 1018 (1972); **46**, 380 (1973).
- 2) H. Inoue and M. Hida, *Yuki Gosei Kagaku Kyokai Shi*, **32**, 348 (1974) and references cited therein. D. Schulte-Frohlinde and C. V. Sontag, *Z. Phys. Chem.*, **44**, 314 (1965), J. M. Bruce, *Quart. Rev.*, **21**, 405 (1967).
- 3) H. Inoue, T. D. Tuong, M. Hida, and T. Murata, *Chem. Commun.*, **1971**, 1347; H. Inoue, T. D. Tuong, M. Hida, and T. Murata, *Bull. Chem. Soc. Jpn.*, **46**, 1759 (1973); H. Inoue, K. Nakamura, S. Kato, and M. Hida, *ibid.*, **48**, 2872 (1975); H. Inoue and M. Hida, *ibid.*, **51**, 1793 (1978); H. Inoue, T. Shinoda, and M. Hida, *ibid.*, **53**, 154 (1980).
- 4) G. O. Phillips, A. K. Davies, and J. F. Mckeller, *Chem. Commun.*, **1970**, 519; A. K. Davies, J. F. Mckeller, and G. O. Phillips, *Proc. R. Soc. London, Ser. A*, **323**, 69 (1971).
- 5) Maki, *J. Soc. Chem. Ind. Jpn.*, **36**, 44 (1933).
- 6) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London*, **1956**, 518.
- 7) B. E. Hulme, E. J. Land, and G. O. Phillips, *J. Chem. Soc., Faraday Trans. 1*, **68**, 2003 (1972).
- 8) G. S. Egerton, N. E. N. Assaad, and N. D. Uffindell, *J. Soc. Dyers and Colourists*, **1967**, 409.
- 9) C. F. Wells, *Trans. Faraday Soc.*, **57**, 1703, 1719 (1961); H. R. Cooper and B. M. Talbot, *ibid.*, **61**, 506 (1965); G. O. Phillips, P. Barber, and T. Richards, *J. Chem. Soc.*, **1964**, 3443; C. F. Wells, *ibid.*, **1962**, 3100; F. Wilkinson *J. Phys. Chem.*, **66**, 2569 (1962).
- 10) G. Eigenmann, *Helv. Chim. Acta*, **46**, 864 (1963); V. A. Kuzmin and A. K. Chibisov, *J. Chem. Soc., D*, **1971**, 1559; V. A. Kuzmin, A. K. Chibisov, and A. V. Karyakin, *Int. J. Chem. Kinet.*, **4**, 639 (1972).
- 11) F. Wilkinson, *J. Phys. Chem.*, **66**, 2569 (1962), G. O. Phillips, J. C. Arthur, Jr., *Text. Res. J.*, **34**, 497, 572 (1964).
- 12) O. P. Studzinskii, N. I. Rtischev, A. V. Devekki, G. V. Fomin, L. M. Gurdzhinyan, and A. V. El'stov, *Zh. Org. Khim.*, **8**, 2130 (1972).
- 13) H. H. Dearman and A. Chan, *J. Chem. Phys.*, **44**, 416 (1966).
- 14) L. W. Sidman, *J. Am. Chem. Soc.*, **78**, 4567 (1956).
- 15) R. S. H. Liu and J. R. Edman, *J. Am. Chem. Soc.*, **91**, 1492 (1969); R. O. Cambell and R. S. H. Liu, *ibid.*, **95**, 6560 (1973).
- 16) C. C. Ladwig and R. S. H. Liu, *J. Am. Chem. Soc.*, **96**, 6210 (1974), **98**, 8093 (1976).
- 17) A. K. Davies, R. Ford, J. F. Mckeller and G. O. Phillips, *J. Chem. Soc., Perkin Trans. 2*, **1972**, 923.
- 18) H. Inoue and M. Hida, *Bull. Chem. Soc. Jpn.*, **51**, 1793 (1978).
- 19) J. B. Birks, "Organic Molecular Photophysics," Wiley-Interscience, New York, N. Y. (1975), Vol. 1, p. 32.
- 20) W. Siebrand, *J. Chem. Phys.*, **47**, 2411 (1967).
- 21) The rate of hydrogen abstraction from alcohols by the excited anthraquinone in its ³nπ* state has been reported to be in the range of ca. 10⁶–10⁷ dm³/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/dm³).
- 23) The observed rate constant ($k_r = 3.3 \times 10^9$ dm³ mol⁻¹ s⁻¹) of the electron transfer from hydroxide ion to **1** coincides reasonably with the calculated value (1.2×10^9 dm³ 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).