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PHOTOCHEMICAL REACTIONS OF CHLOROANTHRAQUINONES

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Irradiation of 1,5-dichloroanthraquinone (1,5-DCAQ) with 366-nm light in ethanol gives anthrahydroquinone (AQH_2) as a final product. This is interpreted in terms of the following consecutive reactions; 1,5-DCAQ $\xrightarrow{h\nu}$ 1,5-dichloroanthrahydroquinone $\xrightarrow{h\nu}$ 1-chloroanthraquinone $\xrightarrow{h\nu}$ 1-chloroanthrahydroquinone $\xrightarrow{h\nu}$ anthraquinone $\xrightarrow{h\nu}$ AQH_2. Similar reactions were also observed for other α-chloroanthraquinones.

It is well known that the photoreduction of anthraquinone originates from its lowest triplet state of an nπ* character. From the measurements of phosphorescence spectra and triplet-triplet absorptions of α-halogenoanthraquinones, we have suggested that the lowest triplet states of α-halogenoanthraquinones are of ππ* character, while an nπ* triplet state is the lowest one for 2-chloroanthraquinone.1,2) Since much shorter lifetimes of the lowest triplet states and small phosphorescence quantum yields are obtained for α-halogenoanthraquinones, it is apparent that the depopulation of the lowest triplet state is mainly due to nonradiative processes. Although the reason for this was not clear, one possibility was thought to be the dehalogenation of α-halogenoanthraquinones, since we found the formation of anthraquinone during the irradiation of α-halogenoanthraquinones in ethanol with 366-nm light.1) This observation leads us to an extensive spectroscopic study on the photochemical reactions of chloroanthraquinones. Among these compounds, we have selected anthraquinone (AQ), 1-chloro-, 2-chloro-, 1,5-dichloro-, and 1,8-dichloroanthraquinones (1-CAQ, 2-CAQ, 1,5-DCAQ, and 1,8-DCAQ, respectively). The details of the methods of purification of these compounds have been given in our previous paper.2)

Spectral-grade ethanol (Nakarai) was used as the solvent without further purification. The sample solutions were degassed by several freeze-pump-thaw cycles. Ushio USH 500-D super-high pressure mercury and UXL-500D xenon lamps were used as the excitation sources. Light of an appropriate monochromatic wavelength was selected using a Shimazu-Bausch-Lomb monochromator or suitable color glass filters. Absorption and fluorescence spectra were taken using a Hitachi 200-20 spectrophotometer and a Shimazu RF-502 fluorescence spectrophotometer. All the experiments were carried out at room temperature and the concentrations of samples were $2\sim5\times10^{-4}$ mol/dm^3.

Fig. 1 shows the result obtained for AQ. The absorption band of AQ with λ_{max}=325 nm decreases upon irradiation with 366-nm light and the new band of the product with λ_{max}=382 nm increases with lapse of time, accompanied by an isosbestic point at 346 nm. By the introduction of air to the sample solution, the absorption spectrum of AQ appears at the expense of that of photoproduct. This is the well-known photoreduction of AQ,[3)] and the photoproduct is identified as anthrahydroquinone (AQH_2).

Irradiation of 2-CAQ with 366-nm light gave the reaction similar to that of AQ. The absorption and emission spectra of the photoproduct are slightly red-shifted compared with those of AQH_2. Thus one can safely conclude that the photoproduct is 2-chloroanthrahydroquinone.

Excitation of 1,5-DCAQ with 366-nm light gave rise to much complicated reactions as shown in Fig. 2. Upon irradiation, the absorption band of the reactant with λ_{max}=343 nm decreases and shifts to blue. The absorption band of spectrum D with λ_{max}=328 nm is very similar to that of AQ. The absorption bands of photoproducts also shift to blue, changing their intensities. Spectrum E with λ_{max}=382 nm is assigned to AQH_2, since the absorption and emission spectra of the final product are identical to those of AQH_2 and the photoproduct changes to AQ by the addition of air.

When irradiation is carried out with 313-nm light, the absorption spectrum of 1,5-DCAQ decreases and the new band of a product increases, accompanied by an isosbestic point at 363 nm (Fig. 3). There are no spectral shifts of the reactant and product during irradiation. Spectrum D with λ_{max}=392 nm is identical to spectra B and C in Fig. 2, and the photoproduct can be identified as 1,5-dichloroanthrahydroquinone (1,5-$DCAQH_2$), since it changes to 1,5-DCAQ by the addition of air.

Upon irradiation of 1,5-$DCAQH_2$ with 465-nm light, a new absorption band appears around 335 nm at the expense of 1,5-$DCAQH_2$ (Fig. 4). The photoproduct is identified as 1-CAQ by comparison of the absorption spectrum with that of the authentic sample of 1-CAQ.

The photochemical reactions of 1-CAQ with 366-nm excitation are also complicated, that is, spectral shifts of the absorption bands of 1-CAQ and photoproducts are observed during irradiation and the final photoproduct is AQH_2. However, irradiation of 1-CAQ with 313-nm light gave a simple reaction as shown in Fig. 5. The photoproduct has an absorption band with λ_{max}=386 nm

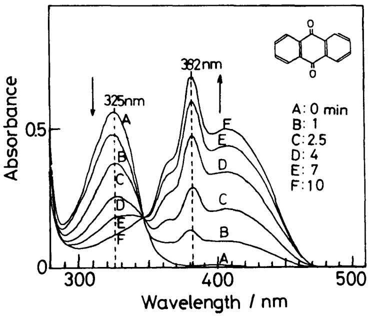

Fig. 1. Absorption spectral change of AQ in EtOH upon irradiation with 366-nm light at room temperature.

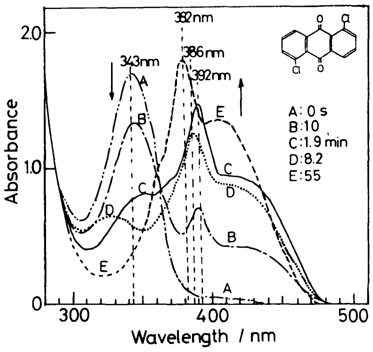

Fig. 2. Absorption spectral change of 1,5-DCAQ in EtOH upon irradiation with 366-nm light at room temperature.

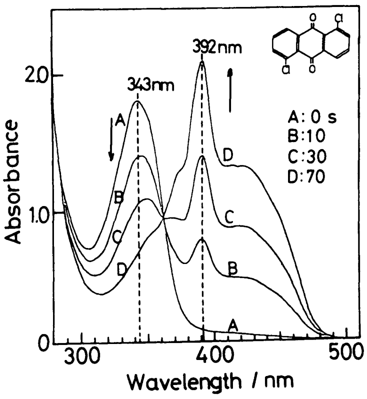

Fig. 3. Absorption spectral change of 1,5-DCAQ in EtOH upon irradiation with 313-nm light at room temperature.

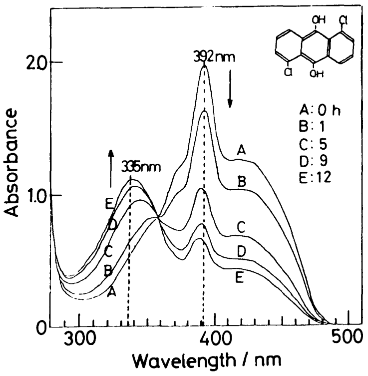

Fig. 4. Absorption spectral change of 1,5-$DCAQH_2$ in EtOH upon irradiation with 465-nm light at room temperature.

which is identical to that of spectrum D in Fig. 2, and it is identified as 1-CAQH$_2$, since it changes to 1-CAQ by the addition of air. As shown in Fig. 6, further irradiation of 1-CAQH$_2$ with 450-nm light gave a photoproduct with λ_{max}=325 nm which was identified as AQ by comparison of the absorption spectrum with that of the authentic sample. (Further irradiation of this photoproduct with 366-nm light yielded AQH$_2$.)

All the results so far obtained indicate that the photochemical reactions of 1,5-DCAQ with 366-nm excitation are interpreted in terms of the following consecutive reactions:

$$\text{1,5-DCAQ} \xrightarrow{h\nu} \text{1,5-DCAQH}_2 \xrightarrow{h\nu} \text{1-CAQ} \xrightarrow{h\nu} \text{1-CAQH}_2 \xrightarrow{h\nu} \text{AQ} \xrightarrow{h\nu} \text{AQH}_2.$$

This is reasonable, since AQ, 1-CAQ, 1,5-DCAQ, and their halogenoanthrahydroquinones have appreciable absorptions at 366 nm.

The photochemical reactions of 1,8-DCAQ with 366-nm excitation are a little different from those of 1,5-DCAQ. Although the spectral shifts of the absorption bands of the reactant and products are observed during irradiation, the absorption around 300 nm increases initially and then decreases. This absorption is also observed when the sample is irradiated with 313-nm light as shown in Fig. 7. There are no spectral shifts of the absorption spectra of the reactant and product, but one can not observe such clear isosbestic points as can be seen in Figs. 2 and 5. The spectrum of the final photoproduct with λ_{max}=392 nm is assigned to 1,8-dichloroanthrahydroquinone (1,8-DCAQH$_2$), since it changes to 1,8-DCAQ by the addition of air. By the 465-nm excitation, the absorption spectrum of 1,8-DCAQH$_2$ changes to that of 1-CAQ, accompanied by an isosbestic point at 358 nm.

The absorption band around 300 nm decreases by the dark reaction as shown in Fig. 8. Upon 12-min irradiation of 1,8-DCAQ with 366-nm light, one can see the spectral increase around 300 nm instead of a small yield of 1,8-DCAQH$_2$, compared to that of 1,5-DCAQH$_2$. By the dark reaction, the absorption around 300 nm decreases and those of 1,8-DCAQ and 1,8-DCAQH$_2$ increase simultaneously, accompanied by an isosbestic point at 322 nm. This suggests that the absorption around 300 nm is due to a precursor which gives the reactant and product simultaneously. A probable candidate for this precursor may be a complex of two 1,8-dichloroanthra-

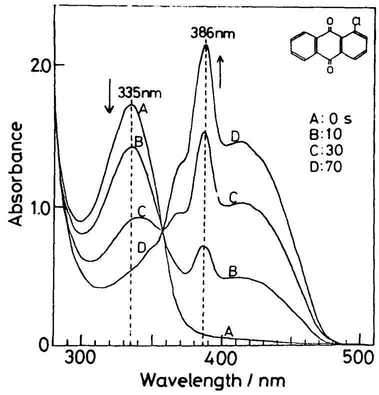

Fig. 5. Absorption spectral change of 1-CAQ in EtOH upon irradiation with 313-nm light at room temperature.

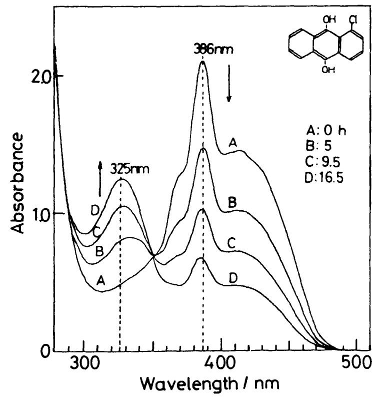

Fig. 6. Absorption spectral change of 1-CAQH$_2$ in EtOH upon irradiation with 450-nm light at room temperature.

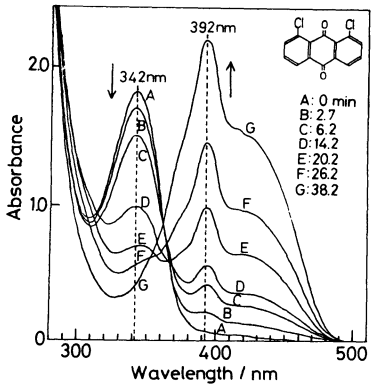

Fig. 7. Absorption spectral change of 1,8-DCAQ in EtOH upon irradiation with 313-nm light at room temperature.

semiquinone radicals (1,8-DCAQH·). This is based on the following reasons: (1) According to the mechanism established by Tickle and Wilkinson for AQ photoreduction,[3)] two anthrasemiquinone radicals (AQH·) disproportionate to form AQH_2 and AQ. (2) Photodimers of anthracenes have absorptions around 300 nm.[4,5)]

An alternative assignment is that the precursor is 1,8-DCAQH·. However, this is unreasonable, since we could not observe any absorption band at about 360∿390 nm and that with peaks at 631 and 687 nm for AQH·, which were observed by Bridge and Porter,[6)] and Carlson and Hercules,[7)] respectively.

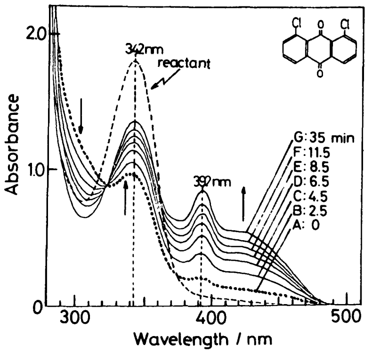

Fig. 8. Dark reaction of 1,8-$DCAQH_2$ in EtOH after 12-min irradiation with 366-nm light at room temperature.

The relative rates of photoreduction of AQ and chloroanthraquinones were roughly estimated by measuring the decrease and/or buildup of absorptions of reactants and/or photoproducts. The values were in the order of 1 (AQ), 0.77 (1-CAQ), 1.1 (1,5-DCAQ), and 0.014 (1,8-DCAQ), which is roughly the same order in the decrease of the lowest triplet lifetimes, i.e., 3400∿3200 (AQ), 170∿160 (1-CAQ), 250∿260 (1,5-DCAQ), and 40∿50 μs (1,8-DCAQ). Thus one can safely conclude that much shorter lifetimes of the lowest triplet state and small phosphorescence quantum yields are not due to the photoreduction but are due to modification of the geometrical molecular structure by the interaction of the carbonyl group with halogen atom(s), causing the lowest triplet states to be of $\pi\pi^*$ character with short lifetimes.[2)]

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