SPECTROSCOPIC STUDIES ON THE PRIMARY PROCESSES IN THE PHOTOREDUCTION OF α-CHLOROANTHRAQUINONES IN ETHANOL AT ROOM TEMPERATURE

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Summary

The hydrogen-atom abstraction of 1,5-dichloroanthraquinone in ethanol at room temperature was studied by picosecond and nanosecond laser photolysis. By combining these results with those previously obtained for 1-chloroanthraquinone and 1,8-dichloroanthraquinone, it was concluded that the picosecond laser photolysis gave the transient absorption spectra due to the second and/or lowest triplet states of α-chloroanthraquinones. Nanosecond laser photolysis revealed that the hydrogen-atom abstraction of α-chloroanthraquinones from ethanol originated from the T_1 state in spite of the mixed $n\pi^*-\pi\pi^*$ or $\pi\pi^*$ character of the lowest triplet state (T_1). The reactivity for the hydrogen-atom abstraction decreased with increasing $\pi\pi^*$ character of the T_1 state.

1. Introduction

The photochemical behaviour of organic carbonyl compounds depends on the nature of their excited states, and it is useful to classify electronically excited states in terms of electronic configurations [1 - 4]. Since the rate of intersystem crossing in aromatic carbonyl compounds is very rapid [5 - 9], the most important electronic configurations are triplet $n\pi^*$ and $\pi\pi^*$, and the hydrogen-atom abstraction by the lowest triplet $n\pi^*$ state of aromatic ketones is well known. For instance, anthraquinone (AQ) in the triplet $n\pi^*$ state abstracts a hydrogen atom from solvent molecules to give the ketyl radical, followed by the disproportionation of anthrasemiquinone radical (AQH·) yielding anthrahydroquinone (AQH$_2$) and AQ [10 - 12].

When $n\pi^*$ and $\pi\pi^*$ triplet states are very close to each other, it is possible to shift the relative energies of the triplet states by changing the solvent [13 - 16]. Fortunately, this may also be achieved by substitution in the molecule itself, this being particularly true of α-halogenoanthraquinones (the

1-chloro, 1,5-dichloro and 1,8-dichloro compounds (1-CAQ, 1,5-DCAQ and 1,8-DCAQ respectively) and the 1-bromo, 1,5-dibromo and 1,8-dibromo compounds) which have the lowest triplet states (T_1) with mixed $n\pi^*-\pi\pi^*$ or $\pi\pi^*$ character, while the $n\pi^*$ triplet states are the lowest in energy for AQ and β-halogenoanthraquinones (2-chloroanthraquinone (2-CAQ) and 2-bromoanthraquinone) [17]. Moreover, we observed that steady state photolysis of α-halogenoanthraquinones with 366 nm light in ethanol at room temperature gave rise to the formation of α-halogenoanthrahydroquinones followed by photochemical dehydrohalogenation giving the corresponding anthraquinones containing one less halogen atom than the original compounds; the final photoproduct was AQH_2. No dehalogenation was observed upon 366 nm photolysis of 2-CAQ and 2-bromoanthraquinone. The quantum yields of photoreduction decreased with increasing $\pi\pi^*$ character of the T_1 states [18 - 20].

Since Inoue *et al.* [21] proposed that the photoreduction of halogeno-anthraquinones (perfluoroanthraquinone, 1,2,3,4-tetrafluoroanthraquinone and 1,2,3,4-tetrachloroanthraquinone) originates via direct electron transfer from ethanol to their triplet $\pi\pi^*$ state, this paper deals with the picosecond and nanosecond laser photolysis of 1,5-DCAQ; in conjunction with our preliminary results for 1-CAQ and 1,8-DCAQ [22], the full kinetic discussion for the primary process of the photoreduction will be given, in order to show that the hydrogen-atom abstraction of α-chloroanthraquinones (1-CAQ, 1,5-DCAQ and 1,8-DCAQ) from ethanol originates from the T_1 state in spite of its mixed $n\pi^*-\pi\pi^*$ or $\pi\pi^*$ character and that no electron transfer occurs from ethanol to triplet α-chloroanthraquinones.

2. Experimental details

We have previously given the details of the method of preparation of 1,5-DCAQ [17]. Spectral grade ethanol (Nakarai) and scintillation grade toluene (Dojin) were used as the solvents without further purification.

All the transient absorption spectra were measured at room temperature. The second harmonics (347.2 nm) from picosecond mode-locked and nanosecond Q-switched ruby lasers were used to excite the sample. The details of our picosecond transient absorption spectrometer, which has a 30 ps instrumental time constant, have been given previously [23]. The Q-switched ruby laser used for the nanosecond photolysis was constructed in our laboratory [22, 24]. The half-peak duration of the second harmonic was 20 ns. The concentration of 1,5-DCAQ for the picosecond laser photolysis was 1.2×10^{-3} M in a cell of path length 2 mm, and the sample solutions were not deaerated. In the nanosecond photolysis, the deaerated sample concentration was 2×10^{-4} M in a cell of path length 10 mm.

3. Results

As reported in a previous paper [22], picosecond laser photolysis of 1,8-DCAQ in ethanol at room temperature gave rise to the appearance of

three absorption band maxima (bands A_1, A_2 and B); band A_1 at 536 nm decreased with the build-up of band B at 502 nm. Moreover, the existence of isosbestic points at 492 and 511 nm could clearly be observed. Since band B is characteristic of the triplet–triplet (T' ← T_1) absorption of 1,8-DCAQ [17], and since the decay constant of band A_1 was equal to the rate constant for the build-up of band B, we proposed that band A_1 was due to the second triplet state (T_2) of 1,8-DCAQ [22, 25, 26]. (Band A_2 at about 460 nm was assigned to a superposition of the absorptions due to T_2 and T_1 states [26].)

Figure 1 shows the transient absorption spectra of 1,5-DCAQ in ethanol at room temperature, observed by picosecond laser photolysis. (The structural formula for 1,5-DCAQ is inserted in Fig. 1.) No A_1-like absorption band was observed; however, band A_2 in Fig. 1 could also be assigned to a superposition of the absorptions due to the T_2 and T_1 states of 1,5-DCAQ. A similar result was obtained for 1-CAQ [22, 26].

In Fig. 2, we display the time variation of the transient absorptions of 1,5-DCAQ in ethanol at room temperature, recorded by nanosecond laser photolysis. A comparison of the T' ← T_1 absorption of 1,5-DCAQ (spectrum b [17]) with spectrum a at 50 ns delay suggests that it is also due to the T_1 state of 1,5-DCAQ. Since AQH· has strong absorption bands at 360 - 390 nm and weak bands at 631 - 687 nm [12, 27, 28], both spectrum c and spectrum d can be assigned to the absorption spectrum of 1,5-dichloro-anthrasemiquinone radical (1,5-DCAQH·), and spectrum e is identical with the absorption of 1,5-dichloroanthrahydroquinone (1,5-DCAQH₂) [18, 19]. The oscilloscope traces of the transmittance at 380 nm (full curves in Fig. 3) support this assignment; that is, there exist two decay components and one non-decay component. (Compared with the T' ← T_1 absorptions of AQ and β-halogenoanthraquinones, spectra a and b have a rather sharp absorption
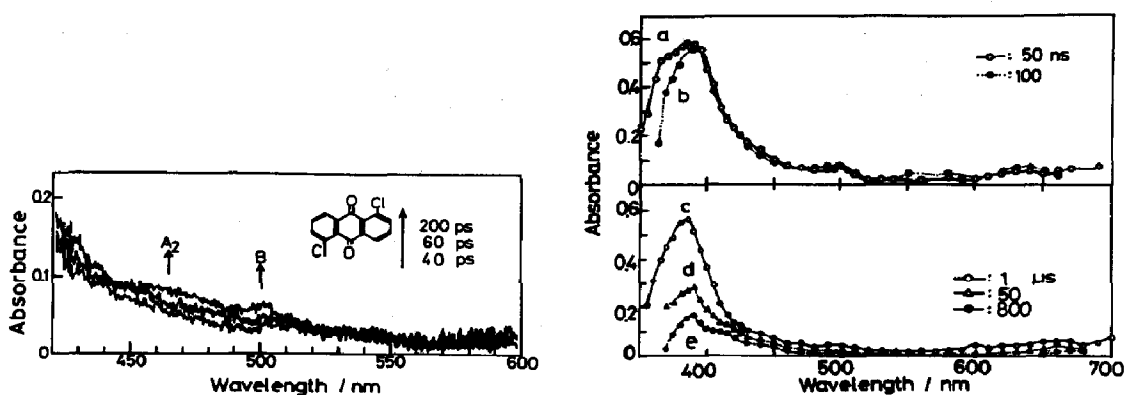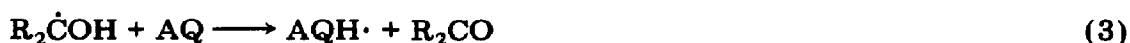

Fig. 1. Time-resolved absorption spectra of 1,5-DCAQ in ethanol at room temperature obtained by picosecond laser photolysis.

Fig. 2. Time variation of the transient absorptions of 1,5-DCAQ (spectra a, c, d and e) in ethanol at room temperature, obtained by nanosecond laser photolysis. Spectrum b is the T' ← T_1 absorption of 1,5-DCAQ at 100 ns delay in EPA (ether–isopentane–ethanol (5:5:2 by volume)) at 77 K.

band at about 500 nm. These bands are characteristic of the $T' \leftarrow T_1$ absorptions of α-chloroanthraquinones and α-bromoanthraquinones [17]. In spectra c and d, the existence of such a band remains uncertain. However, the decay curves in Fig. 3 (curves a and b) indicate that the contribution of the $T' \leftarrow T_1$ absorption to spectra c and d is negligible. Thus, we assigned these spectra to 1;5-DCAQH·.)

According to the mechanism established by Tickle and Wilkinson [11], the photoreduction of AQ in alcohol (R_2CHOH) is given by

$$AQ^*(T_1) \xrightarrow{k} AQ \tag{1}$$

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

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

$$2AQH\cdot \xrightarrow{k_D} AQ + AQH_2 \tag{4}$$

where $AQ^*(T_1)$ is triplet AQ. Since it is estimated that more than 90% of ground state 1,5-DCAQ is excited by a nanosecond laser pulse, the formation of 1,5-DCAQH· via reaction (3) may be negligible. Thus, the absorbance at time t in curve a in Fig. 3 can be given by

$$A = C_0 l(\epsilon_1 - \alpha\epsilon_2) \exp\{-(k + k_R[R_2CHOH])t\} + \alpha\epsilon_2 C_0 l \tag{I}$$

where C_0 is the concentration of triplet 1,5-DCAQ at $t = 0$, l is the optical path length (1 cm), ϵ_1 and ϵ_2 are the extinction coefficients of triplet 1,5-DCAQ and 1,5-DCAQH· respectively and $\alpha = k_R[R_2CHOH]/(k + k_R[R_2CHOH])$ is the efficiency for the formation of 1,5-DCAQH· in reactions (1) and (2).

We determined $\alpha\epsilon_2 C_0 l = A_\infty$ from the absorbance at 3.5 μs in Fig. 3, curve a, and the plots of $-\ln(A - A_\infty)$ *versus* t gave a straight line as shown in Fig. 4, line a. On account of the decrease in the absorbance due to
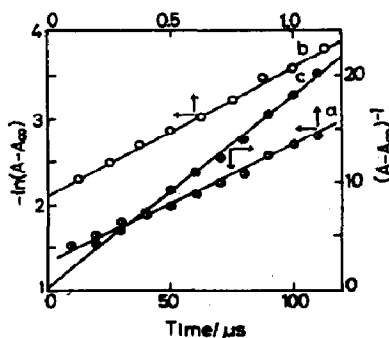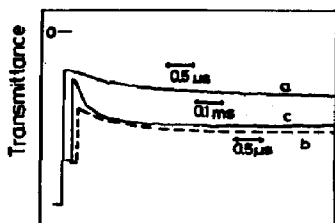

Fig. 3. Oscilloscope traces of the transmittances at 380 nm (———) and 420 nm (– – –).

Fig. 4. First-order (lines a and b) and second-order (line c) plots for the decay of triplet 1,5-DCAQ and 1,5-DCAQH· respectively. (Lines a and c, at 380 nm; line b, at 420 nm.)

1,5-DCAQH·, the value of A_∞ mentioned above contains some errors. However, the absorbance at 420 nm (curve b in Fig. 3) shows no appreciable decrease due to reaction (4), giving the correct value of A_∞. Thus we have also determined the decay constant of triplet 1,5-DCAQ from the change in absorbance at 420 nm (line b in Fig. 4). Lines a and b gave nearly equal values for the decay constant. Thus, the average value of $k + k_R[R_2CHOH]$ in ethanol determined at various wavelengths is listed in Table 1, together with the decay constant of the T_1 states in toluene. (In Table 1, we also show the triplet decay constants of 1-CAQ and 1,8-DCAQ [22].)

The decay of the long-lived component was analysed from Fig. 3, curve c, in which one decay component and one non-decay component can be observed. On this time scale, the absorption due to the T_1 state may be negligible; thus, A is given by

$$\frac{1}{A - A_\infty} = \frac{2k_D}{(2\epsilon_2 - \epsilon_3)l} t + \frac{2}{[AQH\cdot]_0 (2\epsilon_2 - \epsilon_3)l} \tag{II}$$

where $[AQH\cdot]_0$ denotes the concentration of 1,5-DCAQH· at $t = 0$ and ϵ_3 is the extinction coefficient of 1,5-DCAQH$_2$. Plots of $1/(A - A_\infty)$ versus t gave a straight line, as shown in Fig. 4, line c, and the value obtained for $2k_D/(2\epsilon_2 - \epsilon_3)l$ was $1.6 \times 10^5 \, s^{-1}$. A similar result was also obtained for 1-chloroanthrasemiquinone radical (1-CAQH·), giving the value $2k_D/(2\epsilon_2 - \epsilon_3)l = 1.1 \times 10^5 \, s^{-1}$ [22].

In order to estimate the value of k_D, the following two procedures were carried out:

(1) Estimation from ϵ_2. From eqn. (4), $2\epsilon_2 - \epsilon_3$ may be equal to $2\epsilon_2(A_0 - A_\infty)/A_0$, where A_0 is the absorbance at $t = 0$. Thus $k_D = 8.4\epsilon_2 l \times 10^4 \, M^{-1} \, s^{-1}$ for 1-CAQH· and $1.1\epsilon_2 l \times 10^5 \, M^{-1} \, s^{-1}$ for 1,5-DCAQH·. Assuming ϵ_2 for 1-CAQH· and 1,5-DCAQH· to be equal to the ϵ_2 for the semiquinone radicals of anthraquinone-1-sulphonate and anthraquinone-2-

TABLE 1

Decay constants of triplet anthraquinones (k_T) and their semiquinone radicals (k_D)

	k_T (s^{-1})		k_D (M^{-1} s^{-1})	
	In ethanol	In toluene	From ϵ_2	From ϵ_3
1-CAQ	2.3×10^6 $(0.43 \, \mu s)^a$	5.59×10^4 $(17.9 \, \mu s)^a$	9.2×10^8	1.2×10^9 $(14500)^b$
1,5-DCAQ	1.6×10^6 $(0.64 \, \mu s)^a$	4.2×10^5 $(2.4 \, \mu s)^a$	1.2×10^9	1.5×10^9 $(9800)^b$
1,8-DCAQ	4.0×10^5 $(2.5 \, \mu s)^a$	3.0×10^5 $(3.3 \, \mu s)^a$	5.8×10^8 2.2×10^9 $(\epsilon_2 = 42000)^c$ to 4.1×10^9 $(\epsilon_2 = 70000)^c$	

[a]Triplet lifetimes.
[b]Extinction coefficients of the anthrasemiquinone radicals in M^{-1} cm^{-1}.
[c]Estimated from eqn. (III).

sulphonate, i.e. $\epsilon_2 = 1.1 \times 10^4\,\mathrm{M^{-1}\,cm^{-1}}$ at about 380 nm [28], the values of k_D shown in Table 1 were obtained.

(2) Estimation from ϵ_3. The alternative expression $2\epsilon_2 - \epsilon_3 = \epsilon_3 \times (A_0 - A_\infty)/A_\infty$ gives $k_D = 1.7\epsilon_3 l \times 10^5\,\mathrm{M^{-1}\,s^{-1}}$ for 1-CAQH· and $1.9\epsilon_3 l \times 10^5\,\mathrm{M^{-1}\,s^{-1}}$ for 1,5-DCAQH·. Since the results of the steady state photolysis indicate the value of ϵ_3 at 380 nm to be $7 \times 10^3\,\mathrm{M^{-1}\,cm^{-1}}$ for 1-chloroanthrahydroquinone (1-CAQH$_2$) and $8 \times 10^3\,\mathrm{M^{-1}\,cm^{-1}}$ for 1,5-DCAQH$_2$ [18, 19], the ϵ_2 and k_D listed in Table 1 were obtained.

For 1,8-DCAQ, the long-lived component, i.e. 1,8-dichloroanthrasemiquinone radical (1,8-DCAQH·), decayed slowly and the non-decay component cannot be observed [22]; the plots of $1/A$ versus t gave $k_D/\epsilon_2 l = 5.3 \times 10^4\,\mathrm{s^{-1}}$, and thus $k_D = 5.8 \times 10^8\,\mathrm{M^{-1}\,s^{-1}}$ on assuming $\epsilon_2 = 1.1 \times 10^4\,\mathrm{M^{-1}\,cm^{-1}}$.

If we assume a constant extinction coefficient for the triplet states, the value of ϵ_2 may be expressed by the following equation:

$$\epsilon_2 = \frac{A_\infty/A_0}{(A_\infty/A_0)'}\,\frac{\Phi'}{\Phi}\,\epsilon_2' \tag{III}$$

where the primed values are those for 1-CAQ (or 1,5-DCAQ); A_∞/A_0 were calculated from curve a in Fig. 3 and the decay curves of triplet 1-CAQ and 1,8-DCAQ in ref. 22, and Φ are the quantum yields of photoreduction of 1-CAQ, 1,5-DCAQ and 1,8-DCAQ [18, 19]. All results obtained so far are listed in Table 1, indicating that 1,8-DCAQH· decays following a second-order reaction with a rate constant k_D in the range from 5.8×10^8 to about $(2.2 - 4.1) \times 10^9\,\mathrm{M^{-1}\,s^{-1}}$.

4. Discussion

Picosecond laser photolysis gave the transient absorption spectra due to the second and/or lowest triplet states of α-chloroanthraquinones. No absorption due to the radical anions of chloroanthraquinones was observed. In the presence of 0.2 - 1 M triethylamine (TEA) in ethanol, we have actually observed the absorptions due to the ion pairs and/or exciplexes between the triplet state of chloroanthraquinones and TEA at about 495 nm for 1-CAQ [29], about 530 nm for 1,5-DCAQ [30] and about 540 nm for 1,8-DCAQ [31]. Since these absorptions were observed after the build-up of the T_1 states of 1-CAQ, 1,5-DCAQ and 1,8-DCAQ, similar absorptions might be observed on the picosecond time scale in ethanol without TEA, if the electron transfer mechanism proposed for perfluoroanthraquinone, 1,2,3,4-tetrafluoroanthraquinone and 1,2,3,4-tetrachloroanthraquinone by Inoue et al. [21] is correct. Since the 365 nm photolysis of 1,2,3,4-tetrachloroanthraquinone [32] gave results similar to those for 1-CAQ, 1,5-DCAQ and 1,8-DCAQ [18, 19], and since these α-chloroanthraquinones are thought to

be the model compounds for 1,2,3,4-tetrachloroanthraquinone, its photochemical and photophysical behaviour may be similar to those of the model compounds mentioned above. Thus we suspect that their suggestion may be incorrect, at least for 1,2,3,4-tetrachloroanthraquinone.

The triplet lifetimes of 1-CAQ and 1,5-DCAQ in ethanol are much smaller than those in toluene. This indicates that the hydrogen-atom abstraction from ethanol mainly affects the lifetime of the T_1 state in spite of its mixed $n\pi^*-\pi\pi^*$ character. For 1,8-DCAQ, the triplet ($\pi\pi^*$) lifetime in ethanol is of the same order as that in toluene. This means that the hydrogen-atom abstraction and other decay processes from the T_1 state compete with each other. These are consistent with the experimental finding that the quantum yields of photoreduction in ethanol are 1.0 for 1-CAQ, 0.9 for 1,5-DCAQ and 0.04 for 1,8-DCAQ [19], while the corresponding yields in toluene are 0.2, 0.2 and 0.009 [30]. Thus the rates of hydrogen abstraction in ethanol are estimated to be $2.3 \times 10^6 \, s^{-1}$, $1.4 \times 10^6 \, s^{-1}$ and $1.6 \times 10^4 \, s^{-1}$ for 1-CAQ, 1,5-DCAQ and 1,8-DCAQ respectively. From these results, it is concluded that the reactivity of α-chloroanthraquinones decreases with increasing $\pi\pi^*$ character of the T_1 state, in accordance with the results of Porter and Suppan [33] and Formosinho [34] who observed that the $\pi\pi^*$ states of substituted ketones have an intrinsic reactivity for hydrogen abstraction about 10^{-2} - 10^{-4} times lower than that of the $n\pi^*$ states.

The values of k_D for 1-CAQH·, 1,5-DCAQH· and 1,8-DCAQH· are nearly equal to the rate constants for the disproportionation reactions between anthrasemiquinone radicals to form anthrahydroquinones and anthraquinones, i.e. $1.3 \times 10^9 \, M^{-1} \, s^{-1}$ for AQH· [12], $3.0 \times 10^9 \, M^{-1} \, s^{-1}$ and $3.2 \times 10^9 \, M^{-1} \, s^{-1}$ for the semiquinone radicals of anthraquinone-1-sulphonate and anthraquinone-2-sulphonate respectively [28] and $7.0 \times 10^8 \, M^{-1} \, s^{-1}$ and $6.2 \times 10^8 \, M^{-1} \, s^{-1}$ for the semiquinone radicals of 1-piperidinoanthraquinone and 2-piperidinoanthraquinone respectively [28].

No absorption due to 1,8-dichloroanthrahydroquinone (1,8-DCAQH$_2$) was observed even at longer delay times. This is consistent with the result of steady state photolysis of 1,8-DCAQ [18, 19]: upon irradiation of 1,8-DCAQ in ethanol, we observed a spectral increase around 300 nm instead of a small yield of 1,8-DCAQH$_2$. The absorption around 300 nm decreased by a dark reaction and the absorptions 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 equal to the rate constant for the formation of 1,8-DCAQH$_2$ and 1,8-DCAQ, i.e. $5.8 \times 10^{-3} \, s^{-1}$. This suggests that the absorption around 300 nm is due to a precursor which gives both the reactant and the product simultaneously.

Based on the discussion in ref. 19, we assigned this precursor to a complex of two 1,8-DCAQH·. Actually, the rate constant for the build-up of the 300 nm absorption (about $2 \times 10^9 \, M^{-1} \, s^{-1}$ [19]) is nearly equal to the decay constant for 1,8-DCAQH·. Thus the lack of any observation of absorption due to 1,8-DCAQH$_2$ during the decay of 1,8-DCAQH·, in our previous work [22], is reasonable.

5. Conclusions

All results obtained so far indicate that the photoreductions of 1-CAQ, 1,5-DCAQ and 1,8-DCAQ originate via the hydrogen-atom abstraction by the lowest triplet states of mixed $n\pi^*-\pi\pi^*$ or $\pi\pi^*$ character, giving rise to the formation of the corresponding chloroanthrasemiquinone radicals. Similar results have been obtained for other halogenoanthraquinones such as the 1-bromo, 1,5-dibromo and 1,8-dibromo compounds [20], all of which have a lowest triplet state of mixed $n\pi^*-\pi\pi^*$ or $\pi\pi^*$ character [17]. No evidence for electron transfer from ethanol to triplet α-halogenoanthraquinones as suggested for perfluoroanthraquinone, 1,2,3,4-tetrafluoroanthraquinone and 1,2,3,4-tetrachloroanthraquinone by Inoue et al. [21] was obtained.

Upon addition of 0.2 M TEA, the quantum yields of the photoreduction in toluene were 0.6, 0.7 and 0.7 for AQ, 1-CAQ and 1-bromoanthraquinone respectively, while those in the absence of TEA were 0.3, 0.2 and 0.04 respectively [30]. Thus the quantum yield of photoreduction of 1,8-DCAQ in ethanol without TEA should be greater than that of 1-CAQ, if the suggestion of Inoue et al., that a dramatic switch-over from hydrogen abstraction to electron transfer is induced by mixing of $n\pi^*$ character with $\pi\pi^*$ character in the lowest triplet states, were correct. In contrast, the latter value was 25 times greater than that of the former. Moreover, the rate of hydrogen-atom abstraction of triplet 1-CAQ with mixed $n\pi^*-\pi\pi^*$ character is 144 times greater than that of triplet 1,8-DCAQ with $\pi\pi^*$ character.

References

1   G. S. Hammond and P. A. Leermakers, J. Am. Chem. Soc., 84 (1962) 207.
2   E. J. Baum, J. K. S. Wan and J. N. Pitts, Jr., J. Am. Chem. Soc., 88 (1966) 2652.
3   D. S. McClure, J. Chem. Phys., 17 (1949) 905.
4   R. Shimada and L. Goodman, J. Chem. Phys., 23 (1965) 2072.
5   R. W. Anderson, Jr., R. M. Hochstrasser, H. Lutz and G. W. Scott, J. Chem. Phys., 61 (1974) 2500; Chem. Phys. Lett., 28 (1974) 153.
6   D. E. Damschen, C. D. Merritt, D. L. Perry, G. W. Scott and L. D. Talley, J. Phys. Chem., 82 (1978) 2268.
7   K. Hamanoue, T. Nakayama, T. Miyake and H. Teranishi, Chem. Lett., (1981) 39.
8   T. Nakayama, K. Hamanoue, T. Hidaka, M. Okamoto and H. Teranishi, J. Photochem., 24 (1984) 71.
9   T. Nakayama, T. Hidaka, T. Kuramoto, K. Hamanoue, H. Teranishi, Y. Ito and T. Matsuura, Chem. Lett., (1984) 1953.
10 F. Wilkinson, J. Phys. Chem., 66 (1962) 2569.
11 K. Tickle and F. Wilkinson, Trans. Faraday Soc., 61 (1965) 1981.
12 S. A. Carlson and D. M. Hercules, Photochem. Photobiol., 17 (1973) 123.
13 Y. H. Li and E. C. Lim, Chem. Phys. Lett., 7 (1970) 15.
14 W. A. Case and D. R. Kearns, J. Chem. Phys., 52 (1970) 2175.
15 L. Goodman and M. Koyanagi, Mol. Photochem., 4 (1972) 369.
16 A. M. Nishimura and D. S. Tinti, Chem. Phys. Lett., 13 (1972) 278.
17 K. Hamanoue, Y. Kajiwara, T. Miyake, T. Nakayama, S. Hirase and H. Teranishi, Chem. Phys. Lett., 94 (1983) 276.

Y. Kajiwara, *Master Thesis of Faculty of Technology*, Kyoto Institute of Technology, 1982.

18 K. Hamanoue, K. Yokoyama, T. Miyake, T. Kasuya, T. Nakayama and H. Teranishi, *Chem. Lett.*, (1982) 1967.

19 K. Hamanoue, K. Sawada, K. Yokoyama, T. Nakayama, S. Hirase and H. Teranishi, *J. Photochem.*, *33* (1986) 99.

20 K. Hamanoue, T. Nakayama, K. Sawada, Y. Yamamoto, S. Hirase and H. Teranishi, submitted for publication.

21 H. Inoue, K. Ikeda, H. Mihara, M. Hida, N. Nakashima and K. Yoshihara, *Chem. Phys. Lett.*, *95* (1983) 60.

22 K. Hamanoue, K. Yokoyama, Y. Kajiwara, K. Nakajima, T. Nakayama and H. Teranishi, *Chem. Phys. Lett.*, *110* (1984) 25.

23 T. Nakayama, S. Tai, K. Hamanoue and H. Teranishi, *Mem. Fac. Ind. Arts, Kyoto Tech. Univ., Sci. Technol.*, *29* (1980) 46.
K. Hamanoue, T. Hidaka, T. Nakayama and H. Teranishi, *Chem. Phys. Lett.*, *82* (1981) 55.

24 T. Nakayama, T. Miyake, M. Okamoto, K. Hamanoue and H. Teranishi, *Mem. Fac. Ind. Arts, Kyoto Tech. Univ., Sci. Technol.*, *29* (1980) 35.

25 K. Hamanoue, K. Nakajima, Y. Kajiwara, T. Nakayama and H. Teranishi, *Chem. Phys. Lett.*, *110* (1984) 178.

26 K. Nakajima, *Master Thesis of Faculty of Technology*, Kyoto Institute of Technology, 1982.

27 N. K. Bridge and G. Porter, *Proc. R. Soc., Ser. A, 244* (1958) 259.

28 B. E. Hulme, E. J. Land and G. O. Phillips, *J. Chem. Soc., Faraday Trans. I, 68* (1972) 1992.

29 K. Hamanoue, K. Yokoyama, Y. Kajiwara, M. Kimoto, T. Nakayama and H. Teranishi, *Chem. Phys. Lett.*, *113* (1985) 207.

30 T. Nakayama, K. Sawada, K. Hamanoue and H. Teranishi, *Proc. XIIth Int. Conf. on Photochemistry, Tokyo, 1985*, p. 165.

31 K. Hamanoue, M. Kimoto, Y. Kajiwara, T. Nakayama and H. Teranishi, *J. Photochem.*, *31* (1985) 143.

32 H. Inoue, K. Ikeda and M. Hida, *Nippon Kagaku Kaishi*, (1984) 381.

33 G. Porter and P. Suppan, *Pure Appl. Chem.*, *9* (1964) 499; *Trans. Faraday Soc., 61* (1965) 1664.

34 S. J. Formosinho, *J. Chem. Soc., Faraday Trans. II, 74* (1978) 1978.