September, 1986] © *1986 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *59*, *2735—2741 (1986)*

Photochemical Reactions of Bromoanthraquinones in Ethanol at Room Temperature Studied by Steady-State Photolysis and Laser Photolysis

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(Received April 14, 1986)

Photolyses of α-bromoanthraquinones (1-bromo-, 1,5-dibromo-, and 1,8-dibromoanthraquinones) with 366-nm light in ethanol at room temperature gave rise to the formation of debrominated 9,10-anthracenediol as a final product. This was interpreted in terms of the sequence of the formation of α-bromo-9,10-anthracenediols followed by the photochemical dehydrobromination yielding the corresponding anthraquinones with one less bromine atom than original ones. Photolysis of 2-bromoanthraquinone gave rise to the formation of 2-bromo-9,10-anthracenediol, and no dehydrobromination was observed. Combined with the values of the quantum yields of photoreduction, the results of the laser photolyses revealed that the rate constant for the hydrogen-atom abstraction from ethanol decreased as an increase of the ππ* character of the lowest triplet states of α-bromoanthraquinones.

The photochemistry of quinones has been extensively studied on account of its importance in the understanding of the degradative action of light upon biological materials, photophosphorylation and the initiation of biological electron transport via excited quinones.

In connection with our recent interest in photophysics and photochemistry of aromatic carbonyl compounds, we have investigated the phosphorescences and triplet–triplet ($T'\leftarrow T_1$) absorptions of a series of halogenoanthraquinones:[1,2] Our finding is that the lowest triplet states (T_1) of α-haloanthraquinones are of mixed nπ*–ππ* or ππ* character, while the nπ* triplet states are the lowest ones for β-haloanthraquinones. The much shorter lifetimes of the T_1 states and small phosphorescence quantum yields of α-haloanthraquinones were indicative that the depopulation of the T_1 states was mainly due to a special rapid nonradiative process.

Although the reason for this was not clear, a possible conjecture was that the dehalogenation of α-haloanthraquinones affects the triplet lifetimes, because we observed the formation of anthraquinone during the steady-state photolysis of 1-chloroanthraquinone in ethanol with 366-nm light. However, this is ruled out by our findings that: (1) Steady-state photolysis of α-chloroanthraquinones (1-chloro-, 1,5-dichloro-, and 1,8-dichloroanthraquinones) with 366-nm light in ethanol gave rise to the sequence of the formation of α-chloro-9,10-anthracenediols followed by the photochemical dehydrochlorination yielding the corresponding anthraquinones with one less chlorine atom than original ones and the final photoproduct was 9,10-anthracenediol. No dechlorination was observed upon the 366-nm photolysis of 2-chloroanthraquinone.[3,4] (2) The hydrogen-atom abstraction of α-chloroanthraquinones from ethanol originated from the T_1 state in spite of its mixed nπ*–ππ* or ππ* character, though the reactivity for hydrogen-atom abstraction decreased as an increase of the ππ* character in the T_1 state.[5,6]

This paper deals with the photochemical reactions of bromoanthraquinones. Since the lifetimes of the T_1 states of α-bromoanthraquinones (1-bromo-, 1,5-dibromo-, and 1,8-dibromoanthraquinones) are much shorter than those of α-chloroanthraquinons,[1,2] the purpose of our present study is to examine the photochemical reactivity of bromoanthraquinones in order to confirm whether our previous conclusion made for chloroanthraquinones[3–6] can generally be applicable or not.

Experimental

Chemicals. The details of the methods of preparation of 1-bromo-, 2-bromo-, 1,5-dibromo-, and 1,8-dibromoanthraquinones (1-BAQ, 2-BAQ, 1,5-DBAQ, 1,8-DBAQ) have been given in our previous paper.[1] Spectral-grade ethanol (Nakarai) was used as a solvent without further purification. The sample solutions were degassed by several freeze-pump-thaw-cycles.

Steady-State Photolysis. Irradiation of bromoanthraquinones was carried out using a USH-500D super-high pressure mercury lamp. Light of 366-nm monochromatic wavelength was selected by the combination of two Toshiba color glass filters (UV-35 and UV-D35) and a filter solution ($CuSO_4\cdot 5H_2O$, 100 g dm^{-3}; path length, 3 cm), while 313-nm light 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). Photolysis of α-bromo-9,10-anthracenediols was performed with lights of longer wavelengths than 450 nm which were selected by the combination of a USL-500D Xe lamp, two Toshiba color glass filters (UV-35 and VY-46) and a filter solution of $CuSO_4$ (loc. cit). Absorption and fluorescence spectra were recorded using a Hitachi 200-20 spectrophotometer and a Hitachi MPF-4 fluorescence spectrophotometer, respectively. Since we observed a relatively rapid dark reaction immediately after the photolysis of 1,8-DBAQ, the time variation of the absorption spectrum was measured with a Unisoku rapid scan spectrophotometer (USP-450), where a Xe (at 330—450 nm) and a D_2 (at 290—390 nm) lamps were used as the monitoring-light sources. Unless otherwise stated, all experiments were carried out in ethanol at room temperature and the concentrations of sample solutions were 2—5$\times$10^{-4} M (1 M=1 mol dm^{-3}). The quantum yield of the photoreduction was determined by the Hatchard-Parker's potassium trisoxalatoferrate(III) actinometry method.[7] The yield of the photoproduct was determined by measuring its absorbance. To confirm the participation of the solvent in the dehydrobromination reaction, photolysis of 1-bromo-9,10-anthracenediol was carried out in benzene-d_6 (G.R.-grade, Wako) and anthraquinone produced was analyzed by using a Shimadzu QP-1000 GC-MS spectrometer with an OV-101 wall-coated capillary column (Ionization potential, 70 eV).

Laser Photolysis. The decays of the triplet–triplet ($T'\leftarrow T_1$) absorptions of bromoanthraquinones were measured at 380 nm in ethanol at room temperature. The third harmonic (355 nm) from a picosecond mode-locked Nd^{3+}:YAG laser was used for sample excitation, and the pulse width was 15 ps. Although the details of this laser photolysis system have been given elsewhere by Sumitani and Yoshihara,[8] a minor modification was performed: The monitoring light was generated by focusing the fundamental light onto the electrode of a Xe flash lamp (FX265 B203). The detection system for the absorption spectroscopy was composed of a monochromator (Shimadzu-Baush-Lomb, 1350 grooves/mm), a photomultiplier (HTV RI 294UZC318), an osciloscope (Tektronix 7104 with 7A29 and 7B10 plag-in units), a photo-oscillo unit (San-ei Instrument, 5R32) and a microcomputer (NEC PC9801m). The concentrations of the deaerated sample solutions in a cell of 10-mm path length were 3.5$\times$10^{-4}, 1.8$\times$10^{-4}, and 1.6$\times$10^{-4} M for 1-BAQ, 1,5-DBAQ, and 1,8-DBAQ, respectively.

Results

Steady-State Photolysis. Photoreduction of 2-BAQ in ethanol was studied by the absorption spectral change upon photolysis. Figure 1 indicates the depletion of 2-BAQ and the buildup of a photoproduct during 366-nm photolysis. The existence of an isosbestic point at 353 nm supports quantitative conversion of 2-BAQ to the product. Exposure to oxygen caused quantitative oxidation of the product back to 2-BAQ. This reaction is very similar to those of anthraquinone (AQ)[3,4,9–11] and 2-chloroanthraquinone.[4] Moreover, absorption and fluorescence spectra of the photoproduct of 2-BAQ are similar to those of 9,10-anthracenediol (AQH_2) and 2-chloro-9,10-anthracenediol. Thus one can safely conclude that the new absorption in Fig. 1 is due to 2-bromo-9,10-anthracenediol.

Photoreactions of 1-BAQ upon 366-nm photolysis gave rise to rather complicated absorption spectral changes as shown in Fig. 2-a: No isosbestic point could be seen as observed for 2-BAQ, and the absorption bands of the reactant and the products shifted to the blue during photolysis. Spectrum F with λ_{max}=382 nm was assigned to AQH_2, because absorption and fluorescence spectra of the final product were identical with those of AQH_2. Moreover, exposure to oxygen caused quantitative oxidation of the final photoproduct to AQ with λ_{max}=325 nm. On the other hand, photolysis of 1-BAQ with 313-nm light caused a simple absorption spectral change similar to that in photoreduction of 2-BAQ, that is, the depletion of 1-BAQ and the buildup of a product with λ_{max}=387 nm were observed, accompanied by an isosbestic point at 359 nm (Fig. 2-b). No spectral shifts

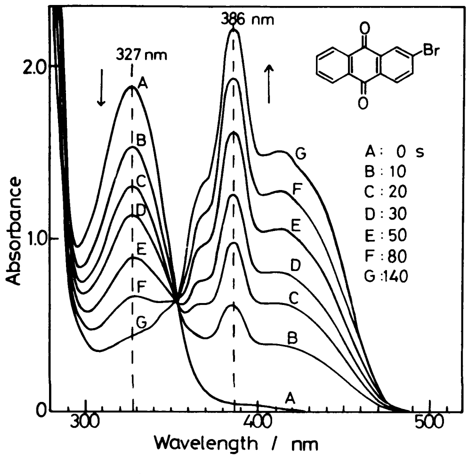


Fig. 1. Absorption spectral change of 2-BAQ in ethanol upon irradiation with 366-nm light at room temperature.

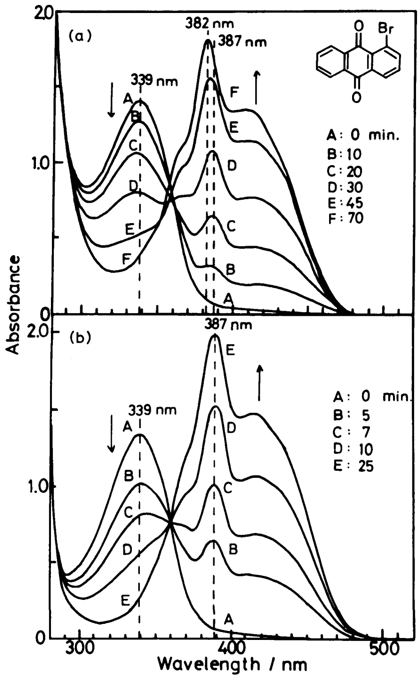


Fig. 2. Absorption spectral changes of 1-BAQ in ethanol upon irradiation with 366-nm (a) and 313-nm (b) lights at room temperature.

of the reactant and the product were observed during irradiation. (Extended photolysis gave rise to the decrease and the blue-shift in the absorption band at 387 nm). Spectrum E with $\lambda_{\max}$=387 nm in Fig. 2-b is identical with Spectra B and C in Fig. 2-a, and the photoproduct can be identified as 1-bromo-9,10-anthracenediol (1-BAQH$_2$) by its reaction with oxygen on exposure to air, giving 1-BAQ.

Figure 3 shows the absorption spectral change of 1-BAQH$_2$ upon the photolysis with lights of longer wavelengths than 450 nm, indicating the formation of a product at the expense of 1-BAQH$_2$, accompanied by an isosbestic point at 348 nm. The photoproduct with $\lambda_{\max}$=325 nm was identified as AQ by comparison of the absorption spectrum with that of the authentic sample of AQ. Further irradiation of this photoproduct with 366-nm light yielded AQH$_2$. The photolysis of 1-BAQH$_2$ was also performed in benzene-d_6, and the result of GC-MS analysis indicated that only AQ (not deuterated AQ) was produced.

In Fig. 4-a, we display much complicated photoreactions of 1,5-DBAQ upon 366-nm photolysis. Spectral shifts of the absorption bands of the reactant and the products can also be seen during photolysis, and the final photoproduct was AQH$_2$. (In Spectrum C, the absorption band with $\lambda_{\max}$=387 nm is identical with that of 1-BAQH$_2$). However, photolysis of 1,5-DBAQ with 313-nm light gave rise to a simple reaction as shown in Fig. 4-b. The photoproduct has an absorption band with $\lambda_{\max}$=393 nm which is identical with that of Spectrum B in Fig. 4-a, and the photoproduct was identified as 1,5-dibromo-9,10-anthracenediol (1,5-DBAQH$_2$), because it changed to 1,5-DBAQ on exposure to air. Further photolysis of 1,5-DBAQH$_2$ with lights of longer wavelengths than 450 nm gave a photoproduct with $\lambda_{\max}$=339 nm which was identified as 1-BAQ by comparison of the absorption spectrum with that of the authentic sample (Fig. 5).

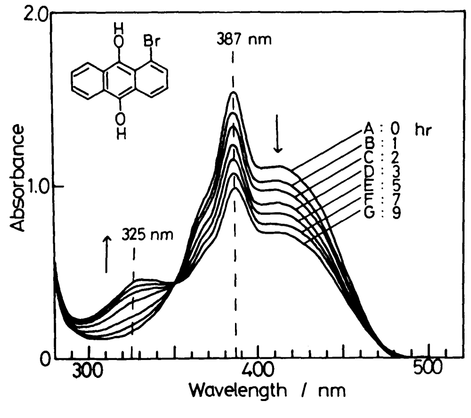


Fig. 3. Absorption spectral change of 1-BAQH$_2$ in ethanol upon irradiation with lights of longer wavelengths than 450 nm at room temperature.

The photochemical reactions of 1,8-DBAQ were not different from those of 1,5-DBAQ as shown in Figs. 6 and 7: The final photoproduct with $\lambda_{\max}$=382 nm in Fig. 6-a was identified as AQH$_2$ and the absorption spectrum of the final photoproduct with $\lambda_{\max}$=393 nm in Fig. 6-b was assigned to 1,8-dibromo-9,10-anthracenediol (1,8-DBAQH$_2$), because it changed to 1,8-DBAQ on exposure to air. By $\lambda \geq 450$-nm excitation (Fig. 7), 1,8-DBAQH$_2$ was dehydrobrominated to 1-BAQ. By using a Unisoku rapid scan spectrophotometer, however, we observed that the absorption spectra taken immediately after the photolysis (7 or 10 min) of 1,8-DBAQ changed with time by a dark reaction (cf. Fig. 8); the absorption around 300 nm decreased and those of 1,8-DBAQ and 1,8-DBAQH$_2$ increased simultaneously, accompanied by an isosbestic point at 325 nm. (Such a spectral change was not observed for 1-BAQ, 2-BAQ, and 1,5-DBAQ.) For the sake of comparison, we also show the similar results for 1,8-

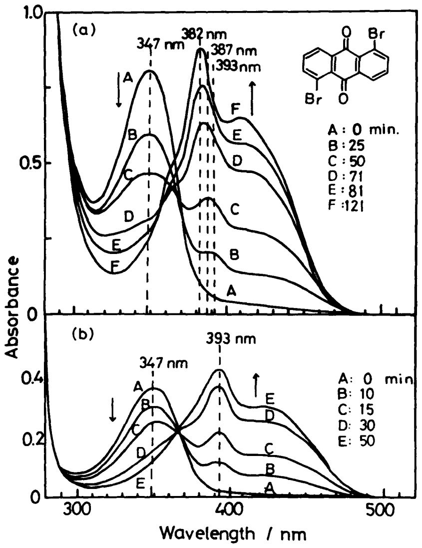


Fig. 4. Absorption spectral changes of 1,5-DBAQ in ethanol upon irradiation with 366-nm (a) and 313-nm (b) lights at room temperature.

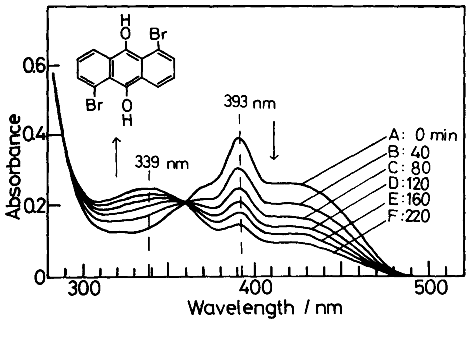


Fig. 5. Absorption spectral change of 1,5-DBAQH$_2$ in ethanol upon irradiation with lights of longer wavelengths than 450 nm at room temperature.

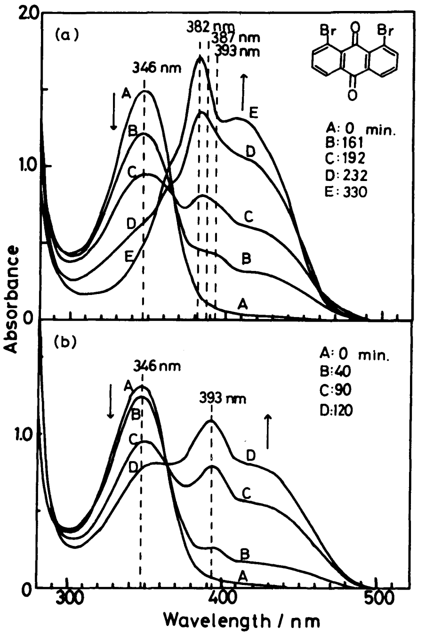


Fig. 6. Absorption spectral changes of 1,8-DBAQ in ethanol upon irradiation with 366-nm (a) and 313-nm (b) lights at room temperature.

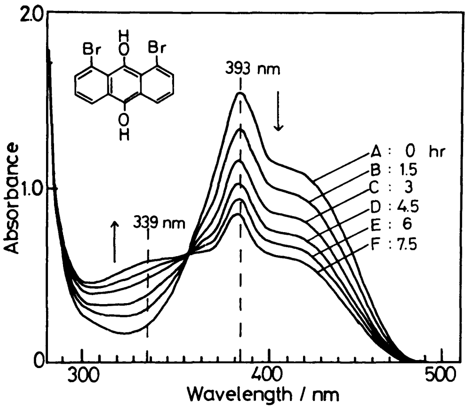


Fig. 7. Absorption spectral change of 1,8-DBAQH$_2$ in ethanol upon irradiation with lights of longer wavelengths than 450 nm at room temperature.

dichloroanthraquinone (1,8-DCAQ) in Fig. 9, where spectra were taken by a Hitachi 200-20 spectrophotometer (a)[3,4] and a Unisoku rapid scan spectrophotometer (USP-450) (b). Since the both results are identical with each other, the result for 1,8-DBAQ in Fig. 8 may be reliable.

In Table 1, we show the quantum yields of photoreduction of α-bromoanthraquinones upon the 313-nm photolysis. For the sake of comparison, we also show the results for α-chloroanthraquinones.[4]

Laser Photolysis. Since the T′←T$_1$ absorptions of α-bromoanthraquinones have the strong absorptions at ≈380 nm and weak one at ≈500 nm,[2] the decays of the T$_1$ states were monitored at 380 nm. In Fig. 10, we display the time variation of the transient absorptions (full curves). According to the mechanism established by Wilkinson[9] and Tickle and Wilkinson,[10] the photoreduction of anthraquinone (AQ) in alcohol (R$_2$CHOH) is given by

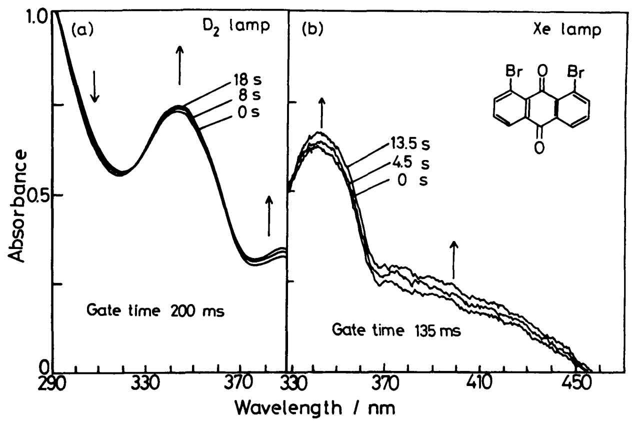


Fig. 8. Dark reactions of the complex of two 1,8-DBAQH· in ethanol at room temperature after irradiation of 1,8-DBAQ for 7 min (a) and 10 min (b), where spectra were taken by a Unisoku rapid scan spectrophotometer (USP-450) using a D$_2$ (a) and a Xe (b) lamps as the monitoring light sources.

$$\mathrm{AQ^*(T_1)} \longrightarrow \mathrm{AQ}, \tag{1}$$

$$\mathrm{AQ^*(T_1)} + \mathrm{R_2CHOH} \longrightarrow \mathrm{AQH\cdot} + \mathrm{R_2\dot{C}OH}, \tag{2}$$

$$\mathrm{R_2\dot{C}OH} + \mathrm{AQ} \longrightarrow \mathrm{AQH\cdot} + \mathrm{R_2CO}, \tag{3}$$

$$\mathrm{2AQH\cdot} \longrightarrow \mathrm{AQ} + \mathrm{AQH_2}, \tag{4}$$

where AQ*(T$_1$) and AQH· are triplet anthraquinone and anthrasemiquinone radical, respectively. Since the transient absorptions decayed monotonously and the quantum yields of photoreduction were very small as shown in Table 1, the absorptions due to anthrasemiquinone radicals may be negligible. Thus, the triplet decay constant (k_T) of α-bromoanthraquinones were determined by analyzing the most probable smooth curves (broken lines) as a single exponential curve. (The first-order plots of the absorbances against time are inserted in Fig. 10 by open circles and dotted lines). The values of k_T thus obtained are also listed in Table 1, together with those for α-chloroanthraquinones.[5,6]

Discussion

The results of the steady-state photolysis indicate that only the photoreduction occurs upon the photolysis of 2-BAQ. For α-bromoanthraquinones, 313-nm photolysis yielded the corresponding bromo-9,10-anthracenediols, and no photochemical dehydrobromination was observed. However, the photolysis of α-bromo-9,10-anthracenedilols with lights of

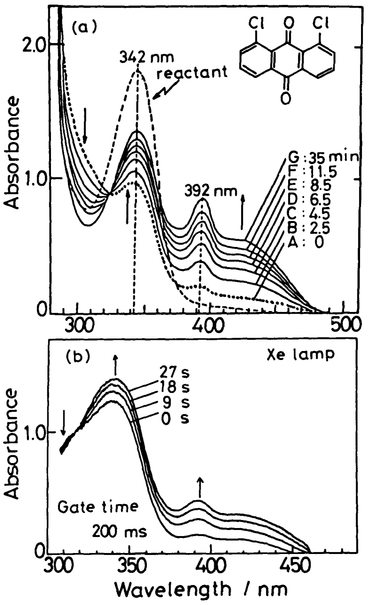


Fig. 9. Dark reactions of the complex of two 1,8-DCAQH· in ethanol at room temperature after irradiation of 1,8-DCAQ for 12 min (a) and 3 min (b), where spectra were taken by a Hitachi 200–20 spectrophotometer (a)[3,4] and a Unisoku rapid scan spectrophotometer (USP-450) (b). In the latter case, a Xe lamp was used as a monitoring light source.

longer wavelengths than 450 nm gave rise to the dehydrobromination yielding AQ (or 1-BAQ), accompanied by a clear isosbestic point. Since AQ and α-bromoanthraquinones (and their bromo-9,10-anthracenediols) have appreciable absorptions at 366-nm, the results of 366-nm photolyses are interpreted in terms of the following consecutive reactions, in accordance with the results for α-chloroanthraquinones:[3,4]

$$\text{1,5- or 1,8-DBAQ} \xrightarrow{h\nu} \text{1,5- or 1,8-DBAQH}_2 \xrightarrow{h\nu} \text{1-BAQ}$$
$$\xrightarrow{h\nu} \text{1-BAQH}_2 \xrightarrow{h\nu} \text{AQ} \xrightarrow{h\nu} \text{AQH}_2.$$

Based on this conclusion, the decrease and the blue-shift in the absorption bands of the photoproducts upon the extended 313-nm photolyses of α-bromoanthraquinones may be due to the consecutive reactions mentioned above.

In Fig. 6-b, a clear isosbestic point can be seen. Such an isosbestic point was not observed for 1,8-DCAQ, where we observed the initial spectral increase around 300 nm instead of a small yield of 1,8-dichloro-9,10-anthracenediol (1,8-DCAQH$_2$):[3,4] By a dark reaction (cf. Fig. 9), the absorption around 300 nm decreased and those of 1,8-DCAQH$_2$ and 1,8-DCAQ increased simultaneously, accompanied by an isosbestic point at 322 nm. The decay constant of the 300-nm absorption was nearly equal to the rate constants for the formation of 1,8-DCAQH$_2$ and 1,8-DCAQ,[4] i.e.,

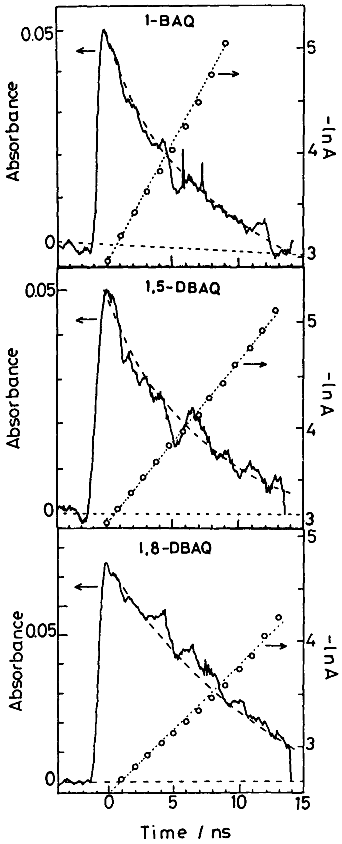


Fig. 10. Decay curves of the T′←T$_1$ absorptions of 1-BAQ, 1,5-DBAQ, and 1,8-DBAQ (full curves), where the absorbances were monitored at 380 nm and the data represent the average of 20 shots of laser pulses. The broken lines are the most probable decay curves and their first-order plots are shown by the dotted lines.

Table 1. The Quantum Yields(Φ) of the Photoreduction of α-Bromoanthraquinones, Their Triplet Decay Constants (k_T) and the Rate Constants (k_r) for the Hydrogen-Atom Abstraction from Ethanol

	1-BAQ	1,5-DBAQ	1,8-DBAQ
Φ	0.04 (1.0)[a]	0.03 (0.9)[a]	0.003 (0.04)[a]
k_T/s^{-1}	2.3×10^8 (2.3×10^6)[b]	1.6×10^8 (1.6×10^6)[b]	1.2×10^8 (4.0×10^5)[b]
k_r/s^{-1}	9.3×10^6 (2.3×10^6)[b]	4.8×10^6 (1.4×10^6)[b]	3.6×10^5 (1.6×10^4)[b]

The values in parentheses are those for the corresponding α-chloroanthraquinones. a) Ref. 4. b) Refs. 5 and 6.

$\approx 5.8\times10^{-3}$ s^{-1}. Thus, we have assigned the 300-nm absorption to a complex of two 1,8-dichloroanthrasemiquinone radicals (1,8-DCAQH·). Actually, the rate constant for the buildup of the 300-nm absorption ($\approx 2\times10^9$ M^{-1} s^{-1})[4] was nearly equal to the decay constant of 1,8-DCAQH·, i.e., 5.8×10^8—2.2—4.1×10^9

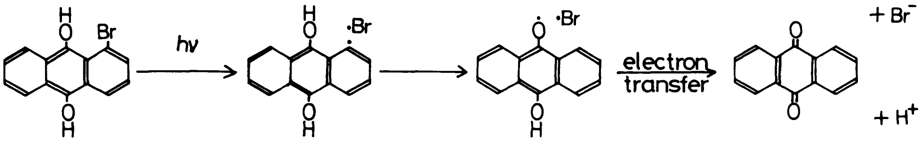
$M^{-1} s^{-1}$, though the value of the decay constant depends on the assumption of the extinction coefficient of 1,8-DCAQH··.[6]

Since we could not observe any absorption due to a complex of two 1,8-dibromoanthrasemiquinone radicals (1,8-DBAQH·) during the spectral measurements using a Hitachi 200-20 spectrophotometer, the complex of two 1,8-DBAQH· may be more unstable than that of 1,8-DCAQH··. This is consistent with our findings that: (1) The result in Fig. 8 clearly shows the existence of a relatively rapid dark reaction. (2) A clear isosbestic point was observed even for 1,8-DCAQ, when each spectrum was taken at the delay time of 20 min after the 313-nm photolysis (1 min) of 1,8-DCAQ.[4]

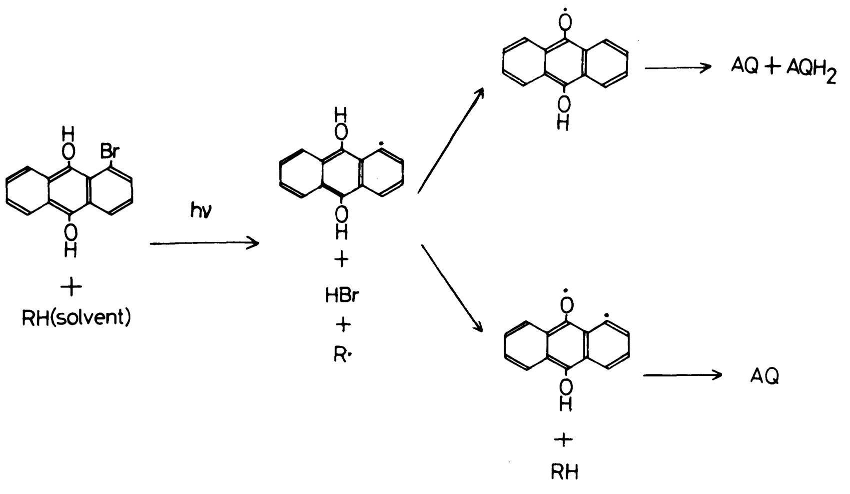
As reported in our previous paper,[4] the quantum yields of photoreduction were 1.0, 1.0, 0.9, and 0.04 for AQ, 1-chloro-, 1,5-dichloro-, and 1,8-dichloroanthraquinones, respectively. This decrease in the quantum yields as an increase of the $\pi\pi^*$ character in the T_1 states of α-chloroanthraquinones was also observed for α-bromoanthraquinones as shown in Table 1. (The value for 2-BAQ was 1.0). Thus one can safely conclude that much shorter lifetimes of the T_1 states and small phosphorescence quantum yields of α-haloanthraquinones are not due to the photoreactions but are due to the modification of the geometrical molecular structure by the interaction of the carbonyl group with halogen atom(s) at the α-positions, causing the T_1 states to be of $\pi\pi^*$ character with short lifetimes. Of course, the internal heavy-atom effect of halogen atoms may also affect the triplet lifetimes.[12]

As can be seen in Table 1, the decay constants (k_T) of the T_1 states of α-bromoanthraquinones are much greater than those of α-chloroanthraquinones.[5,6] Combined with the results of quantum yields of photoreduction, the rate constants (k_r) of hydrogen-atom abstraction from ethanol were estimated as shown in Table 1, indicating that the reactivity of triplet α-bromoanthraquinones decreases as an increase of the $\pi\pi^*$ character of the T_1 state, in accordance with our previous results for α-chloroanthraquinones.[5,6]

Since the result of GC-MS analysis indicated that only AQ (not deuterated AQ) was produced upon the photolysis of 1-BAQH$_2$ in benzene-d_6, a possible reaction mechanism may be given by Scheme 1: Namely, the homolysis of the C–Br bond may give rise to the formation of two caged radicals. If the electron transfer from the semiquinone radical to the bromine radical in the solvent cage is followed by the rapid deprotonation, it looks like that the solvent does not participate in the overall reaction. If this scheme is correct, however, the rate of dehydrochlorination of α-chloro-9,10-anthracenediols should be slower than that of dehydrobromination of α-bromo-9,10-anthracenediols, because the bond dissociation energy of C–Cl bond is expected to be larger than that of C–Br bond. This is inconsistent



Scheme 1.



Scheme 2.

with our present finding that the rates of dehydrobromination are extremely slower than those of dehydrochlorination. (The possibility of Scheme 1 may be also excluded, based on the fact that photolysis of 2-BAQH$_2$ does not give rise to the formation of AQ.)

An alternative reaction mechanism may be given by Scheme 2. However, this is also ruled out based on the discussion in our previous paper,[4] where we proposed that the dehydrochlorination of α-chloro-9,10-anthracenediols occurs via the intramolecular elimination of hydrogen chloride. Since dehydrobromination is also observed only for α-bromo-9,10-anthracenediols, the dehydrohalogenation reaction may be affected by the proximity effect of halogen(s), that is, the structural proximity of the hydroxyl group to the halogen atom(s) may make it possible to cause intramolecular elimination of hydrogen halide. The faster rates of dehydrochlorination than those of dehydrobromination support our previous suggestion[4] that an intramolecular hydrogen bonding between the hydroxyl group and the halogen atom at the α-position enhances the rate of dehydrohalogenation. This is based on the fact that the electronegativity of chlorine atom is larger than that of bromine atom, indicating that the hydrogen-bonding character (or charge-transfer character) between the chlorine atom and the hydroxyl group is larger than that between the bromine atom and the hydroxyl group. For β-halo-9,10-anthracenediols (2-chloro- and 2-bromo-9,10-anthracenediols), therefore, it is expected that the hydroxyl group and the halogen atom are located too much separately to cause the intramolecular dehydrohalogenation.

In summary, one can say that our previous conclusion made for the photochemical reactions of chloroanthraquinones is generally applicable to those of bromoanthraquinones.

We wish to express our sincere thanks to Professor Keitaro Yoshihara and Dr. Minoru Sumitani of Institute for Molecular Science for the help in the measurements of the triplet decay constants using a Nd^{3+}:YAG laser. Thanks are also due to Mr. Toshihiko Nagamura of Unisoku Co. Ltd. for the help in the measurements of the dark reactions using a rapid scan spectrophotometer.

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