PHOTOREDUCTIONS OF α-CHLOROANTHRAQUINONES FOLLOWED BY PHOTOCHEMICAL DEHYDROCHLORINATION IN ETHANOL AT ROOM TEMPERATURE

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Summary

In the 366 nm photolyses of α-chloroanthraquinones (the 1-chloro, 1,5-dichloro and 1,8-dichloro compounds) the absorption bands of the reactants and the products shifted to the blue and anthrahydroquinone was produced as the final product. Combined with the results of the 313 nm photolyses of α-chloroanthraquinones and those of the 450 nm or 465 nm photolyses of α-chloroanthrahydroquinones, the results of the 366 nm photolyses of α-chloroanthraquinones were interpreted in terms of the following consecutive reactions: 1,5-dichloroanthraquinone or 1,8-dichloroanthraquinone $\xrightarrow{h\nu}$ 1,5-dichloroanthrahydroquinone or 1,8-dichloroanthrahydroquinone $\xrightarrow{h\nu}$ 1-chloroanthraquinone $\xrightarrow{h\nu}$ 1-chloroanthrahydroquinone $\xrightarrow{h\nu}$ anthraquinone $\xrightarrow{h\nu}$ anthrahydroquinone. In the step involving the photoreduction of 1,8-dichloroanthraquinone, however, a novel phenomenon was observed: the photolysis gave rise to the formation of a precursor which disappeared by a dark reaction, following a first-order rate law, to yield both the reactant and the product (1,8-dichloroanthrahydroquinone) simultaneously. This precursor was assigned to a complex of two 1,8-dichloroanthrasemiquinone radicals. The photolysis of 2-chloroanthraquinone gave rise to the formation of 2-chloroanthrahydroquinone, and no dehydrochlorination was observed.

1. Introduction

According to the mechanism established by Tickle and Wilkinson [1] for anthraquinone (AQ) photoreduction, a hydrogen atom of the solvent molecule is abstracted by the lowest $n\pi^*$ triplet AQ, followed by the disproportionation of two anthrasemiquinone radicals yielding anthrahydroquinone (AQH_2) and AQ.

From measurements of the phosphorescence spectra and triplet–triplet absorptions of AQ and halogenoanthraquinones (chloro- or bromo-

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substituted anthraquinones) [2], we have suggested that the lowest triplet states of α-halogenoanthraquinones are of mixed $n\pi^*$–$\pi\pi^*$ or $\pi\pi^*$ character, while the $n\pi^*$ triplet states are the lowest ones for AQ and β-halogenoanthraquinones (2-chloroanthraquinone and 2-bromoanthraquinone).

Compared with AQ and β-halogenoanthraquinones, much shorter lifetimes of the lowest triplet states together with small phosphorescence quantum yields were obtained for α-halogenoanthraquinones. Since the lowest triplet states of some derivatives of aromatic carbonyls are of $\pi\pi^*$ character with relatively long lifetimes [3], it is apparent that the depopulation of the lowest triplet states of α-halogenoanthraquinones is mainly due to a special rapid non-radiative process. Although the reason for this was not clear, a possible explanation was that a modification of the geometry of the molecular structure by the interaction of the carbonyl group with halogen atom(s) at the α position(s) caused the lowest triplet states to be of $\pi\pi^*$ character with short lifetimes [2].

An alternative explanation was that the depopulation of the lowest triplet states might be mainly affected by the dehalogenation of the α-halogenoanthraquinones, because we observed the formation of dehalogenated anthraquinones during the irradiation in ethanol with light of wavelength 366 nm. To clarify the relation between the triplet lifetime and the reactivity of triplet anthraquinones, this paper deals with the photochemical reactions of AQ and chloroanthraquinones in ethanol at room temperature, although the preliminary results already have been reported [4]. Of the chloroanthraquinones, we have selected the 1-chloro, 2-chloro, 1,5-dichloro and 1,8-dichloro compounds.

2. Experimental details

The details of the methods of preparation of AQ and chloroanthraquinones have been given in our previous paper [2]. Guaranteed reagent grade triethylamine (TEA; Wako) was refluxed over calcium hydride and distilled under nitrogen. Spectral grade ethanol (Nakarai), acetonitrile (Dojin), benzene (Dojin) and guaranteed reagent grade benzene-d_6 (Wako) were used as the solvents without further purification. The sample solutions were degassed by several freeze–pump–thaw cycles. Monochromatic light of wavelength 366 nm was selected from a USH-500D super-high pressure mercury lamp by a combination of two Toshiba 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 light of wavelength 313 nm was selected by two Toshiba 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). Monochromatic light of wavelengths 450 nm and 465 nm from a USL-500D xenon lamp were selected using a Shimazu–Bausch–Lomb monochromator. Absorption and fluorescence spectra were recorded using a Hitachi 200-20 spectrophotometer and a Shimazu RF-502 fluorescence spectrophotometer respectively. Since we observed a dark reaction

after the photolysis of 1,8-dichloroanthraquinone (1,8-DCAQ) in ethanol, the time variation of the absorbance was measured with a Shimazu UV-200 spectrophotometer. Unless otherwise stated, all experiments were carried out in ethanol at room temperature. The quantum yield of the photoreduction in ethanol was determined by the Hatchard–Parker potassium ferrioxalate actinometry method [5]. The yield of the photoproduct was determined by measuring its absorbance. To confirm the participation of the solvent in the dehydrochlorination reaction, 450 nm photolysis of 1-chloroanthrahydroquinone (1-CAQH$_2$) was carried out in benzene-d_6 and the AQ produced was analysed by using a Shimazu QP-1000 GC–MS spectrometer with an OV-101 wall-coated capillary column (ionization potential, 70 eV).

3. Results

The change in the absorption spectrum of AQ in ethanol is shown in Fig. 1(a). Upon irradiation with light of wavelength 366 nm, the absorption band of AQ with λ_{max} = 325 nm decreased and a new band from a product with λ_{max} = 382 nm built up, accompanied by an isosbestic point at 346 nm. On the introduction of air to the sample solution, the absorption spectrum of AQ appeared at the expense of that of the photoproduct. This is a well-known photoreduction of AQ [1], and the photoproduct was identified as anthrahydroquinone (AQH$_2$).

Irradiation of 2-chloroanthraquinone (2-CAQ) with light of wavelength 366 nm gave rise to a reaction similar to that of AQ, as shown in Fig. 1(b). The absorption and emission spectra of the photoproduct were slightly red shifted compared with those of AQH$_2$. Thus one can safely conclude that the photoproduct is 2-chloroanthrahydroquinone (2-CAQH$_2$).

Excitation of 1-chloroanthraquinone (1-CAQ) with light of wavelength 366 nm gave rise to rather complicated reactions as shown in Fig. 2(a). No

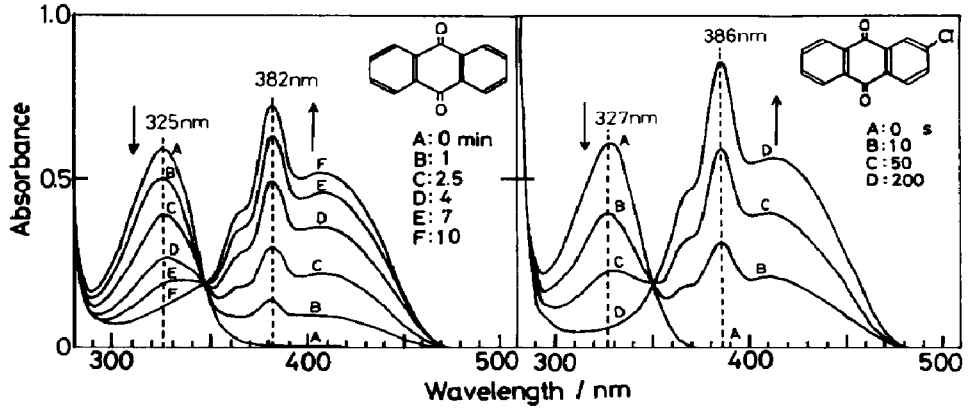


Fig. 1. Changes in the absorption spectra of (a) AQ and (b) 2-CAQ, both in ethanol, upon irradiation with light of wavelength 366 nm at room temperature ([AQ] = 1 × 10^{-4} M; [2-CAQ] = 2 × 10^{-4} M).

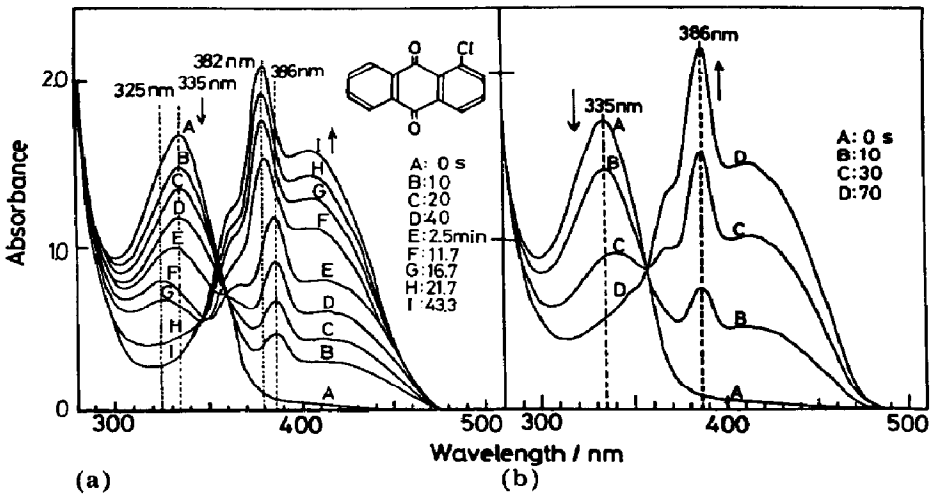


Fig. 2. Changes in the absorption spectra of 1-CAQ (3×10^{-4} M) in ethanol upon irradiation at room temperature with light of wavelength (a) 366 nm and (b) 313 nm.

isosbestic point could be seen as observed in Fig. 1: during irradiation, the absorption band of the reactant with λ_{max} = 335 nm decreased and shifted to the blue. The absorption band with λ_{max} = 325 nm in spectrum G is identical with that of AQ. The absorption bands of the photoproducts also shifted to the blue. Spectrum I with λ_{max} = 382 nm was assigned to AQH_2, because the absorption and emission spectra of the final product were identical with those of AQH_2 and the photoproduct changed to AQ on the introduction of air.

When irradiation was carried out with light of wavelength 313 nm, the absorption of 1-CAQ decreased and a new band from a product increased, accompanied by an isosbestic point at 356 nm (Fig. 2(b)). There were no shifts in the spectra of either the reactant or the product during irradiation. Spectrum D, in Fig. 2(b), with λ_{max} = 386 nm, is identical with spectra B - E in Fig. 2(a), and the photoproduct can be identified as 1-$CAQH_2$, because it changed into 1-CAQ on the introduction of air. Upon irradiation of 1-$CAQH_2$ with light of wavelength 450 nm, a new absorption band appeared around 325 nm at the expense of 1-$CAQH_2$ (Fig. 3(a)). One can see the existence of a clear isosbestic point at 350 nm. The photoproduct was identified as AQ by comparison of the absorption spectrum with that of an authentic sample of AQ. Further irradiation of this photoproduct with light of wavelength 366 nm yielded AQH_2. In Fig. 3(b) we show the relative rates of dehydrochlorination of 1-$CAQH_2$ in benzene, ethanol and acetonitrile, by plotting the logarithm of the absorbance at 450 nm against the irradiation time.

The photochemical reactions of 1,5-dichloroanthraquinone (1,5-DCAQ) on 366 nm excitation were very complicated, as shown in Fig. 4(a), *i.e.* spectral shifts of the absorption bands of the reactant and the products were observed during irradiation, and the final photoproduct was AQH_2 (in Fig. 4(a), spectrum D, the bands with λ_{max} = 386 nm and λ_{max} = 325 nm are

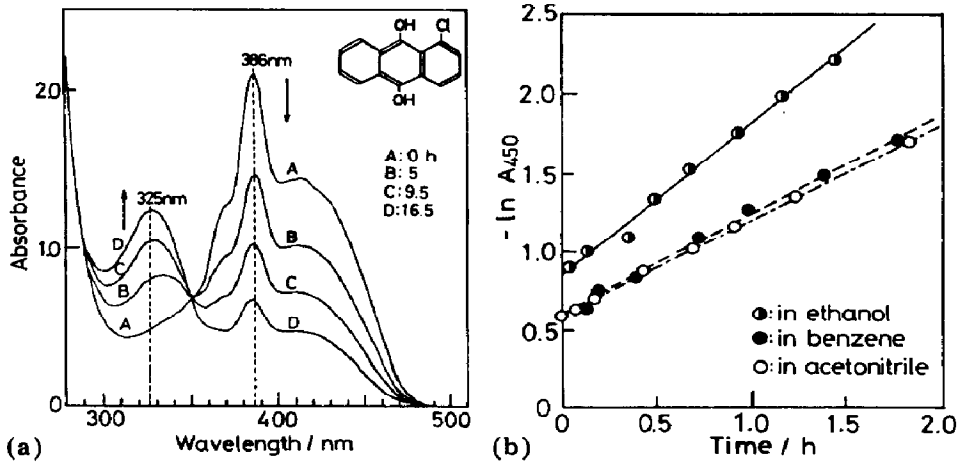


Fig. 3. (a) Changes in the absorption spectra of 1-CAQH$_2$ (about 3×10^{-4} M) in ethanol upon irradiation with light of wavelength 450 nm at room temperature. (b) Relative dehydrochlorination rates in various solvents.

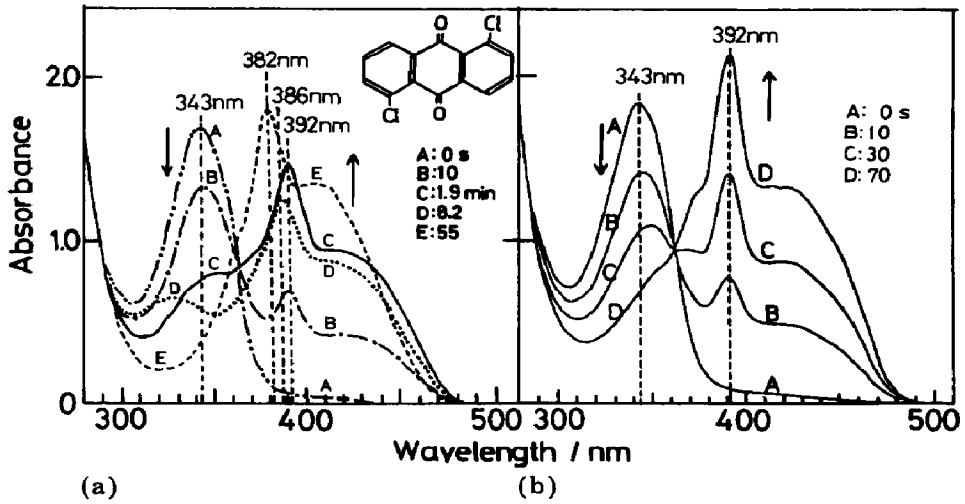


Fig. 4. Changes in the absorption spectra of 1,5-DCAQ (3×10^{-4} M) in ethanol upon irradiation at room temperature with light of wavelength (a) 366 nm and (b) 313 nm.

identical with those of 1-CAQH$_2$ and AQ respectively). However, irradiation of 1,5-DCAQ with light of wavelength 313 nm gave rise to a simple reaction as shown in Fig. 4(b). The photoproduct had an absorption band with λ_{max} = 392 nm which is identical with the bands of spectra B and C in Fig. 4(a), and the photoproduct was identified as 1,5-dichloroanthrahydroquinone (1,5-DCAQH$_2$), because it changed to 1,5-DCAQ on the introduction of air. Further irradiation of 1,5-DCAQH$_2$ with light of wavelength 465 nm gave a photoproduct with λ_{max} = 335 nm which was identified as 1-CAQ by comparison of the absorption spectrum with that of an authentic sample (Fig. 5).

As shown in Fig. 6(a), the photochemical reactions of 1,8-DCAQ on 366 nm excitation were rather different from those of 1,5-DCAQ (*cf.* Fig. 4(a)). Although the spectral shifts of the absorption bands of the reactant

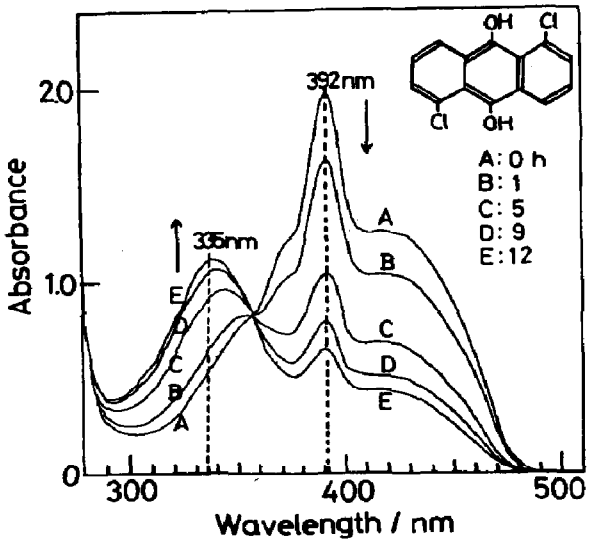


Fig. 5. Changes in the absorption spectra of 1,5-DCAQH$_2$ (about 3×10^{-4} M) in ethanol upon irradiation with light of wavelength 465 nm at room temperature.

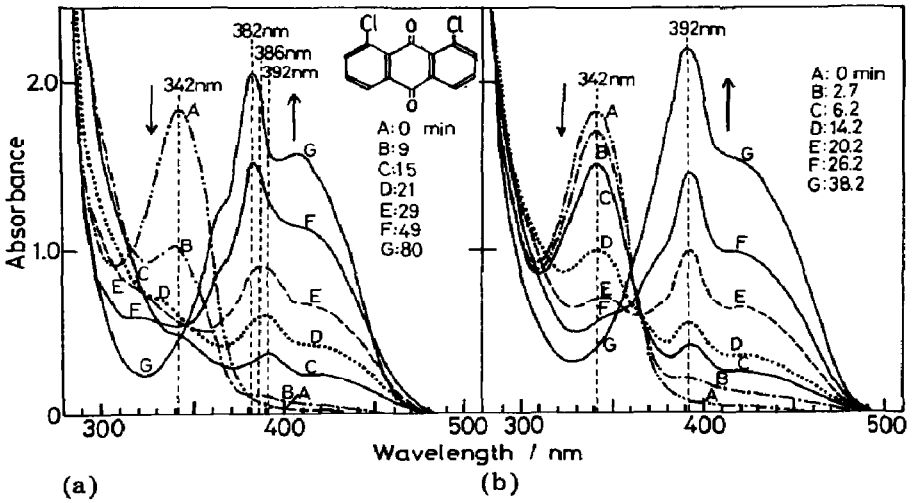


Fig. 6. Changes in the absorption spectra of 1,8-DCAQ (3×10^{-4} M) in ethanol upon irradiation at room temperature with light of wavelength (a) 366 nm and (b) 313 nm.

and the products were observed during irradiation, the absorption around 300 nm increased initially and then decreased. This novel phenomenon was also observed when the sample was irradiated with light of wavelength 313 nm (Fig. 6(b)). In this case there were no spectral shifts of the absorption bands of the reactant and the product, but the clear isosbestic points seen for AQ, 1-CAQ and 1,5-DCAQ could not be observed. The absorption spectrum of the final photoproduct with λ_{max} = 392 nm was assigned to that of 1,8-dichloroanthrahydroquinone (1,8-DCAQH$_2$), because it changed to 1,8-DCAQ on the introduction of air. On 465 nm excitation, the absorption

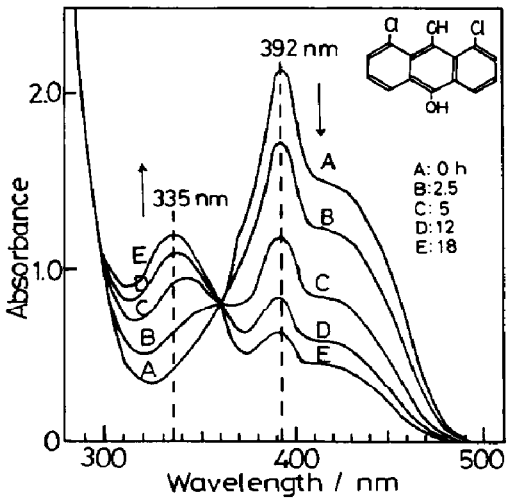


Fig. 7. Changes in the absorption spectra of 1,8-DCAQH$_2$ (about 3 × 10^{-4} M) in ethanol upon irradiation with light of wavelength 465 nm at room temperature.

spectrum of 1,8-DCAQH$_2$ changed into that of 1-CAQ, accompanied by an isosbestic point at 358 nm (Fig. 7).

The absorption band around 300 nm in Figs. 6(a) and 6(b) decreased because of a dark reaction. A typical example is shown in Fig. 8(a): upon irradiation of 1,8-DCAQ with light of wavelength 366 nm for 12 min, an increase in absorbance around 300 nm could be seen instead of a small yield of 1,8-DCAQH$_2$, compared with that of 1,5-DCAQH$_2$. Because of the dark reaction the absorption around 300 nm decreased and those of 1,8-DCAQ and 1,8-DCAQH$_2$ increased simultaneously, accompanied by an isosbestic point at 322 nm. Thus the absence of an isosbestic point in

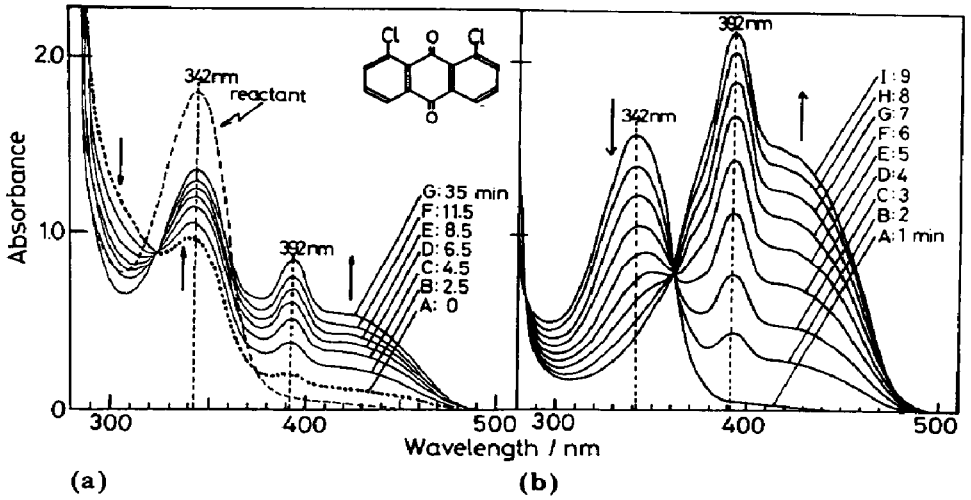


Fig. 8. (a) Dark reaction of the precursor in ethanol after irradiation of 1,8-DCAQ (3 × 10^{-4} M) for 12 min at room temperature. (b) Changes in the absorption spectra of 1,8-DCAQ (2.6 × 10^{-4} M) in ethanol at room temperature where each spectrum was taken at a delay time of 20 min after the 313 nm photolysis (1 min).

Fig. 6(b) can be ascribed to the dark reaction mentioned above, because we could observe a clear isosbestic point at 361 nm, as shown in Fig. 8(b) in which each spectrum was taken after a delay time of 20 min after the 313 nm photolysis (1 min) of 1,8-DCAQ.

In Fig. 9(a), we show the time variation of the absorptions at 290 nm, 342 nm and 392 nm resulting from the dark reaction, and all three absorption bands changed following a first-order rate law (Fig. 9(b)). The decay constant of the 290 nm absorption ($5.9 \times 10^{-3}\ s^{-1}$) was nearly equal to the rate constants for the formation of 1,8-DCAQ ($5.5 \times 10^{-3}\ s^{-1}$ at 342 nm) and 1,8-DCAQH$_2$ ($5.9 \times 10^{-3}\ s^{-1}$ at 392 nm). Based on these results, it can safely be concluded that the absorption around 300 nm is due to a precursor which gives both the reactant (1,8-DCAQ) and the product (1,8-DCAQH$_2$) simultaneously.

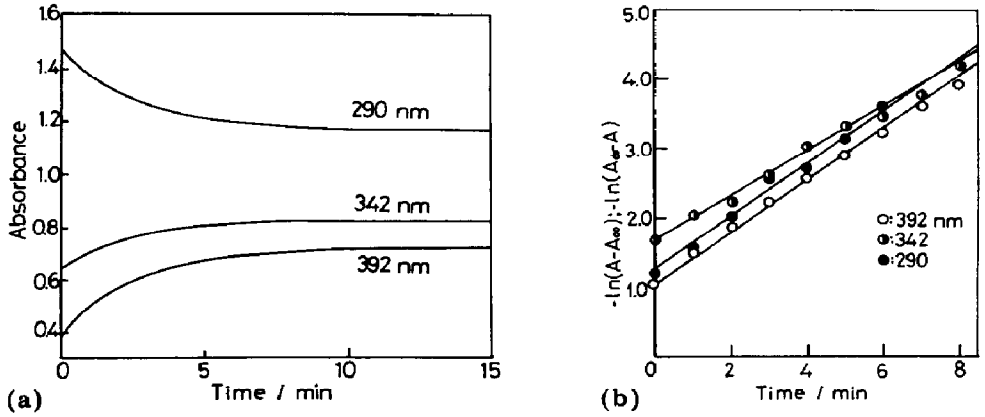


Fig. 9. (a) Time variations in the absorptions at 290 nm, 342 nm and 392 nm due to the dark reaction and (b) their first-order plots.

Exposure to oxygen caused quantitative oxidation of the precursor back to 1,8-DCAQ. This precursor also dissociated into 1,8-DCAQ and 1,8-DCAQH$_2$ immediately after the addition of TEA *in vacuo*, as shown in Fig. 10(a): photolysis of 1,8-DCAQ with light of wavelength 366 nm in ethanol for 3 min gave spectrum B in Fig. 10. Upon addition of TEA (0.2 M), spectrum B changed to spectrum C, indicating that the absorption band (at about 300 nm) due to the precursor decreased and the bands of 1,8-DCAQ (at about 340 nm) and 1,8-DCAQH$_2$ (at about 400 nm) built up. (In spectrum C, we conclude that the absorption band above about 500 nm is due to the monoanion and/or the dianion of 1,8-DCAQH$_2$ based on the following reasons. (1) We have previously reported that the form in which 10-cyano-9-anthrol (or its anion) and 10-benzoyl-9-anthrol (or its anion) exist is dependent on the basicity, polarity and rigidity of medium as well as the temperature [6]. The absorption band due to the base form was observed at a longer wavelength than that due to the acid form. (2) Addition of TEA *in vacuo* to AQH$_2$, 1-CAQH$_2$, 1,5-DCAQH$_2$ and 1,8-DCAQH$_2$ gave rise to results similar to that in Fig. 10(a). (3) Carlson and Hercules [7]

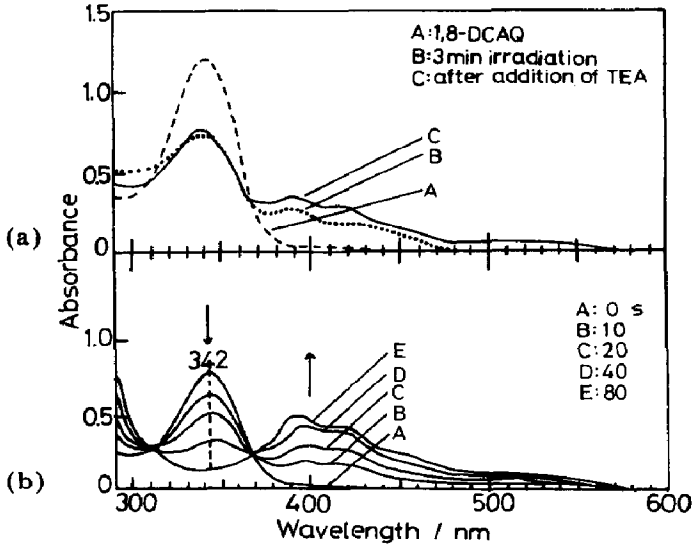


Fig. 10. (a) Effect of TEA (0.2 M) on the stability of the precursor. (b) Changes in the absorption spectra of 1,8-DCAQ (1.4×10^{-4} M) in TEA (0.2 M)–ethanol upon irradiation with light of wavelength 313 nm at room temperature.

have reported that the monoanion and dianion of AQH_2 have absorption bands at 393 nm and 465 nm and at 417 nm and 508 nm respectively.)

In Fig. 10(b), we show the result of the 313 nm photolysis of 1,8-DCAQ–TEA (0.2 M) in ethanol. One can observe the formation of 1,8-$DCAQH_2$ and its base form accompanied by a clear isosbestic point.

4. Discussion

4.1. Photoreductions of anthraquinones

All the results so far obtained indicate that only AQ and 2-CAQ were reduced upon irradiation with light of wavelength 366 nm. For 1-CAQ and 1,5-DCAQ, 313 nm photolysis also gave rise to the formation of the corresponding chloroanthrahydroquinone and no photochemical dehydrochlorination was observed. However, the 450 nm (or 465 nm) photolysis of 1-$CAQH_2$ (or 1,5-$DCAQH_2$) gave rise to dehydrochlorination yielding AQ (or 1-CAQ), accompanied by a clear isosbestic point. Thus the results of the 366 nm photolyses of 1-CAQ and 1,5-DCAQ are interpreted in terms of the following consecutive reactions: 1,5-DCAQ $\xrightarrow{h\nu}$ 1,5-$DCAQH_2$ $\xrightarrow{h\nu}$ 1-CAQ $\xrightarrow{h\nu}$ 1-$CAQH_2$ $\xrightarrow{h\nu}$ AQ $\xrightarrow{h\nu}$ AQH_2. This is reasonable, because AQ, 1-CAQ, 1,5-DCAQ and their halogenoanthrahydroquinones have appreciable absorptions at 366 nm.

The photochemical reactions of 1,8-DCAQ in ethanol were essentially the same as those for 1-CAQ and 1,5-DCAQ. However, a novel phenomenon

was observed in the photoreduction step of 1,8-DCAQ: photolysis of 1,8-DCAQ in ethanol gave rise to the formation of the precursor followed by the dark reaction yielding both the reactant (1,8-DCAQ) and the product (1,8-$DCAQH_2$) simultaneously. At present, no definitive conclusion regarding the structure of this precursor has been obtained, although the precursor in ethanol dissociated into 1,8-DCAQ upon exposure to oxygen or into 1,8-DCAQ and 1,8-$DCAQH_2$ (and its base form) immediately after the addition of TEA. Nor is it clear whether the precursor exists only in ethanol, because the rates of the photoreductions in toluene and cyclohexane were too slow to observe the absorption due to the precursor. The precursor may also dissociate into 1,8-DCAQ and 1,8-$DCAQH_2$ upon excitation with light of wavelength 313 nm, because the ratio of the yield of the precursor to that of 1,8-$DCAQH_2$ upon 313 nm photolysis was smaller than that upon 366 nm photolysis.

A probable candidate for this precursor may be a complex of two 1,8-dichloroanthrasemiquinone radicals (1,8-DCAQH·), based on the following reasons. (1) According to the mechanism established by Tickle and Wilkinson for AQ photoreduction [1], two anthrasemiquinone radicals (AQH·) disproportionate to form AQH_2 and AQ. By performing the nanosecond laser photolysis in ethanol, we have confirmed that the precursor builds up following a second-order reaction with a rate constant of about $2 \times 10^9\ M^{-1}\ s^{-1}$. This value is compatible with that for the disappearance of 1,8-DCAQH·, *i.e.* (5.8×10^8) - $((2.2 - 4.1) \times 10^9)\ M^{-1}\ s^{-1}$ [8]. No absorption due to 1,8-$DCAQH_2$ was observed during the decay of 1,8-DCAQH·. However, the decays of the radicals of 1-chloroanthrasemiquinone and 1,5-dichloroanthrasemiquinone were accompanied by the formation of 1-$CAQH_2$ and 1,5-$DCAQH_2$ respectively. (2) The precursor was quantitatively oxidized back to 1,8-DCAQ upon exposure to oxygen. (3) As shown in Fig. 9(b), the decay constant of the 300 nm absorption was nearly equal to the rate constant for the formation of 1,8-DCAQ and 1,8-$DCAQH_2$, *i.e.* about $5.8 \times 10^{-3}\ s^{-1}$. (4) Photodimers of anthracenes have absorptions around 300 nm [9].

An alternative assignment is that the precursor is 1,8-DCAQH·. However, this is unreasonable, because it was found that almost all the 1,8-DCAQH· decayed within a delay time of 1 ms after the nanosecond laser excitation [8], while the precursor decayed after up to about 20 min as can be seen in Fig. 9(a). Moreover, we could observe neither the strong absorption band at about 360 - 390 nm nor the weak band at 600 - 700 nm (Fig. 8(a)) observed for AQH· by Bridge and Porter [10] and Carlson and Hercules [7] and for semiquinone radicals of α-chloroanthraquinones by us [8].

Since the precursor dissociated into 1,8-DCAQ and 1,8-$DCAQH_2$ (and its base form) immediately after the addition of TEA in ethanol, it is expected that the 313 nm photolysis of 1,8-DCAQ–TEA in ethanol may give rise to the formation of 1,8-$DCAQH_2$ and its base form accompanied by a clear isosbestic point. Actually, we obtained the expected result, as shown in

Fig. 10(b) (the absorption at about 300 nm is not due to the precursor but is due to the base form of 1,8-DCAQH$_2$).

If the complex has a structure consisting of a triplet paired radical of two 1,8-DCAQH· similar to that obtained by radiolysis of *n*-eicosane [11], an electron spin resonance (ESR) spectrum might be obtainable. An ESR study concerning this problem may be inevitable, and experimental work along these lines is in progress.

The quantum yields of photoreduction were 1.0 (AQ), 1.0 (1-CAQ), 0.9 (1,5-DCAQ) and 0.04 (1,8-DCAQ) in ethanol at room temperature. Thus one can safely conclude that both the much shorter lifetimes of the lowest triplet states and the small phosphorescence quantum yields of α-chloroanthraquinones are not due to the photoreaction but are due to the modification of the geometry of the molecular structure by the interaction of the carbonyl group with the halogen atom(s), causing the lowest triplet states to be of $\pi\pi^*$ character with short lifetimes [2].

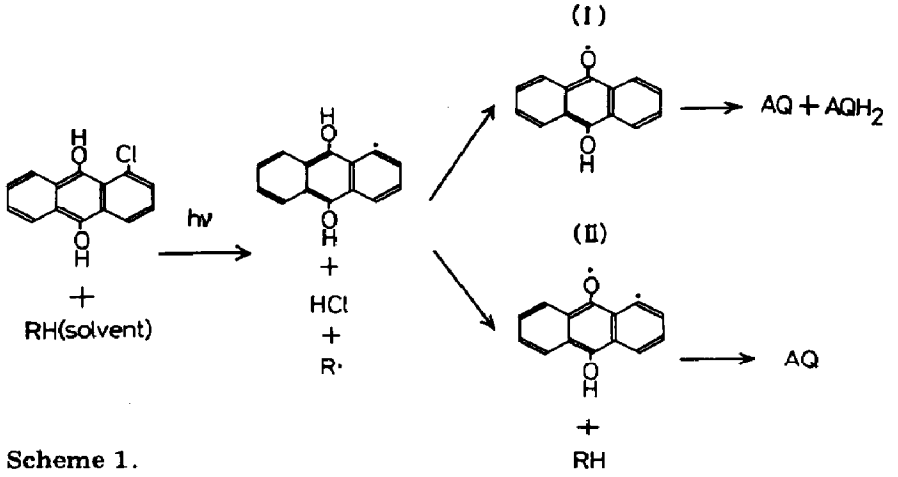
In conjunction with the assumption of $\pi\pi^*$ character for the lowest triplet state of α-chloroanthraquinones, Inoue *et al.* [12] proposed that the photoreduction originated via direct electron transfer from ethanol to the triplet $\pi\pi^*$ states of α-chloroanthraquinones, that is a dramatic switch-over from hydrogen abstraction to electron transfer would be induced by mixing of $n\pi^*$ character with $\pi\pi^*$ character in the lowest triplet state. If this were correct, the much shorter lifetimes of the lowest triplet states of α-chloroanthraquinones might be attributed to the formation of an exciplex between ethanol and triplet $\pi\pi^*$ α-chloroanthraquinones, because the rate of photoreduction was enhanced by the addition of TEA and it was confirmed that the photoreduction originated via the formation of the exciplex between TEA and lowest triplet α-chloroanthraquinones [13]. Moreover, the quantum yield of the photoreduction of 1,8-DCAQ (T_1, $\pi\pi^*$) without TEA should be greater than the quantum yields of 1-CAQ and 1,5-DCAQ (T_1, mixed $n\pi^*-\pi\pi^*$). In contrast, the latter values were 25 times greater than the quantum yield of the former. Thus, we suspect the electron transfer mechanism suggested by Inoue *et al.* to be correct.

The absence of electron transfer from ethanol to triplet α-chloroanthraquinones is also supported by the following facts. (1) We observed the build-up and decay of the absorption due to the second triplet state (T_2) of α-chloroanthraquinones on the picosecond time scale [14]. The decay of the T_2 state was accompanied by the build-up of the lowest triplet state (T_1). No absorption due to an exciplex between ethanol and triplet α-chloroanthraquinones was observed. (2) Nanosecond laser photolysis revealed that the hydrogen-atom abstraction of α-chloroanthraquinones from ethanol originates from the T_1 state, in spite of its mixed $n\pi^*-\pi\pi^*$ or $\pi\pi^*$ character [8]. The rates of hydrogen-atom abstraction decreased with an increase in the $\pi\pi^*$ character of the T_1 state, *i.e.* 2.3×10^6 s^{-1}, 1.4×10^6 s^{-1} and 1.6×10^4 s^{-1} for 1-CAQ, 1,5-DCAQ and 1,8-DCAQ respectively. The value for 1,8-DCAQ was two orders of magnitude smaller than the values for 1-CAQ and 1,5-DCAQ, in accordance with the results of Porter and Suppan [15] and

Formosinho [16]. They observed that $\pi\pi^*$ states of substituted ketones have an intrinsic reactivity for hydrogen abstraction which is 10^{-2} - 10^{-4} times lower than that of the $n\pi^*$ states.

4.2. Dehydrochlorination reactions

The photochemical dehydrochlorination was observed not only in ethanol, but also in benzene and acetonitrile. The result of GC–MS analysis led us to the conclusion that only AQ (not deuterated AQ) was produced upon the 450 nm photolysis of 1-$CAQH_2$ in benzene-d_6. Thus, if the solvent participates in the reaction, a possible reaction mechanism is given by the following scheme.



Scheme 1.

In this mechanism, the formation of AQ via intermediate I (anthrasemiquinone radical) may be excluded, based on the fact that no AQH_2 was detected. If AQ is produced via intermediate II, AQ (not deuterated AQ) is produced in benzene-d_6, in accordance with the results of GC–MS analysis. However, this mechanism may also be excluded, because photolysis of 2-$CAQH_2$ does not give rise to the formation of AQ.

Thus, the probable mechanism is dehydrochlorination via the intramolecular elimination of hydrogen chloride. Since dehydrochlorination was only observed for α-chloroanthrahydroquinones, this reaction may be affected by the proximity effect of the chlorine atom: the structural proximity of the hydroxyl group to the chlorine atom may make possible the intramolecular elimination of hydrogen chloride. For 2-$CAQH_2$, therefore, it is expected that the hydroxyl group and the chlorine atom are located too far apart for intramolecular dehydrochlorination to occur.

As can be seen from Fig. 3(b), the rate of dehydrochlorination in ethanol (ϵ = 24.55) is faster than the dehydrochlorinations in benzene (ϵ = 2.275) and acetonitrile (ϵ = 37.5), while the dielectric constant (ϵ) of the solvent does not affect the reaction. Since ethanol is known to be a protic solvent with high hydrogen-bonding ability, the much faster reaction in this

solvent might be indicative of the enhancement in intramolecular hydrogen bonding between the hydroxyl group and the chlorine atom of 1-$CAQH_2$, resulting in the acceleration of the intramolecular dehydrochlorination.

An alternative explanation might be that the formation of a cyclic intermolecular hydrogen bond involving ethanol, the chlorine atom and the hydroxyl group of 1-$CAQH_2$ accelerates the intermolecular elimination of hydrogen chloride. In this case, if a proton of the hydroxyl group of 1-$CAQH_2$ is transferred to the solvent immediately after the intermolecular elimination of hydrogen chloride, the net reaction appears to be an intramolecular elimination of hydrogen chloride.

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