

Short Communication

Primary photoreduction of 1,8-dichloroanthraquinone by triethylamine studied by laser spectroscopy

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1. Introduction

The photoreduction of benzophenone by amines has been investigated extensively and the generally accepted mechanism is that an electron is transferred from amine to triplet $n\pi^*$ benzophenone, forming a charge transfer complex or an ion pair, followed by proton transfer [1 - 4]. For α -chloroanthraquinones and α -bromoanthraquinones we found that photoreductions still originate from the lowest triplet state (T_1) in spite of its mixed $n\pi^*-\pi\pi^*$ or $\pi\pi^*$ character [5, 6]. No evidence for electron transfer from ethanol to triplet α -halogenoanthraquinones as suggested by Inoue *et al.* [7] was obtained.

The quantum yields of the photoreduction in toluene were 0.3, 0.2 and 0.04 for anthraquinone, 1-chloroanthraquinone and 1-bromoanthraquinone respectively, while they increased to 0.6, 0.7 and 0.7 respectively on the addition of 0.2 M triethylamine (TEA) [6]. Thus it might be expected that an exciplex or an ion pair is produced in the photolysis of TEA-anthraquinone systems. In fact we observed the formation of exciplexes of TEA-anthraquinone and TEA-1-chloroanthraquinone in toluene and ethanol on the first picosecond time scale [8].

It is expected that the second triplet states (T_2) exist below the lowest excited singlet states of anthraquinones [9]. Since the transient absorption due to the T_2 state was clearly observed for 1,8-dichloroanthraquinone (DCAQ) [9], in this paper we report our finding that electron transfer does occur from TEA to the $T_1(\pi\pi^*)$ state but not to the $T_2(n\pi^*)$ state of DCAQ.

2. Experimental details

The details of the methods of preparation of DCAQ have been given elsewhere [5]. Guaranteed reagent grade TEA (Wako) was refluxed over calcium hydride and distilled under a nitrogen atmosphere. Scintillation grade toluene (Dojin) and spectral grade ethanol (Nakarai) were used as solvents without further purification.

All transient absorption spectra were measured at room temperature. Samples were excited using the second harmonic (347.2 nm) from a picosecond mode-locked ruby laser [10] and a nanosecond Q-switched ruby laser [6] and the time resolutions were 30 ps and 20 ns respectively. The sample solutions were placed in a cell of path length 2 mm for the picosecond photolysis and in a cell of path length 10 mm for the nanosecond photolysis; the latter were deaerated while the former were not.

3. Results and discussion

The picosecond photolysis of 1.1 M DCAQ in 1 M TEA-toluene gives the absorption spectra shown in Figs. 1(a) and 1(b). The absorption spectrum at 100 ps delay is identical with that obtained in the absence of TEA [9], where band A_1 decreased in intensity with the build-up of band B. Bands A_1 and B were assigned to the T_2 and T_1 states of DCAQ respectively, and band A_2 was assigned to a superposition of the absorptions of the T_2 and T_1 states. Thus it can be concluded that a new intermediate with $\lambda_{\max} = 566$ nm (band C) is produced at the expense of the T_1 state of DCAQ. A similar result was also obtained in ethanol, where the new intermediate had an absorption maximum at 540 nm.

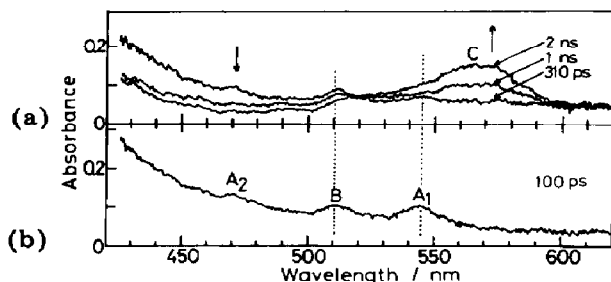


Fig. 1. The transient absorption spectra of DCAQ (1.1×10^{-3} M) in 1 M TEA-toluene solution obtained by picosecond laser photolysis.

In Fig. 2(a) we show the result obtained by the nanosecond laser photolysis of DCAQ in 0.2 M TEA-toluene. The absorption spectrum taken immediately after the laser pulse is identical with that observed on picosecond laser photolysis. Compared with band C, band D at delay times longer than $1.25 \mu\text{s}$ is shifted to the blue by about 5 nm. As can be seen in Fig. 2(b), the transient absorption at 570 nm (full circles) appeared within the duration of a nanosecond laser pulse and it increased initially and then decreased gradually. The decay of band D was accompanied by the build-up of a new absorption at about 440 nm (band E in Fig. 2(a)). This band is identical with the absorption due to 1,8-dichloroanthrahydroquinone.

In ethanol we obtained similar results: bands C and D were observed at 540 and 530 nm respectively. However, the formation of 1,8-dichloroanthrahydroquinone could not be observed up to delay times of $200 \mu\text{s}$. Accordingly, the absorbance at 530 nm increased for $4 \mu\text{s}$ and the maximum

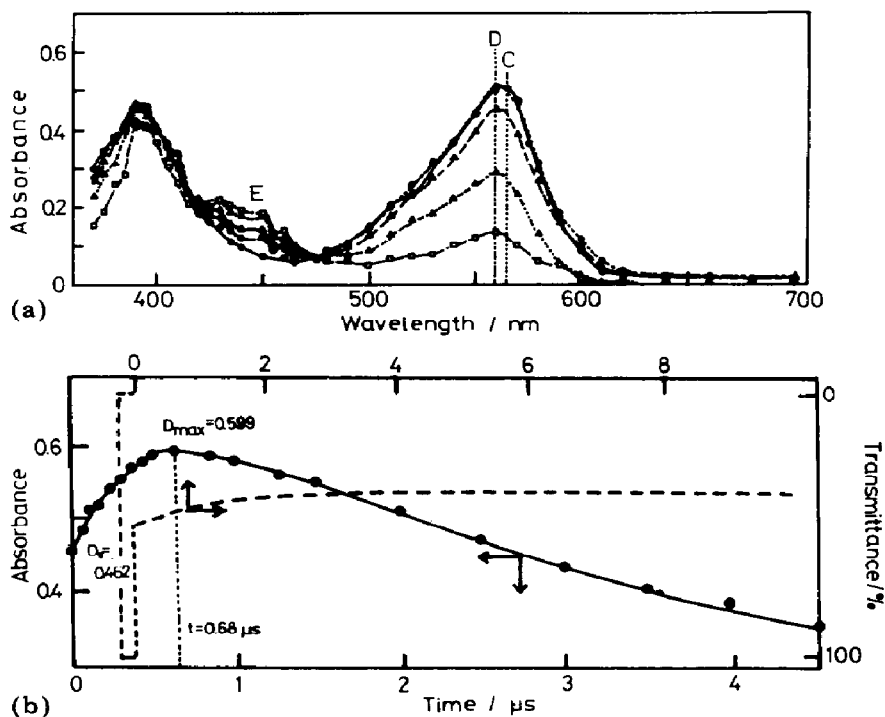


Fig. 2. (a) The transient absorption spectra of DCAQ (1.8×10^{-4} M in toluene) in 0.2 M TEA-toluene solution obtained by nanosecond laser photolysis (\circ — \circ , $t = 0$; \bullet — \bullet , $t = 1.25 \mu\text{s}$; \triangle — \triangle , $t = 2.5 \mu\text{s}$; \blacktriangle — \blacktriangle , $t = 10 \mu\text{s}$; \square — \square , $t = 45 \mu\text{s}$). (b) The time variation of the absorption at 570 nm in toluene (\bullet , $[\text{DCAQ}] = 1.8 \times 10^{-4}$ M) and at 530 nm in ethanol ($---$, $[\text{DCAQ}] = 2.9 \times 10^{-4}$ M in ethanol). The full curve in (b) is the best fit obtained from the equation in the text.

absorbance persisted beyond $200 \mu\text{s}$ with no measurable decay (broken line in Fig. 2(b)).

Except for band E, the absorption spectra in Fig. 2(a) are very similar to those of the DCAQ anion radical (DCAQ^-) produced upon photolysis of DCAQ in alkaline ethanol (ethanol-1 N aqueous sodium hydroxide, volume ratio 20:1) at room temperature and by γ radiolysis of DCAQ in 2-methyltetrahydrofuran at 77 K.

Although no transient photocurrent was detected in toluene, one was observed in ethanol. However, the rise and decay of this photocurrent were different from those of bands C and D. Moreover, the intensity of the initial photocurrent was increased during the repeated measurements, indicating that the photocurrent is due to some electrochemically produced ionic species.

Based on the above results and those for anthraquinone-TEA and 1-chloroanthraquinone-TEA photolyses [8], it is reasonable to conclude the following.

(1) The intermediate observed in the picosecond photolysis is identical with that produced within the duration of a nanosecond pulse. This

intermediate may be assigned to a triplet exciplex between triplet DCAQ(T_1) and TEA.

(2) In ethanol, the exciplex generates a contact ion pair between DCAQ $^-$ and the cation radical of TEA (TEA $^+$). Using simple kinetics, the broken line in Fig. 2(b) can be expressed by a single exponential function with a rate constant of $7.2 \times 10^5 \text{ s}^{-1}$ for the formation of the contact ion pair. This contact ion pair may be relatively stable in a polar solvent such as ethanol, because it was not observed to decay up to 200 μs delay. Since 1,8-dichloroanthrahydroquinone was produced upon the steady-state photolysis of DCAQ-TEA in ethanol, the contact ion pair may finally be quenched by a proton transfer from TEA $^+$ to DCAQ $^-$, generating neutral 1,8-dichloroanthrasemiquinone radical and triethylamine radical. In fact we found that the contact ion pair decayed according to a single exponential function, with a lifetime of 60 ms, and we observed a build-up of absorption due to 1,8-dichloroanthrahydroquinone.

(3) In toluene, the exciplex also generates a contact ion pair followed by proton transfer on the microsecond time scale. If this mechanism is correct and the efficiency for electron transfer is unity, the absorbance at time t is given by

$$D(t) = D_0 \left\{ \left(1 - \frac{\alpha k_1}{k_1 - k_2} \right) \exp(-k_1 t) + \frac{\alpha k_1}{k_1 - k_2} \exp(-k_2 t) \right\}$$

where D_0 is the absorbance of the exciplex at $t = 0$, k_1 and k_2 are the rate constants for the formation and decay of the contact ion pair, and α is the ratio of the extinction coefficient of the contact ion pair to that of the exciplex. If the efficiency of the contact ion-pair formation is less than unity, k_1 and α should be read as τ^{-1} and $\beta\alpha$ respectively, where τ is the lifetime of the exciplex and β is the efficiency for the contact ion-pair formation. Since the quantum yield for the photoreduction of DCAQ-TEA in toluene is estimated to be larger than 0.7, and since the efficiency for the proton transfer in a contact ion pair of *p*-chloranil-durene is thought to be smaller than unity [11], this assumption may be reasonable.

We determined α from the value of D_{max} as a function of k_1 and k_2 (cf. Fig. 2(b)), and the rate constants can be determined by the best fit of the theoretical $D(t)$ curve to the experimental values. A typical D curve is shown in Fig. 2(b) (full curve). The best fitted values were $k_1 = (2.8 \pm 0.2) \times 10^6 \text{ s}^{-1}$, $k_2 = (1.6 \pm 0.2) \times 10^5 \text{ s}^{-1}$ and $\alpha = 1.44$.

Our results are a little different from those found for benzophenone-amine mixtures (amine \equiv TEA, *N,N*-diethylaniline, *N,N*-dimethylaniline or 1,4-diazabicyclo[2.2.2]octane (Dabco)), reported by Peters and coworkers [3, 4]. In their first two papers [3], they proposed that an electron transfers from amine to benzophenone forming an exciplex. Then they changed the assignment of the exciplex to that of a solvent-separated ion pair [4]; however, no explanation has yet been given. Presumably their assignment to the solvent-separated ion pair may be based on their finding that spectral shifts

of anion-radical-like absorptions were observed in acetonitrile on the picosecond time scale.

In our present studies both in toluene and ethanol, however, no spectral shift was observed on the picosecond time scale. Based on the discussion in our previous paper [8], we suggest that the exciplex was produced initially in toluene or ethanol. The spectral shifts observed by Peters and coworkers might be caused by a special solvent effect in acetonitrile. The details will be published elsewhere.

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